

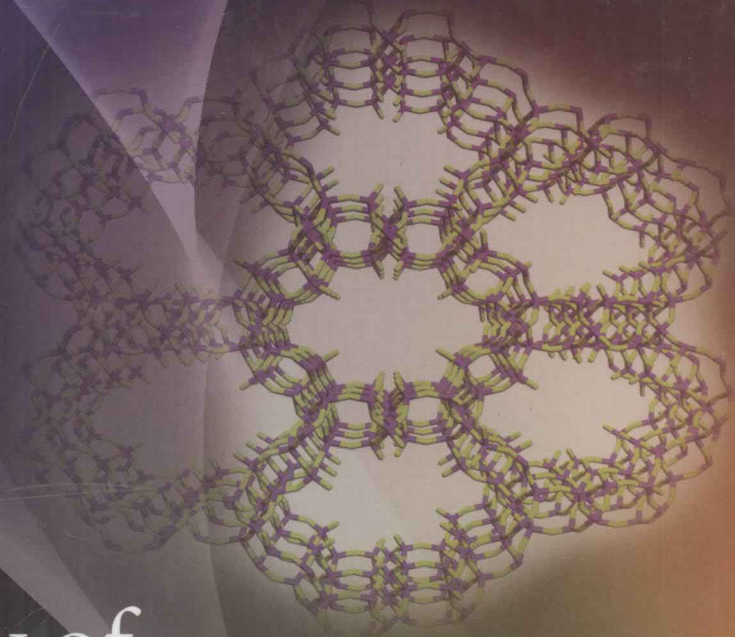
Ruren Xu

Wenqin Pang

Jihong Yu

Qisheng Huo

Jiesheng Chen



# Chemistry of Zeolites and Related Porous Materials

*Synthesis and Structure*

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# Chemistry of Zeolites and Related Porous Materials: Synthesis and Structure

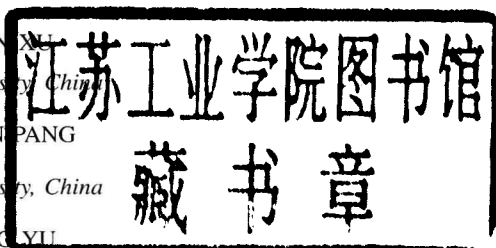
RUREN XU  
*Jilin University, China*

WENQIN PANG  
*Jilin University, China*

JIHONG YU  
*Jilin University, China*

QISHENG HUO  
*Pacific Northwest National Laboratory, USA*

JIESHENG CHEN  
*Jilin University, China*



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# **Chemistry of Zeolites and Related Porous Materials**

# Preface

Our book 'Zeolite Molecular Sieves: Structure and Synthesis' (in Chinese) was first published in 1987. Substantial progress has been made in these 19 years in developing new molecular sieves with microporous structures such as zeolite and aluminophosphate molecular sieves and many new families of molecular sieves with much diversified structural features and compositional elements. Up until 2006, at least 167 types of molecular sieves with unique framework structures had been reported. More than 30 compositional elements have been incorporated into the frameworks. In 1992, scientists at Mobil Corporation for the first time reported the development of a new family of materials (named M41S) characterized by their unique mesoporous structures (diameter ranging from 2 to 50 nm), which instantly became headline news in science. This new discovery has clearly marked a major milestone in this field, opening the door for developing many new types of molecular sieves and porous materials. In 1998, Wijnhoven and Vos reported the successful synthesis of macroporous material  $\text{TiO}_2$ . Since then a number of other new macroporous materials (diameter ranging from 50 to 2000 nm) such as  $\text{SiO}_2$ ,  $\text{ZrO}_2$ , etc., have been synthesized. Parallel to these developments is the emergence of another research area focused on development of porous coordination polymers and hybrid solids with metal-organic frameworks (MOFs). The advent of this family of MOFs has substantially expanded the pool of porous materials that traditionally have their frameworks made of inorganic elements. In addition, the MOF materials with their unique structural and functional characteristics have greatly diversified the existing porous materials. Clearly, the rapid development of microporous compounds and the advent of mesoporous, macroporous, and MOF materials have expanded the already rich and complex molecular sieves and porous materials chemistry, leading to the emergence of a brand new scientific discipline namely the *porous materials chemistry*. Thanks to these new developments and the progress in related theoretical studies, research methodology, and techniques, as well as the expansion in the scope of applications from the traditional areas such as adsorption separation, catalysis and ion-exchange to the making of new and more advanced materials, our understanding about the governing principles and mechanisms and the observations made about molecular sieves and porous material chemistry has improved significantly in the past decade; in particular, our understanding about the relationships of 'function-structure-synthesis' of zeolites and

other porous materials has reached a new level. The idea of this book was conceived and carefully planned in this general context, to which we give a new name 'Chemistry of Zeolites and Related Porous Materials - Synthesis and Structure'. This book will be published in English by John Wiley & Sons, (Asia) Pte Ltd by the time of the 15th International Zeolite Conference (Beijing, 2007).

The present book consists of nine chapters, with the synthetic and structural chemistry of microporous and mesoporous materials as the core. Five chapters (Chapters 3, 4, 5, 6, and 8) are allocated to cover the synthetic aspects of the topic. Chapter 3 introduces the synthesis and related fundamental principles, synthetic strategies, and techniques for the major microporous materials such as zeolites and microporous aluminophosphates. This Chapter serves as Part I of the synthetic aspects of the microporous compounds.

A large number of new microporous materials have emerged in the past decade, with (a) specially interesting structures such as extra-large microporous channels, interconnecting 2- and 3-dimensional channel systems, chiral channels, and various cage structures, (b) special types such as the  $M(III)X(V)O_4$ -type, oxide-, sulfide-, and aluminoborate-type, and (c) specially interesting aggregated states such as nano-size and ultra-fine particles, perfect crystals, and single crystals, microsphere, coating, film, membrane, and special crystal morphologies, etc. All these new developments, along with their increasingly wider range of applications, have motivated us to write a chapter (Chapter 4) about the synthetic chemistry of the microporous materials with special structures, types, and aggregated states. And this chapter serves as Part II of the synthetic aspects of the microporous compounds.

Currently, most molecular sieves and porous materials are synthesized through hydrothermal or solvothermal crystallization. Hence it was considered essential to include a chapter addressing the crystallization process and related chemistry problems, to help the reader better understand the formation of microporous compounds, and their channel-framework structure, and the theory of crystallization, which should provide useful guidance for exploring and developing new synthetic strategies, methodologies, and techniques. This is the core of Chapter 5 (Crystallization of Microporous Compounds), which is focused on three key chemistry issues relevant to crystallization, i.e., (a) the aggregated states and polymerization reactions of the source materials at the pre-crystallization stage; (b) the crystallization mechanism of porous compounds and the templating or structure-directing effects during nucleation and crystallization; (c) crystallization kinetics and the mechanisms of crystal growth. It should be noted that some of the mechanistic issues relevant to crystallization are still not well understood or only partially understood, some of which are still debatable, due to the high complexity of the crystallization processes and the lack of effective techniques for probing them scientifically. So we have honestly presented our current understanding (or lack of it) of these complex scientific issues, and let our readers fully appreciate the complexity of studying the chemistry problems involved in crystallization of porous compounds and understand the feasibility in tackling these problems. The preparation, secondary synthesis, and modification of molecular sieves represent a unique set of problems, different from the issues we have discussed related to crystallization of microporous compounds under hydrothermal (or solvothermal) conditions. These deal with issues related to modifying and refining the crystallized products of microporous compounds and hence their unique process pathways and related mechanistic issues. Chapter 6 is designed to cover such

problems. Mesoporous materials have their unique characteristics from the viewpoint of structural chemistry and their synthesis, different from those of microporous materials though some commonalities exist between the two from the viewpoint of studying porous materials in general. This represents a new and extremely rich research field, playing increasingly important roles in expanding the applications of porous materials. Hence we have included one chapter (Chapter 8) focusing on mesoporous materials.

Microporous materials with regular pore architectures comprise wonderfully complex structures and compositions. Their fascinating properties, such as ion-exchange, separation, and catalysis, and their roles as hosts in nanocomposite materials, are essentially determined by their unique structural characters, such as the size of the pore window, the accessible void space, the dimensionality of the channel system, and the numbers and sites of cations, etc. Traditionally, the term 'zeolite' refers to a crystalline aluminosilicate or silica polymorph based on corner-sharing  $\text{TO}_4$  ( $\text{T} = \text{Si}$  and  $\text{Al}$ ) tetrahedra forming a three-dimensional four-connected framework with uniformly sized pores of molecular dimensions. Nowadays, a diverse range of zeolite-related microporous materials with novel open-framework structures have been discovered. The framework atoms of microporous materials have expanded to cover most of the elements in the periodic table. For the structural chemistry aspect of our discussions, the second key component of the book, we have a chapter (Chapter 2) to introduce the structural characteristics of zeolites and related microporous materials.

In addition to a systematic and in-depth coverage of the above material, we have allocated two chapters (Chapters 7 and 9) to discussion of the cutting-edge research issues in the chemistry of molecular sieves and porous materials, two of the most important growing areas of this field. Chapter 7 focuses on molecular design and rational synthesis of microporous molecular sieves, mainly based on the results of our own research and the knowledge we have gained in the past two decades in the area of molecular engineering of microporous compounds as well as the state-of-the-art research results by other research groups in the world. Both of these areas clearly represent where the science is going in regard to the chemistry of molecular sieves and porous materials. They also demonstrate the ultimate goal that many scientists in different branches of chemistry, such as solid-state chemists, material chemists, and synthesis chemists, have been working diligently to accomplish. Microporous molecular sieves represent one of the most important classes of target systems for molecular engineering studies in recent years, because of the regularity of their framework structures and the large amount of knowledge that scientists have gained about their key structural characteristics and the mechanisms of their formation. Hence we have devoted one chapter (Chapter 7) to presentation of the cutting-edge research issues in molecular engineering of molecular sieves. Chapter 9 focuses on the development of another important area of porous materials, i.e., porous host-guest advanced materials and MOF materials, which represents one of the most promising directions in finding new applications of porous materials in the high-tech materials. Chemistry of molecular sieves and porous materials has increasingly attracted wider attention in the past decade because of the interesting scientific issues that they raise and the prospect of their wide range of applications. This new branch of chemistry is clearly emerging as an exciting new science by itself at the interaction of various scientific disciplines.



While writing this book, we have paid special attention to make sure that the most recent and key developments at the forefront of the field are well covered in the book so that the reader gets a good exposure to the true state-of-the-art of this new field. In addition, we have tried to incorporate as many key research results and applications as possible, wherever appropriate, that have been achieved in the field of molecular sieves and porous materials. The overall design of the book's structure and major content was done by me and Professor Wenqin Pang. The writing of the book was done mainly by Professor Wenqin Pang (Chapter 6), Professor Jihong Yu (Chapters 2 and 7), Professor Jiesheng Chen (Chapter 9) and me (Chapters 1, 3, 4, and 5). Dr Qisheng Huo of the USA, one of the pioneer researchers in the syntheses of mesoporous materials, wrote Chapter 8.

The publication of this book is the result of the hard work by the authors of this book including Prof. Ruren Xu, Prof. Wenqin Pang, Prof. Jihong Yu, Dr Qisheng Huo, and Prof. Jiesheng Chen along with the long-term research experience and accumulation of knowledge of many colleagues of the State Key Laboratory of Inorganic Synthesis and Preparative Chemistry in Jilin University. Particularly, we would like to thank Dr Wenfu Yan, Dr Jiyang Li, Dr Yi Li, and Mrs Fengjuan Zhang for their contribution to the preparation of this book. In addition, we invited Prof. Yushan Yan at the University of California, Riverside, USA, to write a section on 'Preparation and Application of Zeolite Membranes', and Prof. Zi Gao at Fudan University, Shanghai, to write a section on 'Channel and External Surface Modification'. Here we would like to express our heartfelt gratitude for their contribution to this book. Finally, we would like to dedicate this book to the 15th International Zeolite Conference (Beijing, 2007) and colleagues from different parts of the world.

Ruren Xu  
Chairman of 15th IZC  
Professor of Chemistry  
Jilin University  
P. R. China  
November 2006, Changchun



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# 1

## Introduction

Natural zeolites were first discovered in 1756. During the 19th century, the microporous properties of natural zeolites and their usefulness in adsorption and ion exchange were gradually recognized. However, it was not until the 1940s that a series of zeolites with low Si/Al ratios were hydrothermally synthesized through mimicking of the geothermal formation of natural zeolites. The successful synthesis of zeolites laid the foundation for rapid development of zeolite industry in the 20th and 21st centuries. Porous compounds or porous materials share the common feature of regular and uniform porous structures. To describe a porous structure, several parameters may be used and these include pore size and shape, channel dimensionality and direction, composition and features of channel walls, etc. Among these parameters, pore size and pore shape are the most important. According to the aperture size of pores, porous compounds can be classified as microporous (aperture diameter less than 2 nm), mesoporous (aperture diameter of 2–50 nm), and macroporous (aperture diameters larger than 50 nm) materials, respectively.<sup>[1]</sup> The International Zeolite Association (IZA) database shows that the number of structural types of unique microporous frameworks has been growing rapidly, from 27 in 1970, to 38 in 1978, to 64 in 1988, to 98 in 1996, and to 133 in 2001,<sup>[2]</sup> whereas currently (Feb. 2007), this number has reached 174. In fact, during the past half century, a great many microporous compounds with diverse compositional elements and primary building units have been synthesized thanks to the development of synthetic techniques. However, because of a shortage of more powerful characterization techniques, the framework structures of many novel zeolites could not be determined. It has been reported that over 20 elements may be introduced into zeolite frameworks, and taking into account the diversity of zeolite compositions, the number of unique zeolites might be enormous. The announcement of M41S compounds in 1992 by Mobil scientists has stimulated rapid growth of mesoporous materials, whereas the study of macroporous materials has just begun to burgeon, and their special structural features and properties



are very attractive. From microporous to mesoporous to macroporous, the conventional framework compositions of molecular sieves and porous materials are purely inorganic. However, in recent years, the appearance of porous metal-organic frameworks (MOFs) has greatly enhanced the diversity and compositional complexity of porous materials, and has offered further possibilities for the development of porous materials.

## 1.1 The Evolution and Development of Porous Materials

### 1.1.1 From Natural Zeolites to Synthesized Zeolites

The first natural microporous aluminosilicate, i.e., natural zeolite, was discovered more than 200 years ago, and after long-term practical applications, the intrinsic properties of natural zeolites such as reversible water-adsorption capacity were fully recognized.<sup>[3,4]</sup> By the end of the 19th century, during exploitation of ion-exchange capacity of some soils, it was found that natural zeolites exhibited similar properties: some cations in natural zeolites could be ion-exchanged by other metal cations. Meanwhile, natural chabazite could adsorb water, methanol, ethanol, and formic acid vapor, but could hardly adsorb acetone, diethyl ether, or benzene. Soon afterwards, scientists began to realize the importance of such features, and use these materials as adsorbents and desiccants. Later, natural zeolites were also used widely in the field of separation and purification of air.

Natural zeolites were first discovered in cavities and vugs of basalts. At the end of the 19th century, they were also found in sedimentary rocks. As a result of many geological explorations, zeolite formation was considered to include the following genetic types:<sup>[3]</sup>

1. Crystals resulting from hydrothermal or hot-spring activity involving reaction between solutions and basaltic lava flows.
2. Deposits formed from volcanic sediments in closed alkaline and saline lake-systems.
3. Similar formations from open freshwater-lake or groundwater systems acting on volcanic sediments.
4. Deposits formed from volcanic materials in alkaline soils.
5. Deposits resulting from hydrothermal or low-temperature alteration of marine sediments.
6. Formations which are the result of low-grade burial metamorphism.

With geological exploration and study on minerals, more and more natural zeolites have been discovered. Up to now, over 40 types of natural zeolites have been found, but fewer than 30 of them have had their structures solved. Recently, many natural zeolite resources have been discovered around the world, and the applications of these natural species are drawing increasing attention. At present, natural zeolites are widely used in the fields of drying and separation of gases and liquids, softening of hard water, treatment of sewage, and melioration of soils. Some well selected or modified natural zeolites are also used as catalysts or supports of catalysts in industry.

Zeolite science and technology in China has been in great progress as well in the past several decades. According to incomplete statistics, there are many types of zeolite resources in China, and among the natural zeolites discovered in China are mordenite, clinoptilolite, analcime, heulandite, natrolite, thomsonite, stilbite, and laumontite. With further exploration, it is believed that many more zeolite resources will be

discovered in China. As research work on natural zeolites deepens, they will be applied more broadly.

Because natural zeolites cannot meet the huge demands in industry, it becomes an urgent necessity to use synthesized zeolites besides the natural ones. Synthesis of zeolites was first conducted at the end of the 19th century through mimicking of the geothermal conditions for natural zeolite formation, i.e., high-temperature hydrothermal reactions. By the end of the 1940s, a number of scientists started to carry out research on massive synthesis of zeolites.

Abundant natural zeolites were found later in sedimentary rocks. Since these zeolite deposits were usually located near the surface of the earth, it was concluded that they had been produced at temperatures and pressures which were not very high. During a study on strata of Triassic rocks, it was found that zeolites were somehow in a chemical-equilibrium state when they were formed. This state was metastable and was known as the zeolite phase. The equilibrium process for zeolite phases was very similar to that of low-temperature hydrothermal synthesis reactions. Therefore, researchers tried to synthesize zeolites using hydrothermal synthesis techniques at temperatures of around 25–150 °C (usually 100 °C). In the 1940s, low-silica zeolites were first synthesized. The application of low-temperature hydrothermal techniques facilitated the extensive industrial production of zeolites. By the end of 1954, zeolites A and X began to be produced industrially. Following this, a number of companies in the United States, such as Linde, UCC, Mobil, and Exxon, imitated the formation of natural zeolites and produced a series of synthesized zeolites with an intermediate Si/Al ratio ( $\text{Si/Al} = 2\text{--}5$ ), including NaY, mordenite, zeolite L, erionite, chabazite, clinoptilolite, and so on. These zeolites were widely applied in the fields of gas purification and separation, catalytic processes of petroleum refining and petrochemistry, and ion exchange.

In China, zeolites A and X were first synthesized in 1959, followed by the industrial production of zeolite Y and mordenite. With the development of the zeolite industry, zeolites were applied in many fields as well in China. In the 1950s, zeolites were mainly used in drying, separation, and purification of gases. Since the 1960s, zeolites have been widely used as catalysts and catalyst supports in petroleum refining. At present, zeolites have become the most important adsorbents and catalysts in the petroleum industry.

Although, compared with natural zeolites, synthesized zeolites have many advantages such as high purity, uniform pore size, and better ion-exchange abilities, natural zeolites are more applicable when there are huge demands and fewer quality requirements. The reason is that natural zeolites are often located near the surface of the earth and can be easily exploited and used after some simple treatments, which lead to lower costs and hence lower prices. Therefore, natural zeolites have a good prospect of application especially in the fields of agriculture and environmental protection.

### 1.1.2 From Low-silica to High-silica Zeolites

The period from 1954 to the early 1980s is the golden age for the development of zeolites. Zeolites with low, medium, and high Si/Al ratios were extensively explored, and this greatly facilitated the applications of zeolites and stimulated industrial progress.<sup>[5]</sup> In order to increase the thermal stability and acidity of zeolites, Breck et al. synthesized zeolite Y ( $\text{Si/Al} = 1.5\text{--}3.0$ ), which played an extremely important role in the catalysis of