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Guangshan Zhu  
Hao Ren

# Porous Organic Frameworks

Design,  
Synthesis and  
Their Advanced  
Applications



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# Preface

Porous materials are of intensive academic and technological interest because of their vital applications for adsorbent, catalyst, ion exchanger, nanotechnology, etc. The development of porous materials has accompanied the demands of modern society. A large number of porous materials have been designed and synthesized in the past half century, including zeolite, mesoporous materials, metal-organic frameworks (MOFs) also known as coordination polymers, and porous organic frameworks (POFs). Although the above-mentioned porous materials seem to have major differences, they also possess corresponding consistencies. For zeolite, the basic structural unit is  $\text{TO}_4$  tetrahedron. These primary building units ( $\text{TO}_4$ ) are linked by corner sharing oxygen atoms together to form secondary building units (SBUs). SBUs can be connected in the form of cages or channels and finally lead to various zeolites with different structures. MOFs or coordination polymers are assembled by inorganic clusters and organic linkers. POF are constructed by purely organic units via robust covalent bonds. The synthesis procedure could be described as the assembly of building units via specific acting force.

The book *Porous Organic Frameworks: Design, Synthesis and Their Advanced Applications* is aimed at offering researchers with the most pertinent and up-to-date advances of POFs. The development of POF materials has attracted extensive attention thanks to their fascinating characteristics, such as structural designing-ability, high surface area, diverse pore dimensions, chemical functionalities, high chemical and thermal stabilities, etc. Encouragingly, POFs display excellent performances in the fields of gas storage, catalysis, host-guest chemistry, and optical and electronic properties, etc. The main benefit of this book is that it highlights the synthetic principles, and structural merits of most of the advanced POFs. In this book the important relationship between structures and functions of POFs is discussed. It is intended for scientists and researchers focusing on this research field. The material in this book will also benefit engineers concerning the applications of POFs. We would like to take

this opportunity to thank Dr. Yuyang Tang, Qianjun Tang and Changhong Feng for their careful work in fixing grammar errors throughout this book. Special thanks go to Ye Yuan and Dr. Heping Ma, who contributed to the partial writing of Chaps. 3–6, including paperwork, figure design, etc.

August 2014

Guangshan Zhu  
Hao Ren

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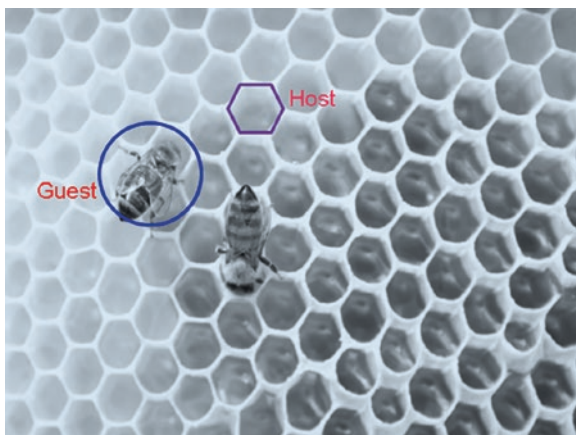
# Chapter 1

## Introduction to Porous Materials

Porous materials have been of intense scientific and technological interest because of their vital applications in adsorption, catalysis, ion exchange, nanotechnology, etc. [1]. Although people might not be familiar with the concept of “porous materials”, they are widely used in our daily lives, such as in removal of harmful gases, dehumidizers, etc. What are porous materials? At microscopic scale, if the atoms of a material are not densely stacked but form voids, the material is defined as porous material. Nature is a magical world, which provides visual examples that help us to understand porous materials. For example, a honeycomb has hexagonal cells, seeming like a “house”, and honeybees can “live” and get in and out of this building. The voids are formed by surrounding walls. The honeycomb could be regarded as the “host” and the honeybee the “guest” (Fig. 1.1).

Doubtless, the void of a honeycomb is very obvious with dimensions in centimeters and can be seen with our naked eyes. However, the voids of studied porous materials are at nanometer scales. According to the nomenclature recommended by the International Union of Pure and Applied Chemistry (IUPAC) [2], porous materials are classified as microporous materials (with pore diameters of less than 2 nm), mesoporous materials (with pore diameters of between 2 and 50 nm), and macroporous materials (with pore diameters of greater than 50 nm) based on their pore sizes. Besides, porous materials include inorganic materials (natural zeolites, synthetic zeolites, microporous aluminum phosphates, silica mesoporous materials, etc.), carbon-based materials, inorganic–organic hybrid materials metal–organic frameworks (MOFs), organic polymers, which are distinguished based on their structural and chemical compositions (Fig. 1.2).

When describing porous materials, several important structural characteristics should be clearly illustrated, including pore geometry, pore opening size, pore surface functionality, and polymeric framework structural features including composition, topology, and functionality (Fig. 1.3) [3]. Porosity is a profound parameter that describes porous materials. Nitrogen and Argon adsorption–desorption isotherms are the most important techniques to investigate the porous properties including the apparent surface area and pore size. The apparent surface area could



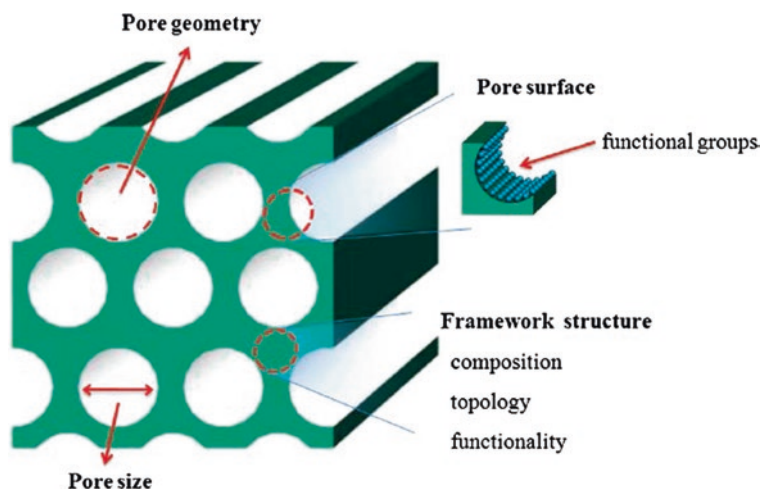
**Fig. 1.1** Illustration of porosity existing in nature. The visual example is honeycomb



**Fig. 1.2** Porous materials could be classified according to their pore size and their components

be calculated from Brunauer–Emmett–Teller (BET) model and Langmuir model, respectively. Commonly, the pore size distribution of porous materials is calculated by density functional theory (DFT) and nonlocal density functional theory (NLDF). It should be mentioned that the model of adsorbent and the type of pores should be carefully selected to ensure the correctness and accuracy of analysis.

The development of porous materials is accompanied with the demands of society. A large number of porous materials have been designed and synthesized

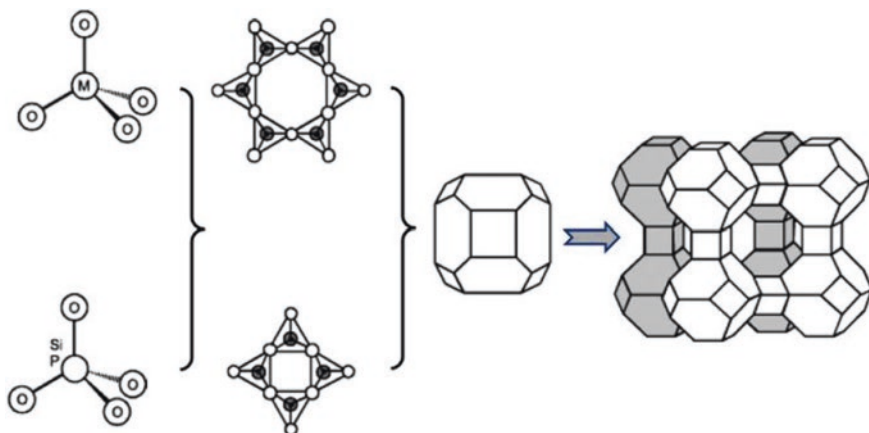


**Fig. 1.3** Illustration of pore geometry, pore surface, pore size, and framework structure of porous polymers. Reprinted with permission from Ref. [3]. Copyright 2009, American Chemical Society

in the past half century. The investigation of porous materials experiences the following representative stages: (1) natural zeolites coined by Swedish mineralogist A.F. Cronstedt in 1756; (2) synthesis of zeolites under hydrothermal or solvothermal conditions; (3) report of the MCM family ordered mesoporous materials (MCM-41, MCM-48, etc.) in 1992 [4, 5]; (4) MOFs or coordination polymers through assembling inorganic units and organic linkers started at the beginning of the 1990s [6, 7]; (5) porous organic frameworks (POFs) constructed with purely light elements via robust covalent bonds [3, 8–18]. Although the above-mentioned porous materials seem to have major differences, they also possess certain similarities.

For zeolites, their basic structural unit is  $\text{TO}_4$  tetrahedron, where  $\text{TO}_4$  is  $[\text{SiO}_4]^{4-}$  or  $[\text{AlO}_4]^{5-}$ . These primary building units ( $\text{TO}_4$ ) are linked together by corner sharing oxygen atoms to form secondary building units (SBUs). SBUs can be connected in the form of cages or channels within the structure. Finally, constructing cages and rings of different sizes leads to various zeolites with different framework structures (Fig. 1.4).

Despite zeolites and microporous solids being widely applied in gas adsorption and separation catalysis, their pores are restrained to the subnanometer scale ( $<2.0$  nm), limiting their application for larger molecules, especially for biological molecules in the areas of adsorption and catalysis. The report of MCM family materials with ordered mesopores has attracted considerable attention in the research field of mesoporous materials. In the process of synthesizing mesoporous materials, templates formed by the assembly of special molecules plays a vital



**Fig. 1.4** Illustration of the formation of zeolite, from the primary TO<sub>4</sub> to secondary building units (SBUs), and SBUs further assemble to form extended zeolite

role, which can affect the final structure of mesoporous materials. The control of surfactant template is a fruitful strategy to design the pore and topology of mesoporous materials. Typical structures of mesoporous materials include [19]: (1) MCM-41, which has a two-dimensional hexagonal structure; (2) MCM-48, which has a cubic channel structure; (3) MCM-50, which has a lamellar structure.

Along with the development of purely inorganic porous materials, remarkable innovation for synthesis of porous materials has been made with the introduction of organic molecules as building composition of the structure, forming inorganic–organic hybrid compounds. Among these coordination compounds, MOFs, or coordination polymers constructed from metal ions or clusters as connectors and bridging organic ligands (Fig. 1.5) have been intensively investigated [6, 7]. In 1999, two robust MOFs, MOF-5 ( $\text{Zn}_4\text{O}(\text{bdc})_3$ , bdc = 1,4-benzenedicarboxylate) [20] and HKUST-1 ( $\text{Cu}_3(\text{btc})_2$ , btc = 1,3,5-benzenetricarboxylate) [21] considered as milestones in the development of MOFs, greatly promoted this fruitful research field. Compared with inorganic porous solids, MOFs have their intrinsic characters such as: (a) mild synthetic conditions, even at room temperature; (b) various organic ligands, which could be readily designed and modified; (c) abundant inorganic building connectors, metal ions, or metal clusters; (d) the structures and properties of MOFs could be tuned through pre-synthetic and post-synthetic design of organic ligands, inorganic SBUs, and synthetic conditions, etc.

In 2005, Yaghi et al. reported two 2D covalent–organic frameworks (COF) materials, COF-1 and COF-5 [23]. Their crystalline and nanoporous textures have changed researchers' understanding of porous materials and polymers. In fact, more than 40 years ago, hyper-cross-linked polymer (HCP) networks had already been successfully synthesized possessing amorphous and organic porous textures [24]. In this book, we introduce the concept of POFs [3, 8–18] constructed by purely light elements via robust covalent bonds, and present this new family