

CRYSTALLINE MICROPOROUS AND OPEN FRAMEWORK MATERIALS

XIANHUI BU

Chemistry Department, University of California, CA93106, USA

PINGYUN FENG

Chemistry Department, University of California, Riverside, CA92521, USA

A variety of crystalline microporous and open framework materials have been synthesized and characterized over the past 50 years. Currently, microporous materials find applications primarily as shape or size selective adsorbents, ion exchangers, and catalysts. The recent progress in the synthesis of new crystalline microporous materials with novel compositional and topological characteristics promises new and advanced applications. The development of crystalline microporous materials started with the preparation of synthetic aluminosilicate zeolites in late 1940s and in the past two decades has been extended to include a variety of other compositions such as phosphates, chalcogenides, and metal-organic frameworks. In addition to such compositional diversity, synthetic efforts have also been directed towards the control of topological features such as pore size and channel dimensionality. In particular, the expansion of the pore size beyond 10Å has been one of the most important goals in the pursuit of new crystalline microporous materials.

1 Introduction

Microporous materials are porous solids with pore size below 20Å [1,2,3,4]. Porous solids with pore size between 20 and 500Å are called mesoporous materials. Macroporous materials are solids with pore size larger than 500Å. Mesoporous and macroporous materials have undergone rapid development in the past decade and they are covered in other chapters of this book. A frequently used term in the field of microporous materials is “molecular sieves” [5] that refers to a class of porous materials that can distinguish molecules on the basis of size and shape. This chapter focuses on crystalline microporous materials with a three-dimensional framework and will not discuss amorphous microporous materials such as carbon molecular sieves. However, it should be kept in mind that some amorphous microporous materials can also display shape or size selectivity and have important industrial applications such as air separation [6].

The development of crystalline microporous materials started in late 1940s with the synthesis of synthetic zeolites by Barrer, Milton, Breck and their coworkers [7,8]. Some commercially important microporous materials such as zeolites A, X, and Y were made in the first several years of Milton and Breck’s work. In the following thirty years, zeolites with various topologies and chemical compositions (e.g., Si/Al ratios) were prepared, culminating with the synthesis of ZSM-5 [9] and

aluminum-free pure silica polymorph silicalite [10] in 1970s. A breakthrough leading to an extension of crystalline microporous materials to non-aluminosilicates occurred in 1982 when Flanigen *et al.* reported the synthesis of aluminophosphate molecular sieves [11,12]. This breakthrough was followed by the development of substituted aluminophosphates. Since late 1980s and the early 1990s, crystalline microporous materials have been made in many other compositions including chalcogenides and metal-organic frameworks [13,14].

Crystalline microporous materials usually consist of a rigid three-dimensional framework with hydrated inorganic cations or organic molecules located in the cages or cavities of the inorganic or hybrid inorganic-organic host framework. Organic guest molecules can be protonated amines, quaternary ammonium cations, or neutral solvent molecules. Dehydration (or desolvation) and calcination of organic molecules are two methods frequently used to remove extra-framework species and generate microporosity.

Crystalline microporous materials generally have a narrow pore size distribution. This makes it possible for a microporous material to selectively allow some molecules to enter its pores and reject some other molecules that are either too large or have a shape that does not match with the shape of the pore. A number of applications involving microporous materials utilize such size and shape selectivity.

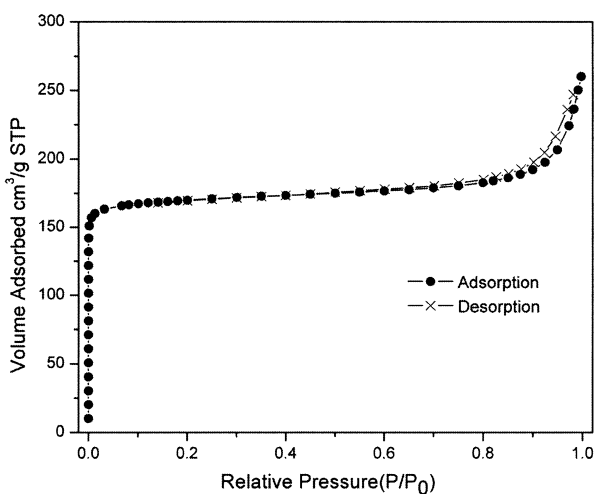


Figure 1. Nitrogen adsorption and desorption isotherms typical of a microporous material. Data were measured at 77K on a Micromeritics ASAP 2010 Micropore Analyzer for Molecular Sieve 13X. The structure of 13X is shown in Fig. 3. The sample was supplied by Micromeritics.

Two important properties of microporous materials are ion exchange and gas sorption. The ion exchange is the exchange of ions held in the cavity of microporous materials with ions in the external solutions. The gas sorption is the ability of a

microporous material to reversibly take in molecules into its void volume (Fig. 1). For a material to be called microporous, it is generally necessary to demonstrate the gas sorption property.

The report by Davis *et al.* of a hydrated aluminophosphate VPI-5 with pore size larger than 10\AA in 1988 generated great enthusiasm toward the synthesis of extra-large pore materials [15]. The expansion of the pore size is an important goal of the current research on microporous materials [16]. Even though microporous materials include those with pore sizes between 10 to 20\AA , The vast majority of known crystalline microporous materials have a pore size $<10\text{\AA}$. The synthesis of microporous materials with pore size between 10 and 20\AA is desirable for applications involving molecules in such size regime and remains a significant synthetic challenge today.

In the following sections, we will first review oxide-based microporous materials followed by a review on related chalcogenides. We will then discuss metal-organic frameworks, in which the framework is a hybrid between inorganic and organic units. The research on metal-organic frameworks is a rapidly developing area. These metal-organic materials are being studied not only for their porosity, but also for other properties such as chirality and non-linear optical activity [17]. The last section gives a discussion on materials with extra-large pore sizes. There exist many excellent reviews and books from which readers can find detailed information on various zeolite and phosphate topics [1,4,13,18,19,20,21,22,23,24,25].

2 Microporous Silicates

From a commercial perspective, the most important microporous materials are zeolites, a special class of microporous silicates. A strict definition of zeolites is difficult [5] because both chemical compositions and geometric features are involved. Zeolites can be loosely considered as crystalline three-dimensional aluminosilicates with open channels or cages. Not all zeolites are microporous because some are unable to retain their framework once extra-framework species (e.g., water or organic molecules) are removed. The stability of zeolites varies greatly depending on framework topologies and chemical compositions such as the Si/Al ratio and the type of charge-balancing cations. In addition to aluminum, many other metals have been found to form microporous silicates such as gallosilicates [26], titanosilicates [27,28], and zincosilicates [16]. Some microporous frameworks can even be made as pure silica polymorphs, SiO_2 [10].

2.1 Chemical compositions and framework structures of zeolites

Natural zeolites are crystalline hydrated aluminosilicates of group IA and group IIA elements such as Na^+ , K^+ , Mg^{2+} , and Ca^{2+} . Chemically, they are represented by the empirical formula: $\text{M}_{2/n}\text{O} \cdot \text{Al}_2\text{O}_3 \cdot y\text{SiO}_2 \cdot w\text{H}_2\text{O}$ where y is 2 or larger, n is the