Porous Materials

Process Technology and Applications

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Preface

Approximately four million years of human history has passed. We have been using materials to make a variety of tools. The first materials used were naturally occurring materials such as animal bones, stones, wood etc.; and some of these familiar materials are porous. Porous materials are so familiar that they are sometimes forgotten or ignored.

The taste experience of ice cream is created not only by adjusting ingredients, but also by including air as an ingredient, i.e. pores that give the smooth texture of ice cream.

This book is designed to describe and explain about pores, the synthesis of materials with pores (porous materials), and applications of porous materials. This book is intended for engineers and scientists of different disciplines and specialities, and is expected to be useful in the design and synthesis of porous materials for existing as well as potential new applications.

Let us rediscover pores.

K. Ishizaki,
S. Komarneni and
M. Nanko
January 1998

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Introduction

1.1 WHAT ARE POROUS MATERIALS?

Porous materials are defined as solids containing pores. Figure 1.1 shows different porous materials. Generally speaking, porous materials have a porosity of 0.2–0.95. The porosity means the fraction of pore volume to the total volume. Porous materials have been used in various applications from daily necessities, such as purifying drinking water by activated carbon or porous ceramics, to uses in modern industries, for example removing dusts from high purity process gases for semiconductor production.

Pores are classified into two types: open pores which connect to the outside of the material, and closed pores which are isolated from the outside and may contain a fluid. Penetrating pores are a kind of open pores; these have at least two openings located on two sides of a porous material.

Figure 1.2 illustrates schematically the different morphology of pores. Porous metals, ceramics and glasses are particularly important for industrial applications, in chemistry, mechanical engineering, biotechnology and electronics. For most industrial applications of porous materials, open pores are required. Porous materials for filters and carriers for catalysts and bioreactors need to have a high fraction of open porosity. In open pores, penetrating pores are necessary for industrial applications such as in filters or for gas distribution.

Closed porous materials are used mainly for sonic and thermal insulators, or low-specific-gravity structural components.

Introducing open pores in material (producing open porous materials) changes material properties. Two essential changes are the decreased density and the increased specific surface area. The changes generate useful properties (which are not observed in dense bodies) such as fluid permeability,

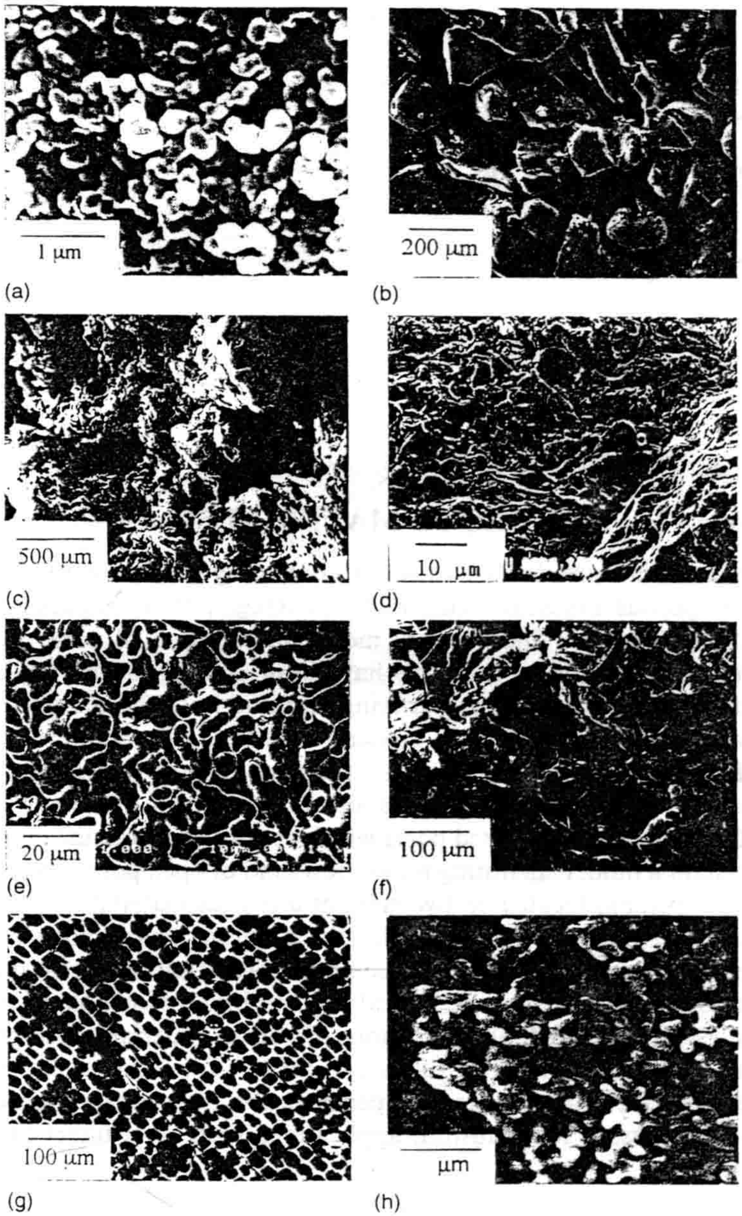

FIGURE 1.1 Examples of porous materials: (a) shows porous titania sintered fine powder; (b) grinding wheel, abrasive grains with a vitrified bonding agent; (c) sponge titanium; (d) a traditional ceramic; (e) porous copper sintered electrolytic powder; (f) porous silicon carbide produced by reaction sintering; (g) charcoal; and (h) porous glass prepared by leaching method.

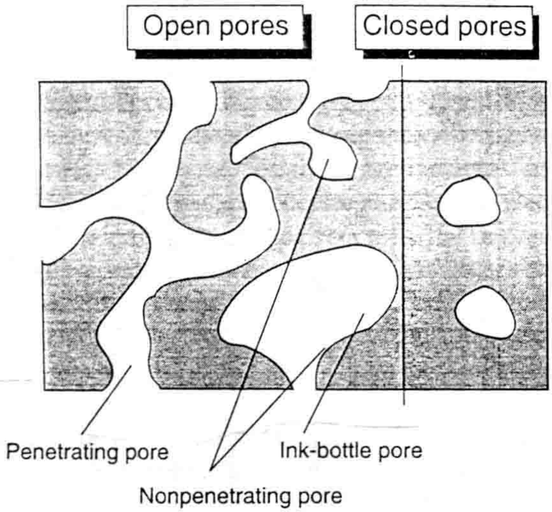

FIGURE 1.2 Schematic illustration of different morphology of pores. Pores are classified into two major types: open and closed pores. In open pores, penetrating pores are permeable for fluid, and therefore are important in applications such as filters.

filtration effects and thermal and acoustic insulation capability. Table 1.1 shows the required properties for different applications of porous materials. Narrow pore size distribution is important for porous filters, and allows selective filtration. Materials with a bimodal pore size distribution are required for bioreactors, in which enzymes or bacteria are immobilized in small pores and large open pores are used as channels for transporting reactants and products [1]. Narrow pore size distribution for each pore mode is required for these applications.

Large specific surface area is necessary for catalysis. In many applications of porous materials, high open porosity is desirable to increase the specific surface area or fluid permeability. An increase in porosity decreases mechanical strength. Low mechanical strength limits the operating conditions for porous materials, and consequently increases the required dimensions of porous materials. Both high open porosity and high mechanical strength may be required simultaneously in order to use porous materials under severe operating conditions.

Different applications of porous materials require different pore sizes. For instance, pores of atomic scale are required for gas separation or catalysis. Zeolites, silica gel, intercalated layered materials etc. are used in these applications due to their atomic scale pores. Particles are removed from

TABLE 1.1 Porous materials and their requirements for different applications

	Filter	*Catalyst*	*Bioreactor*	*Gas distributor*	*Sensor*	*Oil-containing bearing*
Open porosity (%)	> 30	> 30	> 30	> 30	> 30	20–40
Pore size	Appropriate size, depending on applications	Appropriate size, depending on applications	For bacteria: 5–30 μm For enzymes: 10–100 nm	> μm	Depending on applications	> μm
PSD[a]	Narrow	Narrow (depending on application, bimodal)	Narrow (depending on applications, bimodal)	Narrow	Narrow	Insensitive
SSA[b]	Depending on applications	1–2000 m^2/g	> 1 m^2/g	Depending on pore size	> 1 m^2/g	Insensitive
Permeability	High	Depending on applications	Depending on applications	High	Depending on applications	Insensitive
Mechanical strength	High	Depending on applications	High	High, depending on applications	Depending on applications	High
Others	Chemical resistance	Catalysis function	Appropriate surface potential		Sensing function Appropriate surface condition	Chemical and wear resistance

[a] PSD = pore size distribution.
[b] SSA = specific surface area per unit volume

water by using porous materials of pore size 0.1–100 μm, depending on the size of particles to be removed. Porous materials with micron-scale pores are often made by sintering.

Nowadays, ecological problems and energy-saving efforts are keen industrial issues. The design of industrial processes may be improved in order to overcome these issues, but these design improvements have unavoidable limitations. More improvement of processes can be achieved by developing and improving the materials used in the processes. In the case of filtration of high temperature gas, ceramic filters can be used at higher temperatures than metallic ones. Engineering design will inevitably be changed if new materials are used, as occurred in electronics owing to the introduction of semiconductors.

Recently porous ceramics have been developed with high-temperature stability, strength, catalytic activity, erosion resistance and corrosion resistance. These excellent properties of porous ceramics make it possible to use them in severe operating conditions, compared with the porous polymers, glasses and metals. In spite of these excellent properties, the potential of porous ceramics has not been fully realized because of their well-known problems [2]. These include:

1. brittleness,
2. absence of integrated materials and manufacturing system,
3. lack of pore size control,
4. lack of continuous processing methods,
5. use of processing/sintering aids that limit toughness,
6. absence of joining technologies, and
7. absence of a model relating pore structure to mechanical properties.

Problems 1, 2, 4, 5 and 6 are also applicable to dense ceramics. To overcome these difficulties, researchers of porous ceramics have to approach scientifically the technological problems of materials, from powder production of raw materials to quality control of final products.

1.2 CLASSIFICATION OF POROUS MATERIALS

Many porous materials have been used in many applications. They can be classified by different criteria such as pore size, pore shape, materials and production methods. Classification by pore size and by pore shape is useful in considering applications of porous materials.

Figure 1.3 shows the relationship between pore size and applications of porous materials, and is based on the reports by Chan and Brownsten [3] and Yamamoto [4]. Note that a remarkably wide range of pore sizes from atomic size to millimeters is required in applications of porous materials. These

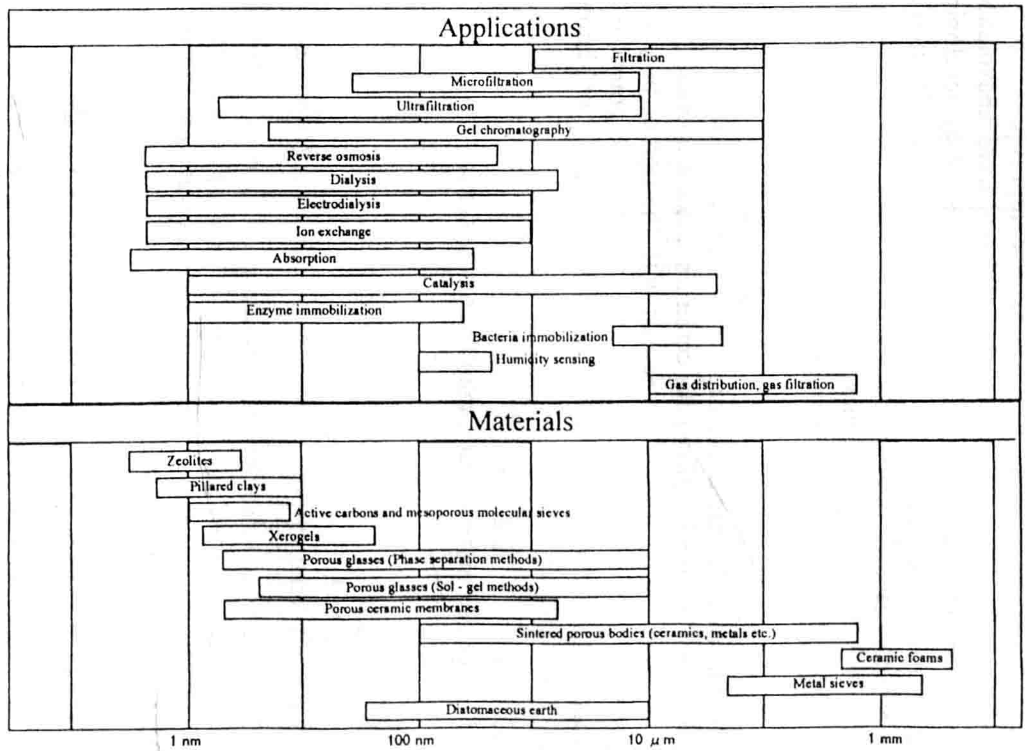

FIGURE 1.3 The relationship between pore size and applications of porous materials. This figure is derived from the reports by Chan and Brownsten [3] and Yamamoto [4]. Different applications require different pore sizes, which can range from the atomic scale to millimeter scale.

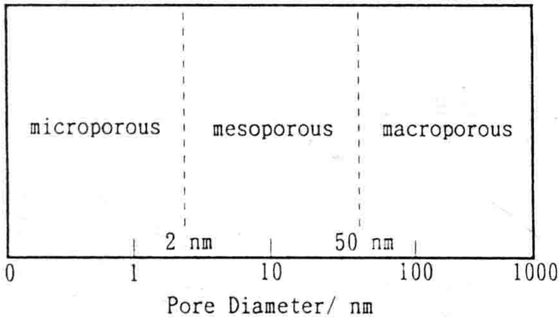

FIGURE 1.4 Classification of porous materials based on pore size. The International Union of Pure and Applied Chemistry (IUPAC) has recommended specific nomenclature for porous materials: microporous (pore diameter < 2 nm), mesoporous (2 nm < pore diameter < 50 nm), or macroporous (50 nm < pore diameter). Based on [2].

porous materials are produced by various methods in order to meet the required pore size. The International Union of Pure and Applied Chemistry (IUPAC) has recommended specific nomenclature [2]. Based on these recommendations, the classification of porous materials by pore size is shown in Figure 1.4. Most sintered porous materials are classified as macroporous materials.

Table 1.2 summarizes the possible different configurations of pore geometry and different production methods of porous materials. Figure 1.5 illustrates pore geometry. The properties of porous materials depend on the nature of the materials, pore geometry, porosity, and pore size. Table 1.2 also lists the properties of porous materials with pore geometry. For example, the mechanical strength of a porous material is a function of the nature of a material, porosity, its pore size and pore geometry. Open porosity relates to the volume ratio of open pores and solid parts, so that it can be understood easily that the pore configurations of foam have higher open porosity than openings among particles. In actual cases, pore geometry is complex, as shown in Figure 1.1. There are porous materials with not only combinations or intermediates of pore geometry, but also individual special geometry of materials. This complexity makes it difficult to understand the properties of porous materials.

As a new approach to understanding pore geometry, fractal analysis of pore geometry has been developed. Tsuchinari *et al.* evaluated fractal dimension aspects of pore shape and investigated the relationship between the fractal dimension and permeability [5, 6]. The fractal dimension of pore shape changes depending on the amounts of sintering additives [5], sintering