

1 Introduction

Materials science is one of the most important subjects of sciences and technologies in the twenty-first century. Its importance has been emphasized by the governments via formulating their national policies in the developed countries, as well as many developing countries. New materials not only greatly promote the developments of industry, agriculture, medicine, environment, aerospace, and information science and so on, but may also demonstrate some revolutionary changes of their forms and novel functions, and thereby bring about tremendous changes to human life. Unlike the traditional materials science dominated by metals and metallurgy, modern materials science has become a typical interdisciplinary field. Any major development of new materials, for example high-temperature superconductors, novel catalysts, many functional nanomaterials, etc., requires collaboration of scientists from many different disciplines.

Porous silicates are a huge family of inorganic materials, possessing open-pore frameworks and large surface area (including the inner and outer surfaces). Based on IUPAC, porous materials according to the pore diameter can be classified into three categories: those with pore diameters less than 2 nm are microporous; pore sizes between 2 and 50 nm are mesoporous; and pore diameters greater than 50 nm are called macroporous materials. “Nano” is a concept with the size from 1 to 100 nm; therefore all the above three kinds of porous materials can be designated as nanoporous materials. However, in most of the literature, nanoporous materials refer to mesoporous or/and microporous materials.

Conventional microporous molecular sieves have a uniform sieve-like pore structure and large surface area. They are excellent adsorbents, catalysts, carriers (catalyst supports), ion-exchange agents and nanoreactors. They have been extensively used in chemical, petrochemical, gas separation industries, and other fields. The vast majority of such materials possess perfect atomic crystal structures, that is, the position of each atom in the unit cell is fixed. For example, in a zeolite A with a cubic (space group $Pm\bar{3}m$) structure (unit cell parameter of 11.9 nm) (see Figure 1.1a), 24 of the silicon and aluminum atoms occupy (24 k) lattice sites (atomic coordinates: 0.370, 0.183, 0); and 48 of the oxygen atoms occupy the positions of the (24m) (0.110, 0.110, 0.345), (12h) (0, 0.220, 0.5) and (12i) (0.289, 0.289, 0) [1]. Uniform pore arrays in microporous molecular sieves offer good spatial

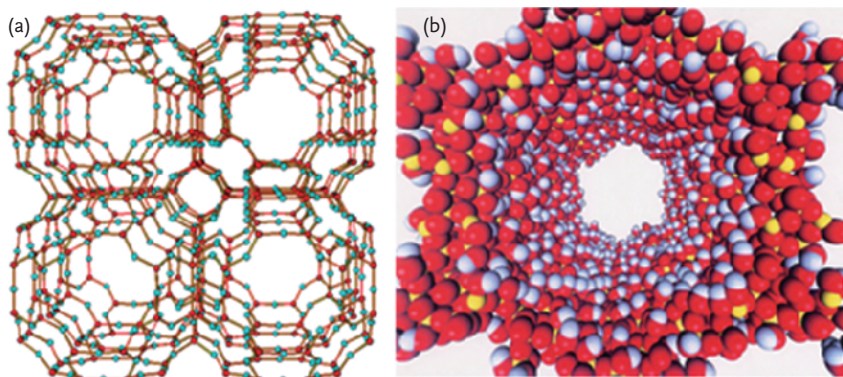


Figure 1.1 Structural models of microporous molecular sieve zeolite LTA (a) and mesoporous aluminosilicate MCM-41 (b).

selectivity (shape selectivity) in catalysis. However, the pore sizes of zeolites, microporous molecular sieves are typically less than 1.3 nm, and therefore limit the applications that involve transfer and conversion of macromolecules. Consequently, the creation and development of mesoporous materials have become an important branch in catalysis and inorganic chemistry. In addition, the nanoscale mesopores can be utilized as the hard template for fabricating other nanomaterials, which offer good opportunities in exploring new applications.

Mesoporous materials with ordered pore arrays became a hot research topic in 1992, when Mobil Oil Corporation (Mobil) scientists first reported the M41S series of mesoporous silica materials [2, 3]. Long-chain cationic surfactants were used as a structure-directing agent to synthesize ordered mesoporous (alumino-) silicate materials. However, this approach was not a brand new method, it was actually demonstrated 20 years earlier. In a patent by French scientists in the early 1970s, a method was recorded to tune the density of silica gels by using long-chain cationic surfactants. Following the synthesis batch mentioned in the patent, workers could easily prepare 2D hexagonal mesoporous silica that is exactly the same as the most famous MCM-41 (Figure 1.1b). However, the patent did not produce enough attention, mainly due to the lack of XRD and electron microscopy characterization data. Japanese scientists, earlier than 1990, also started the synthesis of mesoporous materials. They utilized a cationic surfactant to support a so-called Kanemite layered clay. The clay structure was destroyed in a high-alkalinity solution (high concentration of NaOH). A new mesostructured material was generated, which was later named as FSM-16 mesoporous silica. Once again, attention was not given because the products were mixed phases, no TEM images and XRD patterns were provided. Furthermore, at that time, because of the lack of indepth understanding on formation mechanisms, the concept of “mesoporous” was not realized. On the other hand, Mobil researchers not only developed a family of mesoporous materials with ordered pore arrangements, but also proposed a

general “liquid-crystal templating” mechanism with detailed synthesis method. A new inorganic synthetic chemistry research area began to rise.

It has been well known that dealumination can produce mesopores in zeolites. However, both the pore sizes and numbers are very dependent on the dealumination conditions, so that the mesopores are disordered and out of control. Layered materials such as clays and phosphates, can be pillared by large molecules including polycations (such as alumina oligmers Al_{13}^{7+}) and silicates, and accordingly mesopores are generated. These materials are so-called pillared clays or pillared molecular sieves. Clays include vermiculites, montmorillonites, and typical phosphates such as zirconium phosphates. Mesoporous pillared clays were considered to be the future catalysts for heavy-oil cracking. Unfortunately, it was later discovered that the drawbacks, including weak surface acidity, easy coke deactivation, and low thermal stability, make them unfeasible for catalytic cracking. In addition, the pillars are amorphous and irregularly arranged despite the ordered atomic crystals of clays and phosphates, which leads to nonuniform mesopore sizes and disordered pore arrangement. Although the aluminosilicate gels with narrow pore-size distribution prepared from a well-controlled sol-gel process can serve as pillars, the disordered pore arrays are maintained and cannot be avoided.

Workers have witnessed a rapid development in ordered mesoporous materials, including the new mesostructures and compositions, the formation mechanisms, and applications [4]. If we refer to SCI expanded system (The Web of Science) and use “mesoporous” as the subject, we can clearly find a predominantly increasing publication numbers (Figure 1.2). This demonstrates the emerging development trends in this field. The establishment of the International Mesostructured Materials Association (IMMA) has promoted the development of mesoporous materials.

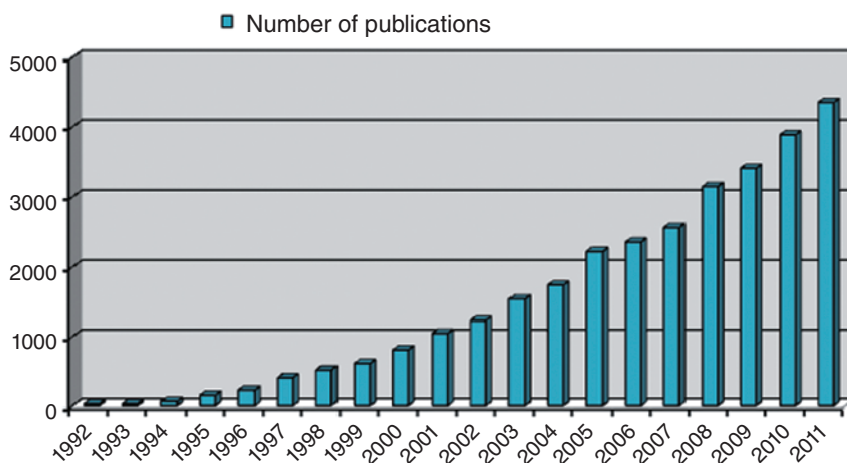


Figure 1.2 The published paper numbers originated from the SCI expanded system using mesoporous as a subject since 1992.

The theme of the 13th International Zeolite Conference held in July 2001 in Montpellier, France, was “zeolites and mesoporous materials in the dawn of the 21st century”. Mesoporous molecular sieves have since been officially accepted as an important branch of the zeolite materials in IZA.

So far, dozens of mesoporous molecular sieves have been synthesized, most of them have ordered mesostructures and pore arrangements. Since the first series of mesoporous silica materials M41S reported by Mobil Corporation, the most striking materials are explored by the Stucky group from University of California, Santa Barbara, and so-called SBA series. In addition, scientists from various countries, including Japan, Korea, China, Canada, UK, and France have contributed much to the mesoporous families. Among them, the KIT series from a Korea scientist, Prof. Ryoo’s group in KAIST and the FDU series by Prof. Zhao’s group in Fudan University, China have been extensively investigated.

Despite crystalline frameworks as one of the major goals, almost all mesoporous silicates possess amorphous pore-wall structures, which limit their applications in petrochemistry, optoelectronic devices, etc. In terms of the structure, mesoporous materials are “amorphous”, compared to atomic crystals. The general designation of “ordered mesoporous materials” is basically referred to the pore space structure instead of the traditional crystal structures in atomic scale. Workers follow the concept of “crystal”, “space group” to describe the pore structure of mesoporous materials, only because no more appropriate terms are available. Recent studies have revealed that skeletons for some mesoporous materials have fine structures, including micropore distribution, ordered domain boundaries in nanoscale, ordered atomic arrangement in framework by adjusting the compositions, etc. Deep understanding of their microstructures will attract increasing attention.

It is necessary to review the research on mesoporous materials in the past decade. The purpose of this book is a comprehensive review of this field, and together with it, a summary. We hope that this book can be a good reference for researchers, scientists, graduate and undergraduate students in chemistry, chemical engineering, physics, materials, who are interested in mesoporous materials.

References

- 1 Reed, T.B., and Breck, D.W. (1956) *J. Am. Chem. Soc.*, **78**, 5972.
- 2 Kresge, C.T., Leonowicz, M.E., Roth, W.J., Vartulli, J.C., and Beck, J.S. (1992) *Nature*, **359**, 710.
- 3 Beck, J.S., Vartulli, J.C., Roth, W.J., Leonowicz, M.E., Kresge, C.T., Schmitt, K.D., Chu, C.T.W., Olson, D.H., Sheppard, E.W., McCullen, S.B., Higgins, J.B., and Schlenker, J.L. (1992) *J. Am. Chem. Soc.*, **114**, 10834.
- 4 Ying, J.Y., Mehnert, C.P., and Wong, M.S. (1999) *Angew. Chem. Int. Ed.*, **38**, 56.