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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.^[1] 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,^[2] 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.^[3,4] 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:^[3]

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.^[5] 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

hydrocarbon conversion. From then on, a variety of zeolites with an Si/Al ratio of 2~5, i.e., 'intermediate silica' zeolites which include mordenite, zeolite L, erionite, chabazite, clinoptilolite, zeolite Ω , etc, have been synthesized. At the beginning of the 1960s, scientists at Mobil Corporation started to use organic amines and quaternary alkylammonium cations as templates in the hydrothermal synthesis of high-silica zeolites, and this is considered a milestone in the progress of zeolite synthesis. In 1972, Argauer and Landelt synthesized the first important member of the pentasil family, ZSM-5, using Pr_4NCl or Pr_4NOH as the template at 120 °C, whereas in 1973, Chu synthesized ZSM-11 using Bu_4N^+ as the template. In 1974, Rosinski and Rubin prepared ZSM-12 using Et_4N^+ as the template, followed by the syntheses of ZSM-21 and ZSM-34 in 1977 and 1978; later on, Wadlinger and Kerr synthesized high-silica zeolite beta (BEA).

The pentasil family, which includes high-silica zeolites with hydrophobic surfaces and interconnected two-dimensional (2-D) 10-membered-ring channels, has played an important role in shape-selective catalysis since its inception. In 1970, Flanigen at UCC first synthesized pure-silica forms of ZSM-5 (silicalite-I) and ZSM-11 (silicalite-II), which were the end members of the pentasil family. Meanwhile, the rapid progress in synthesis of high-silica zeolites facilitated the study of the secondary synthesis of zeolites. Some high-silica zeolites such as zeolite Y (Si/Al > 3), which were difficult to synthesize directly, could be prepared from zeolites with medium Si/Al ratios through steam treatment or de-alumination in framework by reaction with Si. For instance, ultra-stable zeolite Y (USY), high-silica mordenite, erionite, BEA, and clinoptilolite were all successfully synthesized in this way. In the past 25 years, the emergence of zeolites with low (Si/Al = 1.0~1.5), medium (Si/Al = 2.0~5.0), and high Si/Al ratios (Si/Al = 10~100), as well as pure-silica zeolites, facilitated the study of both the structure and property of molecular sieves and porous compounds, and promoted their applications.

The increase in type and structural diversity of zeolites, as well as deep insight into zeolite properties such as thermal stability, acidity, hydrophobicity/hydrophilicity of surfaces, and ion-exchange capacity, has led to application of a series of zeolites in industry. These zeolites include synthesized ones such as zeolite A (Na, Ca, K), zeolite X (Na, K, Ba), zeolite Y (Na, Ca, NH_4), zeolite L (K, NH_4), zeolite Ω (Na, H), zeolon (MOR-H, Na), ZSM-5, zeolite F (K) and zeolite W (K), and natural ones such as mordenite, chabazite, erionite and clinoptilolite. These materials have been widely used as commercial adsorbents for drying and purification of gases and for bulk separation of, for example, normal-/iso-paraffins, isomers of xylenes and olefins, and O_2 from air, as catalysts for petroleum refining and petrochemistry, and as ion exchangers. Because of their excellent ion-exchange capacities, zeolites A and X can be used as auxiliary agents in the detergent industry, in radioactive waste treatment and storage, and in the treatment of industrial liquid wastes.

1.1.3 From Zeolites to Aluminophosphate Molecular Sieves and Other Microporous Phosphates

In 1982, Wilson, Lok, and Flanigen et al. successfully synthesized a novel family of molecular sieves, that is, microporous aluminophosphates $\text{AlPO}_4\text{-}n$.^[6] The discovery of $\text{AlPO}_4\text{-}n$ is regarded as a milestone in the development of porous materials. Not only

were large-, medium-, and small-pore AlPO_4 - n molecular sieves prepared, but also SAPO- n ($\text{S} = \text{Si}$), MeAPO- n ($\text{Me} = \text{Fe}, \text{Mg}, \text{Mn}, \text{Zn}, \text{Co}, \text{etc}$), MeASO- n , ElAPO- n ($\text{El} = \text{Ba}, \text{Ga}, \text{Ge}, \text{Li}, \text{As}, \text{etc}$) and ElAPSO- n could be obtained through introduction of elements other than Al and P into the microporous frameworks of AlPO_4 - n . At present, the aluminophosphate-based family of microporous compounds has over 200 members. These compounds were synthesized through the crystallization of Al, P, and other element sources together under hydrothermal or solvothermal conditions. Differing from the aluminosilicate molecular sieves, normally the AlPO_4 -based compounds must crystallize in the presence of templates or structure-directing agents. There are a large number of structure types for AlPO_4 -based microporous materials and the compositions of these materials also vary to a considerable degree.^[7] Except for a few members which are isostructural with zeolites, most aluminophosphate molecular sieve structures are novel, and their elementary compositions are quite different from those of conventional zeolites containing only silicon and aluminum. By 1986, 16 elements had been successfully incorporated into frameworks of aluminophosphate molecular sieves. The incorporation of heteroatoms into aluminophosphates has played an important role in enhancing the diversity of structures and compositions of microporous compounds and molecular sieves.

Since 1982, two major accomplishments have been achieved for aluminophosphate-based molecular sieves. One is the discovery of various aluminophosphate microporous compounds with an Al/P ratio less than unity.^[8] For instance, JDF-20 ($[\text{Et}_3\text{NH}]_2[\text{Al}_5\text{P}_6\text{O}_{24}\text{H}]\bullet 2\text{H}_2\text{O}$) is a microporous aluminophosphate with the largest aperture size (20-membered ring, $14.5 \times 6.2 \text{ \AA}$); AIPO-CJB1 ($[(\text{CH}_2)_6\text{N}_4\text{H}_3][\text{Al}_{12}\text{P}_{13}\text{O}_{52}]$) is the first microporous aluminophosphate with Brönsted acidity. These 3-D microporous aluminophosphates with anionic frameworks are different from AlPO_4 - n with a neutral framework constructed by the alternation of AlO_4 and PO_4 tetrahedra. The anionic frameworks are constructed by Al-centered units (AlO_4 , AlO_5 , AlO_6), and $\text{P}(\text{O}_b)_n(\text{O}_t)_{4-n}$ tetrahedra (b = bridging, t = terminal, $n = 1 \sim 4$), and this construction manner results in rich structural chemistry. The existence of terminal oxygen of P—OH and P=O groups strengthens the nonbonding interaction between the framework and template molecules, rendering the templates hard to remove. The other accomplishment is the synthesis of other families of metal phosphates, including zinc, gallium, titanium, iron, cobalt, nickel, vanadium, and molybdenum phosphates.^[9] The compositional and structural diversity of aluminophosphates and their derivatives leads to potential applications in the fields of adsorption, separation, formation of host–guest advanced materials, redox catalysis, chiral catalysis, and macromolecular catalysis.

1.1.4 From 12-Membered-ring Micropores to Extra-large Micropores

For nearly 50 years, chemists failed to synthesize molecular sieves with channels larger than 12-membered rings. It was not until 1988 that Davis et al. successfully synthesized the first aluminophosphate molecular sieve, VPI-5 ($(\text{H}_2\text{O})_{42}[\text{Al}_{18}\text{P}_{18}\text{O}_{72}]$), with 18-membered-ring apertures ($12.7 \times 12.7 \text{ \AA}$).^[10] The synthesis of VPI-5 is another milestone in the development of microporous materials.

It has been found that, except for a few silica or germanium oxide porous compounds, most of the microporous molecular sieves with a large aperture are metal phosphates with

1-D channels. The structures of large-pore microporous materials share the following common features:

1. The frameworks are constructed by metal-centered primary building units with various coordination states, such as $[\text{AlO}_4]$, $[\text{AlO}_6]$, $[\text{GaO}_4]$, and $[\text{GaO}_4(\text{OH})_2]$;
2. There are terminal groups in the frameworks, such as $\text{P}=\text{O}$, $\text{P}-\text{OH}$, and $\text{Al}-\text{OH}$, which make the structures less stable than zeolites and aluminophosphate molecular sieves with (4,2) networks. These terminal groups also favor the formation of interrupted frameworks, such as cloverite and JDF-20;
3. The structure-directing agents used in the synthesis of these compounds usually possess multiple amino groups, long chains, or large molecular weights, and occasionally the synthesis also involves F^- ions. Usually, F^- ions exist in the open frameworks and are located between two metal centers as bridging atoms or inside the double 4-ring (D4R) cages. On the other hand, the oxygen atoms in the terminal groups normally have strong non-bonding interactions with structure directing agents.

On the basis of these structural features, it is easy to understand why zeolites constructed by Si and Al cannot have extra-large pores. Nevertheless, pure-silica zeolites with 14-membered rings, i.e. CIT-5 and UTD-1, have been synthesized recently, and further investigation into crystallization mechanisms in combination with the vast experimental data available and with theoretical simulation and computation may help us to rationally design and synthesize extra-large microporous aluminosilicate molecular sieves with special channels such as multidimensionally interconnected and chiral ones.

The discovery of extra-large microporous materials facilitates research on the catalytic reaction of large and medium molecules, and also promotes host-guest chemistry and related advanced materials.

1.1.5 From Extra-large Micropores to Mesopores

The discovery of mesoporous materials, which usually refer to materials with ordered pores of diameter size 2~50 nm, is another leap in the development of molecular sieves and porous materials.

In fact, the synthesis of ordered mesoporous materials began as early as 1971. Kuroda et al. also started to synthesize mesoporous materials before 1990. However, it was not until 1992, when Kresge et al. reported the discovery of M41S materials, that mesoporous compounds started to attract real increasing attention.^[11,12] Using surfactants as templates, scientists at Mobil synthesized a series of mesoporous compounds, the M41S family, including MCM-41 (hexagonal), MCM-48 (cubic), and MCM-50 (layered). This discovery is comparable with the other great accomplishments in the history of zeolite science and technology; for instance, the synthesis of ZSM-5 also by Mobil scientists. For microporous zeolites used as catalysts, the reactants in their pores and/or channels are usually smaller than 10 Å due to the microporous features of the catalysts, even after modification of the channels. However, the successful synthesis of mesoporous materials with channels of 2~50 nm might break this limitation.

Mesoporous materials have the advantages of ordered mesoporous channels with size of 2~50 nm, as well as very large specific surfaces and pore volumes. However, since the

channels in these materials are surrounded by amorphous walls, mesoporous materials have less thermal and hydrothermal stability than do microporous molecular sieves. Recently, the synthesis of SBA-15, MAS-7, and MAS-9 showed that the stabilities of mesoporous materials could be enhanced. Another advantage of mesoporous materials is that there are far fewer restrictions on their composition. Theoretically, any oxides, oxide composites, inorganic compounds, or even metals could form mesoporous materials. In fact, many oxides, such as TiO_2 , ZrO_2 , Al_2O_3 , Ga_2O_3 , MnO_2 , and other non-silicon oxides, have been successfully synthesized in a mesoporous form. Recently, many highly ordered mesoporous materials have been obtained, and these include MCM-41 ($P6m$), MCM-48 ($Ia3d$), MCM-50 (layered), FSM-16, SBA-1, SBA-6 ($Pm3n$), SBA-2, SBA-12 ($P6_3/mmc$), SBA-11 ($Pm3m$), and SBA-16 ($Im3m$). Low-ordered ones such as HMS, MSU- n , and KIT-1 have also been reported.

According to their compositions and structures, the periodic mesoporous materials can be divided into 6 categories:

1. Mesoporous silicon oxides with different channel networks, sizes, and shapes;
2. Mesoporous silicon oxides with modified surfaces;
3. Mesoporous silicon oxides with organic compositions;
4. Mesoporous silicon oxides with other metal atoms on their channel walls;
5. Inorganic mesoporous materials without silicon;^[13]
6. Mesoporous materials without oxygen.

There will be many more categories if we consider specific polymorphs. The rapid development and constant improvement of mesoporous materials as well as the progress in related research areas will render mesoporous materials more widely applicable.

1.1.6 Emergence of Macroporous Materials

Ordered macroporous materials have special optical features due to their pore diameters. Since the synthesis of macroporous materials has just started, there are no general synthetic strategies for this type of materials at present, and hence only a few examples will be mentioned here.

By using modified colloidal particles as templates, silicon oxide macroporous materials with uniform submicrometer-sized pores can be synthesized.^[14] Modified polystyrene emulsion microspheres (200~1000 nm) can be electronegative (sulfates) or electropositive (amidines). After these microspheres are packed in an orderly fashion, they can interact with surfactants and silicon oxides to form macroporous solid composites, and further to form macroporous materials after the removal of the templates by calcination. The sizes of the macropores in the products range from 150 to 1000 nm. Macroporous TiO_2 can also be prepared in a similar way.

Mineralization on hyphae can also generate macroporous materials.^[15] Using this method in the synthesis of mesoporous materials, mesoporous and macroporous composites can be obtained. The long channels in these composites are parallel to each other. The pores are at a micron level, and the thickness of the walls ranges from 50 to 200 nm.

By using colloid as the template, inorganic oxides can be deposited on the outer surface of the colloidal droplet to form macroporous materials with apertures of 50 nm

to several microns in size.^[16] Oil can form uniform droplets in formamide colloid and can further be used as the template. Polymers, such as the triblock copolymer formed by ethylene glycol and propylene glycol, can stabilize this colloid. Many macroporous materials have been synthesized using this method, such as macroporous titanium oxides, silicon oxides, and zirconium oxides.

1.1.7 From Inorganic Porous Frameworks to Porous Metal-organic Frameworks (MOFs)

From natural zeolites to the recently discovered meso- and macro-porous materials, the ordered porous frameworks are all constructed by inorganic species. However, in the past ten years, a new family of porous compounds composed of metal-organic frameworks (MOFs) has attracted enormous attention. The main reason is that the poor thermal and chemical stability of MOFs has been somewhat improved. In addition, the discovery of some advantages of MOFs that are lacking in molecular sieves and mesoporous materials has also stimulated the research on MOFs.

In 2001, Chen et al. synthesized a coordination polymer, $\text{Cu}_3(\text{BTB})_2(\text{H}_2\text{O})(\text{DMF})_9(\text{H}_2\text{O})_2$ (MOF-14) (BTB-4,4',4''-benzene-1,3,5-triyltribenzoic acid), from which the DMF could be removed by heating at 250 °C under inert gas flow.^[17] The N_2 and Ar adsorption isotherms of MOF-14 are of type-I, confirming its microporous structure. The adsorption isotherms of MOF-5 are also characteristic of type-I. Adsorptions of CO , CH_4 , CH_2Cl_2 , CCl_4 , C_6H_6 , C_6H_{12} and *m*-xylene in these materials are all reversible, as in zeolites. However, the pore volume for MOF-14 is 0.53 cm³/g whereas the specific surface area is 1502 cm²/g, and these two values are distinctly higher than the corresponding ones for inorganic microporous compounds. In 2002, Yaghi and coworkers reported the synthesis of a microporous compound (MOF-5), $\text{Zn}_4\text{O}(\text{R}^1\text{-BDC})_3$ ($\text{R}^1 = \text{H}$), by the crystallization of $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and 1,4-benzenedicarboxylate (terephthalate (BDC) in *N,N*-diethylformamide (DEF) solvent at 85~105 °C.^[18] The microporous framework of this compound is constructed by the primary building unit of the $[\text{Zn}_4\text{O}(\text{CO}_2)_6]$ octahedron and bridging R groups. Yaghi and coworkers used different BDC derivatives and related naphthalene -2,6-dicarboxylic acid (2,6-NDC) and triphenyldicarboxylate (TpDC) compounds to obtain a series of microporous compounds with various pore diameters (3.8~28.8 Å), and they found that the pore diameter varies with R. The free porous volume increases remarkably from $\text{C}_5\text{H}_{11}\text{O-BDC}$ (55.8%) to TpDC (91.1%), both of which are much larger than the free volume of the zeolite FAU. The adsorption properties of the compound are similar to those of zeolites.

MOF-6 has a great adsorption capacity for CH_4 (240 cm³/g; 36 atm, 298 K), which could be exploited for storage and transportation of CH_4 . In addition, it has been demonstrated that a number of MOF compounds exhibit promising H_2 -storage capacities. Furthermore, other groups, such as -Br, - NH_2 , - OC_3H_7 , - OC_5H_{11} , - C_2H_4 , and - C_4H_4 , could be added into the R groups. Therefore, the MOFs may be functionalized to meet special catalysis or adsorption demands. Conventional inorganic porous compounds have no such advantages, and therefore, in a sense, the emergence of MOFs has broadened the applications of porous materials and facilitated their development.

1.2 Main Applications and Prospects

As mentioned earlier in this chapter, it is the social demands and wide applications of porous materials that keep them under continuous exploration. From natural zeolites to synthesized ones, from low-silica zeolites to high-silica ones, from aluminosilicate molecular sieves to aluminophosphate-based ones, from extra-large microporous materials to mesoporous materials, and from inorganic porous frameworks to MOFs, together with newly emerging macroporous materials, all these porous materials have ordered and uniform porous systems.

Here, we would like to take ZSM-5 as an example to illustrate the relationship between structure and function. ZSM-5 has an interconnected 2-D 10-membered-ring channel system ($[100] \ 10 \ 5.1 \times 5.5^* \leftrightarrow [010] \ 10 \ 5.3 \times 5.6^*$). Since the Si/Al ratio of ZSM-5 can be varied from 10 to infinity as found in pure-silica silicalite-I, the type, acidity, and distribution of acidic sites can also be controlled accordingly. Furthermore, because of its special channel system, ZSM-5 may function very differently for different molecules. For example, the diffusion, the adsorption/desorption, the reaction rate, and the formation of intermediate and final product of molecules may vary to a great extent. ZSM-5 has been widely used in petroleum refining as a catalyst with good shape-selectivity.

Since 1950s, there have been three traditional fields of application for molecular sieves and porous materials: 1) separation, purification, drying and environment treatment process; 2) petroleum refining, petrochemical, coal and fine chemical industries; 3) ion-exchange, detergent industry, radioactive waste storage, and treatment of liquid waste. In addition to the traditional application fields, zeolites and related porous materials may also find applications in new areas such as microelectronics and molecular device manufacture.

1.2.1 The Traditional Fields of Application and Prospects of Microporous Molecular Sieves

Since the first application of NaA in the separation of normal and isoalkanes by the Linde company in the 1950s, and X- and Y- zeolites as catalysts for cracking reactions of hydrocarbon conversion in the 1960s, NaA, NaX, and NaY have been widely used in the petroleum industry in reactions such as cracking, alkylation, isomerization, shape-selective reforming, hydrogenation and dehydrogenation, methanol-to-gasoline conversion (MTG), etc. These porous materials have also been extensively used in the detergent industry and in a variety of adsorption and separation processes such as the drying, the removal of CO₂ from, and the desulfurization for natural gas, and the separation of xylene isomers, of alkenes, and of O₂/N₂ from air.^[5] In the past half century, molecular sieves have played increasingly important roles as catalysts in the petroleum refining, petrochemical, and other chemical industries. According to the statistics studies conducted by Marcilly in 2001, the annual output of synthesized molecular sieves exceeded 1.6 million tons, and the annual output of natural zeolites rose to 0.3 million tons (about 18% of the total output).^[19] The value of the annual gross product of synthesized molecular sieves exceeded 2.0 G\$. Furthermore, the value of annual gross product of other catalysts, adsorbents, and ion-exchangers related to molecular sieves and their

derivatives greatly exceeded the values of molecular sieves themselves.^[5] Despite this, there are still many prospects for development of molecular sieves in the above three main traditional fields. First, there are 174 known molecular sieve frameworks. Considering the differences in their composition, there should be more space for further development. However, currently only a few frameworks, including LTA, FAU, MOR, LTL, MFI, BEA, MTW, CHA, FER, AEL, and TON, have been widely used in industry. Second, at present, molecular sieves are mainly used in petroleum related industries and intermediary chemistry processes. It is believed that, in the next 20 years, molecular sieves will be more widely used in catalysis, adsorption, and separation, with the development of petroleum refining, petrochemical, intermediary chemical, and fine chemical industries.

According to Marcilly's proposal in 2001, in the next 20 years, there will be several new application fields in petroleum refining and petrochemical industries:^[19]

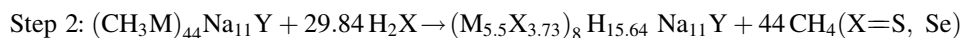
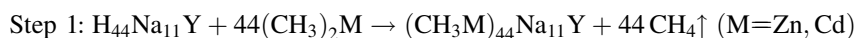
- FCC (fluid catalytic cracking): to develop novel molecular sieves which are comparable with or better than ZSM-5 in shape-selectivity of light olefins ($C_3=$ – $C_5=$).
- HDC (hydrocracking): to develop novel zeolitic catalysts dedicated to the production of middle distillates, integrating both the activity and stability of zeolites.
- Aliphatic alkylation: to develop novel molecular sieves with a three-dimensional open framework and catalytic activity higher than BEA.
- Alkane isomerization of paraffins: to develop novel molecular sieves with high selectivities (2 branches or more) for isomerizations of C_7 – C_9 middle paraffins in gasoline (petrol).

In addition, in the field of dewaxing (gas oils, HDC residues, lubricating oil, etc.), synthesis of novel molecular sieves with better adsorption and separation abilities is highly desired. In the past 20 years, thanks to the discovery of many molecular sieves with new compositions and structural features [secondary building units (SBUs) and pores], there have appeared a number of new application fields for molecular sieves, such as basic catalysis, extra-large microporous molecular sieve catalysis, redox catalysis, asymmetric catalysis, and dual- and multi-functional catalysis.^[20] All of these will lay a further solid foundation for the development of molecular sieves in catalysis, adsorption, and separation.

1.2.2 Prospects in the Application Fields of Novel, High-tech, and Advanced Materials

In molecular sieves and microporous crystalline compounds, there exist channels with apertures of 12-, 14-, 16-, 18-, 20-, or 24-membered rings, and cages or cavities constructed by interconnected 2- or 3-D channels. For example, the FAU cavity (11.8 Å) is constructed by the intersection of three 12-membered-ring channels; the α cage (11.4 Å) in LTA by the intersection of three 8-membered-ring channels; the EMT cage (13.5 Å) in EMC-2 by the intersection of three 12-membered-ring channels; the AFS cage (14.0 Å) in MAPSO-46 by the intersection of a 12-membered-ring channel and two 8-membered-ring channels, the DFO cage (15.5 Å) in DAF-1 by the intersection of 12-, 8-, and 10-membered-ring channels; the CLO cavity (30 Å) by the intersection of 20- and 8-membered-ring channels. These large cages or cavities can act as favorable reaction venues. For example, through the

so-called ‘ship-in-bottle’ synthetic strategy,^[21] a dye composite can be prepared in the cavities of FAU or channels of $\text{AlPO}_4\text{-5}$,^[22,23] and through using nanoscale chemical synthesis techniques, Cd_4S_4 semiconductive nanometer-sized clusters can be obtained in the FAU cages.^[24] The overall process takes two steps:



Another approach to the preparation of zeolite composite materials is to add on some complicated molecules, complexes, metal-organic compounds, supermolecules, clusters, or polymers with specific functions in the nanometer-sized cages or channels in molecular sieves through grafting or other reaction routes. As Pool mentioned in 1994, ‘zeolites – crystalline materials riddled with nanometer-sized cavities – can exert exquisite control over chemical reactions and produce devices on the smallest scale’.^[25] In the mid -1990s, Ozin, Herron, Bein,^[26] and others extensively studied the preparation of quantum dot arrays, molecular wires, and magnetons inside porous materials. They also carried out a variety of basic research on microdevices, molecular circuits, molecular switches, sensors, and optical memory. In the past decade, with the development of meso- and macro-porous materials and the successful preparation of molecular sieve membranes and millimeter- to centimeter-sized single crystals, the application of novel advanced materials based on porous materials has undergone great progress. The following are several examples of progress achieved in recent years. With the aid of poly-(propylene glycol), Fan et al. synthesized porous materials with low dielectric constant ($k = 1.3$),^[27] which are promising for commercial use,^[1] whereas gadolinium zeolite has been used as a radiography reagent for magnetic resonance imaging (MRI).^[1] Another new field of application for microporous materials is the utilization of zeolite-dye composites as microlasing materials.^[1,23] In a word, microporous materials have promising prospects, but there is still a long way to go before the application potential of these materials is fully realized.

1.2.3 The Main Application Fields and Prospects for Mesoporous Materials

Since the ordered mesoporous material MCM-41 was reported in 1992,^[1–3] comprehensive research on the potential applications of mesoporous materials has been carried out, with focus on their catalysis, adsorption, and the preparation of novel advanced materials. Their applications in catalysis have attracted the most intense attention.

The unique properties of mesoporous materials arise from their high specific surface areas ($>1000\text{ m}^2/\text{g}$) and their uniform mesopores (diameters range from 2 to 50 nm).^[11,28,29] In the past decade, mesoporous materials have been widely used in the field of catalysis, such as in petroleum processing, the fine-chemicals industry, and in reactions involving large molecules. For petroleum processing, the conventional catalysts are usually microporous zeolites, such as zeolite Y and ZSM-5. However, with the decrease of petroleum resources in the world and the increase of heavy components in crude oil, the applications of conventional zeolites are more and more restricted due to their small pores. Mesoporous materials have ordered mesopores which might have potential applications in the catalysis of heavy oil processing.^[29] For example, Al-MCM-41 has

shown better catalysis performance in hydrocracking, hydrodesulfurization, and hydrodenitrogenation reactions than do traditional microporous materials.^[30]

In green oxidation reactions, zeolite TS-1 is the typical catalyst. Since the size of its channels ranges from 5 to 6 Å, TS-1 can be used as the catalyst only for benzene and phenol conversion. However, ordered mesoporous titanium silicate materials have pores large enough for the catalytic reactions of bulkier molecules, and this is very important for the production of fine chemicals. For example, for the oxidation reaction of terpineol, Ti-MCM-41 performs much better than do microporous titanium silicate molecular sieves as a catalyst.^[29]

However, on the other hand, the hydrothermal stability and catalytic activity of ordered mesoporous materials are still lower than those of conventional microporous molecular sieves. In recent years, many measures have been taken to solve this problem, such as adding inorganic salts during the synthesis of mesoporous materials,^[31] intensifying the post treatment,^[32,33] using triblock copolymers as templates to obtain thicker channel walls of mesoporous materials,^[28] using neutral surfactants to synthesize mesoporous materials,^[34] using mixed templates,^[35–37] and synthesizing mesoporous materials at high temperatures.^[38] Although these methods more or less help enhance the hydrothermal stability of mesoporous materials, their catalytically active centers are still not comparable with those of conventional microporous molecular sieves. In recent years, scientists have tried to prepare novel ordered mesoporous materials through the self-assembly of nanoparticles consisting of microporous building units and surfactant micelles. Using this approach, both the hydrothermal stability and the catalytic activity of mesoporous materials have been enhanced.^[39–41] For instance, the novel mesoporous titanium silicate material, MTS-9, has shown better catalytic activity than have Ti-MCM-41 and TS-1 in the synthesis of an intermediate product of vitamin E.^[41]

Mesoporous materials have great application potential in novel and high-technology areas as well. They can be used for the stabilization or separation of enzymes and proteins, the degradation of organic wastes, the purification of water, and the transformation of exhaust gas. They can also be used for energy storage. Many functional materials are able to be assembled into mesoporous materials. For example, advanced mesoporous optical materials may be prepared through assembly of laser-generating species or materials with optical activities.^[42–44] Ordered mesoporous conducting polymers may form through polymerization in ordered mesopores followed by chemical removal of the inorganic host.^[45] Ordered mesoporous carbon materials can be obtained through complete mixing of mesoporous materials and a glucoside followed by carbonization and dissolution of the inorganic species.^[46] It has been demonstrated that the mesoporous carbon thus formed exhibits better performance than do conventional carbon materials when used as electrodes of fuel cells.^[47] Through using the ordered channels in mesoporous materials as micro-reactors, fine nanoparticles and other quantum composite materials can be synthesized. Because of small-size or quantum-size effects arising from the confinement of ordered channels, these composite materials exhibit unique optical, electrical, and magnetic properties. For example, it has been demonstrated that modified mesoporous zirconium oxides show unusual photoluminescence at room temperature.

In contrast with carbon nanotubes, mesoporous materials composed of silica and non-silica species exhibit rich surface chemical activity. The ordered channels in mesoporous materials may act as micro-reactors to assemble nanometer-sized homogeneous guest

materials, and, as a result, the application fields of mesoporous materials can be further broadened on the basis of the host–guest effects. Through using stable mesoporous materials as hosts, a variety of inorganic photoelectric nano-sized materials such as Si, BN, SiC, AgI, and AlN, and giant magneto-resistant transition metals such as Ni, Cu, and Co can be prepared. Assembly of some semiconductor clusters with a wide band-gap such as ZnO, ZnS, and CdS into mesoporous materials may greatly increase the fluorescence intensities of the former due to the host–guest interactions and quantum-size effects, implying promising applications of these composites in the field of optoelectronics.

In view of the many applications in the fields of separation, purification, biology, medicine, chemical industry, catalysis, information, environment, energy, and advanced composite materials, it is believed that mesoporous materials will play more important roles in the 21st century as an increasing number of mesoporous materials with advanced functions are designed and synthesized.

1.3 The Development of Chemistry for Molecular Sieves and Porous Materials

In the past half century, with the expansion of structure types and compositions of porous materials, the number of application fields and the total demand for these materials have been continuously growing, and meanwhile, the characterization techniques and instrumentation have been greatly improved. As a result, our comprehension of the chemistry of molecular sieves and porous materials has been deepened to a great extent. Here, we take two main branches in the chemistry of molecular sieves and porous materials as examples to illustrate how zeolite science has been developed.

1.3.1 The Development from Synthesis Chemistry to Molecular Engineering of Porous Materials

In 1968, the first International Zeolite Conference (IZC) was held in London. This was the first international conference focusing on zeolites and microporous aluminosilicates, and various issues related to zeolite research were addressed. Because only a few natural zeolites had been discovered and about 20 synthesized at that time, all the scientific topics about the synthesis of zeolites were focused on the formation of aluminosilicate microporous materials, and the influence of synthetic conditions on reactions and products (for example, crystallization zone diagrams, and crystallization kinetic curves, etc). In the past 30 years, the compositional elements have increased from 2 to over 30, and the framework types have increased to 174 (Feb. 2007). Therefore, it is important to summarize the synthetic chemistry for pore construction, and to conduct an in-depth study on related scientific issues, such as the structures of intermediates and products, the polymerization of reactants, the structures and transformation of sols and gels, nucleation and crystallization, the templating and structure-directing effects, the metastable state and crystal transformation, and the growth of crystals and their aggregation. Inorganic synthesis and preparative chemistry, hydrothermal and solvothermal chemistry, sol–gel chemistry, crystallization and

crystal-growth, host-guest chemistry, and combinatorial chemistry all help to paved the way for the progress of the synthetic chemistry of porous materials or the so-called 'pore-construction' synthetic chemistry.

On the other hand, the most important goal for chemistry is to create new materials. Synthesis and preparative chemistry is the core of chemistry, and it is always on the frontier of development. During the process of development, the research mode of 'synthesis-structure-function' is formed. With the progress of science and technology, it has become a key issue to explore ways to avoid creating new materials without clear goals and to develop rational, effective, and environment-friendly synthetic routes in the 21st century. As chemistry and related disciplines have gained deep insight into and reasonable control over molecules, a new research field, that of molecular design and molecular engineering, has emerged. In recent years, molecular design and engineering has attracted increasing attention in chemistry, materials science, and life sciences, leading the development of chemistry into the age of molecular engineering.

Differing from traditional chemistry, molecular engineering involves the design of structures based on their required function. Molecular engineering focuses on the formation and assembly of primary building units, and, with the aid of computational simulations, gradually realizes the rational synthesis of compounds with specific functions and structures. In some sense, molecular engineering is the chemistry of rational design and synthesis. The key impact of molecular engineering on chemistry is that it broadens the perspectives on function, structure, and synthesis, draws more attention to 'function-structure-synthesis', and promotes a better understanding of structure types and levels beyond molecular structures, rather than excessively focusing on the synthesis of individual compounds.

The channels in porous molecular sieves are rather regular and uniform. The framework features, the secondary building units (SBUs), and the interactions between building units and structure-directing agents for porous materials have been thoroughly investigated. Furthermore, the formation behavior, the crystallization mechanism, and the movement and reactions of reactant molecules in the channels have also been elucidated for over half a century. Therefore, in contrast with other materials, porous materials, with molecular sieves as their representatives, have been well studied in terms of the relations among function, structure, and synthesis. With the aid of computers, ideal porous structure models can be designed to meet specific function requests. Then feasible structures and corresponding synthesis conditions can be selected under the guidance of structure and synthesis databases. Finally, rational synthesis can be achieved using combinatorial chemistry. At present, several research groups, including the authors' own group, in the world have been engaged in this work, and satisfactory results have been obtained in some aspects. Although there is still a long way to go, molecular engineering has pushed the chemistry of porous materials to a new level, and more challenging research directions and scientific issues will come up in this emerging field.

1.3.2 Developments in the Catalysis Study of Porous Materials

The first use of molecular sieves in catalysis occurred in 1959 when zeolite Y was used as a catalyst for isomerization reactions. In 1962, the Mobil Company used zeolite X in the

catalysis of cracking reactions. In 1969, Grace developed ultra-stable zeolite Y (USY) as a catalyst. At that time, besides the catalysis of cracking and hydrocracking reactions, molecular sieves were also used for the isomerization of normal alkanes, C₈ aromatics, and the disproportionation of toluene in industry.^[48] With increasing applications of molecular sieves in industry, the theories of acid catalysis, of B- and L-acids,^[49] and on carbonium ion reaction mechanisms were established in the field of molecular sieve catalysis. At the same time, study on another important feature of molecular sieves, that is, catalytic shape-selectivity, was also carried out. This study was initiated in 1960 by Weisz and Frillette, followed by investigation in shape-selective catalysis of zeolites erionite,^[50] ZSM-5, mordenite, and CaA were studied until the early 1980s.^[51] Naccache et al. summarized the shape-selective issues in several different catalytic processes involving molecular sieves, such as the diffusion and adsorption of reactants, the generation of active intermediates, and the desorption and diffusion of intermediates and final products.^[52] They believed that shape selectivity depended mainly on the sieving effect, the reverse molecular-size selectivity, and the selectivity of intermediate products. Since the beginning of the 1980s, applications of molecular sieves and porous materials have been continuously increasing due to several reasons: 1) the demands of industry, such as the transformation of hydrocarbons in petroleum processing, the catalysis of intermediates in the fine chemicals and medicine industries,^[52,53] and the use of catalysis in the treatment of environmental pollutants;^[54,55] 2) the development of secondary synthesis, modification, and treatment of zeolites, including ion-exchange, dealumination of framework, isomorphous substitution, and assembly techniques in channels or cavities, etc.; and 3) the emergence of new molecular sieves and porous materials, such as extra-large microporous molecular sieves and mesoporous materials. On the basis of solid acid and shape-selective catalysis theories, new catalytic processes have been developed, and these include metal–molecular sieve dual functional catalysis,^[51,56] redox catalysis,^[55] alkali catalysis,^[57] catalysis in the channels of extra-large microporous and mesoporous materials,^[57] and chiral catalysis of molecular sieves.^[57] Furthermore, the enormous amount of experimental data and the rapid development in theory allow for a deep understanding of the relationship between the catalytic functions and the structures of molecular sieves. Our extensive knowledge of the relationships between catalytic functions, structures, and synthesis enables molecular sieves and porous materials to enter the era of molecular engineering ahead of many other types of catalyst. All the above reasons contribute to the prominent position of research on the catalysis of molecular sieves and porous materials in the whole field of catalysis. According to some internationally renowned experts in catalysis research and development, ‘the grand challenge for catalysis science in the 21st century is to understand how to design catalyst structure to control catalytic activity and selectivity’. This preludes a very prosperous future for molecular sieves and porous materials as catalysts.

In the past decades, great progress has been made in various fields related to molecular sieves and porous materials, such as synthesis and catalysis, structural chemistry, adsorption and diffusion, characterization, and porous composite chemistry. In particular, the overlap of molecular sieve science with other related sciences, including physics, mathematics, computer science, materials science, and biology, has promoted the in-depth development of the chemistry of molecular sieves and porous materials.

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