Recent advances in the synthesis of hierarchically nanoporous zeolites

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ABSTRACT

Hierarchically nanoporous zeolites possessing mesopores as well as the inherent micropores of zeolite structures are garnering attention as a solution to the diffusion limitation problem of solely microporous classical zeolites. The hierarchical structure enables zeolites to have maximum structural functions in a limited space and volume owing to the high diffusion efficiency. Hierarchical zeolites are in high demand for the development of advanced materials for applications in adsorption, separation and catalysis. Herein, recent advances in synthesis routes to hierarchically nanoporous zeolites are reviewed with their catalytic contributions. Particular emphasis is given to the recently developed synthesis method which uses surfactants that are functionalized with a zeolite-structure-directing group. This type of surfactants can direct porous structures in micro- and meso-length scales simultaneously.

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1. Introduction

Zeolites are a family of crystalline aluminosilicate mineral, whose structure is composed by regular array of uniform micropores in a molecular dimension (micropores are defined as pores with diameters of less than 2 nm) [1–3]. The micropore diameters are selectable, typically, in the range of 0.3–1.5 nm depending on zeolite structures. Currently, *ca.* 200 types of zeolite are crystallographically classified. Zeolites have high gas adsorption capacity due to the high specific surface area of the microporous structure. Zeolite pores can selectively sort molecules depending on their sizes and shapes. This '*molecular sieving*' effect has enabled the development of molecular size- or shape-selective applications in adsorption, separation and catalysis. New applications, such as optoelectronics, sensing, and drug delivery, were considered in recent years [4]. However, catalysis is still the most important application of zeolites. Zeolites are essential as a solid catalyst for oil refining, petrochemical processing and also organic synthesis, for the production of fine and specialty chemicals [1–3]. Zeolites are known to occupy more than 40% of the entire solid catalysts in the current chemical industry [5]. The tremendous success of zeolites in catalysis is owing to their ion-exchange capacity, solid acidity and framework stability, as well as shape-selective pore diameters. In most zeolites, trivalent Al atoms are tetrahedrally coordinated by oxygen in the crystalline silicate framework. This causes a charge mismatch between Al and the oxide framework, which is compensated by extra-framework Na^+ ions. These Na^+ ions

can be exchanged by other cations like K^+ and H^+. In some zeolites, H^+-ion exchanged form can exhibit Lewis acidity and also Brönsted acidity, which is comparable to sulfuric acid. Furthermore, the acidity can often be tailored in strength and concentration by the choice of the framework composition. Transition metals with reduction–oxidation property, such as Ti, Co and Sn, can be incorporated into zeolite frameworks. The surface nature is tunable from hydrophobic to hydrophilic according to Si/Al ratios. Zeolites have excellent thermal stability, hydrothermal stability and mechanical strengths, allowing convenient recycling after removal of organic contaminants through calcination.

Despite much of the outstanding features of the microporous structure, the sole presence of micropores often imposes significant limitations. Reactants and products with sizes beyond the micropore dimensions cannot diffuse into and out of zeolite crystals. Even in the case of smaller molecules, the catalytic performance can be seriously limited by the diffusion of reactants or products. Bulk zeolite crystals are often several thousand times larger than the pore diameter. In such a diffusion-controlled regime, less than 10% of zeolite active sites at the edge of the bulky crystal might actually participate in the catalytic reaction simply due to the limited mass transport to and from the active sites [4]. In addition, slow diffusion can cause polymerization of by-products or reaction intermediates covering catalytic active sites within the microporous channels. This can cause serious loss of catalytic activity, that is, catalytic deactivation. To overcome the diffusion limitations imposed by the microporous structure, various efforts have been made during over the past few decades. Generally, the efforts can be categorized into three different approaches. Synthesis of zeolites with extra-large micropores is one of these approaches [6–17]. Another approach is to synthesize zeolites in the form of small nanoparticles for rapid diffusion [18]. A third

class of approach is to obtain zeolite samples with intracrystalline mesopores (defined as pores with diameters ranging from 2 to 50 nm), generating mesopores during the zeolite crystallization using a template, or through a post-synthetic treatment using acid or base [19–77].

After the discovery of VPI-5 (pore diameter = 1.2 nm) [6], extensive efforts have been devoted to the development of new zeolitic materials having extra-large pores. Extra-large pores mean micropore apertures composed of more than 12-membered ring (12MR) [7]. These materials were hydrothermally synthesized by use of bulky organic amine as a pore-generating agent ('*porogen*' in short) [6–13]. High-throughput methods were adopted to optimize the synthesis conditions very quickly [8]. Incorporation of germanium into the synthesis composition increased the synthesis opportunities dramatically [14–17]. Germanosilicate zeolites having even 30MR pore apertures were synthesized via rational design of bulky porogens using high-throughput synthesis method [17]. However, most of such materials were phosphate-based or germanosilicate, which were catalytically less active or chemically less stable than aluminosilicate zeolites [7].

In the approach to nanocrystalline zeolites, the synthesis conditions have to be controlled very delicately in order to stop crystallization before growth to bulk crystals. The synthesis should often be carried out under diluted conditions, at low temperatures, and under Na+-deficient conditions by using a hydroxide form of structure-directing agent (SDA). The synthesis often has to stop at a very low yield. The zeolite nanoparticles are usually obtained in colloidal dispersion, which is cumbersome to filtrate. The synthesis conditions are difficult to generalize because the crystal growth rate and mechanism is very greatly influenced by the detailed structures and Si/Al ratios of the zeolites. There are quite a few reports on the synthesis of zeolite nanoparticles. The synthesis information is valuable for the investigation of the zeolite crystallization mechanism, using electron microscopy and *in situ* dynamic light scattering measurement [18]. However, from the viewpoint of catalyst preparation, the synthesis of zeolite nanoparticles is considered yet impractical.

Post-synthetic dealumination and/or desilication of pre-synthesized zeolite crystals can be used to generate intracrystalline mesopores. This method is suitable for a large-scale production. However, it is difficult to generate uniform mesopores. In addition, the raw zeolite samples should be treated properly, to prevent complete dissolution or the loss of crystallinity [19,20]. The direct generation of intracrystalline mesopores can be achieved by the addition of a hard template of a mesopore diameter [21]. Various kinds of nanotemplates are available, such as carbon nanoparticles and nanotubes. Soft-templates such as surfactant micelles and silylated polymers may also be added into the initial synthesis gel. The zeolite should be crystallized with the inclusion of the template. However, this process is a thermodynamically unfavourable in terms of entropy. Hence, the zeolite crystallization should be directed to occur in the confined space between the template particles or inside the template pores, in a manner similar to dry-gel synthesis [51]. In the case of soft templates, the templates or mesoporogens should have sufficiently high affinity with zeolite frameworks. After removal of the template through calcination, the zeolite can possess open mesoporous structure in addition to the zeolitic micropores in a hierarchical manner. This type of zeolites is often called '*hierarchically nanoporous zeolites*' or '*hierarchical zeolites*' for short. This material can exhibit the dual merits of two different pore structures. The micropores could provide a size- or shape-selective catalytic process for guest molecules while the mesopores provide a facile diffusion pathway to catalytic sites inside the micropores or on the mesopore wall. At the same time, the mesopore walls are useful for catalyzing reactions of bulky molecular species that cannot diffuse into the micropore.

Herein, we briefly review the post-synthetic treatments that were developed to obtain hierarchical zeolites. Then, we move into the direct synthesis routes using nanotemplates. Particular emphasis is given to the recently developed synthesis method from our laboratory using surfactants that are functionalized with a zeolite-structure-directing group. This type of surfactant can direct porous structures in micro- and meso-length scales simultaneously.

2. Post-synthetic demetallation of zeolite framework

In this method, the framework constituents, Al and silica, are partially extracted from a pre-synthesized zeolite crystal through chemical degradation in acids or bases. Depending on the dissolved framework constituent, it can be classified into dealumination or desilication. In an ideal case, the selective extraction can generate mesopores inside the zeolite crystal without destroying crystallinity. Consequently, microporous zeolites having intracrystalline mesopores can be obtained. In addition to the porous properties, the demetallation process leads to a significant change in acidity. Among the two demetallation methods, dealumination is typically applied to the high-Al zeolites. The steam-thermal dealumination of zeolite Y is the most well-known example [22–28]. Typically, the dealumination procedure is performed by repeating high temperature steaming of NH4Y zeolite, followed by an acid treatment with mineral acid. By transforming the framework Al into the extraframework Al species, the dealumination process results in a local destruction of crystal structure. This produces mesoporous channels (mostly 5–100 nm in diameter) as a defect region inside the zeolite crystal. Such secondary mesoporosity increases the accessibility to framework acid sites for bulky molecules in oil refining [3]. As revealed by 3D-transmission electron micrograph (TEM) tomography in combination with N_2 adsorption and mercury porosimetry, a significant fraction of mesopores exists as isolated cavities inside the zeolite crystal, which is in principle much less effective in enhancing the diffusion of large molecules into the zeolite structure than mesoporous channels open to the external surface (Fig. 1) [27,28]. It is reported that hydrothermal dealumination processes involving other zeolites such as mazzite [29,30], mordenite [31,32] and ZSM-5 also generate mesoporosity inside zeolite crystals [33–35]. In addition to the hydrothermal dealumination, extraction of framework Al can be achieved in aqueous solutions containing ammonium hexafluorosilicate (AHFS) [36,37] and $SiCl_4$ [37–40]. The resultant pore textural properties and Al distribution depend very much on the types of dealumination procedure [37]. The dealumination process involves an inevitable change of acid property, which is generally difficult to control. Since the mesopores are generated by the extraction of framework Al which was originally an acid site, the dealumination causes the number of acid sites to decrease. The acid strength generally increases as the number density decreases. As a result of dealumination, many of the Brönsted acid sites in the zeolite frameworks are converted to the extraframework Lewis acid sites.

Another demetallation strategy is the local dissolution of framework silica in basic solution. The desilication process is more effective for high-silica zeolites (usually Si/Al >20) than high Al zeolites [41–48] since it is difficult to remove SiO- that is directed bonded to Al. The desilication can be readily performed at a low concentration of alkali metal hydroxide. Mesoporous textures generated by the desilication process strongly depend on the concentration and distribution of Al within the zeolite crystals [41,45,46]. Silica-rich domains are easily leached out to generate large mesopores while Al-rich domains remain relatively unchanged. In the case of large ZSM-5 crystals, desilication resulted in the selective dissolution of the interior of the zeolite, which is due to the high concentration of Al at the exterior surface of the crystals [41,46]. These results