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## Review

## Nanosized and hierarchical zeolites: A short review



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## ABSTRACT

Zeolites are crystalline aluminosilicates with three-dimensional microporous structures. They have been used as ion-exchangers, catalysts, and adsorbents in various fields such as oil refining, petrochemistry, agriculture, and water and wastewater treatment. Their wide use is because of their many beneficial properties, such as framework and compositional flexibilities, physical and hydrothermal stabilities, non-toxicity, high surface areas, exchangeable cations, and good cost-benefit ratios. Although many zeolite applications depend on their microporous structures, this can cause diffusional constraints for bulky reactant and product molecules. There have been many efforts to overcome the intrinsic limitations of conventional zeolites by preparing nanosized and hierarchically structured zeolites. As a result of these efforts, several strategies have been established and the use of new zeolitic materials in various catalytic and adsorptive reactions has been investigated. Longer lifetimes, high catalytic performances, and postponed coking and catalyst deactivation can be achieved using hierarchical and nanosized zeolites. The aim of this review is to provide an overview of the enhanced properties of hierarchical and nanosized zeolites, and recent development methods for their synthesis. The advantages and disadvantages of each route are discussed, and the catalytic applications of nanozeolites and zeolites with secondary porosity, and a comparison with conventional zeolites, are briefly presented.

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## 1. Introduction

Zeolites, glasses, carbons, and oxides are members of a large group of porous materials known as molecular sieves. Among these, zeolites are the most attractive candidates for industrial applications because of their unusual features. Many aspects of our daily lives are affected directly or indirectly by zeolites. Zeolites are crystalline materials with well-defined porous structures and pore sizes of molecular dimensions in the range 0.3–2 nm; they are microporous solids, according to the IUPAC classification. They consist of  $\text{TO}_4$  tetrahedra (T is Al or Si in a natural zeolite and can be other elements such as Ti, Ge, P, and B in synthetic ones), which are connected with each other by sharing corner oxygen atoms [1–6]. The final framework

structure of a typical zeolite is obtained from secondary structures formed by primary tetrahedra [7].

Crystalline zeolites are usually prepared by hydro/solvothermal methods under appropriate conditions such as time and temperature of reaction, type of mineralizing agent, source of T atoms, structure-directing agents (SDAs), and calcination temperature [8–11]. In addition to three-dimensional channel systems occupied by water molecules and alkali or alkaline-earth metal cations, one- or two-dimensional zeolites are also possible [12]. Although synthetic zeolites are excellent choices for catalytic, adsorptive, and ion-exchange applications, inexpensive and abundant natural zeolites have not been widely used because of their impurities and structural defects [13]. Hydrophilic natural zeolites such as clinoptilolite, which

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have high cation-exchange capacities, have many benefits in water and wastewater treatment [14,15]. Natural zeolites also have applications in areas such as agriculture [16], gas separation [17], and animal husbandry [18]. Up to 2014, the Structure Commission of the International Zeolite Association (IZA-SC) had accepted 218 types of zeolite framework structure; other IZA structures may have been synthesized but not yet reported (Fig. 1) [19].

The most important applications of zeolites are in the oil-refining and petrochemical industries, in which synthetic zeolites with MFI, FAU, and  $\beta$  frameworks have been commercialized as well-known catalysts [1]. The high selectivities of zeolites are important with respect to the requirements for certain petrochemical products. No corrosive and hazardous mineral acids are needed and fewer byproducts are formed [7].

The successful use of zeolites is based on their inherent shape-selective structures. There are three types of shape selectivity provided by the size and shape of zeolite inner vacancies. The first is reactant selectivity, which allows the introduction of certain small reactants into zeolite channels; the second is transition-state selectivity, in which intermediates of appropriate size are formed; and the third is product selectivity, enabling specific products to be obtained [20]. These features enable discrimination among molecules with regard to their size and shape, control of their passage through the porous system, and reactions with active sites. Although many excellent and unexpected results have been obtained using zeolites in a wide range of reactions, they cannot work properly in the presence of bulky molecules because such molecules cannot diffuse into the zeolite microporous structures; therefore, the efficiency and activity are lower in media containing such substrates. Only active sites close to the zeolite pore entrances or on their external surfaces, which represent at most 5% of the total number of active sites, are available for bulky molecules [21,22]. These constraints have stimulated research on zeolitic structures. Two main strategies have been developed to overcome these limitations, namely introducing secondary pores with diameters larger than 2 nm (meso- or macro-pores) and reducing the zeolite crystal size to the nanometer scale, to give

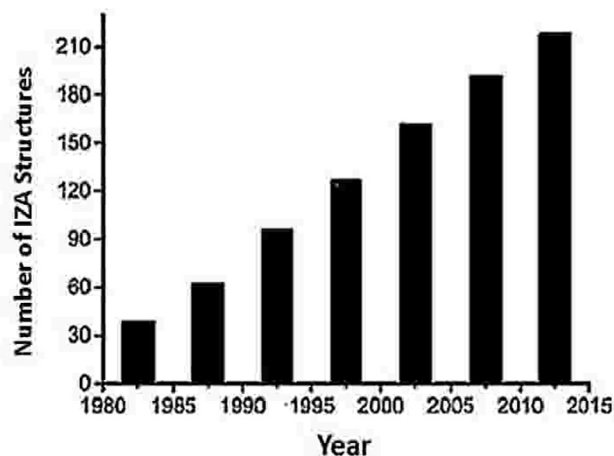


Fig. 1. Zeolite framework types recorded by IZA-SC. Reprinted with permission from Ref. [19]. Copyright 2014, American Chemical Society.

hierarchical and nanosized zeolites, respectively. These improved structures with larger pores systems enhance diffusion of bulky reactant molecules into the pores and of large product molecules out of the pores. This shortens the distance to the active sites and facilitates adsorptive and catalytic reactions.

Fig. 2 shows different methods for nanozeolite and hierarchical zeolite synthesis from conventional zeolites. Some excellent reviews on hierarchical and nanosized zeolites have been published [23,24]. However, to the best of our knowledge, there is no review paper describing the properties and syntheses of both structures. The aim of this paper is to give a comprehensive review of zeolites and the improvements provided by hierarchical and nanosized structures; it will provide a good tutorial guide. We describe synthetic methods for both types of material (the syntheses of hierarchical structures are discussed in more detail than those of nanosized zeolites, in accordance with their importance) and briefly discuss their catalytic applications.

## 2. Nanozeolites

Since the beginning of the new millennium, much attention has been paid to nanosized porous materials [25]. Many chemical and physical processes involving a solid component are clearly affected by the differences between bulk and surface atoms in the solid. Increasing the amount of atoms exposed at solid surfaces with enhanced specific surface areas can be achieved by reducing the solid particle size or introducing an open pore system (Fig. 3) [26,27]. This is particularly important when zeolites are used as a main component of the reaction system in the form of adsorbents, ion-exchangers, or catalysts. As already mentioned, using zeolites with micron-diameter pores and micrometer-scale crystallites can hinder diffusion of bulky molecules because the extensive surface areas of the internal parts of the framework can only be accessed by molecules with kinetic diameters less than 1.5 nm, and most natural and synthetic zeolites consist of micrometer-sized crystallites [28].

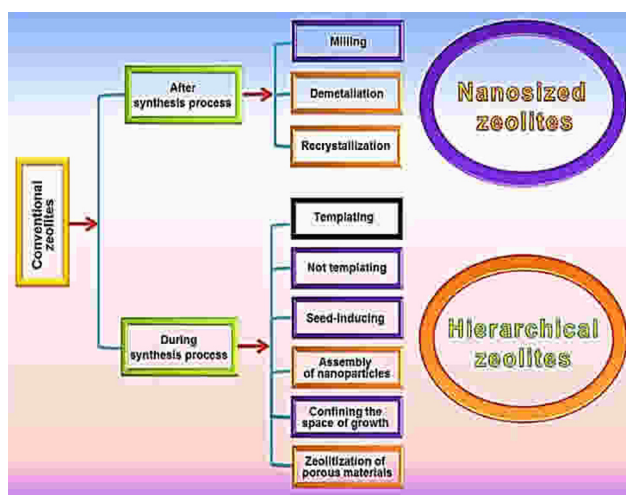


Fig. 2. Overview of synthetic methods for nanozeolites and hierarchical zeolites (colors indicate methods related to each type of zeolite; templating is used for both types).

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