



Innovations in hierarchical zeolite synthesis



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ABSTRACT

There has been growing interest in the research and development of hierarchical zeolites possessing at least two levels of porosity in order to reduce diffusion limitations in reactions catalyzed by microporous zeolites. Engineering and manipulation of the hierarchy of pore structures are required to facilitate transport of large reactants and to improve the accessibility of active sites in zeolite catalysts. Various strategies and approaches have been proposed and developed in order to introduce secondary porosity, which is usually in the mesopore range, for conventional zeolites. From controllable post-synthetic modifications to designed direct synthesis with or without mesopore templating agents, significant progress has been made over the past several years in making hierarchical zeolites. In this paper, recent innovations in the synthesis of hierarchical zeolites by different methods will be reviewed, including post-synthetic demetallation, hard- and soft-templating approaches, and template-free routes. We will also discuss separately the progress of hierarchical structures derived from two-dimensional (2D) zeolite nanosheets. A summary and outlook will also be discussed with the focus on providing industrial perspectives of this field.

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1. Introduction

Zeolites are a class of aluminosilicates constructed from SiO_4 and AlO_4 tetrahedrons connected to form crystalline structures with various framework compositions [1–5]. More than 225 different topologies have been catalogued (<http://www.iza-online.org/>) by the International Zeolite Association and assigned a three-letter code for each distinct topology. The realization of large-scale production of synthetic zeolites as solid-acid catalysts in the 1950s and the discovery of new zeolite materials in the following two decades revolutionized the petrochemical and chemical industries in many applications, such as catalytic cracking, alkylation, and isomerization. The industrial interest in zeolites is due to a combination of several unique properties, including high surface area, good ion-exchange capability, strong acidity, and most importantly, high thermal/hydrothermal stability. Moreover, the regular crystalline channels allow zeolites to perform shape-selective reactions, thus enabling discrimination of reactants, products, and transition states on a molecular scale. Conventional zeolites are crystalline materials constructed typically by 8, 10, or 12 tetrahedral atoms (T-atoms) arranged as rings with pore sizes less than 1 nm. These are classified as *small-*, *medium-*, and *large-pore* zeolites [6], terms identified from the perspective of their ‘microporous’

region. For these microporous zeolites, the active sites become inaccessible when reactants with sizes greater than the dimensions of the pores are present due to strong diffusion limitation resulting from the relative rigid zeolite framework. The diffusion limitation also increases the possibility of coking, which deactivates the catalysts and shortens their catalytic life. To alleviate these limitations, hierarchical zeolites were conceived with the aim of adding secondary porosity to traditional zeolites. In this usage, *hierarchical* refers to the presence of at least one additional pore system, typically in the mesopore size range, in addition to the intrinsic zeolite microporosity. Ideally, hierarchical zeolites should facilitate access of bulky reactants to catalytically active sites while simultaneously preserving the acidity and crystallinity of the original zeolites.

Within the past two decades, intense attention and research activities have been devoted to enhancing the accessibility of active sites in microporous zeolite frameworks. Although a variety of different synthetic strategies have been proposed and demonstrated to obtain hierarchical structures, they can all be classified into two major categories, namely “top-down” and “bottom-up” approaches. The top-down approach starts with microporous zeolites that are then post synthetically modified to create hierarchical zeolite structures. Dealumination and desilication represent the two most frequently investigated post synthesis routes for the top-down approach. Alternatively, the bottom-up approach builds hierarchical zeolites through the engineering of microporous and mesoporous domains. The bottom-up approach is considered to be more synthetically challenging as it often involves complicated

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templating routes, such as hard- and soft-templating. The bottom-up approach can also utilize template-free syntheses. In hard templating, a solid template is added to the synthesis reaction to create confined spaces around which the growing zeolite crystallizes. The hard-templating materials are then removed by high temperature combustion, leaving behind mesoporous voids where the hard template was removed. In contrast to hard templates, soft templates are more flexible in nature and usually interact with zeolite precursor or framework via covalent bonds, van der Waals forces, hydrogen bonds, or electrostatic forces. The soft templates are incorporated into the growing zeolite during the synthesis and create a pore system upon their removal. Thus, hard templating is also known as “exotemplating”, whereas soft-templating is known as “endotemplating” [7]. Template-free bottom-up routes refer to synthesis methods that do not utilize templates in directing the formation of mesoporosity. It should be mentioned that the use of ‘template’, especially organic species for microporosity formation, may not be entirely accurate despite the term’s widespread use. This is due to the fact that the channel/pore structures of zeolites are not exactly the same as the structures of the template molecules. Furthermore, organic molecules are not necessarily incorporated in the zeolites. Instead, templates should be more accurately viewed as structure-directing agents (SDAs) and “there is no example of true templating (for the synthesis of zeolites)” [8].

In this article, we will provide an account of recent innovations in the research of hierarchical zeolites by different strategies, such as post-synthetic demetallation, templating, and template-free approaches. The hierarchical structures from zeolite nanosheets will be discussed under the concept of two-dimensional (2D) zeolites. The review will conclude with a summary and outlook with respect to emerging trends in the development of hierarchical zeolites using various approaches. Several excellent review papers published in the past decade are recommended for a comprehensive chronology of this field [9–15]. While the discussion of nano-sized crystals is inevitable in the following sections, a detailed review of their preparation and application will not be the focus of this paper. Also excluded in this review are developments and synthesis strategies of *extra-large pore* zeolites (pore systems that contain more than 12 T-atom rings) due to the limited number of such zeolites and to the smaller micro-scale pores, which exclude them from being considered mesoporous [16–19]. We refer to recent publications for those who are interested in these topics [20,21].

2. Hierarchical zeolites by top-down approaches

As previously mentioned, top-down synthesis approaches begin with existing microporous zeolites that are then post synthetically modified to create hierarchical zeolite structures. Dealumination is a well-known post-synthetic treatment for zeolites that was first reported by Barrer et al. in the early 1960s to extract Al from clinoptilolite with mineral acids [22]. The concept of dealumination by leaching was then successfully applied to other chemical agents, such as H_4EDTA and $(NH_4)_2SiF_6$ in the liquid-phase and $SiCl_4$ in gas/vapor phase reactions [23–25]. Most of this pioneering work focused on optimizing the dealumination of zeolite Y to obtain its ultra-stable form (USY) with a higher Si/Al ratio for catalytic cracking, since it is difficult to experimentally synthesize NaY with a Si/Al ratio > 3. Another widely applied dealumination route is via a high-temperature (873–1073 K) steaming process for NH_4Y , during which the steam-assisted hydrolysis of $-Si-O-Al-$ occurs and framework Al atoms become detached from their original tetrahedral sites. The combination of steaming and chemical leaching was found to be necessary to obtain better dealumination performance [26–28], e.g. a mild acid treatment after steaming for

extra-framework aluminum (EFAl) removal or a steaming process after chemical leaching for hydroxyl defect reduction.

In general, the removal of Al from a zeolite framework would lead to generation of silanol nests and reinsertion of Si atoms into the framework with mesopores created around non-silicated silanol nests and the partially collapsed region in the framework. Since zeolites are usually composed of silica with minor amounts of alumina, dealumination can significantly change the framework Si/Al ratio and the corresponding acidity of zeolites by altering the strength and distribution of acidic sites. Moreover, it is not currently possible to control the size, shape, and density of mesopores by dealumination. Transmission electron microscopy (TEM) and pulsed field gradient magnetic resonance spectroscopy (PFG NMR) diffusion studies also revealed that the hierarchical structure resulting from steaming USY creates mainly isolated cavities rather than the preferred well-connected mesopore network that can effectively facilitate diffusion of bulky molecules [29].

In 2000, Ogura et al. reported the formation of mesopores in ZSM-5 with preserved crystallinity measured by X-Ray Diffraction (XRD) via an alkaline treatment, during which Si is predominantly extracted from the framework [30]. Since then, a sizeable effort has been devoted to developing alkaline-based desilication techniques for synthesizing hierarchical zeolites [31–43]. In addition to the common variables, such as temperature, concentration of alkaline solutions, and duration of treatment, one critical discovery is the significant effect of Al (i.e. framework Si/Al ratio) on the extent and efficiency of desilication (Fig. 1). Upon a standard alkaline treatment in 0.2 M NaOH solution for 30 min at 65 °C, a framework Si/Al ratio of 25–50 has been identified as the optimal value for the formation of intracrystalline mesopores in the range of 5–20 nm for ZSM-5 zeolites. Of note is that mesopore sizes of USY by dealumination are within a broad range of 2–50 nm. At lower Si/Al ratios (high Al contents), very limited mesopore formation and Si extraction occurs since the negatively charged framework (by the existence of Al either in its original tetrahedral position or realumination onto external surfaces) hinders the hydrolysis of $Si-O-Al$ bonds in the presence of hydroxide ions, while higher Si/Al ratios lead to excessive Si extraction and framework dissolution with larger pores yet lower mesopore surface area. The shielding effect of EFAl species is evidenced by the limited mesoporosity development following alkaline desilication of steamed ZSM-5 zeolites. In such circumstances, a mild acid treatment like oxalic acid is needed to remove EFAl. Hierarchical zeolites formed by appropriate desilication methods provided good mesopore accessibility evidenced by mercury intrusion porosimetry as well as preserved acidity, in stark contrast with the formation of isolated mesopores by dealumination.

With pioneering work mainly focusing on MFI-type zeolites, the post-synthetic alkaline treatment approach was gradually applied to other zeolite topologies, such as BEA, FER, CHA, FAU, MTW, MWW, MOR, etc. [44–52]. The results revealed the challenges to obtaining ideal mesoporosity with preserved microporosity/acidity for different zeolites through similar NaOH post-treatments due to the differences in framework Al stability and variant crystalline morphologies. Further efforts toward more controlled desilication involved the introduction of a secondary base in the solution to fine tune the process, especially for less stable zeolite types that are difficult to handle in NaOH solutions. The inspiration started with the use of aqueous solutions of tetraalkylammonium (TAA) hydroxides (TPAOH, TBAOH, TMAOH) as the base media (Fig. 2) [53,54]. This process is less selective toward Si extraction with the formation of smaller mesopores and produces better microporosity preservation and higher solid yields than the standard NaOH route. More importantly, due to their larger sizes and less effective water solvation compared to sodium cations, TAA cations have higher affinity with zeolites and better protect the framework from OH^- attack,

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