

Review

# Research Progress on the Synthesis of Nanosized and Hierarchical Beta Zeolites

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**Abstract:** Beta zeolite, a crystal material with a three-dimensional twelve-ring cross-channel structure, has many advantages, such as high Brønsted acid concentration, high Si/Al ratio, thermal/hydrothermal stability, and large surface area. Due to these advantages, beta zeolite shows excellent catalytic performance in petroleum refining and petrochemical processes. However, traditionally microporous beta zeolite has strong steric hindrance and diffusion restrictions, which hinder large molecules from passing through its internal channels. In addition, carbon deposition occurs, resulting in catalyst deactivation. The main strategy to solve this problem is to prepare nanosized or hierarchical beta zeolites, which allow for large molecule conversion and shortening diffusion pathways. Therefore, researchers have explored different synthesis strategies to prepare beta zeolite with different particle sizes and porosities to obtain better zeolite catalysts. This paper briefly describes the recent research progress in the preparation of nanosized and hierarchical beta zeolite. Additionally, the mechanisms of various preparation methods, structural characteristics, and applications of the materials are introduced in detail. Furthermore, the main problems existing in its industrial application are describing by comparing the advantages and disadvantages of the different methods to prepare optimally nanosized and hierarchical zeolite to meet the requirements of industrial development.

**Keywords:** hierarchical; beta zeolites; nanosized; preparation method



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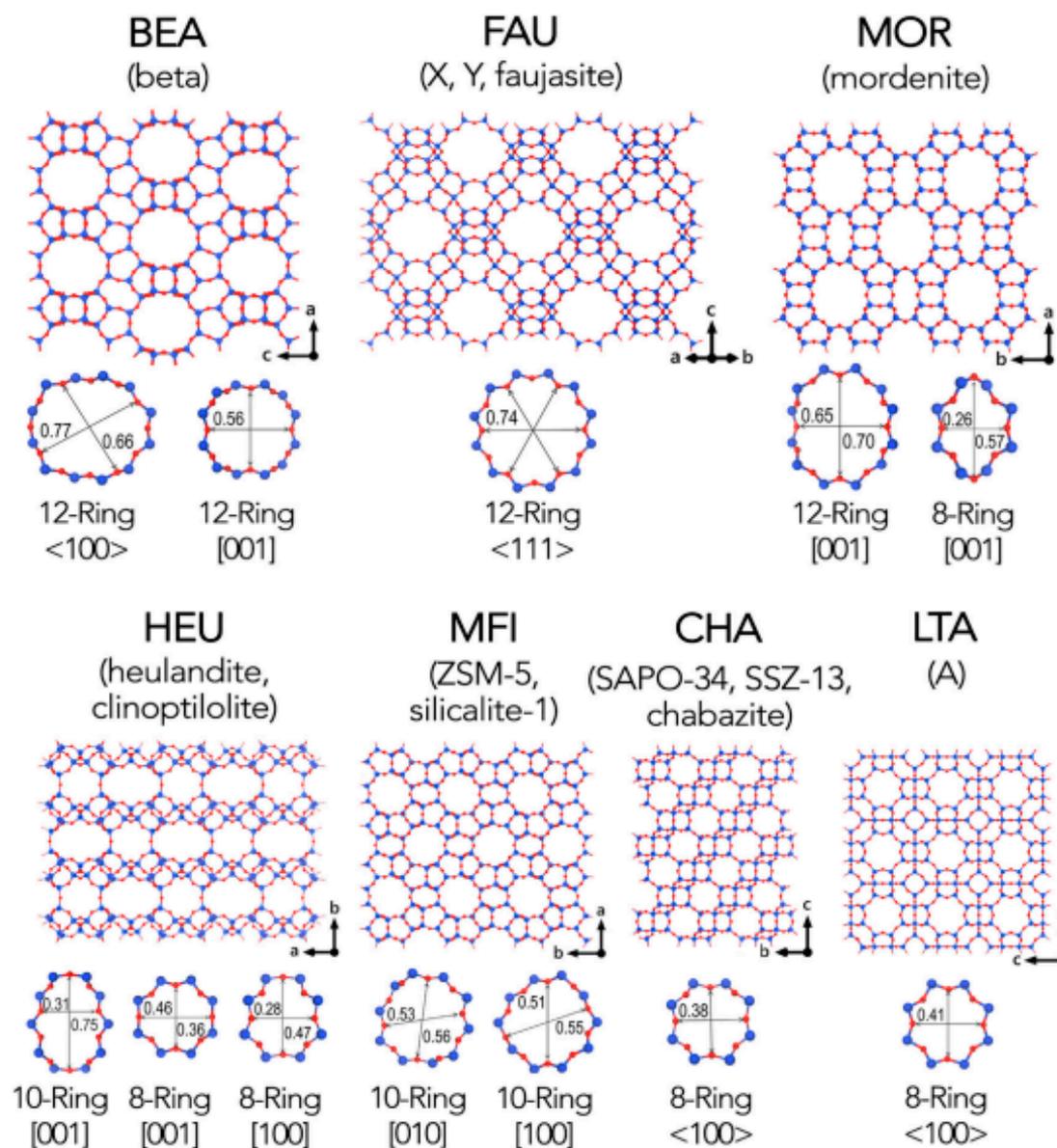


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## 1. Introduction

Zeolite is a material with regular pores; the pore size has the function of sieving fluid molecules of different sizes. Zeolite is characterized by selective adsorption, large specific surface area, and excellent thermal/hydrothermal stability, so is widely used in the fields of adsorption and separation, ion exchange, and catalysis [1–9].

According to the regulations of the International Union of Pure and Applied Chemistry (IUPAC), pores are classified based on their size. A pore size less than 2 nm is a micropore material; a pore size in the range of 2–50 nm is a mesopore material; a pore size greater than 50 nm is a macropore material. The strict definition of zeolite is a three-dimensional ordered inorganic microporous crystal material (<2 nm) that is made up of TO<sub>4</sub> tetrahedrons (T = Si, Al, P, Ti, Fe, Sn, Ge, B, etc.) as the basic structural unit that are connected by sharing vertex oxygen atoms. Micropore zeolite can be divided into small-pore zeolite (eight rings), medium-pore zeolite (ten rings), large-pore zeolite (twelve rings), and ultralarge-pore zeolite (more than twelve rings) based on the number of pore cycles. Common zeolite structures are shown in Figure 1.



**Figure 1.** Skeletal structure of the widely used zeolites. Reprinted with permission from ref. [10]. Copyright 2017, Chemistry. BEA, FAU, MOR, HEU, MFI, CHA, and LTA are the framework codes of beta, X or Y, mordenite, heulandite, ZSM-5, SAPO-34, and A zeolites, respectively.

As a solid acid catalyst, zeolite plays an irreplaceable role and is currently the most widely used solid acid catalyst in the petrochemical and fine chemical fields [11–15]. The H proton, as the cation, can combine with the bridging oxygen connected to aluminum to form hydroxyl groups. Zeolite can act as a proton donor, thus playing the role of a Brønsted acid. There is another important acid site in zeolite, in which the nonframework aluminum and other compensating cations are Lewis acid sites. As shown in Figure 2, zeolite contains both Brønsted and Lewis acid centers. The catalytic reaction mainly occurs at the Brønsted acid center, but Lewis acid can also play a catalytic role or have a synergistic effect [16]. Due to the significant differences in properties such as the morphology, structure, chemical composition, pore size, and acidity of different zeolites, the appropriate zeolite can be selected as the catalyst according to the different catalytic requirements. Currently, the most common zeolites (including Y, ZSM-5, mordenite, and beta) have unique properties such as a strong Brønsted acid concentration, high specific surface area, and hydrothermal stability, making them particularly suitable for the petrochemical industry.

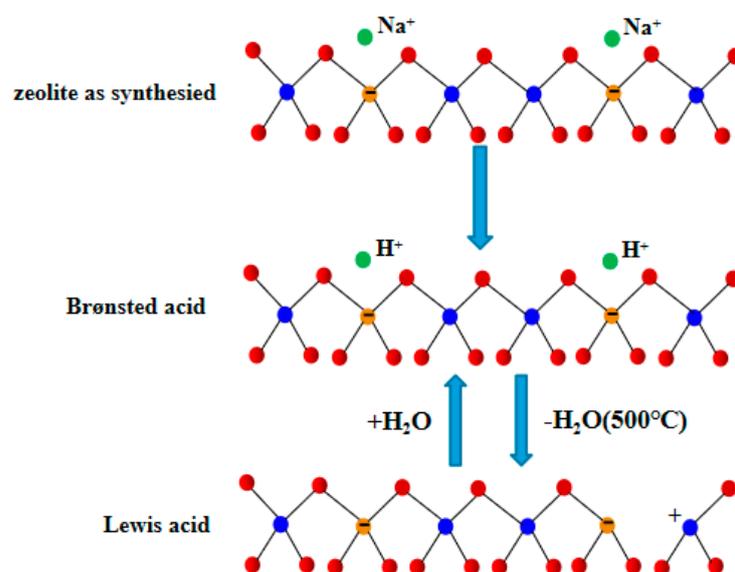


Figure 2. Schematic diagram of Brønsted and Lewis acid centers in zeolite.

## 2. Characterization

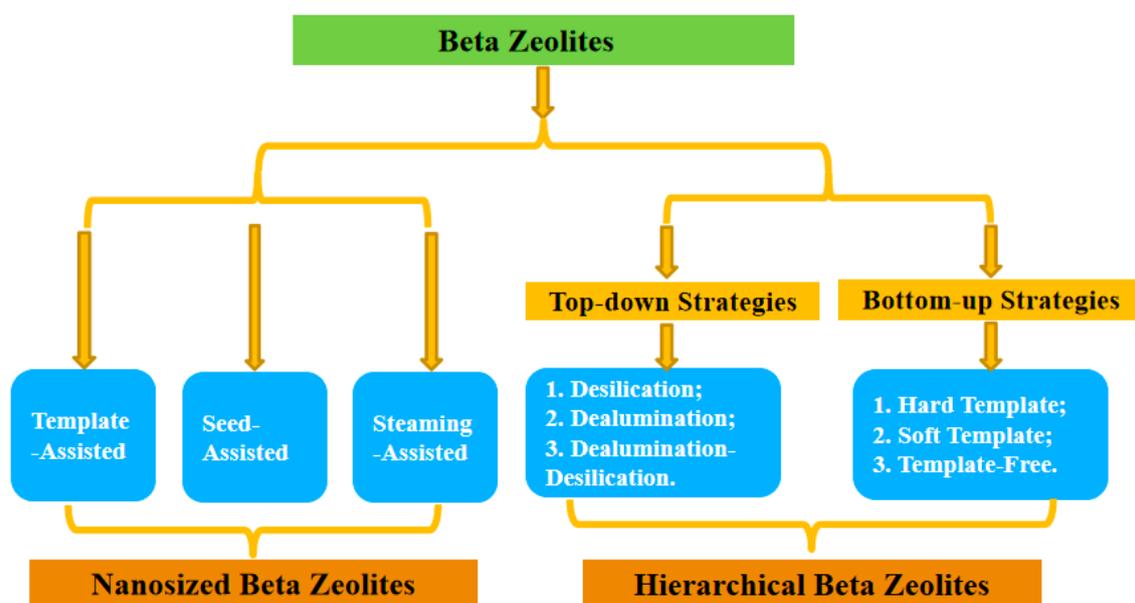
The structure and crystallinity of beta crystals were characterized by X-ray diffraction analysis, which were recorded in the range of  $5\text{--}40^\circ$ . The morphology and the particle size of the samples were tested with scanning electron microscopy and transmission electron microscopy. The textural properties and the pore size distribution were characterized by  $\text{N}_2$  adsorption–desorption analyses. The apparent surface areas were determined with the Brunauer–Emmett–Teller (BET) method in the range of  $P/P_0 = 0.02\text{--}0.10$ . The mesopore size distribution was obtained by the Barrett–Joyner–Halenda (BJH) model, which was applied to the adsorption branch of the isotherm. The acid properties were characterized by ammonia temperature-programmed desorption analysis. All samples' bulk element composition were characterized with an X-ray fluorescence spectrometer [17].

## 3. Beta Zeolite

Beta zeolite is an important high-silica zeolite, which was first synthesized in 1967 by Mobil Corporation's Wadlinger through the hydrothermal method with silicon gel, aluminum, alkali, and tetraethyl ammonium hydroxide at  $75\text{--}200^\circ\text{C}$ . It is widely used as a catalyst in petrochemical production due to its unique three-dimensional twelve-membered ring structure, hydrothermal stability, and appropriate acidity [18–20]. However, the microporous structure of beta zeolite affects the diffusion rate of the reactant molecules, product molecules and the utilization of active sites. In addition, the microporous structure can cause carbon deposition and deactivation in the process of catalytic reactions such as petroleum refining [21,22], reducing the catalytic life and catalytic efficiency of beta zeolite. Currently, the main methods used for the preparation of beta zeolite are preparing nanosized zeolites [23], synthesizing ordered mesoporous zeolites [24], and preparing hierarchical zeolites by introducing mesopores or large pores in the micropores [23–25] to address the issues faced by traditional beta zeolites in large molecular catalytic reactions.

Beta zeolites have been commercialized in the petrochemical, fine chemical, and environmental fields. For example, in the petrochemical industry, beta zeolites have been used as an efficient fluid catalytic cracking additive to increase light olefins and as a solid acid catalyst for the liquid-phase alkylation of benzene with ethylene. In the fine chemical industry, Ti-beta zeolite exhibited high activity for the selective oxidation of alkenes and alkanes [26]. Sn-beta zeolite is regarded as the most important catalysts for the conversion of carbohydrates into lactic acid and because of its stability and unique Lewis acidity [27]. In the environmental field, siliceous and high-siliceous Beta zeolites have a wide range of applications in the treatment of volatile organic compounds [28].

Currently, researchers have employed various synthesis strategies and methods, such as novel structure-directing agents, specialized silicon sources, additives, and different crystallization methods, to prepare beta zeolite with different particle sizes, porosities, and morphologies to produce better zeolite catalysts [29–36]. However, no comprehensive review article has been published on the properties and preparation methods of nanosized and hierarchical beta zeolites. In this paper, the recent research progress in the preparation of nanosized and hierarchical beta zeolites is briefly described; the research progress in the development of different preparation methods, structural characterization, and applications of materials are introduced in detail. A diagram of the preparation methods for hierarchical and nanosized beta zeolite is shown in Figure 3.



**Figure 3.** Schematic illustration for the preparation of hierarchical and nanosized beta zeolite.

#### 4. Nanosized Beta Zeolite

Zeolites with a particle size less than 100 nm are referred to as nanosized zeolites. Compared with micronsized zeolites, nanosized zeolites have a larger specific surface area and a shorter mass transfer path, which enable the rapid transfer of reactants and products, thereby improving the turnover rate of active sites and enhancing catalytic reaction performance [37–39].

The process of synthesizing zeolites is complex and requires adjusting synthesis parameters to obtain nanosized zeolites. The usual zeolite beta synthesis system is the aluminosilicate gel system, in which aluminosilicate gel undergoes crystallization and growth by the induction of mineralizing agents ( $\text{OH}^-$ ,  $\text{F}^-$ ) or structure-directing agents (SDAs). SDAs can be positively charged organic molecule, such as tetraalkylammonium cations, which are the most popular SDAs and are usually used to prepare nano zeolites. The size, shape, and nature of the SDAs affect the formation of the zeolitic phase. These SDAs modify the crystallite size and morphology and improve the crystallization efficiency. The type of tetraalkylammonium cation produces a specific zeolite framework, e.g., tetramethylammonium hydroxide is an efficient template for \*BEA zeolite formation. In summary, The synthesis of nanosized sieves is mainly affected by the following factors: (1) the type and amount of structure-directing agent; (2) the composition of precursor synthesis gel; (3) the type of crystallization raw materials in the initial gel; (4) the external conditions of crystallization synthesis, such as crystallization temperature, crystallization time, static crystallization or rotational crystallization, and crystallization pressure. In summary, the key factor in the synthesis of nanosized sieves is the nucleation stage. If the system can produce enough crystal nuclei, it can provide more raw material growth

sites for the subsequent crystallization growth stage, which is conducive to the synthesis of nanosized zeolites [40].

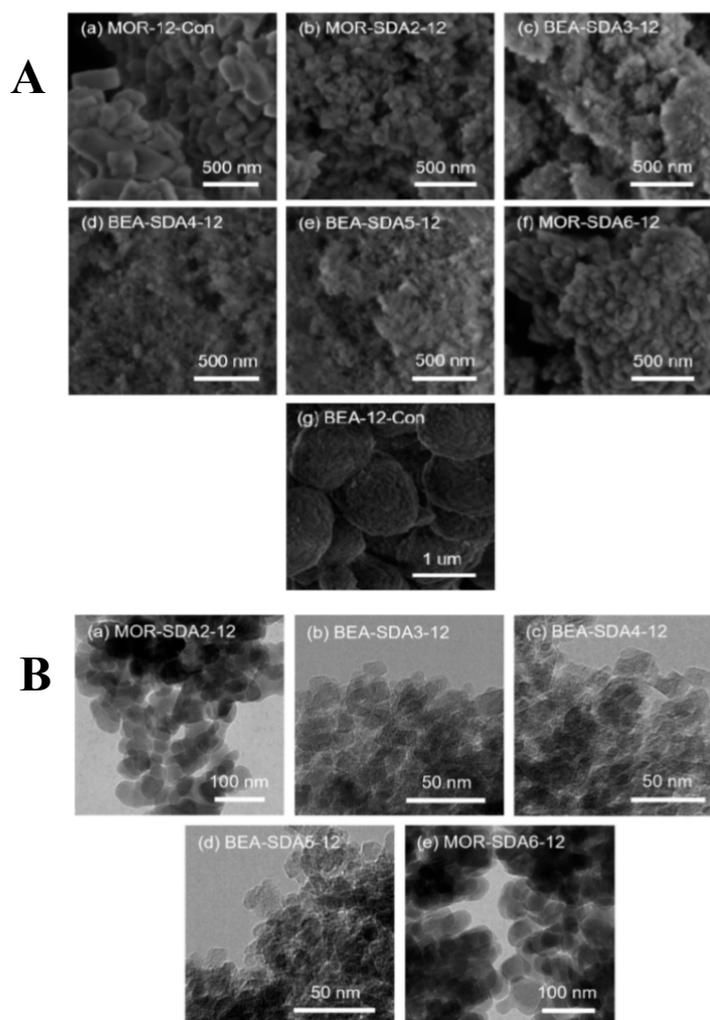
The main synthesis methods of nanosized zeolites include template synthesis, seed-assisted approach, confined synthesis, and steam-assisted synthesis methods [40]. More information on each procedure is given in Table 1.

**Table 1.** Methods for nanosized zeolite synthesis.

Synthesis Method	Characteristics	Advantages/Disadvantages	Refs.
Template-assisted	Synthesis of certain zeolite framework structure with template assistance	Simplicity and obtaining desired homogenous zeolitic phase nanoparticles/Environmental and economic issues in accordance to SDA and time consumption	[41–45]
Seed-assisted	Adding small amount of seeds to synthetic gel without template	Desired zeolitic phase with high yield/Seed introduction	[46–53]
Steam-assisted	Crystallization of dry gel containing organic template under water-steaming treatment	Efficient collection of nanosized zeolite and template utilization/Not suitable for operation, and not used in mass production	[54,55]

#### 4.1. Template-Assisted Synthesis Method

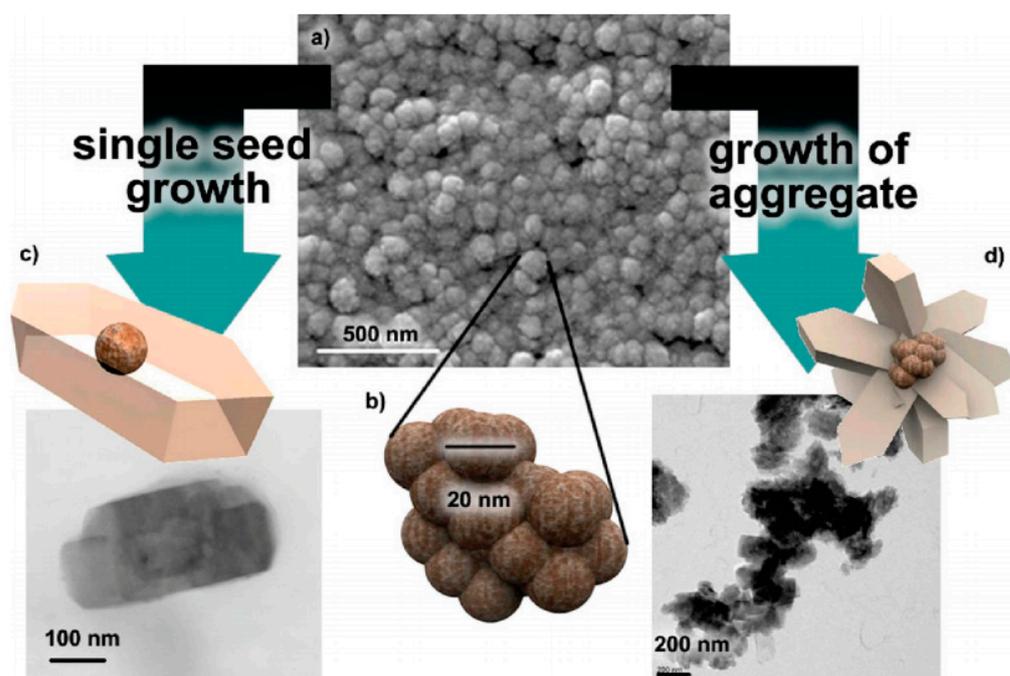
The template synthesis method refers to the synthesis of nanosized beta zeolite guided by a template, which includes quaternary ammonium cations. Here, the quaternary ammonium cations are the most common template for the synthesis of nanosized beta zeolite. The morphology, size, and chemical properties of the template significantly affect the nucleation and growth process of zeolites. Increasing the amount of organic template in the initial gel can accelerate the nucleation rate, meet the requirements for alkalinity and supersaturation in the gel system for nucleation, and facilitate the preparation of nanocrystals. Li et al. synthesized nanosized beta zeolite (15–30 nm) via a one-step hydrothermal method with nonsurfactant diquaternary ammonium compounds. By investigating the solid products obtained during hydrothermal synthesis, the formation of nanocrystals could be related to the strong interaction between diquat templates and aluminosilicate species during the induction stage, which limits the size of amorphous precursor. Nanosized beta is more active than its corresponding bulk counterparts in the alkylation of benzene with benzyl alcohol and the acylation of anisole with acetic anhydride, due to the enhanced mass transport ability and better accessibility of the Brønsted acid sites. Figure 4 shows SEM and TEM images of nanosized beta zeolite obtained by template-assisted synthesis method [41]. Corma et al. [42] successfully synthesized homogeneous nanosized high-silica beta zeolites (~10–20 nm) with high solid yields (above 95%) by using a simple alkyl-substituted flexible dicationic organic structure-directing agent (OSDA), which allowed the synthesis of nanosized beta zeolites with different Si/Al ratios (15–30) in alkaline and fluoride media. Compared with other commercially available nanosized beta zeolites, these nanosized beta zeolites showed better catalytic behavior toward the alkylation of benzene. Xiao et al. [43] achieved the rapid synthesis of zeolite by reducing the solvent content of the synthesis system and significantly reducing the crystal size of the zeolite, resulting in nanosized beta zeolite with particle size of 50–200 nm, which had a low synthetic cost and higher yields of zeolite. With the development of template synthesis and characterization methods, metal–organic ligands can also serve as structural guides in the crystallization process of zeolites. For example, complexes of metal and amine  $[M(\text{NH}_3)_4]n^+$  ( $M = \text{Cu}, \text{Pd}, \text{Pt}, \text{etc.}$ ) can be introduced into the synthesis system of zeolites as templates to obtain nanosized beta zeolite [44,45].



**Figure 4.** SEM and TEM images of the nanosized beta zeolites. (A) SEM images of calcined zeolites. (B) Representative TEM images of calcined zeolites. Reprinted with permission from ref. [41]. Copyright 2022, Inorganic Chemistry Frontiers.

#### 4.2. Seed-Assisted Synthesis Method

Seed-assisted synthesis is an environmentally friendly and efficient strategy to prepare nanosized zeolites, in which product properties can be adjusted, crystallization time can be shortened, and crystal size can be controlled. Crystal seeds can introduce a large number of structural fragments for the crystallization of zeolites into the synthesis system. They act as crystal nuclei, skipping the original nucleation stage of zeolites and directly entering the growth stage. The introduction of crystal seeds not only shortens the crystallization time but also facilitates the formation of nanosized zeolites [46–49]. As shown in Figure 5, the size and dispersion of the seeds significantly impact the morphology of the final zeolites. Isolated and well-dispersed seeds crystals induce the formation of zeolites with regular morphologies, while aggregated seeds often lead to the serious aggregation of zeolites [50]. Zhang et al. [51] used a radicalized seed strategy to prepare an aluminum-rich Beta zeolite with particle size of 100–200 nm. The results showed that those synthesized in the presence of radicalized seeds milled for 30 min exhibited higher crystallinity, higher yields, and larger BET specific surface areas and the crystallization time was shorter. Therefore, in the seed-assisted synthesis strategy, the use of high-concentration organic template agents is not required, so the strategy has important application value in industrial production.



**Figure 5.** Schematic illustration of the preparation of nanosized zeolite by seed-assisted synthesis method. SEM micrograph of silicalite-1 nanocrystals used for seeding of initial gels (a), a sketch of a seed aggregate (b), and the result of the secondary growth of a monocrystalline particle and a polycrystalline aggregate exemplified by TEM images (c and d, respectively). Reprinted with permission from ref. [50]. Copyright 2009, Industrial & Engineering Chemistry Research.

Additionally, compared with complex organic compounds as structure-directing agents, the amount of template required in the seed-assisted method is lowered, thus reducing the synthesis cost of zeolite. Liu et al. [52] prepared nanosized beta zeolite with different Si/Al ratios through the seed-assisted method using a small amount of template and silica gel as the silicon source. The beta seeds were synthesized by the traditional hydrothermal method using tetraethylammonium hydroxide as the template [53]. Hexane was used as the model compound for evaluating the catalytic cracking performance. The results showed that beta zeolites had good crystallinity, an appropriate specific surface area and pore structure, higher B/L acid, and strong acidic sites, so exhibited a high yield of low carbon olefins, a relatively low hydrogen transfer reaction, and coke activity in catalytic cracking reaction.

#### 4.3. Steam-Assisted Conversion Method

The water steam-assisted conversion method consumes less water and improves the utilization of reactor space, thus improving the efficiency of zeolite synthesis. At the same time, the generation of water in the steam-assisted conversion method is reduced to a certain extent, so the method is more environmentally friendly. Nanosized beta zeolite aggregates with a hierarchical structure were synthesized by Jia et al. [54] via the steam-assisted conversion method of dry gel in presence of seeds and a cationic polymer of polydiallyldimethylammonium chloride. The nanosized beta zeolite aggregates consisted of nanocrystals with a size of around 10 nm and possessed rich interconnected mesopores and relatively mild acidity. Compared with traditional beta zeolites, the beta aggregate had higher catalytic activity in the Friedel–Crafts acylation reaction of benzene with acetic anhydride. Highly dispersed nanosized beta zeolites with different Si/Al ratios were prepared by Yu et al. [55] via steam-assisted crystallization from ball-milled solid powder. Due to the adequate mixing of solid raw materials and the good migration of the solid mixture, nanosized beta zeolite was assembled from ultra-small nanoparticles with a size

of around 15 nm and possessed abundant interconnected intraparticle mesopores, which exhibited outstanding catalytic performance in the conversion of lactic acid to lactide.

In conclusion, although nanosized beta zeolite has solved the problem of mass transfer in micropores and improved the conversion rate of reactants and catalytic life [56], there are still some problems in the synthesis and application of nanosized zeolites in catalysis based on the current level of research. Firstly, the crystal structure of nanosized zeolites is more susceptible to damage. Secondly, the hydrothermal and thermal stabilities of zeta zeolites are poor. Thirdly, the grain size of nanosized zeolite is not easy to control, so particle size is prone to being uneven. In addition, nanosized zeolites are smaller, so they require high-speed centrifugation or other methods to separate them from the liquid, increasing the synthesis cost [57]. These problems limit the large-scale commercial application of nanosized zeolites. The introduction of mesopores or macropores into the microporous structure to prepare hierarchical zeolites is currently considered to be the most effective solution and has become a hot spot for researchers [58].

## 5. Hierarchical Beta Zeolites

Hierarchical beta zeolites not only retain the adjustable acidity and excellent hydrothermal stability of microporous zeolites: they can effectively improve the diffusion rate of reactants and products and the utilization efficiency of active sites. Therefore, hierarchical beta zeolites are considered as one of the most effective methods in different catalytic fields. The preparation of hierarchical beta zeolites can be divided into two methods: top-down and bottom-up. The top-down strategies include the methods of desilicication, dealumination, and dealumination-desilicication. The bottom-up strategies include the hard template, soft template, and template-free methods. This paper focuses on the latest research progress and catalytic applications of hierarchical beta zeolites prepared by the above methods. Information on each procedure is given in Table 2.

**Table 2.** Methods for hierarchical beta zeolite synthesis.

Synthesis Method	Characteristics	Advantages/Disadvantages	Refs.
Dealumination	Introducing mesopores by selectively removing aluminum atoms from the zeolite framework	The process is simple and easy to industrialization/Decreasing the crystallinity of the zeolite	[59–64]
Desilication	Introducing mesopores by selectively removing silica atoms from the zeolite framework	Simple technique and low cost/Reduces the number of zeolite acid centers and the pores are not connected	[65–72]
Dealumination-desilication	Combination of desilication and dealumination methods	Controllable pore structure/The process is complex	[73,74]
Hard template	Adding small amount of hard template into the synthetic gel	Wide secondary pore size distribution/Poor thermal stability and mechanical stability	[75–93]
Soft template method	Adding small amount of soft template into the synthetic gel	Good compatibility with precursor of zeolite, pore size distribution is adjustable/Templates are expensive, process is complex	[94–110]
Template-free method	Using the microporous template agent	Rich in intragranular mesopores and low cost/Poor thermal and mechanical stability	[111–116]

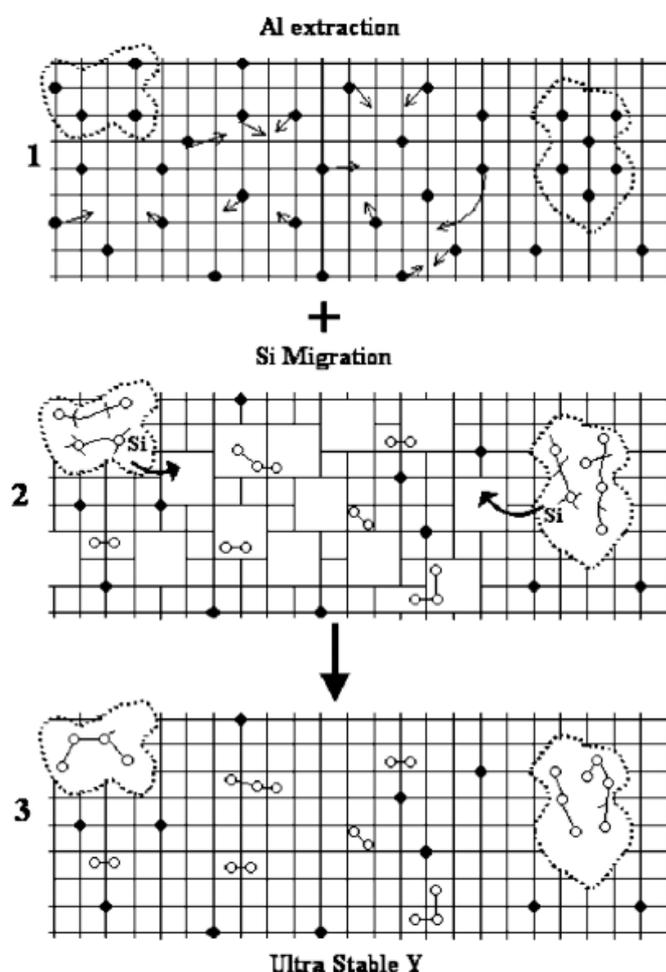
### 5.1. Top-Down Method

The top-down approach, also known as the post-treatment method, involves introducing mesopores by selectively removing atoms from the zeolite framework. For conventional

silicoaluminates, the post-treatment methods mainly include the dealumination and desilication methods.

### 5.1.1. Dealumination Method

The dealumination method is the most traditional method used to form intracrystalline mesopores [59–61]. It achieves dealumination by calcination, steam treatment, acid washing, or chemical treatment to hydrolyze the Si-O-Al bonds in the zeolite framework, producing defects in the zeolite lattice and then forming mesopores. The most widely used of this method is the Y zeolite shown in Figure 6 [62]. Shen et al. [63] prepared hierarchical beta zeolites enriched with 10 nm mesopores by acid-steaming treatment to adjust the aluminum site of beta zeolite, and they confirmed that they exhibited high conversion and gasoline yield in the catalytic cracking reactions of n-octane and vacuum gasoline. Suarez et al. [64] employed different concentrations of HF/NH<sub>4</sub>F mixture solution to treat beta zeolites (Si/Al = 19). When the HF concentration was 0.5 M and the treatment temperature was 40 °C, hierarchical beta zeolites with an intracrystalline pore size of 5–20 nm could be prepared by selective removal of Al atoms within 30 min. The mesopore capacity was increased by 80%, and the ratio of B to L acid was improved without reducing the relative crystallinity of the zeolite. However, the activity of the samples in the isomerization/disproportionation of m-xylene was lower than that of the beta zeolite matrix, which could be due to the higher B/L ratio.

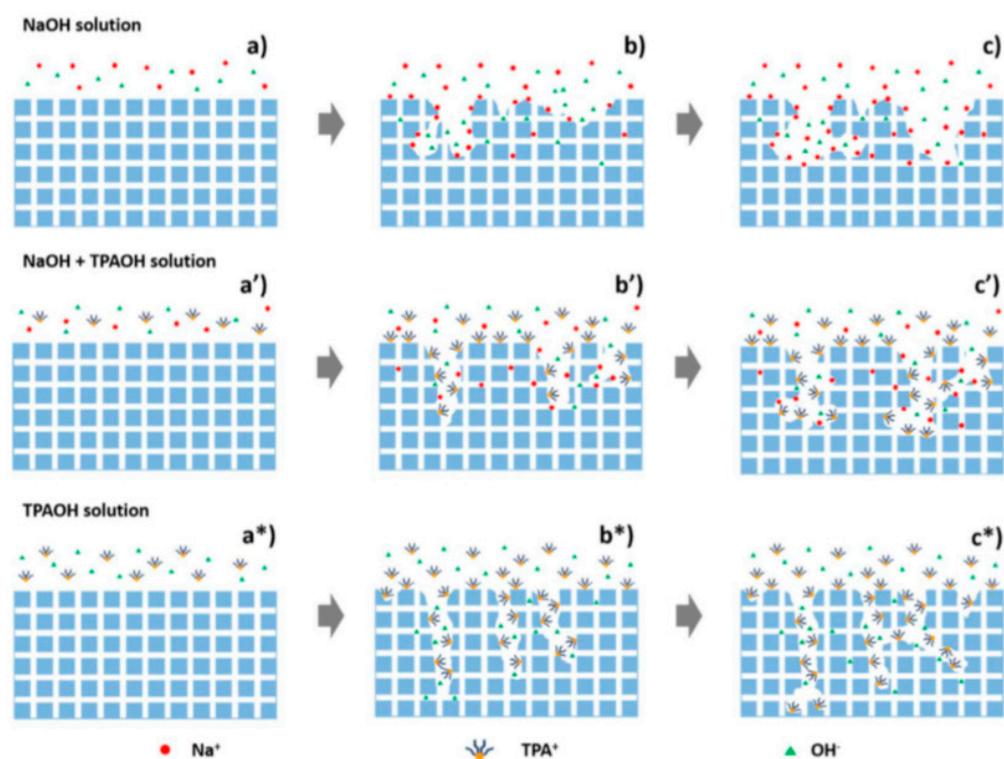


**Figure 6.** Schematic diagram for the preparation of hierarchical ultra-stable Y zeolites via dealumination method. Reprinted with permission from ref. [62]. Copyright 2012, Angewandte Chemie International Edition.

Although the dealumination method can be used to prepare hierarchical beta zeolites, the following drawbacks exist: The removal of aluminum atoms significantly reduces the number of zeolite acid centers. The hierarchical zeolites prepared by the dealumination method have a wide pore size distribution, and the pores are not connected.

### 5.1.2. Desilication Method

The desilication method refers to the treatment of zeolites with alkali solutions to selectively dissolve silicon atoms in the framework to obtain hierarchical zeolites, which are rich in intracrystalline mesopores [65–68]. This method has an impact on the acidity of zeolite [68]. The mesopores produced by the desilication method are mainly concentrated at the crystal edges or surface defects, but the structure and size of the mesopores are strongly influenced by the Si/Al ratio of the zeolite, the type of alkali solution, and the stability of the zeolite framework structure. As shown in Figure 7, it was found that Si/Al = 25–50 is considered to be the best Si/Al ratio range for the preparation of intracrystalline mesopores by desilication, where the skeletal Si atoms are selectively removed while the Al atoms can be preserved [69]. However, when the Si/Al ratio is higher than 50 or the stability of Al in the zeolite framework is relatively low, it is more likely to cause skeleton damage due to desilication and, therefore, cause the removal of the aluminum framework and the Brønsted acidic sites.



**Figure 7.** Schematic diagram of desilication mechanism of different types of alkali solution. (a–c) Fabrication mechanism of mesopores for ZSM-5 in NaOH solutions. (a’–c’) Fabrication mechanism of mesopores for ZSM-5 in NaOH + TPAOH solutions. (a\*–c\*) Fabrication mechanism of mesopores for ZSM-5 in TPAOH solutions. Reprinted with permission from ref. [65]. Copyright 2016, Industrial & Engineering Chemistry Research.

Groen et al. [70] treated microporous beta (Si/Al = 35) zeolite with 0.2 M sodium hydroxide solution and found that the silica removal process of beta zeolite was not easily controlled under the same alkali treatment conditions compared with that of MFI and MOR zeolites. The micropore volume and acidity both significantly decreased, which was due to the large number of defects in the beta zeolite and the poor stability of its aluminum skeleton, leading to uncontrollable silica removal during the alkali treatment

process. Consequently, alkaline-treated beta zeolites show lower catalytic activity in acid-catalyzed liquid-phase benzene alkylation than matrix zeolite. Tian et al. [71] used urea solution to treat microporous beta zeolite, obtaining a hierarchical beta zeolite with a pore size concentrated between 7.6 and 11.2 nm, which exhibited excellent activity in the norbornene synthesis reaction. Using urea as the treatment agent can avoid the destruction of the zeolite micropore structure caused by inorganic alkali modification such as NaOH. Furthermore, using a mild treatment agent can avoid the reduction in relative crystallinity and an ammonium ion exchange process after alkali treatment. Verboekend et al. [72] added structure-directing agents such as tetrapropyl ammonium and hexadecyltrimethylammonium bromide to the sodium hydroxide solution to treat USY and beta zeolites, thus improving the proportion of intracrystalline mesoporosity in the zeolites. The use of pore-directing agents in NaOH leaching was demonstrated as a generic approach to introduce extensive mesoporosity in USY and beta zeolites while preserving the intrinsic zeolite properties, for example, microporosity, crystallinity, and composition. However, the introduction of surfactants during the silica removal process increased the cost of preparing hierarchical zeolites and resulted in serious environmental pollution issues.

Aluminosilicate zeolites can be prepared by the desilication method to achieve intragranular pore formation. This method is easy to carry out for industrial production. It can be used to prepare high Si/Al ratios zeolites (beta, ZSM-5, etc.) to obtain interconnected hierarchical pores. However, the desilication method still has shortcomings, such as the decrease in crystallinity of the zeolite due to alkali treatment, the high price of the organic template agents, and the small number of secondary pores that can be adjusted in the zeolite. Therefore, the alkali treatment desilication is the focus of future research.

### 5.1.3. Dealumination–Desilication Method

The combination of desilication and dealumination methods can produce a zeolite with a controllable pore structure and excellent catalytic performance. Zhang et al. [73] found that inserting a mild acid treatment step before the alkali treatment can produce hierarchical beta zeolites from microporous zeolites with high Al contents with by a template-free method. Firstly, the beta zeolite was dealuminated in a diluted nitric acid, which broke the Si-O-Al framework structure in some parts of the zeolite and produced certain amount of defects. Then, the hierarchical structure was created on the appropriate dealumination of beta zeolites in alkaline solutions under hydrothermal conditions. The desilication processes during high-temperature treatment can protect the crystallinity, microporosity, acid site strength, and total acidity of the zeolite, which be negatively affected during conventional desilication.

Leng et al. [74] also proposed that crystal defects contribute to the diffusion and transportation of  $H^+$  within the crystal, thus aiding in the formation of mesopores during the dealumination process. Compared with the mesopore zeolites prepared by direct silica or aluminum removal, the hierarchical pore Ti-beta zeolite prepared from hierarchical pore beta zeolite as the parent material showed significantly higher removal efficiency for benzothiophene and 4,6-dimethylbenzothiophene in deep oxidation desulfurization of gasoline due to the presence of highly active sites and rich mesoporosity.

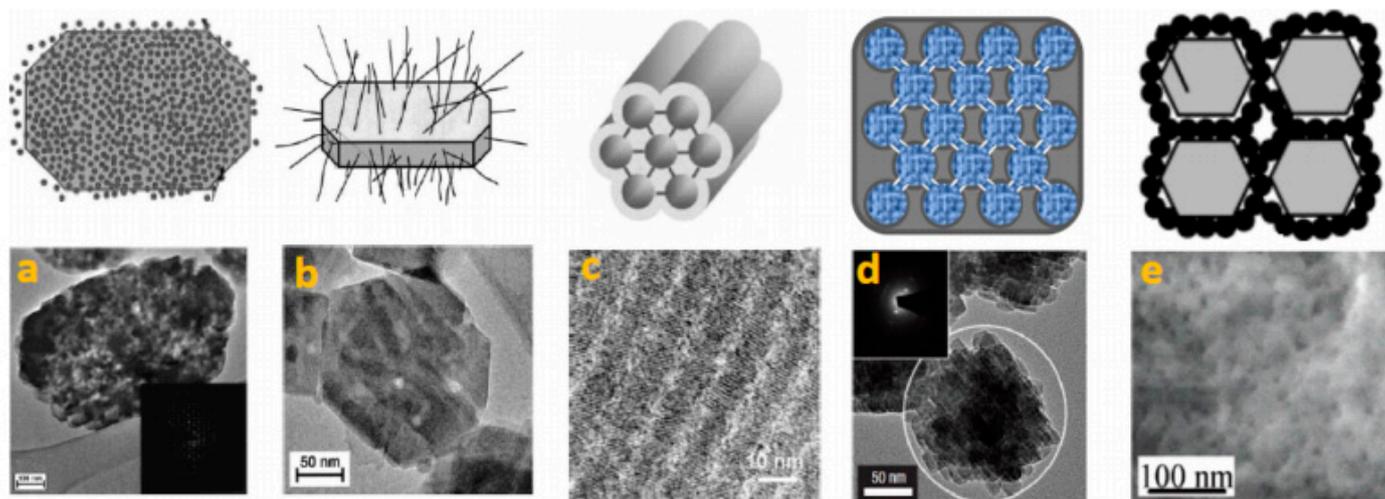
## 5.2. Bottom-Up Method

The bottom-up methods includes template and template-free methods. The template method refers to the method of directly synthesizing hierarchical zeolites by adding template agents during the synthesis process, which is divided into hard [75–82] and soft template methods.

### 5.2.1. Hard Template Method

The hard template method refers to the addition of a hard template that cannot act with the silica aluminum gel in the process of synthesizing zeolite, thereby occupying space to limit crystal growth. Then, the mesoporous channels are produced by removing the

template through calcination. The hard template agents are typically carbon materials that are stable in chemical properties and easy to remove through calcination, thereby producing hierarchical pore zeolites, as shown in Figure 8. The common carbon materials mainly include carbon black [83], carbon nanotubes [84], ordered mesoporous carbon [85], three-dimensional ordered macroporous carbon [86], and carbon aerosols [87].

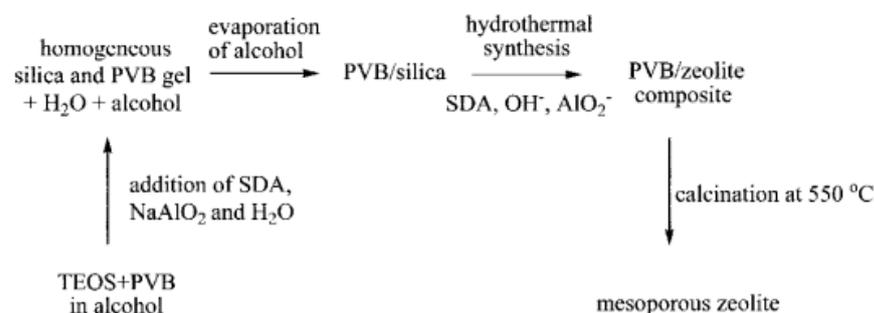


**Figure 8.** TEM images of hierarchical zeolites prepared with different carbon templates. (a) Carbon black pearls, (b) carbon nanotubes, (c) ordered CMK carbon, (d) 3DOM carbon, (e) carbon aerogel. Reprinted with permission from ref. [88]. Copyright 2015, Catalysis Today.

Sun et al. [89] reported the synthesis of hierarchically ordered macro–mesoporous single-crystalline beta zeolite with a rare micron-scale crystal size via an in situ bottom-up confined zeolite crystallization strategy. Beta zeolite single crystals with intracrystalline hierarchical porosity at the macro-, meso-, and microscales were developed, which have improved accessibility to active sites and outstanding hydrothermal stability. The catalytic conversion of this kind of beta zeolite is nearly 4.0 and 2.0 times higher than that of conventional microporous beta and nanosized beta both in the gas-phase cracking reaction of bulky 1,3,5-triisopropylbenzene and the liquid-phase Friedel–Crafts alkylation of benzene with benzyl alcohol, respectively. The strategy has been extended to the synthesis of ZSM-5, TS-1, and SAPO-34. Tsapatsis et al. [90] used a three-dimensional ordered mesoporous carbon template as the confined space and injected a zeolite precursor into the confined space to obtain beta zeolite with sizes ranging from 100 to 200 nm and mesopores diameters ranging from 10 to 40 nm. Jacobsen et al. [91] used carbon black BP2000 as a hard template and confinement space to prepare nanosized beta zeolite with particle sizes ranging from 7 to 30 nm.

However, most carbon material templates are expensive. So, researchers have synthesized hierarchical zeolites using relatively cheap sugars and starches as hard template agents, making the hard template method feasible for industrial production. Jin et al. [92] used cationic ammonium-modified chitosan as the mesoporous template agent, prepared mesoporous Sn-beta with a 300 nm nanocrystalline structure through hydrothermal synthesis. It was revealed that the addition of cationic chitosan induced nanocrystal aggregation to particle sizes of ~300 nm, giving rise to intercrystalline/interparticle mesoporosity. Hierarchical Sn-beta zeolites were prepared using the gas–solid-phase method, which showed good activity and stability in  $\alpha$ -pinene isomerization and Baeyer–Villiger oxidation reactions. Xie et al. [93] used polyvinyl butyral (PVB) as the mesoporous template agent, first prepared a PVB/SiO<sub>2</sub> precursor by the sol-gel method, and then added the precursor as a silica source into the beta zeolite synthesis system to prepare hierarchical beta zeolites. Hierarchical beta zeolite consists of two levels of porosity, which are well-defined and irregular mesoporosities. Mesoporous zeolites exhibited excellent catalytic performance in

the 1,3,5-triisopropylbenzene cleavage reaction compared with conventional zeolites. The synthesis procedure of mesoporous zeolites templated by PVB gel is shown in Figure 9.



**Figure 9.** Schematic diagram of preparing hierarchical zeolites with PVB as template. Reprinted with permission from ref. [93]. Copyright 2008, The Journal of Physical Chemistry C. TEOS and PVB are abbreviations of tetraethoxysilane and polyvinyl butyral.

Hierarchical beta zeolites can also be synthesized using polystyrene microspheres, resin microspheres,  $\text{CaCO}_3$ , and biomolecules as the hard template. During the synthesis process, zeolite appears in the form of nanocrystalline aggregates around the hard template. However, the hierarchical zeolites prepared with the above hard template have a wide secondary pore size distribution. In addition, compared with carbon materials, these materials have poor thermal and mechanical stabilities, which limit their large-scale application in the field of hierarchical zeolites synthesis.

### 5.2.2. Soft Template Method

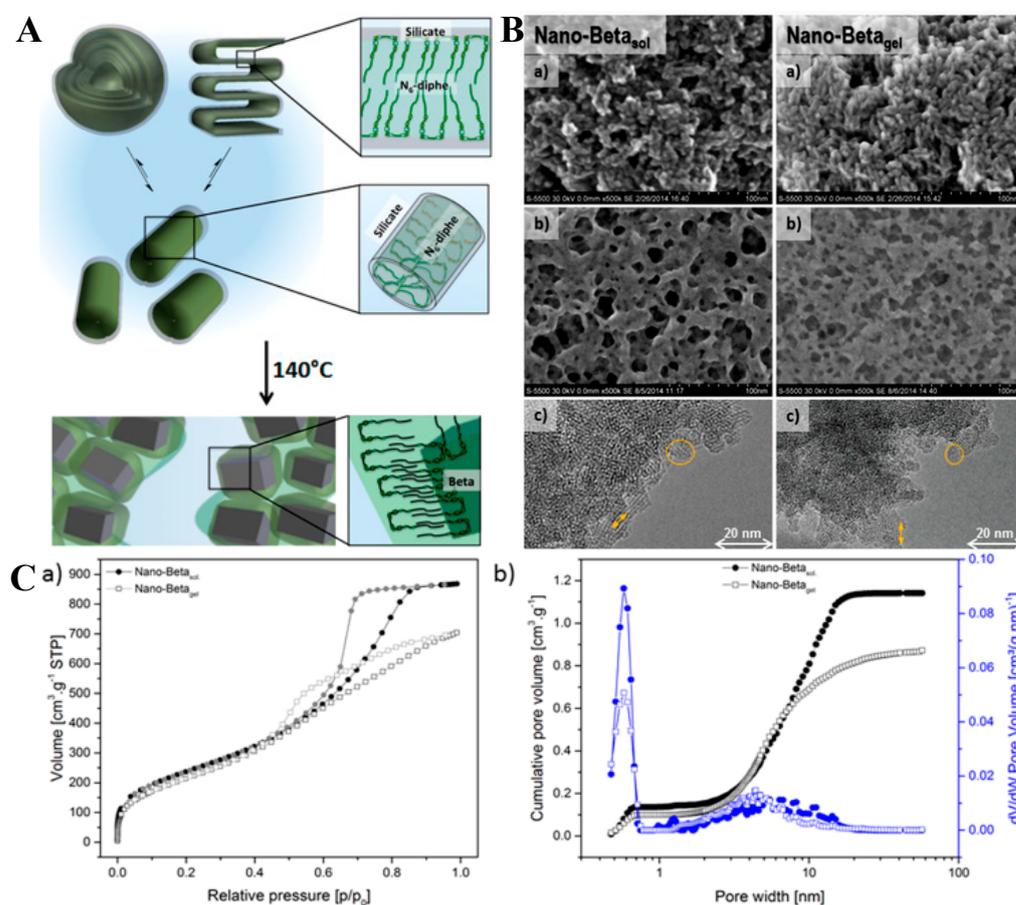
The structure of the hard template is fixed, and its chemical composition is poorly adjustable. Soft templates have strong surface charge modification capabilities and flexible structural compositions, so have been used in the field of zeolite synthesis [94–101]. Soft templates, such as surfactants, macromolecular polymers, and other amphiphilic macromolecular polymers or silane coupling agents, are composed of hydrophilic and hydrophobic groups. With the structural guidance of the hydrophilic groups, the organic long chain can be anchored in the zeolite crystal. Hydrophobic groups have a confinement effect on the crystallization of zeolite, eventually forming small nanocrystalline zeolite or layered zeolite [102–104].

Möller et al. [105] successfully prepared hierarchical beta zeolite by adding poly (diallyldimethylammonium chloride) (PDDA) as an intermediates template to the synthesis system of tetraethyl ammonium hydroxide. PDDA, as a cationic polyelectrolyte, can interact with negatively charged silicon precursor species and be inserted into zeolite crystal. The hydrophobic alkyl can effectively limit the growth of the zeolite, producing interparticle pores with very high mesopore volumes and surface areas in hierarchical beta zeolite. It was shown that the mesopore/macropore size can be adjusted between about 40 nm and 400 nm by increasing the amount of polymer in the synthesis gel. In another study, Aguado [106] synthesized beta zeolite rich in mesopores and high acidity by functionalization of the zeolite seeds with organosilanes to prevent their further aggregation. The mesopore size and specific surface area of the mesoporous beta zeolite can be regulated by adjusting the molecular size and amount of siloxane coupling agents. Unlike cetyltrimethylammonium bromide (CTAB) templates, organic siloxanes are more compatible with the zeolite framework, resulting in more stable hierarchical structures. The beta zeolite synthesized by means of this procedure have a very high total surface area with a considerable acid strength, so they present a superior higher catalytic activity than common beta zeolite in the catalytic conversion of low density polyethylene.

Vinícius et al. [107] added both CTAB and silane coupling agents to beta zeolite seeds solution and successfully synthesized hierarchical beta zeolites with different pore size distributions. The experiments showed that the sample prepared with CTAB exhibited a

narrower pore size distribution, more uniform and stable tetrahedral aluminum species, and stronger acidity. It exhibited excellent selectivity and stability in the polymerization reaction of propene. Although the sample prepared with the silane coupling agent as the template had a large external specific surface area, its acidity was weaker, resulting in poor cracking performance in the reaction.

Hierarchical beta zeolites were prepared by using a gemini-type piperidine-based multiammonium surfactant ( $N_6$ -diphe) as the mesoporous template, as shown in Figure 10 [108]. The mesopore formation mechanism was studied by means of dynamic light scattering, XRD, and NMR. First,  $N_6$ -diphe and aluminosilicate formed core-shell cylindrical micelles with  $N_6$ -diphe as the core and aluminosilicate as the shell. Under hydrothermal conditions, the aluminosilicate connected with hydrophilic groups crystallized at high temperature to form nanosized beta zeolite. Hydrophobic groups played a limiting role in the crystallization of zeolites, and finally formed spongy hierarchical beta zeolites. On the basis of BJH model, the mesopore size distribution centered at 6–8 nm and 10–30 nm, which would provide auxiliary benefits in catalysis. Figure 10 illustrates the surfactant employed as well as the main features of the hierarchical beta zeolite obtained by the soft template method.



**Figure 10.** Preparation process of hierarchical beta zeolites with gemini-type piperidine-based multiammonium surfactant. (A) Schematic illustration of the formation of zeolite beta particles, (B) SEM and TEM images, and (C) pore size distribution from  $N_2$  adsorption isotherm. Reprinted with permission from ref. [108]. Copyright 2018, Chemistry of Materials.

The synthesis of high-performance hierarchical zeolites can be achieved by using quaternary ammonium salt or siloxane coupling agents as large molecular template agents. The templates are expensive, and the synthesis process is complex, which hinder large-scale production and application. Zhang et al. [109] innovatively adopted the molecular trimming method to trim the molecular structure of dual-function quaternary ammonium surfactants. By using this simple organic molecule  $N_2$ -P- $N_2$  as the template, they obtained

hierarchical beta zeolites containing intercrystalline mesopores with higher catalytic activity and stability through the benzene and propylene polymerization reaction, which confirmed that the long hydrophobic alkyl chain of quaternary ammonium surfactants is not a necessary additive for synthesizing hierarchical pores. Liu et al. [110] introduced small-molecule N-methyl pyridinone into a beta zeolite synthesis system to obtain single-crystal hierarchical beta zeolites with high crystallinity and rich intracrystalline mesopores. The zeolite showed excellent activity and selectivity in large molecule catalytic reactions, such as weak acidic  $\alpha$ -olefin isomerization, strong acidic benzaldehyde, and primary alcohol formaldehyde condensation.

The difficulty of synthesizing hierarchical zeolites with soft templates is avoiding phase separation. Therefore, it is necessary to overcome the phase separation problem by changing the type of template, controlling the crystallization time, and changing the pH value of the solution, thereby achieving one-step hydrothermal synthesis to prepare hierarchical beta zeolites.

In summary, the preparation of hierarchical beta zeolites using soft template methods is an easy industrial process that prevents the framework damage that occurs with the desilication and hard template methods.

### 5.2.3. Template-Free Method

The template-free method is a synthesis method that uses a microporous template agent only without adding hard or soft templates. It is mainly divided into the following three categories: controlling the size of the zeolite crystal through small grain accumulation to form interstitial pores between crystals [111], controlling the transformation process of amorphous silica gel to produce intrapores, changing the growth direction of the zeolite crystal through regulating the cogrowth of the zeolite to form intrapores [112–114].

Xiong et al. [115] used the aerosol-assisted hydrothermal method to synthesize hierarchical beta zeolites with Si/Al ratios ranging from 44 to 392 in NaF media. Two different morphologies, including nanoaggregates with interparticle mesopores and plate-like zeolites with intracrystalline mesopores, were formed depending on the Si/Al ratios of the synthesis gels. The obtained hierarchical beta zeolites showed good Al species distribution and fewer internal defect sites and exhibited good activity and stability for the reaction of 1,3,5-trimethylbenzene cracking. Zhao et al. [116] developed a fast and mesopore-free strategy to synthesize high-silica hierarchical beta zeolites by conducting crystallization in low-water conditions ( $H_2O/SiO_2 = 1$ ). Further research results showed that a low water dosage can facilitate nucleation and crystal growth but restrains the fusion of individual nanocrystallites inside the particles, which help with the formation of hierarchical structures. In the reaction of methanol to olefins, hierarchical beta zeolite showed a much longer catalytic lifetime and slower coking rate than conventional zeolite due to the improved utilization of interior acid sites and enhanced molecular diffusion.

Although nanosized zeolites can be stacked into hierarchical zeolites rich in intragranular mesopores by self-assembly through controlling the crystal growth process, such hierarchical zeolites are relatively unstable, especially under harsh hydrothermal reaction conditions, where nanosized zeolites are prone to dissociation, resulting in structural collapse.

## 6. Conclusions and Outlook

In this paper, the research progress for the methods of synthesizing nanosized and hierarchical beta zeolites was reviewed. Additionally, its application in catalytic reactions was introduced. Nanosized zeolite reduces the occurrence of side reactions to a certain extent by shortening the diffusion path and improving the selectivity of products. Hierarchical zeolites can effectively reduce the diffusion resistance of guest molecules through the introduction of mesopores and increasing the effective utilization of active sites on the surface of zeolite, which significantly expands the application range of traditional microporous zeolites. The smallest particle size achieved for nanosized beta zeolite was 10–20 nm, which was obtained by using simple alkyl-substituted flexible dicationic as the OSDA,

while the best mesopore size distribution achieved for hierarchical Beta zeolite centered at 6–8 nm and 10–30 nm with the template-assisted synthesis method under the optimization of synthesis methods and parameters. However, it is still a challenge to promote the use of nanosized and hierarchical zeolites in large-scale industrial applications. The laborious and expensive synthesis process may be one of the main reasons limiting their large-scale production. In addition, the separation of nanosized zeolites and the preparation of hierarchical zeolites with a large number of secondary pores without sacrificing micropores are still a challenge. Therefore, researchers have been working to develop more effective methods to solve these problems. In order to achieve the industrial production of nanosized and hierarchical zeolites, the following are required: (1) The synthesis process must be simple. The steps in the process of synthesizing nanosized zeolite are complicated, and the solid–liquid separation of products is difficult, thereby hindering industrial application. For the seed orientation method, guiding agent or seed needs to prepare in advance, and the storage of the guiding agent needs the appropriate temperature and humidity; otherwise, efficacy can be easily lost. (2) The cost of the production must be low. The main selection principles of industrial raw materials are low cost and not producing a large amount of waste water, thereby creating higher economic value. (3) The scale-up of the process must be stable. The shift from laboratory-scale to industrial-production needs to be scaled up step-by-step. The most important aspect in the process of scaling up is to ensure that the samples have the same properties as the zeolite produced on the laboratory scale.

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### Abbreviations

The following abbreviations are used in this manuscript:

SDA	Structure-directing agent
OSDA	Organic structure-directing agent
PVB	Polyvinyl butyral
TEOS	Tetraethoxysilane
PDDA	Poly(diallyldimethylammonium chloride)
CTAB	Cetyltrimethylammonium bromide
N <sub>6</sub> -diphe	Gemini-type piperidine-based multiammonium surfactant
BJH	Barrett–Joyner–Halenda

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