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Review

# Research Progress on Modifications of Zeolite Y for Improved Catalytic Properties

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**Abstract:** Zeolite Y, as a solid acid catalyst with excellent performance, is a landmark in petroleum refining and chemical industry production–especially in catalytic cracking reactions. Improving the SAR of Y zeolite, enriching its pore structure, and modifying it with heteroatoms can realize the multifunctional catalysis of Y zeolite, improve the application value of it, and then meet the demands of petroleum refining. In this review, the synthesis of Y zeolites with high SAR, multistage pores, and heteroatom modification is summarized.

**Keywords:** zeolite Y; synthesis; high Si/Al ratio; hierarchical porous structure; heteroatom modification

## 1. Introduction

Zeolites are highly crystalline aluminosilicates with silica and aluminum trioxide as the main components; their structures are composed of $SiO_4$ tetrahedra and $Al_2O_3$ tetrahedra. The center of the tetrahedron is a silicon (or aluminum) atom, which is surrounded by four oxygen atoms. The individual tetrahedra are interconnected by oxygen atoms at the vertices and are arranged in different proportions and manners [1]. Silicon or aluminum in the framework can be replaced or partially replaced by phosphorus, gallium, titanium, chromium, iron, and other elements to form heteroatomic zeolites. Due to its unique crystal pore structure, variable acidity, high specific surface area, and good thermal and hydrothermal stability, zeolite has special "shape-selecting" catalytic properties and adsorption and separation properties, and has a very wide range of applications in various fields such as petrochemical, fine chemical, and environmental protection [2–4].

Y zeolites are composed of sodalite cages and hexagonal column cages connected according to the structure of diamond; a new three-dimensional cavity structure–the supercage–with a diameter of around 1.2 nm is formed between multiple sodalite cages in the framework. The supercages are mainly interconnected by a 12 membered ring with a diameter of about 0.74 nm, which creates a major channel for the substance transport. The schematic of the framework structure of Y zeolites is shown in Figure 1 [5]. Due to their 3D unobstructed framework structure, and excellent thermal and hydrothermal stability, Y-type zeolites can serve as a solid acid catalyst with excellent properties, which shows its irreplaceable roles in petroleum refining and chemical industry production, especially in fluidized bed catalytic cracking (FCC) reactions [6]. Ultra-stable Y zeolite (USY) treated by steam is the most commonly used industrial catalyst. The average particle size of Y zeolite crystals used in commercial FCC catalysts is generally less than 1 μm [7]. The active site of Y zeolite is located in its micropore, and only the reactant molecules adsorbed by the active site can react. Therefore, the acid and structural properties of zeolites have a great influence on the catalytic effect. The micropore size of Y zeolite is 0.74 nm, and there are many molecules whose molecular size is larger than 0.74 nm in the raw materials of FCC reaction. Therefore, the pore structure of Y zeolite seriously limits the diffusion of reactants and leads to the decrease in catalytic efficiency and selectivity. Therefore, it is very attractive to improve the transport properties of industrial Y zeolite catalysts, and the

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construction of mesoporous Y zeolites is a promising method to improve mass transfer. In industrial applications, the stability of the catalyst must be considered [8]. The stability of zeolite is largely determined by its Si/Al ratio, so the synthesis of Y zeolite with a high Si/Al ratio is an important direction of industrial research. The addition of heteroatoms will also affect the stability and catalytic activity of zeolites, so the synthesis of heteroatom Y zeolites is also very attractive [9].

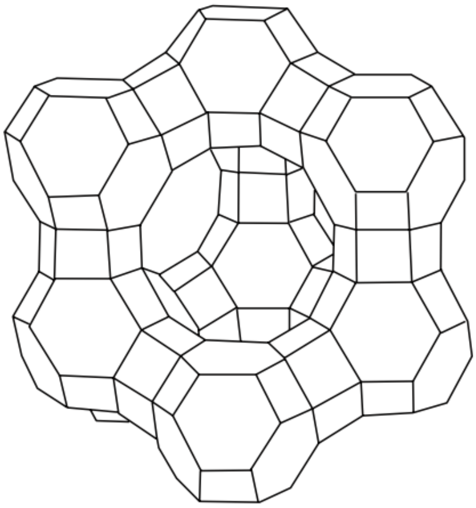

**Figure 1.** Schematic diagram of Y zeolite structure [5].

As the quality of crude oil decreases worldwide, the physicochemical properties of zeolites prepared by conventional synthesis methods have been unable to meet the current demand in petroleum refining, therefore, the modification of Y zeolites is widely concerned. This article collates a part of the different modification methods on Y zeolites in recent years and summarizes the advantages and disadvantages of different methods.

## 2. High $SiO_2/Al_2O_3$ Ratio Y Zeolites

Fluidized catalytic cracking (FCC) and hydrocleavage are currently important secondary processing processes of crude oil in the petroleum refining industry, and they are widely used to convert the high boiling, high molecular weight hydrocarbon components in crude oil into more valuable products–such as gasoline and olefin gases. Figure 2 gives the situation of specific weight occupied by different crude oil refining processes worldwide [10]. Y zeolites with FAU topology are the main active component of current industrial catalytic cracking agents [10–12]. FCC catalysts need to withstand harsh hydrothermal conditions in the process of reaction and regeneration; therefore, increasing the hydrothermal stability of Y zeolites–the active component of FCC catalysts–is of great importance to improve their catalytic performance. Studies have shown that increasing the framework SAR of Y zeolite can make part of the Al–O bonds be replaced by Si–O bonds; due to the shorter bond length and greater bond energy of Si–O bonds, Y zeolites with high SAR have stronger thermal and hydrothermal stability. Additionally, increasing the framework silicon to aluminum ratio of Y zeolites can also reasonably reduce the density and enhance the relative strength of acid centers, thereby reducing coke yield and improving product distribution [13,14]. Generally, the framework $SiO_2/Al_2O_3$ ratio (SAR) of NaY zeolite synthesized by conventional methods is about 3.0–5.0. Conventionally, we refer to NaY zeolite with a framework SAR greater than 6.0 as high-SAR Y zeolite. The inherent low-silicon framework characteristics and the resulting structural instability of Y zeolite synthesized by conventional methods have become the main bottleneck for direct industrial application. Increasing the SAR of Y zeolite is the best way to improve the acid property and structural stability of it, thereby enhancing its catalytic performance.

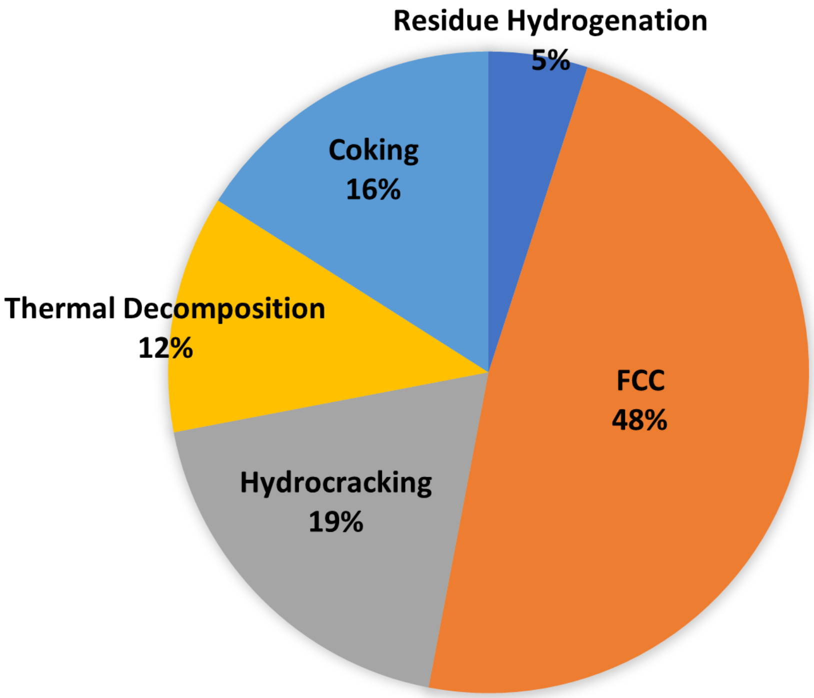

**Figure 2.** The proportion of different crude oil refining processes.

In order to obtain Y zeolite products with a higher framework SAR, much research work has been undertaken. At present, there are two main methods for preparing Y zeolites with high SAR: the direct synthesis method and post-treatment method [15]. The post-treatment method is to use a series of physical or chemical methods to treat the NaY zeolite synthesized by the conventional method to improve its framework SAR, while the direct synthesis method refers to the direct synthesis of NaY zeolite with high SAR by an appropriate method without any post-processing.

### *2.1. Post-Treatment Method*

For conventional Y zeolites, due to their low framework SAR and high number of aluminum atoms, they have a high density of acid centers, weak acid strength, and poor hydrothermal stability. To improve the catalytic cracking activity and hydrothermal stability of Y zeolites, it is necessary to post-treat Y zeolites to improve their framework SAR. After modification, the removal of aluminum and the migration of silicon atoms would increase the thermal and hydrothermal stability, decrease the acid density, enhance the acidic strength, and increase the catalytic activity of zeolites. At present, hydrothermal dealumination, chemical methods dealumination, and composite dealumination are the most predominant dealumination methods.

Hydrothermal dealumination is the most commonly used industrial NaY zeolite modification method. In 1968, Mc Danniel et al. first proposed a process for the super-stabilization of Y zeolite. By treating the ammonium-exchanged NaY zeolite with high-temperature water steam, part of the framework aluminum is hydrolyzed and removed, and then the amorphous silicon or framework silicon inside the Y zeolite will migrate and reorganize by high-temperature roasting to form a silica-rich Y zeolite, which is usually called ultrastable Y zeolite (USY). Bazyaril et al. [16] pointed out that hydrothermal treatment causes partial destruction of the Y zeolite crystal structure, making the crystallinity decline. The consequence of hydrothermal treatment is the change of aluminum atoms from framework aluminum to non-framework aluminum, and these framework-extracted aluminum atoms usually aggregate near the crystal surface, causing a gradient distribution of aluminum content [17]. In addition, a large amount of non-framework aluminum can adversely affect the catalytic performance and mass transfer, thus requiring subsequent chemical reagent treatment for dealumination [18]. Yurtaeva et al. [19] subjected Y zeolite to dealumination at high temperatures in a steam environment. The increase in SAR decreases the concentration of acid sites as well as strengthens them. HTVGO cracking was carried out to examine the effect of SAR on the catalytic properties. The results show that a rise in SAR enhances the yield of $C_2$–$C_4$ olefins from 25.3 to 27.1 wt % as a result of the smaller contribution of hydrogen transfer reactions due to the acidity decrease.

Chemical dealumination is the method in which the dealumination of zeolite framework occurs in a solution with the aid of interactions between acids, salts, or chelating agents and zeolites. López-Fonseca et al. [20] modulated the aluminum content of commercial HY zeolite by adjusting the $(NH_4)_2SiF_6$/zeolite ratio, and removed 16%, 32%, 50%, and 64% of aluminum from the zeolite, respectively. The experimental results show that when the dealumination degree is lower than 50%, the zeolite structure is almost unaffected, and the pore structure is well maintained. However, when the dealumination degree reaches 64%, the zeolite exhibits obvious structural collapse due to the extraction of a large amount of aluminum from the zeolite framework. These modified Y zeolites exhibit higher catalytic activity compares to the parent zeolites, and the increase in activity is related to the strong acidity due to the dealumination. Yan et al. [21] systematically investigated the dealumination of USY zeolites by nitric acid and oxalic acid under different conditions. Studies have shown that the removal of different types of aluminum species can be achieved by controlling the acid type and concentration as well as the treatment temperature. Oxalic acid can extract aluminum at a high rate, even at low concentrations; additionally, acid treatment of USY zeolite can increase its Bronsted acid strength. Ainul et al. [22] achieved controllable dealumination of Y zeolites in an oxalic acid solution by introducing tetraalkylammonium into Y zeolites via the impregnation method. Experiments show that the presence of tetramethylammonium cations can protect the zeolite framework without affecting the dealumination process. By adjusting the concentration of oxalic acid solution, dealuminated Y zeolite with a SAR in the range of 4.0–4.9 was obtained, and the crystallinity of Y zeolite was maintained while increasing its SAR. Yu Yun et al. [23] mixed aqueous solutions of acid fluoride salts ($NaHF_2$, $KHF_2$, $NH_4HF_2$) with Y zeolite to obtain modified Y zeolite with a SAR of 6–12. Acid fluoride salts can slowly electrolyze out $H^+$ and $F^-$, have a strong buffer effect on the change of solution pH, and the ionized $F^-$ can complex with $Al^{3+}$, further improving the dealumination efficiency. Therefore, this method can obtain Y zeolites with a high crystallinity and high SAR without additional buffers. Yakimov et al. [24] investigated the difference between the $(NH_4)_2SiF_6$ treatment and hydrothermal treatment on the dealumination of nanoscale Y zeolites. The results show that for Y zeolites with a grain size less than 700 nm, hydrothermal treatment can make them completely amorphous. However, $(NH_4)_2SiF_6$ treatment can dealuminate zeolites under mild conditions and increase their SAR to 7.6–10 while maintaining their crystallinity. The $(NH_4)_2SiF_6$ treatment method can also be used on zeolites with a grain size less than 50 nm, but this method has the disadvantage of forming a layer of $SiO_2$ membrane on the surface of zeolites, which can greatly limit the catalytic effect of treated zeolites. M Hosseini et al. [25] used acetylacetone as chelator to dealuminate Y zeolites using ultrasound method. The results show that the combination of ultrasonic treatment and acetylacetone treatment greatly increases the dealumination degree of Y zeolite, especially for HY and NaY zeolite. Buttersack et al. [26] studied the stability of highly dealuminated Y-zeolite in liquid aqueous media. Through the stability test of Y zeolite in pure water and NaCl solution with different PH, it was found that the hydrothermal stability of high-silica zeolite is higher, but the existence of $Na^+$ will accelerate the decomposition of zeolite.

Although hydrothermal dealumination can significantly improve the framework SAR, it will produce a large amount of non-framework aluminum, which affects the catalytic performance. The chemical method can remove the non-framework aluminum and increase the content of secondary pores, but it will seriously damage the framework structure of zeolites and cause a large loss of crystallinity. The modification of zeolites by a combination of chemical dealumination and hydrothermal dealumination can not only improve the SAR and framework stability of zeolite, but also remove non-framework aluminum. Wang et al. [27] modified Y zeolite by a combination of hydrothermal treatment, acid dealumination, and hydrothermal crystallization in the presence of surfactants. The results show that the presence of a small amount of surfactant cetyltrimethylammonium bromide (CTAB) can significantly improve the relative crystallinity, SAR, pore structure, and hydrocracking performance of Y zeolite. The results of the hydrocracking reaction of vacuum gas oil (VGO) showed that the hydrocracking activity and middle distillate yield of the Y zeolite modified in the presence of CTAB were 2.42% and 4.20% higher than that of the commercial catalyst, respectively.

In general, the modified zeolites obtained by the post-treatment method have a large loss of crystallinity and low product yield; further, this method also has disadvantages such as high cost, complicated process, and environmental pollution. At present, the high-silica Y zeolites widely used in the industry are mainly obtained by the post-treatment of conventionally synthesized Y zeolites. This method not only has a complicated operation and high energy consumption, but also presents aluminum gradients both on the crystal surface and inside it, causing the uneven distribution of acid centers. Therefore, although it is difficult to synthesize NaY zeolite with high SAR by the direct method, it can compensate the deficiency of tge post-processing method to some extent and is very important for the preparation of catalytic cracking catalysts.

### 2.2. Direct Synthesis Method

It is known that the lower the SAR of Y zeolite, the easier it is to prepare, while the higher the SAR, the harsher the preparation conditions required. The direct synthesis method refers to the direct synthesis of high SAR Y zeolites without any post-treatment process. High-silica Y zeolite synthesized by the direct method has a perfect structure and uniform aluminum distribution, which is an ideal catalytic material and has been pursued by the industry and researchers. However, the direct synthesis of high-silica Y zeolites has been a great challenge in the field of zeolite synthesis for the past 60 years. At this stage, the methods for the direct synthesis of high SAR NaY zeolites mainly include the organic templating method and non-organic templating method.

The organic template method is to synthesize high SAR NaY zeolites by adding organic templates to the initial gel of zeolite synthesis as structure directing agent. In 1990, Delprato et al. [28] directly synthesized high-silica Y zeolite with SAR of about 9 by one-step hydrothermal method using 15-crown ether-5 as the structure directing agent. Despite the simplicity of the one-step hydrothermal synthesis method, the high cost and toxicity of crown ether limit its industrial application. Therefore, many research groups are devoted to developing a nontoxic and inexpensive organic template to synthesize high-silica Y zeolites. Zhu et al. [29] synthesized high-silica Y zeolite at a crystallization temperature of 120–130 °C using a low toxicity, inexpensive organic template N-methylpyridinium iodide (NMPI) as a new structure directing agent. The Y zeolite obtained by this method has high crystallinity, and its framework SAR can reach 6.35–6.85. Compared with Y-zeolites obtained by conventional synthesis methods, this zeolite exhibited high hydrothermal stability and larger adsorption capacities for water, acetone, and n-hexane. In the cumene cracking reaction, the initial activity was 84.9%, which is obviously higher than those of ordinary Y zeolite with a low Si/Al ratio (60.6%). Yuan et al. [30] synthesized a high-silica Y zeolite with a SAR of 6.20–6.40 using alkyl-substituted imidazole ionic liquids 1-ethyl-3-methylimidazole bromide and 1-butyl-3-methylimidazole bromide as organic templates. The imidazolium cations can partially replace $Na^+$ to balance the negative charges in the zeolite framework and promote the formation of faujasite structures with a high SAR. He et al. [31] directly synthesized high-silica Y zeolites with the framework SAR between 6.0–7.0 using choline-based organic ammonium salts (e.g., choline chloride, choline hydroxide) as structure directing agents under basic conditions. However, it is difficult to obtain Y zeolites with a SAR greater than 7 in one-step synthesis without using crown ether as the structure directing agent. He et al. [32] successfully synthesized high-silica Y zeolite with a SAR up to 7.76 using a commonly used organic template tetraethylammonium hydroxide (TEAOH) as the structure directing agent. It was found that the $TEA^+/Na^+$ ratio of the initial gel has an important influence on the SAR of the product, and the pure **FAU** topology zeolite was synthesized in the phase region with a relatively narrow $TEA^+/Na^+$ and $OH^-/Al$ ratio in the initial gel: $TEA^+/Na^+$ ratios of 0.32–1.25, and $OH^-/Al$ ratios of 1.8–2.0. It was found that the $TEA^+/Na^+$ ratio of the initial gel is positively related to the SAR of zeolite and therefore, in order to increase the SAR of Y zeolite, the $TEA^+/Na^+$ ratio should be as high as possible. However, the **FAU** to **BEA** phase transition can be observed in the high $TEA^+/Na^+$ ratio system. Considering the high SAR and pure **FAU** phase, the most suitable $TEA^+/Na^+$ ratio is 1.15. Yan et al. [33] synthesized high-silica Y zeolite with a framework SAR of up to 21.35 in one step in a dual-template system using high-silica Y zeolite as the seed. The specific steps are as follows: two organic templating agents (the first templating agent preferably tetramethylammonium hydroxide and the second templating agent preferably any tetraalkylammonium hydroxide other than tetramethylammonium hydroxide) are dissolved to obtain a double template solution, it is then mixed with the aluminum source and base source, and then the silicon source and high-silica Y zeolite seed ($Si/Al > 50$) are added to the solution, followed by sequential aging and the hydrothermal crystallization process, in order to obtain high-silica Y zeolite. The dual template can play a role of space filling for the specific pore channel structure, in which the second template agent with a longer molecular chain is able to occupy more space, thus reducing the amount of aluminum source introduced into the framework. Meanwhile the high-silica Y zeolite seeds can provide high-silica crystal nuclei for crystallization, and therefore the synergistic effect of the double template system and seeds increases the SAR of the Y zeolite framework.

The obstacle in the way of increasing the Y zeolite framework SAR is the mismatch between the basicity required for nucleation/crystallization and that is required for the high framework silicon aluminum ratio. High alkalinity systems facilitate nucleation and crystallization, but usually lead to the formation of zeolites with low framework SAR due to the increased solubility of silica [34]. Recently, Tian Peng's team [35] proposed a new synthesis strategy for high-silica Y zeolite. This method involves the use of FAU nuclei, a bulky organic structure-directing agent (OSDA), and a gel system with low alkalinity and named NOA-co strategy (Figure 3). The direct synthesis of high-silica Y zeolite with a SAR up to 15.6 was first achieved under the synergistic effect of three factors: highly dispersed **FAU** nucleate solution, bulk organic template, and low basicity initial gel. It was shown that **FAU** microcrystals provide highly active nanocrystals nuclei and can help overcome the difficulties of zeolite nucleation. The introduction of bulky organic structure directing agent with low charge density can direct the crystal growth of a high-silica **FAU** structure. Researchers have discovered eight bulky quaternary ammonium ions that can act as effective organic structure directing agents, of which tetrabutylammonium hydroxide (TBAOH) is the strongest, with a relatively broad synthetic phase region and the highest framework SAR (15.6). Materials synthesized by the NOA-co method show excellent catalytic activity in cracking reactions of macromolecular feedstocks, and this method provides a new idea for the synthesis of high-silica zeolites.

Due to the high cost and environmental pollution of most templates, the large-scale industrial production of the organic template method is limited. At present, the preparation of high-silica Y zeolites by the organic template free method has become a research hotspot. Matthew et al. [36] synthesized high-silica Y zeolites with a SAR of 6 using a one-step organic template free method. Research shows that the crystallization rate of Y zeolite in this synthesis system is slow, and the longer crystallization time is helpful for the incorporation of Si into the zeolite framework. In addition, the concentration of $Na^+$ and $OH^-$ in the system is low, $OH^-$ is the mineralizer in zeolite synthesis, and $Na^+$ acts as the inorganic structure directing agent and balances the negative charge of the framework Al site, so the concentration of $Na^+$ and $OH^-$ also affects the number and position of framework Al. Ferdov et al. [37] further optimized the synthesis conditions of the organic template free method to prepare Y zeolites, and achieved the best balance between a high SAR and high crystallinity by adjusting the crystallization time, temperature, $NaAlO_2$ and $H_2O$ content; a high crystallinity Y zeolite with SAR of more than 5 was successfully prepared. Experiments show that a synthesis temperature lower than 100 °C is beneficial to the improvement of the SAR of Y zeolite. Yu Jihong's team [38] published the work on the preparation of Y zeolite with high SAR by combining the hydroxyl radical-assisted method and post-treatment method. In this study, Y zeolite with a SAR of 6.35 was synthesized in one step without an organic template through a hydroxyl radical-assisted route, breaking the challenge of synthesizing Y zeolite with a SAR over 6 without a template. Studies have shown that $OH^-$ radicals can promote the formation of Si-O-Si bonds, so the SAR of Y zeolite can be increased to 6.35. To further increase the SAR, a dealumination process was carried out using citric acid, which decreased the crystallinity of zeolites. To heal the zeolite, a subsequent second-step hydrothermal crystallization was carried out. Thus, the sample with an SAR of up to 7.5 and good crystallinity was obtained. The improvement of the catalytic performance of the zeolite was studied using cumene cracking as a model reaction. The experimental results show that the increase in SAR is beneficial to the catalytic activity. The sample with a SAR of 7.5 showed a higher conversion with the highest initial conversion of 32.2%, which was much better than that of the contrast sample with a SAR of 5.

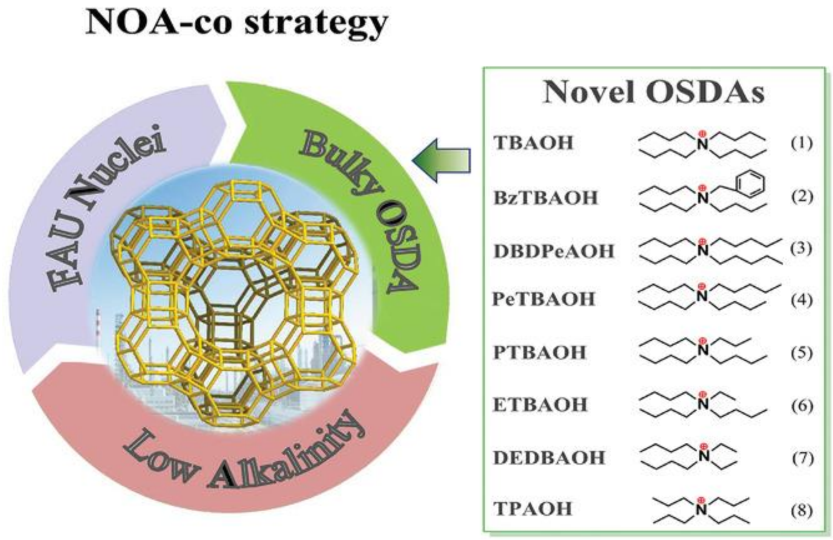

**Figure 3.** NOA-co strategy and novel OSDA for the synthesis of high-silica Y zeolite [36].

## 3. Hierarchically Porous Y Zeolite

Y zeolite has unobstructed three-dimensional pore structures, good thermal and hydrothermal stability, and tunable acidity; these characteristics make Y zeolite widely used in petrochemical production processes, such as catalytic cracking, hydro cracking of hydrocarbons, and alkylation reactions. The pore structure of Y zeolite is an important factor affecting its catalytic performance. In general, the active centers inside the micropores of zeolites is much more than that on the external surface, so the catalytic reaction mainly occurs inside the micropore channels. However, the micropore size of conventional zeolite is less than 2 nm whereas the size of molecules in crude oil is generally larger than that, and thus it is difficult for reactant molecules to enter the micropores and interact with the active centers inside them, which leads to the reduction of catalytic efficiency [39]. In addition, the narrow space severely restricts the diffusion and transport of reactant/product molecules, leading to the occurrence of secondary reactions or the generation of carbon deposits, thus affecting the lifetime of the catalyst [40,41]. Currently, petroleum refining is facing serious challenges due to the reduction in light crude oil production [42]. As the leading catalyst in catalytic cracking, Y zeolite's microporous structure limits its wide application in industrial catalysis because of its mass transfer of large molecules.

In order to alleviate the problem of diffusion and improve the utilization rate of active centers, much research focuses on introducing mesopores into microporous zeolite crystals, using the pore size advantage of mesopores to overcome the diffusion limitation, thus improving the catalytic performance of zeolites [43,44].

Hierarchically porous zeolite alleviates the diffusion limitation of micropores for macromolecules and has more advantages in industrial application compared with microporous zeolite. Currently, the main methods to introduce mesopores into the Y zeolites structure include the bottom-up method and top-down method. The bottom-up method is a constructive approach that utilizes templates to build micropores and mesopores simultaneously during the synthesis process of zeolite. The top-down method is a destructive approach that introduces mesopores by the post-treatment of zeolites with acid or alkali species, and this process is accompanied with desilication and dealumination reactions.

### *3.1. Bottom-Up Method*

In the bottom-up method, specific chemical reagents or solid materials will be added to the zeolite synthesis system as a mesoporous template, and the mesopores can be obtained by removing the template by means of calcination or extraction. Commonly used templating agents are divided into hard templates and soft templates.

Hard templates are solid materials with relatively stable structural properties and chemical properties. In the hydrothermal crystallization process, zeolites grow around the template, and after removing the template by calcination or other chemical methods, the spatial positions occupied by the template become mesopores. Commonly used hard templates are carbon nanomaterials, carbon black, and carbon aerogels, etc. [45–48]. Tao et al. [49] successfully synthesized Y zeolite with uniform mesopores using carbon aerogels prepared by the pyrolysis of resorcinol-formaldehyde aerogels as a mesoporous template. Infiltrating the synthesis liquid into carbon aerogel, and Y zeolite with regular mesopores, could be formed by removing the template after hydrothermal crystallization. The pore size of mesopore is about 10 nm, and the mesoporous volume is 1.37 $cm^3/g$. Samer et al. [50] prepared Y zeolite with intracrystalline mesopores using carbon nanotubes (CNTs) and nanocrystalline cellulose (NCC) as hard templates. The research shows that the effect of NCC in introducing mesopores is better than that of CNTs, and mesoporous Y zeolites with a mesopore volume up to 0.21 $cm^3/g$ could be prepared by using NCC as a template agent. In addition, NCC is more economical and efficient, so it is more suitable for it to be a hard template.

However, due to the particularity of the Y zeolite synthesis system, complex steps are generally required to resolve the incompatibility between the hard template and the precursor. In addition, the calcination progress of template removal will also cause some damage to the zeolite framework. Therefore, the hard template method has some limitations in industrial applications. Compared with the hard template method, the soft template method has a higher flexibility in adjusting the mesoporous structure. The soft template method uses self-assembleable organic polymer as a template, and the mesopores are formed through the interaction between the template and the aluminosilicate precursor. At present, commonly used soft templates include surfactants, cationic polymers, and silane coupling agents.

Xiao et al. [51] synthesized mesoporous Y zeolite in a quaternary ammonium salt N,N-dimethyl-N-octadecyl-N-(3-triethoxysilylpropyl) (TPOAB) dispersed sodium silicate system. This template can be uniformly dispersed in the precursor solution, and hierarchically porous Y zeolite containing both mesopores (8–30 nm, centered at 18 nm) and ordered micropores can be synthesized in one step. The pore distribution curve of zeolite is shown in Figure 4. It can be seen that the Y zeolite shows mesopores in the range 8–30 nm, centered at 18 nm. Jin et al. [52] reported a facile method to synthesize mesoporous Y zeolite with a mesoporous volume up to 0.29 $cm^3/g$ using the amphiphilic silane octadecyldimethyl[trimethoxysilylpropyl]ammonium chloride TPOAc as template. The schematic diagram of its synthesis mechanism is shown in Figure 5. The hydrolysable methoxysilyl groups in the amphiphilic silanes could link to the zeolite surface via Si-O bonds, and the micelles formed by the long hydrophobic organic chains act as mesoporous templates. This method effectively solves the phase separation problem between the template and the aluminosilicate gel. Compared with conventional Y zeolites, this mesoporous Y zeolite shows superior catalytic performance in the catalytic cracking reaction of vacuum gas oil (VGO). This catalyst can significantly increase the yield of gasoline and reduce the yield of coke and dry gas. The improvement of its catalytic performance can be attributed to the improved accessibility of zeolite active centers by the introduction of mesopores. Zhao et al. [53] developed a novel aggregation assembly method to synthesize hierarchically porous Y zeolite with mesoporous channels using the triblock copolymer F127 (PEO106-PPO70-PEO106) as a template. Two types of mesopores exist in this zeolite: smaller mesopores of 6.5 nm and larger mesopores of 35 nm. The addition of F127 not only introduces mesopores into zeolites, but can also adjust the acidity of zeolites. These properties make mesoporous Y zeolites exhibit an excellent catalytic performance in fluidized catalytic cracking, and the reaction catalyzed by this zeolite has a high gasoline yield and low coke yield. Wang et al. [54] achieved a one-step hydrothermal synthesis of hierarchically porous Y zeolites using organosilanes as a co-structure directing agent and anionic surfactants ($C_nH_{2n+1}AM$, n = 8–18, A=COO, $OSO_3$, M=H, Na, K) as a mesoporous template. In this method, the quaternary ammonium salt sites of organosilanes can interact with the negatively charged anionic surfactant heads, and the alkoxy groups can interact with inorganic silicon species, therefore, the co-structure directing agent can connect the organic template and inorganic precursors, which solves the problem that the microporous template and mesoporous template cannot be reasonably matched, connected, and co-built during the self-assembly process, prompting the formation of hierarchically porous Y zeolites. Alexander et al. [55] synthesized Y zeolites with mesopores of different morphologies using imidazolium ionic liquid-based surfactant [$C_{16}$MIm]Cl and pyridine ionic liquid-based surfactant [$C_{16}$MPy]Cl as mesoporous templates. Researchers compared mesoporous Y zeolites synthesized by this method with those synthesized using the classical mesoporous template–ammonium based surfactant CTAC–and found significant differences in the templating behavior of CTAC with [$C_{16}$MIm]Cl and [$C_{16}$MPy]Cl, that is, the mesopore size distribution of Y zeolite synthesized using the latter as a template was wider. This indicates that the difference in the micellization ability within limited space of three surfactants affected the structure of zeolites. Aasif et al. [56] hierarchically synthesized porous Y zeolite by a one-step method using cationic polymer polydiallyldimethylammonium chloride (PDDA) as a bifunctional template. This zeolite contains mesopores with an average pore size of 3.7 nm, and its crystallinity, Si/Al ratio, and pore properties are all affected by PDDA and NaOH concentrations. The $CO_2$ adsorption test shows that the adsorption capacity of hierarchically porous Y zeolite can reach 5.4–5.9 mmol/g, which is 20% higher than that of microporous Y zeolite. Tian Peng's team [57] synthesized high-silica Y zeolite with a large number of intracrystalline mesopores in one step using the TPOAC-assisted NOA-co method. This zeolite has abundant mesopores and high hydrothermal stability. At the same time, its SAR is as high as 9.8, and its acid density and acid strength are both higher than that of USY. In catalytic reactions involving macromolecules, this mesoporous Y zeolite exhibits significantly higher catalytic activity and lifetime than the mesoporous-free Y zeolite prepared by the NOA-co method and commercial USY. Martins et al. [58] prepared hierarchical Y zeolites through the surfactant-assisted methodology. The results show that the mesoporous properties of Y zeolite are closely related to the kinds of surfactants used. Compared with the samples prepared by DTAB under the same conditions, the mesoporous porosity of the samples modified in the presence of the larger surfactant molecule CTAB was higher, and the yield and rate constant of the products significantly increased in the catalytic reaction.

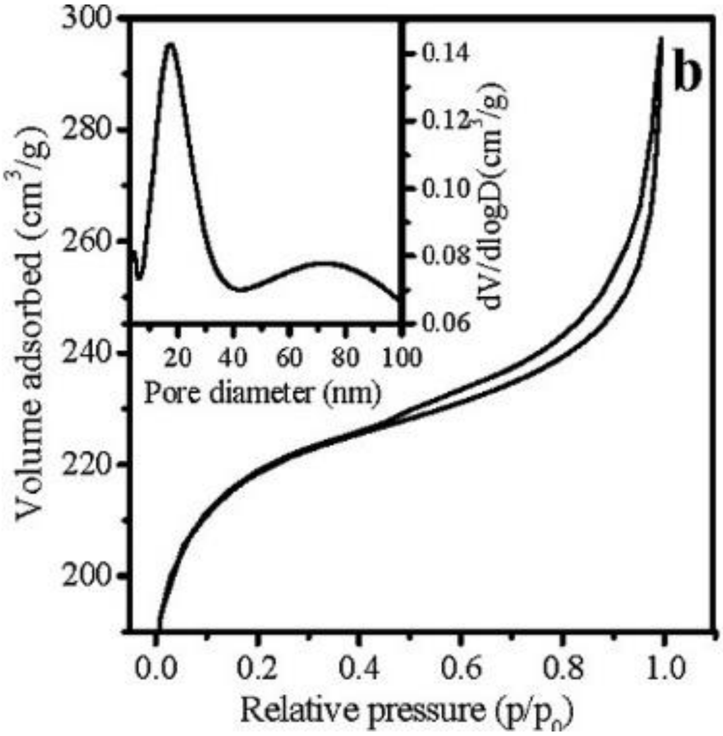

**Figure 4.** Pore distribution diagram of mesoporous zeolite Y synthesized using TPOAB as template [51].

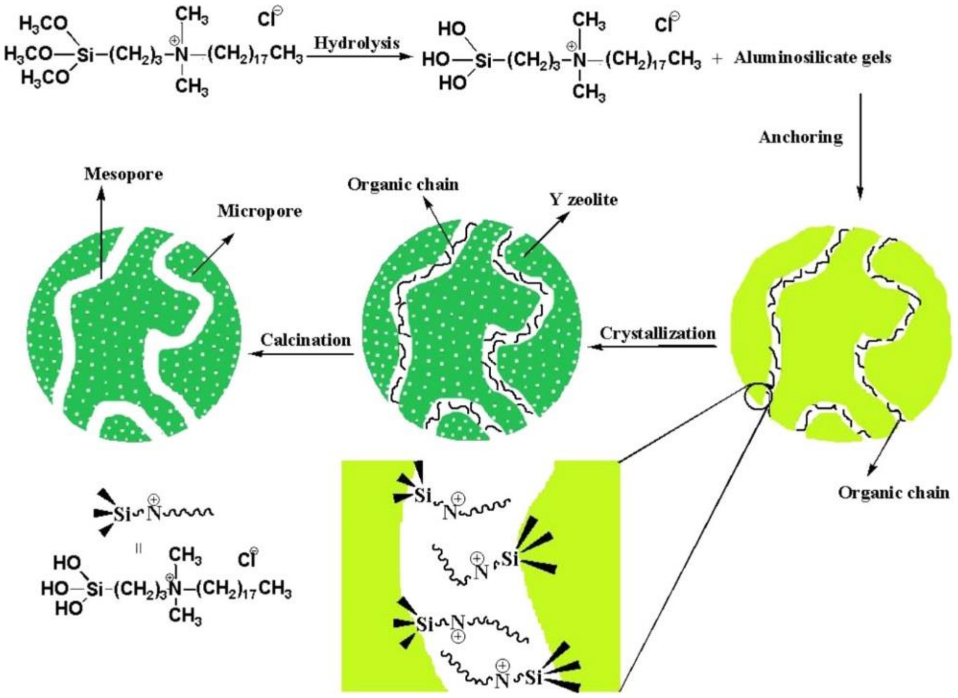

**Figure 5.** Schematic diagram of the synthesis mechanism of mesoporous Y zeolite [52].

From a synthetic point of view, the template method usually suffers from the phase separation between the mesopores and zeolite crystals, and some templates are expensive and not suitable for large-scale industrial applications. In addition, the amount of mesopores is closely related to the concentration of the synthesis system, and the adjustable range of it is relatively small, which is unfavorable for the synthesis of high-silica Y zeolites. From the point of acid centers, the zeolites prepared by this method maintained the intact structure of microporous zeolites, and no adjustment occurred to the framework structure, so the ratio between different acid centers is difficult to match reasonably, which means it cannot meet the demand of industrial production.

### *3.2. Top-Down Method*

The top-down method is a destructive approach in which zeolites will be subjected to desilication or dealumination, causing partial collapse of the framework and thus introducing mesopores into the structure. Commonly used treatment methods include hydrothermal treatment, chemical treatment, and combined treatment.

Hydrothermal treatment is the most commonly used method. Treating Y zeolite with high-temperature steam can remove part of the framework aluminum and silicon, thus improving the hydrothermal stability of zeolites and tuning their pore structure properties and catalytic effects. The process of this method is shown in Figure 6. Under suitable conditions, high-temperature steam can hydrolyze the Si-O-Al bonds, and the Al atoms are removed from the zeolite framework to generate hydroxyl nests and silicon-rich regions. The hydroxyl nests are occupied by Si atoms, resulting in the rearrangement of the framework structure. The vacancies created by dealumination cannot be completely filled by Si atoms, so mesopores appear in the zeolite framework [59]. Jong et al. [60] analyzed the pore structure of the as-prepared USY zeolite by nitrogen adsorption and three-dimensional TEM. The results show that the mesopores in zeolites are mostly isolated and occluded when the mesopore volume is small. Additionally, when the mesopore volume becomes large, part of the mesopores begin to connect with each other and with the outer surface.

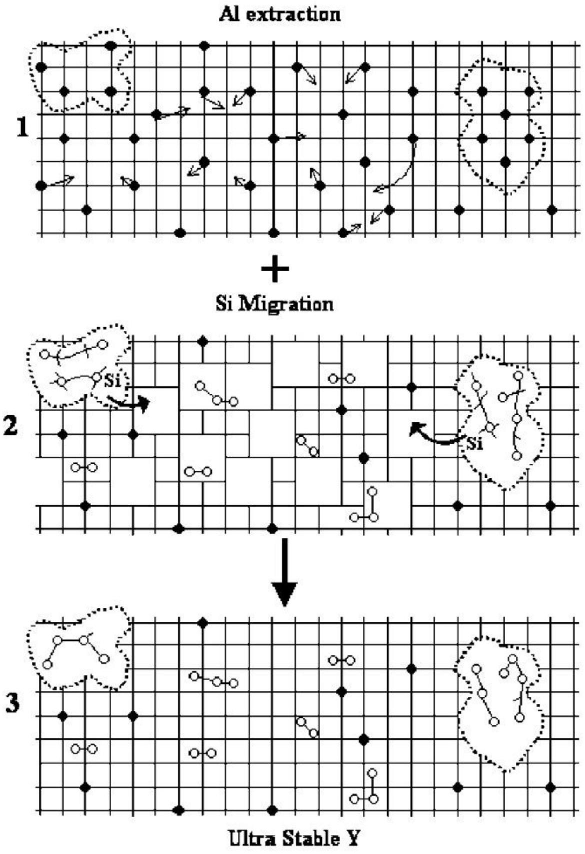

**Figure 6.** Formation progress of mesopores by dealumination [59].

Chemical treatment refers to a method of treating the zeolites with chemical reagents such as acids, bases, salts, or complexing agents to partially dealuminate or desilicate the framework [61]. Li et al. [62] successfully prepared Y zeolite with abundant mesopores and controllable pore size distribution by sequential ammonium fluorosilicate and alkali treatments. The results showed that after ammonium fluorosilicate treatment, the surface of zeolite particles has many defects and is in a silicon-rich state, which is unstable and easy to desilicate under alkaline conditions to form a large number of mesopores. Meanwhile, the pore channels formed by ammonium fluorosilicate treatment improved the efficiency and depth of desilication by subsequent alkali treatment. The catalytic performance of zeolites was evaluated by the cracking reaction of 1,3,5-triisopropylbenzene, and the results showed that the catalytic activity was closely related to the mesoporous system. Gackowski et al. [63] used NaOH solution, tetrabutylammonium hydroxide (TBAOH) solution, and NaOH/TBAOH mixed solution to alkali-treat Y zeolite with SAR of 31, respectively. The results show that NaOH solution will dissolve 78% of the framework silicon, which will lead to amorphization of the zeolite and loss of micropores and acidity. The TBAOH solution only dissolves a small amount of framework silicon and slightly increases the mesoporosity, and most of the microporous structure is retained. Treatment with NaOH/TBAOH mixed solution can dissolve 43% of the framework silicon while maintaining the microporous structure, which greatly improves the mesoporosity of the zeolite without changing the strength of acid centers. These outstanding properties make it exhibit higher catalytic activity in the $\alpha$-pinene isomerization reaction. Subsequently, this group optimized the desilication conditions using infrared spectroscopy and NMR methods [64]. In order to obtain zeolites with optimal crystallinity, porosity, and acid properties, the optimal condition was sought by adjusting the ratio between NaOH and TBAOH as well as the treatment temperature. Considering the desilication effect and economic factors, the desilication agent should contain 10 mol% TBAOH, and the optimum temperature is 353 K. Duan et al. [65] obtained hierarchical porous Y zeolites using an oxalic acid-ammonia co-treatment method. After treatment, the surface area of zeolite increased more than three times, and the mesoporous volume increases more than four times. Qin et al. [66] achieved the controllable extraction of framework cations (Si, Al) in Y zeolites, and the formation of mesopores by etching Y zeolites with $NH_4F$ solution. A small amount of $H_2F^-$ produced by double hydrolysis of $NH_4F^-$ can extract Si and Al from the framework at the same rate. Due to the low content of $H_2F^-$, the whole process is mild and controllable. Additionally, $H_2F^-$ is well distributed in the zeolite crystal, avoiding the problem of concentration gradient. The generation of mesopores can be observed when the treatment time reaches 20 min. Feng et al. [67] prepared hierarchical porous Y zeolites using $NH_4HF_2$ as a dealuminizer. Compared with other systems containing $H^+$ and $F^-$, the crystallinity of NaY zeolite treated with $NH_4HF_2$ solution is better maintained, which is due to the slow ionization rate of $NH_4HF_2$, and the buffering effect means the concentration of $H^+$ and $F^-$ will not rise suddenly. Therefore, the dealumination reaction of NaY zeolite in $NH_4HF_2$ solution is more persistent and milder. It was found that the concentration of $NH_4HF_2$ solution had a great influence on the pore structure of NaY zeolite. With the increase in $NH_4HF_2$ concentration, the Si/Al ratio and mesoporosity of modified NaY zeolite increased. The NaY zeolite treated with 0.3 M $NH_4HF_2$ has high crystallinity and suitable mesopore content and exhibits the best toluene adsorption performance in the toluene adsorption experiment. Zhang et al. [68] proposed a post-synthetic method combining the microwave-assisted dealumination and hydrothermal alkaline treatment to obtain mesoporous Y zeolite. The results show that when using inorganic acid (i.e., hydrochloric acid, HCl) for dealumination, the acid will destroy the crystal structure of zeolite and will not produce obvious mesoporous. The carboxylic acid with the function of chelation was very capable of extracting Al species and creating mesopores.

The combined treatment method refers to the combined use of hydrothermal treatment and chemical treatment, which can combine the advantages of the two methods. Gola et al. [69] treated USY zeolite with high-temperature steam followed by nitric acid, ammonium fluorosilicate, and EDTA, and investigated the state of non-framework aluminum and its effect on catalytic performance. It was found that this combination can not only remove non-framework aluminum, but also improve the crystallinity and structural stability of the zeolite. Zečević et al. [70] studied the pore structure of commercial Y zeolite after steam-acid treatment. The results confirmed that the Y zeolite treated by this combined method contained a large number of mesopores, most of which were connected, and only a few of the pores were blocked. Qin et al. [71] used NaOH solution/oxalic acid solution to desiliconize/dealuminate Y zeolite, introduced Si-defects/Al-defects into them, and then carried out hydrothermal treatment on the defects containing Y zeolite. In this way, the effect of different kinds of defects on the formation of mesopores during hydrothermal treatment was studied. The experiments show that Si-defects are beneficial to the formation of mesopores, while the presence of Al-defects has an inhibitory effect on the mesopores.

Generally speaking, the top-down method of preparing mesoporous Y zeolite is simple and low in cost, but the crystal structure of the obtained zeolite will inevitably be destroyed to a certain extent. The zeolite has low crystallinity and poor thermal and hydrothermal stability, which restricts its industrial application. The mesoporous Y zeolites synthesized by the bottom-up methods have various and adjustable mesoporous structures, and high crystallinity and good stability. However, the high price of organic template is a major limitation for its industrial application. In addition, the process of removing the template by roasting not only consumes energy, but also pollutes the environment. These problems need to be solved urgently. Therefore, it is an attractive topic to develop an economical and environmentally friendly method to produce high crystallinity zeolites with excellent mesoporous structure.

## 4. Heteroatomic Y Molecular Sieve

Heteroatomic molecular sieves are formed by partially replacing Si or Al in the framework with transition metal elements (Ti, Fe, Zr, Cu, Mn, V, W, etc.) or main family elements (as, Ga, Sn, Ge, etc.) whose properties are similar to those of Si or Al [72,73]. The heteroatom introduced into the framework is generally one type, but it can also be more than one in some cases. The introduction of framework heteroatoms can significantly influent the catalytic activity, redox, hydrophobicity, acidity, and other properties of the parent molecular sieve, and effectively improve the weak acidity and insufficient catalytic ability of conventional molecular sieves. The special properties of heteroatoms endow zeolites with some new physical and chemical properties, which are beneficial for realizing multi-functional catalysis and improving the application value of molecular sieves, so more and more attention has been paid to the synthesis and application of heteroatomic molecular sieves [74].

Y zeolites are widely used in catalytic cracking, hydrocracking, isomerization, and other refining processes as a catalyst active component or catalyst carrier. In order to improve the catalytic performance of Y zeolites to meet the industrial demand, the introduction of framework heteroatoms is of practical significance. The highly active heteroatomic molecular sieve not only requires a highly ordered framework structure, but also requires that the heteroatoms that play the role of active centers can enter the framework. At present, the synthetic methods of heteroatomic molecular sieves mainly include the direct synthesis method and post-treatment method [75–79].

### 4.1. Direct Synthesis Method

The direct synthesis method is to introduce heteroatoms into the silica-alumina sol in the form of metal organics, metal salt solutions, or metal complexes, and then carry out the crystallization process to directly obtain the heteroatom molecular sieve.

Shen et al. [80] synthesized a heteroatomic TiY molecular sieve by the direct hydrothermal method. The XRD characteristic diffraction peaks of the TiY molecular sieve shifted to lower angles, and the absorption peaks around 1139 $cm^{-1}$ and 787 $cm^{-1}$ in the IR spectra shifted to lower wave numbers; these phenomenons proved that Ti had entered the framework. On this basis, the effect of different contents of Ti on the crystal structure of Y zeolite was further investigated. The results show that with the increase in Ti content, the unit cell constant of the TiY molecular sieve increases, and the thermal and hydrothermal stability are enhanced. Framework Ti can obviously tune the surface acidity of Y zeolites, resulting in improved cracking reaction activity and significantly reduced carbon accumulation [81,82]. Liu et al. [83] synthesized a NiY molecular sieve containing framework Ni via the hydrothermal crystallization method. Researchers used Y zeolite and NiY molecular sieve as carriers to support metal active components Ni and Mo to prepare hydrocracking catalysts. The results show that the introduction of Ni can modulate the surface acidity of the catalyst and improve its cracking activity and anti-coking ability. Zhou et al. [84] obtained a Ni modified USY zeolite by an in situ synthesis method, and prepared NiMo-supported catalyst by using this zeolite to support Mo. The presence of framework Ni, which could tune the structural parameters and acidity of zeolites, endowed the USNiY zeolites with a high specific surface area and porosity as well as suitable acidity. These properties favor the dispersion of active metals, making the USNiY catalyst exhibit high catalytic activity and a long lifetime. Compared with Ni-containing Y zeolite prepared by impregnation method or ion exchange method, in situ synthesized USNiY zeolite has the best catalytic performance. The catalytic effect of USNiY zeolite with different Ni content in diesel HDS process was investigated [85]. Experiments show that the catalytic effect is the best when the mass fraction of NiO is 3%. This team also synthesized Ga-containing mesoporous Y zeolite by the hydrothermal method [86]. The zeolite acidity can be tuned by adjusting the Ga/Al ratio of the initial gel. The researchers used this zeolite to load Ni, Mo, and synthesized the NiMo/Y-Ga catalysts. The Ga specie can promote the sulfurization of Ni/Mo and change the morphology of active phase. A small amount of Ga can promote the entry of Ni atoms into the $MoS_2$ phase, thereby forming the real NiMoS active component. Cui et al. [87] directly synthesized Zr-doped Y zeolite nanocrystals by the hydrothermal method, and prepared NiW supported catalysts with this zeolite as a precursor. Framework Zr can enhance the reducibility of W species and regulate the growth of $WS_2$ phase. This catalyst has a better balance of cracking activity and hydrogenation/dehydrogenation activity. Compared with Y zeolite-based catalyst, the ZrY zeolite catalyst has higher middle distillate conversion and selectivity.

The heteroatomic molecular sieves synthesized by the direct method have high crystallinity, stable active sites, and are reproducible, which make them easy to produce in industrial scale. However, the long crystallization time and high cost of this method limit its application. In addition, the direct synthesis method is limited by the strong base of the synthesis system, and few metal heteroatoms can enter the molecular sieve structure, which restricts the activity of the heteroatom-modified molecular sieve.

### 4.2. Post-Treatment Method

Due to the low metal content in the heteroatomic molecular sieves obtained by the direct method, and to the fact that some heteroatomic molecular sieves' initial gel cannot nucleate spontaneously under hydrothermal conditions, the post-treatment method is gradually applied. In the post-treatment method, framework heteroatoms are introduced by isomorphous substitution.

In 1984, Breck et al. [88] first published the isomorphous substitution of Y zeolite for dealumination and silicon supplementation. Treating Y molecular sieve with $NH_4SiF_6$ solution can increase its framework SAR, thus changing its thermal stability, acidity, and catalytic activity. The principle of this method is that the $F^-$ dissociated from $SiF_4{}^{2-}$ can complex with $Al^{3+}$ to remove them, and then $Si^{4+}$ will fill the vacancies to form high-silica Y zeolites. If silicon is replaced by another element M with similar properties, as long as the dissociation degree of $MF_4{}^{2-}$ is suitable, the M element can also exist stably in the framework in the form of four-coordination. As an extension of this method, Gao et al. [89] synthesized Zr-Y, Ti-Y, Fe-Y, and Cr-Y molecular sieves by isomorphous substitution of Y zeolite using $(NH_4)_3ZrF_7$, $(NH_4)_2TiF_6$, $(NH_4)_3FeF_6$, and $CrF_3{\cdot}3NH_4F$ as substituents. In addition, from the perspective of isomorphic substitution mechanism, the author discussed the main factors affecting the heteroatom substitution degree: ionic radius of heteroatom, polymerization equilibrium constant of hydrolyzate, cationic hydrolysis equilibrium constant, and cumulative stability constant of fluorine-containing complexes.

Liu et al. [90] synthesized Ga-containing Y molecular sieves using ammonium fluorogallate under mild condition. The mechanism is as follows: ammonium hexafluorogallinate hydrolyzes to generate $GaO_4^{5-}$ and $F^-$, of which $F^-$ is strong complexing agent and can complex with aluminum ions to remove them from the framework. $GaO_4^{5-}$ then enter the vacancy of aluminum ion, forming Ga-Y molecular sieves. Dwyer et al. [91,92] added $NH_4$-Y molecular sieves to the mixed solution of gallium nitrate and ammonium fluoride and treated them at 70–80 °C for 3–4 h to obtain Ga-Y zeolite molecular sieves. The changes in the cell parameters and the solid NMR characterization indicated that Ga successfully replaced a portion of aluminum in the Y molecular sieve. Tang et al. [93] synthesized a Ga-containing Y molecular sieve by the above method and studied its adsorption desulfurization performance. The adsorption desulfation capacity of Ga-Y zeolites was improved compared to that of $NH_4$-Y zeolites.

According to the above results, a two-step isomorphous substitution method can be obtained. In this method, aluminum in conventional aluminosilicate molecular sieves is first removed with strong acid, leaving vacancies, and other metal ions fill in the vacancies to obtain heteroatomic molecular sieves. Sano et al. [94] obtained Ti-USY molecular sieves by treating dealuminated USY zeolites with $(NH_4)_2TiF_6$ solution. Series characterization such as XRD, $^{27}$Al MAS NMR, FT-IR, SEM, TEM, UV-vis, and XANES proved that Ti species exist in the framework of a USY molecular sieve in the form of tetracoordination. The catalytic activity of the Ti-USY molecular sieve is obviously better than that of the TS-1 molecular sieve in the cycloolefin epoxidation reaction using hydrogen peroxide solution as oxidant.

Zhu et al. [95] successfully synthesized hierarchically porous Sn-Y molecular sieves using a two-step isomorphous substitution method. The specific steps are as follows: first, the H-USY zeolite (Si/Al = 6) was dealuminated with strong acid ($HNO_3$, 6 mol/L) under reflux for 0–18 h, and then treated with $SnCl_4$ vapor at 773 K for 2 h. The residual $SnCl_4$ species were removed with dry nitrogen gas, and the hierarchically porous Sn-Y molecular sieve was obtained after drying in air at 373 K overnight (shown in Figure 7). Compared with other Sn-containing molecular sieves with different topologies, Sn-Y molecular sieves showed excellent catalytic performance in Baeyer Villiger oxidation reaction of 2-adamantanone. The reaction catalyzed by Sn-Y zeolite can reach 97.5% conversion and almost 100% lactone selectivity within 40 min. The good performance of this catalyst is attributed to the open pore channels formed by three-dimensional 12-membered ring channels and dealumination-derived mesopores. Wang et al. [96] studied the replacement of Al or Si in the framework of Y zeolites by Ti using density function theory (DFT) calculation. The substitution energy indicates that it is easier for Ti to replace skeleton Al than Si. For Ti/Si substitution, the substitution probability is related to the position of Si in the zeolite framework. The researchers compared the substitution energies of 17 silicon sites and found that the preferred substitution is the Si near Al, while the diagonal position away from Al on the six-membered ring of zeolite was the least easy to be replaced.

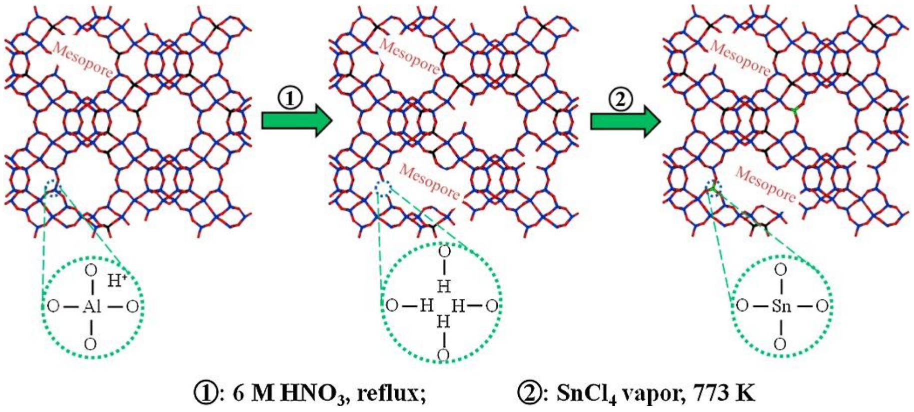

**Figure 7.** Synthesis of Sn-Y molecular sieves by two-step post-treatment method [95].

The post-treatment method can obtain heteroatom molecular sieves that cannot be prepared with the conventional hydrothermal synthesis method and can improve the content of heteroatoms in the molecular sieves, but each post-treatment method also has its disadvantages. The liquid-solid phase isomorphous substitution method requires solvents to dissolve the heteroatom source, and the waste liquid will bring environmental pollution problems; the gas-solid phase isomorphous substitution method is to metallize molecular sieves at a high temperature, which has strict requirements on equipment. Therefore, the post-treatment method also has limitations, and not all heteroatomic molecular sieves can be synthesized by this method.

## 5. Conclusions

This review summarized different methods for the synthesis of high SAR Y zeolites, hierarchically porous zeolites, and heteroatomic molecular sieves. Modification of Y zeolites improves its stability, selectivity, and catalytic properties, leading to improved utilization efficiency. High SAR Y zeolite has improved acidity and stability; hierarchically porous Y zeolite accelerates diffusion and improves the utilization rate of active centers; heteroatomic Y zeolite improves the catalytic activity, redox, hydrophobic, acidic, and realize the multifunctional catalysis of Y zeolites. The comprehensive use of these methods to modify Y zeolite can greatly improve its industrial application value. For example, high-silica hierarchically porous Y zeolite can be obtained by selective desilication of dealuminated zeolite Y [97]. Oxalic acid leaching modification of rare-earth-containing USY zeolite can adjust its pore structure and acid content, thus greatly improving its catalytic stability and activity. When it is used in the industrial aromatics catalytic deolefin reaction, its lifetime is up to two years, which is 13 times that of the commonly used catalyst activated clay [98]. Although there are many ways to synthesize Y zeolites, there are still many deficiencies such as expensive template agents and tedious synthesis steps. Therefore, low-cost and efficient modification methods should be sought.

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