

# Synthesis and mechanism of porous molecular sieves

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**Abstract:** Porous molecular sieve was a kind of material with different pore structure. Porous molecular sieve had molecular sieve separation ability and rapid mass transfer ability. These materials effectively solved the mass transmission problem of traditional molecular sieve. And allowed substrate molecules to enter the active site located in the micropore, thus improving the reaction rate and lifetime. In addition, the secondary porosity of the porous zeolite created an ideal space for the deposition of the products, controlling their size and allowing high dispersion and strong interactions between the zeolite and the medium. In this paper, the synthesis and mechanism of porous molecular sieve were summarized and summarized, which laid a theoretical foundation for the synthesis of porous molecular sieve.

**Keywords:** Porous; Molecular sieve; Synthesis mechanism.

## 1. Introduction

Because of the special skeleton and pore structure of molecular sieve, it had been widely used in ion exchange, gas separation, catalysis, adsorption and other fields. However, molecular sieves containing only a single pore structure had certain shortcomings in the diffusion of guest molecules. For example, in the reaction of methanol to olefin, the active sites of the microporous molecular sieves themselves were reduced and the pores of the molecular sieves were blocked by the formation of coke, thus affecting the intermolecular diffusion [1]. Although nano-sized molecular sieves or nano-sized molecular sieves with reduced crystal size shorten the diffusion path of reactants/products, the synthesis yield was low and there was a tendency to aggregate during the treatment process [2]. Recently, there had been great interest in developing multistage pore structures in order to more efficiently improve mass transfer between reactants/products. With the development of research methods and synthesis methods, the types of porous molecular sieves with special structure and function were becoming more and more abundant. Porous molecular sieves with different structural characteristics and functions could be obtained by adjusting the removal of skeleton atoms, designing and selecting different template agents or structure guiding agents, and designing the synthesis conditions of molecular sieves. So far, a variety of methods for porous adsorption materials had been developed.

Therefore, the synthesis method and mechanism of porous molecular sieve would be summarized in detail in this paper, providing a theoretical basis for the synthesis of porous molecular sieve.

## 2. Remove the skeleton atoms

One of the most common ways to synthesize porous molecular sieves was to remove the skeleton atoms (such as Si and Al) from the structure. The removal of skeleton atoms from molecular sieve results in mesoporous formation. As shown in Figure 1, after acid-based desilication / dealumination, obvious defect sites were generated in the molecular sieve framework, providing conditions for the formation of mesoporous pores. The following was a detailed description of the preparation of porous molecular sieves by

removing skeleton atoms.

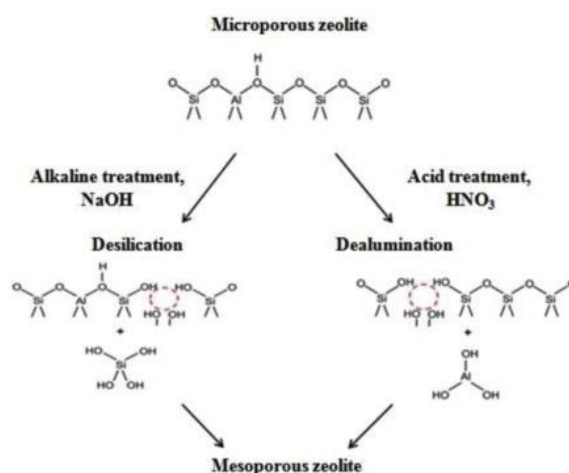


Figure 1. Desilication and dealumination[3]

Desilication was mainly to remove silicon atoms from microporous molecular sieve structure under alkaline conditions, thus obtaining porous molecular sieve containing mesoporous structure in each grain, and basically does not change the structure and acidity of the molecular sieve itself [4]. For example, Sharon [5] calcined commercial NH<sub>4</sub>-ZSM-5 molecular sieve powder to generate H-ZSM-5 molecular sieve, and treated it with NaOH. Part of Si in the molecular sieve skeleton would react with NaOH to form silicate, which would break away from the skeleton, thus generating mesoporous pores in the molecular sieve (Figure 2).

Sun Yu [6] added 0.2M sodium hydroxide into the synthesized ZSM-5 molecular sieve to obtain mesoporous/microporous molecular sieve with uniform mesoporous pores. Among them, the desilification reaction was mainly due to the reaction between the existing sodium hydroxide and part of silicon in the zeolite skeleton to produce silicate, and then part of silicon in the skeleton was removed. After desilication, the molecular sieve had obvious defect sites (nestlike defect sites), in which mesoporous pores were mainly concentrated around 10 nm, which also made the molecular sieve have higher specific surface area and pore volume, and extended the service time of the molecular sieve

catalyst for 32 hours.

Sadowska K [7] used 0.2M NaOH/TBAOH to desilicize high-silicon ZSM-5 molecular sieve (Si/AL =164) at high temperature, resulting in small diameter and narrow pore size distribution mesoporous. In the desilication process of the high silicon molecular sieve (Si/Al = 164), the TBA<sup>+</sup> cations are combined with the nanoparticles on the surface of the molecular sieve through physical adsorption. The formation of the organic Synthesis and mechanism of porous molecular sieves cationic-silicon core-shell structure [8] protects the Si on the surface of the molecular sieve from being eroded by OH<sup>-</sup> through the coating form, so that the OH<sup>-</sup> erodes the Si inside the molecular sieve. Furthermore, narrow pores with uniform distribution are generated, which increases pore volume and specific surface area, so that the catalytic performance is good.

Chemical agents or hydrothermal treatment can also be used to remove aluminum from the skeleton of the molecular sieve structure to produce graded molecular sieves. During dealuminization, the removal of aluminum atoms is accompanied by the destruction of some molecular sieve structures and the formation of vacancy, which generates additional porosity, mainly in the mesoporous range of molecular sieve microporous structure.

The most common method was to remove aluminum by

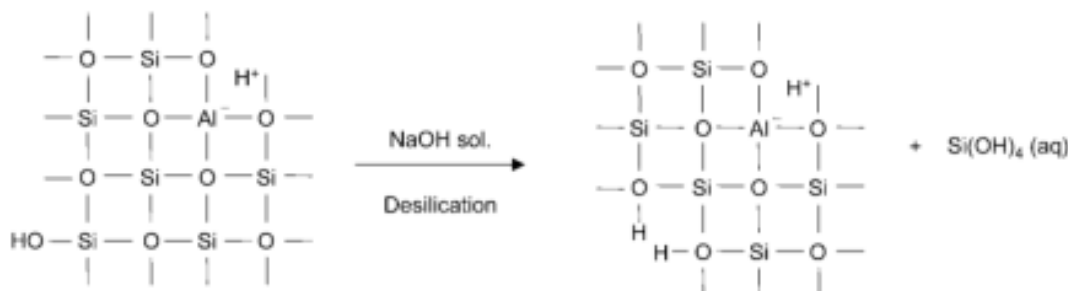


Figure 2. Introduction of mesoporous ZSM-5

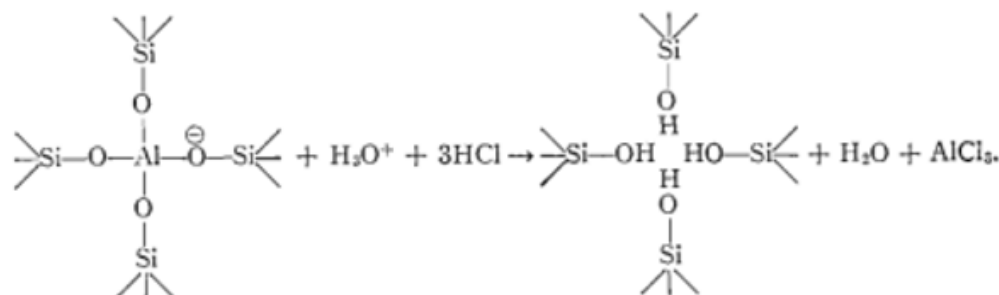


Figure 3. Hydrolysis of aluminium in molecular sieve

According to the literature on preparation of porous molecular sieves by removing skeleton atoms, it is found that this method is mostly applied to high silicon molecular sieves. And high silica molecular sieves are only limited to specific Si/Al ratio. For example, Moller [14] studied ZSM-5 molecular sieve with Si/Al ratio ranging from 25 to 50 and found that at a low Si/Al ratio, when NaOH was used to remove skeleton atoms, Si and Al in the molecular sieve skeleton would be removed. Al whose skeleton fell off inside the molecular sieve was reassembled on the defective surface of the molecular sieve to form an amorphous layer containing AlO<sub>4</sub><sup>-</sup>, which prevented further dissolution and closed the mesoporous pores. After pickling, porous mesoporous pores could be obtained (Figure 5a). For molecular sieves with moderate Si/Al ratios, mesoporous molecular sieves can be obtained by one-step desilication with NaOH (Figure 5b).

pickling at high temperatures. This method was first described by Barrer[9] in the 1960s. When inorganic acid was used to treat oblique molecular sieve, the hydrolysis of Al-O-Si bond in the skeleton was shown in Figure 3, to achieve the effect of dealuminization. Silaghi M C [10] further elaborated the mechanism of molecular sieve skeleton dealuminization (Figure. 4): First, the aluminum is removed from the position of microporous skeleton, leaving atomic gap and silanol nest ( $\equiv\text{SiOH}$ ); And then interface defects within the crystal structure of silicon atoms shifting and repopulate the clearance, the silicon migration will some silicon alkoxide nest into silicon structure, and to provide the silicon atoms clearance area evolved into mesoporous, end up with medium/microporous molecular sieves. High temperature steam treatment can also lead to the dealuminization of molecular sieve to obtain porous molecular sieve. For example, Ji Yuewei[11] treated RHO and KFI microporous molecular sieve with high temperature (600-800 °C) steam. The aluminum at the strong acid site in the molecular sieve was removed first, the bridge hydroxyl structure (O<sub>3</sub>Si-OH-AlO<sub>3</sub>) in the molecular sieve skeleton was reduced, and the aluminum site was dissolved. The internal structure of molecular sieve channels was severely damaged and secondary mesoporous pores were generated [12].

However, for zeolites with high Si/Al ratio, excessive dissolution of zeolites will be caused by the above alkali desilication, and alternative treatments should be used to prevent the dissolution of zeolites, including (I) using milder alkali (such as NaOH/TBAOH[7]), (II) adding pore guide agent (PDA), (III) recrystallization with surfactant[15], and (IV) partial removal of templates: The microporous template (dark blue area) was only partially removed before desilication (Figure 5c).

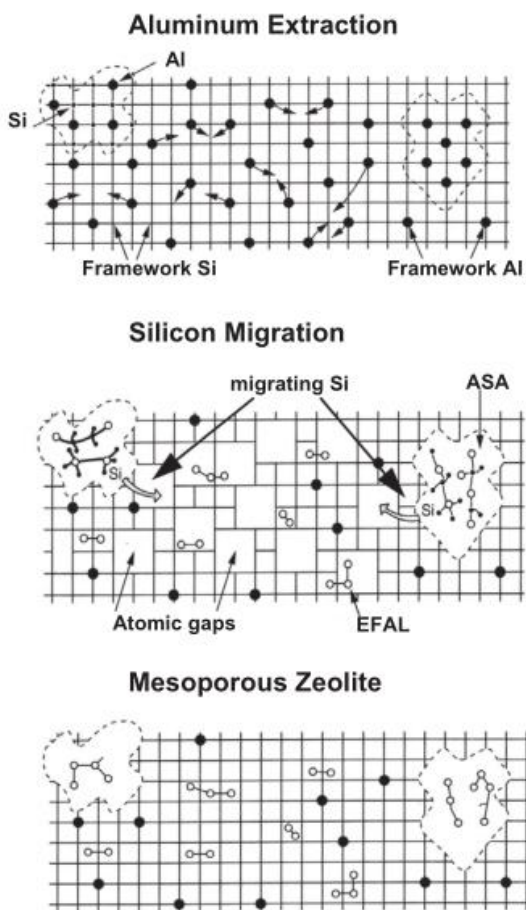


Figure 4 Schematic diagrams of Marcell's mechanism showing mesopore formation after dealuminization [13]

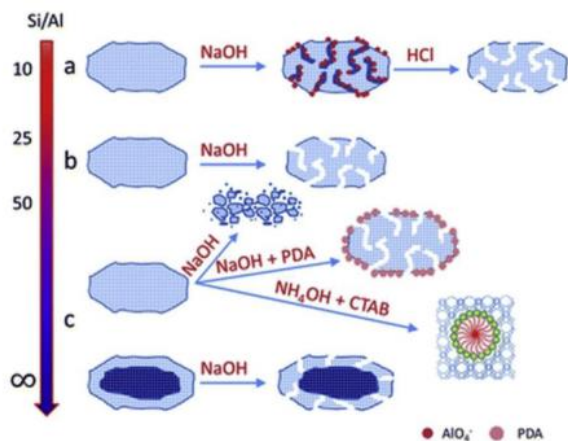


Figure 5 Desilication at different Si/Al ratios

### 3. Template assisted synthesis

Synthesis of porous molecular sieves with "hard" or "soft" templates [16] is also a common method for the synthesis of porous molecular sieves.

The template agent has the following functions in the synthesis of molecular sieve [16] : (1) structure-oriented effect: Structure orientation has strict structure orientation and general structure orientation, strict structure orientation refers to a special structure can only use a kind of organic guided synthesis, general orientation refers to organic matter is easy to guide some small structural units, cage or pore generation, thus affecting the generation of the whole skeleton structure; (2) Space filling effect: template agent has space filling effect in the skeleton, which can stabilize the

generated structure; (3) Balance skeleton charge: template agent affects the skeleton charge density of products. Compounds in molecular sieve all contain anionic skeleton, which requires cationic balance skeleton charge in template agent.

Hard templates Rigid templates held together primarily by covalent bonds, such as those containing carbon, aerogel, mesoporous silicates, etc.

Because the large pore channel is larger, it is conducive to the transport of materials, so the mass transfer is accelerated. Synthesis on macroporous molecular sieves is usually carried out by using a preset template. The growth of molecular sieve on the template is mainly carried out by layer-by-layer assembly, by alternately depositing molecular sieve nanoparticles and polyelectrolytes with opposite charges onto the template that does not change during the crystallization of the molecular sieve, and then removing them by calcination to release macropores[17].

As reported by Zhang [18], mesoporous silica microspheres were first synthesized as sacrificial templates in the synthesis process, and then large/microporous LTA zeolites were synthesized by steam-assisted crystallization. In the process of steam assisted crystallization, mesoporous silica gradually dissolved and transformed into zeolite, and finally the product formed a large pore structure.

Soft templates are often formed by aggregating surfactant molecules. It mainly includes various ordered polymers formed by amphiphilic molecules, such as liquid crystals, vesicles, micelles, microemulsions, self-assembled membranes, and self-organizing structures of biomolecules and polymers. The intermolecular or intramolecular weak interaction is the force that maintains the template, thus forming aggregates with different spatial structural characteristics. This kind of aggregate has obvious structural interface, and it is through this special structural interface that the inorganic materials show specific tendency distribution, and then obtain the nanomaterials with special structure of the template.

Cationic surfactants such as cetyltrimethylammonium bromide (CTABr) or cetyltrimethylammonium chloride (CTACl) can also be used and the mesoporous molecular sieves can be effectively introduced into the molecular sieve structure under relatively mild synthetic conditions, namely through the recrystallization of microporous molecular sieves into micro/mesoporous or mesoporous molecular sieves. In this process, the interaction between surfactant and molecular sieve is needed to prevent crystal dissolution, and almost complete reorganization of the molecular sieve network around the surfactant micelle can be achieved [19, 20].

Among the many reports on porous materials, the three-stage pore structure of micro-pore, mesoporous and macropore is rarely reported. However, this structure enables the material to have many advantages of micro-pore, mesoporous and macropore structure, and it is also a kind of porous material that many people dream about.

Nowadays, there are various methods for the synthesis of tertiary porous zeolite. In the synthesis process, mesoporous and macroporous template are added at the same time. However, the phase and phase will separate from each other, so it is difficult to get the microporous - mesoporous - macroporous structure. Some zeolite materials with three-stage pore structure use mesoporous and macroporous materials as templates, and copy the mesoporous and macroporous structures on the templates through the

subsequent crystallization zeolite process, so as to form microporous, mesoporous and macroporous structures. For example, Chen et al first synthesized hierarchical mesoporous macroporous titanosilicate with amorphous structure and used it as a precursor substance, then added them into the solution containing structure guide agent tetrapropylammonium ion (TPA+) and tetraethyl orthosilicate, and carried out crystallization transformation in a quasi-solid system to obtain zeolite molecular sieve material with micropore, meso-pore and macropore structure [21].

Li et al. selected polyacrylamide as the structure guide agent, introduced polyacrylamide hydrogel through one-step hydrothermal synthesis, and used polyacrylamide micelles to enter the crystal to produce mesoporous structure. At the same time, the excess aluminum in the molecular sieve framework would form defects, resulting in the formation of macroporous structure, and finally synthesized SAPO-34 molecular sieve with three-stage porous structure [22].

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#### 4. Change the synthesis conditions

In order to find a simpler method to synthesize porous molecular sieve, some people found that by changing the synthesis conditions of molecular sieve, porous molecular sieve can also be obtained. For example, Wang [24] used organic functionalized mesoporous silica as a silicon source to hydrothermal synthesis CaA molecular sieve with microporous, mesoporous and macroporous structures through bond resistance principle. Moreover, their research also showed that the zeolite process retained micropores during the generation of macropores and mesoporous. The molecular sieve surface and large mesoporous porosity can be adjusted by changing the degree of organic functionalization on the surface of mesoporous silica, which has great flexibility.

Pan [25] proposed that by independently changing the amount of NaOH added to the initial gel, that is, by controlling the nutrients required in the zeolite process, the defects in the crystallization process - mesoporous and macroporous - would be generated, so as to regulate the crystallization kinetics. Moreover, the pore size structure and morphology of ZSM-5 molecular sieve were realized, and molecular sieve with tertiary pores was obtained.

#### 5. Conclusion

The common methods for the synthesis of porous molecular sieves include removing the skeleton atom, template assisted synthesis, changing the synthesis conditions, etc. Using these methods, we can easily prepare and adjust the pore structure of the molecular sieve, and realize the controlled synthesis of porous molecular sieve. Because of its unique pore structure, porous molecular sieve has the advantages of porous structure, but also has the advantages that a single pore structure does not have, and has a wide range of applications in the fields of catalysis, adsorption, energy and so on.

In this paper, the synthesis and mechanism of porous molecular sieves are summarized and summarized. According to the application requirements, we can synthesize specific porous molecular sieves by controlling the pore size, connectivity, shape, etc., and lay a theoretical foundation for the synthesis of porous molecular sieves.

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