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# Low Cost Raw Material for One Step Synthesis of Small Crystal ZSM-5 Molecular Sieve

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**Abstract**: High crystallinity small crystal ZSM-5 molecular sieves were prepared by one step direct synthesis method using low cost raw materials such as aluminum sulfate, water glass, *n*-butylamine, water, seed, NaCl, concentrated sulfuric acid, etc. Effect of gel aging process, solution addition sequence, crystallization time, crystallization temperature, water content and $SiO_2/Al_2O_3$ ratio on the crystallinity and crystal size of molecular sieve were investigated. By means of XRD and SEM on the characterization of synthesized ZSM-5 molecular sieve was investigated in detailed. Research results showed that a high crystallinity small crystal ZSM-5 molecular sieve were obtained under the crystallization condition of 160 ~ 170 ℃ for 30 h with low temperature water bath reflux stir-aging method. The solution addition sequence has little effect on the crystallinity of molecular sieve.

**Key words**: small crystal molecular sieve; ZSM-5; synthesis
**CLC number**: O643.3 **Document code**: A

In the 1970s, the Mobil Corporation developed ZSM-5 molecular sieve in the first time, which is a kind of shape selective microporous molecular sieve with unique channel structure and acid strength distribution. ZSM-5 molecular sieve owns two kinds of pores, one is a ten ring straight pore with pore size of 0.51×0.55 nm, and another is a ten ring Zigzag shape pore with pore size of 0.53×0.56 nm. Since it has the characteristics of high Si/Al ratio, oil drain, thermal stability and high catalytic activity, ZSM-5 molecular sieve used in catalytic cracking reaction can improve the quality of FCC gasoline and maximize ethylene and propylene and other important chemical raw materials[1]. ZSM-5 molecular sieve can also be used as a catalyst in diesel hydrodewaxing, xylene isomerization and butene catalytic cracking reaction [2-4].

The physicochemical properties of molecular sieve powder play an important role on the catalytic performance of the catalyst. Such as, crystal size of molecular sieve determines the pore length, can affect the diffusion of reactant and product in the catalyst surface, which is closely related to the stability of catalyst. Compared with the conventional ZSM-5 molecular sieve, small crystal ZSM-5 molecular sieve has the characteristics of small crystal size, short pore, large external surface area and abundant pores, which shows unique performance in the catalytic reaction [5-7]. Such as, Agustin Martinez et al. [8] studied the influence of crystal size of ZSM-5 molecular sieve for the direct conversion of syngas to high octane gasoline. The result showed that the stability of molecular sieve was substantially improved by decreasing its crystal size, probably by favoring the diffusion of aromatics preventing their further transformation into coke. In the catalytic

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cracking reaction, reduction of crystal size of ZSM-5 molecular sieve is conducive to improve propylene yield and octane number of gasoline [9]. Small crystal molecular sieve is very helpful to improve the catalytic performance in some catalytic reaction. Therefore, how to synthesis of small crystal ZSM-5 molecular sieve is one of hot topics in catalysis and materials science research.

At present, many literatures had widely reported the synthesis of small crystal ZSM-5 molecular sieve[10-13], but most synthesis process used expensive templates. Fan et al. [10] used NaOH, silicon sol, sodium aluminate and tetrapropyl ammoniumhydroxide as raw materials for the synthesis of ZSM-5 molecular sieve, by changing the ratio of PEG-800 to modulate crystal size of ZSM-5 molecular sieve. Parikh et al. [11] used triethylbutyl ammoniumbromide and ethylene diamine as co-templates to synthesize small crystal size ZSM-5 molecular sieve. ZSM-5 zeoilite preparing with these expensive templates are difficult to achieve industrial application, thus it is particularly important to develop low cost raw material for direct synthesis of small crystal ZSM-5 molecular sieve. Wang et al. [14] used NaOH, aluminum sulfate, sulfuric acid and sodium silicate as raw material to prepare small crystal ZSM-5 molecular sieve aggregates by two step synthesis processes. While the small crystal ZSM-5 molecular sieve can be synthesized, the two step synthesis increases the reaction process. In this paper, low cost raw materials, for example aluminum sulfate, water glass, n-butylamine, water, seed, NaCl, concentrated sulfuric acid and other cheap materials were used to synthesize the high crystallinity, small crystal and size-controlled ZSM-5 molecular sieve by one-step direct synthesis method.

# 1 Experimental

## 1.1 Synthesis of ZSM-5 molecular sieve

The synthesis process of ZSM-5 molecular sieve was described as following. Taking a certain amount of aluminum sulfate, mixing evenly with sulfuric acid, distilled water, NaCl, isopropyl alcohol, the mixture was denoted as solution A. Taking a certain amount of water glass, followed by adding a certain amount of distilled water, *n*-butylamine, seed, and then the solution was mixed evenly and denoted as solution B. The addition of solution A drop by drop into solution B was called as positive addition method. The addition of solution B drop by drop into solution A was called as reverse addition method. After dropped, the gel was aged at a certain temperature for a period of time, and then placed in an autoclave and crystallized for a period of time. In final, the solution was filtered, dried and calcined to obtain small crystal ZSM-5 molecular sieve.

## 1.2 Characterization of ZSM-5 molecular sieve

Powder X-ray diffraction (XRD) analysis was performed to verify the species present in the samples. XRD patterns of the samples were recorded on a Rigaku D/MAX-RB X-ray diffractometer with a target of Cu Kα operated at 60 kV and 55 mA with a scanning speed of 0.5°/min and a scanning angle ($2\theta$) range of 5°~50°. The relative crystallinity of samples was defined as diffraction peak area percentage ratio of experimental and reference sample at the 22.5°~25° ($2\theta$). The commercial ZSM-5 molecular sieve samples were purchased as the reference samples.

The surface morphologies of the molecular sieves were also determined by using Scanning Electron Microscopy (SEM) on a JSM-5600 instrument operating at 20 kV.

BET surface areas were determined by nitrogen adsorption with a micromeritics ASAP 2010 instrument.

# 2 Results and discussion

## 2.1 Formation mechanism of small crystal ZSM-5 molecular sieve

In the synthesis conditions of high temperature and no salt, many small scattered crystals (including the amorphous phase) formed in the early stages of crystallization, and then these small scattered crystals were agglomerated into pellets. Small crystals and intergranular amorphous phases were fused gradually and disappeared at last, and then large crystals body formed. However, under the conditions of low temper-

ature stir with salt, formed nuclei will be scattered without time to gather due to low temperature and stir. Adding the suitable amount of NaCl to solution before the crystallization, the nucleus was easier to form, the nucleation rate accelerated and the number of nuclei formation also increased. Competitive growth between crystal nucleuses inhibited the growth of grains and resulted in small crystal size. The increase of the crystallinity of ZSM-5 molecular sieve in the crystallization process was mainly due to an increase of crystal nucleus number. Therefore, using the measure of low temperature water bath stir-aging and adding NaCl, a large number of crystal nucleuses formed in the first crystallization process, the crystal nucleus competitively grew in the subsequent process, and a large number of small crystal molecular sieve produced in final.

## 2.2 Influence of gel aging method

In the experiment, the effect of two kinds of gel aging method on the crystallinity and crystal size of molecular sieves was investigated. While using the method of low temperature water bath stir-aging gel, the crystallinity of preparing ZSM-5 molecular sieve was high and crystal size was small. However, using the method of the oven aging gel, the crystallinity of preparing ZSM-5 molecular sieve was low (65%) and a large part of amorphous $SiO_2$ formed in the synthesis process. Using water bath reflux aging method, the temperature and concentration gradients of system was eliminated, and nucleation and crystallization carried out at the same time in the whole system. As a result, a large number of crystal nucleus formed, and excessive nucleus resulted in the small crystal size. Eddy current of gel produced by stirring and each crystal nucleus was in constant motion. Stir process affected the diffusion-deposition of crystal nucleus and formed the small crystal size ZSM-5 molecular sieve at last.

The crystal size obtained by oven aging was obvious bigger than those obtained by using water bath stir-aging. Due to the poor thermal conductivity of gel, temperature gradient obviously existed in the system using static aging. The temperature of outer wall of the gel layer was significantly higher than the central place, resulting in concentration gradient in the system. The high concentration crystal nucleus constantly spreading to low concentration crystal nucleus, leaded to the formation of large crystal size ZSM-5 molecular sieves. At the same time, the gel dispersed unevenly on the oven conditions and a part of gel can not generate molecular sieve, thus the relative crystallinity is low.

## 2.3 Influence of the sequence of solution addition

In the synthesis process of molecular sieve, the sequence of solution addition may produce some effects on the physicochemical properties of molecular sieve. Fig. 1 was XRD patterns of ZSM-5 molecular sieves preparing with different solution addition sequences. The standard ZSM-5 spectrum was also putted in Fig. 1c. As can be seen from Fig. 1, the XRD partterns of two molecular sieves were almost the same, showing that the sequence of solution addition had no obvious effect on the performance of molecular sieve. The positive or reverse addition can prepare high crystallinity small crystal ZSM-5 molecular sieve. The peak of synthesized ZSM-5 zeolite was higher than that of standard ZSM-5, showing that the relative crystallinity of synthesized ZSM-5 was higher.

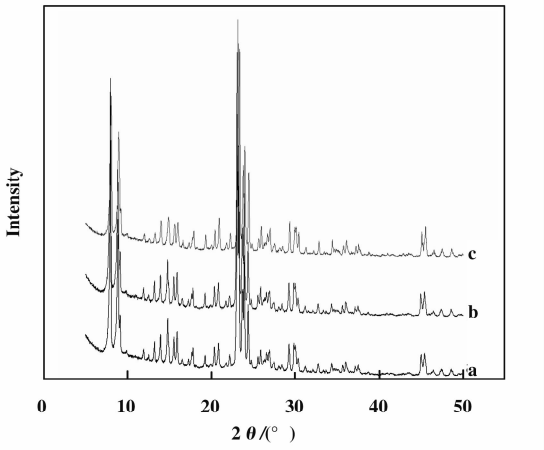


Fig. 1 XRD patterns of synthesized ZSM-5 molecular sieve preparing with different solution addition sequences.
(a) positive addition, (b) reverse addition,
(c) standard ZSM-5.

## 2.4 Influence of crystallization temperature

Crystallization temperature was one of the important factors in the synthesis process of molecular sieve. The increase of crystallization temperature will speed

up grew up of crystal nucleus, and accelerate crystal growth. At 140 ℃, the crystallization product was amorphous. Fig. 2 was TEM graph under different temperatures (160 ℃, 170 ℃ and 180 ℃) after 36 h crystallization. As can be seen from Fig. 2, when the crystallization temperature was 160 ℃, the typical ZSM-5 molecular sieve formed. The average size of corresponding molecular sieve was about 1.5 μm, and evenly dispersed. With the increase of temperature, reunion phenomenon of molecular sieve began to appear. When the temperature increased to 180 ℃, adhesion between molecular sieves formed large crystals. This may be due to that ZSM-5 was formed according to the reaction mechanism of solid phase. When hydrothermal crystallization temperature increased, the silicon aluminate gel formed the crystal nucleuses by self-assembly and growth rate also gradually increased. At this time, silicon aluminate gel structure became more conducive to the nucleation and crystal growth of ZSM-5. Solubility of gel solid and crystal growth rate increased, resulting in the thorough crystallization process. However, too high crystallization temperature can lead to agglomeration of molecular sieve. Therefore, the appropriate crystallization temperature for preparing small crystal ZSM - 5 molecular sieve was 160 ~ 170 ℃.

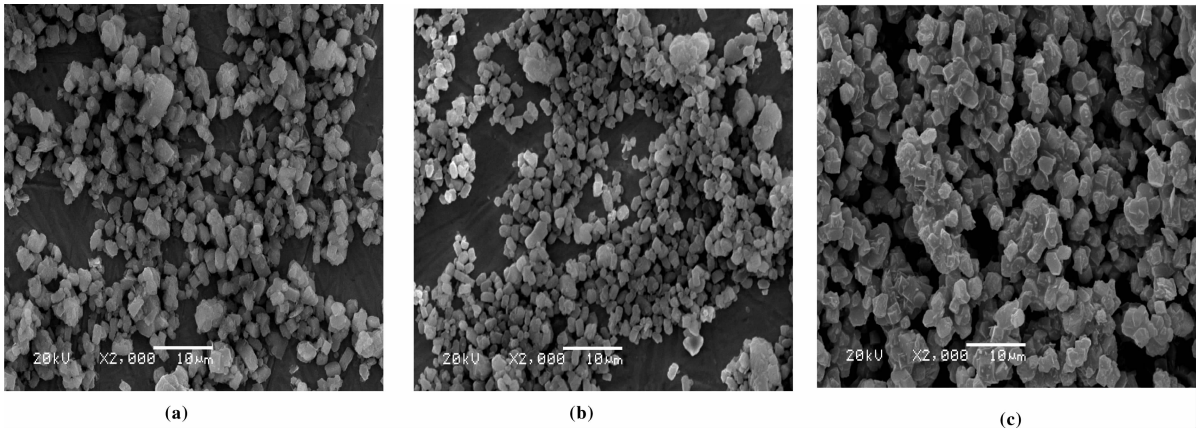


Fig. 2 SEM graphs of synthesized ZSM-5 molecular sieves preparing with different crystallization temperatures. (a)160 ℃, (b)170 ℃, (c)180 ℃.

## 2.5 Influence of crystallization time

As the molecular sieve materials are metastable phase, it can transform into the other phase, so the crystallization time is a very important factor in the synthesis process of molecular sieve. Under the conditions of the same raw materials, different crystallization time can influence the properties of synthesized ZSM-5 molecular sieve. Generally speaking, in the synthesis process of ZSM-5 molecular sieve, it should have a suitable crystallization time in a specific crystallization temperature.

Fig. 3 was XRD patterns of crystallization products under 160 ℃ with different crystallization time. $2\theta$ = 7.9°, 8.8°, 23.1°, 23.3°, 23.9° in Fig. 3 showed characteristic X-ray diffraction peaks of ZSM-5 molecular sieves, showing that ZSM-5 molecular sieve formed. The relation of relative crystallinity of ZSM-5 molecular sieve with crystallization time was shown in Fig. 4. It can be seen from Fig. 4 that relative crystal-

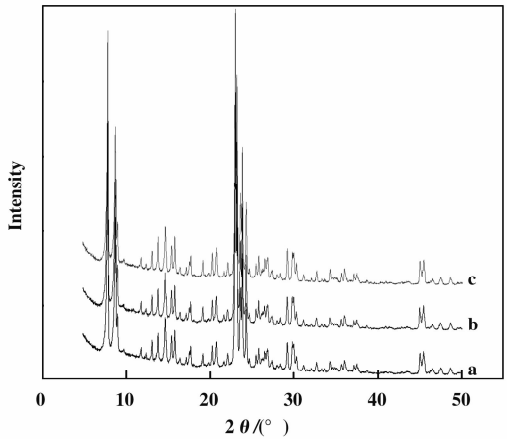


Fig. 3 XRD patterns of synthesized ZSM-5 molecular sieves preparing with different crystallization time. (a)36 h, (b)30 h, (c)24 h.

linity of ZSM-5 molecular sieve increased along with the increase of the crystallization time. When the crystallization time is 24 h, the relative crystallinity of ZSM-5 molecular sieve is 95%. When the crystallization time was prolonged to 30 h, the relative crystallinity of ZSM-5 molecular sieve increased to 101%. Further increase of the crystallization time, the crystallinity of molecular sieve changed little. Generally speaking, relative crystallinity increased first and then decreased with the increase of crystallization time. In the given crystallization temperature, when crystallization time was too short, the crystallization process was not complete and relative crystallinity was low. Along with the crystallization time prolonged, aluminosilicate gel may continue to nucleate and grow to form ZSM-5 crystal. Since the crystallization process continued, the relative crystallinity increased gradually into the stable period. But with the further increase of crystallization time, molecular sieves may turn into amorphous $SiO_2$ powders. Therefore, the most suitable crystallization time was 30 h.

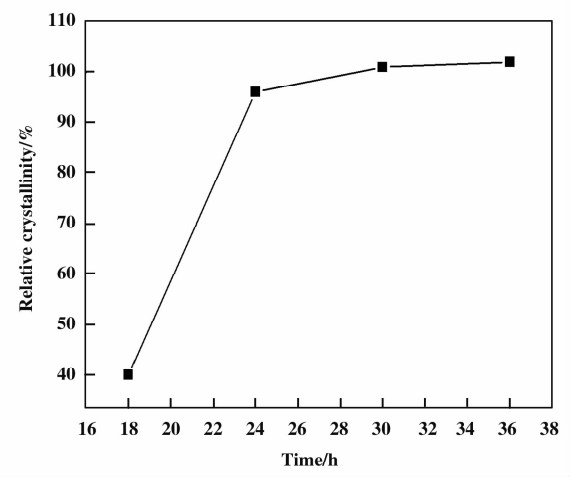


Fig. 4 Influence of crystallization time on the relative crystallinity

## 2.6 Influence of water content

Change of water content mainly influenced the concentration and alkalinity of silicon-aluminum gel. It also significantly affected nucleation, crystal growth, crystallinity and particle size of ZSM-5 molecular sieve. The feed was carried out according to the mole ratio of $37Na_2O : 107SiO_2 : 2Al_2O_3 : yH_2O$, by changing the y value to examine the influence of water content on the synthesis of ZSM-5 molecular sieves. Fig. 5 was XRD spectra of the synthesized ZSM-5 molecular sieve with different water contents. $2\theta = 7.9°$, $8.8°$, $23.1°$, $23.3°$, $23.9°$ in Fig. 5 showed characteristic X-ray diffraction peaks of ZSM-5 molecular sieves, indicating that ZSM-5 molecular sieve formed. It can be seen from Fig. 5, when y value of the water amount was 7 334 and 5 334, the relative crystallinity of ZSM-5 molecular sieve was around 102%. While y value decreased to 4 334, relative crystalline of ZSM-5 molecular sieve began to decrease. As we all known, the content of silicon and aluminum increased and high concentration aluminosilicate gel formed with the decrease of water content. As a result, it favored interaction and assembly of gel particles and the formation and growth of ZSM-5 molecular sieve crystal nucleus. Too lower water content will excessively elevate the alkalinity, which easily leads to form mixed crystal and decrease the crystallinity. Therefore, the appropriate y value of water content was 4 334 ~ 5 334.

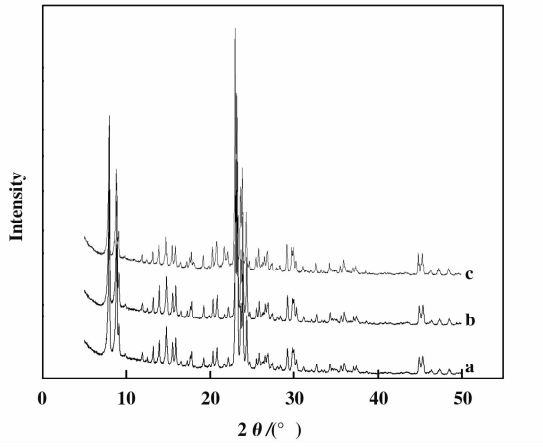


Fig. 5 XRD patterns of ZSM-5 molecular sieves preparing with different water contents.
y value : (a)7334, (b)5334, (c)4334.

## 2.7 Influence of $SiO_2/Al_2O_3$ ratio

Silicon and aluminum are main chemical elements in the framework of molecular sieve, which forms Si-Al tetrahedron with skeleton oxygen. The $SiO_2/Al_2O_3$ ratio of feed directly affected the $SiO_2/Al_2O_3$ ratio and the crystallinity of product. Fig. 6 was the XRD patterns of ZSM-5 molecular sieves with three kinds of different

$SiO_2/Al_2O_3$ ratios. The relative crystallinity according to Fig. 6 was shown in Table 1. It can be seen from Fig. 6 and Table 1, with the increase of $SiO_2/Al_2O_3$ ratio of feed, the crystallinity gradually decreased. XRD showed that the synthesized product was ZSM-5 molecular sieve with no mixed crystal. Fig. 7 was the corresponding SEM figure. As can be seen from Fig. 7, with the increase of $SiO_2/Al_2O_3$ ratio, average particle diameter of molecular sieves increased, and coexistence state of small and large crystal ZSM-5 molecular sieve emerged gradually.

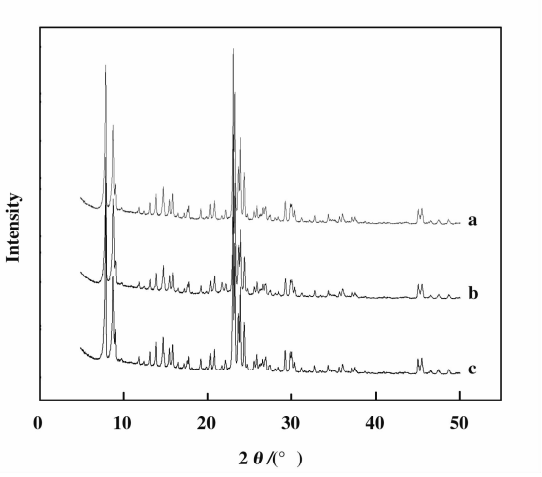


Fig. 6 XRD patterns of synthesized ZSM-5 molecular sieves preparing with different $SiO_2/Al_2O_3$ ratios. (a)300, (b)100, (c)50.

$SiO_2/Al_2O_3$ ratio of gel plays a decisive role on the structure and composition of final product. From the difficulty of bonding, Si-O-Al is easier to form than Si-O-Si, especially in high $SiO_2/Al_2O_3$ ratio system, and Al element is more easily into the framework of molecular sieve. After an Al atom into molecular sieve skeleton frame causes a unit of negative charge, skeleton attracts positive ions to balance the electric charge, thus stabilize molecular sieve structure. However, no charge produces after Si into the molecular sieve frame. Therefore, excessive Si into the crystallization product in the crystallization process will decrease the stability, resulting in the decrease of the crystallinity. With the increase of the $SiO_2/Al_2O_3$ ratio of feed, the resistance of Si species from the crystallization system into the crystallization product is also growing. Therefore, the crystallinity gradually decreased with the increase of $SiO_2/Al_2O_3$ ratio of feed.

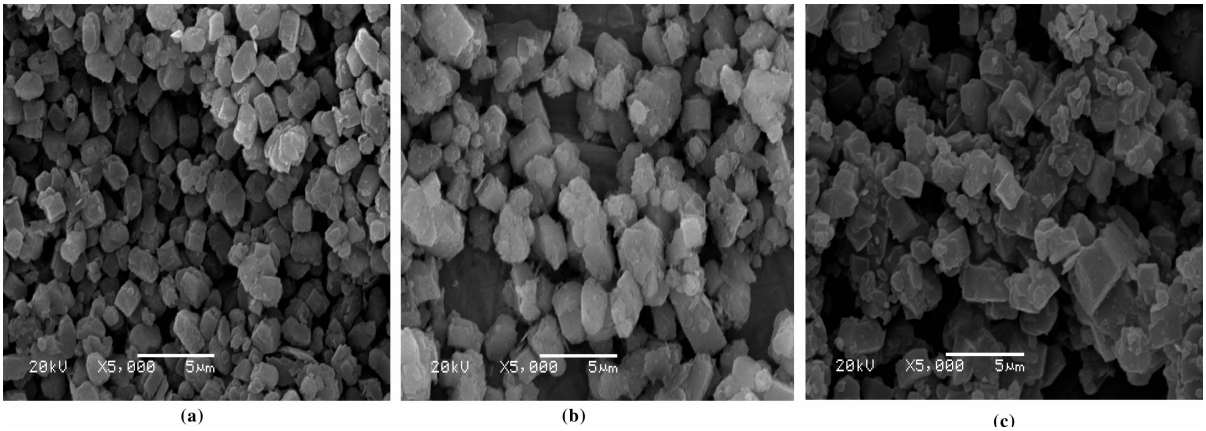


Fig. 7 SEM graphs of synthesized ZSM-5 molecular sieves preparing with different $SiO_2/Al_2O_3$ ratios. (a) 50, (b) 100, (c) 300.

**Table 1 Influence of $SiO_2/Al_2O_3$ ratios on the properties of ZSM-5 molecular sieves**

| $SiO_2/Al_2O_3$ | Relative crystallinity /% | Component | Average particle size/μm |
|---|---|---|---|
| 50 | 101 | ZSM-5 | 1.5 |
| 100 | 98 | ZSM-5 | 2.5 |
| 300 | 94 | ZSM-5 | 3.6 |

BET analysis of the obtained small-sized ZSM-5 zeolite was shown in Table 2. As can be seen from Table 2, the BET surface area of small-sized ZSM-5 zeolite was obviously higher than routine zeolite (about 120 $m^2g^{-1}$). Pore distribution of small-sized ZSM-5 zeolite was shown in Fig. 8. The average pore width of synthesized small-sized ZSM-5 zeolite was about 5.0 nm, which was consistent with literature [15].

**Table 2 BET results of small-sized ZSM-5 zeolite**

| Sample | BET surface area/($m^2 \cdot g^{-1}$) | Pore volume/($cm^3 \cdot g^{-1}$) | Pore size/Å |
|---|---|---|---|
| ZSM-5 | 268.83 | 0.18 | 27.2 |

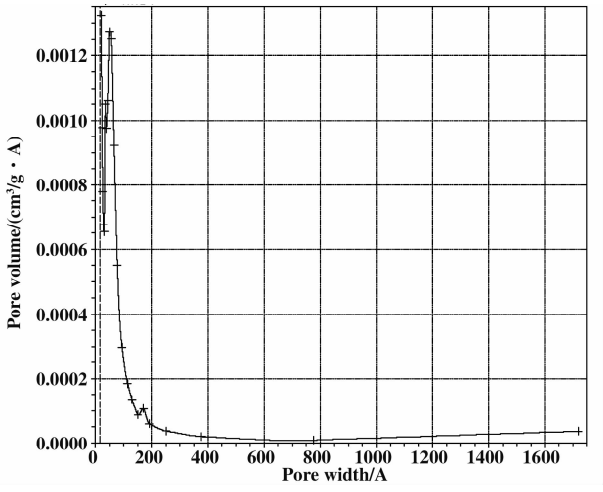


Fig. 8 Desorption pore distribution of small-sized ZSM-5 zeolite

## 3 Conclusions

In this paper, with aluminum sulfate as aluminum source and water glass as silicon source, template and crystal seed composite technology were used to prepare high crystallinity small crystal ZSM-5 molecular sieve. Research results showed that high crystallinity small crystal ZSM-5 molecular sieves can be synthesized in the crystallization conditions of 160 ~ 170 ℃ for 30 h by using low temperature water bath reflux stir-aging way.

Adding thesuitable amount of NaCl to gel before crystallization was helpful for forming nucleus and accelerating the nucleation rate, increased the number of nuclei formation. Under the conditions of low temperature and water bath stir, formed nuclei will be scattered without time to gather due to low temperature and stirring. The competition growth of a large number of crystal nucleus restrained the growth of crystals, which resulted in the formation of small crystal size ZSM-5 molecular sieve.

**Acknowledgements**

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# 低成本原料一步直接合成小晶粒 ZSM-5 分子筛

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**摘要:** 以硫酸铝、水玻璃、正丁胺、水、晶种、NaCl、浓硫酸等低成本试剂为原料, 一步直接合成法制备了高结晶度小晶粒 ZSM-5 分子筛, 详细考察了凝胶陈化方式、滴加顺序、晶化时间、晶化温度、水量及原料硅铝比对分子筛结晶度及粒度的影响. 通过 XRD、SEM 等对合成的分子筛进行了详细表征. 研究结果表明: 采用低温水浴回流搅拌陈化方式、在 160 ~ 170 ℃、晶化 30 h 可获得高结晶度小晶粒 ZSM-5 分子筛. 正反加顺序对分子筛结晶度影响不大.

**关键词:** 小晶粒分子筛; ZSM-5; 合成; 催化剂; 石油化工