Preparation and characterization of NaY zeolite in a rotating packed bed

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Abstract: NaY Zeolite was synthesized in a rotating packed bed (RPB) for the first time. A Si-Al gel with a specific composition was used as the structure-directing agent. The as-synthesized NaY Zeolite was characterized with scanning electron microscopy (SEM), X-ray diffraction (XRD) and specific surface area (BET). The characterization result showed that the NaY Zeolite had a particle size of approximately 200 nm, $n(SiO_2)/n(Al_2O_3)$ ratio of 5.03, crystallinity of 96% and specific surface area of 714 m^2/g. The experimental results indicated that the structure of NaY Zeolite was related to the synthesis conditions (such as reactors, crystallization time and so on). The micromixing efficiency was proven to be the most important factor for synthesis of NaY Zeolite in the high-gravity environment in RPB.

Key words: NaY zeolite, crystallinity, high-gravity, preparation characterization, rotating packed bed

1 Introduction

Synthesis of microsized NaY zeolite has received much attention owing to its valuable properties, such as high catalytic activity, high surface-atom ratio, large specific surface area and high surface energy (Wang et al, 2002; Camblor et al, 1989). Fluid catalytic cracking (FCC) catalysts prepared from microsized NaY zeolite with high Si/Al ratio have high catalytic activity and can be used in the refining of residual and heavy oils (Gilson and Derouane, 1984; Hamilton et al, 1993; Wang and Ma, 1998). It is also reported that the usage of small sized NaY zeolite can improve catalytic cracking selectivity, reduce coke formation, increase the yield of diesel oil and improve gasoline quality; and small sized NaY zeolite can also be used in the fine chemical industry (Yang et al, 1999; Kyotani et al, 2003; Albemarle Netherlands, 2005; Yamamura et al, 1994). So it is important to develop a feasible technology for preparation of small sized NaY zeolite.

A rotating packed bed (RPB), as a high-gravity apparatus for better multiphase contact, can generate an acceleration of 1-3 orders of magnitude larger than the gravitational acceleration on the earth (Chen et al, 1996; Foley, 1995). Since this apparatus can intensify gas-liquid or liquid-liquid mass transfer and micromixing, it has been successfully applied to the synthesis of well-defined nano inorganic powders, such as calcium carbonate, silica and pseudoboehmite, by the reactive precipitation method (Chen et al, 1999; 2003; Zhao et al, 2006). RPB has advantages over the conventional reactors in production of nano inorganic powders, such as short reaction time, small particle size, narrow size distribution, and easy industrial application. In this paper, small sized NaY zeolite is synthesized in RPB for the first time. The influence of the high-gravity environment on microporous structure was confirmed by comparison of experimental results in RPB with that of conventional hydrothermal synthesis. The effect of high-gravity level on NaY zeolite structure was investigated.

2 Experimental

2.1 Synthesis

All the chemicals used in this work were A.R. grade. The reaction apparatus is shown in Fig. 1.

#### 2.1.1 Preparation of structure-directing agent

Sodium aluminate solution (with a concentration of 20 wt%) was intensively mixed with sodium silicate solution (with a concentration of 30 wt%) for 10 min in RPB. Then the mixed solution was aged, and the structure-directing agent was obtained with a typical composition of $9.5Na_2O \cdot Al_2O_3 \cdot 10SiO_2 \cdot 720H_2O$.

2.1.2 Preparation of initial solution

Sodium aluminate solution (with a concentration of 30 wt%) was intensively mixed with sodium hydroxide solution (with a concentration of 7 wt%) and sodium silicate solution (with a concentration of 30 wt%) for 10 min in RPB, and then the initial solution was obtained with a typical composition
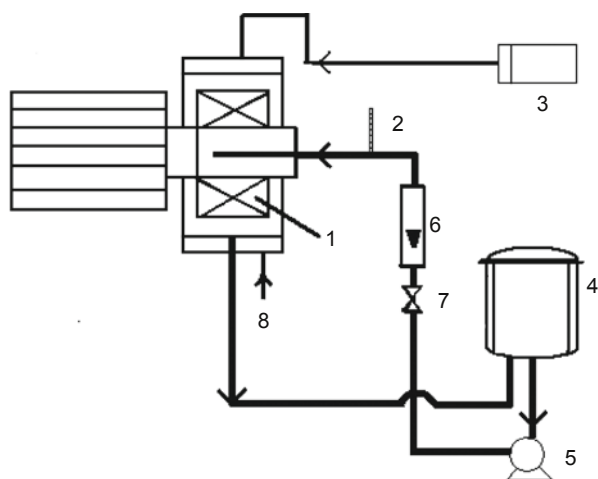
Fig. 1 Reaction apparatus of rotating packed bed
1-rotating packed bed, 2-thermometer, 3-pump, 4-stirred tank,
5-circulating pump, 6-rotor flow meter, 7-valve, 8-heating water

Fig. 2 SEM image of NaY zeolite synthesized
by the conventional hydrothermal method

Fig. 3 SEM image of NaY zeolite synthesized in RPB

$2.5Na_2O \cdot Al_2O_3 \cdot 4SiO_2 \cdot 240H_2O$.

2.1.3 Mixing

The rotating packed bed (RPB) was filled with wire mesh packings. The prepared initial solution was put into the agitating tank, and then circulated with a pump between RPB under a High-Gravity level of 170 g and the agitating tank. Then the directing agent was slowly added into this solution with a constant-flow pump which can control the adding rate accurately.

2.1.4 Crystallization and calcination

The resulting gel-like mixture was aged for 24 h and crystallized at 100 °C for 12 h, and then calcined at 450 °C for 3 h in air.
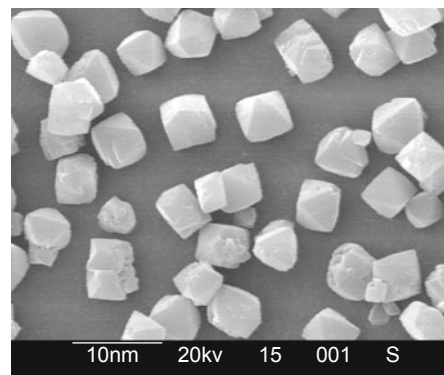
2.2 Characterization

The powder X-ray diffraction (XRD) patterns of NaY zeolite were recorded on a Siemens D500 diffractometer using CuKa radiation (λ=0.154 nm). The crystallinity of NaY zeolite was determined by comparing the intensity of the peaks in the X-ray diffraction patterns (Shimazu, Japan). Specific surface area (BET) of NaY zeolite was measured using an ASAP 2010 Analyzer (Beijing Best Technology Limited Company, China). Scanning electron microscopy (SEM) was performed on an E5431 electron microscope (Hitachi, Japan).

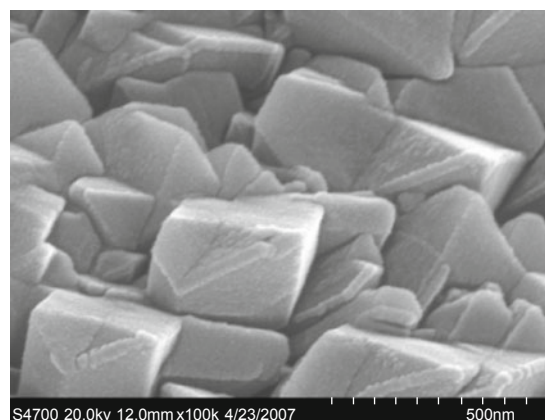## 3 Results and discussion

3.1 Comparison of NaY zeolite synthesized in RPB and by conventional hydrothermal method

The conditions for synthesis of NaY zeolite in RPB and by a conventional hydrothermal method are as follows: Si/Al of structure-directing agent of 7:1; Si/Al of initial solution of 4:1; Aging time of 24 h; Crystallization time of 12 h; Crystallization temperature of 100 °C. The SEM images of the obtained NaY zeolite samples are shown in Fig. 2 and Fig. 3.

From Fig. 2 and Fig. 3, it is found that the particle size of NaY zeolite prepared in RPB was significantly reduced compared to that prepared by the conventional hydrothermal method. The particle size of NaY zeolite prepared by hydrothermal synthesis method was about 5 μm, whereas the NaY zeolite prepared in RPB had a particle size of about 200 nm and exhibited uniform particle size distribution, indicating that high-gravity technology is superior to hydrothermal synthesis in preparation of NaY zeolite. The reason is that high-gravity technology in the form of RPB has better mass transfer and micromixing property than hydrothermal synthesis, resulting in homogenous mixing of structure-directing agent with initial solution, so that the size of the nuclei is small, and the number is large. Thus the crystal nuclei in RPB synthesis system have a large surface area, adsorbing solute on their surface for crystallization. The grain size of the NaY zeolite product is also small.

Compared with the conventional hydrothermal method, the NaY zeolite particle size which is synthetized by RPB is significantly small, which should be attributed to the "high-gravity effect". In the high-gravity field where strong shear stress exists, a large number of silicate and aluminum ions collide at the same time, and a large number of nucleation events occur in the system. The larger the number of nuclei with size smaller than the critical size in the synthesis system, the smaller the crystals that are generated. The size of molecular sieve grains also depends on the crystal growth rate and the nucleation rate. If the nucleation rate is faster than the

crystal growth rate, the size of synthesized molecular sieve is small and tends to be uniform. Because the nuclei greater than the threshold can grow to crystals almost at the same time, and new generated grains are allowed to exist until they reach a rapid growth period. Under high gravity, the nucleation rate is accelerated, the induction period is shortened, and the nucleation rate is faster than the crystal growth rate, so the NaY zeolite synthesized in RPB is small and uniform.

Fig. 4 shows the XRD patterns of NaY zeolite synthesized using two different methods. The characteristic peaks of NaY zeolite prepared in RPB shows it has the structure of standard NaY zeolite, but it has weak peak intensity, indicating that NaY zeolite prepared in RPB has a smaller particle size.
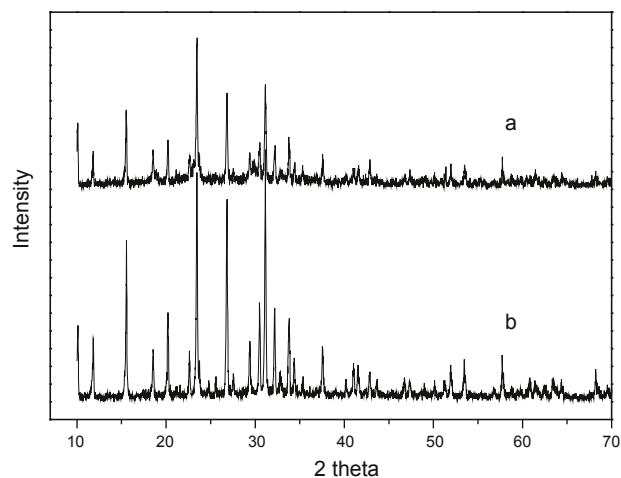
Fig. 4 XRD patterns of NaY zeolite synthesized in RPB (a) and by hydrothermal method (b)

3.2 Synthesis of NaY zeolite with different crystallization times

Generally, the NaY zeolite synthesized by different methods has a regular structure and works well in applications. But the synthesis time is long, especially the crystallization time (usually 24−48 hours), which greatly restricts its commercial application. Therefore, it is significant to shorten the crystallization time. In this work, NaY zeolite was separately synthesized in RPB and by conventional hydrothermal synthesis, with different crystallization times, to investigate the effect of crystallization time on its structure.

The effect of different crystallization times on NaY zeolite structure, synthesized by a conventional hydrothermal method as shown in Table 1.

Table 1 Effect of crystallization time on NaY zeolite structure, by conventional hydrothermal method

Crystallization time, h	12	20	24	30	40
$n(SiO_2)/n(Al_2O_3)$	2.19	3.28	3.24	3.17	3.21
Crystallinity, %	42	91	90	84	67
Surface area, m^2/g	425	703	711	609	543

Table 1 shows that with crystallization time of 20 h, the synthetized NaY zeolite by conventional hydrothermal method had higher Si-Al ratio and crystallinity. The surface area is 703 m^2/g. Crystallization time of 20 h is the optimal time for the conventional hydrothermal synthesis method.

The effect of crystallization time on the NaY zeolite structure, synthesized in RPB under the same condition as by the conventional hydrothermal method (i.e. the Si-Al ratios of structure-directing agent and mother liquor, crystallization, aging time, etc.), is shown in Table 2.

Table 2 The effect of crystallization time on the NaY zeolite structure, synthesized in RPB

Crystallization time, h	9	12	15	18	24
$n(SiO_2)/n(Al_2O_3)$	4.8	5.03	5.0	4.8	4.3
Crystallinity, %	78.0	96.0	92.0	89.0	67.0
Surface area, m^2/g	623	714	617	608	596

Table 2 shows that with crystallization time of 12 h, the synthetized NaY zeolite in RPB had the largest Si/Al ratio of 5.03, crystallinity of 96% and surface area of 714 m^2/g. So, crystallization time of 12 h is the optimal time for NaY zeolite synthesis in RPB, significantly shorter than the 20 h by the conventional hydrothermal method.

The SEM images of the synthesized NaY zeolite in RPB with crystallization time of 9 h, 12 h and 24 h are shown in Fig. 5.
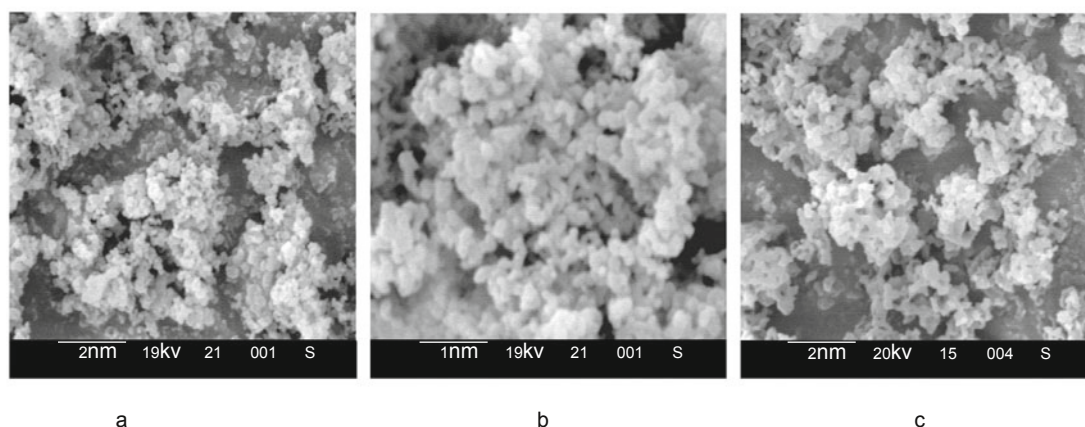
Fig. 5 SEM image of synthesized NaY zeolite in RPB with different crystallization times (a: 9h; b: 12h; c: 24h)

Zeolite crystallization is a micromixing process and a rapid reaction. In a conventional stirred tank reactor silicon and aluminum crystallization does not occur quickly and completely. Thus it will greatly prolong the crystallization time. High-gravity technology in RPB can greatly intensify the mass transfer and micromixing. A high-gravity reactor can enhance the mass transfer and mixing between silica and aluminum sols in the nucleation process and the reaction system will be uniformly mixed in a very short time, which will greatly shorten the crystallization time and improve the crystallinity of the molecular sieve. As a result the zeolite particles will be small and uniform.

Grain growth process can be divided into three stages. Stage 1 is referred to "nucleation preparation phase". The concentration of silicon tetrahedral structure and aluminum tetrahedral structure at this time has not yet reached the minimum saturation C^*_{min} required for grain nucleation, and no nucleation occurs; Stage 2 is called "nucleation phase". At this point the concentration is higher than C^*_{min}, and a large number of nuclei forms. With the formation of nuclei, the concentration decrease; Stage 3 is called "the growth phase", when the nuclei grow and become grains. To obtain small and uniform grains, nucleation rate must be as high as possible, while the growth rate should be low. In High-Gravity reactor, silicon and aluminum are highly decentralized, and can instantly reach the minimum saturation C^*_{min} required for grain nucleation. In a short time the system can enter the second stage — nucleation phase, and a large number of small nuclei are produced. Competition occurs between nucleation and crystal growth. The faster the rate of nucleation, the slower the growth rate of corresponding grains, as a result the grains will be small and uniform. Therefore, nanoscale zeolite NaY can be synthesized by using RPB. The crystallization process can be regarded as a continuation of the growth process, but it requires a specific temperature and pressure. Since a large number of nuclei is formed at the early stage and particle size is small, resulting in large surface area and a large number of growing points, crystallization will be completed in a short time.

4 Conclusions

In this study, ultrafine (about 200 nm) NaY zeolite with a uniform particle size distribution was synthesized in a RPB reactor. Compared with conventional methods for NaY zeolite synthesis, the as-prepared ultrafine NaY zeolite has a much smaller particle size and higher surface area, suggesting higher catalytic performance. The experimental results indicated that the structure of NaY Zeolite was related to the synthesized condition. Especially the efficiency of micromixing which was the most important condition for the synthesis of NaY Zeolite has been greatly intensified by the high-gravity environment in the RPB. RPB technology provides a promising and efficient pathway for mass production of ultrafine NaY zeolite.

Acknowledgements

References

Albemarle Netherlands B V. Process for the preparation of doped pentasil-type zeolite using doped faujasite seeds. Patent 1678528. 2005-10-05

Camblor M A, Corma A and Martínez A. Catalytic cracking of gasoil: Benefits in activity and selectivity of small Y zeolite crystallites stabilized by a higher silicon-to-aluminium ratio by synthesis. Applied Catalysis. 1989. 55: 65-74

Chen J F, Chen J T and Zheng C. Interaction of macro- and micromixing on particle size distribution in reactive precipitation. Chemical Engineering Science. 1996. 51(10): 1957-1966

Chen J F, Shao L, Guo F, et al. Synthesis of nano-fibers of aluminum hydroxide in novel rotating packed bed reactor. Chemical Engineering Science. 2003. 58: 569-575

Chen J F, Wang Y H and Guo K. Synthesis of nano-cubic $CaCO_3$ by high-gravity reactive precipitation. Acta Metallurgica Sinica. 1999. 35: 179-182

Foley H C. Carbogenic molecular sieves: synthesis, properties and applications. Microporous Materials. 1995. 4: 407-433

Gilson J P and Derouane E G. On the external and intracrystalline surface catalytic activity of pentasil zeolites. J Catal. 1984. 88: 538-541

Hamilton K E, Coker E N, Sacco A, et al. The effects of the silica source on the crystallization of zeolites NaX. Zeolites. 1993. 13: 645-653

Kyotani T, Ma Z X and Tomita A. Templated synthesis of novel porous carbons using various types of zeolites. Carbon. 2003. 41(7): 1451-1459

Wang B and Ma H Z. Factors affecting the synthesis of microsized NaY zeolite. Microporous and Mesoporous Materials. 1998. 25: 131-136

Wang B, Ma H Z and Shi Q Z. Synthesis of nanosized NaY zeolite by confined space method. Chinese Chemical Letters. 2002. 13: 385-388 (in Chinese)

Yamamura M, Chaki K, Wakatsuki T, et al. Synthesis of ZSM-5 zeolite with small crystal size and its catalytic performance for ethylene oligomerization. Zeolites. 1994. 14(6): 643-649

Yang P D, Zhao D Y, Margolese D I, et al. Block copolymer templating syntheses of mesoporous metal oxides with large ordering lengths and semicrystalline framework. Chemistry of Materials. 1999. (10): 2813-2826

Zhao R H, Guo F, Hu Y Q, et al. Self-assembly synthesis of organized mesoporous alumina by precipitation method in aqueous solution. Microporous Mesoporous Material. 2006. 93: 212-215

(Edited by Zhu Xiuqin)