

Synthesis of small crystals zeolite NaY

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Received 18 November 2004; accepted 8 October 2005

Available online 21 November 2005

Abstract

Zeolite NaY with small crystals was hydrothermally synthesized using a two-stage variable-temperature program without the presence of organic templates, structure-directing agent, seeding crystals and other additives. The as-synthesized samples were characterized by X-ray diffraction (XRD), laser particle size analyzer, scanning electron microscopy (SEM), and Fourier-Transformation Infrared (FT-IR) spectroscopy and Raman spectroscopy. The temperature was found to be a crucial factor for the control of the crystal size.

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Keywords: Synthesis; Small crystal; Zeolite NaY; Catalysts; Nanomaterials

1. Introduction

Zeolite Y, a highly versatile member of the faujasite family, plays a great role in the petrochemical industry [1,2]. It has been found that the size of zeolite crystals could exert a significant impact on the catalytic performance [3]. Recently, the synthesis of zeolite Y with small particle size has received much attention, because the use of such zeolite Y can noticeably improve the catalytic cracking selectivity with reduced coking, and increase both the diesel yield and the gasoline quality [4]. In most syntheses, organic templates, structure-directing agent, seeding crystals and many other additives were often added to induce the formation of zeolite NaY with small crystals [1–3,5–8].

In the present work, we successfully developed a two-stage variable-temperature program for the synthesis of zeolite NaY with uniform small crystals without the addition of organic templates, directing-agent, seeding crystals and other additives.

2. Experimental

All of the syntheses were performed according to the following gel composition of $10\text{Na}_2\text{O} : 1.0\text{Al}_2\text{O}_3 : 15\text{SiO}_2 : 300\text{H}_2\text{O}$ (molar

ratio). The initial precursor was prepared by mixing the required amounts of aluminum isopropoxide, sodium hydroxide, colloidal silica and distilled water together, and then transferred into an autoclave, where the hydrothermal crystallization was carried out at 313, 333, 373, and 393 K for some time, respectively. The crystallization controlled by a two-stage variable-temperature program was conducted at 313 K for 24 h, subsequently at 333 K for 48 h. After the completion of crystallization, the solid products were washed several times with distilled water until $\text{pH}=7-8$, then dried at 373 K overnight. X-ray diffraction (D/max-rb) was performed to determine the crystal phase. The particle size was measured by laser beam scattering technique (BT-9300 Particle Size Analyzer) and scanning electron microscopy (SEM). FT-IR was used to analyze sample structures.

3. Results and discussion

In comparison with the variable-temperature synthesis, the isothermal syntheses of zeolite NaY were performed. The effect of temperature on the crystallization of zeolite NaY was examined at temperatures ranging from 313 to 393 K. Fig. 1(A) shows the XRD patterns of the samples synthesized by an isothermal program. Zeolite NaY could be achieved at 373 and 333 K. However, the crystallization at 393 K induced the formation of zeolite P instead of zeolite Y. When the temperature was decreased to 313 K, only amorphous solid could be produced. Very distinctly, along with the decrease of the crystallization temperature, X-ray diffraction peaks of as-synthesized samples gradually weaken and widen (in Fig. 1(A)), possibly attributed

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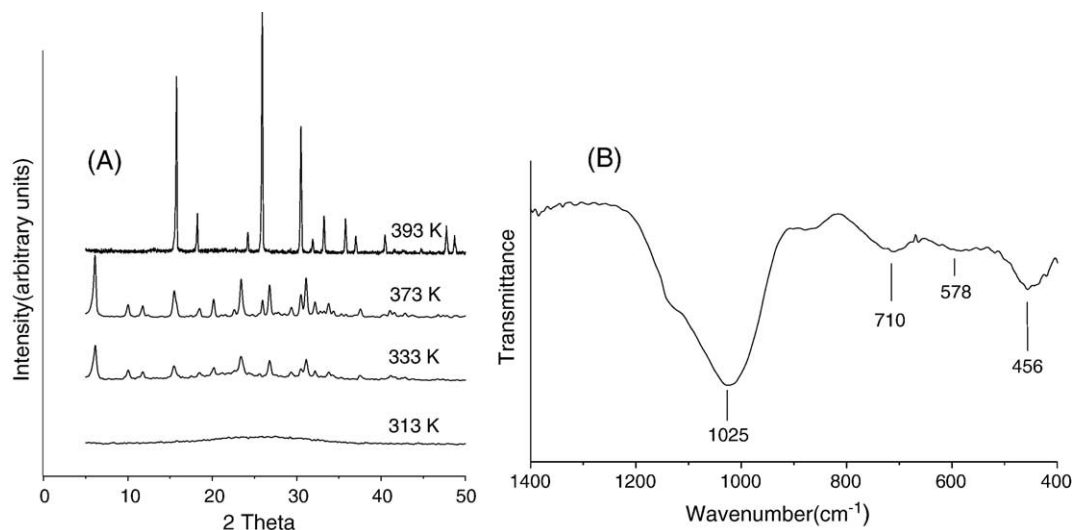


Fig. 1. (A) XRD patterns of as-synthesized samples crystallized by an isothermal program at different temperatures. (B) FT-IR of as-synthesized NaY zeolite by a two-stage variable-temperature program at 313 K for 24 h.

to the smaller particle size of the samples, in accordance with observations reported elsewhere [9]. The particle size distributions of as-synthesized samples by an isothermal program at 333 and 373 K were shown in Fig. 2(A). With decreasing crystallization temperature, the average crystal size of products becomes smaller, and the particle size distribution becomes narrower, as shown in Fig. 2(A). These results are consistent with XRD results. This is because the higher temperature could accelerate the growth of crystal, resulting in larger crystals. The lower temperature was always favorable to the formation of zeolite NaY with small crystals, possibly because decreasing the temperature was more favorable to the nucleation than crystal growth, resulting in smaller zeolite crystals [10].

In order to synthesize smaller NaY crystals, a two-stage variable-temperature program was employed, starting crystallization at 313 K and rapidly increasing the temperature to 333 K. XRD indicated pure zeolite Y was obtained. As shown in Fig. 2(A), it can be observed that the particle size distribution of the sample synthesized by a two-stage variable-temperature program (0.12~0.85 μm) is much narrower than that by an isothermal program (0.36~1.45 μm). The average crystal diameter is <0.4 μm , consisting of >85% of micron-sized NaY smaller than 0.5 μm . SEM image in Fig. 2(B) further reveals a uniform particle size of the sample with a regular shape. We presume that the lower temperature in the initial stage is favorable for the fast nucleation of

zeolite NaY with negligible crystal growth, and that the subsequent higher temperature is beneficial to the crystal growth. Thus, the fast nucleation in the initial stage may allow the formation of a big number of crystal nuclei, further leading to smaller zeolite crystals [11]. In order to confirm our viewpoint, XRD and FT-IR were used to characterize the sample synthesized by a two-stage program at 313 K for 24 h. Although the XRD showed no peaks, FT-IR (Fig. 1(B)) showed some peaks of tetrahedral vibration. The peaks at 456 and 1025 cm^{-1} are both assigned to tetrahedral vibration; the appearance of the band at 578 cm^{-1} (although very weak) is attributed to the double ring external linkage peak associated with the FAU structure [12]. This showed that the nucleation is major at low temperature.

4. Conclusion

A two-stage variable-temperature program promoted the synthesis of zeolite NaY with small crystals (<0.4 μm) from a precursor mixture without organic templates, structure-directing agent, seeding crystals and other additives. XRD showed the as-synthesized NaY was pure. LPA results indicated a narrow distribution of particle size, with an average crystal size of <0.4 μm . And SEM image confirmed the LPA results further.

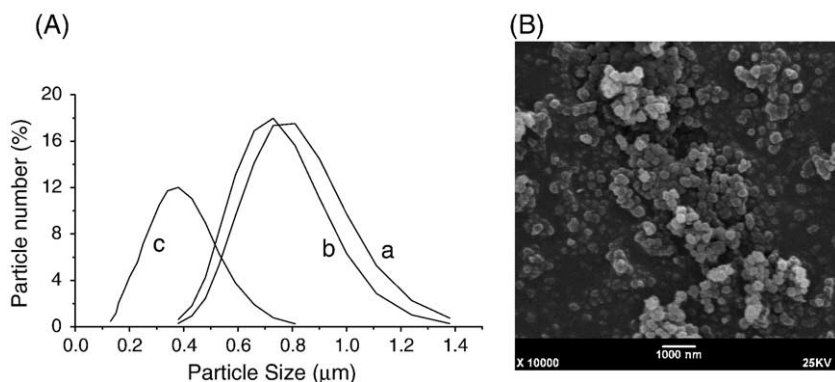


Fig. 2. (A) Particle size distribution of the samples synthesized by an isothermal program at different temperatures and a two-stage variable-temperature program (a) 373 K, (b) 333 K, and (c) a two-stage variable-temperature program. (B) SEM image of as-synthesized NaY zeolite by a two-stage variable-temperature program.

Acknowledgments

The authors thank the assistant Shuanghe Meng for SEM photographs. We are grateful to assistant Yue Yang for XRD tests.

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