Synthesis of a high-quality NaP zeolite from epidesmine by a hydrothermal method

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Abstract. Epidesmine as a silicon source was used to synthesize NaP zeolite by a hydrothermal method. Parameters such as $\text{SiO}_2/\text{Al}_2\text{O}_3$ and $\text{H}_2\text{O}/\text{Na}_2\text{O}$ molar ratios, reaction temperatures and reaction times were investigated for regulating the purity of the final product. The samples were characterized by X-ray diffraction, infrared spectroscopy and scanning electron microscope. The experimental results evidenced that a high-quality NaP zeolite was obtained at $\text{SiO}_2/\text{Al}_2\text{O}_3$ and $\text{H}_2\text{O}/\text{Na}_2\text{O}$ molar ratios of 3.7 and 55, respectively, and at a temperature of 95°C for 6.5 h of ageing. The BET surface area and total pore volume of the powders were $17.1359 \text{ m}^2 \text{ g}^{-1}$ and $0.006845 \text{ cm}^3 \text{ g}^{-1}$, and the pore size was $\sim 3.2 \mu\text{m}$.

Keywords. Epidesmine; NaP zeolite; hydrothermal method; molar ratios; reaction temperature; reaction time.

1. Introduction

Zeolites are kinds of crystalline solids with an extending three-dimensional framework of silicon and aluminium tetrahedra linked by sharing oxygen atoms. Well-defined channels, morphology as well as crystal size of these zeolites have a significant role in industries [1]. NaP is a kind of most interesting structured zeolite with two sets of intersecting channels and its structure is called 'Gismondine' (GIS). The NaP zeolite can be used not only as a cation exchanger and an adsorbent, but also it has been found to have widespread application in the purification of metal ions, separation of gases and as a carrier of antibacterial agents [2].

In recent years, the preparation of synthetic zeolites has been increasing by using natural minerals, such as clinoptilolite, pyrophyllite, mordenite, chabazite, epidesmine, etc., because the preparation of chemical reagents was expensive [3]. A hydrothermal method enables effective solvability of water and the solubility and reactivity of the reactants for the synthesis of zeolite, rearranging and dissolving the initial primary gel, which increases the crystallization rate. This method is beneficial to control the grain size and morphology of the product crystal [4,5].

Epidesmine is considered as one of the most abundant natural minerals in Guangxi. As a type of inorganic mineral, epidesmine possesses good thermostability, acid stability and high quality of whiteness. One of the effective utilization is to convert epidesmine into zeolitic materials and synthesizing

zeolites is considered as an environmental friendly application of epidesmine [6].

In the present investigation, we attempted the hydrothermal synthesis of NaP under controlled different conditions. Optimization of crystallization conditions was adapted through variation of the following parameters: $\text{SiO}_2/\text{Al}_2\text{O}_3$ and $\text{H}_2\text{O}/\text{Na}_2\text{O}$ molar ratios, ageing times and ageing temperatures.

2. Experimental

2.1 Materials and chemicals

Epidesmine (table 1) from the Guangxi province of China, hydrochloric acid (HCl, 36–38 wt%) from Xilong-Guangdong, sodium hydroxide (96 wt% NaOH) from Xilong-Guangdong and sodium aluminate (45% of Al_2O_3) from Guangfu-Tianjin were obtained.

Experimental apparatus: DF-101S Hot type thermostatic magnetic stirring apparatus from Yuhua Instrument Limited, Liability Company, Gongyi city, Henan province; TDZ5-WS multi-tube frame automatic balancing centrifuge from Xiangyi Lab instrument exploitation limited company, Hunan province; PHB-3 pen type meter from Sanxin instrument and meter plant, Shanghai province and electric heating constant temperature drying oven from Yuejin medical apparatus factory, Shanghai province, were obtained.

Table 1. Chemical composition of epidesmine (%).

SiO ₂	Al ₂ O ₃	CaO	K ₂ O	Na ₂ O	Fe ₂ O ₃	H ₂ O ⁺	H ₂ O ⁻	Si/Al	Loss on ignition	Total
58.76	14.13	8.8	0.11	0.18	0.44	16.87	1.25	3.529	17.79	100.1

2.2 Synthesis of NaP zeolite

In the first step, epidesmine and 15% hydrochloric acid in a 1:3 ratio were mixed in a three-necked flask, a stirring bar was added into the solution and the solution was stirred at 150rpm for 2h. Reaction temperature was 90°C. Then, the mixture was washed with distilled water up to pH 6–7 and dried at 60°C for 12h to obtain a precursor.

In the second step, 3g of the precursor was placed in a reactor, then sodium aluminate, sodium hydroxide and distilled water were mixed in the three-necked flask according to SiO₂/Al₂O₃ = 3.3–3.7, Na₂O/SiO₂ = 1.1 and H₂O/Na₂O = 45–55. Hydrothermal crystallization was continued under continuous magnetic stirring for 6h at 95°C.

In the third step, the synthesized zeolite was filtered, washed thoroughly with deionized water to remove unreacted and water-soluble components, and then, dried overnight at 60°C for 12h to obtain the NaP zeolite. This was characterized by means of different instrumental techniques.

2.3 Characterization

The crystal structure of NaP zeolite was analysed by using an X-ray diffractometer (XRD) (X'Pert PRO, PANalytical, Almelo, Holland) using CuK α radiation at a scanning rate of 10° min⁻¹ and the 2 θ range from 5 to 80°.

The presence of functional groups of NaP zeolite was analysed by using a Fourier transform infrared (FTIR) spectrophotometer (IRAffinity, Shimadzu, Japan) using KBr as a reference material in the range of 400–4000 cm⁻¹ with a resolution of 0.5 cm⁻¹.

The morphology of the NaP zeolite was investigated using a field emission scanning electron microscopic (FESEM) system (Hitachi, S-4800).

3. Results

3.1 Effect of SiO₂/Al₂O₃ ratios

The characteristic peaks of the NaP zeolite at 12.5, 17.6, 21.7, 28.1 and 33.4° [7] were identified in XRD patterns of zeolite powders (figure 1A) obtained in a SiO₂/Al₂O₃ ratio ranging from 3.3 to 3.7, indicating the formation of the NaP zeolite crystalline phase (JCPDS no. 71-0962) [8]. Besides, the characteristic peaks of quartz at 20.8 and 26.9° were always existed in the three curves, correspondingly, the conventional step of alkali dissolution was skipped [9]. Notably, a diffraction peak of the NaX zeolite at SiO₂/Al₂O₃ = 3.3

and 3.5 was also observed (figure 1A; a, b), indicating that the chemical compositions were analogous between the NaP zeolite and NaX zeolite. The NaP zeolite with higher purity was synthesized in a SiO₂/Al₂O₃ ratio = 3.7 (figure 1A; c).

Figure 1B depicts the IR spectra of the NaP zeolite synthesized from the hydrothermal process with variable SiO₂/Al₂O₃ ratios. The strong vibration at around 1000 cm⁻¹ was observed and the intensity of this band declined with an increase in SiO₂/Al₂O₃ ratio, which can be attributed to an increase in the number of Al–O bonds [10]. The bands at 740 and 665 cm⁻¹ are attributed to the Si–O and Al–O symmetrical stretching vibrations, respectively. Si–O–Si is responsible for the band at 600 cm⁻¹. The band at 440 cm⁻¹ is assigned to the tetrahedron bending vibration [11]. The bending vibration shifted from 450 (figure 1B; a, b) to 440 cm⁻¹ (figure 1B; c) resulting in the disappearance of the NaX zeolite. These peaks were in accordance with those reported by Albert *et al* [12].

The morphological evaluation and particle size of the NaP zeolite with different SiO₂/Al₂O₃ (3.3, 3.5 and 3.7) molar ratios were investigated by FESEM (figure 1C). The octahedral structures of the NaX zeolite were observed (figure 1C; a, b), but these crystal structures are incomplete, which means that the complete NaX zeolite cannot be produced under this condition. The crystals of the NaP zeolite have a rounded shape, which is similar to the ones observed in previous research [13]. The diameter of the spherical particle was 1.5 μ m (figure 1C; c).

3.2 Effect of H₂O/Na₂O ratios

Alkalinity plays an important role in the synthesis of the zeolite by impacting polymerization aluminate and aluminosilicate oligomers, controlling the state of silicate anions and maintaining the balance of ingredient in the system, ensuring the formation of particles and promoting the crystallization process [14,15]. When the H₂O/Na₂O ratio increased from 45 to 55, the crystallinity of the product gradually increased (figure 2A; a, b and c). However, as the ratio increased from 55 to 60, the crystallization of the NaP zeolite slightly diminished and the characteristic peaks of the NaX zeolite were observed (figure 2A; d), so the alkalinity too high or too low will affect the formation and stability of the crystal [16], suggesting that H₂O/Na₂O = 55 was suitable condition for the synthesis of the NaP zeolite.

SEM observations of the samples after hydrothermal treatment with H₂O/Na₂O = 45, 50, 55 and 60 are presented

Figure 1. (A) XRD pattern, (B) FTIR and (C) SEM images of the NaP zeolite synthesized with different $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios (a. 3.3, b. 3.5 and c. 3.7).

Figure 2. (A) XRD patterns and (B) SEM images of the NaP zeolite synthesized with different $\text{H}_2\text{O}/\text{Na}_2\text{O}$ ratios (a. 45, b. 50, c. 55 and d. 60).

in figure 2B. Compared to figure 2B; a, b, c and d, figure 2B; d presents an octahedral morphology [17], confirming the results of XRD measurements (figure 2A; d). SEM images (figure 2B; c) showed that the NaP zeolite has a fine crystal when $\text{H}_2\text{O}/\text{Na}_2\text{O} = 55$.

3.3 Effect of hydrothermal temperature

The NaP zeolite was obtained at four different temperatures 80, 85, 90 and 95°C, and the hydrothermal sample is shown in figure 3A. Only amorphous substance is observed in

Figure 3. (A) XRD patterns, (B) FTIR and (C) SEM of the NaP zeolite synthesized at different temperatures (a. 80, b. 85, c. 90 and d. 95°C).

figure 3A; a, it was the incomplete dissolution of the Si and Al atoms from the precursor [18].

The characteristic peak of XRD does not change significantly, when the temperature was gradually increased

Figure 4. (A) XRD patterns and (B) SEM of the NaP zeolite synthesized at different times (a. 5, b. 5.5, c. 6.0, d. 6.5 and e. 7.0 h).

from 85 to 95°C (figure 3A; b, c and d). This result indicated that the NaP zeolite was completely formed and crystal transformation was not observed when the material ratio was controlled.

Figure 3B presents the IR spectra of the zeolite. The peaks at 400–1500 cm^{-1} were significantly weakened at 80°C (figure 3B; a) from the infrared contrast chart, indicating that the NaP zeolite has not been synthesized at this temperature. The band at 1000 cm^{-1} is assigned to a Si–O or Al–O asymmetric stretch. By increasing the hydrothermal treatment temperature from 80 to 95°C, the peak position shifted from high to low wavenumber (1000–988 cm^{-1}), which meant that the Si–O bond was weakened due to a part of the O atom of the Si–O bond combining with the Al atom.

The SEM images of the synthesized products are shown in figure 3C. The particles of the product are small and irregular at 80°C (figure 3C; a), proving that the nucleus of the NaP zeolite was not formed [19]. The crystal grown rapidly at 85°C (figure 3C; b), leading to the NaP zeolite with a spherical shape was observed [20], and the crystal morphology did not change as the temperature increases from 85 to 95°C (figure 3C; b, d). Particles with an average diameter of 1.5 μm are presented in figure 3C; d, and they have a larger particle size compared to the particle size shown in figure 3C; b, c.

Figure 5. N_2 adsorption–desorption isotherms of the NaP zeolite prepared with $\text{SiO}_2/\text{Al}_2\text{O}_3 = 3.7$, $\text{Na}_2\text{O}/\text{SiO}_2 = 1.1$ and $\text{H}_2\text{O}/\text{Na}_2\text{O} = 55$ at 95°C for 6.5 h. The inset shows the pore-size distributions of the NaP zeolite.

3.4 Effect of hydrothermal time

The effect of the hydrothermal time on the crystallization of the NaP zeolite under similar conditions, i.e., $\text{SiO}_2/\text{Al}_2\text{O}_3 = 3.7$, $\text{Na}_2\text{O}/\text{SiO}_2 = 1.1$ and $\text{H}_2\text{O}/\text{Na}_2\text{O} = 55$, respectively, were determined. The XRD powder patterns of samples at 95°C for different crystallization times (5, 5.5, 6, 6.5 and 7 h) are shown in figure 4A. The obvious characteristic peaks of the NaP zeolite and heterocrystalline stilbite at 9.68° were observed in five-diffraction patterns (figure 4A); however, it could be clearly observed that the crystal diffraction intensity of stilbite is low and is shown in figure 4A; d. When the hydrothermal time increased to 7 h, the NaX zeolite and stilbite are observed in figure 4A; e [21]. Mixed crystals appeared when the reaction time was prolonged and the crystallization time should be controlled at 6.5 h for the preparation of the NaP zeolite.

Figure 4B shows the microstructure of the products prepared at different hydrothermal times. The regular shape of the NaP zeolite has been formed when the hydrothermal time was 5 h. The size of the NaP zeolite increased and the surface became rough in the product as the temperature increased to 6 h. When the hydrothermal time is 7 h, the octahedral angle of the NaX zeolite became clear and the size was uniform (2–3 μm) [22]. The products were identified as NaP zeolite from XRD analysis. In figure 4B; d, the size of the samples was larger and more uniform compared to others, the average particle size of the NaP zeolite was about 1.5 μm .

3.5 Surface area texture

Figure 5 shows the N_2 adsorption–desorption isotherms of the zeolite at liquid nitrogen temperature (77 K). In mesoporous zeolites, the sorption behaviour is a function of fluid wall interaction strength and the attractive interactions between the fluid molecules [23]. NaP zeolite samples show a type IV isotherm characteristic of solids with a predominantly mesoporous channel (figure 5). The mesopore region represents a relative pressure range of 0.5–0.95, the hysteresis loop of the sample is H3-type, which is a typical system with a ‘bottle’ pore distribution [24]. Besides, the pore size distribution found by the Barrett–Joyner–Halenda method as shown in figure 5 (inset), exhibited the main mesoporous distribution. The sample exhibits a broad pore size distribution of 2–16 nm and is mainly concentrated at 3.2 nm. Table 2 shows that the BET surface area is 17.1359 $\text{m}^2 \text{g}^{-1}$ and the total pore volume is 0.006845 $\text{cm}^3 \text{g}^{-1}$.

Table 2. Surface characteristics of the NaP zeolite at $\text{SiO}_2/\text{Al}_2\text{O}_3 = 3.7$, $\text{Na}_2\text{O}/\text{SiO}_2 = 1.1$ and $\text{H}_2\text{O}/\text{Na}_2\text{O} = 55$ at 95°C for 6.5 h.

Sample	BET surface area	<i>t</i> -plot micropore area	<i>t</i> -plot external surface area	<i>t</i> -plot micropore volume
NaP zeolite	17.1359 $\text{m}^2 \text{g}^{-1}$	13.2565 $\text{m}^2 \text{g}^{-1}$	3.8794 $\text{m}^2 \text{g}^{-1}$	0.006845 $\text{cm}^3 \text{g}^{-1}$

4. Conclusion

The NaP zeolite was synthesized using epidesmine as a silicate source via a simple hydrothermal process. The effects of $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios, $\text{H}_2\text{O}/\text{Na}_2\text{O}$ ratios, crystallization times and crystallization temperatures in zeolites on the crystalline were investigated. The experimental results illustrated that the NaX zeolite gradually disappeared as the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios increased from 3.3 to 3.7 by the hydrothermal method at 95°C for 6.5 h. $\text{SiO}_2/\text{Al}_2\text{O}_3$ and $\text{H}_2\text{O}/\text{Na}_2\text{O}$ ratios were found to play an important role in the zeolite structure and composition. The NaP zeolite with high crystalline was obtained at $\text{H}_2\text{O}/\text{Na}_2\text{O} = 55$ and reaction time = 6.5 h. Furthermore, a well-developed NaP zeolite could be obtained after hydrothermal treatment at 85°C for 6.5 h. The formation of the target product NaP zeolite was accompanied by the appearance of the stilbite after 5 h of hydrothermal treatment at 95°C and the NaX zeolite appeared when the time increases to 7 h. Besides, a long-crystallization time results in miscellaneous compounds being developed. Thus, the optimal synthesis conditions to obtain a NaP zeolite were $\text{SiO}_2/\text{Al}_2\text{O}_3 = 3.7$ and $\text{H}_2\text{O}/\text{Na}_2\text{O} = 55$ at 95°C for 6.5 h. The NaP zeolite has a uniform mesoporous structure with a pore size of about $3.2\ \mu\text{m}$. The surface area is $17.1359\ \text{m}^2\ \text{g}^{-1}$ and the total pore volume is $0.006845\ \text{cm}^3\ \text{g}^{-1}$.

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