Synthesis of ultra-small NaA zeolite nanocrystals at near room temperature

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Research Article

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Abstract

The NaA zeolite nanocrystalline aggregates composed of 6 nm ultra-small were synthesized for the first time by refluxing at near room temperature and atmospheric pressure. NaA zeolite samples had been characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and N2 adsorption-desorption isotherms. The XRD of the obtained samples at different synthesis temperatures demonstrated that their crystallinity was high. Furthermore, the SEM images of NaA zeolite synthesized at 30, 40 and 60°C showed that its particle sizes were 100, 100 and 150 nm, respectively. Moreover, the TEM images confirmed that the NaA zeolite aggregates synthesized at 40°C and 60°C consisted of ultra-small crystals with a size of 6 nm, while the NaA zeolite synthesized at 30°C was a single crystal. Compared with the previously reported synthetic zeolite crystals, the use of a reflux system under atmospheric pressure in this study not only synthesized the ultra-small zeolite nanocrystals（6 nm）with large specific surface area, but also avoided many safety issues brought by traditional synthesis methods under high autogenous pressure. Therefore, this study provides a precise and safe synthetic method for the development of ultra-small zeolite nanocrystals.Moreover, the large specific surface area makes them have great potential for development.

1. Introduction

Zeolite is an alumino silicate crystal with regular pore structure, composed of silicon-oxygen tetrahedron (-SiO_4) or aluminum-oxygen tetrahedron (-AlO_4) [1]. Nano-zeolites have attracted extensive research attention for adsorption and catalysis because of their higher surface activity, larger external surface area, lower mass and heat transfer resistance than micron-zeolites [2]. The small zeolite crystal size facilitates intra-crystalline diffusion and has positive effects on the catalytic reaction. Although previous studies have reported the synthesis of ZSM-5 and EMT nanocrystals [3–4], the synthesis of ultra-small NaA zeolite nanocrystals smaller than 6 nm under a hydrothermal reflux system has not yet been reported.

The first method considered in zeolite synthesis is hydrothermal [5]. Although hydrothermal synthesis is easy to perform and the raw materials are inexpensive [6–7], it has certain limitations such as high temperature requirement, crystallization under autogenous pressure and product formation was difficult to monitor. Hence, we prepared NaA zeolite nanocrystalline aggregates using the atmospheric pressure hydrothermal reflux method that allows for monitoring the reaction, avoids the use of autoclaves, and reduces the equipment cost.

The highly crystalline NaA zeolite nanocrystalline aggregates with a particle size of about 130 nm were successfully synthesized. Moreover, TEM revealed that NaA zeolites are aggregates composed of 6 nm ultra-small nanocrystals. The ultra-small nanocrystal is conducive to intra-crystalline diffusion, easy access to the active center and and contribute to increase adsorption rate; thus, it has many potential applications and warrants further investigation.

2. Experimental

2.1 Materials

Analytically pure chemical reagents were purchased from Sinopharm Chemical Reagent Co., Ltd. and were used directly without additional purification. The following chemical reagents were used: tetramethylammonium hydroxide (TMAOH; 25 wt%), aluminum isopropoxide (AIP), sodium hydroxide (NaOH), and tetraethyl orthosilicate (TEOS).

2.2 Synthesis of NaA zeolites

In a typical synthesis of NaA zeolites, H_2O, TMAOH, NaOH, AIP, and TEOS were mixed together. The molar composition of mixed solution was 2 Al_2O_3: 15 SiO_2: 30 TMAOH: 1350 H_2O. The clear solution was transferred to a three-necked flask and refluxed for several days at 30, 40, and 60℃. The resulting crystalline white solid was centrifuged, washed, and air dried overnight at 100℃ in an oven. The zeolite synthesis time is that the product quality does not change with time (complete reaction). The synthesized NaA zeolite samples were labeled as NaA-30, NaA-40, and NaA-60.

2.3 Characterization

X-ray diffraction (XRD) patterns for the samples were recorded in a 2θ range of 5°~50°, with a step size of 0.02°, using a Dandong Tongda TD-3500 powder diffractometer. Additionally, scanning electron microscopy (SEM) images were captured at an acceleration voltage of 5 kV on an FEI Scios microscope. Transmission electron microscopy (TEM) was performed using a JEOL JEM-2800 F microscope at 200 kV. The Beishide 3H-2000PS2 surface area and pore size analyzer was used to measure the N_2 adsorption-desorption isotherms. The samples were degassed at 200°C for 2 hours under vacuum conditions before the test. The Brunauer-Emmet-Teller (BET) method was used to calculate the specific surface area.

3. Results And Discussion

3.1 Zeolite/SiO_2 quality analysis

The samples of the same volume of zeolite were taken at different times, dried at the same temperature, and weighed. The time for complete reaction was determined by calculating the mass growth curve of zeolite, as shown in Fig. 1. The results showed that the mass of the zeolite synthesized at 30°C hardly increased with time after 92 days, indicating that it had completely reacted. At 40°C and 60°C, the mass of the synthesized zeolite hardly changed after 25 and 14 days, respectively.

3.2 XRD analysis

Figure 2 shows the XRD patterns of NaA-30, NaA-40, and NaA-60 zeolites. The characteristic peaks for NaA zeolites appeared at 2θ = 7.3°, 10.3°, 12.6°, 16.3°, 21.9°, consistent with the typical structure of NaA

zeolites [8]. Moreover, the absence of contaminated phases in the XRD patterns indicates that the NaA zeolites were synthesized with high purity and good crystallinity.

3.3 SEM and TEM analysis

Figure 3 shows the SEM and TEM of the samples. The morphology and particle size of the NaA zeolites were observed through SEM. The prepared NaA zeolites exhibit spherical particles. The particle size of NaA-30 (Fig. 3a) and NaA-40 (Fig. 3c) is 130 nm, whereas that of NaA-60 (Fig. 3e) is 180 nm. The crystal structure of NaA zeolites were observed through TEM. Although the particle size of NaA-30 (Fig. 3a) and NaA-40 (Fig. 3c) was similar as seen in the SEM images, the TEM images revealed their distinct crystal structures. NaA-30 (Fig. 3b) exhibits a single nanocrystalline structure, whereas NaA-40 (Fig. 3d) is a multi-crystal aggregate composed of ultra-small nanocrystals. The size of the ultra-small crystals was 6 nm. The difference in structure occurs because of the slow nucleation of zeolites at low temperatures, leading to the gradual growth into a larger single nanocrystalline structure [9]. NaA-60 (Fig. 3f) is also composed of ultra-small nanocrystals, but its aggregate size increases significantly, which is attributed to the fact that the increase of temperature will accelerate the nucleation rate, which in turn leads to the conversion of single crystals into single crystal aggregates. But continuing to increase the temperature leads to an increase in the zeolite growth rate, resulting in larger aggregates [10]. The preparation of ultra-small nanocrystals is conducive to intracrystalline diffusion, which provides more possibilities for the application of zeolite in the field of catalysis in the future.

3.4 N_2 adsorption-desorption analysis

The analysis results of the zeolite samples by N_2 adsorption and desorption are shown in Fig. 4 and Table 1. The N_2 adsorption and desorption isotherm of zeolite ((Fig. 4) has steep N_2 uptake in the low pressure region, showing a type I curve [11], which is a typical feature of microporous materials. All samples have a hysteresis loop at $P/P_0 > 0.9$, which is caused by the accumulation of pores between nanoparticles. And compared with the zeolite synthesized by Haijun Yu et al (678 m^2/g) [12], the zeolites synthesized at different temperatures in this study have large specific surface areas as shown in Table 1. The specific surface area of NaA-40 is larger than that of other samples because it is an aggregate composed of ultra-small nanocrystals. And the aggregate particle size is smaller than that of NaA-60.

Table 1
BET specific surface area of the samples

Sample	$S_{BET}(m^2/g)$	$S_{micro}(m^2/g)$	$V_{micro}(cm^3/g)$
NaA-30	913.72	856.48	0.33
NaA-40	986.59	944.09	0.37
NaA-60	802.25	753.64	0.30

4. Conclusion

The NaA zeolite aggregates had been successfully synthesized in this study with high crystallinity and good dispersibility. NaA zeolite aggregates composed of 6 nm ultra-small crystals were synthesized under reflux conditions at 40°C with a particle size of 130 nm and a specific surface area of 986.59 m^2/g. The ultra-small nanocrystals could not be formed at temperatures lower than 40°C, but rather giving rise to larger single crystals. Although ultra-small nanocrystals were formed at temperatures higher than 40℃, the aggregate particle size increased from 130 nm to 180 nm. Since ultra-small NaA zeolite nanocrystals could shorten the diffusion path and increase the specific surface area, they have great application potential in catalysis and adsorption.

Declarations

CRediT authorship contribution statement

YuHan Huang: Investigation, Writing - original draft, Software, Methodology.

Min Li: Writing - review & editing, Methodology

Chenxi Shi: Writing - review & editing, Data curation.

Zhanjun Liu: Supervision, Writing - review & editing.

Bo Ren: Conceptualization, Project administration, Writing - review & editing.

Conflicts of interest

The authors report no conflicts of interest. The authors alone are responsible for the content and writing of this article.

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Figures

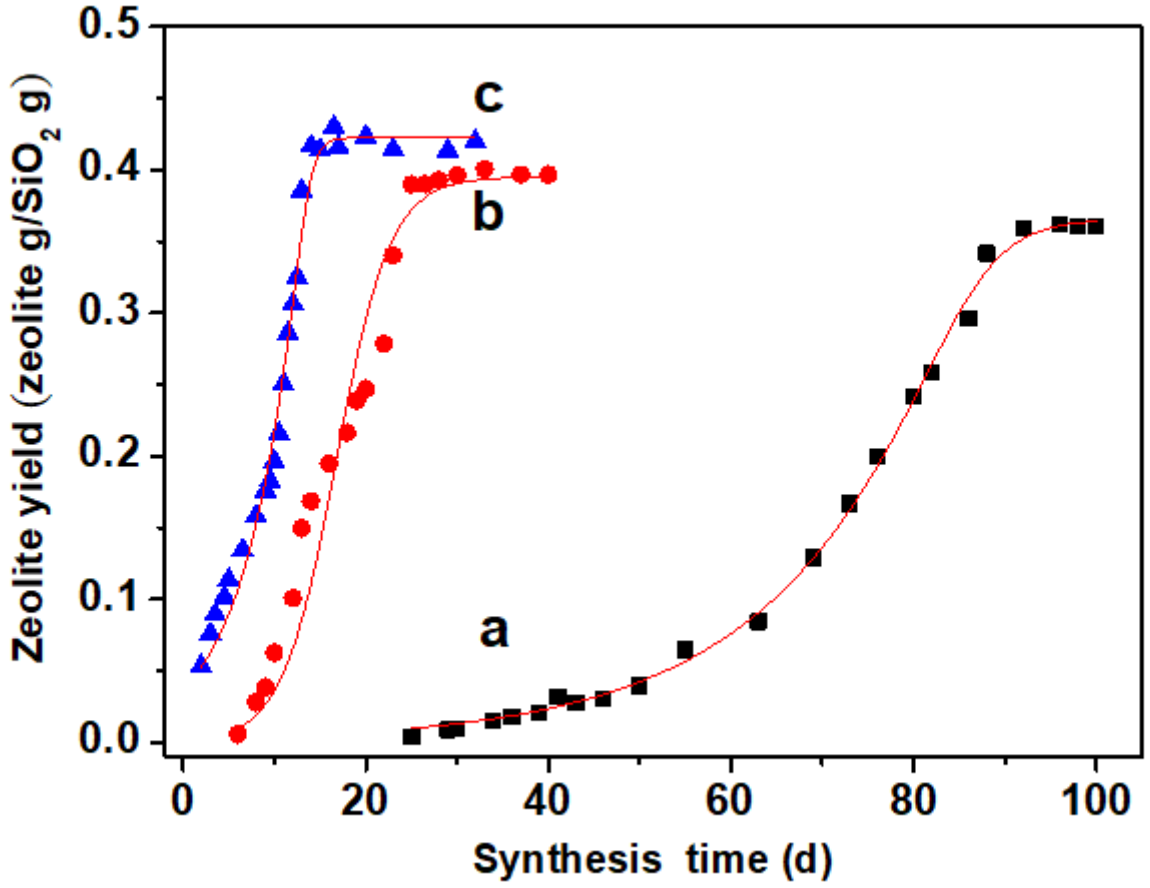

Figure 1

Calculated mass growth curves for the synthesis of zeolite at different temperatures (a) NaA-30, (b) NaA-40, and (c) NaA-60

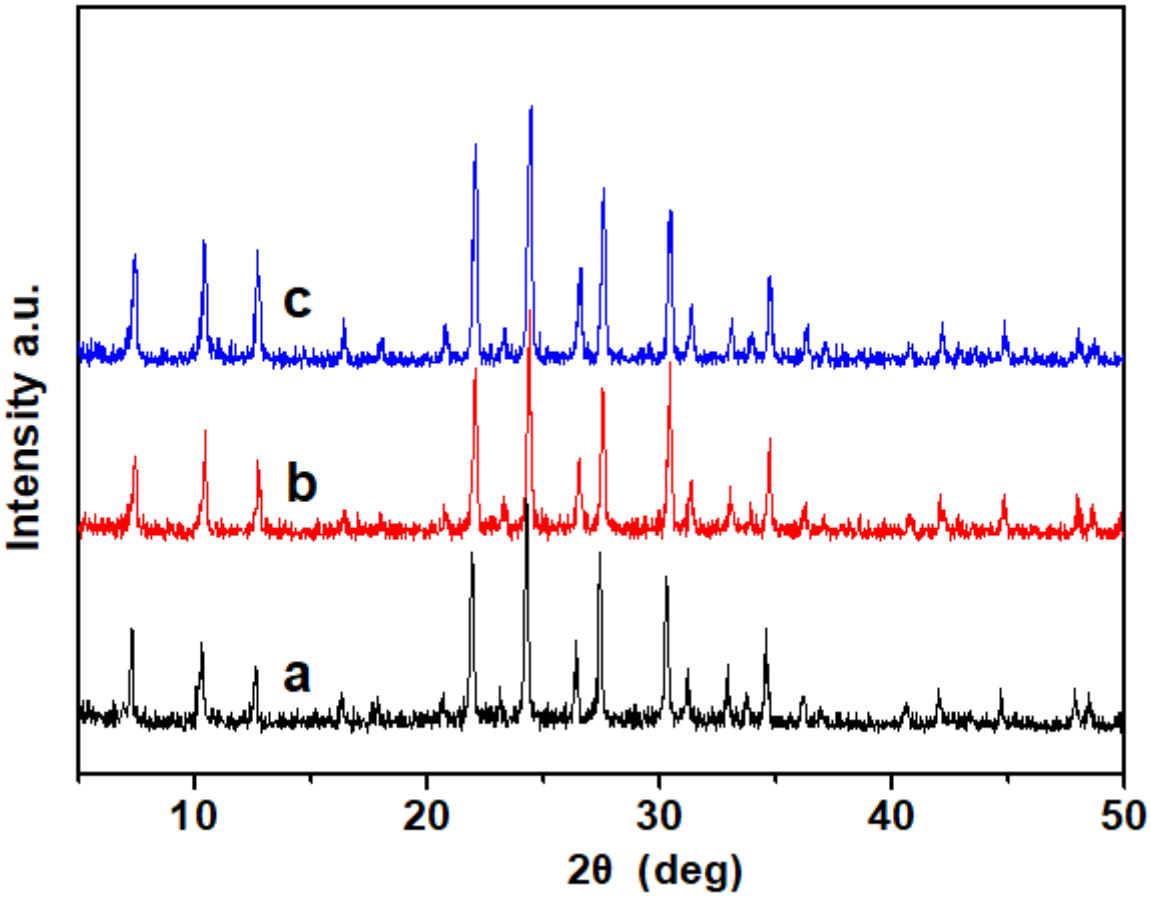

Figure 2

XRD patterns of (a) NaA-30, (b) NaA-40, and (c) NaA-60

Figure 3

SEM images of (a) NaA-30, (c) NaA-40, and (e) NaA-60;

TEM images of (b) NaA-30, (d) NaA-40, and (f) NaA-60

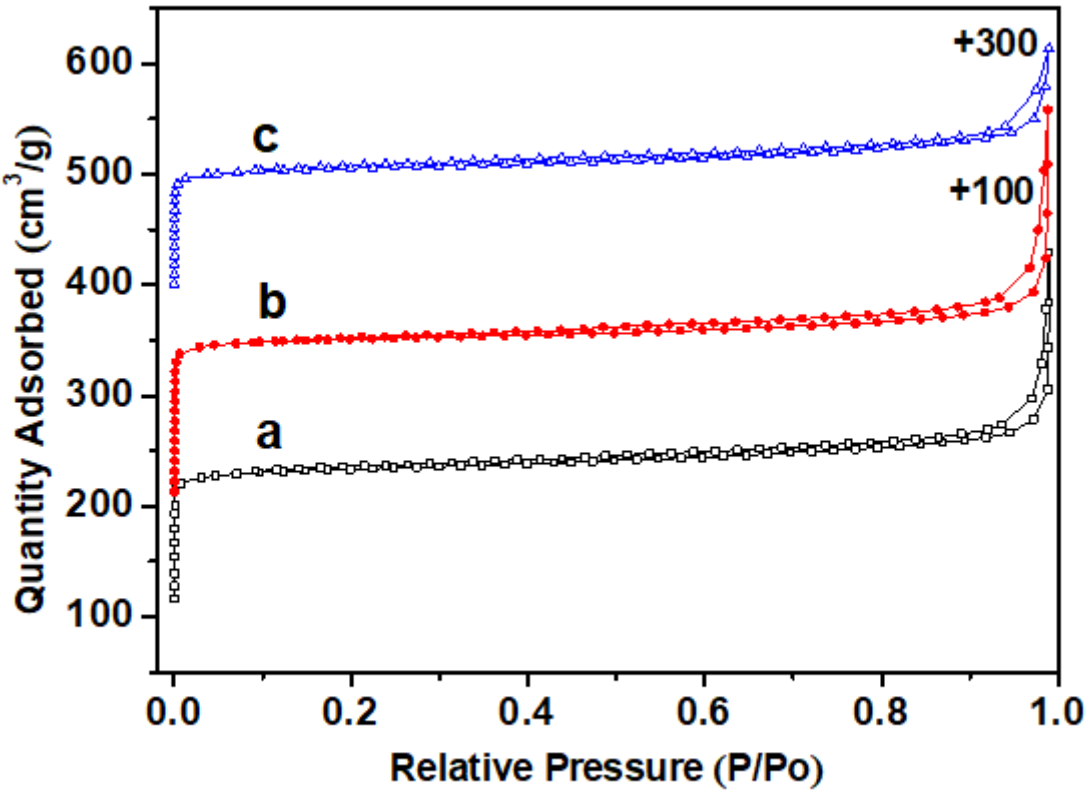

Figure 4

N_2 sorption isotherms of (a) NaA-30, (b) NaA-40, (c) NaA-60