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Hydrothermal synthesis of nanostructure NaA zeolite: The effect of synthesis parameters on zeolite seed size and crystallinity

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Abstract

In this research, nanostructure NaA zeolite was synthesized via hydrothermal method. As mentioned in the literature, the recommended molar composition for NaA zeolite synthesis was Na_2O/Al_2O_3 ratio of 2–3, but in our work, NaA zeolite was synthesized with new molar compositions by the emphasis on both molar ratios of Na_2O/Al_2O_3 and SiO_2/Al_2O_3. Also, the effects of reaction time and temperature on morphology and crystallinity of the synthesized zeolites were investigated. The final products were characterized by X-ray diffraction and scanning electron microscopy (SEM). The obtained results showed that both of the investigated molar ratios are controlling parameters in the synthesis of zeolites. In addition, it is found that the reaction time has a great effect on the crystallinity of the synthesized zeolites. Also, the zeolite seeds size increases significantly by increasing reaction temperature. Finally, to obtain NaA zeolite with desirable particle size, crystallinity and morphology, an optimum synthesis conditions can be proposed.

Keywords: NaA zeolite; Crystallinity; Nanostructure; Hydrothermal synthesis; Composition

1. Introduction

Zeolites or crystalline aluminosilicates are widely used in separation and refinery industries as catalysts, adsorbents and ion exchangers due to their meso and microporous structures.[1,2] The significant catalytic activity and selectivity of zeolite materials are attributed to the large internal surface area and highly distributed active sites that are accessible through uniform pores size,[3] high thermal resistance; chemical inertness and high mechanical strength.[4]

Nanostructure NaA zeolite is one of the microporous crystalline aluminosilicate zeolites which has a channel opening size of 0.4 nm. The small pore size of NaA zeolite makes the separation of small molecules by difference in size possible. The molecular kinetic diameters of short-chain alkanes are close to or larger than the pore size of NaA zeolite. Thus, small molecules, such as hydrogen (0.29 nm) and nitrogen (0.364 nm), are expected to be separated from short-chain alkanes by molecular sieving or configuration diffusion using nanostructure NaA zeolite membrane, which may find application in the separation of refinery gases.[4–8]

Due to unique applications of NaA zeolite, various works have been focused on the synthesis of this kind of zeolite by different methods. Sathupunya et al.[2] have synthesized NaA zeolite from alumatrane and silatrane by sol–gel microwave techniques. Xu et al.[6] have synthesized NaA zeolite by molar ratio of $3Na_2O{:}Al_2O_3{:}2SiO_2{:}200H_2O$ via hydrothermal synthesis method in a stainless steel autoclave contain a Teflon holder. Also, Huang et al.[9] reported the hydrothermal synthesis of NaA zeolite from a clear solution with molar ratio of $50Na_2O{:}Al_2O_3{:}5SiO_2{:}1000H_2O$ at 333 K for 24 h. But, Pak et al.[10] recommended that the suitable Na_2O/Al_2O_3 ratios for NaA zeolite synthesis is in the range of 2–3 and higher molar ratios (typically $\geq$50) are suitable for the hydroxy sodalite synthesis. Also, their results show that for making NaA zeolite and hydroxy sodalite zeolite, suitable SiO_2/Al_2O_3 ratios are 2 and 1, respectively. By considering these contrast results, investigating the effect of molar ratios (i.e. Na_2O/Al_2O_3 and SiO_2/Al_2O_3) in the synthesis of zeolites, especially NaA and sodalite, is necessary.

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Table 1
Composition of the synthesis solutions and reaction conditions employed in this study

Recipe	Synthesis composition			Reaction temperature (°C)	Reaction time (h)	Crystallite size (nm)	Synthesized zeolite type
	x	*y*	*z*				
A	10	5	15	60	24	27	NaA
B	10	5	15	90	24	30	NaA
C	10	5	15	100	3	34	NaA
D	5	1	50	60	24	–	Sodalite
E	10	1	50	60	24	39	NaA

In this research, we synthesized NaA and sodalite zeolites via hydrothermal synthesis method. Also, the effects of the reaction time and temperature were investigated on the crystallinity and morphology of the synthesized zeolite seeds. Moreover, we synthesized NaA zeolite using new molar ratios based on the original molar composition that was usually used for the synthesis of sodalite, in order to indicate the important role of both Na_2O/Al_2O_3 and SiO_2/Al_2O_3 ratios in the synthesis of different types of zeolites. On the other hand, the appearance of the synthesized NaA zeolite with new molar composition was investigated, which might enable the preparation of zeolite with special structures, morphology and convenient form such as membrane layers.

2. Experimental

2.1. Material

The used silica source was silica sol (SiO_2 27 wt%, $\rho = 1.07$ g/ml) and the used alumina source was aluminum foil and the used sodium source was sodium hydroxide (Solid white plate) that were purchased from Merck company.

2.2. Zeolite seeds synthesis

NaA zeolite seeds were prepared by dissolving sodium hydroxide and aluminum foil in deionized water, and then silica sol was added to above solution under stirring at high speed. The molar compositions of the resulting synthesis mixture were $xSiO_2$:yAl_2O_3:zNa_2O:$1000H_2O$. The solutions were transferred to a Teflon-lined stainless steel autoclave and hydrothermally treated for 3–24 h in an oven at temperatures 60–100 °C. The molar composition (*x*, *y* and *z*), heat treatment (reaction) time and temperature for all type of the synthesized seeds have been presented in Table 1. After the hydrothermal treatment, the products were recovered, thoroughly washed with deionized water, and then dried in air at 100 °C for 3 h.

2.3. Characterization

The crystalline structure of the synthesized zeolite seeds was determined by X-ray diffraction (XRD) patterns. XRD was carried out on a TW3710 Philips X'Pert diffractometer using Cu Kα($\lambda = 1.54$ Å) radiation operating at 40 kV and 50 mA. Crystallite size of zeolite seeds was estimated using the standard Scherrer's formula:[11]

$$D = \frac{0.9\lambda}{\beta \mathrm{Cos}\theta} \quad (1)$$

where D is the crystallite size (nm), λ is the radiation wavelength (0.15406 nm), θ is the diffraction peak angle and β is the corrected half-width at half-maximum intensity (FWHM) of the reflex at $2\theta = 7.18°$. The morphology and size of the synthesized zeolite seeds were investigated with scanning electron microscopy (SEM, LEO 440I, 3×10^5, LEO, UK).

3. Results and discussion

3.1. Reaction temperature effect

Fig. 1 indicates XRD patterns of A and B samples (Table 1) with the same synthesis mixture composition and reaction time, at different reaction temperatures. The XRD patterns of the obtained samples (A and B) were compared to the standard NaA zeolite XRD pattern[12] (see Fig. 1c). The findings emerge that both patterns of samples confirmed that NaA zeolite phase was formed, but the structural parameters (peaks intensity) of sample B is more desirable in comparing with the standard XRD pattern.

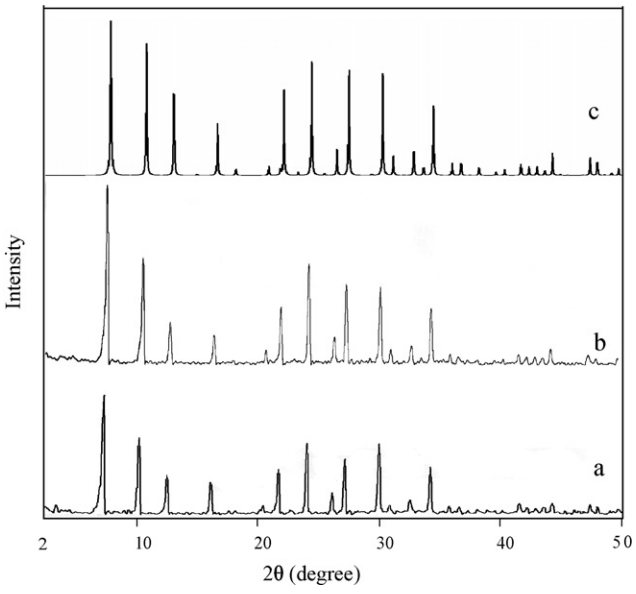

Fig. 1. XRD patterns of (a) A sample, (b) B sample and (c) the standard NaA zeolite.[12]

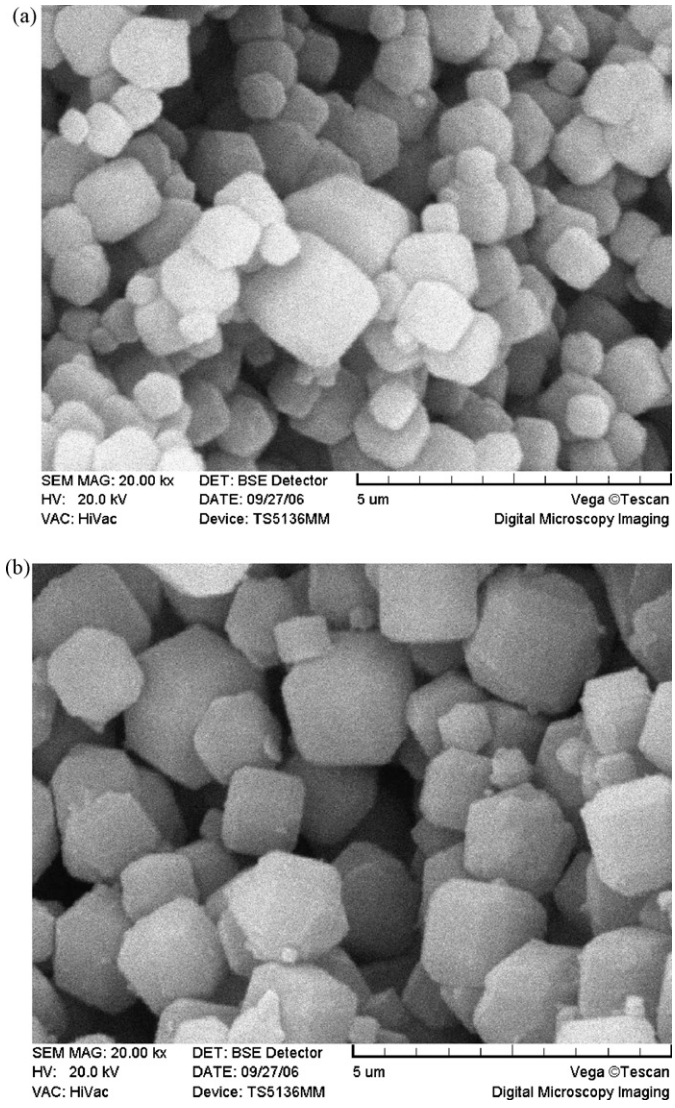

Fig. 2. SEM micrographs of (a) A sample and (b) B sample.

Also, the effect of reaction temperature on the zeolite seeds size and morphology is shown in Fig. 2. As can be seen, similar morphology is observed for both samples as cubic particles. But, by increasing of crystallization temperature, average particle size of the synthesized zeolite increases dramatically. Therefore, the reaction temperature has significant effect on the crystallinity and size of the synthesized NaA zeolite seeds. This trend can be confirmed by crystallite size of the samples A and B obtained based on the Scherrer formula (see Table 1), indicating polycrystalline structures for the synthesized samples.

3.2. Reaction time effect

The B and C samples (Table 1) were synthesized with the same molar composition and at the nearly same reaction temperature but at different reaction times. The XRD patterns of samples were presented in Fig. 3. The obtained results show that both samples formed as NaA zeolite. But regarding to the standard XRD pattern, peaks intensity of sample B is more desirable in comparing with sample C.

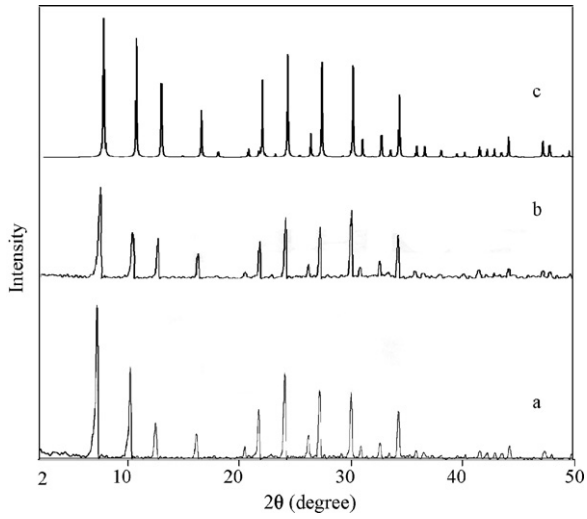

Fig. 3. XRD patterns of (a) B sample, (b) C sample and (c) the standard NaA zeolite.[12]

Fig. 4 shows the SEM micrographs of B and C samples which indicate that reaction time effect on morphology of the synthesized zeolite is similar to the reaction temperature. But, unlike the strong effect of reaction temperature, reaction time does not have significant effect on the average particle size of the synthesized NaA zeolite seeds. The obtained crystallite size as presented in Table 1, confirm this tendency. Therefore, it can be concluded that reaction temperature has more significant effect on the average particle size of the synthesized NaA zeolite seeds in comparison with reaction time.

Due to important role of particle size and crystallinity of the NaA zeolite seeds in various applications, especially in zeolite-composite membranes, optimum conditions should be predicted for the synthesis of NaA zeolite seeds. In zeolite-composite membranes, in order to form thin and uniform NaA zeolite membranes on the supports, the nucleation zeolite seeds should be small and uniform in size. On the other hand, in order to inhibit the penetration of NaA zeolite seeds in the support pores, the seeds size should be larger than the support pore size. By considering the effects of reaction time and temperature on the crystallinity and average particle size of the synthesized NaA zeolite (as mentioned earlier), to obtain zeolite seeds with suitable particle size and crystallinity an optimum temperature range (60–90 °C) and a maximum time (24 h) is proposed. It is our experience that further increasing of reaction time causes to synthesis NaA zeolite with low purity which is in good agreement with literature.[5]

3.3. Molar composition effect

The XRD patterns of D and E samples (Table 1) synthesized with the same reaction time and temperature at different molar compositions are shown in Figs. 5 and 6. Comparing XRD patterns of samples with the standard XRD patterns[12] confirms that D sample is sodalite zeolite, but E sample is NaA zeolite unlike the previous works which had emphasis on higher molar

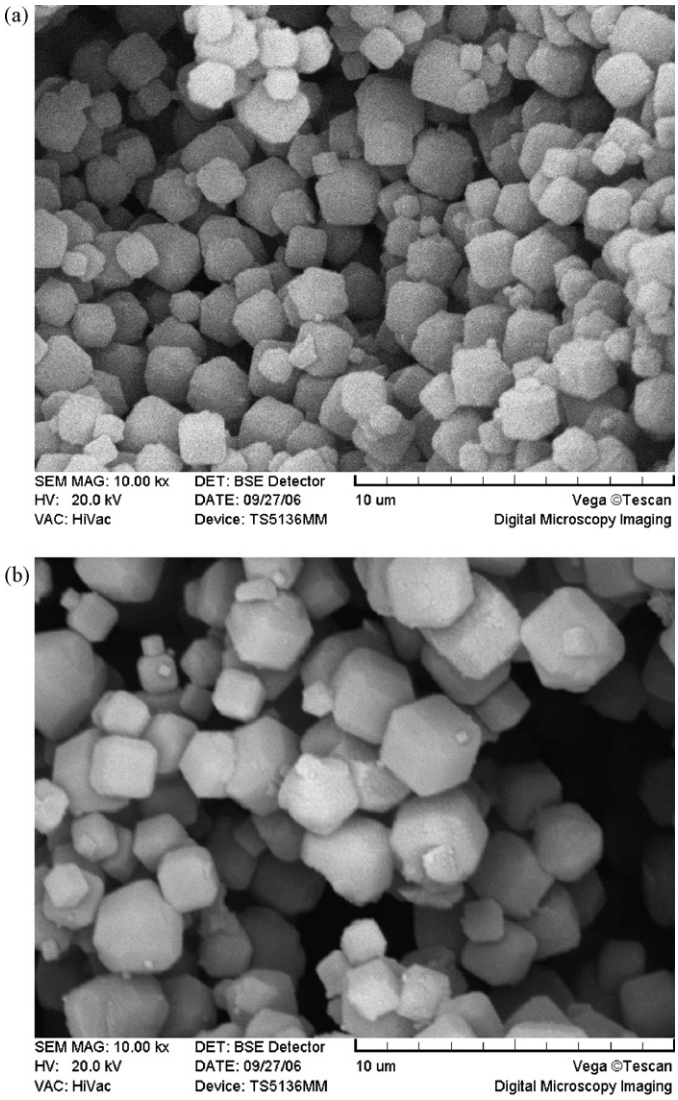

Fig. 4. SEM micrographs of (a) B sample and (b) C sample.

ratios of Na_2O/Al_2O_3 (typically $\geq$50) in the synthesis of sodalite zeolite.[10] Therefore, in this work, NaA zeolite was synthesized via a new molar ratio based on the original molar composition that was usually used for the synthesis of sodalite zeolite with

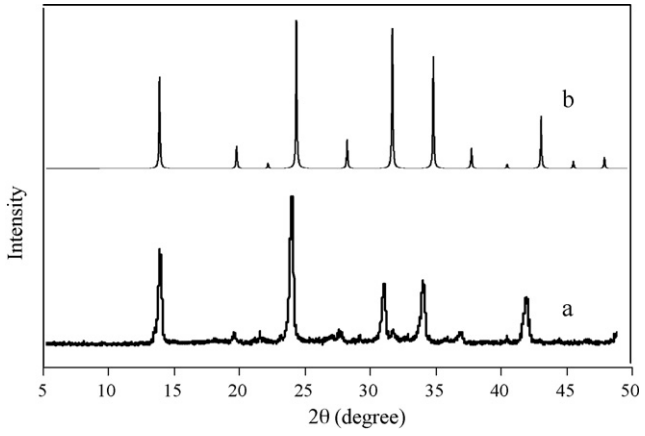

Fig. 5. XRD patterns of (a) D sample and (b) the standard Sodalite zeolite.[12]

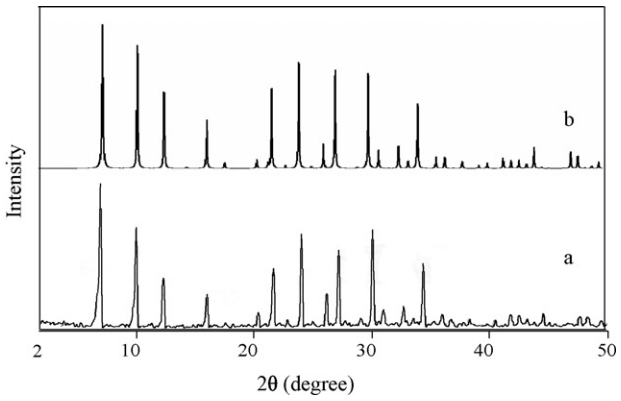

Fig. 6. XRD patterns of (a) E sample and (b) the standard NaA zeolite.[12]

emphasis on SiO_2/Al_2O_3 ratio of 10. SEM micrographs of D and E samples were presented in Fig. 7.

Also, as can been seen in Table 1, A and E samples were synthesized with the same reaction time and temperature at different molar compositions. The obtained XRD results show that both of the samples have the same zeolite phase (NaA), though the peaks intensity of E sample is relatively higher than that of A sample (see Figs. 2a and 6a). But, SEM micrographs of A

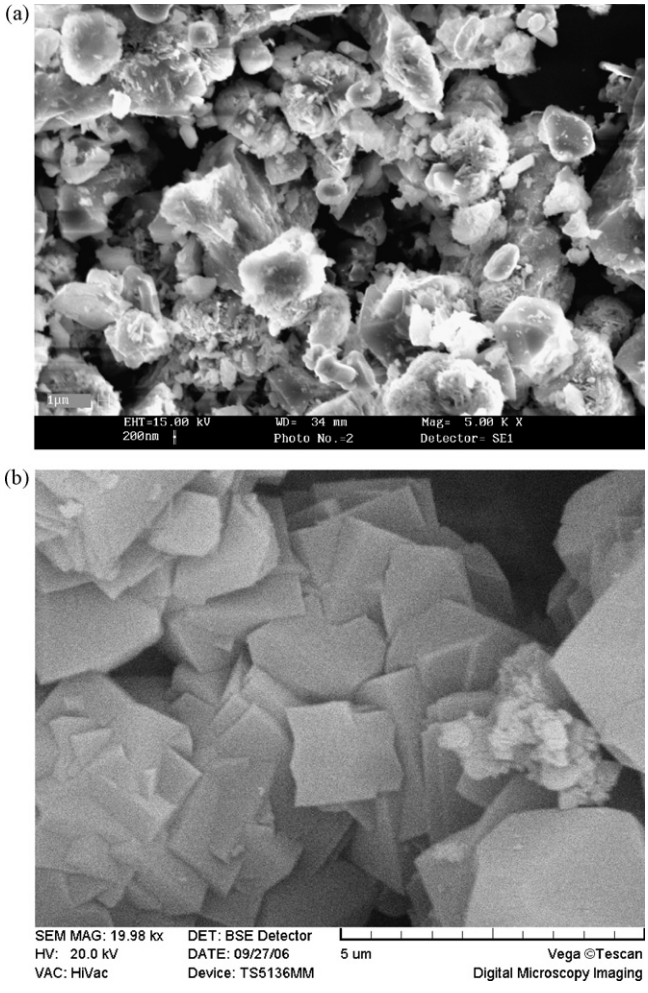

Fig. 7. SEM micrographs of (a) D sample and (b) E sample.

and E samples, as presented in Figs. 2a and 7b, show different morphologies for both of the synthesized samples. These results confirm the significant effect of the molar composition on morphology of the synthesized zeolite seeds.

4. Conclusions

Nanostructure NaA zeolite was synthesized successfully via hydrothermal synthesis method. The effects of different parameters such as molar composition, heat treatment (reaction) time and temperature on the crystallinity and morphology of the synthesized zeolites were investigated. The obtained results are presented as follows:

- *Heat-treatment* (*reaction*): By increasing of reaction temperature, average particle size and crystallinity of the synthesized NaA zeolite increases dramatically. Although crystallinity of the synthesized NaA zeolite increases dramatically by increasing of reaction time, but reaction temperature has more significant effect on the average particle size of the synthesized NaA zeolite seeds in comparison with reaction time. Therefore, to obtain NaA zeolite seeds with suitable particle size and desirable crystallinity an optimum temperature range (60–90 °C) and a maximum time (24 h) is proposed.
- *Molar composition*: NaA zeolite was synthesized via a new molar ratio based on the original molar composition that was usually used for the synthesis of sodalite zeolite with emphasis on SiO_2/Al_2O_3 ratio of 10. The obtained results showed that in the synthesis of different types of zeolites (NaA and sodalite) not only Na_2O/Al_2O_3 ratio but also SiO_2/Al_2O_3 ratio are controlling parameters of the morphology and phase behavior. Moreover, both XRD and SEM results showed that the morphology and microstructure of the synthesized NaA zeolite with a new molar ratio ($10Na_2O{:}Al_2O_3{:}50SiO_2{:}1000H_2O$) can be convenient form for the preparation of zeolite membrane layers, but more details are under investigation.

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