

Influence of NaOH concentrations on synthesis of pure-form zeolite A from fly ash using two-stage method

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Abstract

Synthesis of pure-form zeolite A were investigated using four concentrations of NaOH solution to dissolve Si source from fly ash, and with the addition of Al source, to prepare initial gel. Experimental results demonstrated, for two-stage method, that NaOH concentrations in initial gel played an important role in synthesis of pure-form zeolite A using fly ash as raw materials. Generally, pure-form zeolite A could be synthesized when following conditions were used: NaOH concentrations, 1.67, 5 and 6.67 M; the synthesis temperature, 100 °C; the corresponding crystallization time, 340, 250 and 190 min. However, a mixture phases of zeolites A and X were obtained at the condition of 3.33 M NaOH solution during various crystallization times. It was found that the higher NaOH concentration was used, the shorter crystallization time of zeolite A was required and the narrower particle size distribution of zeolite A was achieved. In addition, zeolite A submicron-crystals were first synthesized from fly ash using two-stage method in our study.

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Keywords: NaOH concentrations; Zeolite A; Fly ash; Submicron-crystals; Two-stage method

1. Introduction

A huge amount of fly ash has been generated from electric power plants and approximate 500 million tonnes of fly ash is discharged per year throughout the world. Because fly ash has a pozzolanic property after reacted with lime [1], about 20% of fly ash is used in building materials related applications. However, the remaining fly ash disposed of in landfill still causes an increasing threat to the environment due to its fine structure and toxic elements. Thus, it is urgent to develop more effective techniques for converting fly ash into the more valuable materials. Because amorphous material (aluminosilicate glasses) of fly ash can be used typically as raw materials for the manufacture of zeolites, the conversion of fly ash into zeolites is one of promising techniques in the recent years [1–20]. By applying many synthesis methods, many researchers have synthesized different types of zeolites from fly ash, such as zeolite Na–P1 [1–5], zeolite A [6–11], zeolite X [6,7,12] and zeolite ZSM-5 [13], etc. However, these synthesis methods, such as classical hydrothermal

method [1–4,14,17], dry or molten-salt conversion [16,17,19] and fusion method [6,12], were adopted to produce zeolitic materials which not only vary widely but also contain a significant amount of non-zeolitic phases. Moreover, the obtained zeolites, such as Na–P1 and hydroxyl-sodalite (HS), usually have a more condensed structure (low pore volume). This greatly limits the potential applications of zeolites from fly ash. To improve it, Hollman et al. [20] presented a two-stage method that enables to obtain pure-form zeolites from initial gel prepared from fly ash. The method is based on the fact that pure-form zeolites can be synthesized by adopting NaOH solution to dissolve Si source from fly ash, with the addition of Al source, to prepare initial gel. Then, prepared initial gel is crystallized under static condition during hydrothermal treatment.

Because zeolite A has been found widespread application both laboratories and industries, several modified two-stage methods have been developed to synthesize pure-form zeolite A from fly ash at present [7–11]. Tanaka et al. [7] synthesized pure-form zeolite A from waste solution obtained after conversion of fly ash into zeolites. Tanaka et al. [8] synthesized pure-form zeolite A from fly ash by dialysis process using a semipermeable membrane tube. The process is based on the fact that fly ash was mixed with NaOH–NaAlO₂ solution to obtain a homogeneous

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mixture; this was then added into a semipermeable membrane tube and aged in same NaOH–NaAlO₂ solution at 85 °C for 24–30 h. Hui and Chao [9] applied step-change of synthesis temperature to synthesize pure-form zeolite A during hydrothermal treatment of fly ash prepared solution. However, these reports required long crystallization time and rather complex process. Furthermore, they did not investigate the influence of different NaOH concentrations on synthesis of pure-form zeolite A from fly ash using two-stage method.

The purposes of the present work were to investigate the influence of four concentrations of NaOH solution (1.67, 3.33, 5 and 6.67 M) on structural formation, morphology and particle size distribution of synthetic pure-form zeolite A samples from fly ash using two-stage method, in order to provide an economically viable means for the recycling of fly ash. All samples obtained from fly ash were characterized and confirmed by XRD patterns. In addition, controlling crystallization time is crucial for avoiding the formation of other zeolitic phases during the crystallization of zeolite A.

2. Experimental procedure

2.1. Raw fly ash

Raw fly ash was obtained from a Chinese power plant located in Henan province using electrostatic precipitators. The chemical composition of raw fly ash was determined by XRF (ARL9800XP+) and is listed in Table 1. Fig. 1 indicates that main crystalline phases of raw fly ash are the quartz and mullite by XRD analysis and trace phases of calcite, portlandite and anhydrite are also identified. The average diameter of raw fly ash determined by a particle size analyzer (Malvern instrument) is 1.44 μm and the surface area of its calculated from N₂ isotherms at –196 °C is 2.44 m²/g.

Before synthesis, raw fly ash was pretreated by acid-washing process performed on a mixture of HCL solution (10%) and fly ash (ratio, 25:1(L/S)) in a breaker. The breaker was kept in a water bath at 80 °C for 1 h and stirred constantly (300 rpm). Then, fly ash was filtered off, washed repeatedly with distilled water and dried finally at 100 °C for 24 h for further use. Table 2 shows the three major composition of fly ash (involved composition for zeolites A synthesis) obtained after acid-washing process.

Table 1
Chemical composition of raw fly ash (wt%)

Component	%
SiO ₂	49.29
Al ₂ O ₃	33.07
Fe ₂ O ₃	5.76
K ₂ O	2.58
TiO ₂	1.18
CaO	2.05
MgO	0.27
Na ₂ O	2.22
MnO	0.13

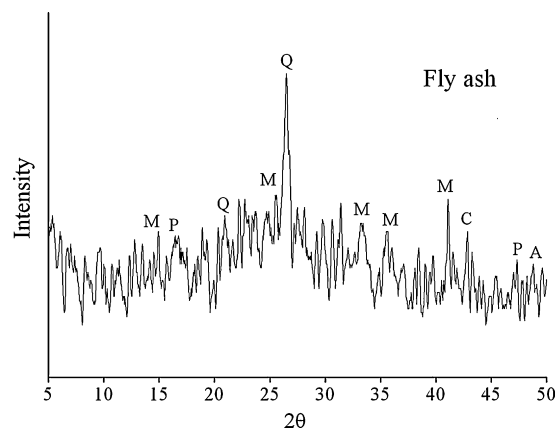


Fig. 1. XRD pattern of raw fly ash. M, Q, C, P and A represent mullite, quartz, calcite, portlandite and anhydrite, respectively.

2.2. Zeolite A synthesis processes

2.2.1. Preparation of initial gel

Preparation of initial gel involves three stages: (1) 9 g of fly ash was mixed with 90 ml of NaOH solutions (Guangdong, analytical reagents) in a breaker. Four NaOH concentrations (1.67, 3.33, 5 and 6.67 M) were used. The breaker was placed in a water bath and heated at 80 °C for 2 h with stirring constantly (300 rpm). The solution was separated from the mixture by a filtration process and the volume obtained in the solution was about 90 ml; (2) NaOH–NaAlO₂ solution was prepared by vigorously mixing 2.4 g of NaAlO₂ (Shanghai, chemical reagents) and 30 ml of 1.67 M NaOH solution; (3) the NaOH–NaAlO₂ solution prepared was poured into the solution obtained at first stage to form initial gel and then about 120 ml of initial gel obtained was stirred intensely at 25 °C for 30 min. Synthesis of zeolite A was investigated from four initial gel with the following composition $x\text{Na}_2\text{O}:1.0\text{Al}_2\text{O}_3:y\text{SiO}_2:444.44\text{H}_2\text{O}$, where $x=7.67, 12.64, 17.64$ and 22.64 and the corresponding $y=2.22, 3.06, 3.75$ and 4.19 .

2.2.2. Zeolite A synthesis

The synthesis experiments were performed in specially designed stainless alloy autoclaves with thin walls which allow a fast heat transfer. The autoclaves containing about 120 ml of initial gel were kept in a conventional air oven at 100 °C at auto-genous pressure. After various crystallization times, the solids were obtained by high-speed centrifugal process, washed repeatedly with distilled water, dried at 100 °C and kept in powder form for further characterization. Hereafter, labeling of the sample was denoted as A1–340 min, where A1 was NaOH concentra-

Table 2
Chemical composition of pretreated fly ash (wt%)

Component	%
SiO ₂	59.62
Al ₂ O ₃	30.95
Fe ₂ O ₃	1.40

tion (1.67 M) and 340 min was the corresponding crystallization time (min) during hydrothermal treatment.

2.3. Characterization

XRD pattern was taken on a Bruker D8 Advance X-ray diffraction instrument (Cu, $K\alpha$), the diffraction angle (2θ) in the range $2\text{--}35^\circ\text{C}$ was scanned. SEM images were obtained using a JEOL JSM-6380LV electron microscope. The particle size measurements were performed by laser beam scattering technique (Malvern instrument); the sample was dispersed in aqueous ethanol by ultrasonic stirring. Cation exchange capacity (CEC) values were determined using the ammonium acetate method [12]. The results were expressed as milliequivalents per 100 g of solids.

3. Results and discussion

3.1. Characterization of pretreated fly ash

Fig. 2 illustrates that the CEC values of the synthetic zeolite A (A1–340 min) from fly ash using two-stage method with raw and pretreated fly ash as starting materials. It is evident from Fig. 2 that acid-washing process prior to synthesis contributes to improve the CEC values of samples and the CEC values increased about 38%. This behavior could be explained in the light of the synthesis method used. For two-stage method, iron oxides bearing composition in fly ash can be dissolved by NaOH solution; and can then be form the precipitates (insoluble iron hydroxides) [21]. This yields not only a brownish tinge [10] but also the undesirable products which have a deleterious effect on CEC values. Thus, the proportion of iron oxides in fly ash affects significantly performance of the synthetic zeolites from fly ash. As shown in Table 2, a reduction of iron oxides in fly ash is about 76% after acid-washing process. As a rule, magnetic separation process [12] was also used for removal of iron oxides in fly ash except for acid-washing process. Acid-washing process has an impact on superficial structure of fly ash when compare with magnetic separation process. The acid solution enables spherical smooth surface of fly ash to become rough so

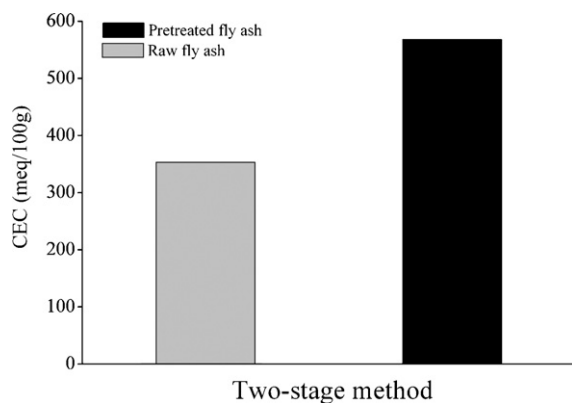


Fig. 2. CEC values of pure-form zeolite A sample (A1–340 min) synthesized from raw and pretreated-fly ash (synthesis conditions—NaOH concentrations: 1.67 M, crystallization time: 340 min).

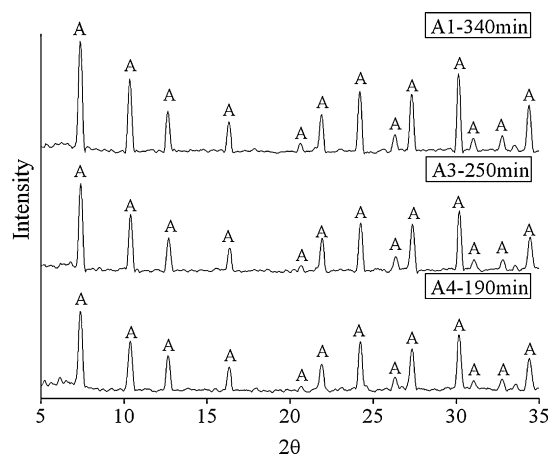


Fig. 3. XRD pattern of three pure-form zeolite A samples synthesized from fly ash (synthesis conditions—NaOH concentrations: 1.67, 5 and 6.67 M).

as to increase the surface area of fly ash, which help to increase the amount of Si source dissolved from fly ash and take full advantage of raw materials.

Since acid-washing process clearly demonstrated a benefit effect on synthesis, only the pretreated fly ash was used for subsequent two-stage synthesis processes.

3.2. Influence of NaOH concentrations on structural formation of zeolite A

According to XRD patterns of all samples obtained, only three samples (A1–340 min, A3–250 min and A4–190 min) were confirmed by pure-form zeolite A without the formation of other types of zeolites. Fig. 3 illustrates the XRD patterns of three pure-form zeolite A samples synthesized from fly ash at the condition of 1.67, 5 and 6.67 M NaOH solution during the corresponding crystallization time for 340, 250 and 190 min.

The structural formation of zeolite A may be explained in terms of its crystallization kinetics which is affected by composition molar ratios of initial gel (i.e. $\text{SiO}_2/\text{Al}_2\text{O}_3$ and $\text{Na}_2\text{O}/\text{H}_2\text{O}$ molar ratios). Hui and Chao [9] pointed out that synthesis of zeolite A depends on the rate of gel dissolution, the number and distribution of nuclei in prepared initial gel, and the crystal growth rate during hydrothermal treatment. All of them in turn depend on other factors such as synthesis temperature, crystallization time, composition molar ratios of initial gel, etc.

It is known that amorphous materials (aluminosilicate glasses) in fly ash is dissolved readily in NaOH solution when compare with crystal phases such as the quartz and mullite. Because the content of amorphous SiO_2 (about 47%) of fly ash is remarkably higher than that of amorphous Al_2O_3 (about 9%), the amount of Si source dissolved from fly ash is very higher than that of Al source. Furthermore, Si and Al source dissolved from fly ash can react to form the Pc, Po and Pt type zeolites on the surface of fly ash so as to hinder the amount of Al source dissolved from fly ash [7,8]. The amount of Al source dissolved from fly ash by different concentrations of NaOH solution was negligibly small as confirmed by XRF (ARL9800XP+) in our work. It is believed that $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of prepared

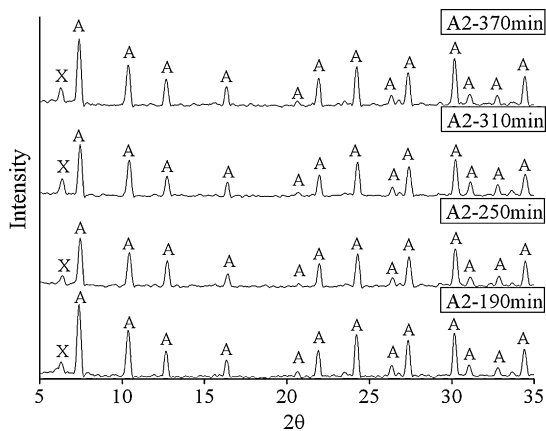


Fig. 4. XRD pattern of zeolites samples synthesized from fly ash (synthesis conditions—NaOH concentration: 3.33 M, crystallization time: 190, 250, 310 and 370 min).

initial gel is controlled by the addition of Al source. Generally, $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of initial gel should be controlled a range from 2 to 2.4 for synthesizing zeolite A. At the condition of 1.67 M NaOH solution, $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio was adjusted to 2.22 when 2.4 g of NaAlO_2 was added to the solution containing Si obtained from fly ash. The pure-form zeolite A can be synthesized from fly ash during crystallization time for 340 min. At the condition of 5 and 6.67 M NaOH solution, the amount of Si source dissolved from fly ash is higher when compare with using 1.67 M NaOH solution. The $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratios of prepared initial gel reached to 3.75 and 4.19 with the addition of 2.4 g of NaAlO_2 , respectively. This overstepped a proper range of $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio for synthesizing zeolite A. Owing to the increase of rate of initial gel dissolution at the condition of 5 and 6.67 M NaOH solution, pure-form zeolite A could be also synthesized during crystallization time for 250 and 190 min, respectively. However, when 2.4 g of NaAlO_2 was added to the solution containing Si source, followed by hydrothermal treatment at 100 °C, a mixture crystalline phases of zeolites A and X were synthesized from fly ash. At the condition of 3.33 M NaOH solution, the XRD patterns of the samples synthesized from fly ash during various crystallization times indicate the structural formation of zeolites A and X, as shown in Fig. 4. Fig. 5 also illustrates that small peaks of zeolite X were detected at the condition of 5 M NaOH solution when prolong crystallization time. The XRD patterns in Figs. 4 and 5 indicate that they are synthesized from initial gel differing essentially in $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio (higher for zeolites X than for A). The $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratios of 3.06 and 3.75 favor the formation of zeolite X at the condition of 3.33 and 5 M NaOH solution. Similar results were obtained by Tanaka et al. [7]. It is concluded that the lower $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio favor the formation of zeolite A, which later transform into zeolite X with an increase of $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio. The structural formation of zeolite X requires longer crystallization time due to its more complex and larger polymeric silicate units (D6R) and sparser structure [22]. Thus, zeolite A was the main crystalline phase during the shorter crystallization time at the condition of 3.33 M NaOH solution. At the condition of 6.67 M NaOH solution, the situa-

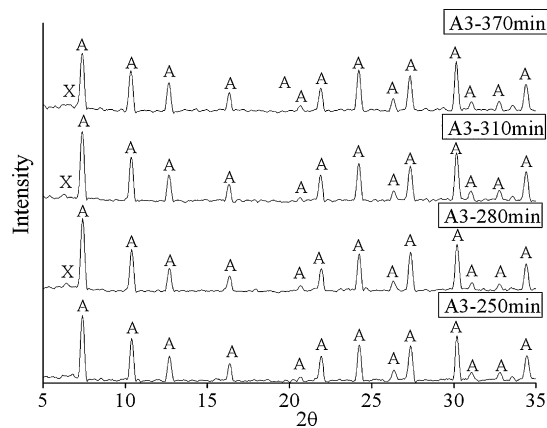


Fig. 5. XRD pattern of zeolites samples synthesized from fly ash (synthesis conditions—NaOH concentration: 5 M, crystallization time: 250, 280, 310 and 370 min).

tion is somewhat difference. Fig. 6 shows that metastable phase, namely. Zeolite A synthesized from fly ash, are replaced gradually by the more stable zeolite, namely. Hydroxyl-sodalite (HS), with an increase of crystallization time. This result accords with Ostwald's rule of successive transformation reported in other literatures [9,12]. From these facts, it can be inferred that high NaOH concentrations can lead to the formation of other types of zeolites. However, as previously mentioned in Fig. 3, crystallization time of zeolite A samples can be reduced with an increase of NaOH concentrations. It is clear that controlling crystallization time is very important to maintain purity of the synthetic zeolite A samples from fly ash. However, NaOH concentrations used should be limited for dissolving Si source of fly ash in order to avoid flocculation of prepared initial gel particles.

3.3. Influence of NaOH concentrations on morphology of zeolite A

Morphological analysis of three zeolite A samples (A1–340 min, A3–250 min and A4–190 min) synthesized from fly ash performed by SEM is shown in Fig. 7. It was observed that three zeolite A samples were all in the formation of chamfered-

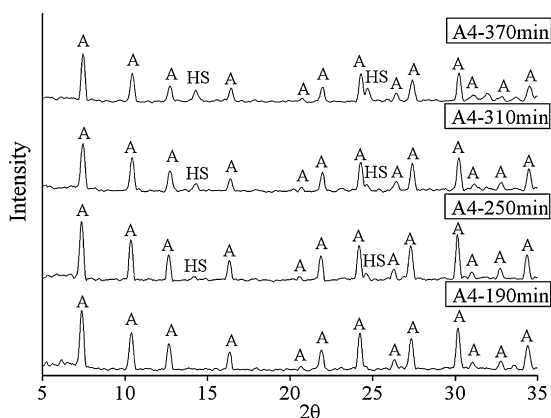


Fig. 6. XRD pattern of zeolites samples synthesized from fly ash (synthesis conditions—NaOH concentration: 6.67 M, crystallization time: 190, 250, 310 and 370 min).

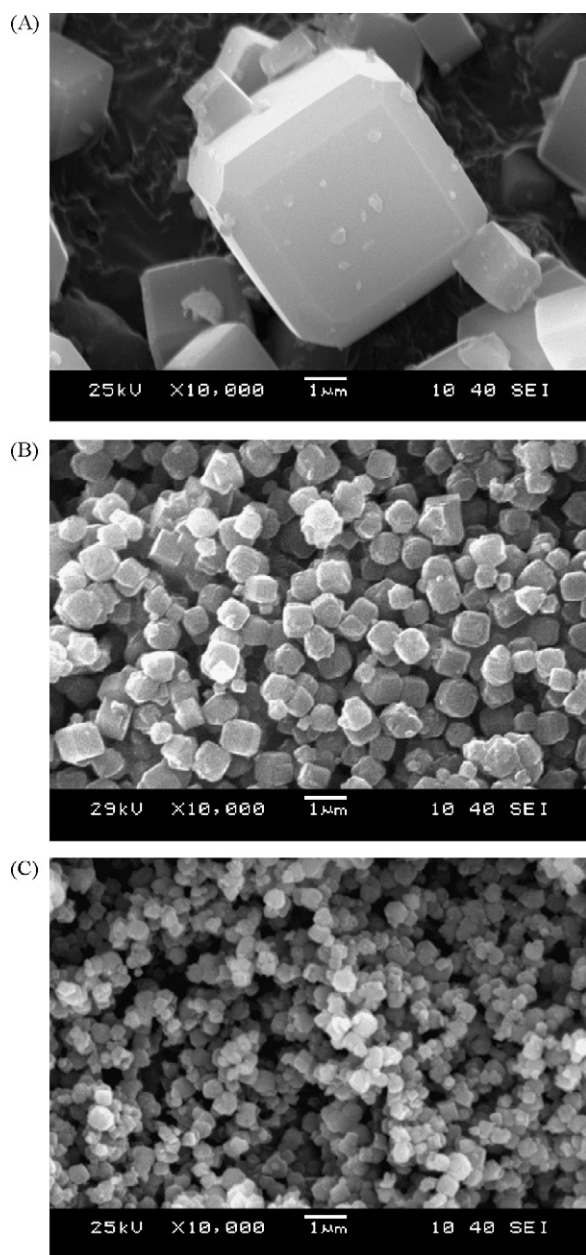


Fig. 7. SEM photographs of three pure-form zeolite A samples synthesized from fly ash. (A) A1–340 min, (B) A3–250 min, (C) A4–190 min.

edged cubes. Moreover, the XRD patterns in Fig. 3 also proved that crystalline particles with lattice fringes that can be assigned to the $\{110\}$ faces of the cubic structure of zeolite A were synthesized [23]. The structure of zeolite A is conformed by a β -cage (the basic structure of sodalite) interconnected with double 4-ring units (D4R) [12]. Due to chamfered-edged cubes morphology of its, zeolite A will not lead to excessive incrustation of

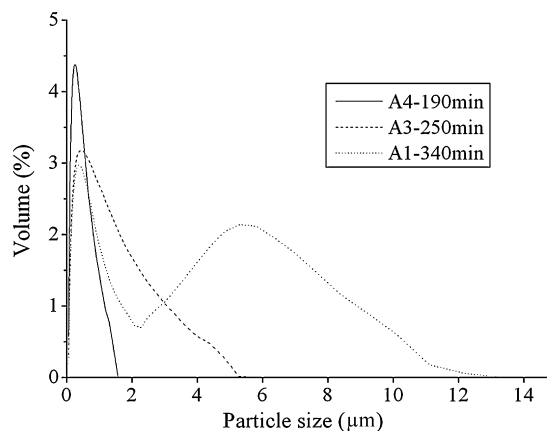


Fig. 8. Particles size distribution curves of three pure-form zeolite A samples synthesized from fly ash (NaOH concentrations: 1.67, 5 and 6.67 M, the corresponding crystallization time: 340, 250 and 190 min).

fibers during the laundry process and is suitable for substituting conventional phosphatic builder, viz. sodium tripolyphosphate (STP) so as to resolve effectively the serious eutrophication problem caused after discharging into nature water [10]. It has been demonstrated that the synthetic zeolite A from pure chemicals result in no hazards to the environment and public health [11]. In order to investigate if there was any toxic element existing in zeolite A synthesized from fly ash, a comparative study of elemental composition between zeolite A (synthesized from fly ash) and commercial zeolite A was conducted. Table 3 lists various trace elements of zeolite A sample (A1–340 min) synthesized from fly ash and commercial zeolite A. The results show that the synthetic zeolite A from fly ash do not pose any serious threat to the environment and public health when compare with commercial zeolite A. Apparently, the presence of these elements, such as Fe, Mn, Mg, Ti, Ca and K, existing in zeolite A samples may be due to the dissolution of these elements of fly ash under alkaline conditions, and may then be incorporated into framework structure of zeolite A sample during hydrothermal treatment. Similar toxicological studies were also reported by Hui and Chao [11].

In addition, the yielding (quantity) of three zeolite A samples synthesized from fly ash in our study was about 13–15%. Yielding was calculated as [9] (weight of pure-form zeolite A synthesized from fly ash)/(weight of reactive reagents used in the synthesis: fly ash, NaOH pellets and NaAlO_2 powder) $\times 100$.

3.4. Influence of NaOH concentrations on particle size distribution of zeolite A

Fig. 8 indicates that the influence of NaOH concentrations on particle size distribution (PSD) of three zeolite A samples (A1–340 min, A3–250 min and A4–190 min) synthesized from

Table 3

A comparison of elemental composition (wt%) of the synthetic zeolite A sample (A1–340 min) from fly ash and commercial zeolite A

Zeolite	SiO ₂	Al ₂ O ₃	Na ₂ O	Fe ₂ O ₃	K ₂ O	TiO ₂	CaO	MgO	MnO
Zeolite A (two-stage)	42.79	35.27	19.89	0.36	0.35	1.15	0.41	1.02	nd ^a
Commercial zeolite A	42.88	34.72	18.87	0.50	0.30	nd ^a	0.48	1.03	0.32

^a Not detected.

fly ash using two-stage method. It is evident that the PSD of zeolite A sample (A1–340 min) shows fairly broader than that of zeolite A samples (A3–250 min and A4–190 min). Moreover, the zeolite A sample (A4–190 min) of smallest particle size existing in narrowest PSD was synthesized from fly ash and the PSD of zeolite A sample (A4–190 min) covered a range from 90 to 700 nm. A reduction of the ultimate zeolites crystals size requires conditions that favor nucleation over crystal growth in initial gel [24]. Due to the dissolution rate of initial gel accelerated by high OH⁻ concentrations (A3, A4), this forms the abundant viable nucleus with uniform size distribution. Moreover, high synthesis temperature (100 °C) contributes to increase crystal growth rate of zeolites so as to obtain high-crystallinity zeolite A samples. Consequently, two factors result in the fact that the ultimate crystals size and crystallization time of zeolite A samples are all reduced based on maintaining crystallinity of them. As shown in Fig. 3, it is believed that a slight decline of apparent intensity observed from XRD patterns of three zeolite A samples with an increase of NaOH concentrations was due to the extinction effects of small zeolite A crystals, rather than the reduction in crystallinity of zeolite A samples.

Generally, high supersaturation and steric stabilization of the proto-nuclei are the key factors for minimize the ultimate zeolites crystal sizes [25]. These conditions are usually achieved by utilization of abundant amounts of organic template. However, the cost of organic template is very expensive and it can be converted into toxic organic gas to emit atmosphere after combustion. Another important factor that influences zeolites crystal size is the temperature [24]. Lower temperature favor nucleation because the activation energy needed for crystal growing is generally higher. However, lower synthesis temperature suffers from some drawbacks such as long crystallization time and high operational costs. Thus, high NaOH concentrations and temperature (100 °C) are the best synthesis conditions for obtaining small zeolites crystals from fly ash from an economic and environmental point of view. Hui and Chao [9] reported the PSD of zeolite A samples was controlled by applying step-change synthesis temperature during hydrothermal treatment. The method is based on the fact that the first stage of synthesis (the first synthesis temperature, *T*₁) acted as an introduction of small zeolite A nuclei in the system; the second stage of synthesis (the second synthesis temperature, *T*₂) acted as direct crystallization of the nuclei towards the given zeolite A. However, average diameter of the synthetic zeolite A samples from fly ash in their study reached to about 2–3 μm. Compared with their results, zeolite A submicron-crystals with narrow particle size distribution was synthesized from fly ash in our study. Average diameter of zeolite A samples (A3–250 min and A4–190 min) determined by a particle size analyzer are about 450 and 250 nm, respectively. The reduction of zeolites crystal size from micrometer to submicrometer scale, especial nanometer scale, can lead to substantial changes in the properties of zeolites.

4. Conclusions

Four NaOH concentrations have been evaluated for synthesis of pure-form zeolite A using fly ash as raw materials by

two-stage method. The study have demonstrated that pure-form zeolite A were synthesized from fly ash at the condition of 1.67, 5 and 6.67 M NaOH solution during hydrothermal treatment and the corresponding crystallization time is 340, 250 and 190 min. Moreover, zeolite A crystals (A3–250 min and A4–190 min) of smaller particle size existing in a narrower particle size distribution were synthesized from fly ash and average diameter of zeolite A samples (A3–250 min and A4–190 min) were reduced to 450 and 250 nm, respectively.

Based on our results, NaOH concentrations determine compositions molar ratio of prepared initial gel, and then affect structural formation, morphology, particle size distribution of zeolite A samples. Crystal sizes and crystallization time of zeolite A samples are all reduced with an increase of NaOH concentrations. For avoiding the presence of other zeolitic phases at the condition of high NaOH concentrations, controlling crystallization time is necessary during hydrothermal treatment. The influence of NaOH concentrations on pure-form zeolite A synthesized from fly ash using two-stage method investigated in our study provides an alternative approach for the massive recycling of fly ash.

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