

Continuous synthesis of zeolite NaA in a microchannel reactor

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Abstract

We demonstrate the application of a stainless steel microchannel reactor for the continuous synthesis of zeolite NaA. Some influence parameters such as the aging time of the synthesis solution, the residence time and the crystallization temperature had been studied. It was found that aging of the synthesis solution was a key procedure to avoid the blockage of the microchannel. By using the aged synthesis solution, it took 1/10 of the crystallization time needed in the batch system to synthesize zeolite NaA in the microchannel reactor. On the other hand, the mean particle size and the particle size distribution of zeolite NaA synthesized in the microchannel reactor were, respectively, smaller and narrower than in the batch system. In the microchannel reactor, long aging time of the synthesis solution led to small mean particle size and narrow particle size distribution of the products. When synthesized at high temperature, zeolite NaA with big mean particle size but narrow particle size distribution could be produced even within short residence time, which would result from the fast heat transfer and auto-creation segmented flow of the synthesis solution in the microchannel.

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1. Introduction

Zeolites are crystalline aluminosilicates with uniform nanometer-sized pores [1]. Their unique frameworks and high internal surface areas make them widely used in chemical and petrochemical processes, such as production of fuels, fine chemicals and pharmaceuticals synthesis [2,3], pollution abatement [4], membranes [5], membrane reactors [6,7], sensors [8,9], and optoelectronic materials [10].

Synthesis of most zeolites is carried out as a batch operation [1], though there are few reports of continuous synthesis of zeolites in continuous stirred tanks, tubular reactors and semicontinuous reactors with the successful synthesis of ZSM-5 crystals [11–13]. A continuous process would be desirable because it would: (1) be energy efficient by eliminating the high energy consumption that is required for repeated heat-up and cool-down in batch crystallizers; (2) require smaller equipment and possibly lower capital costs that are inherent in a continuous process as compared to a batch process at the same produc-

tion rate; and (3) produce a more uniform product because of the readily controlled operating conditions [11]. However, it was reported that plug flow continuous crystallization of zeolites had not been very successful because the relatively slow kinetics of crystallization required operation at low flow rates in order to obtain the required residence times. On the other hand, mass and heat transfer rate were low at such low flow rates and could result in non-uniform products and poor energy efficiency [11,14].

Microreactors, generally defined as miniaturized reactors with characteristic dimension in micrometers and reaction volumes in the nanoliter-to-microliter range, have attracted increasing interests in recent 10 years [15–18]. They have been used in the synthesis of various organic [19–23], inorganic [24], and biological materials [25]. Significant advantages over the conventional reactors in respect of safety, cost, kinetics, throughput and scale-up have been demonstrated by many researchers in the past few years [26,27]. In general, mass and heat transfer rate in microreactors are much higher than in microscopic reactors [28–30]. For example, a heat conduction simulation showed that only 0.28 s was needed to heat the reaction solution from 20 to 299 °C for a flow rate of 100 $\mu\text{L min}^{-1}$ inside a 200 μm channel [31].

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Recent research in the application of microchannel reactors for particle production has largely focused on the synthesis of various semiconductor nanoparticles, such as CdSe [31–36], CdS [37,38] and CdSe/ZnS [39,40]. Several other groups have used microchannel reactors to produce titania [41,42], colloidal silica [43,44], silver [45], and gold nanoparticles [46,47]. All these works demonstrated that microchannel reactors were quite suitable for continuous preparation of inorganic particles and showed great advantages for the control of reaction conditions and particle properties. Particles could be immediately obtained and measured at the outlet of the microchannel reactors with different residence times, which is convenient for studying the synthesis mechanism. In this paper, we tried to use a simple microfluidic system to synthesize zeolite NaA. Zeolite NaA was chosen for its wide range of batch compositions and synthesis temperatures. Results were compared with normal hydrothermal synthesis.

2. Experimental

Stainless steel capillary (inner diameter, 0.75 mm; outer diameter, 1.2 mm; length, 1.5 m) was connected with a constant-flow pump by a PTFE tube (inner diameter, 2 mm; outer diameter, 3 mm; length, 0.5 m) to make a microfluidic system and the capillary was immersed in an oil bath (Fig. 1).

Zeolite NaA synthesis solution was prepared by following the composition and preparation steps in Ref. [48]. First, 0.724 g sodium hydroxide was completely dissolved in 80 mL deionized water. Then the solution was divided into two equal volumes in polypropylene bottles. The aluminate solution and the silicate solution were prepared by adding 8.254 g sodium aluminate and 11.560 g sodium silicate to each half of the caustic solution at room temperature, respectively. Afterwards, the silicate solution was added to the aluminate solution and the synthesis mixture was vigorously stirred for 2 h. The molar ratio of the mixture was $2.446\text{Na}_2\text{O}:1\text{Al}_2\text{O}_3:1.187\text{SiO}_2:145\text{H}_2\text{O}$.

In the batch synthesis, the synthesis mixtures, aged for certain periods of times (50, 100 and 150 h), were transferred into autoclaves equipped with a Teflon liner and then crystallized at 90 and 100 °C. After crystallization for several hours, the autoclaves were taken out and cooled by tap water. The crystallization products were obtained after filtrating, washing with deionized water and drying at 90 °C overnight.

For synthesis in microchannel reactors, the capillary was immersed in the oil bath, which was accurately controlled at

reaction temperature (90 or 100 °C). The aged synthesis mixture was injected into the capillary at a constant flow rate ($0.20\text{--}0.85\text{ mL min}^{-1}$) by a constant-flow pump without mixing, which corresponds to residence times (RT) ranging from about 3.5 to 13.5 min. Samples were immediately collected at the outlet. NaA crystals were obtained after five cycles of centrifuging and washed with deionized water, followed by drying at 90 °C overnight.

The zeolite samples were characterized by the following techniques: powder X-ray diffraction (XRD), scanning electron micrographs (SEM) and particle size distribution (PSD). XRD data were collected on a D8-Advance diffractometer (Bruker Company) using Cu K α radiation with an accelerating voltage of 40 kV and intensity of 30 mA. The diffraction pattern was collected in the 2θ range of 5–50°, using a step size of 0.05° and a collection time at each step of 0.2 s. SEM pictures were obtained on a Quanta 200 scanning electron microscope (FEI Company). Particle size distribution and mean particle size were determined with a laser scattering particle size distribution analyzer (Malven Zetasizer 3000 HS_A) with water used as the medium for dispersion of the zeolite sample. The solution was ultrasonicated for 30 min to break down the flocculates before the measurement.

3. Results and discussion

The synthesis mixture without aging was first used to synthesize zeolite NaA in the microfluidic system at 90 or 100 °C. It was observed that the products coming out of the outlet were, alternately, clear solution and viscous gel, as shown in Fig. 2, where black blocks represent the gels and the spaces between the black blocks are clear solutions, which indicated that crystallization process was going on when homogenous reactant solution was passing through the capillary. Unfortunately, the viscous gels were amorphous as determined by XRD, no matter what residence time (from 1 to 15 min, restricted by the length of microchannel and the flow rate of the constant-flow pump) was chosen. Even worse, as the experiment was carried out for more than 2.5 h, the capillary was always blocked that the experiment could not go on. The unsuccessful synthesis of zeolite NaA in the capillary would relate to not-enough long residence time since the capillary is only 1.5 m in length and the flow rate of the pump could not be adjusted to a very low level. So the initial state of the synthesis solution should be adjusted to shorten the required crystallization time. It is well known that aging of the synthesis solution can shorten the crystallization time [1]. Therefore, the fresh synthesis mixture was aged for certain time before it was used for zeolite NaA synthesis in the microfluidic system.

As we know, the crystallization time plays a very important role on the synthesis of zeolites. Because of the extremely high heat transfer rate in the microchannel, the residence time

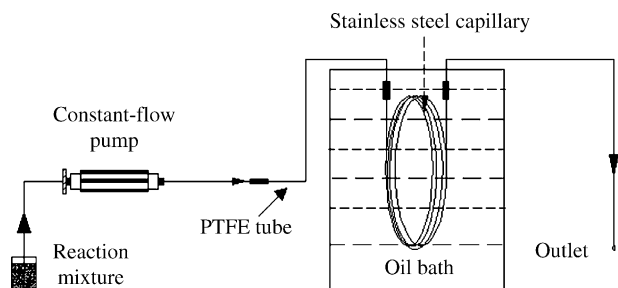


Fig. 1. Scheme of the microfluidic system for zeolite synthesis.

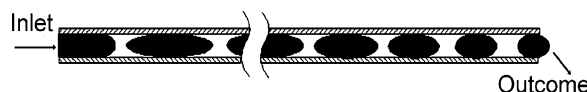


Fig. 2. Scheme of the alternate flow patterns during successful synthesis of zeolite NaA in microchannel.

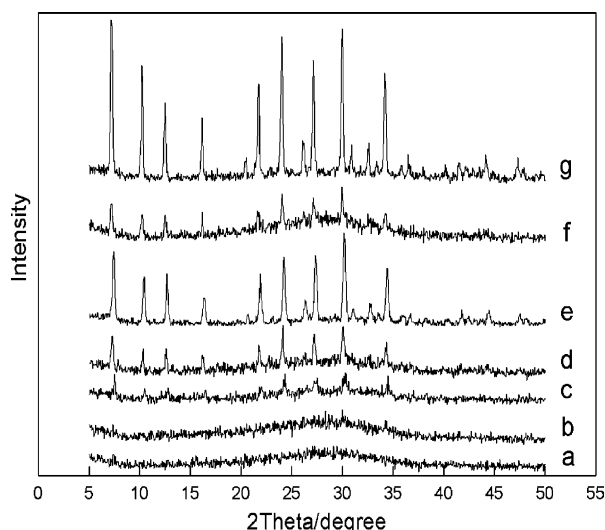


Fig. 3. XRD patterns of the evolution of zeolite NaA synthesized at 90 °C with various residence times: (a) 5.1 min, (b) 6.4 min, (c) 9.9 min, (d) 11.2 min, (e) 13.3 min, (f) 105 min, and (g) 135 min from synthesis solutions aged for 50 h at room temperature, where (a)–(e) were prepared in the microchannel reactor; (f) and (g) were prepared in the batch systems.

equals to the crystallization time for continuous synthesis of zeolite in the microchannel reactor. Fig. 3 shows XRD patterns of zeolite crystals synthesized in the microreactor at 90 °C with various synthesis times from the synthesis solution aged for 50 h. It could be seen that, no XRD peaks could be detected from the products synthesized with the residence time of 5.1 and 6.4 min (Fig. 3a and b). When the residence time was increased to 9.9 min, XRD patterns ascribed to zeolite NaA of the resulting products could be observed (Fig. 3c), but they were very weak, indicating that the crystallization of NaA was not complete. When the residence time was increased to 11.2 min, the peaks became stronger (Fig. 3d). When the residence time was further increased to 13.3 min, well-resolved XRD patterns of the products could be observed, suggesting successful synthesis of NaA with good crystallinity (Fig. 3e). On the other hand, by using the same synthesis solution, it took 105 min for a batch synthesis process without or with stirring to synthesize zeolite NaA which exhibited weak XRD patterns (Fig. 3f). After synthesis for 135 min in the batch synthesis, the products showed strong zeolite NaA XRD patterns. Therefore, the required crystallization time for the synthesis of zeolite NaA using the synthesis solution aged for 50 h in the microchannel reactor was only 1/10 of the crystallization time needed for the synthesis of the same product in a batch system.

The above results indicated that aging of the synthesis solution resulted in the successful synthesis of zeolite NaA in the microchannel reactor. Then the influence of aging of the synthesis solution for a longer period of time was examined. Fig. 4 presents the XRD patterns of products synthesized in the microchannel reactor at 90 °C with various residence times from synthesis solutions aged for long period of times. Comparing samples (a) and (b), (c) and (d), respectively, it could be seen that, when the synthesis solution was aged for 100 h, the resulting products demonstrated obvious diffraction peaks

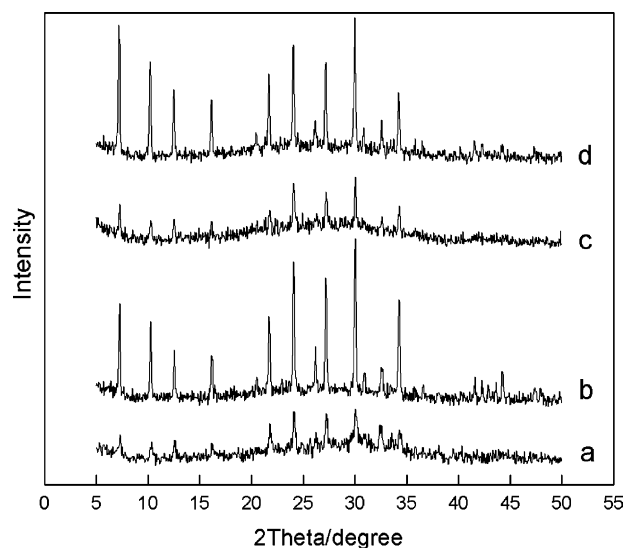


Fig. 4. XRD patterns of products synthesized in the microchannel reactor at 90 °C with various residence times from synthesis solutions aged for 100 h ((a) 9.1 min and (b) 10.6 min), and for 150 h ((c) 6.5 min and (d) 9.9 min).

of NaA with the residence time of 9.1 min (Fig. 4a), and much stronger diffraction peaks with the residence time of 10.6 min (Fig. 4b). Further increase of the aging time to 150 h resulted in the successful synthesis of NaA in even shorter residence times. It was apparent that the products synthesized from the synthesis solution aged for 150 h with residence times of 6.5 min (Fig. 4c) and 9.9 min (Fig. 4d) exhibited almost the same intense XRD peaks as that synthesized from synthesis solution aged for 100 h with residence times of 9.1 min (Fig. 4a) and 10.6 min (Fig. 4b), respectively. From the above results and by comparing the results in Figs. 3 and 4, we could concluded that, with the increase of the aging time of the synthesis solution, shorter residence time was needed to synthesize zeolite NaA possessing almost the same crystallinity.

The particle size distributions of zeolite crystals in Fig. 5 showed that NaA synthesized at 90 °C for the residence time of 13.3 min from the synthesis solution aged for 50 h had a mean particle size of 426 nm with the wide range from 230 to 710 nm. When the aging time was prolonged to 100 h, the mean particle size of the resulting products synthesized with residence time of 10.6 min decreased to 368 nm with a particle size distribution ranged from 220 to 570 nm (Fig. 5b). When the synthesis solution was aged for 150 h, the mean particle size of the products synthesized with residence time of 9.9 min decreased to 278 nm with a narrow particle size distribution ranged from 190 to 400 nm (Fig. 5c). On the other hand, zeolite NaA synthesized from synthesis solutions aged for 50 h at 90 °C with a crystallization time of 135 min in the batch system without and with stirring showed a mean particle size of 512 nm with a wide particle size distribution ranged from 280 to 800 nm (Fig. 5d) and a mean particle size of 589 nm with a particle size distribution ranged from 350 to 950 nm (Fig. 5e), respectively. Therefore, zeolite NaA synthesized in the microchannel reactor had smaller mean particle size with narrower particle size distribution than that produced in the batch synthesis from the synthesis solution

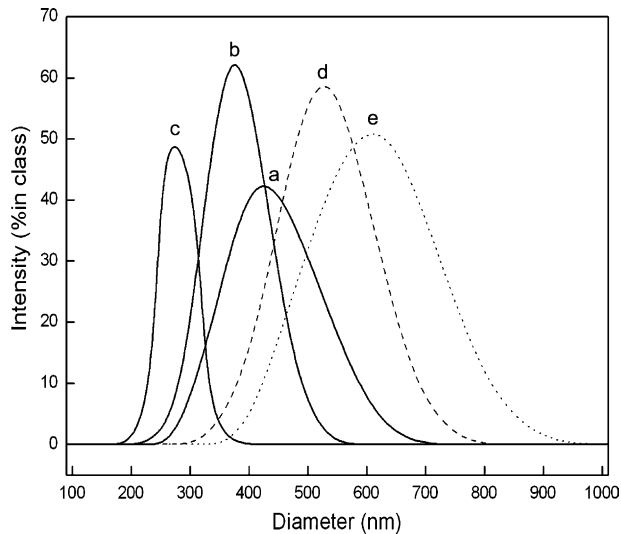


Fig. 5. Particle size distributions of zeolite NaA synthesized at 90 °C from synthesis solutions aged for different periods of times with various residence times: (a) aged for 50 h, RT of 13.3 min; (b) aged for 100 h, RT of 10.6 min; (c) aged for 150 h, RT of 9.9 min; (d) aged for 50 h, crystallization time of 135 min; (e) aged for 50 h, crystallization time of 135 min with stirring; where (a)–(c) were prepared in the microchannel reactor; (d) and (e) were prepared in the batch systems.

aged for 50 h. For zeolite NaA synthesized in the microchannel reactor, NaA with smaller mean particle size and narrower particle size distribution could be produced from the synthesis solution aged for a longer period of time even in less residence time. Fig. 6 shows the SEM pictures of the products shown in Fig. 5. It could be seen from the SEM pictures that the trend of the particle size of the zeolite NaA was the same as the results of the particle size distribution analyses presented in Fig. 5. On the other hand, the morphology of zeolite NaA synthesized in the microchannel reactor was all round in shape, while the shape of zeolite NaA produced in the batch system was mostly cubic.

The synthesis temperature was also examined for the synthesis of zeolite NaA in the microchannel reactor. Fig. 7 presents the XRD patterns of the products synthesized at 100 °C from synthesis solutions aged for different periods of times with various residence times. Samples (a)–(c) were prepared in the microchannel reactor and sample (d) was prepared in the batch system. It could be seen that, when the synthesis solution was aged from 50 to 100 h and to 150 h, zeolite NaA with close crystallinity could be synthesized in the microchannel reactor in decreasing residence times. Sample (c), which was synthesized from the synthesis solution aged for 150 h with a residence time of 7.5 min, exhibited stronger XRD peaks than sample (a), which was synthesized from synthesis solution aged for 50 h with a residence time of 11.9 min. On the other hand, samples (a) and (d),

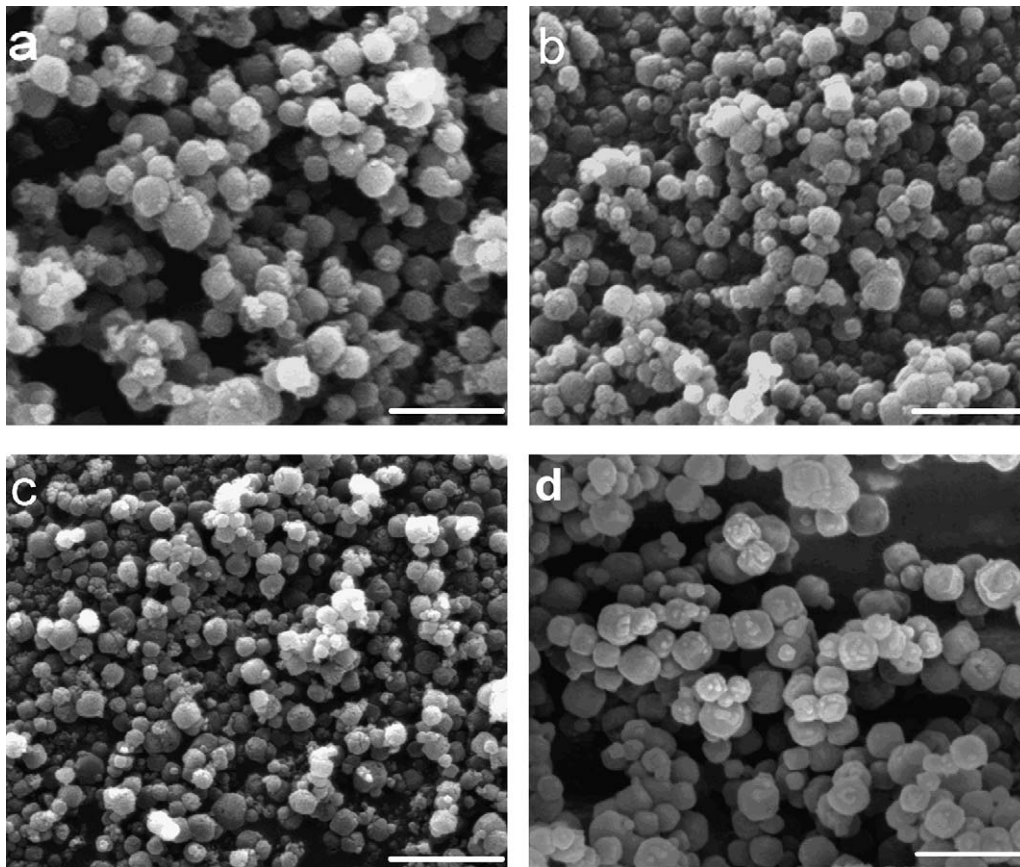


Fig. 6. SEM pictures of zeolite NaA synthesized at 90 °C from synthesis solutions aged for different periods of times with various residence times: (a) aged for 50 h, RT of 13.3 min; (b) aged for 100 h, RT of 10.6 min; (c) aged for 150 h, RT of 9.9 min; (d) aged for 50 h, crystallization time of 135 min; where (a)–(c) were prepared in the microchannel reactor, (d) was prepared in the batch system. In all SEM micrographs, the scale bar corresponds to 2 μm.

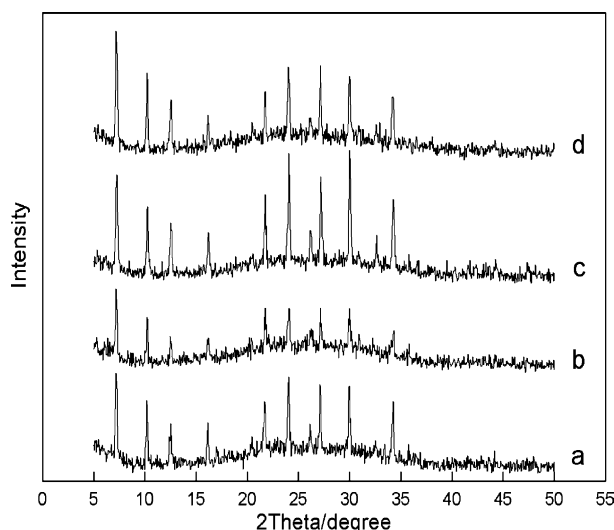


Fig. 7. XRD patterns of zeolite NaA synthesized at 100 °C from synthesis solutions aged for different periods of times with various residence times: (a) aged for 50 h, RT of 11.9 min; (b) aged for 100 h, RT of 9.3 min; (c) aged for 150 h, RT of 7.5 min; (d) aged for 50 h, crystallization time of 115 min; where (a)–(c) were prepared in the microchannel reactor, (d) was prepared in batch system.

both synthesized from the synthesis solution aged for 50 h, with former synthesized in the microchannel reactor and latter in the batch system, exhibited almost the same XRD intensity. However, the crystallization time for sample (a) was only 1/10 of that for sample (d). Corresponding particle size distributions of the samples (Fig. 8) showed that, zeolite NaA synthesized from synthesis solutions aged for 50, 100, and 150 h in the microchannel reactor at 100 °C had the mean particle sizes of 497, 416, and 357 nm with the particle size distribution ranges of 310–730, 320–620, and 310–400 nm, respectively. While zeolite NaA syn-

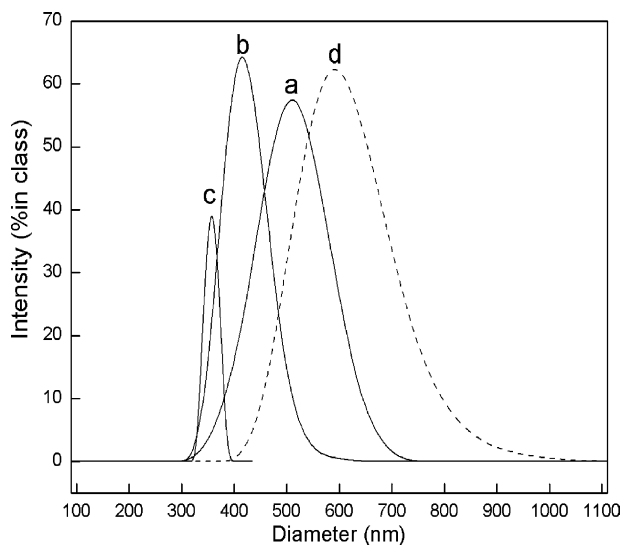


Fig. 8. Particle size distributions of zeolite NaA synthesized at 100 °C from synthesis solutions aged for different periods of times with various residence times: (a) aged for 50 h, RT of 11.9 min; (b) aged for 100 h, RT of 9.3 min; (c) aged for 150 h, RT of 7.5 min; (d) aged for 50 h, crystallization time of 115 min; where (a)–(c) were prepared in the microchannel reactor; (d) was prepared in batch system.

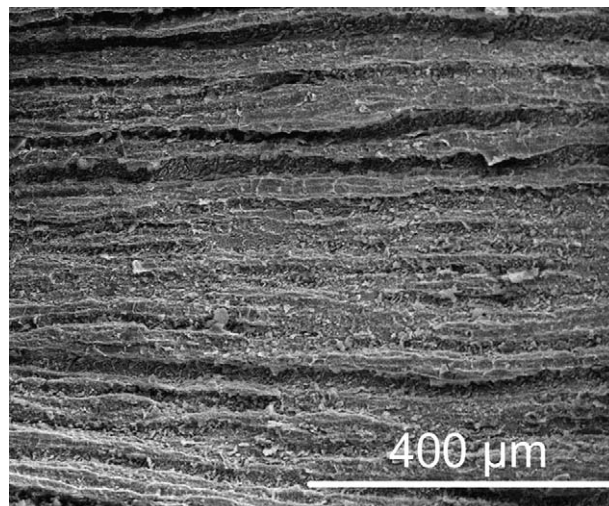


Fig. 9. SEM picture of the inside surface of the stainless steel capillary after the hydrothermal synthesis.

thesized from the synthesis solution aged 50 h at 100 °C with a crystallization time of 115 min in the batch system showed a mean particle size of 596 nm with a wide range from 400 to 1150 nm. This trend was the same as that when the synthesis was conducted at 90 °C. It could be concluded that zeolite NaA with smaller mean particle size and narrower particle size distribution could be produced within less residence time from the synthesis solutions aged for longer period of times in the microchannel reactor. SEM pictures of the products exhibited the same trend for the particle size as that from the particle size analysis results shown in Fig. 8. Similar to the morphology of the samples produced at 90 °C, zeolite NaA crystals synthesized at 100 °C in the microchannel reactor were also round in shape, but they were mostly cubic when synthesized in the batch system, as could be seen from SEM pictures.

In order to know the appearance of the capillary after the hydrothermal synthesis, the stainless steel capillary, which had been used with an accumulative synthesis time for more than 60 h, was cut off, and its inside surface was observed by SEM (see Fig. 9). It could be seen that the inside wall of the stainless steel capillary was coated with sheaves of small particles. This coating could be served as a preventing layer from the corrosion of the stainless steel capillary in the strong alkali zeolite synthesis solution.

We observed that segmented flow was always obtained during the synthesis of zeolite NaA in the microchannel reactor, no matter whether the synthesis solution was aged or not. This was because zeolite synthesis solution was composed of an amorphous gel phase and a solution phase during the synthesis, as we know that most zeolite syntheses are preceded by the formation of an amorphous gel phase, which dissolves to replace reagents consumed from the solution by crystal growth [49]. Formation of two phases was observed by Brar et al. [48] when they heated the zeolite NaA synthesis solution, which was pre-cooked in conventional oven at 60 °C for 3 h, in microwave oven for 105 s. When the synthesis mixture was pumped through the microchannel, the two phases was gradually formed along the microreactor,

and they separated with each other. Consequently, segmented flow was formed in the microchannel. We also observed that formation of segmented flow was earlier when the synthesis solution was aged for longer time. Brar et al. [48] also reported that no separation of the phases was seen to occur when the above microwave radiation time was less than 90 s. This was because of more structure rearrangement after aging for longer time, which was described in the next paragraph.

Our results revealed that aging of the synthesis solution had apparent influence on the particle size and particle size distribution of zeolite NaA synthesized in a microchannel reactor. Longer aging time could result in the production of NaA crystals with smaller particle size and narrower particle size distribution, as shown in Figs. 5 and 8. This trend is the same as that in conventional batch synthesis of zeolite NaA [48]. As we know, structure rearrangement occurred during the aging of the synthesis solution, which led to the formation of zeolite nuclei [50]. The prolongation of the aging time resulted in the decrease in the size of aggregates formed during the structure rearrangement [51] and the increase of the numbers of the nuclei [1]. When the synthesis mixture aged for a long time was injected into the microchannel, it was quickly heated to crystallization temperature. Thereafter, the growth of the nuclei occurred while the nutrients were consumed. At the same time, separation of two phases occurred and segmented flow was formed in the microreactor. The longer the aging time was, the more the nuclei were formed, and the earlier the two phases formed. Both the consumption of the nutrients and the big number of the nuclei in each segment limited the further nucleation and grow-up of the crystals, since the nutrients could not be supplied from the adjacent segments. As a result, smaller particles with narrower particle size distribution could be produced from the synthesis mixture aged for a longer time.

By comparing the results in Figs. 5 and 8, it could be seen that the mean particle size and particle size distribution of zeolite NaA synthesized at 100 °C were, respectively, bigger and narrower than those of zeolite synthesized at 90 °C in microchannel reactor system, when the same synthesis solution was used. It was believed that lower temperatures favored nucleation, and at relatively higher temperatures, crystal growth surpassed nucleation [48]. When higher temperature was applied, the rate of crystal growth was increased, which resulted in the formation of bigger crystals, and the rate of nucleation was decreased. At the same time, the faster consumption of the nutrients at higher temperature also led to less formation of nuclei in the segments. Therefore, at higher temperature, most of the nuclei in each segment were formed at almost the same time and they were grown up at almost the same rate, which resulted in the formation of crystals with bigger particle size and narrower particle size distribution. However, the influence of temperature on the particle size distribution of zeolite NaA prepared in batch synthesis was different from our results, as reported by Brar et al. [48]. Their results indicated that the particle size distribution of zeolite NaA was broader at high temperature (100 °C) than at low temperature (60 °C). This would result from the low heating rate in the batch reactor, where more nuclei were formed during the heating process; while the early formed nuclei were growing up at the

same time. Consequently, broader particle size distribution was obtained. In fact, they thereafter applied microwave radiation on the synthesis and obtained a narrower particle size distribution [48].

The above results revealed that, for zeolite NaA synthesis in a microreactor, both long aging time and high crystallization temperature resulted in zeolite NaA crystals with narrow particle size distribution in short residence time. However, Khan et al. [43] found that colloidal silica with broad particle size distribution was synthesized in short residence time (high flow rate) in a laminar flow microreactor during their early research. They found that, as the residence time was prolonged, the particle size distribution was narrowed. They attributed this to axial dispersion of the growing colloidal particles as the synthesis solution flew through the reactor, which could be explained by a modified Taylor–Aris dispersion coefficient K showed in Eq. (1):

$$K = D + \frac{U^2 r_0^2}{48D} \left(1 - \frac{a}{r_0}\right)^6 \quad (1)$$

where K is the modified Taylor–Aris dispersion coefficient, U the area-averaged mean flow velocity, a the particle radius, r_0 the radius of the capillary, and D is the particle diffusivity in an unbounded fluid.

In their opinion, the Taylor–Aris dispersion coefficient K was mainly affected by the average flow rate U in the laminar flow microreactor. Under such circumstance, the axial dispersion was dominated, and in turn the axial dispersion coefficient varied as the square of the average flow velocity. Then, shorter residence time meant higher flow rate and bigger dispersion coefficient, which led to wider distribution of residence time and, consequently, broader particle size distribution. In order to eliminate the axial dispersion, the authors proposed a segmented flow, which was formed by injecting gas into the liquid, for the synthesis of colloidal silica with narrow particle size distribution in short residence time [43,44]. The segmented flow reactor was equivalent to a flow of small batch reactors passing in succession through a plug flow reactor, with the residence time distribution of fluid elements approaching a delta function centered at the value of mean residence time [43,44]. Since all the small batches spent the same amount of time in the reactor, a segmented flow reactor was equivalent to be composed of many small batch reactors, which therefore eliminated the problem of axial dispersion as encountered in the case of the laminar flow reactor. In the course of zeolite NaA synthesis in the microchannel reactor, segmented flow, consisted of clear solution and viscous gel, was always observed. The connection between the adjacent gel segments was hence isolated by the clear solution, which resulted in the narrow residence time distribution of the nutrients in the gels. As a result, zeolite NaA with narrow particle size could be synthesized even in short residence time from long time aged synthesis mixture at high crystallization temperature. On the other hand, the minimum crystallization time required for zeolite NaA synthesis in the microchannel reactor was determined by the crystal growth rate. If the residence time was too short, zeolite NaA could not be synthesized (see Fig. 3a and b). However, if the residence time were too long, zeolite NaA crystals

would be transformed [1]. Therefore, there must be an optimum residence time for the synthesis of zeolite NaA with narrow particle size distribution.

4. Conclusions

A stainless steel microchannel reactor was utilized for continuous synthesis of zeolite NaA. It was found that aging of the synthesis solution was necessary to avoid the blockage of the reactor before it was pumped into the microchannel in our study. The required crystallization time for the synthesis of zeolite NaA with close crystallinity in the microchannel reactor was remarkably decreased compared to that needed in the batch system. On the other hand, the mean particle size and the particle size distribution of zeolite NaA synthesized in the microchannel reactor were, respectively, smaller and narrower than in the batch system. In the microchannel reactor, zeolite NaA could be produced in short residence time when the synthesis solution was aged for long time. Consequently, the mean particle size and the particle size distribution of the resulting products were, respectively, small and narrow. When synthesized at high temperature, zeolite NaA could be produced within short residence time and it had big mean particle size but narrow particle size distribution. This phenomenon would result from fast heat transfer and auto-creation segmented flow of the synthesis solution in the microchannel reactor, which led to narrow particle size distribution of zeolite NaA at high temperature even within short residence time. Therefore, zeolite NaA with different particle size and particle size distribution could be synthesized in the microchannel reactor by adjusting the aging time, quick, accurate control of the crystallization temperature and the residence time.

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