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Preparation of Ultrafine Zeolite A Crystals with Narrow Particle Size Distribution Using a Two-Phase Liquid Segmented Microfluidic Reactor

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A method for synthesizing ultrafine zeolite A crystals with narrow particle size distribution (PSD) using a water–liquid paraffin two-phase segmented microfluidic device assembled by coaxial dual tubes is reported. The influence of the sizes of the outer tubes, the aging of the synthesis solution, and the reaction temperature was examined. As-synthesized zeolite crystals were characterized by X-ray diffraction, Fourier transform infrared spectroscopy, dynamic light scattering, energy dispersive X-ray spectroscopy, scanning electron microscopy, and field-emission scanning electron microscope. Zeolite A crystals with mean particle sizes (MS) of 408 and 262 nm and PSDs of 150–620 and 100–420 nm were prepared in the segmented microfluidic reactor (inner tube i.d. of 0.6 mm, outer tube i.d. of 1 mm) at 80 °C for 20 min using the fresh synthesis solution and for 5 min using the aged synthesis solution, respectively. The MS and PSD of zeolite A can be controlled by adjusting the temperature and the sizes of the outer tube. The crystallization performance of zeolite A in the segmented microfluidic reactor was compared with those in the conventional and microwave-heated batch reactor and the single-phase microfluidic reactor at 90 °C. It was found that the rate of crystallization in the segmented microfluidic reactor was a bit slower than that in the microwave-heated batch reactor, but was much higher than those in the conventional batch reactor and single-phase microfluidic reactor. The MS and PSD of the resulting zeolite A synthesized in the segmented microfluidic device are smaller and narrower than those produced in the conventional batch reactor, single-phase microfluidic reactor, and microwave-heated reactor.

1. Introduction

Zeolite A, an aluminosilicate with unique pore size and high capacity of ion exchange, has of a wide range of applications in detergent, drying, gas separation, and so on.^{1–3} Usually, zeolite A is prepared in conventional batch reactors, resulting in products with a wide particle size distribution (PSD) ranging from one to several micrometers.¹ For optimal practical applications, uniform submicrometer zeolite A crystals need to be developed since they have advantages such as short diffusion paths, high external surface area-to-volume ratio, and uniform properties.^{4–6}

Several strategies have been developed to synthesize submicrometer-sized zeolite A. One is to use homogeneous clear solutions containing abundant amounts of organic structure directing agents, mainly TMA⁺ (tetramethylammonium hydroxide cation).^{1–3} Utilization of TMA⁺ by encompassing of a lot of silica tetrahedron and aluminum tetrahedron around TMA⁺ can favor the formation of secondary structure units (sodalite cage) during the gelation or nucleation period,^{3,7} resulting in easy formation of zeolite A with small sizes. Zeolite NaA crystals with a particle size distribution (PSD) of 100–300 nm have been thus obtained at 100 °C for 2–13 days.^{8,9} However, this strategy has to use expensive organic additives, which are removed by calcination. Another strategy is to confine synthesis of zeolite A in very small spaces, such as nanopores of carbon blacks,¹⁰ three-dimensional pores in thermoreversible polymer hydrogels,¹¹ and vesicles of microemulsions.¹² Nevertheless, this confined space synthesis method requires either sacrificial inert media with high quality or complex synthesis procedures. On the other hand, efforts have been made to manipulate synthesis

parameters, such as the Si/Al molar ratios and water content in the initial synthesis solution, the crystallization temperature, and aging of the synthesis solution, to synthesize zeolite A with particle sizes ranged from 100–500 nm without adding any extra substances.^{13–15} Under such circumstance, accurate controls of synthesis parameters or quite long synthesis times (for example, aging the synthesis solution for 6 days followed by crystallization at 100 °C for 1 day¹³ or conducting the synthesis at room temperature for 3 days¹⁵) are needed. Furthermore, all of the above cited works have been conducted in batch reactors.

Recently, we have demonstrated a continuous process for synthesis of zeolite A with a smaller mean particle size (MS) and narrower PSD within much shorter times using a single-phase microfluidic reactor than using the batch system.¹⁶ However, several problems remained to be resolved. First, the aged synthesis solution should be used to avoid the blockage of the channel. Second, the aging time was too long (~6 days). Third, the PSD of zeolite A synthesized was broad, ranging from 150 to 800 nm. It was reported that a two-phase liquid segmented flow pattern in microreactor for hydrothermal synthesis of particles could keep the solid products away from the tube inner walls to avoid clogged channels.^{17–20} Moreover, the segmented droplets experienced a self-recirculation flow due to the shear interaction with the carrier fluid,^{21,22} resulting in intensification of the mixing and elimination of axial dispersion. Thus, the reaction time could be reduced and the residence time distribution of the solution in microchannels became narrower, leading to narrower PSD of final products.^{17,23–28} For example, Takagi et al.¹⁹ used a coaxial dual pipe microreactor to generate the segmented flow pattern, and TiO₂ particles with a narrow PSD of 40–150 nm can be prepared. On the contrary, the PSD of the same products prepared in batch reactor was broader, ranging from 20 to 400 nm. On the basis of the above literature work, we tried to synthesize ultrafine zeolite A crystals with

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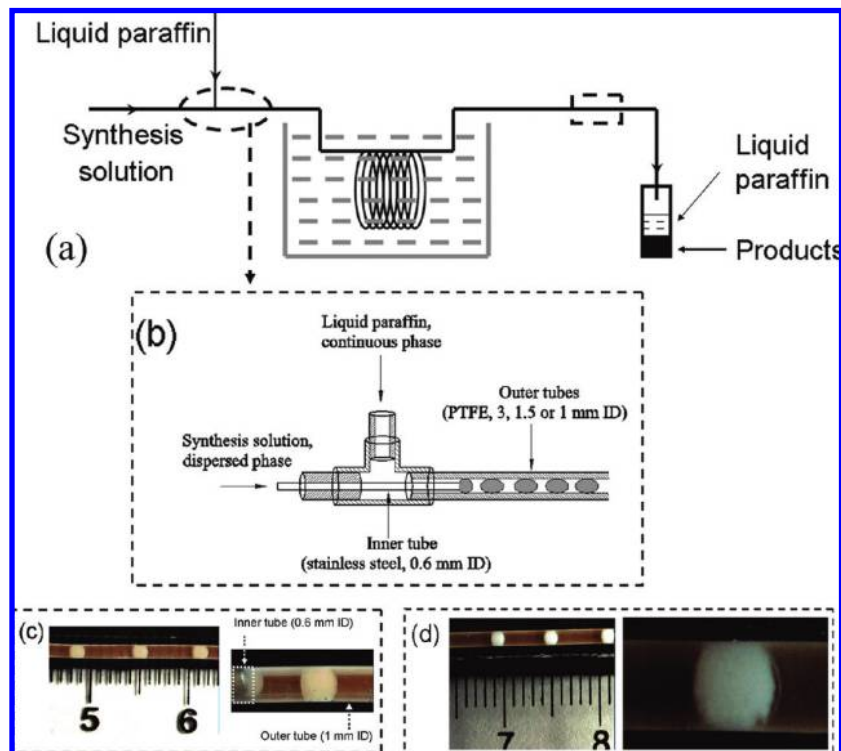


Figure 1. Scheme of a two-phase liquid segmented microfluidic system for zeolite A synthesis and flow patterns in the reaction tube. (a) General flowchart of the microfluidic system. (b) Detailed illustration of the coaxial dual pipe assembly. (c) General (left) and close view (right) of flow patterns at the outlet of the 0.6 mm i.d. inner tube in the 1 mm i.d. outer tube. (d) General (left) and close view (right) of flow patterns at the outlet the 1 mm i.d. outer tube (rectangle in part a). The experiment was carried out with the aged synthesis solution at 80 °C with the residence time of 5 min.

narrow PSD using a water–liquid paraffin two-phase segmented microfluidic device assembled by coaxial dual tubes, in an attempt to resolve the above problems existing in the synthesis of zeolite A in single-phase microfluidic reactors. The influence of the sizes of the tubes, the aging of the synthesis solution, and the reaction temperature were examined. In addition, synthesis of zeolite A in conventional and microwave-heated batch reactors and a single-phase flow microreactor were also examined.

2. Experimental Section

2.1. Preparation of the Synthesis Solution. Zeolite A synthesis solution was prepared following the composition and preparation steps in ref 15 with a little increase of the amount of sodium hydroxide (NaOH), which resulted in decrease of the mean particle size of zeolite A, as indicated from our preliminary experiment results and the work of Kuanchertchoo and co-workers.²⁹ First, NaOH aqueous solution was prepared by dissolving 9.14 g NaOH in 60 mL deionized water, and then, the solution was divided into two equal volumes. Then, one NaOH solution was added with 6.44 g sodium aluminate, and the other was added with 3.0 g sodium silicate. After completely dissolving, the silicate solution was added to the aluminate solution with vigorous stirring to obtain the fresh synthesis solution. The molar ratio of the final mixture was 6.2 Na₂O:0.6 Al₂O₃:1.0 SiO₂:150 H₂O. In some cases, the fresh synthesis solution was aged at 30 °C for 20 h and denoted as the aged synthesis solution.

2.2. Synthesis of Zeolite A. Zeolite A was prepared in a water–liquid paraffin two-phase segmented microfluidic reactor, which was assembled by positioning a stainless steel inner tube with fixed outer diameter (o.d.) of 0.8 mm and inner diameter (i.d.) of 0.6 mm directly in the axis of a PTFE outer tube (i.d. 1–3 mm, length 1.5–10 m), as shown in Figure 1. The synthesis

solution, as a dispersed phase, was pumped into the inner tube by a constant flow pump. Liquid paraffin, as a continuous phase, was conveyed to the outer tube by a piston pump. The outer tube was immersed in an oil bath; the temperature of which was accurately controlled at 80, 90, or 100 °C. The flow rates of the synthesis solution and liquid paraffin were fixed at 8 and 20 mL h⁻¹, respectively, to maintain the smallest size of the synthesis solution segments under our experiment conditions (S-Figure 1 in the Supporting Information). Formation of segmented flow patterns with uniform and stable segments can be obviously seen from pictures of the flow at the outlet of the inner tube and the outlet of the outer tube shown in Figure 1. The synthesis time was changed by adjusting the lengths of the outer tube from 5 to 30 min. After synthesis, the upper liquid paraffin was decanted, and then, the products were separated by centrifugating (8000 rpm, 10 min) and washing with acetone and deionized water by five repetitions until the pH of the solution was 8, followed by washing with hexane five times to remove the residual paraffin. Finally, the products were dried at 80 °C for 24 h. The yield of the products was calculated by the ratio of the weight of dried products to the dry weight of Al₂O₃ and SiO₂ in the synthesis solution.³⁰

For comparison, syntheses of zeolite A were also conducted in a conventional batch reactor, a microwave-heated batch reactor, and a single-phase flow microreactor. For the conventional batch synthesis, the synthesis solution was charged into a polypropylene bottle and then kept in an oven preheated at 90 °C for 5–80 min. The microwave-heated batch syntheses were conducted in a microwave oven (Mars-5, CEM, USA) with the fresh synthesis solution loaded in a Teflon autoclave and crystallized at 90 °C for 5–40 min with a power of 800 W. Synthesis in the single-phase microfluidic reactor was carried out by pumping the aged synthesis solution into a PTFE microchannel reactor (1 mm i.d.), which was immersed in the

Table 1. Experimental Conditions and Results for Synthesis of Zeolite A Crystals in Different Reactors

sample	reaction temperature (°C)	aging of the synthesis solution	residence time (min)	size of outer tube (i.d., mm)	mean particle size (nm)	particle size distribution (nm)	CV value (%)
1 ^a	80	no	30	3.0	755	200–1500	39.5
2 ^a	80	no	24	1.5	566	100–800	34.2
3 ^a	80	no	20	1.0	408	150–620	26.2
4 ^a	80	yes	5	1.0	262	100–420	28.2
5 ^a	90	no	13	1.5	615	200–900	36.6
6 ^a	90	no	12	1.0	570	100–700	34.6
7 ^a	90	yes	5	1.0	258	80–400	29.3
8 ^a	100	no	10	1.5	700	300–1100	35.9
9 ^a	100	yes	5	1.0	263	70–440	28.7
10 ^b	80	yes	15	1.0	358	170–600	38.7
11 ^c	90	no	80		620	100–1500	49.4
12 ^d	90	no	10		632	120–850	40.5

^a The synthesis was carried out in the two-phase segmented flow microfluidic reactor. ^b The synthesis was carried out in the single-phase microfluidic reactor. ^c The synthesis was carried out in the conventional batch reactor. ^d The synthesis was carried out in the microwave-heated batch reactor.

oil bath at 80 °C with a flow rate of 8 mL h⁻¹. The products were separated, washed, and dried following the same procedures as mentioned above. The conditions and results for synthesis of zeolite A crystals in the two-phase segmented microfluidic reactor, single-phase microfluidic reactor, conventional batch reactor, and microwave-heated batch reactor are all listed in Table 1.

2.3. Characterization. The flow patterns in the two-phase segmented microfluidic reactor were recorded by macro lenses (Pentax, Japan) connected to a high-speed CCD video camera (Microview, Beijing) with a frequency of 50 images per second. X-ray diffraction (XRD) patterns were collected on the Bruker D8 ADVANCE powder diffractometer using Ni-filtered Cu K α radiation source at 40 kV and 20 mA. Crystallinities were calculated³¹ by dividing the sum of intensities of the prominent peaks ($2\theta \approx 7, 10, 12.5, 21.5, 24, 26, 27, 30,$ and 34°) of a sample by that of the reference standard prepared following ref 14. Fourier transform infrared (FTIR) spectra were obtained on the Nexus 870 FTIR spectrometer. Samples were mixed and ground with KBr for FTIR measurement in the wavenumber range of 2000–400 cm⁻¹. Dynamic light scattering (DLS) (Malven Zetasizer 3000 HSA) was used to determine the MS and PSD of products by preparing a suspension with a zeolite concentration of ~ 3.5 wt %.^{15,32} Element analysis was carried out on an energy dispersive X-ray analytical system (EDX, Genesis). The size and morphology of zeolite crystals were observed with a scanning electron microscope (SEM, Quanta 200) and field-emission scanning electron microscope (FESEM, Hitachi S-4800). The MSs and PSDs of samples were also determined by manual measurement of about 300 crystals in SEM pictures by Adobe Photoshop 7.0 software,^{33–36} for comparing the difference of results measured by DLS. The coefficient variation (CV) value was defined as the following equation. The lower the CV value, the more uniform particle size of crystals becomes.^{34,36}

$$CV = \frac{\left[\sum_{i=1}^n \frac{(d_i - d)^2}{n} \right]^{1/2}}{d}$$

Where, d_i is the diameter of the i th zeolite crystal, d is the average diameter, and n is the total number of the crystals counted.

3. Results and Discussion

3.1. Effects of the Temperature. The effect of temperature on zeolite A crystallization in the segmented microfluidic device

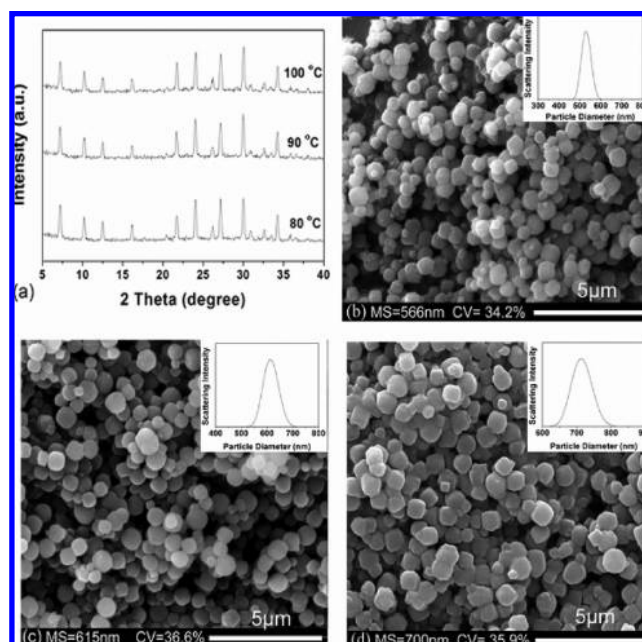


Figure 2. XRD patterns (a) and SEM pictures of zeolite A synthesized by fresh synthesis solution in the segmented microfluidic device (1.5 mm i.d. outer tube) at 80 °C for 24 min (b), 90 °C for 13 min (c), and 100 °C for 10 min (d). Insets in the SEM pictures are DLS analysis curves of the corresponding samples.

with the 1.5 mm i.d. outer tube was examined at 80, 90, or 100 °C using the fresh synthesis solution. Figure 2 shows the XRD patterns, PSD analysis curves, and SEM pictures of synthesized samples. We can see from Figure 2a that all samples present well-resolved zeolite A XRD peaks. More XRD characterizations of the products synthesized at different resident times (S-Figure 2 in the Supporting Information) reveal that fully crystalline products are just obtained at 80 °C for 24 min, at 90 °C for 13 min, and at 100 °C for 10 min, indicating that the reaction time for fully crystallized zeolite A production is shortened with an increased synthesis temperature. High crystallinities of these products were also verified from their FTIR spectra (see the Supporting Information, S-Figure 3).^{37,38} The Si/Al ratios of the products are 1.067, 1.046, and 1.053, respectively, as indicated from EDX analyses.

SEM pictures of these products (Figures 2b–d) show that most of zeolite A particles are round and trace amounts of particles are in cubic morphology. The measured MSs and PSDs of the three samples are 566, 615, and 700 nm and 100–800, 200–900, and 300–1100 nm, with corresponding CV values of 34.2%, 36.6%, and 35.9%, respectively. From the DLS curves

(insets in Figures 2b–d), we can see that the MSs and PSDs of the three samples are 540, 613, and 725 nm and 470–600, 540–710, and 675–800 nm, respectively. Apparently, the PSD results obtained from SEM pictures are significantly different from those obtained from DLS analyses, while the MS measured by these two methods are very close. This result is consistent with that reported by Valtchev et al.¹⁵ Since some quite small particles with sizes smaller than the results detected by DLS can be obviously observed in SEM pictures, the DLS results may be not accurate enough to interpret the MS and PSD of the resulting zeolite A crystals. Therefore, the MSs and PSDs of products studied in the following experiments were determined from SEM pictures. From Figure 2, we also find that the elevation of crystallization temperature leads to increase of the MS as well as little difference on the changes in the PSD span (i.e., the CV value) of the products. This is ascribed to the similar concentration of the nuclei and nutrients in each synthesis solution segment formed right at the outlet of the inner tube and the fast crystal growth rate at high temperature. As for zeolite synthesis, the MS and PSD are, respectively, determined by crystallization rate and the number and distribution of nuclei in the synthesis solution.^{1,14} Lower temperatures favor the nucleation while higher temperatures favor the rapid crystallization.¹⁴ Since each segment formed right at the outlet of the inner tube contains the similar concentration of the nuclei and nutrients,³⁹ the crystallization rate of the nuclei and the consumption rate of the nutrients in each segment can be considered to be similar during the course of the synthesis at elevated temperature. On the other hand, the secondary nucleation is restrained⁴⁰ because of fast heat transfer in the microreactor and fast consumption of the nutrients in the limited volume of each segment. Under such circumstances, changing the synthesis temperature changes the crystallization rate and hardly changes the concentration of the nuclei, leading to the change of the MS and little difference on the changes in the PSD span. From the above results, the nucleation and crystallization rates can be calculated (S-Table 1 in the Supporting Information). The activation energies of nucleation (E_n) and crystallization (E_g) are 24.7 and 37.9 kJ/mol, respectively (S-Figure 4 in the Supporting Information), which are smaller than those in batch synthesis of zeolite NaA.^{41–43} Furthermore, it was worth noting that the PTFE outer tube was not clogged during the experiments using the fresh synthesis solution carried out for 20 h, implying that application of the two-phase segmented flow system can avoid blockage of the microchannels occurred in the single-phase flow.¹⁶

3.2. Effect of the Size of the Outer Tube. The effect of the outer tube sizes on zeolite crystallization at 80 °C with 3.0, 1.5, and 1 mm i.d. outer tubes using the fresh synthesis solution was examined, and XRD characterization (S-Figure 5 in the Supporting Information) shows that the crystallization time to just obtain fully crystallized zeolite A are 30, 24, and 20 min, respectively. Figures 3a–c show SEM pictures of zeolite A synthesized in the segmented microfluidic reactors assembled with 3.0, 1.5, and 1.0 mm i.d. outer tubes, respectively, and the three-dimensional columns of the PSDs of three samples are shown in Figure 3d. We can see that the MSs of samples are 755, 566, and 408 nm, with the PSDs in the range of 200–1500, 100–800, and 150–620 nm, and the CV values of 39.5%, 34.2%, and 26.2%, when the inner diameters of the outer tubes are 3.0, 1.5, and 1 mm, respectively. The CV value of products prepared in the segmented microfluidic reactor with 1 mm i.d. outer tube is close to 26%, indicating that the PSD of the products is narrow.^{34,35} These above results suggest that the

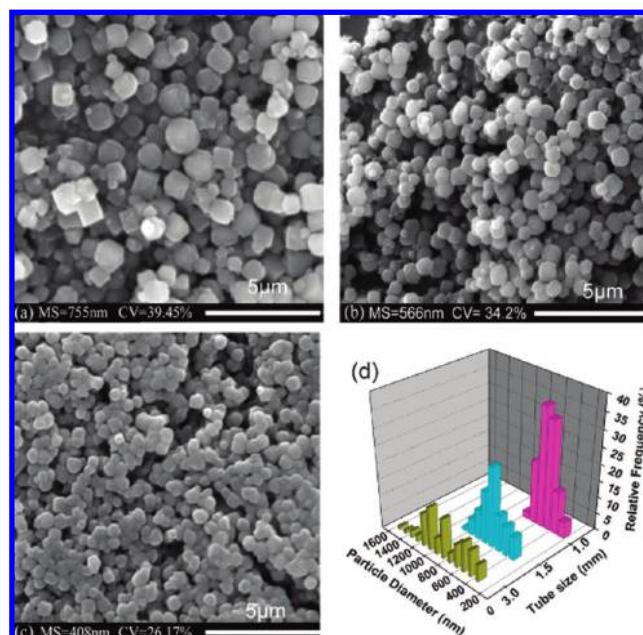


Figure 3. SEM pictures of zeolite A synthesized by the fresh synthesis solution at 80 °C in segmented microfluidic reactors with various inner diameters of outer tubes and times: 3.0 mm for 30 min (a), 1.5 mm for 24 min (b), 1.0 mm for 20 min (c), and three-dimensional columns of PSDs of three samples (d).

needed reaction time for synthesizing highly crystalline zeolite A is shortened when the inner diameter of the tube is decreased, and the MS and PSD of the resulting zeolite A crystals are reduced and sharpened, respectively. The possible reason is that decrease of the outer tube size results in a decrease of the dimension of the separated segments, which achieves the strong internal recirculation.^{39,44} Thus heat and mass transfer are intensified and the homogeneous distribution of the nuclei and nutrient is promoted. As a consequence, the crystallization rate is enhanced and the PSD and CV value of products become narrower and smaller, respectively, when the small-sized outer tube is applied.

3.3. Effect of Aging of the Synthesis Solution. The effect of aging of the synthesis solution on crystallization of zeolite A by the segmented microfluidic device (with 1 mm i.d. outer tube) was examined. XRD characterization shown in Figure 4a indicates that the dried aged synthesis solution is amorphous and highly crystalline zeolite A particles are synthesized at 80, 90, and 100 °C in 5 min using the aged synthesis solution. The samples (Figures 4b–d) have the MSs of 262, 258, and 263 nm, with the PSDs in the range of 100–420, 80–400, and 70–440 nm, and the CV values of 28.2, 29.3, and 28.7%, respectively. These results indicate that aging the synthesis solution also shortens the crystallization time in the segmented flow synthesis, which is consistent with the general recognition in zeolite synthesis.¹ At the consequent synthesis stage at the high temperature, a burst of high energy is applied, leading to rapid crystallization of these nuclei and fast and complete consumption of the left nutrients within a short time.^{1,14} In our case, the synthesis solution was aged at 30 °C for 20 h. Prolongation of the aging time to 22 h results in the formation of zeolite A crystals, as revealed from XRD characterization of the aged gels (S-Figure 6 in the Supporting Information), indicating that the induction period of zeolite A growth is almost completed after aged for 20 h. Thus, each segment contains the maximum amount of nuclei and little nutrients. The nutrients are quickly consumed, leading to impossibly further growth of

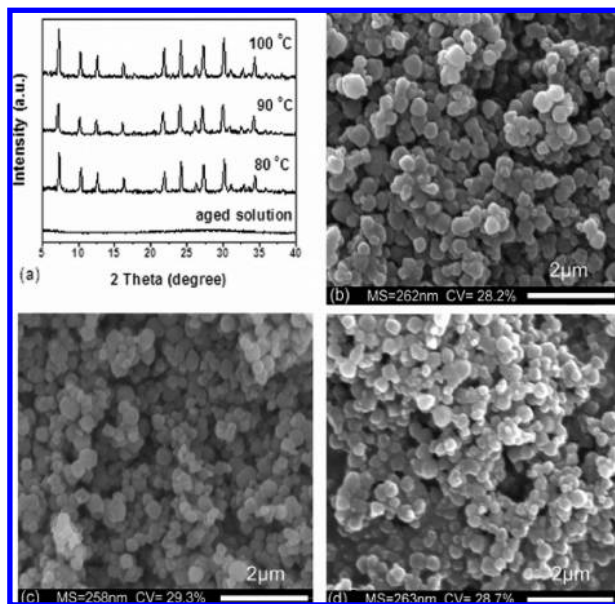


Figure 4. XRD patterns (a) and SEM pictures of zeolite A synthesized by aged synthesis solution in the segmented microfluidic reactor (1.0 mm i.d. outer tube) for 5 min at 80, (b) 90, (c) and 100 °C (d).

the crystals during the synthesis periods. As a result, the variation of crystallization temperature (80–100 °C) does not remarkably affect the MS and PSD of final products. On the other hand, CV values of products synthesized with fresh and aged synthesis solutions in the segmented microfluidic reactor with 1 mm i.d. outer tube (samples 3 and 4) at 80 °C are quite close. This is possibly attributed to the synergy of temperature and the size of the outer tube of the reactor. As indicated in the last section, the CV value of products synthesized in the microfluidic reactor with a smaller-sized outer tube becomes smaller. Brar et al.¹⁴ observed a narrower PSD of zeolite A crystals synthesized using the fresh synthesis solution at lower temperature, probably due to the fact that lower temperatures favor nucleation and crystal growth decreases more rapidly with temperature than gel dissolution.¹⁴

3.4. Discussion. No blockage of the channels occurred during the synthesis of zeolite A using the fresh synthesis solution in two phase segmented microfluidic devices. Furthermore, the yields of the resulting products were around 90%. We think this is really a progress for practical application of zeolite synthesis in microstructured reactors, since the microchannels are always blocked during in the single-phase synthesis of zeolite A using the fresh synthesis solution.¹⁶ This contributes to encompassing of the synthesis solution by liquid paraffin, thus avoiding direct contact of the wall of the microchannel with the gels formed from the synthesis solution in the course of synthesis.^{18–20}

Zeolite A was also synthesized in a single phase microfluidic reactor with a 1.0 mm i.d. tube using the aged synthesis solution at 80 °C. The time for just obtaining fully crystalline zeolite A is 15 min in this case. Figure 5 shows the SEM image and PSD of the corresponding products. We can see that the MS and PSD of the resulting zeolite A are, respectively, larger and wider than those produced in the two-phase segmented microfluidic reactor with the 1.0 mm i.d. outer tube at 80 °C for 5 min using the aged synthesis solution (Figure 4b and S-Figure 7 in the Supporting Information). Apparently, the crystallization time for obtaining highly crystalline zeolite A at 80 °C is shorter in the two-phase segmented microfluidic reactor than in the single-phase microfluidic reactor. Furthermore, the MS, PSD and CV

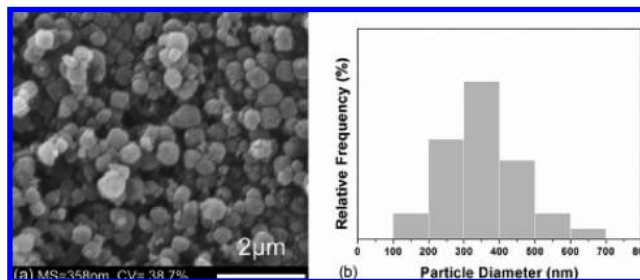


Figure 5. SEM image (a) and PSD (b) of zeolite A synthesized at 80 °C for 15 min in a single-phase microfluidic reactor (1 mm i.d. tube) using the aged synthesis solution.

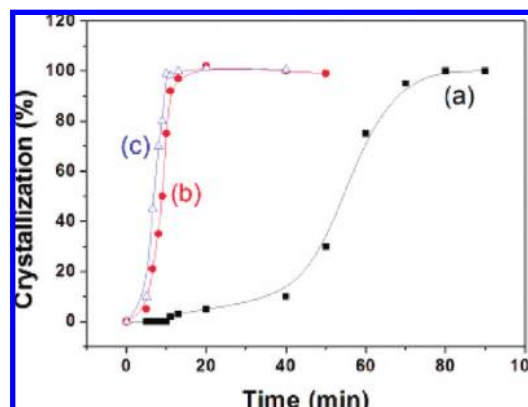


Figure 6. Crystallization curves of the fresh synthesis solution conducted in the conventional batch reactor (a), the segmented flow microreactor with the 1.0 mm i.d. outer tube (b), and the microwave-heated reactor (c).

value of the products synthesized in the single-phase microfluidic reactor are, respectively, larger, wider, and higher than those synthesized in the two-phase segmented microfluidic reactor (358 vs 262 nm, 170–600 vs 100–420 nm, and 38.7% vs 28.2%). For synthesis in the two-phase segmented microfluidic reactor, the reduction of reaction time may attribute to the recirculation and mixing occurred within the segments, leading to intensify the crystallization of zeolite A. On the other hand, both the consumption of the nutrients and the large number of the nuclei in each segment limit the further nucleation and grow-up of the crystals, since the nutrients can not be supplied from the adjacent liquid paraffin segments. Furthermore, segmented flow pattern eliminates the axial dispersion effects associated with the single-phase flow^{16,45} and sharpens the residence time distribution of synthesis solution.^{28,39} As a result, smaller particles with a narrower PSD can be produced in the segmented microfluidic reactor.

It is well-known that the synthesis time can be shortened significantly using a microfluidic reactor.^{17,23,39} For comparison, experiments of zeolite A syntheses were conducted in a microwave-heated batch reactor and a traditional oven-heated batch reactor with the fresh synthesis solution, since microwave is well-known as a means of quite fast synthesis of zeolites.^{40,46–48} Figure 6 shows the crystallization curves of zeolite A synthesized at 90 °C in the two batch reactors and the two-phase segmented microfluidic reactor (1.0 mm i.d. outer tube) and Figure 7 shows SEM pictures of the fully crystallized relevant products and the PSDs of these samples. We can see from Figure 6 that the crystallinities of products increase with the prolongation of crystallization time to a plateau of 100%. The crystallization rate in the microwave-heated batch reactor and the two-phase segmented microfluidic reactor are very close, with the time for completing crystallization of about 10–12 min (Figure

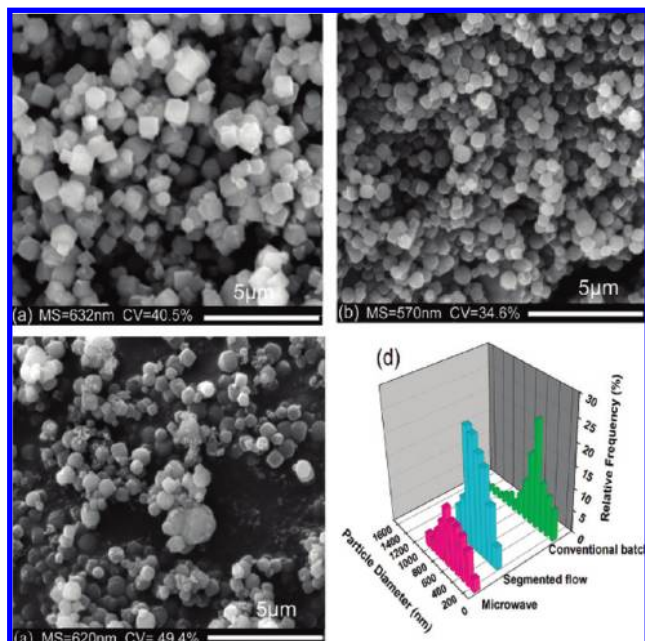


Figure 7. SEM images of zeolite A synthesized from the fresh synthesis solution at 90 °C in the microwave-heated batch reactor for 10 min (a), the segmented microfluidic reactor (1.0 mm i.d. tube) for 12 min (b), and the conventional batch reactor for 80 min (c) and three-dimensional columns of PSDs of the three samples (d).

6a and b). In contrast, the crystallization rate in the conventional batch reactor is much lower, with the time for completing crystallization of about 80 min (Figure 6c). The high crystallization rate in the microwave-heated batch reactor is ascribed to fast dissolution of the gel resulted from the rapid heat-up of the synthesis solution.^{1,40,46} This explanation can also be used to elucidate the high crystallization rate in the two-phase segmented microfluidic reactor. Furthermore, the shearing interactions of the fluid inside the segment can cause the development of recirculation flow, which can enhance mixing efficiency and accelerate the crystallization process in the two-phase segmented microfluidic reactor^{27,39} by intensifying mass transfer of the nutrients in the gel; the bulk phase and the liquid phase filled in the cavities in the gel mass.⁴⁹ We can see from Figure 7 that all zeolite A crystals synthesized in the microwave-heated batch reactor exhibit cubic morphology, with the MS, PSD, and CV values of 632 nm, 120–850 nm, and 40.5%, respectively. Zeolite A crystals synthesized in the two-phase segmented microfluidic reactor are mostly round and partially cubic in shape, with the MS, PSD, and CV values of 570 nm, 100–700 nm, and 34.6%, respectively. The morphology of products synthesized in the conventional batch reactor is all round. The MS, PSD, and CV values are 620 nm, 100–1500 nm, and 49.4%, respectively. Apparently, the MS and PSD of the products prepared in the segmented microfluidic reactor are smaller and narrower than those prepared in microwave-heated and conventional batch reactors. This may be attributed to the more uniform distribution of nuclei in the synthesis solution in the segmented microfluidic reactor than that in both microwave-heated and conventional synthesis batch reactors.^{39,50} Furthermore, the nutrients cannot be supplied from the adjacent liquid paraffin segments in the segmented microfluidic reactor, avoiding the excessive growth of zeolite crystals. In addition, the mean particle sizes of zeolite A crystals synthesized in the microwave-heated and conventional batch reactors are very close. This is consistent with that reported by slangen and co-

workers, due to the usage of the fresh synthesis solution rather than the aged synthesis solution.⁴⁷

4. Conclusion

Ultrafine zeolite A crystals with narrow particle size distribution can be synthesized using water–liquid paraffin two-phase segmented microfluidic reactors. The microchannels were not clogged for tens of hours of continuous synthesis even though the fresh synthesis solution was used. When the fresh synthesis solution was applied, elevation of the reaction temperature could lead to reduction of crystallization time, increase of the MS and no obvious change of the PSD span of final products. On the other hand, aging of the synthesis solution resulted in reduction of crystallization time of zeolite A, but no obvious change of both the MS and PSD span of final products in the temperature range of 80–100 °C. Decreasing the size of outer tube could reduce the crystallization time, MS, and PSD. The crystallization rate in the segmented microfluidic reactor was comparable to that in the microwave-heated batch reactor, but was much higher than that in the conventional batch reactor and single-phase microfluidic reactor. The MS and PSD of the resulting zeolite A synthesized in the segmented microfluidic device were smaller and narrower than those produced in the conventional and microwave-heated batch reactor and the single-phase microfluidic reactor. By using the fresh synthesis solution and aged synthesis solution, zeolite A crystals with MSs of 408 and 262 nm and PSDs of 150–620 and 100–420 nm were prepared in the segmented microfluidic reactor (0.6 mm i.d. inner tube and 1 mm i.d. outer tube) at 80 °C for 20 and 5 min, respectively. The MS and PSD of zeolite A are believed to be further decreased by reducing the sizes of the inner and outer tubes, and this method is applicable to the synthesis of other types of zeolites.

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Supporting Information Available: (1) Selection of flow rate of synthesis solution and liquid paraffin. (2) Formation of fully crystalline zeolite A in the segmented microfluidic device (1.5 mm i.d. outer tube) at 80, 90, and 100 °C using fresh synthesis solution. (3) FTIR spectra of highly crystalline zeolite A synthesized using fresh synthesis solution in the segmented microfluidic device (1.5 mm i.d. outer tube) at 80, 90, and 100 °C. (4) Calculation of activation energies of nucleation and crystallization. (5) XRD patterns of zeolite A synthesized using the fresh synthesis solution at 80 °C in segmented microfluidic reactors with outer tubes of 1, 1.5, 3 mm i.d. at various times. (6) XRD patterns of the solids separated from the synthesis solutions aged at 30 °C for 20 and 22 h. (7) FESEM images of zeolite A synthesized using the aged synthesis solution at 80 °C for 5 min in the segmented microfluidic reactor with 1 mm i.d. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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