Synthesis of Template-Free Zeolite Nanocrystals by Reverse Microemulsion−Microwave Method

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Many new applications for zeolite materials such as low dielectric constant films for chips and polymer−zeolite nanocomposite membranes for fuel cells require small, uniform, dispersible, and template-free zeolite nanocrystals, whose synthesis has so far proved difficult. Here we report an effective strategy to produce such zeolite nanocrystals by using microwave heating in reverse microemulsion (water in oil). The reverse microemulsion possibly acts as a space-confining nanoreactor, and microwave provides fast, homogeneous, and preferential heating of the aqueous phase (not the oil phase) where zeolite crystals are produced. As an example, the synthesis of template-free zeolite A nanocrystals (40−80 nm) is presented. The method demonstrated can potentially provide a general route to synthesize small, uniform, dispersible, and template-free zeolite nanocrystals.

1. Introduction

Zeolite nanocrystals have been demonstrated as excellent “building blocks” for constructing hierarchical porous materials[1−4] and as a component for functional films such as low dielectric constant (low-k) films for future generation computer chips[5,6] and polymer−zeolite nanocomposite membranes for gas separation and fuel cells.[7,8] Most of these applications require dispersible nanocrystals with small and uniform diameter. The synthesis of zeolite nanocrystals has also been used as a model system for fundamental studies of zeolite nucleation and crystal growth.[9−11] At present, zeolite nanocrystals are mostly synthesized under conventional hydrothermal conditions and with the use of organic structure-directing agents (SDA).[1−11] Note that many zeolites (e.g., LTA, FAU), which can be readily synthesized into microcrystals (diameter > 100 nm) without the use of a template, have interestingly all required template for their nanocrystal synthesis. The template approach has several drawbacks. First, removal of the template is normally carried out by calcination, which leads to irreversible aggregation of the nanocrystals. Second, the use of template in the synthesis tends to change the Si/Al ratio of the final products that could drastically affect their applications (e.g., air separation). For example, zeolite A, synthesized by using template (tetramethylammonium), has a Si/Al ratio greater than 1, and as a result, after Na^+ exchange, it has a pore size larger than 4 Å.[7,8] In contrast, template-free synthesis leads to Si/Al = 1 and zeolite 4A after Na^+ exchange. The slight change in pore size impacts the air separation capability of zeolite A dramatically.[12] Last, template is expensive. Thus synthesis of zeolite nanocrystals with small uniform diameter and without the use of template is highly desirable.

Efforts have been made to minimize template-free zeolite crystal size by manipulating synthesis parameters.[13−15] Space-confined synthesis using carbon black[16] and starch[17] as space confinement additives has recently been developed to produce both templated and template-free zeolite nanocrystals.[16,17] But the carbon and starch have to be burned off at high temperatures (e.g., >400 °C) after synthesis, which may lead to nanocrystal aggregation and lower nanocrystal crystallinity. In our previous work,[18] dispersible template-free zeolite crystals have been synthesized using a thermoreversible polymer hydrogel. However, the size of the zeolite A crystals obtained is in a range of 20−180 nm.

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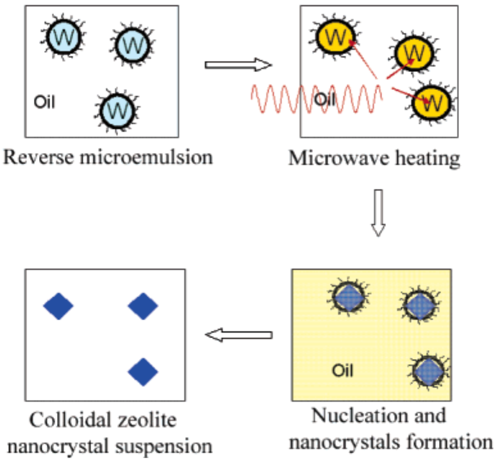

Figure 1. Schematic representation of microemulsion−microwave synthetic method.

Microemulsion−microwave method has been used to control zeolite crystal morphologies.[19−23] Here we report a method to prepare uniform and smaller template-free zeolite nanocrystals in reverse microemulsion by microwave heating. The reverse microemulsion consists of aqueous domains dispersed in a continuous oil phase. Under appropriate conditions, a variety of reactants can be introduced into the nanometer-sized aqueous domains for reaction, leading to materials with controlled size and shape. These small aqueous domains can be viewed as nanoreactors for synthesis of zeolite nanocrystals.[24,25] Microwave heating has found a number of applications in synthetic chemistry.[26] Compared with conventional heating, microwave heating has the advantages of short reaction time, producing small particles with a narrow size distribution and high purity. The combination of reverse microemulsion and microwave heating in our present study has the added advantage that the oil phase in the reverse microemulsion system is transparent to microwave so that the aqueous domains are heated directly, selectively, and rapidly. By contrast, in conventional heating, the heat is transferred from the oil phase to the aqueous domains through conduction so temperature gradient is expected. The microemulsion−microwave synthesis theme is schematically illustrated in Figure 1. To the best of our knowledge, this is the first report on the synthesis of template-free zeolite nanocrystals by reverse microemulsion−microwave method.

2. Experimental Procedures

2.1. Preparation of Synthesis Gel. First, a 250-mL polypropylene bottle containing a magnetic stir bar was washed with double deionized water (DDI H_2O) under ultrasonication. Then weighed amounts of DDI H_2O (161.1 g), sodium hydroxide (97% Aldrich, 20.0 g), and sodium aluminate ($Na_2O{\cdot}Al_2O_3{\cdot}3\ H_2O$, Spectrum, 10.9 g) were added, in that order, and stirred vigorously until the solution became clear. Aqueous 30 wt % colloidal silica (Ludox HS-30, Aldrich, 27.0 g) was then added to complete the solution. The solution became turbid at this time. The final molar composition of the synthesis gel for zeolite NaA was 5.85 Na_2O:2.7 SiO_2: 1.00 Al_2O_3:182 H_2O. The corresponding weight ratio was 3.56 Na_2O: 1.59 SiO_2:1.00 Al_2O_3:32.12 H_2O. The synthesis gel was sealed and aged overnight at room temperature (RT) with vigorous stirring. The solution was still turbid after the overnight aging.

2.2. Preparation of Reverse Microemulsion and Zeolite Nanocrystals. Microemulsion was prepared by solubilizing the synthesis gel prepared above into a mixture of cetyltrimethylammonium bromide (CTAB, Aldrich), *n*-butanol (99.8%, Aldrich), and cyclohexane (99.5%, Aldrich), in which CTAB and *n*-butanol were used as the surfactant and cosurfactant and cyclohexane as the oil phase. Note that the final mixture was transparent although the zeolite synthesis gel and the mixture of CTAB, *n*-butanol, and cyclohexane were not transparent before the mixing, indicating that microemulsion was formed in the final mixture. The molar ratios of cyclohexane/CTAB, *n*-butanol/CTAB, and water (in the synthesis gel)/CTAB were 130, 10, and 5, respectively. The preparation of zeolite nanocrystals was achieved by heating the microemulsion in a microwave (Denoted as MM-*x*, *x* is heating time in minutes) oven with a microwave frequency of 2450 MHz. Three control experiments were carried out, and they were microemulsion with conventional heating (MC-*x*), conventional synthesis mixture with microwave heating (CM-*x*), and conventional synthesis mixture with conventional heating (CC-*x*). The heating temperature of the all experiments was 75 °C.

Microwave heating was carried out in a microwave oven (MARS5, CEM Corporation, with 12 100-mL Teflon vessels). The heating profile was from room temperature to 75 °C within 2 min and then at 75 °C for a controlled amount of time without stirring. The maximum power output of the microwave was adjusted to 600 W. Conventional heating was conducted in a Teflon-lined pressure vessel in a convection oven preset at 75 °C for a desired amount of time without stirring.

For all of the experiments, the product was first cooled to room temperature. All samples were washed by five repetitions of centrifugation with relative centrifugal force of 48 500 g for 2 h, then decanting, and redispersion in ethanol and water with ultrasonication before analyses preparations were performed. Centrifugations were performed in a Beckman J2-HS centrifuge at 20,500 rpm using a JA-21 rotor.

2.3. Characterization. Zeolite type and crystallinity were determined by X-ray diffraction (XRD; Siemens D-500 diffractometer using Cu Kα radiation). Data were collected in step mode every 0.05 degrees for a 1-s duration. Particle size and crystal morphology of the samples were examined with a scanning electron microscope (SEM, Philips XL30-FEG at 20 kV). Dilute suspensions of washed nanocrystals in ethanol were used to prepare samples for transmission electron microscopy (TEM, Philips CM 300 at 200kV). Dynamic light scattering (DLS; ZetaPALS, Brookhaven Instruments Corporation) measurements were performed on dilute aqueous suspensions of washed nanocrystals.

3. Results and Discussion

Powder X-ray diffraction patterns of products from microemulsion with various microwave heating times at 75 °C are shown in Figure 2. After crystallization for 5 min, the

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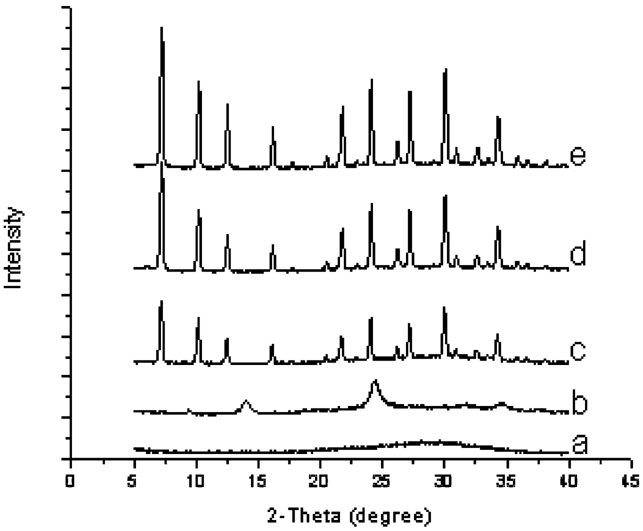

Figure 2. XRD patterns of samples from reverse microemulsion−microwave method at 75 °C: (a) MM-5; (b) MM-10; (c) MM-20; (d) MM-40; (e) MM-60.

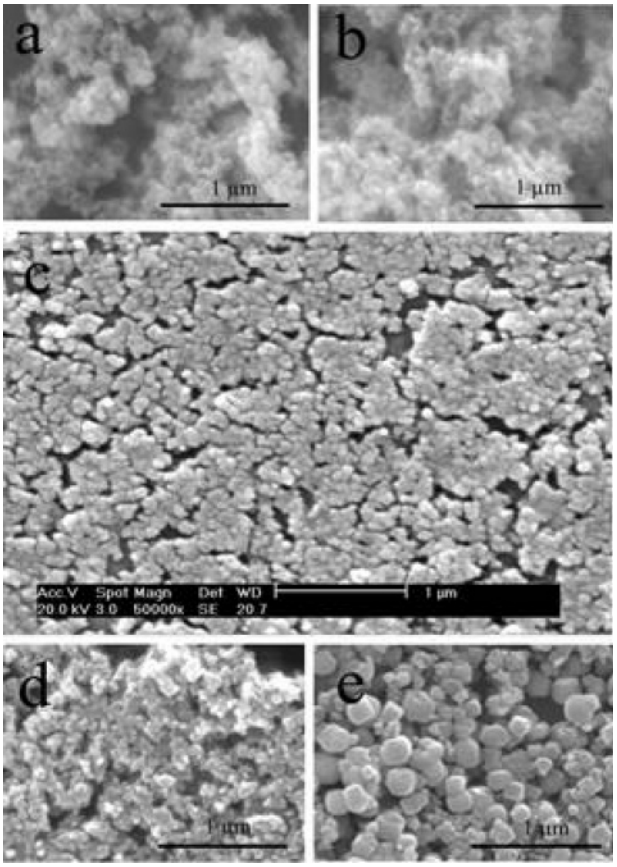

Figure 3. SEM images of samples from reverse microemulsion−microwave method at 75 °C: (a) MM-5; (b) MM-10; (c) MM-20; (d) MM-40; (e) MM-60. All scale bars here are 1 μm.

product MM-5 was amorphous. Crystalline material emerged in MM-10, and pure zeolite A crystals were formed after 20 min heating (MM-20). The XRD peak intensity increased with further increase of heating time (MM-4 and MM-60). The corresponding crystal morphologies of these samples are shown in Figure 3. Consistent with XRD, samples MM-5 and MM-10 appear to be amorphous (parts a and b of Figure 3). MM-20 contains nanocrystals with very uniform size (Figure 3c). With the increase of heating time from 20 to 60 min (parts c−e of Figure 3), the zeolite crystals become larger and the crystal size distribution becomes wider. This might be due to the fact that a stable microemulsion is difficult to maintain at elevated temperatures during the crystallization process. It is possible that, with the increase of heating time, some of the water droplets and nanocrystals in the microemulsion become unstable and they merge together. Under our experimental conditions, it is clear that 20 min is the optimal crystallization time to obtain uniform zeolite A nanocrystals (40−80 nm) using microwave heating. TEM image confirms that zeolite nanocrysyals from MM-20 are highly crystalline and have a narrow particle size distribution (about 60 nm) (Figure 4). Aqueous suspensions of washed nanocrystals were analyzed by DLS, and the mass median diameter was 78 nm for MM-20. This suggests good redispersibility for the nanocrystals.

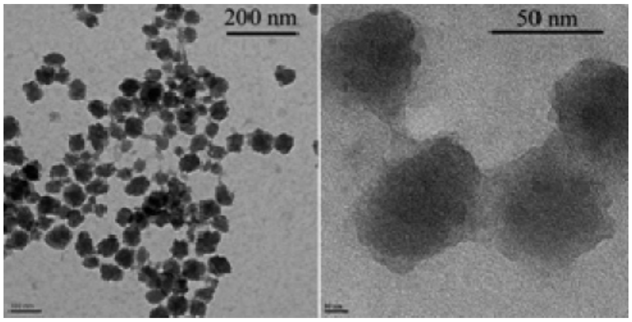

Figure 4. TEM micrographs of MM-20.

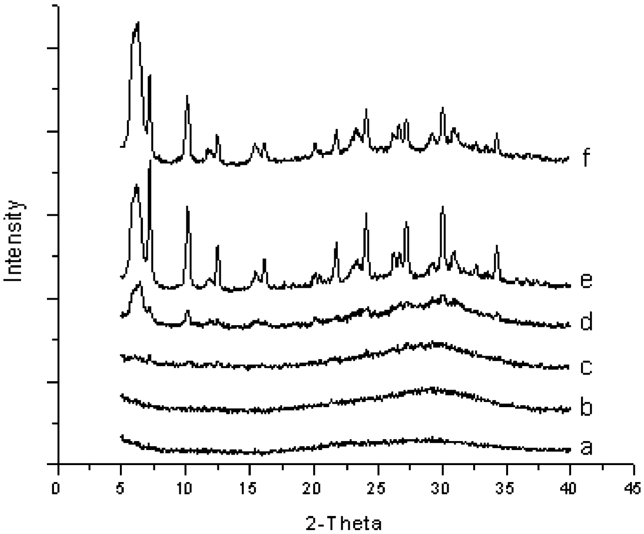

Figure 5. XRD patterns of samples from reverse microemulsion with conventional heating at 75 °C: (a) MC-20; (b) MC-40; (c) MC-60; (d) MC-90; (e) MC-120; (f) MC-150.

To demonstrate the favorable effect of the microemulsion−microwave method, three control experiments have been carried out. These three experiments are microemulsion with conventional heating (MC-*x*), conventional synthesis mixture with microwave heating (CM-*x*), and conventional synthesis mixture with conventional heating (CC-*x*).

XRD patterns of the samples from microemulsion with conventional heating method (MC-*x*) are shown in Figure 5. Only an amorphous solid appeared after crystallization for 20, 40, and 60 min (parts a, b, and c of Figure 5, respectively). Weak diffraction peaks were observed after

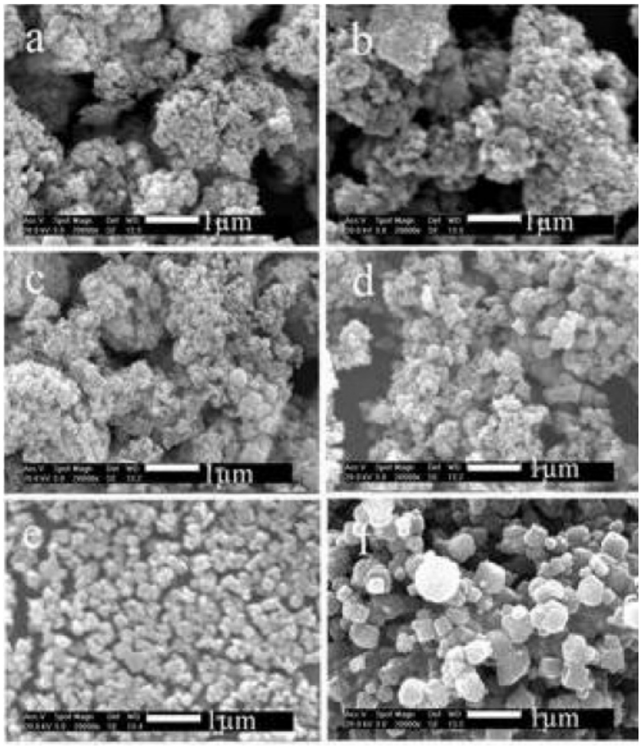

Figure 6. SEM images of samples from reverse microemulsion by conventional heating at 75 °C: (a) MC-20; (b) MC-40; (c) MC-60; (d) MC-90; (e) MC-120; (f) MC-150. All scale bars here are 1 *μ*m.

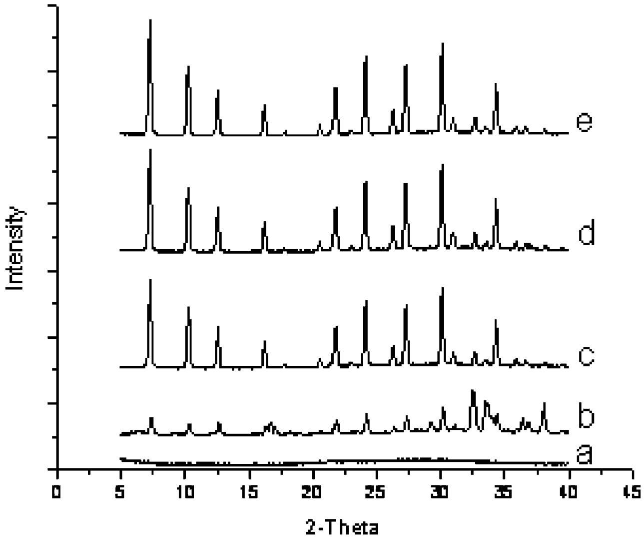

Figure 7. XRD patterns of samples from conventional synthesis mixture by microwave heating at 75 °C: (a) CM-5; (b) CM-10; (c) CM-20; (d) CM-40; (e) CM-60.

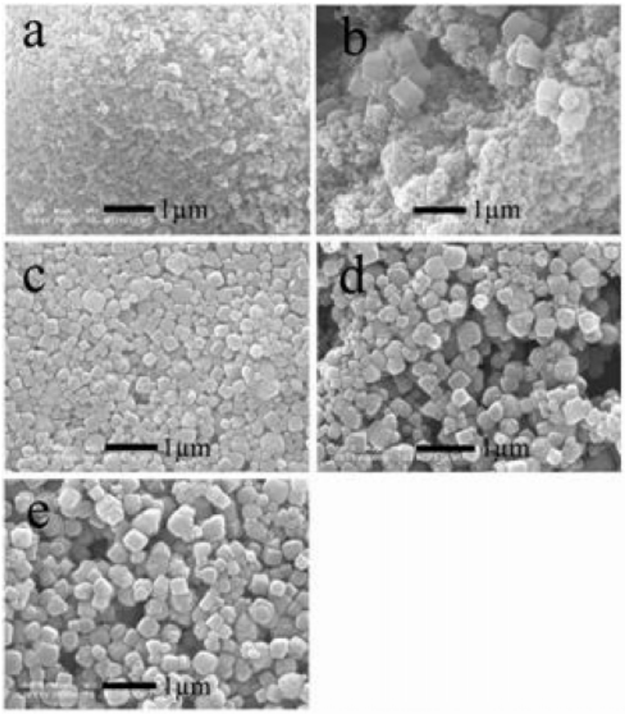

Figure 8. SEM images of samples from conventional synthesis mixture by microwave heating at 75 °C: (a) CM-5; (b) CM-10; (c) CM-20; (d) CM-40; (e) CM-60. All scale bars here are 1 *μ*m.

heating for 90 min (Figure 5d). Zeolite crystals were clearly formed after 120 min (Figure 5e). Parts e and f of Figure 5 both have features of a mixture of zeolite A and zeolite X. The corresponding crystal morphologies are shown in Figure 6. Only samples MC-120 (Figure 6e) and MC-150 (Figure 6f) appear crystalline consistent with XRD results (Figure 5).

For conventional synthesis mixture with microwave heating (CM-*x*), crystals were observed after heating for 10 min (Figure 7b). Zeolite A was clearly formed after 20 min (Figure 7c), and the diffraction peaks became stronger after heating for 40 min (Figure 7d). However, heating to 60 min did not result in significant further increase in the diffraction peak intensity (Figure 7e). The crystal morphologies of the CM-*x* samples are shown in Figure 8. It shows that it is amorphous solid after 5 min of heating (Figure 8a). After 10 min of heating it is a mixture of zeolite crystals and amorphous solid (Figure 8b). Figure 8c shows uniform zeolite A crystals. Parts d and e of Figure 8 show similar crystals, but in both cases, the crystals are larger than the crystals in Figure 8c. The XRD results are consistent with SEM observations.

The XRD patterns and SEM images of samples from conventional synthesis mixture with conventional heating (CC-*x*) are shown in Figures 9 and 10, respectively. Parts a−c of Figure 9 indicate that after heating for 60 min the samples were still amorphous. Only weak diffraction peaks were observed after heating the synthesis gel for 90 min. Zeolite crystals were clearly formed after 120 min (Figure 9d). Heating to 150 min lead to slightly stronger diffraction peaks. Similar to the cases of MC and CM samples, the XRD results for CC samples are confirmed by SEM observations.

To clearly demonstrate the advantages of the MM method, XRD patterns of four selected samples are presented in Figure 11 and the corresponding SEM micrographs are as shown in Figure 12. We selected MM-20, MC-120, CM-20, and CC-120 because each of these samples is the one that is fully crystalline and has the smallest crystal diameter in its own series.

Microemulsion−microwave method (Figures 11a and 12a, MM-20, 40−80 nm) produces smaller, more uniform, and purer zeolite nanocrystals than the conventional synthesis mixture and conventional heating method (Figures 11d and 12d, CC-120, 100−800 nm). MM-20 is pure zeolite A, while CC-120 is a mixture of zeolite A and X. The improved size

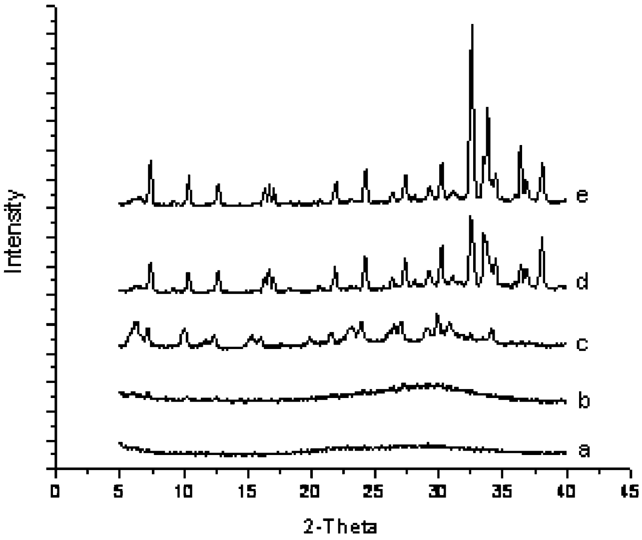

Figure 9. XRD patterns of samples from conventional synthesis mixture by conventional heating at 75 °C: (a) CC-30; (b) CC-60; (c) CC-90; (d) CC-120; (e) CC-150.

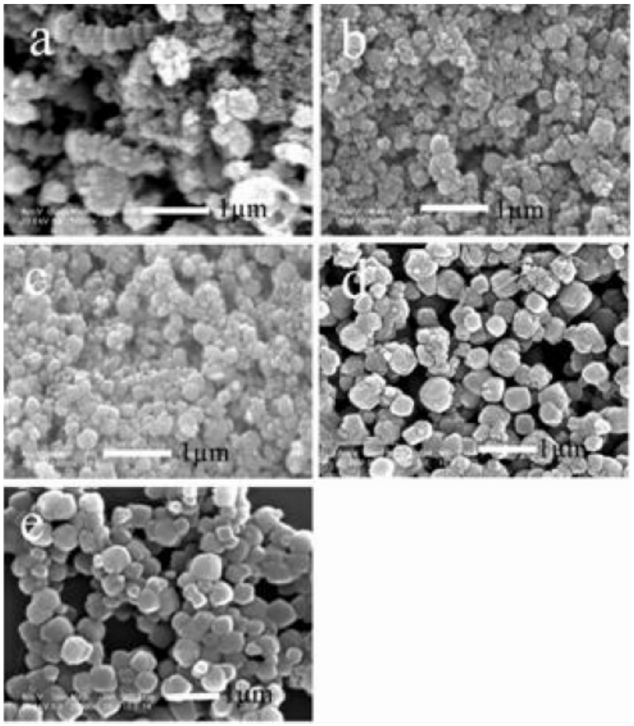

Figure 10. SEM images of samples from conventional synthesis mixture by conventional heating at 75 °C: (a) CC-30; (b) CC-60; (c) CC-90; (d) CC-120; (e) CC-150. All scale bars here are 1 μm.

uniformity and purity of the nanocrystals seem to be general for microwave heating (MM-20, pure zeolite A, diameter 40−80 nm; CM-20, pure zeolite A, diameter 100−400 nm; MC-120, mixture of zeolite A and X, diameter 50−200 nm; CC-120, mixture of zeolite A and X, diameter 100−800 nm). It is believed that microwave heating offers faster and more uniform heating than conventional heating and thus leads to more uniform generation and growth of nuclei and avoids the formation of impurity phase.

The advantage of reverse microemulsion over conventional synthesis mixture is clear by comparing MM-20 (40−80 nm) with CM-20 (100−400 nm) and MC-120 (50−200 nm) with CC-120 (100−800 nm). The crystals from reverse microemulsion are much smaller than those from conventional synthesis mixture. The surfactant-covered water droplets in reverse microemulsion offer a unique microenvironment for the formation of nanoparticles. They may have possibly served as nanoreactors for nucleation and crystal growth and inhibited the excess aggregation of particles because the surfactants can absorb on the particle surface.

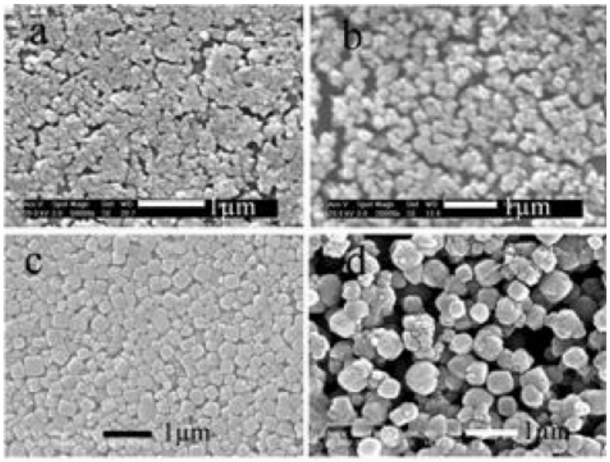

Figure 11. SEM images of zeolite A crystals: (a) MM-20; (b) MC-120; (c) CM-20; (d) CC-120. All scale bars are 1 μm.

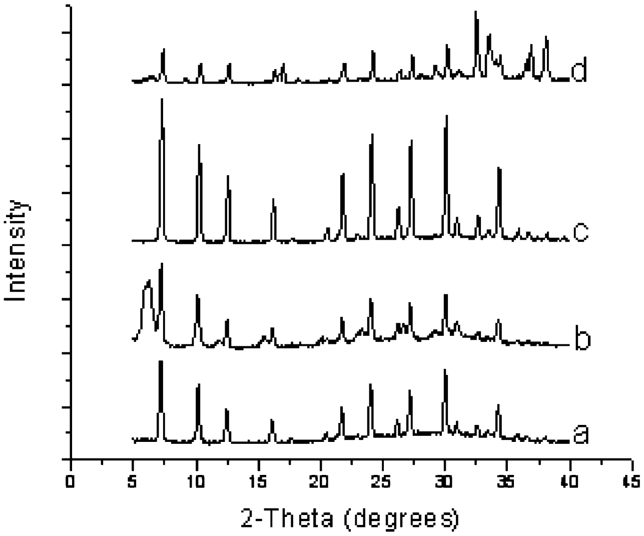

Figure 12. XRD patterns of zeolite A crystals (a) MM-20; (b) MC-120; (c) CM-20; (d) CC-120.

In summary, we have provided the essential results necessary to demonstrate the effectiveness of reverse microemulsion−microwave synthesis method. As an example, we have successfully synthesized pure zeolite A nanocrystals with uniform and small size (40−80 nm). It is believed that the strategy developed here provides a unique, effective, and potentially general methodology to the preparation of uniform and high purity nanocrystals of template-free zeolites (zeolite Y and X are obvious examples) and zeolite-like materials.

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