

## **Electronic supplementary information (ESI)**

# **Preparation of Uniform Nano-Sized Zeolite A Crystals in Microstructured Reactors Using Manipulated Organic Template-Free Synthesis Solutions<sup>†</sup>**

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## **Experimental Section**

### **Materials**

Sodium aluminate, sodium silicate, sodium hydroxide (NaOH) and liquid paraffin were all purchased from Sinopharm Chemical Reagent Co., Ltd., and **deionized water** was all used in the synthesis. All chemicals were used as received without further purification.

### **Preparation of the milky gel solution (MGS)**

The MGS was prepared following the composition and preparation steps in ref 12. First, a NaOH aqueous solution was prepared by dissolving 9.14 g NaOH in 60 mL deionized water. Then, the solution was divided into two equal volumes. One NaOH solution was added with 3.0 g sodium aluminate to get an aluminate solution, and the other was added with 6.44 g sodium silicate to get a silicate solution. After completely dissolving, the silicate solution was added to the aluminate solution with vigorous stirring to obtain a heterogeneous solution with a molar composition of the final mixture of 6.5 Na<sub>2</sub>O: 0.6 Al<sub>2</sub>O<sub>3</sub>: 1.0 SiO<sub>2</sub>: 150 H<sub>2</sub>O. This heterogeneous solution was aged at 30 °C for 20 h.

### **Preparation of the silica-aluminum clear solution (SACS), the silica clear solution (SCS), the aluminum clear solution (ACS) and the zeolite A synthesis solutions**

The SACS was prepared following the composition and preparation steps in ref 19. First, a NaOH aqueous solution was prepared by dissolving 34.2 g NaOH in 200 mL deionized water. Then, the solution was divided into two volumes. One third of the NaOH solution was added with 3.34 g

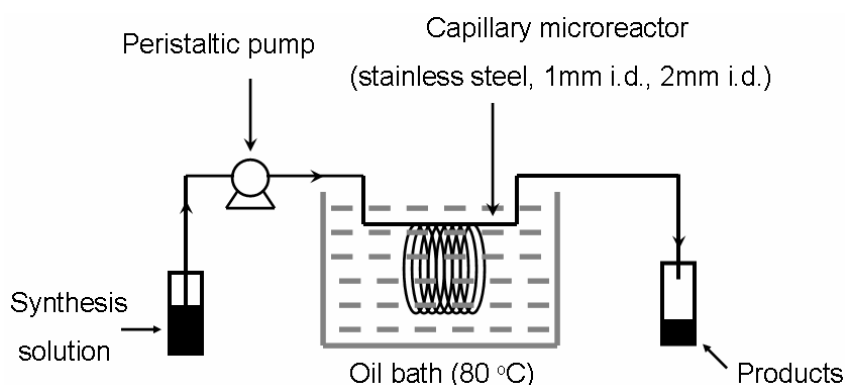
sodium aluminate to get an aluminate solution, and two thirds of the NaOH solution was added with 21.86 g sodium silicate to get a silicate solution. After completely dissolving, the silicate solution was added to the aluminate solution with vigorous stirring to obtain a clear solution with a molar composition of  $8.6 \text{ Na}_2\text{O} : 0.18 \text{ Al}_2\text{O}_3 : 1.0 \text{ SiO}_2 : 150 \text{ H}_2\text{O}$ . This clear solution was denoted as SACS.

The SCS was prepared by successively mixing 1.71 g NaOH and 1.093 g sodium silicate in 10 mL deionized water. The ACS was prepared by successively mixing 1.71 g NaOH and 0.167 g sodium aluminate in 10 mL deionized water. The molar compositions of the SCS and the ACS were, respectively,  $8.6 \text{ Na}_2\text{O} : 1.0 \text{ SiO}_2 : 150 \text{ H}_2\text{O}$  and  $8.6 \text{ Na}_2\text{O} : 0.18 \text{ Al}_2\text{O}_3 : 150 \text{ H}_2\text{O}$ .

The zeolite A synthesis solutions were prepared by mixing 20 mL MGS and 0–40 mL SACS (or SCS, ACS) for 30 min at room temperature. The detailed composition of the synthesis solution is listed in Table 1.

### Synthesis of nano-sized zeolite A

Nano-sized zeolite A crystals were first prepared in a single-phase flow stainless steel capillary microreactor as shown in Figure S1. The synthesis solution was injected into the stainless steel capillary (1 mm i.d., 2 mm o.d.), which was immersed in a 80 °C oil bath, by a peristaltic pump at a fixed flow rate of 0.4 mL/min. The residence time of the synthesis solution inside the microreactor was adjusted from 4.5 to 7.5 min by changing the length of capillary from 2.0 to 3.5 m. The effluent was collected at the outlet of the capillary. The product was separated from the collected effluent after five cycles of centrifuging (10000rpm, 10min) and washing with deionized water. It was finally dried at 80 °C overnight.

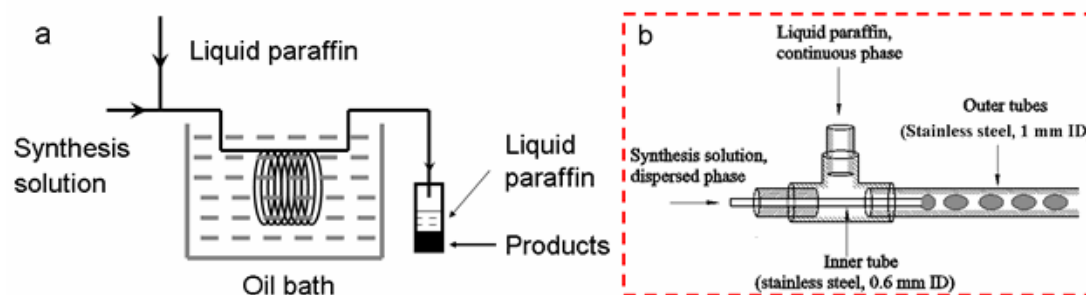


**Fig. S1** Scheme of the single-phase flow stainless steel capillary microreactor for preparation of nano-sized zeolite A crystals.

Nano-sized zeolite A crystals were also prepared a water-liquid paraffin two-phase segmented

microfluidic reactor as shown in Figure S2. The reactor was assembled by positioning a stainless steel inner tube (0.6 mm i.d., 0.8 mm o.d.) directly in the axis of the stainless steel capillary microreactor (i.d. 1 mm, length 12 m). The synthesis solution, prepared by mixing 10 mL SACS into 20 mL MGS, as a dispersed phase, was pumped into the inner tube by a peristaltic 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, and the temperature of which was accurately controlled at 80 °C. The flow rates of the synthesis solution and liquid paraffin injected were fixed at 0.4 and 1 mL/min, respectively, and the residence time of the synthesis solution was 7.5 min. The synthesis solution was broken up into highly uniform segments by the paraffin flow, resulting from the competition between viscous stress and capillary stress.<sup>17</sup> After synthesis, the upper liquid paraffin was decanted, and then the products were separated by centrifuging and washing with hexane and deionized water by five repetitions. Finally, the products were dried at 80 °C for 24 h.

For comparison, the syntheses of zeolite A crystals from synthesis solution of 20 mL MGS and 10 mL SACS were also conducted in a conventional batch reactor. The synthesis solution was charged into a sealed 100 mL polypropylene bottle, which is kept in an oven preheated at 80 °C. Small aliquots of the synthesis solution were taken at different periods of time, i.e., 20, 40 and 60 min. Finally, samples were obtained after five cycles of centrifuging and washed with deionized water, followed by drying at 80 °C overnight.



**Fig. S2** Scheme of a two-phase liquid segmented microfluidic system for nano-sized zeolite A synthesis (a) and detailed illustration of the coaxial dual pipe assembly (b).

### Characterization

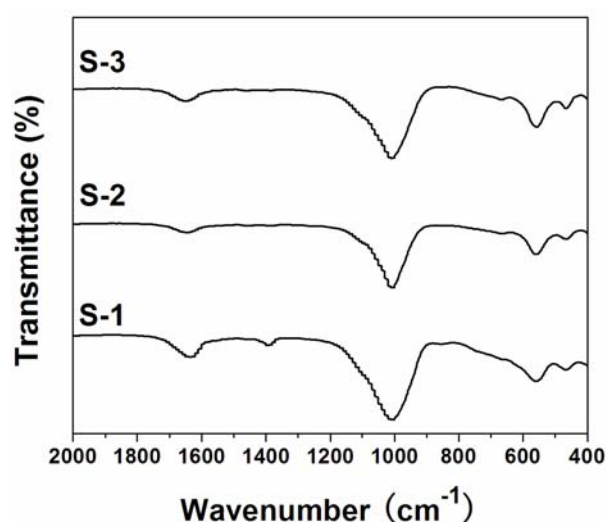
X-ray diffraction (XRD) patterns were collected on the Bruker D8 ADVANCE powder diffractometer using Ni-filtered CuK $\alpha$  radiation source at 40 kV and 20 mA. The Fourier transform infrared (FTIR) spectra were obtained on the Nexus 870 FTIR spectrometer. Samples were mixed

and ground with KBr for FTIR measurement in the wave number range of 2000–400  $\text{cm}^{-1}$ .  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios of the samples were estimated from energy dispersive X-ray spectroscopy (EDXS) on the PHILIPS-Quanta200 microscope. Nitrogen adsorption measurements were carried out on a Micromeritics ASAP2020 surface area analyzer at 77 K, after outgassing the samples at 300  $^\circ\text{C}$  for 2 h. The specific surface area was determined from the linear part of the BET equation ( $P/P_0 = 0.05\text{--}0.15$ ). The size and morphology of zeolite crystals were observed with field-emission microscopy (LEO-1530 or Hitachi-S4800). The mean particle size and particle size distribution of samples were also determined by manual measurement of about 300 crystals in SEM pictures by Adobe Photoshop 7.0 software, and the coefficient variation (CV) value was defined as the following equation. The lower the CV value, the more uniform particle size of crystals becomes.<sup>21</sup>

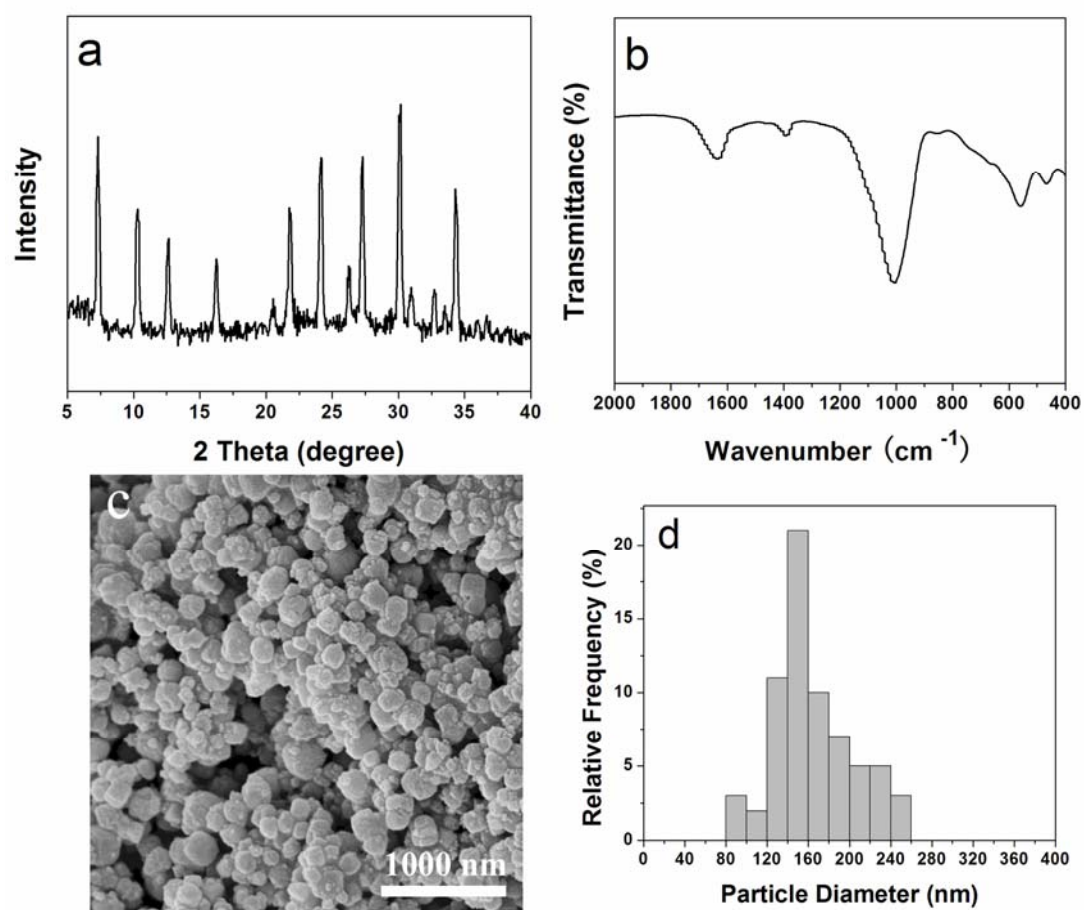
$$CV = \frac{\left[ \sum_{i=1}^n \frac{(d_i - d)^2}{n} \right]^{\frac{1}{2}}}{d}$$

Where  $d_i$  is the diameter of the  $i^{\text{th}}$  zeolite crystal,  $d$  is the average diameter and  $n$  is the total number of the crystals counted.

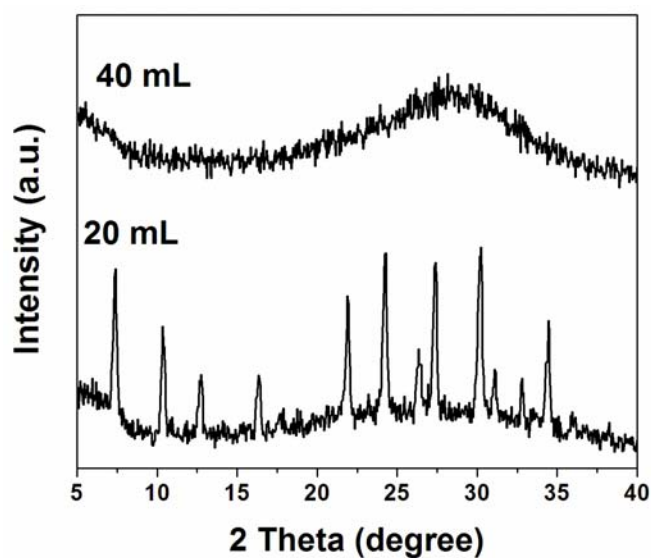
## Figures



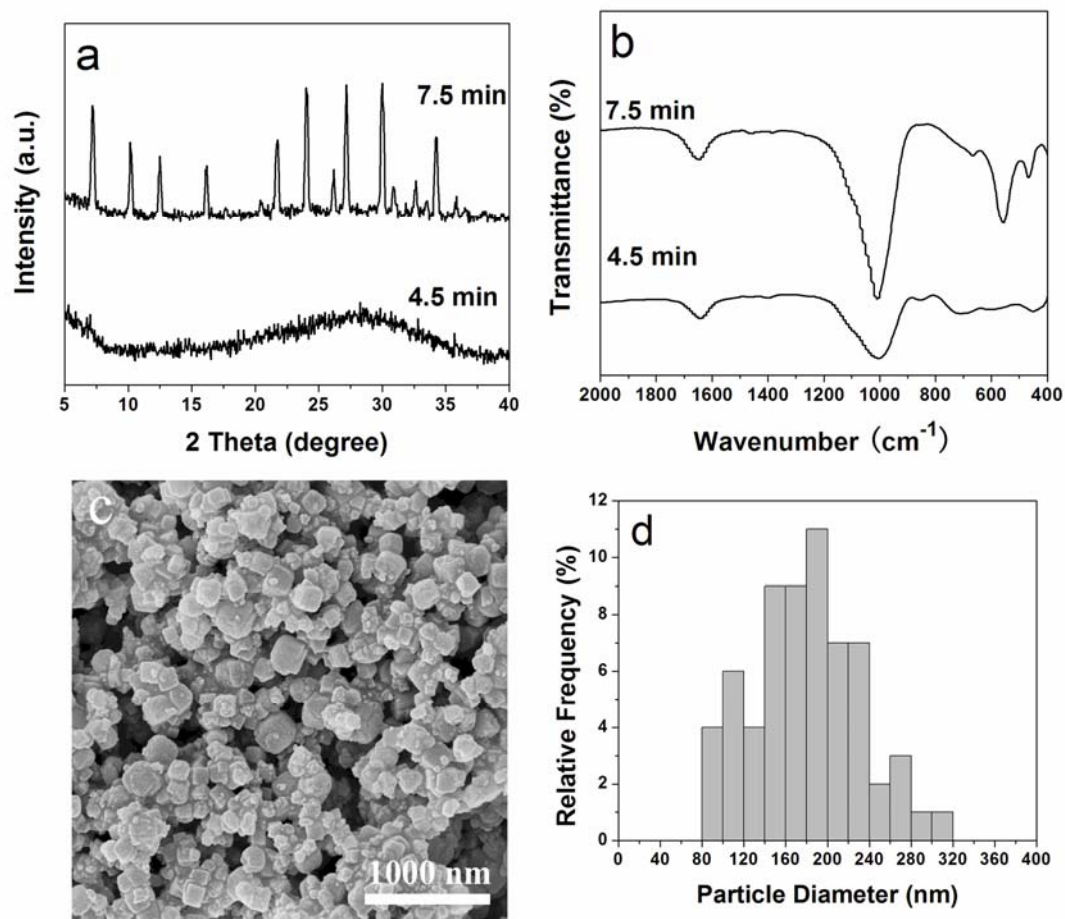
**Fig. S3** FTIR spectra of nano-sized zeolite A crystals (samples S-1, S-2 and S-3).



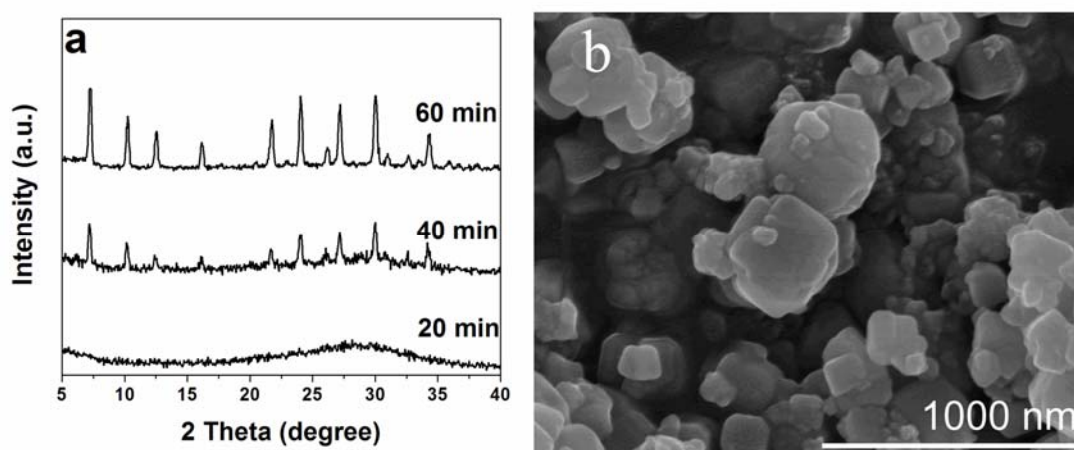
**Fig. S4** XRD pattern (a), FTIR spectrum (b), SEM image (c) and particle size distribution (d) of sample S-4.



**Fig. S5** XRD patterns of products prepared at 80 °C for 7.5 min in microreactors with the synthesis solution of 20 mL MGS and 20–40 mL SACS.



**Fig. S6** XRD patterns (a), FTIR spectra (b) of products synthesized at 80 °C for 4.5 and 7.5 min using only 20 mL MGS, and SEM image (c) and particle size distribution (d) of products with a residence time of 7.5 min (sample S-5).



**Fig. S7** XRD patterns (a) of products synthesized at 80 °C for 20–60 min in 100 mL conventional batch reactor with the synthesis solution of 20 mL MGS and 10 mL SACS, and SEM image (b) of products synthesized for 60 min (sample S-7).