Supporting Information

Addressing the Viscosity Challenge:
Ultrafast, Stable-Flow Synthesis of Zeolites with An Emulsion Method

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Contents

1, Experimental section

1.1 Design of the continuous flow system

1.2 Continuous flow synthesis of ERI zeolite with emulsion method

1.3 Synthesis of ZSM-5 zeolite in the sealed pipe reactor with emulsion method

1.4 Continuous flow synthesis of *BEA zeolite with emulsion method

1.5 Continuous flow synthesis of CHA zeolite with emulsion method

2, Characterization

3, Supplementary Tables

Table S1 Conductivity test results of emulsions prepared with different surfactants

4, Supplementary Figures

Figure S1 Continuous flow system components

Figure S2 Photographs of the reactant mixture over different heating periods

Figure S3 Typical pressure profile for the continuous flow synthesis of ERI zeolite without emulsion method

Figure S4 Optical micrograph of the emulsions prepared with different surfactants

Figure S5 Viscosity change after the addition of different surfactants to the initial reactant mixture

Figure S6 Hydrothermal stability test results of ERI product and ERI seed

Figure S7 Typical temperature profile for the continuous flow synthesis of ERI zeolite with emulsion method

Figure S8 SEM image of ERI product synthesized with different amounts of surfactant in
the sealed pipe reactor

Figure S9  Powder X-ray diffraction patterns of ZSM-5 zeolite synthesized with different amounts of surfactant in the sealed pipe reactor

Figure S10  SEM images of ZSM-5 products synthesized with different amounts of surfactant in the sealed pipe reactor

Figure S11  Typical temperature profile for the continuous flow synthesis of *BEA zeolite with emulsion method

Figure S12  Typical pressure profile for the continuous flow synthesis of *BEA zeolite with emulsion method

Figure S13  SEM images of *BEA product synthesized in the continuous flow reactor and conventional *BEA synthesized in the autoclave

Figure S14  SEM image of milled SSZ-13 seed crystals

Figure S15  XRD patterns of SSZ-13 zeolite synthesized at different temperatures in the continuous flow reactor with emulsion method
1, Experimental section

1.1 Design of continuous flow system

The schematic layout of the continuous flow system is presented in Figure S1. The apparatus consists of the following key components: HPLC pumps, electronic heaters and temperature controller (MTCS, Misumi), pressure gauges (PGI-63B-MG10-LAQX, Swagelok), compressed-air-driven vibrator, back-pressure regulator (TESCOM 26–1700, Emerson, US), and an in-house-assembled computer control system. All the continuous flow reactors and necessary connecting units are made from stainless steel standard parts (purchased from Swagelok).

In a typical operation, the system was gradually preheated to the target temperatures using water as a circulating medium, and accordingly, the system pressure was adjusted to 16 MPa using the back-pressure regulator. Once the temperature and pressure conditions were steady, the synthesis reactant was fed to replace the circulating water, and the continuous flow synthesis started. The homogenized emulsion flowed in a pipe-in-pipe system, in which a Teflon tube was placed inside a stainless tube to prevent the formed solid phase from sticking to the wall of the reactor. The length of the continuous flow reactor was 1400 mm. The inlet and outlet diameter of the stainless tube were 4.4 mm and 6.4 mm, respectively. The inlet and outlet diameter of Teflon tube were 2.0 mm and 4.0 mm, respectively. In the case of ERI and *BEA zeolites, the residence time is 7 min and the residence volume is calculated as 4.41 cm³. While for SSZ-13, the residence time is 2 min and the residence volume is calculated as 1.26 cm³. The flow rates for the synthesis reactant mixture and the hot water were maintained at 0.63 mL/min and 2.0 mL/min, respectively, which resulted in a synthesis temperature of 210 °C or 240 °C, respectively. At the outlet of the continuous flow reactor, cooling water was fed to cool down the slurry at a flow rate of 10 mL/min. To minimize the precipitation of the solids, the compressed air-driven vibrator kept shaking the continuous flow reactor at a frequency of about 100 Hz under a pressure of 0.1 MPa. The product flowing out of the continuous flow reactor was centrifuged, washed, and dried to obtain the final zeolite crystals.

1.2 Continuous flow synthesis of ERI zeolite with emulsion method

The composition of the initial reactant mixture was as follows: 1.63 RBr₂/10.4 KOH/0.8 Al₂O₃/16 SiO₂/258 H₂O, where RBr₂ represents hexamethonium bromide. First, aluminum sec-butoxide (Al[OCH(CH₃)C₂H₅]₃, 97%, Aldrich) was dissolved in potassium hydroxide
solution (Wako Pure Chemical Industries, Ltd. 30 wt.%), followed by the dropwise addition of a solution containing hexamethonium bromide dissolved in deionized water. Colloidal silica (LUDOX® AS-40, 40 wt.% suspension) and deionized water were then slowly added to form an aluminosilicate reactant. The reactant mixture was homogenized for 2 h and aged for 20 h at 95 °C in an oven. To this aluminosilicate mixture, 20 wt.% ERI seed crystals synthesized via the charge density mismatch (CDM) method were added and the resulting reactant was stirred for 10 min.[1] The emulsion was prepared by mixing the aluminosilicate reactant mixture with the surfactant(sorbitan monooleate, span 80) and organic solvent (cyclohexane) and then homogenizing with an ultrasonic vibration machine. The mass ratio of the aluminosilicate reactant mixture: cyclohexane: span 80 was fixed at 1: 1: 0.1. Finally, 10ml of the homogenized emulsion was fed into the continuous flow reactor at 240 °C/ 210 °C for 7 min. The product flowing out of the continuous flow reactor was centrifuged, washed, and dried overnight at 80 °C in an oven to obtain the final zeolite crystals. The Si/Al ratio of ERI product was 4.2 with a yield of 26wt.%.  

1.3 Synthesis of ZSM-5 zeolite in the sealed pipe reactor with emulsion method  

The composition of the initial reactant mixture was as follows: 50 NaOH/Al₂O₃/300 SiO₂/20 TPAOH/2300 H₂O. The reagents used for the preparation of ZSM-5 zeolite included colloidal silica (LUDOX AS-40, 40 wt. % suspension in H₂O), aluminum hydroxide (crystalline, Wako, 100%), TPAOH solution (40wt% aqueous solution, Merck), and NaOH aqueous solution (Wako Pure Chemical Industries, Ltd. 20 wt.%). Initially, aluminum hydroxide, TPAOH solution and NaOH aqueous solution were mixed and stirred for 5 min, followed by the addition of colloidal silica. After homogenization for 30 min, the well-mixed reactant mixture was aged at 90 °C in an oven under rotation with a speed of 20 rpm. The aged reactant mixture was added to the surfactant-organic solvent and mixed using an ultrasonic vibration machine to achieve adequate homogenization. The mass ratio of the aluminosilicate reactant mixture: cyclohexane: span 80 was fixed as 1: 1: 0.1. Finally, 10ml of the homogenized emulsion was fed into the sealed pipe reactor, and heated at 210 °C for 10 min. The solid products were recovered by centrifugation, washed with deionized water and dried at 80 °C. The Si/Al ratio of ZSM-5 product was 105 with a yield of 60 wt.%.  

1.4 Continuous flow synthesis of *BEA zeolite with emulsion method  

The synthesis mixture had a composition of 0.15 TEAOH/0.6 NaOH/0.022 Al₂O₃/1.0
SiO$_2$/18 H$_2$O, which was prepared as follows: sodium hydroxide (NaOH) solution (Wako Pure Chemical Industries, Ltd. 20 wt.%), aluminum hydroxide (Al(OH)$_3$) (non-crystalline, Sigma-Adrich, 99% as Al$_2$O$_3$), and tetraethylammonium hydroxide (TEAOH) solution (35 wt.% aqueous solution, Sigma-Aldrich) were mixed and stirred for 30 min, and the colloidal silica (LUDOX® HS-40, 40 wt.% suspension) was then added and stirred for an additional 1 h. Afterward, 10 wt.% of as-synthesized *BEA was added into the aluminosilicate mixture as seed crystals and the resulting reactant was well mixed with the surfactant-organic solvent. The seed crystals were synthesized with the following chemical compositions: 0.2TEAOH/0.12NaOH/0.04Al$_2$O$_3$/1.0SiO$_2$/20H$_2$O. Firstly non-crystalline aluminum hydroxide was dissolved with TEAOH and 20 wt% sodium hydroxide. The mixture was stirred for 30 min, followed by the addition of colloidal silica. The homogenized reactant mixture was then transferred into a 23 ml stainless steel Teflon®-lined autoclave and heated at 160 °C for 2 days. The emulsion was prepared by using an ultrasonic vibration machine. The mass ratio of the aluminosilicate reactant mixture: cyclohexane: span 80 was fixed as 1:1:0.1. Finally, 10ml of the homogenized emulsion was fed into the continuous flow reactor, and heated at 210 °C for 7 min. The solid products were recovered by centrifugation, washed with deionized water and dried at 80 °C. The Si/Al ratio of *BEA product was 8.2 with a yield of 20wt%.

1.5 Continuous flow synthesis of CHA zeolite with emulsion method

The composition of the synthesis mixture was 1.0 SiO$_2$ /0.025 Al$_2$O$_3$/0.40 TMAdaOH/16 H$_2$O, which was prepared as follows: Al(OH)$_3$ was dissolved in TMAdaOH overnight at 80 °C in an oven. Deionized water and colloidal silica were then slowly added to form the aluminosilicate reactant. The reactant mixture was homogenized for 1 min at 2000 rpm, followed by the addition of 10 wt.% milled SSZ-13 seed crystals. The resulting reactant was stirred for 10 min and well mixed with cyclohexane and polyoxyethylene (20) oleyl ether to prepare an emulsion by using an ultrasonic vibration machine. The mass ratio of the aluminosilicate reactant mixture: cyclohexane: polyoxyethylene (20) oleyl ether was fixed as 1:1:0.1. The homogenized emulsion was fed into a sealed pipe reactor (4.4 mm i.d., 6.6 mm o.d, 13.5 cm length), and aged at 95 °C for 24 h. Finally, 10ml of the aged emulsion was injected into the continuous flow reactor at 230 °C for 2 min. The solid products were recovered by centrifugation, washed with deionized water and dried at 80 °C. The Si/Al ratio of SSZ-13 product was 12.8 with a yield of 59 wt.%.
2, Characterization

The crystalline phases of all the solid products were identified using a Rigaku Ultima IV X-ray diffractometer using CuKα radiation (λ = 0.15406 nm, 40 kV, 40 mA) at a scan rate of 4°/min. The crystallinity of the solid product was calculated according to the areas of the peaks ranging from 20° to 30°. The crystal size and morphology of the zeolite products were confirmed by scanning electron microscopy (JSM-7000F, JEOL, Japan) at an acceleration voltage of 15 keV. Elemental analysis of the products was carried out using an inductively coupled plasma–atomic emission spectrometer (ICP-AES, iCAP-6300, Thermo Scientific) after dissolving the solid products in a potassium hydroxide solution. Nitrogen adsorption–desorption measurements were performed to evaluate the specific surface area of the zeolite products using a Quantachrome Autosorb-iQ2-MP at −196 °C. Prior to the measurements, all samples were preheated at 400 °C for 4 h under vacuum. The emulsion was prepared with an ultrasonic processor (UP400S, Hielscher, Germany) at a power of 400 W and 24kHz. The shear rate of the initial reactant mixtures and emulsion prepared with different surfactants were measured using a viscosometer (Viscometer RVDV II+P, Brookfield). The morphology and droplet size of the emulsions were examined using an optical microscope (BX51, OLYMPUS, Japan). The samples were placed on viewing slides with cover slips. The conductivity of the initial reactant mixtures and emulsion prepared with different surfactants were evaluated with a compact water quality meter (LAQUAtwin B-771, HORIBA) under ambient conditions.
3. Supplementary table

**Table S1** Conductivity test results of the emulsions prepared with different surfactants

<table>
<thead>
<tr>
<th>Surfactant/cyclohexane</th>
<th>Span 80 Conductivity [mS/cm]</th>
<th>Polyoxyethylene (10) oleyl ether Conductivity [mS/cm]</th>
<th>Polyoxyethylene (20) oleyl ether Conductivity [mS/cm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminosilicate mixture</td>
<td>56.0</td>
<td>56.0</td>
<td>56.0</td>
</tr>
<tr>
<td>x=0.1</td>
<td>14.3</td>
<td>39.0</td>
<td>25.0</td>
</tr>
<tr>
<td>x=0.2</td>
<td>2.2</td>
<td>7.4</td>
<td>14.1</td>
</tr>
<tr>
<td>x=0.4</td>
<td>1.4</td>
<td>3.8</td>
<td>11.6</td>
</tr>
<tr>
<td>x=0.6</td>
<td>1.2</td>
<td>2.4</td>
<td>not measurable</td>
</tr>
</tbody>
</table>

x denotes the mass ratio of surfactant to cyclohexane.
Figure 1. Continuous flow system components. The length of the continuous flow reactor was 1400 mm, and four heaters were set at 280, 560, 840 and 1120 mm, respectively. The temperatures at different points were denoted as T1, T2, T3, T4.
Figure S2. Photographs of the reactant mixture over different heating periods. a to d, Reactant mixture synthesized for 0 min, 5 min, 10 min and 20 min, respectively.
Figure S3. Typical pressure profile for the continuous flow synthesis of ERI zeolite without emulsion method.
Figure S4. Viscosity change after the addition of different surfactants to the initial reactant mixture.

Figure S5. Optical micrograph of the emulsions prepared with different surfactants: (a) span 80; (b) polyoxyethylene (20) oleyl ether; (c) polyoxyethylene (10) oleyl ether as a surfactant.
Figure S6. Hydrothermal aging of the (a) ERI product and (b) ERI seed at 750 °C for 5 h in flowing air containing 10% H₂O.
Figure S7. Typical temperature profile for the continuous flow synthesis of ERI zeolite with emulsion method. The length of the continuous flow reactor was 1400 mm, and four heaters were set at 280, 560, 840 and 1120 mm, respectively. The temperatures at different points were denoted as T1, T2, T3, T4, as shown in Figure S1.

Figure S8. SEM images of ERI products synthesized with different amounts of surfactant in the sealed pipe reactor. (a) span 80/cyclohexane = 0.1; (b) span 80/cyclohexane = 0.2; (c) span 80/cyclohexane = 0.4. x denotes the mass ratio of span 80 to cyclohexane.
Figure S9. Powder X-ray diffraction patterns of ZSM-5 zeolite synthesized with different amounts of surfactant in the sealed pipe reactor. (a) span 80/cyclohexane = 0.1; (b) span 80/cyclohexane = 0.4. x denotes the mass ratio of span 80 to cyclohexane.

Figure S10. SEM images of ZSM-5 products synthesized with different amounts of surfactant in the pipe sealed reactor. (a) span 80/cyclohexane = 0.1; (b) span 80/cyclohexane = 0.4. x denotes the mass ratio of span 80 to cyclohexane.
Figure S11. Typical temperature profile for the continuous flow synthesis of *BEA zeolite with emulsion method. The length of the continuous flow reactor was 1400 mm, and four heaters were set at 280, 560, 840 and 1120 mm, respectively. The temperatures at different points were denoted as T1, T2, T3, T4, as shown in Figure S1.
**Figure S12.** Typical pressure profile for the continuous flow synthesis of *BEA zeolite with emulsion method.

**Figure S13.** (a) SEM image of *BEA product synthesized in the continuous flow reactor with emulsion method (same as Figure 4(b)); (b) SEM image of *BEA zeolite synthesized in the conventional autoclave.
Figure S14. SEM image of milled SSZ-13 seed crystals.

Figure S15. Powder X-ray diffraction patterns of SSZ-13 zeolite synthesized at different temperatures for 2 min in the continuous flow reactor with emulsion method.