## **Electronic Supporting Information**

## for

# Choline-mediated synthesis of zeolite ERS-7 via an excess fluoride approach

Juna Bae and Suk Bong Hong\*

Center for Ordered Nanoporous Materials Synthesis, Division of Environmental Science and Engineering, POSTECH, Pohang 37673, Korea

#### **Experimental Details**

**Synthesis.** The reagents employed included choline hydroxide (ChOH, 20% aqueous solution, Aldrich), aluminum hydroxide (Al(OH)<sub>3</sub>·1.0H<sub>2</sub>O, Aldrich), tetraethylorthosilicate (TEOS, 98%, Aldrich), HF (48%, J.T. Baker) and deionized water. The final composition of the synthesis mixture was 0.5ChOH·xAl<sub>2</sub>O<sub>3</sub>·1.0SiO<sub>2</sub>·yHF·zH<sub>2</sub>O, where *x* and *y* are varied between  $0 \le x \le 0.10$  and  $0.25 \le y \le 1.50$ , respectively, and *z* is 5 or 10. When necessary, a small amount (4 wt% of the silica in the synthesis mixture) of calcined ERS-7 with Si/Al = 14 was added as seed crystals to the synthesis mixture and stirred for 24 h, before heating the resulting mixture at 80 °C to remove the ethanol molecules generated by the hydrolysis of TEOS and some water for the desired composition. The final synthesis mixture was charged into Teflon-lined 23-mL autoclaves and heated under rotation (60 rpm) at 175 °C for 1-14 days. The synthesis was also carried out using boric acid (H<sub>3</sub>BO<sub>3</sub>, 99%, Aldrich) or gallium nitrate (Ga(NO<sub>3</sub>)<sub>2</sub>·8.5H<sub>2</sub>O, 99.9%, Aldrich) instead of aluminum hydroxide. The solid product was recovered by filtration, washed repeatedly with deionized water, and dried overnight at room temperature.

As-made ERS-7 was calcined in air at 650 °C for 8 h to remove the organic structuredirecting agents (OSDAs) occluded. The calcined sample was refluxed twice in 1.0 M NH<sub>4</sub>NO<sub>3</sub> or 1.0 M NaNO<sub>3</sub> solutions (1.0 g solid per 100 mL solution) at 80 °C for 6 h. Cu-ERS-7 was prepared by stirring NH<sub>4</sub>-ERS-7 three times in 0.01 M Cu(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>·H<sub>2</sub>O solutions at room temperature for 6 h followed by drying at 90 °C overnight and calcining at 550 °C in air for 8 h.<sup>S1</sup> For catalytic comparison, SAPO-34 with Si/(Si + Al + P) = 0.1 and SSZ-13 with Si/Al = 16 were synthesized according to the procedures in the literature.<sup>S2</sup> Cu-SSZ-13 was prepared following the procedures similar to the Cu-ERS-7 preparation. Elemental analysis indicates that the Cu content (0.3 wt%) of Cu-ERS-7 is much smaller than that (3.2 wt%) of Cu-SSZ-13. It thus appears that the 8-ring (3.5 × 4.7 Å) windows in ERS-7 may not be large enough to freely allow Cu<sup>2+</sup> ion exchange in aqueous solution. For adsorption comparison, chabazite with Si/Al = 2.2 was synthesized according to the procedures given elsewhere<sup>S3</sup> and converted to their Na<sup>+</sup> form following the procedure described above.

Analytical methods. Powder X-ray diffraction (XRD) patterns were recorded on a PANalytical X'Pert diffractometer (Cu K $\alpha$  radiation) with an X'Celerator detector. The relative

crystallinities of a series of solid products recovered at different time intervals during ERS-7 crystallization were determined by comparing the area of the intense X-ray peak around  $2\theta = 19.3^{\circ}$ , corresponding to the (114) reflection of the ESV structure,<sup>S4</sup> with that of a fully crystallized ERS-7 sample synthesized at Si/Al = 10 after 14 days of heating at 175 °C. The yield of each product was calculated by dividing the weight of the product obtained after crystallization for a given time by the total weight of the oxide forms of all of the components in the synthesis mixture except water. Crystal morphology and size were determined by a JEOL JSM-6510 scanning electron microscope (SEM). Elemental analysis for Si and Al was performed by the analytical laboratory of the Pohang Institute of Metal Industry Advancement. Thermogravimetric analyses (TGA) were carried out on an SII EXSTAR 6000 thermal analyzer, where the weight losses related to the combustion of OSDAs were further confirmed by differential thermal analyses (DTA) using the same analyzer. The N<sub>2</sub> sorption experiments were performed on a Mirae SI nanoPorosity-XG analyzer.

Solid-state multinuclear NMR measurements were performed using Bruker DRX500 (<sup>1</sup>H-<sup>13</sup>C CP, <sup>27</sup>Al, and <sup>29</sup>Si) and Bruker Avance II plus 400 (<sup>19</sup>F) spectrometers at a spinning rate of 21.0 and 12.0 kHz, respectively. The <sup>1</sup>H-<sup>13</sup>C CP magic-angle-spinning (MAS) NMR spectrum was recorded at a <sup>13</sup>C frequency of 125.758 MHz with a  $\pi/2$  rad pulse length of 4.0  $\mu$ s, a contact time of 2.0 ms, a recycle delay of 3.0 s, and an acquisition of ca. 500 pulse transients. The <sup>29</sup>Si MAS spectra were recorded at a <sup>29</sup>Si frequency of 99.372 MHz with a  $\pi/2$  rad pulse length of 4.0  $\mu$ s, recycle delay of 20 s, and an acquisition of ca. 500 pulse transients. The <sup>13</sup>C and <sup>29</sup>Si shifts are referenced relative to TMS. The <sup>27</sup>Al MAS NMR spectra were recorded at a <sup>27</sup>Al frequency of 130.351 MHz with a  $\pi/6$  rad pulse length of 1.0  $\mu$ s, a recycle delay of 2.0 s, and an acquisition of ca. 100 pulse transients. The <sup>27</sup>Al chemical shifts are referenced relative to an Al(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup> solution. The <sup>19</sup>F MAS NMR spectrum was recorded at a <sup>19</sup>F frequency of 376.574 MHz with a  $\pi/4$  rad pulse length of 2.1  $\mu$ s, a recycle delay of 8.0 s, and an acquisition of ca. 200 pulse transients. The <sup>19</sup>F chemical shifts are referenced relative to CFCl<sub>3</sub>.

**Catalysis.** The methanol-to-olefins (MTO) conversion was conducted under atmospheric pressure in a conventional continuous-flow microreactor. Prior to the experiments, the catalyst was routinely activated under flowing  $N_2$  (130 mL min<sup>-1</sup>) at 550 °C for 2 h and kept at 350 °C to establish a standard operating procedure, allowing time for the reactant/carrier gas

distribution to stabilize. Then, methanol vapor was fed at a rate of 0.085 mL h<sup>-1</sup> (0.67 h<sup>-1</sup> weight hourly space velocity (WHSV)) into the reactor containing 0.1 g of catalyst at the same temperature. The total gas flow at the reactor inlet was kept constant at 30 mL min<sup>-1</sup>. The reaction products were analyzed online in a Varian CP-3800 gas chromatograph equipped with a CP-PoraPLOT Q capillary column (0.25 mm × 25 m) and a flame ionization detector, with the first analysis carried out after 5 min on stream. CO<sub>2</sub> was separated using a packed Carbosphere column and analyzed with a thermal conductivity detector. The conversion of methanol was defined as the percentage of methanol consumed during MTO conversion. Dimethylether was not considered as a product. The yield of each product was calculated as the percentage of the amount (in mol) of methanol converted to hydrocarbons.

The deNOx activity tests were conducted under atmospheric pressure in a fixed-bed flow reactor (3/8-in.-od. Al tube).<sup>S5</sup> Prior to each experiment, 0.6 g of catalyst in the 20/30 mesh size packed into the reactor were pretreated from room temperature to 500 °C at a heating rate of 10 °C min<sup>-1</sup> under 21%  $O_2/N_2$  flow (2,000 mL min<sup>-1</sup>) and keep at the final temperature for 2 h. A feed gas mixture containing 500 ppm NH<sub>3</sub>, 500 ppm NO, 5%  $O_2$ , 10% H<sub>2</sub>O and N<sub>2</sub> balance was supplied through mass flow controllers, and the gas hourly space velocity (GHSV) was maintained at 100,000 h<sup>-1</sup>. The inlet and outlet concentrations of NO were determined by an online Nicolet 6700 FT-IR spectrometer.

**Gas adsorption.** The CO<sub>2</sub> (Linde, 99.999%), CH<sub>4</sub> (Linde, 99.995%), and N<sub>2</sub> (Linde, 99.995%) adsorption isotherms were recorded at 25 °C and pressures up to 1.2 bar using a Mirae SI nanoPorosity-XG analyzer. Prior to the experiments, 0.1 g of sample was evacuated at 250 °C for 6 h. The temperature of the samples was subsequently reduced under vacuum until the target temperature was reached. The criterion of equilibration at a given pressure point depends on the rate of adsorption, as such, a maximum equilibration time of 30 min was set for each isotherm point.

|          | Product <sup>b</sup> |                    |                             |  |
|----------|----------------------|--------------------|-----------------------------|--|
| Si/Al    | $HF/Ch^{+} = 0.5$    | $HF/Ch^{+} = 1.0$  | $HF/Ch^{+} = 2.0$           |  |
| 5        | Amorphous            | Amorphous          | Amorphous <sup>c</sup>      |  |
| 7        | Amorphous            | Amorphous          | ERS-7                       |  |
| 10       | Amorphous            | Amorphous          | ERS-7 + nonasil + amorphous |  |
| 20       | RUB-10 + ZSM-39      | Amorphous + ZSM-39 | Nonasil                     |  |
| $\infty$ | ZSM-39               | Dense              | Dense                       |  |

**Table S1** Syntheses from gel composition 0.5ChOH·xAl<sub>2</sub>O<sub>3</sub>·1.0SiO<sub>2</sub>·yHF·10.0H<sub>2</sub>O<sup>a</sup>

a x and y are varied between  $0 \le x \le 0.10$  and  $0.25 \le y \le 1.00$ , respectively. All syntheses were performed under rotation (60 rpm) at 175 °C for 14 days, unless otherwise stated. <sup>b</sup> The product appearing first is the major phase. <sup>c</sup> The product obtained using a small amount (4 wt% of the silica in the synthesis mixture) of calcined ERS-7 with Si/Al = 14.0 as seed crystals.

|          | Ploduct             |                            |                     |
|----------|---------------------|----------------------------|---------------------|
| Si/T     | T = B               | T = A1                     | T = Ga              |
| 5        | Amorphous + nonasil | Ferrierite                 | Layered + amorphous |
| 7        | Nonasil             | Amorphous + ZSM-39 + ERS-7 | Layered + amorphous |
| 10       | Nonasil             | ERS-7                      | Layered + amorphous |
| 20       | Nonasil             | Nonasil + ERS-7            | Layered + amorphous |
| $\infty$ | -                   | Nonasil + unknown          | -                   |

Table S2 Syntheses from gel composition 0.5ChOH· $xT_2O_3$ · $1.0SiO_2$ ·1.0HF·5.0H $_2O^a$ Product<sup>b</sup>

 $\overline{a}$  T is B, Al, or Ga and x is varied between  $0 \le x \le 0.10$ . All the syntheses were performed under rotation (60 rpm) at 175 °C for 14 days, unless otherwise stated. <sup>b</sup> The product appearing first is the major phase.

| Table 55 Room temperature CO2/CI14 and CO2/112 Selectivities |                         |                        |  |  |  |
|--|-------------------------|------------------------|--|--|--|
| Material   | $CO_2/CH_4$ selectivity | $CO_2/N_2$ selectivity |  |  |  |
| Na-ERS-7   | 13                      | 20                     |  |  |  |
| Na-chabazite   | 4                       | 29                     |  |  |  |

Table S3 Room-temperature  $CO_2/CH_4$  and  $CO_2/N_2$  selectivities



**Fig. S1** (a) Powder XRD patterns, (b) relative crystallinities ( $\blacksquare$ ) and solid yields ( $\bullet$ ) and (c) organic contents ( $\blacktriangle$ ) and Si/Al ( $\nabla$ ) ratios for a series of solid products obtained after ERS-7 crystallization from the synthesis mixture with Si/Al = 10 for different times. The Si/Al ratio and organic content in each solid product were determined by elemental and thermal (the exothermic weight loss by TGA/DTA at 200-1000 °C) analyses, respectively.



**Fig. S2** Powder XRD patterns for a series of solid products obtained after ERS-7 crystallization from the synthesis mixture with Si/Al = 15 for different times. X-ray reflections from the NON structure are indicated by closed circles ( $\bullet$ ).



**Fig. S3** TGA/DTA (black/red) profiles of as-made ERS-7 synthesized using Ch<sup>+</sup> via an excess fluoride approach.



Fig. S4 <sup>27</sup>Al MAS NMR spectra of the (a) as-made and (b) proton forms of ERS-7.



**Fig. S5**<sup>29</sup>Si MAS NMR spectra of the (a) as-made (from top to bottom: experimental, simulated, and deconvoluted components) and (b) proton forms of ERS-7.



**Fig. S6** Methanol conversion as a function of time on stream in the MTO reaction over H-ERS-7 ( $\blacksquare$ ) and H-SAPO-34 ( $\bullet$ ) at 350 °C and 0.67 h<sup>-1</sup> WHSV.



Fig. S7 Yield of lower olefins as a function of time on stream in the MTO reaction over (a) H-ERS-7 and (b) H-SAPO-34 at 350  $^{\circ}$ C and 0.67 h<sup>-1</sup> WHSV.



**Fig. S8** NO conversion as a function of temperature in NH<sub>3</sub>-SCR reaction over Cu-ERS-7 ( $\blacksquare$ ) and Cu-SSZ-13 ( $\bullet$ ). The feed contains 500 ppm of NH<sub>3</sub>, 500 ppm of NO, 5% O<sub>2</sub>, 10% H<sub>2</sub>O balanced with N<sub>2</sub> at 100,000 h<sup>-1</sup> GHSV.

### References

- S1 I. J. Heo, Y. M. Lee, I.-S. Nam, J. W. Choung, J.-H. Lee and H.-J. Kim, *Microporous Mesoporous Mater.*, 2011, 141, 8.
- S2 (a) H. G. Jang, H.-K. Min, J. K. Lee, S. B. Hong and G. Seo, *Appl. Catal., A*, 2012, 437, 120; (b) S. I. Zones, US Pat., 4,544,538, 1985; (c) S. I. Zones, *J. Chem. Soc., Faraday Trans.*, 1991, 87, 3709.
- S3 C. G. Goe, T. R. Gaffney and R. S. Srinivasan, US Pat., 4,925,460, 1990.
- S4 C. Baerlocher and L. B. McCusker, *Database of Zeolite Structures*, http://www.iza-structure.org/databases/.
- S5 J. H. Park, H. J. Park, H. J. Baik, I.-S. Nam, C. H. Shin, J.-H. Lee, B. K. Cho and S. H. Oh, *J. Catal.*, 2006, **240**, 47.