Supplementary Information

Crucial Factors for Seed-Directed Synthesis of CON-type Aluminoborosilicate Zeolites Using Tetraethylammonium

Sibel Sogukkanli,^{§a} Koki Muraoka,^a Kenta Iyoki,^a Shanmugam P. Elangovan,^a Yutaka Yanaba,^b Watcharop Chaikittisilp,^{‡a} Toru Wakihara,^a and Tatsuya Okubo^{*a}

^aDepartment of Chemical System Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

^bInstitute of Industrial Science, The University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo, 153-8505, Japan

§Present address: Institute of Industrial Science, The University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo, 153-8505, Japan

‡Present address: Research and Services Division of Materials Data and Integrated System (MaDIS), National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan

*Author to whom correspondence should be addressed.

E-mail: okubo@chemsys.t.u-tokyo.ac.jp

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3. References

1. Experimental Section

Preparation of N,N,N-Trimethyl-(-)-cis-myrtanylammonium as organic structure **directing agent.** According to a previous report.^[1] the typical synthesis of *N*,*N*,*N*-Trimethyl-(-)-cis-myrtanylammonium is carried out as follows: 10 g of (-)-cis-myrtanylamine((1S)- $[1\alpha,2\beta,5\alpha]$ -2-methanamine-6,6-dimethylbicyclo[3.1.1] heptane) was dissolved in 100 mL methanol, then 27 g of K₂CO₃ and 55 g of metyliodide were added into this solution. The mixture was stirred for overnight at room temperature in the absence of light. Later, the reaction mixture was filtered, and the solid filtrate was washed with additional 50 mL of methanol to remove unreacted K₂CO₃. In order to separate the methanol from the solid material, the combined solution was heated at 50 °C by using evaporator. A white solid was formed in the flask which is then extracted with 2 portions each of 100 mL of chloroform. The combined chloroform solution which contains trimethylmyrtanylammonium were filtered again and were heated in an evaporator until the chloroform was evaporated. Generally, a very viscous oily liquid was obtained after the evaporation of chloroform. In this case, the ammonium salt can be easily recrystallized by the addition of 50 mL of diethyl ether. After the solid was formed, the crystals were washed with 200 mL of additional ether. Then, the ether was allowed to be evaporated from the solid at room temperature in a hood. Later, the recovered solids were recrystallized from a 9:1 tetrahydrofuran/methanol solution, approximately 17 g white crystals of N,N,N-Trimethyl-(-)-cis-myrtanylammonium iodide were recovered. The ¹³C NMR of this iodide salt is: ¹³C NMR δ = 23.2, 23.7, 25.6, 27.2, 31.5, 35.6, 38.2, 40.2, 47.6, 53.8, 76.9 ppm. Finally, ion exchange was accomplished from iodide form to hydroxide.

Synthesis of borosilicate beta seed crystals. The synthesis of borosilicate beta zeolite was performed by using the general dry gel technique as previously reported.^[2,3] In a typical synthesis procedure, the prepared gel with the molar composition was 1.0SiO₂: 0.033B₂O₃: 0.056NaOH: 1.0 TEAOH. First, an appropriate amount of TEAOH was mixed with colloidal

silica under continuous stirring, and was further stirred for 10 min. Then, NaOH was added in this mixture, and continued stirring for extra 30 min. Meanwhile, sodium tetraborate decahydrate was dissolved in a certain amount of deionized, distilled water, then added into the above mixture. The final mixture was further stirred for 2h. Then the gel was dried at 80 °C by using a hot plate with continuous stirring, allowing evaporation of water. When the gel became thick and viscous, it was homogenized by hand using a teflon rod until it dried. After formation of white solid, it was ground into a fine powder, and the powder was poured into a small teflon cup (20 mm × 20 mm). Later, this teflon cup was placed in a Teflon-lined autoclave (No. 4749, Parr Instrument) which had 0.25 g water as the source of steam to avoid direct contact between gel and water. The crystallization of the dry gel was carried out at 175 °C for 96 hours in autogenous pressure. After the crystallization was over, the solid products could be recovered by consecutively washing with deionized water, centrifuging, and drying at 80 °C for overnight.

Synthesis of aluminosilicate beta seed crystals. Zeolite beta seeds were synthesized using TEAOH by hydrothermal treatment of aluminosilicate reaction mixtures with the following chemical composition: 0.035Na₂O: 0.175TEA₂O: 0.04Al₂O₃: SiO₂: 14H₂O. Initially, TEAOH and sodium aluminate were dissolved in distilled water to obtain a clear solution. Then, Mizukasil was slowly added into the solution and mixed by a mortar and pestle to obtain a homogenous aluminosilicate reaction mixture. A mortar and pestle were then used to mix the solution and to obtain a homogenous aluminosilicate reaction mixture. Aluminosilicate reaction mixture slurry (40 g) was transferred to a stainless-steel autoclave with a volume of 60 mL and was then subjected to hydrothermal treatment at 165 °C for 96 h under 20 rpm rotation in an oven under autogenous pressure. The product was then filtered, washed thoroughly with hot distilled water, dried at 60 °C.

Milling conventional CIT-1 zeolites. The conventional borosilicate CIT-1 seed crystals were milled using a bead milling apparatus (LMZ015, Ashizawa Finetech Ltd.). CIT-1 powder (10 g) was dispersed in 50 mL of water and milled with the bead milling apparatus for 30 min at 3000 rpm using zirconia beads with a diameter of 300 µm. After the milling

treatment, the slurry was centrifuged, and the residual solid was recovered and dried overnight in an oven at 80 $^{\circ}$ C.

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