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Supplementary Information
for
Charge density mismatch synthesis of MEI- and BPH-type zeolites in the TEA^+-TMA^+-Li^+-Sr^{2+} mixed-structure-directing agent system

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Experimental Details

Synthesis. In a typical synthesis of PST-11 and PST-12, a clear aluminosilicate solution with the composition $4.0TEAOH\cdot 1.0TMACl\cdot 0.075LiCl\cdot 0.15Sr(NO_3)_2\cdot 0.5Al_2O_3\cdot 2.5SiO_2\cdot 100H_2O$ was prepared by combining tetraethylammonium hydroxide (TEAOH, 35% aqueous solution, Sachem), tetramethylammonium chloride (TMACl, 97%, Aldrich), LiCl (99+%, Aldrich), $Sr(NO_3)_2$ (99+%, Aldrich), aluminum tri-*sec*-butoxide (Al[O(*s*-Bu)]$_3$, 97%, Aldrich), tetraethylorthosilicate (TEOS, 98%, Aldrich), and deionized water. Al[O(*s*-Bu)]$_3$ was first mixed with a solution of TEAOH in water and stirred at room temperature for 2 h. To this clear solution, a given amount of TEOS was added and stirred at room temperature for another 2 h. The resulting aluminosilicate solution was heated at 80 °C for 3 h under stirring to remove the ethanol molecules generated by the hydrolysis of TEOS. Then, a solution of TMACl, LiCl, and $Sr(NO_3)_2$ in water was slowly added with vigorous stirring to the charge density mismatch (CDM) solution prepared above. The final synthesis solution was stirred at room temperature for 1 day, charged into Teflon-lined 45-mL autoclaves, and then heated under rotation (60 rpm) at 120 or 160 °C for a total period of 21 days. The solid products were separated by centrifugation (15000 rpm, 10 min). The recovered solids were redispersed in deionized water using an ultrasonic bath (100 W, 42 kHz) for 60 min and followed by centrifugation, which was repeated three times. Finally, the resulting solids were dried overnight at room temperature.

UZM-4 was synthesized using a CDM aluminosilicate solution with the composition $4.0ChOH\cdot 0.25LiCl\cdot 0.25NaCl\cdot 0.5Al_2O_3\cdot 5.0SiO_2\cdot 150H_2O$. The reagents used included choline hydroxide (ChOH, 20% aqueous solution, Aldrich), aluminum hydroxide ($Al(OH)_3\cdot 1.0H_2O$, Aldrich), and colloidal silica (Ludox AS-40, DuPont), NaCl (≥99.5%, Aldrich), and LiCl was the same as those used in PST-11 and PST-12 syntheses. The final synthesis solution was stirred at room temperature for 1 day, charged into Teflon-lined autoclaves, and heated under rotation (60 rpm) at 100 °C for 7 days. UZM-22 was synthesized using a CDM aluminosilicate solution with the composition $4.0ChOH\cdot 0.15LiCl\cdot 0.15Sr(NO_3)_2\cdot 0.5Al_2O_3\cdot 5.0SiO_2\cdot 150H_2O$. After being stirred at room temperature for 1 day, the final synthesis solution was heated under rotation (60 rpm) at 100 °C for 7 days. To determine the relative amount of a sodalite impurity in a series of the solid products isolated after PST-11 crystallization at 120 °C for different times, in addition, a sodalite sample was prepared by heating an aluminosilicate gel with the composition $4.0TMAOH\cdot 0.25LiCl\cdot 0.25NaCl\cdot 0.5Al_2O_3\cdot 5.0SiO_2\cdot 150H_2O$ under rotation (60 rpm) at 100 °C for 14 days.

As-made zeolites were calcined at 550 °C for 8 h to remove the organic species occluded. The calcined samples were then refluxed twice in 1.0 M $NH_4(NO_3)$ solutions at 80 °C for 6 h followed by calcination at 550 °C for 2 h to make their proton form. If necessary, as-made zeolites were directly exchanged twice in 1.0 M $NH_4(NO_3)$ solutions (1.0 g solid per 100 mL solution) at 80 °C for 6 h and then calcined at 550 °C for 2 h.

Analytical Methods. Powder X-ray diffraction (XRD) patterns were recorded on a PANalytical X′Pert diffractometer (Cu K_α radiation) with an X′Celerator detector. The relative crystallinities of a series of solid products recovered after PST-11 synthesis at 120 °C for different times were determined by comparing the areas of intense X-ray peaks around $2\theta = 7.7$ and 24.5°, corresponding to the (100) and (211) reflections of the MEI and SOD structures, respectively,[S1] with those observed for the fully crystallized PST-11 and sodalite samples. The yield of each product was calculated by dividing the mass of the product obtained after crystallization for a given time by the total mass of the oxide forms of all of the components in the synthesis mixture except water. The synchrotron diffraction data were collected on the 9B beamline at Pohang Acceleration Laboratory (PAL; Pohang, Korea) using monochromated X-rays ($\lambda = 1.46390$ Å). The detector arm of the vertical scan diffractometer consists of seven sets of Soller slits, flat Ge(111) crystal analyzers, anti-scatter baffles, and scintillation detectors, with each set separated by 20°. Data were obtained on the sample at room temperature in flat plate mode, with a step size of 0.01° and overlaps of 0.5° to the next detector bank over the 2θ range 3 – 123.5°.

Crystal morphology and average size were determined by a JEOL JEM-2200FS transmission electron microscope (TEM) operating with an acceleration voltage of 200 kV. The N_2 sorption experiments were performed on a Mirae SI nanoPorosity-XG analyzer. Thermogravimetric analyses (TGA) were performed on an SII EXSTAR 6000 thermal analyser, where the weight losses related to the combustion of organic SDAs were further confirmed by differential thermal analyses (DTA) using the same analyser. Elemental analysis for Si, Al, Li, and Sr was carried out by a Jarrell-Ash Polyscan 61E inductively coupled plasma spectrometer in combination with a Perkin-Elmer 5000 atomic absorption spectrophotometer. The C, H, and N contents of the samples were analysed by using a Vario EL III elemental organic analyser.

The ^{13}C, ^{27}Al, and ^{29}Si MAS NMR spectra were measured on a Varian Inova 300 spectrometer at a spinning rate of 6.0 kHz or on a Bruker AVANCE 400 spectrometer at a spinning rate of 7.0 kHz. The ^{13}C MAS NMR spectra were recorded at a ^{13}C frequency of 75.43 MHz with a $\pi/2$ rad pulse length of 7.0 μs, a recycle delay of 2 s, and an acquisition of *ca.* 10000 pulse transients. The ^{27}Al MAS NMR spectra were measured at a ^{27}Al frequency of 78.16 MHz with a $\pi/8$ rad pulse length of 1.8 μs and a recycle delay of 0.5 s. Approximately 3000 pulse transients were accumulated. The ^{29}Si MAS NMR spectra were measured at a ^{29}Si frequency of 59.59 or 79.54 MHz with a $\pi/2$ rad pulse length of 5.0 or 4.0 μs, a recycle delay of 60 s, and an acquisition of about 5000 pulse transients. The ^{13}C and ^{29}Si chemical shifts are referenced relative to TMS and the ^{27}Al chemical shifts are reported relative to $Al(H_2O)_6^{3+}$.

The minimum lattice energies of MEI- and BPH-type zeolites were acquired using the force field method and shell model for silicates.[S2] All calculations were performed using GULP (general utility lattice program) following the procedure previously reported.[S3]

[S1] Ch. Baerlocher and L. B. McCusker, Database of Zeolite Structures: http://www.iza-structure.org/databases/.

[S2] M. J. Sanders, M. Leslie and C. R. A. Catlow, *J. Chem. Soc., Chem. Commun.*, 1984, 1271.

[S3] N. J. Henson, A. K. Cheetham and J. D. Gale, *Chem. Mater.*, 1994, **6**, 1647.

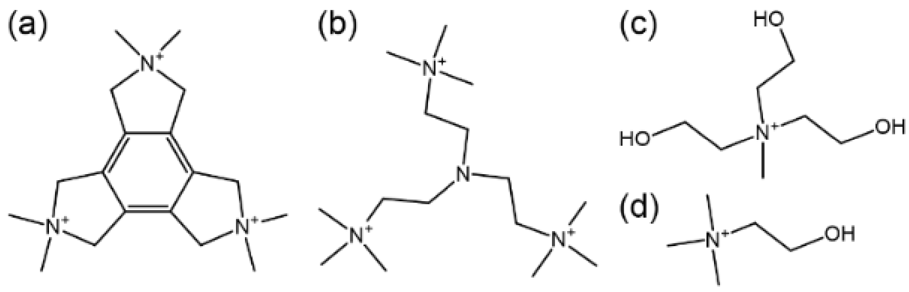

Fig. S1 The organic species which have thus far been used in MEI-type zeolite syntheses: (a) 2,3,4,5,6,7,8,9-octahydro-2,2,5,5,8,8-hexamethyl-1*H*-benzo[1,2-*c*:3,4-*c*':5,6-*c*'']tripyrrolium, (b) tris(2-trimethylammonioethyl)amine, (c) triethanolmethylammonium and (d) choline.

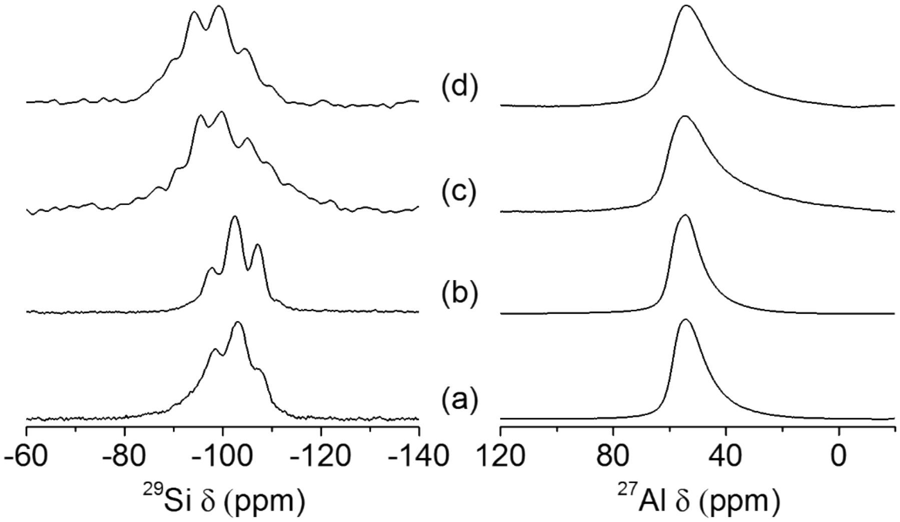

Fig. S2 ^{29}Si (left) and ^{27}Al (right) MAS NMR spectra of as-made (a) PST-11, (b) UZM-22, (c) PST-12 and (d) UZM-4.

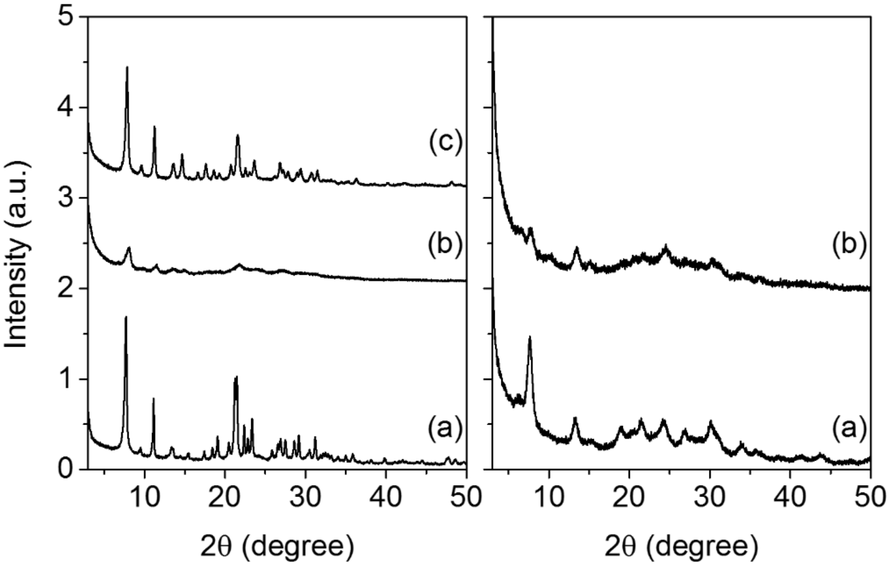

Fig. S3 Powder XRD patterns of (a) as-made and (b) calcined forms of (left) PST-11 and (right) PST-12. The XRD pattern given as trace c above the pattern of calcined PST-11 was obtained from the PST-11 sample first exchanged twice with 1.0 M NH_4NO_3 solutions at 80 °C for 6 h and then calcined at 550 °C for 2 h.

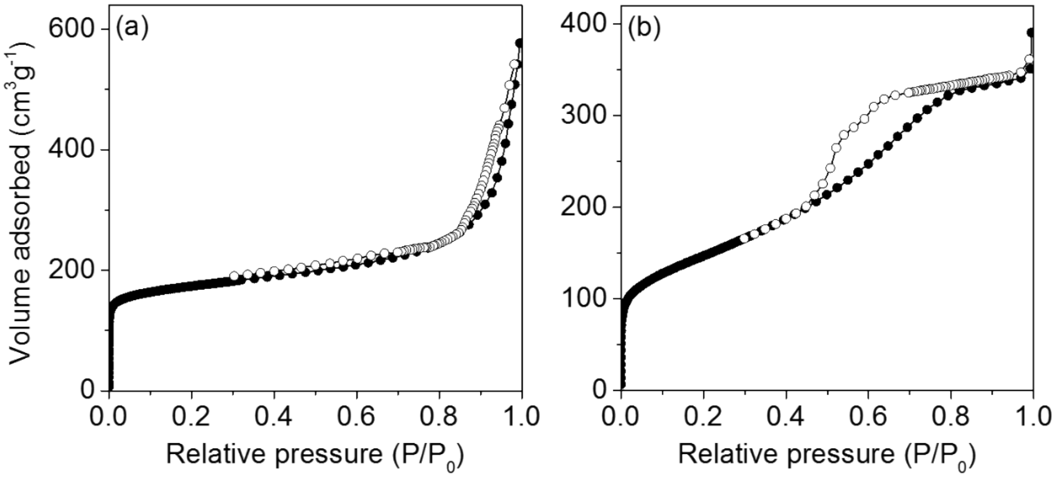

Fig. S4 N_2 adsorption-desorption isotherms of (a) H-PST-11 and (b) calcined PST-12.

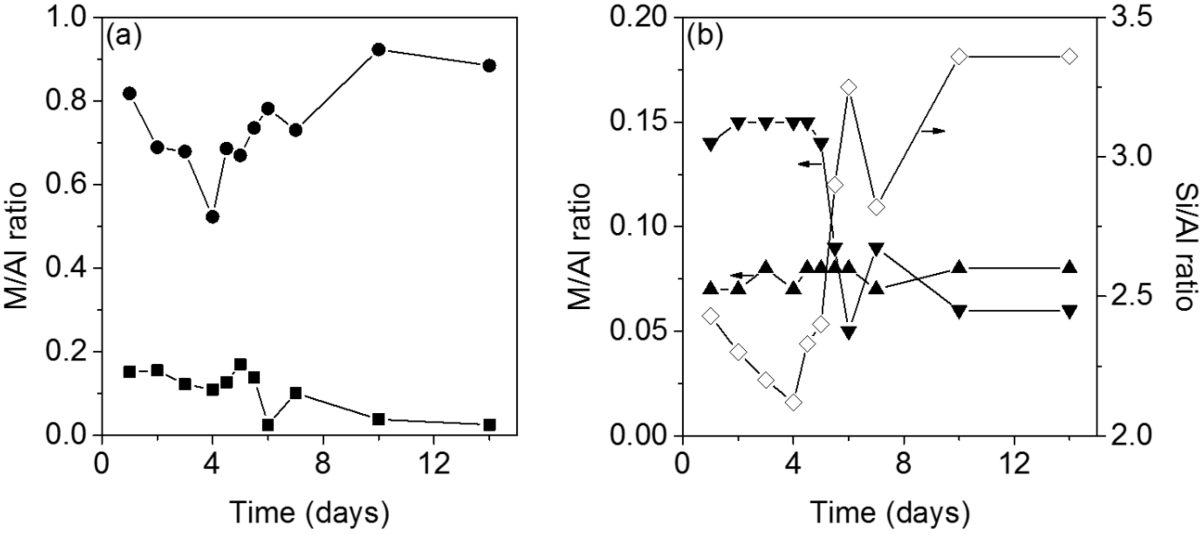

Fig. S5 (a) TEA/Al (■) and TMA/Al (●) ratios and (b) Li/Al (▲), Sr/Al (▼) and Si/Al (◇) ratios in the solid products obtained after PST-11 synthesis at 120 °C for different times.

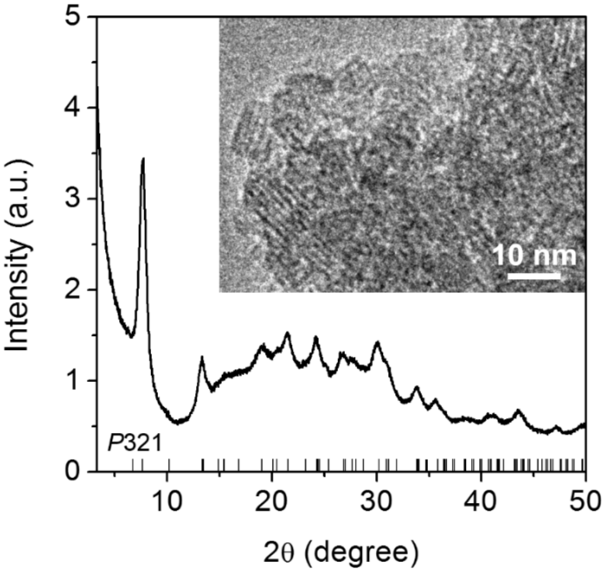

Fig. S6 Synchrotron powder diffraction pattern and TEM image of the solid product isolated after PST-11 synthesis under rotation (60 rpm) at 120 °C for 3 days. Diffraction data are adjusted with respect to Cu K_α, radiation (λ = 1.5419 Å), and the tick marks indicate the positions of allowed reflections for UZM-4 in *P*321 symmetry.

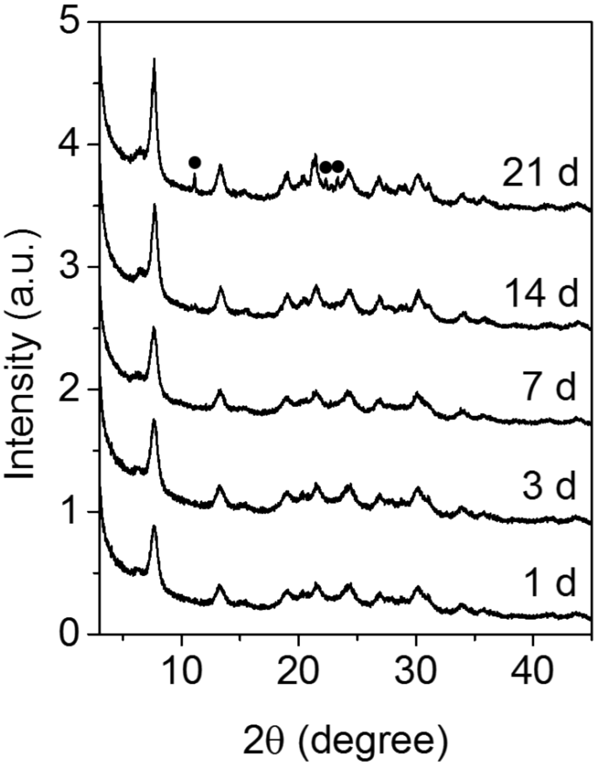

Fig. S7 Powder XRD patterns for the solid products obtained after PST-12 synthesis at 160 °C for different times. X-ray reflections from the MEI structure are indicated by closed circles (●).