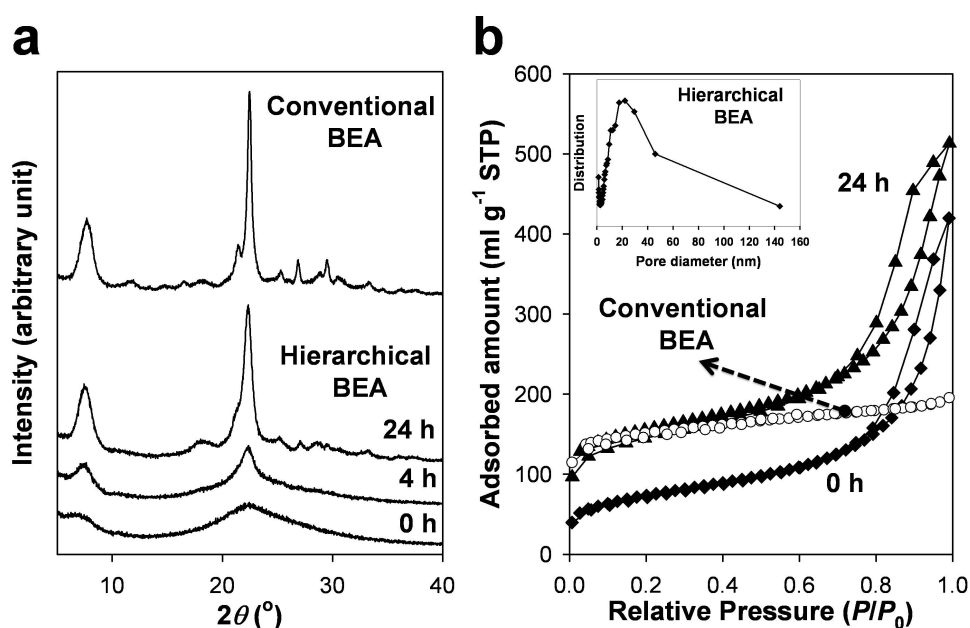# Electronic supplementary information (ESI)

The synthesis of a hierarchically porous BEA zeolite *via* pseudomorphic crystallization [†]

Minkee Choi, Kyungsu Na and Ryong Ryoo*

Figure S1. a) XRD patterns, and b) N_2 adsorption-desorption isotherms and a pore size distribution (inset) of solid products collected during the crystallization of hierarchical BEA zeolite at 170°C. For comparison, XRD pattern and N_2 adsorption isotherm of conventional BEA zeolite are also shown.

Table S1. Catalytic properties of BEA zeolites in isopropylation of naphthalene.

Time on stream (h) [a]	Hierarchical BEA zeolite [b] (Si/Al = 15, BET = 631 $m^2 g^{-1}$)					Conventional BEA zeolite [b] (Si/Al=13, BET = 457 $m^2 g^{-1}$)				
	Conv. (%) [c]	Selectivity [d]				Conv. (%) [c]	Selectivity [d]			
		IPN	2,6-DIPN	2,7-DIPN	PIPN		IPN	2,6-DIPN	2,7-DIPN	PIPN
1	42	45	24	16	15	41	43	21	16	20
3	33	55	19	14	12	18	61	15	15	9
5	31	59	17	14	10	<<1	-	-	-	-

[a] Reaction conditions: 200°C, 1 atm, WHSV (total liquid feed) = 5.4 h^{-1}, feed composition (naphthalene/isopropanol/cyclohexane) = 1/ 2/10. [b] Hierarchical BEA zeolite was synthesized using water glass as a silica source at 130°C. Conventional BEA zeolite was purchased from Zeochem. [c] Naphthalene conversion. [d] IPN: monoisopropylnaphthalene, DIPN: diisopropylnaphthalene, PIPN: polyisopropylnaphthalene

Experimental Section

Material Synthesis: The cyclic diammonium (CD) in Scheme 1 was synthesized via a single step reaction between α,α'-dichloro-p-xylene and N,N,N',N'-tetramethyl-1,6-hexanediamine in acetonitrile under the reflux condition (isolated yield > 95%). In a typical synthesis of hierarchical BEA zeolite, water glass (29 wt% SiO_2 Si/Na=1.75), NaOH, H_2SO_4, $Al_2(SO_4)_3 \cdot 18H_2O$, CD and distilled water were mixed to obtain the composition; 30 Na_2O: 2.5 Al_2O_3: 100 SiO_2: 10 CD: 15 H_2SO_4: 6000 H_2O. The resultant gel was transferred to a Teflon-lined autoclave and hydrothermally crystallized at 170°C under tumbling condition (60 rpm). The product was filtered, washed with distilled water and dried at 130°C. CD in the product zeolite could be removed by calcination at 550°C under air. Alternatively, it can be extracted by 0.1 M HCl solution for recycling.

To investigate the effect of TPA^+ as a competing SDA, tetrapropylammonium bromide (TPABr) was added into the aforementioned synthesis composition of BEA zeolite. The final gel composition was 30 Na_2O: 2.5 Al_2O_3: 100 SiO_2: 10 CD: 10 TPABr: 15 H_2SO_4: 6000 H_2O. The resultant gel was crystallized, following the same procedure.

BEA zeolite crystallization from diatomaceous earth was carried out by using Hyflo Super Cel® (Sigma-Aldrich) as a major inorganic source. In the synthesis, approximately 90% of silica source was provided from diatomaceous earth and 10% from water glass (29 wt% SiO_2 Si/Na=1.75). In a typical synthesis, initial gel was prepared by mixing 4.1 g water glass, 3.2 g NaOH, 7.0 g CD, 0.29 g $Al_2(SO_4)_3 \cdot 18H_2O$ and 190 g H_2O, followed by the addition of 10.8 g diatomaceous earth. The resultant mixture was crystallized at 150°C for 2 d in a tumbling autoclave. BEA zeolite was also synthesized from diatomaceous earth by using TEAOH (35 wt%) as an SDA. Synthesis gel was prepared by mixing 5.2 g water glass, 0.23 g NaOH, 0.06 g KOH, 52.6 g TEAOH, 0.37 g $Al_2(SO_4)_3 \cdot 18H_2O$ and 30 g H_2O, followed by addition of 13.5 g diatomaceous earth.

Characterization: XRD patterns were taken with a Rigaku Multiflex diffractometer equipped with CuKα radiation (40 kV, 40 mA). Scanning electron micrograph (SEM) images were taken at a low electron acceleration voltage (2 kV, Hitachi S-4800) without metal coating, after mounting on a carbon-coated tape. Transmission electron micrograph (TEM) images were obtained with a JEM-210F (JEOL corp.) transmission electron microscope with the operating voltage of 200 kV. N_2 adsorption isotherms were measured at liquid nitrogen temperature with an ASAP2020 volumetric adsorption analyzer. Geometrical optimization (Fletcher-Reeves algorithm) and molecular dynamics simulation of CD were carried out by using HyperChem (version 6.03) software.