†Electronic Supplementary Information (ESI)

Zeolite Nanosheet of a Single-Pore Thickness Generated by a Zeolite-Structure-Directing Surfactant

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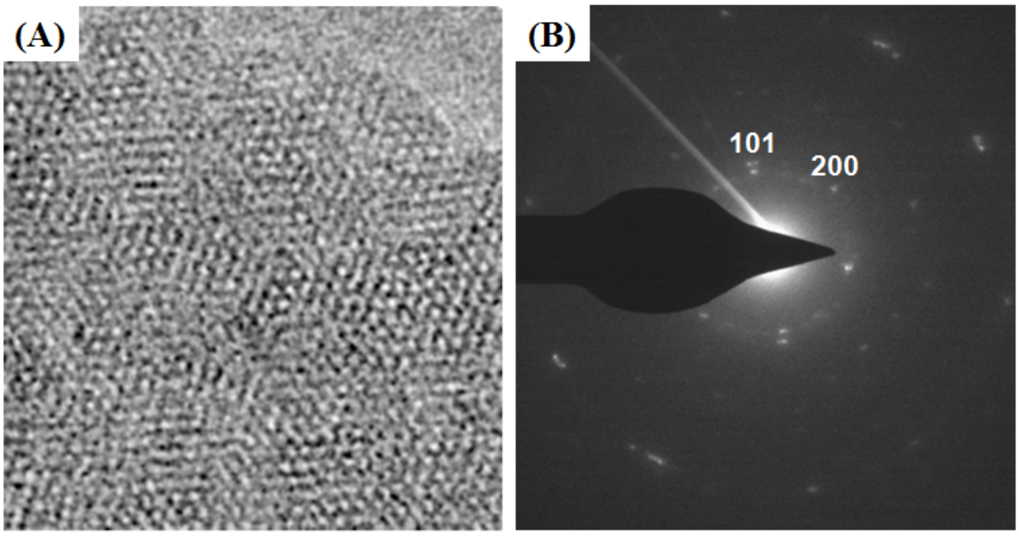

Fig. S1 1.5 nm thick zeolite nanosheet synthesized with $[C_{18}H_{37}\text{-}N^{+}(CH_3)_2\text{-}C_6H_{12}\text{-}N^{+}(CH_3)_2\text{-}C_6H_{12}\text{-}N^{+}(CH_3)_2\text{-}C_{18}H_{37}][Br^{-}]_3$ molecule as structure-directing agent (SDA). (A) TEM image projected down [010] axis and (B) its electron diffraction pattern.

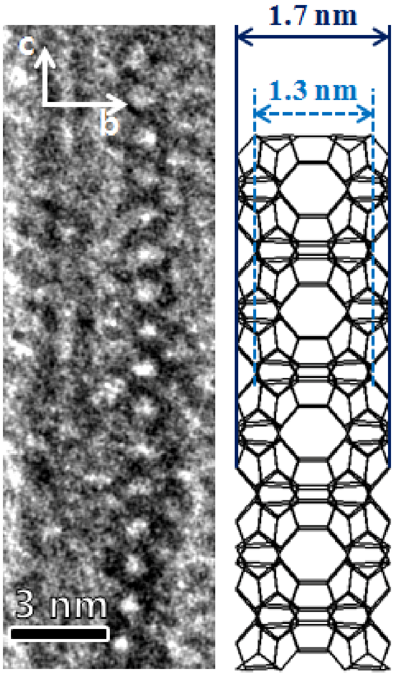

Fig. S2 The thickness of single-layer zeolite framework. It is not much precise to measure the framework thickness on the TEM micrographs, so that the measurement was based on the MFI zeolite structure which was provided by the International Zeolite Association. The 1.5-nm thickness is a mean value between the maximum thickness of 1.7 nm and the minimum thickness of 1.3 nm.

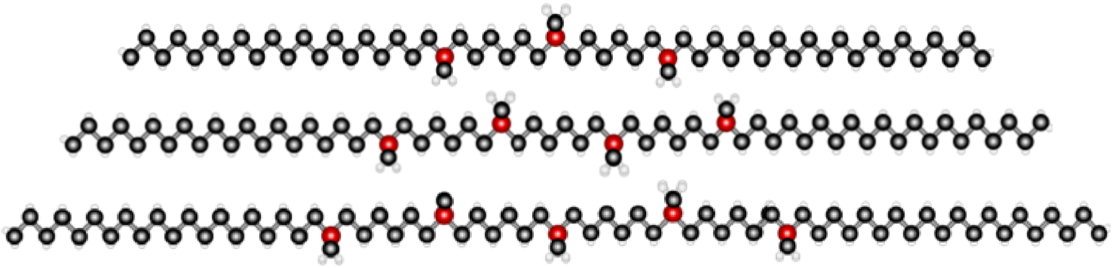

Fig. S3 Molecular structures of the gemini-type surfactants containing multi quaternary ammonium groups as zeolite SDA (black: carbon, red: nitrogen, and white: hydrogen atoms). All quaternary ammonium groups are connected by hexamethylene bridges in a row, and two docosyl chains are attached on two outer ammonium groups. Molecular formulae of the surfactants, from the top to bottom, are $[C_{18}H_{37}\text{-}N^{+}(CH_3)_2\text{-}C_6H_{12}\text{-}N^{+}(CH_3)_2\text{-}C_6H_{12}\text{-}N^{+}(CH_3)_2\text{-}C_{18}H_{37}][Br^{-}]_3$, $[C_{18}H_{37}\text{-}N^{+}(CH_3)_2\text{-}C_6H_{12}\text{-}N^{+}(CH_3)_2\text{-}C_6H_{12}\text{-}N^{+}(CH_3)_2\text{-}C_6H_{12}\text{-}N^{+}(CH_3)_2\text{-}C_{18}H_{37}][Br^{-}]_4$, and $[C_{18}H_{37}\text{-}N^{+}(CH_3)_2\text{-}C_6H_{12}\text{-}N^{+}(CH_3)_2\text{-}C_6H_{12}\text{-}N^{+}(CH_3)_2\text{-}C_6H_{12}\text{-}N^{+}(CH_3)_2\text{-}C_6H_{12}\text{-}N^{+}(CH_3)_2\text{-}C_{18}H_{37}][Br^{-}]_5$. These surfactants are designated as ‘GS-3N’, ‘GS-4N’, and ‘GS-5N’, respectively. ‘GS’ means gemini-type surfactant, and the number following ‘GS-’ means the number of ammonium-groups in a molecule.

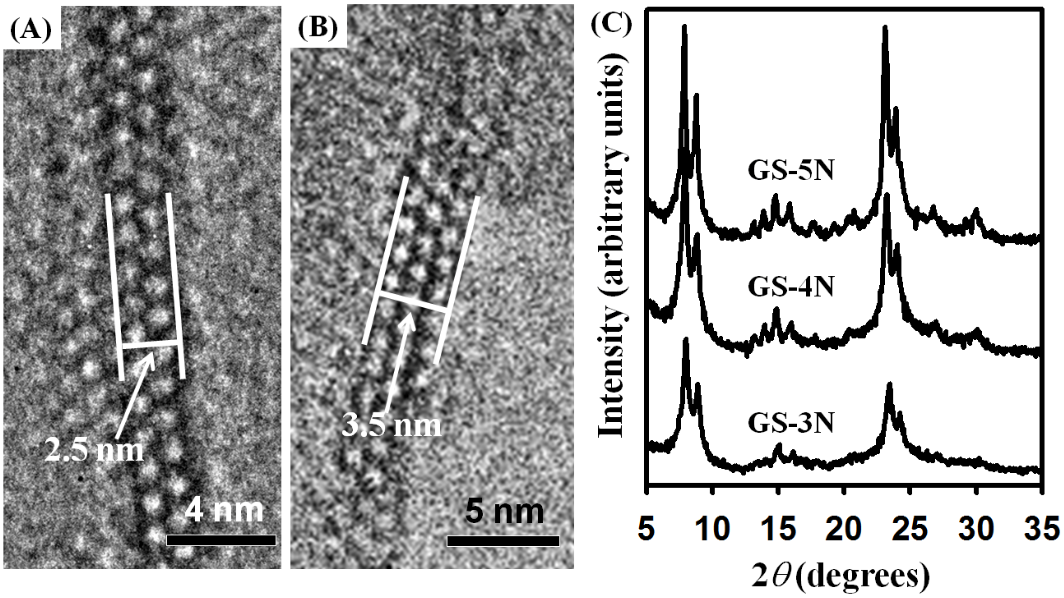

Fig. S4 (A), (B) TEM images of resultant zeolites synthesized with GS-4N and GS-5N surfactant, respectively. Maximum thickness of resultant zeolite increased with ammonium groups in a surfactant. (C) XRD patterns of calcined zeolites synthesized with gemini-type surfactants containing various quaternary-ammonium groups.

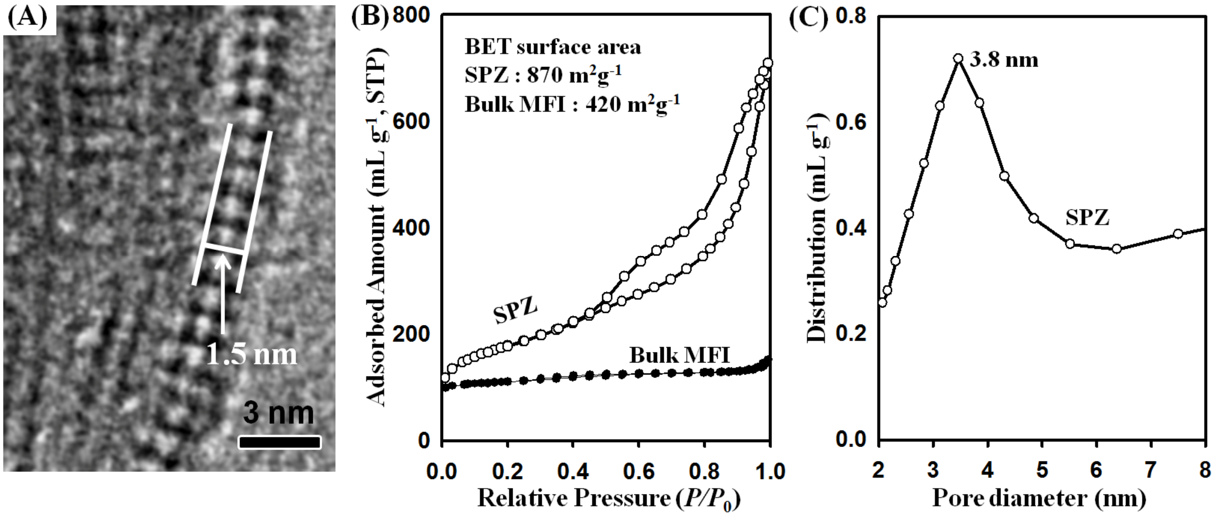

Fig. S5 (A) TEM image, (B) N_2 adsorption-desorption isotherms of SPZ (disordered single layer) and bulk MFI, and (C) pore size distribution of SPZ obtained from adsorption branch of N_2 adsorption-desorption isotherm. This SPZ showed remarkable N_2 adsorption capacity in the mesoporous region (i.e., $0.2 \leq P/P_0 \leq 0.95$), in contrast to bulk MFI.

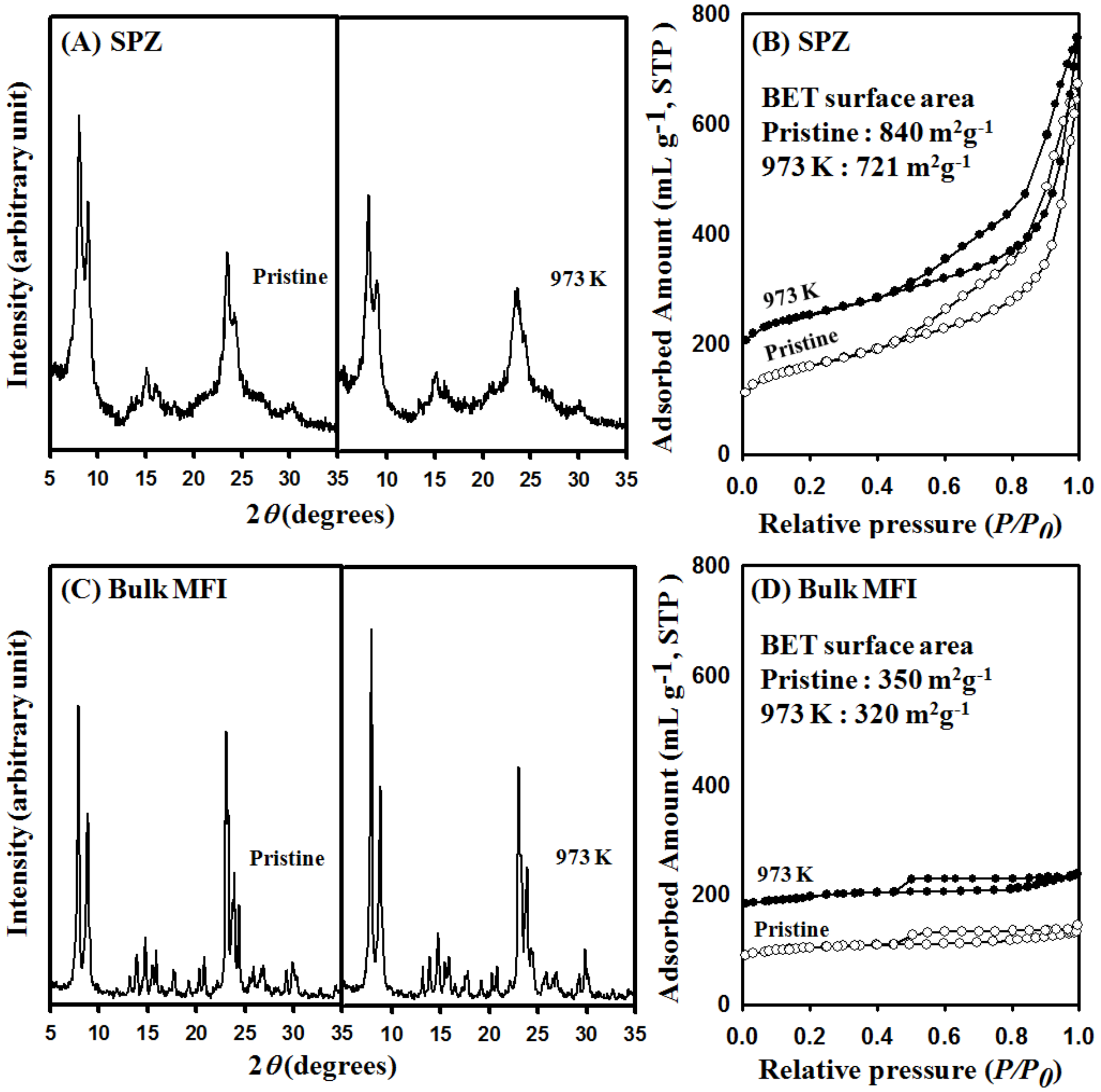

Fig. S6 Steam stability of 1.5-nm thick SPZ and bulk MFI zeolite. (A), (C) X-ray diffraction patterns and (B), (D) N_2 adsorption-desoprtion isotherms are of the SPZ and bulk MFI zeolite sample, before and after the steaming treatment at 973 K. The N_2 adsorption-desorption isotherms of the SPZ and bulk MFI which were steamed at 973 K in (B) and (D) were vertically offset by 100 mL g^{-1}. For the steaming treatment, each 50 mg of two zeolite samples were heated in fused silica tubing with 100% steam flow at the rate of 0.25 mL min^{-1}. Temperature was increased from room temperature to 973 K over 2 h, and maintained there for 2 h.

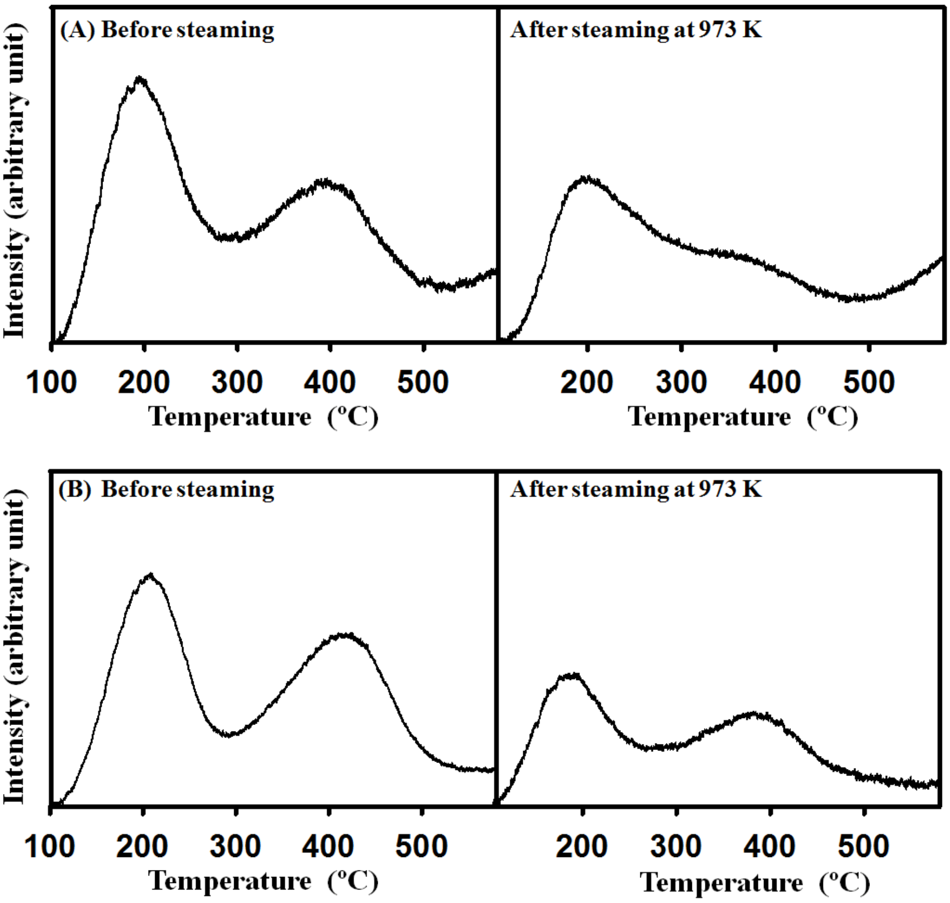

Fig. S7 Temperature-programmed desorption (TPD) of ammonia profiles of (A) 1.5-nm thick SPZ and (B) bulk MFI zeolite, before and after the steaming treatment at 973 K. Ammonia TPD was measured in a He flow using an instrument (BELCAT-M, BEL Japan) equipped with a thermal conductivity detector (TCD). Before the measurement, 50 mg of the zeolite was degassed in a He stream (20 mL min^{-1}) at 773 K for 1 h. After cooling to 373 K, the sample was put in a mixed gas flow of 10 mol% NH_3 and 90% He (20 mL min^{-1}) for the sufficient adsorption of the NH_3. Subsequently, the sample was exposed to flowing He for 3 h to remove weakly adsorbed NH_3. Finally, a TPD profile was obtained while the sample was heated from 373 to 923 K at a ramping rate of 10 K min^{-1} under flowing He (20 mL min^{-1}). The TPD profile thus obtained was deconvoluted with the assumption of Gaussian distributions.

Table S1 Distribution fitting data of TPD spectra using Gaussian distribution function

Sample	1st peak (~473 K), weak acid, mmol g^{-1}	2nd peak (~753 K), strong acid, mmol g^{-1}
SPZ	0.12	0.17
Bulk MFI zeolite	0.19	0.22

Catalytic experiments

Before the catalytic tests, all the zeolite samples were ion-exchanged three times with 1 M NH_4NO_3 solution NH_4^+ form, and then converted to the H^+ form via calcination in air at 773 K. Synthesis of jasminadlhehyde, and Friedel-Crafts alkylation of benzene with benzyl alcohol were chosen as acid-catalyzed reactions of large molecules to investigate the catalytic ability of the out surfaces of the SPZ nanosheet. The catalytic conversion of methanol to gasoline was performed as probe reaction to measure the steam-stability of acidity of the SPZ nanosheet. Detailed processes of the catalytic reaction were described as follows:

Synthesis of jasminaldehyde: This reaction was carried out under N_2 ambient, in a Pyrex batch reactor equipped with a reflux condenser. Before the reaction, 50 mg of the zeolite catalysts was degassed at 573 K under vacuum condition. Typically, heptanal (3 mmol), benzaldehyde (15 mmol) and the catalyst (50 mg) were mixed, and the mixture was heated at 125°C for 20 h. After cooling to room temperature, the solid catalyst were removed by the syringe filter and the remained reaction solution was analyzed by a gas chromatograph (GC, Younglin, Acme-6000) equipped with a flame ionization detector and a capillary column (HP-Innowax, J&W).

Friedel-Crafts alkylation of benzene with benzyl alcohol: Gas-phase Friedel-Crafts alkylation of benzene with benzyl alcohol was performed in gas-phase. The reaction was carried out over the 100 mg of the powder sample in a fixed bed quartz reactor (inner diameter = 15 mm) at 493 K in a benzene-benzyl alcohol mixture (molar ratio 5:1) carried by N_2 gas stream (flow rate = 50 mL min^{-1}). Before reaction, catalysts were activated at 823 K for 2 h in a flowing air (30 mL min^{-1}). The feed rate of the benzene-benzyl alcohol mixture was 5 mL h^{-1} (weight hourly space velocity of benzyl alcohol = 10.4 g g^{-1} h^{-1}). The product was condensed as liquid phase. The product obtained at 30 min of the reaction was analyzed by a gas chromatograph (GC, Younglin, Acme-6000) equipped with a flame ionization detector and a capillary column (HP-Innowax, J&W).

Methanol to gasoline reaction: The reaction was performed at 623 K in a fixed-bed Pyrex reactor using 100 mg of catalyst. Before reaction, catalysts were activated at 823 K for 2 h in a flowing air (30 mL min^{-1}). Methanol was introduced as vapor phase, after diluting the liquid phase methanol injected by HPLC pump by N_2 flow (50 mL min^{-1}). The weight hourly space velocity of the methanol was 14.1 g g^{-1} h^{-1}. The reaction effluent was analyzed by two online GC (Younglin, Acme-6000) equipped with a flame ionization detector and a capillary column (HP-Plot-Q, J&W). The conversion rate of methanol was measured at 30 min of the reaction.