Electronic Supplementary Information (ESI)

Synthesis of hierarchical zeolites using an inexpensive mono-quaternary ammonium surfactant as mesoporogen

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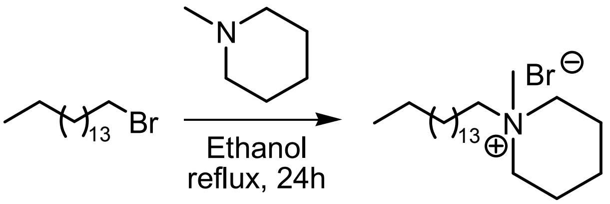
Experimental details

1. Synthesis of surfactants

(**C_{16}MP**) Synthesis of $C_{16}H_{33}$-[N^+-methylpiperidine]



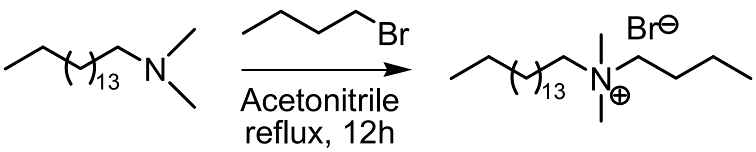
0.01 mol of 1-bromohexadecane (TCI Europe n.v., > 96 %, 72.15 €/500 g) and 0.012 mol of N-methylpiperidine (Aldrich, 98 %, 333 €/4 kg) were dissolved in 50 ml of ethanol (Biosolve, 99.9 %). The solution was refluxed in an oil bath at 80 °C for 24 h. After evaporation of ethanol, the product was filtered, washed with diethyl ether (Biosolve, 99.5 %), and dried in vacuum oven at 50 °C for overnight. The product was $C_{16}H_{33}$-[N^+-methylpiperidine] (denoted as **C_{16}MP**). The product yield was 86 %.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.75 (m, 2H), 3.59 (m, 4H), 3.30 (s, 3H), 1.76 (m, 8H), 1.26 (m+ br s, 26H), 0.82 (t, J = 6.6 Hz, 3H)

^{13}C NMR (101 MHz, $CDCl_3$) δ 62.81 (s), 60.77 (s), 48.42 (s), 31.85 (s), 29.61 (br), 29.54 (s), 29.43 (s), 29.36 (s), 29.29 (s), 29.25 (s), 26.36 (s), 22.62 (s), 22.03 (s), 20.64 (s), 20.19 (s), 14.06 (s).

ESI-MS: Calcd. $C_{22}H_{46}N^+$ ([template **C_{16}MP**]$^+$) 324.36. Found: 324.60 (100 %).

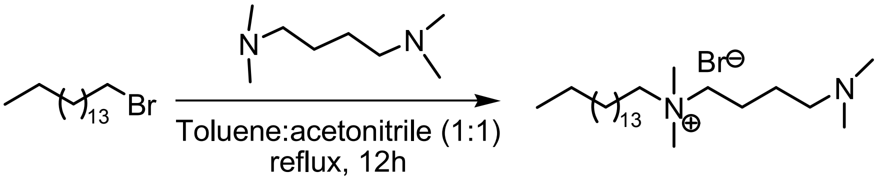
(**C_{16} N_1**) Synthesis of $C_{16}H_{33}$-$N^+(CH_3)_2$-C_4H_9



0.01 mol of N, N-dimethylhexadecylamine (Aldrich, ≥ 95 %) and 0.012 mol of 1-bromobutane (Aldrich, 99 %) were dissolved in 50 ml of acetonitrile (Biosolve, 99.8 %). The solution was refluxed in an oil bath at 80 °C for 12 h. After evaporation of acetonitrile, the product was filtered, washed with diethyl ether (Biosolve, 99.5 %), and dried in vacuum oven at 50 °C for overnight. The product was $C_{16}H_{33}$-$N^+(CH_3)_2$-C_4H_9 (denoted as **C_{16} N_1**). The yield was 81 %.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.51 (m, 4H), 3.40 (s, 6H), 1.74 – 1.61 (m, 4H), 1.48 – 1.17 (m, 28H), 0.99 (t, J = 7.3 Hz, 3H), 0.86 (t, J = 6.9 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 63.89 (s), 63.69 (s), 51.30 (s), 31.89 (s), 29.65 (br), 29.43 (s), 29.34 (s), 29.19 (s), 26.24 (s), 24.67 (s), 22.78 (s), 22.66 (s), 19.61 (s), 14.10 (s), 13.70 (s).
ESI-MS: Calcd. $C_{22}H_{48}N^+$ ([template **C_{16} N_1**]$^+$) 326.38. Found: 326.60 (100 %).

(**$C_{16}N_2$**) Synthesis of $C_{16}H_{33}$-$N^+(CH_3)_2$-C_4H_8-$N^+(CH_3)_2$-C_4H_9

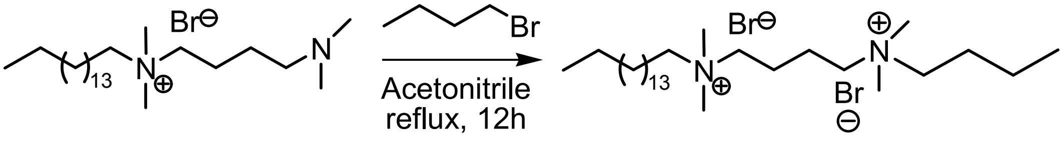


0.01 mol of 1-bromohexadecane (TCI Europe n.v., > 96 %, 72.15 €/500 g) was dissolved in 20 ml toluene (Biosolve, 99.5 %) and added dropwise into a 20 ml solution of 0.08 mol of N, N, N', N'-tetramethyl-1,4-butanediamine (TCI Europe n.v., 98 %, 62.9 €/25 ml) in acetonitrile (Biosolve, 99.8 %). The solution was refluxed in an oil bath at 70 °C for 12 h. After cooling to room temperature, the solution was kept at 4 °C for 1 h, and then was filtered and washed with diethyl ether (Biosolve, 99.5 %). The resulting solid product $C_{16}H_{33}$-$N^+(CH_3)_2$-C_4H_8-$N(CH_3)_2$ was dried in a vacuum oven at 50 °C, the yield was 53.4 %.

^1H NMR (400 MHz, $CDCl_3$) δ 3.55 – 3.45 (m, 2H), 3.40 (m, 2H), 3.30 (s, 6H), 2.27 (t, J = 6.7 Hz, 2H), 2.13 (s, 6H), 1.78 – 1.58 (m, 4H), 1.56 – 1.42 (m, 2H), 1.37 – 1.06 (m, 26H), 0.80 (s, J = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 63.81 (s), 63.57 (s), 58.21 (s), 51.26 (s), 45.28 (s), 45.24 (s), 31.83 (s), 29.61 (br), 29.42 (s), 29.34 (s), 29.27 (s), 29.17 (s), 26.20 (s), 23.83 (s), 22.69 (s), 22.61 (s), 20.38 (s), 14.05 (s).

ESI-MS: Calcd. $C_{24}H_{53}N_2^+$ 369.43. Found: 369.20 (66 %) + 185.20 (33%, $[C_{24}H_{53}N_2]^{+}$+H^+).



Secondly, 0.01 mol of $C_{16}H_{33}$-$N^+(CH_3)_2$-C_4H_8-$N(CH_3)_2$ and 0.02 mol of 1-bromobutane (TCI Europe n.v., > 98 %, 24 €/500 g) were dissolved in 100 ml of acetonitrile and subsequently stirred under reflux at 70 °C for 12 h. The resulting solution was cooled in a refrigerator at 4 °C for 1 h, and then filtered, washed with diethyl ether (Biosolve, 99.5 %) and dried in a vacuum oven at 50 °C. The product was $C_{16}H_{33}$-$N^+(CH_3)_2$-C_4H_8-$N^+(CH_3)_2$-C_4H_9 (denoted as **$C_{16}N_2$**), the yield was 69.7 %.

^{1}H NMR (400 MHz, CDCl$_3$) δ 3.40 – 3.29 (m, 4H), 3.06 – 2.99 (br, 4H, overlap with unidentified impurity), 2.87 (s, 6H), 2.86 (s, 6H), 1.63 (br, 4H), 1.35 – 1.23 (m, 4H), 1.02 – 0.73 (m, 28H), 0.56 (t, J = 6.0 Hz, 3H), 0.43 (t, J = 6.9 Hz, 3H).
^{13}C NMR (101 MHz, CDCl$_3$) δ 64.98 (s), 64.63 (s), 63.51 (s), 63.34 (s), 51.04 (s), 50.94 (s), 31.86 (s), 29.66 (br), 29.52 (br), 29.30 (s), 29.26 (s), 26.34 (s), 24.61 (s), 22.85 (s), 22.63 (s), 19.82 (s), 19.65 (s), 14.07 (s), 13.73 (s).
ESI-MS: Calcd. $C_{28}H_{62}N_2^{2+}$ 213.25. Found: 213.20 (65 %) + 507.24 (35%, $[C_{28}H_{62}N_2Br]^+$).

2. Cost of surfactants

We estimated the raw materials cost of $C_{16}MP$ and $C_{16}N_2$. This analysis does not include the cost of solvents, which is a reasonable assumption as the major part can be reused. We also did not include cost for electricity, labor etc. To facilitate comparison, we assume 100 % yield for each step in the synthesis. The cost for $C_{16}MP$ and $C_{16}N_2$ are 133 €/kg and 6363 €/kg, respectively. The price of [3-(trimethoxysilyl)propyl]octadecyl-dimethylammonium chloride (TPOAC, Acros, 60 % in methanol, 78.4 €/100 ml) is 1468 €/kg if we only take into account the weight of TPOAC.

3. Synthesis of zeolites

(1) Synthesis of SSZ-13 zeolites

Mesoporous SSZ-13 zeolites were synthesized as follows: aluminium hydroxide (Aldrich, reagent grade), sodium hydroxide (EMSURE, 50 wt%), TMAdaOH (SACHEM Inc. 25 wt%), and $C_{16}MP$ (bromide form) were dissolved in deionized water. Then, Ludox AS 40 (Aldrich, 40 wt%) was added into the clear solution. The final gel had a molar composition of 15 TMAdaOH : 5 $C_{16}MP$: 7.5 Na_2O : 2.5 Al_2O_3 : 100 SiO_2 : 4400 H_2O (25 % of TMAdaOH was replaced by $C_{16}MP$). After vigorous stirring at room temperature for 2 h, the resulting gel was transferred into a 45 mL Teflon lined steel autoclave and crystallized at 160 °C for 8 days. The obtained solid is denoted as SSZ-13-$C_{16}MP$. The influence of lowering the $C_{16}MP$ amount was investigated by replacing 5 % (instead of 25 %) of TMAdaOH by $C_{16}MP$, forming a final gel with the composition 19 TMAdaOH : 1 $C_{16}MP$: 7.5 Na_2O : 2.5 Al_2O_3 : 100 SiO_2 : 4400 H_2O. This zeolite is denoted as SSZ-13-$C_{16}MP$(5%). Using the same approach, zeolites were prepared using $C_{16}N_1$ and $C_{16}N_2$ and the final materials are denoted as SSZ-13-$C_{16}N_1$ and SSZ-13-$C_{16}N_2$, respectively. The same molar amount of the bromide form of these mesoporogens ($C_{16}N_1$ or $C_{16}N_2$) was added into the gel, forming a gel with composition 15 TMAdaOH : 5 mesoporogen : 7.5 Na_2O : 2.5 Al_2O_3 : 100 SiO_2 : 4400 H_2O. SSZ-13-bulk was synthesized without mesoporogen using a gel with the composition 20 TMAdaOH : 7.5 Na_2O : 2.5 Al_2O_3 : 100 SiO_2 : 4400 H_2O. Furthermore, SSZ-13-bulk, SSZ-13-$C_{16}N_2$ and SSZ-13-$C_{16}MP$ were synthesized at an gel Si/Al ratio of 50. This was achieved by using less aluminium hydroxide to compose the otherwise similar gel.

(2) Synthesis of ZSM-5 zeolites

Mesoporous ZSM-5 zeolite was synthesized as follows: aluminum sulfate octadecahydrate (Aldrich, 98 %), sodium hydroxide (EMSURE, 50 wt%), 1,6-diaminohexane (DAH, Aldrich, 98 %), and C_{16}MP (OH form) were dissolved in distilled water under 70 °C until the solution is clear. Then, the solution was cooled to room temperature and Ludox AS 40 (Aldrich, 40 wt%) was added into the solution at once. The final gel had a molar composition of 1.5 C_{16}MP : 6 DAH : 4 K_2O : 0.3 Al_2O_3 : 30 SiO_2 : 1333 H_2O. After vigorous stirring at room temperature for 2 h, the resulting gel was transferred into a 45 mL Teflon lined steel autoclave and crystallized at 160 °C for 4 days with tumbling at 50 rpm. The resulting zeolite is denoted as ZSM-5-C_{16}MP-DAH. Two further zeolites were synthesized using tetrapropylammonium hydroxide (TPAOH, Merck, 40 wt%) and diethylamine (DEA, Aldrich, 99.5 %) at similar SDA/C_{16}MP ratios. These zeolites are denoted as ZSM-5-C_{16}MP-TPAOH and ZSM-5-C_{16}MP-DEA, respectively. Conventional ZSM-5 was prepared with TPAOH as the sole SDA (ZSM-5-bulk).

After crystallization, the zeolite products were filtered, washed with deionized water and dried in air at 110 °C. The zeolites were calcined at 550 °C for 10 h under flowing air and subsequently ion-exchanged three times with 1.0 M NH_4NO_3 solutions followed by calcination at 550 °C for 4 h in flowing air in order to obtain their proton forms.

4. Characterization

X-ray diffraction patterns were recorded on a Bruker D4 Endeavor diffractometer using Cu Kα radiation in the 2θ range of 5−60°. Surface area and porosity of zeolites were determined by Ar physisorption at −186 °C on a Micromeritics ASAP 2020 instrument in static mode. The samples were outgassed at 400 °C for 8 h prior to the sorption measurements. The Langmuir surface area of SSZ-13 zeolite was from data in the relative pressure range p/p_0 = 0.05–0.20. The BET surface area of ZSM-5 zeolite was obtained using the p/p_0 range of 0.10–0.20. The total pore volume was determined at p/p_0= 0.97. The mesopore volume and the micropore volume were determined by *BJH* and the *t*-plot methods, respectively. To determine the mechanical stability of SSZ-13-C_{16}MP, the calcined sample was pressed in a stainless steel die at 150 or 300 MPa for 2 min prior to the Ar physisorption measurement. Thermogravimetric analysis (TGA) of the as-synthesized zeolites was performed using a TGA/DSC (Mettler Toledo). The temperature was increased to 850 °C at a rate of 5 °C min^{-1} in air (20 ml min^{-1}). Scanning electron microscopy (SEM) images were taken on a FEI Quanta 200F scanning electron microscope at an accelerating voltage of 3 kV. The zeolites were coated with gold prior to measurement. High-resolution LV-SEM was done with an in-column detector on a JEOL JSM-7800F Prime at an electron landing energy of 300 eV without conductive coating and the samples were prepared on Carbon stub that was dried at 250 °C for 30 min before mounting. Transmission electron microscopy (TEM) pictures were taken on a FEI Tecnai 20 at 200 kV. The samples were suspended in ethanol and dispersed over a carbon coated holey Cu grid with a film prior to measurements. FT-IR spectra of samples were recorded on a Bruker Vertex 70v instrument. The spectra were acquired at 2 cm^{-1} resolution and 64 scans. The samples were prepared as thin wafers of 10 mg/cm^2 and placed inside a controlled-environment infrared transmission cell, capable of heating and cooling, gas dosing and evacuation. For CO adsorption, the wafer was heated to 550 °C at a rate of 10 $°C{\cdot}min^{-1}$ under evacuation. Subsequently, the sample was cooled to −196 °C. CO (Praxair, 99.999 %) was introduced into the sample cell via a sample loop (5 μL) connected to a six-port valve. For pyridine adsorption, pyridine was introduced to the cell from an ampoule kept at room temperature. The exposure time was 20 min followed by desorption for 1 h under evacuation at temperatures of 150, 300 and 500 °C. Spectra were recorded after cooling the sample to 150 °C. IR Spectra were normalized by the weight of catalyst wafer. ^1H MAS NMR measurements were recorded on a 11.7 Tesla Bruker DMX500 NMR spectrometer. The sample was loaded in a ZrO_2 rotor placed in a 4 mm MAS probe head. The sample rotation rate was 10 kHz. Prior to NMR measurement, the zeolite sample was dehydrated at a temperature of 450 °C at a pressure lower than 10^{-5} mbar for 6 h. To quantify the concentration of Brønsted acid sites (BAS), the ^1H MAS NMR signal intensity was calibrated using adamantane as the reference. ^{27}Al MAS NMR spectroscopy was measured on the same spectrometer in a 2.5 mm MAS probe head using a spinning rate of 20 kHz. To confirm the composition of the template, liquid state NMR spectra were recorded on a Varian Mercury 400 MHz spectrometer. The chemical shifts were referenced to residual solvent peaks. ESI-MS measurements were performed on a Thermo Scientific LCQ Fleet apparatus using CH_3CN with 0.1 % formic acid as solvent.

5. Molecular simulations

The classical force-field COMPASS in the forcite+ module in Materials Studio V6.0 (Accelrys

Software inc.) (MSt) was used. Silanol terminated SSZ-13 zeolite slabs with the size of $a \times b \times c = 4 \times 3 \times 4$ unit cells separated by a vacuum layer of 180 Å in the *c*-direction were used using periodic boundary conditions. In this model, we embedded the templates of interest. Silanol terminated MFI nanosheets with the size of $a \times b \times c = 3 \times 1.5 \times 2$ unit cells (25 Å thick excluding external silanol groups) separated by a vacuum layer of 180 Å in the *b*-direction were used to model ZSM-5 nanosheets. Two templates were placed on opposite side of the sheet at the two channel intersections. Prior to the single-point energy calculations, the geometry of the structures were optimized, subjected to a 10 ps dynamics run in the NVE-ensemble and followed by another geometry optimization step. Interaction energies were obtained by referencing the final geometries to vacuum based models of the individual components of the model of interest. $C_{16}N_2$ situation (I) is characterized by an ammonium group at the surface and in the cavity below it and $C_{16}N_2$ (II) by two consecutive cavities below the surface that are both occupied by an ammonium group. The destabilization energies of the ZSM-5 and SSZ-13 zeolite slabs were calculated by referencing the final geometry of the zeolites obtained from the dynamic runs to geometry optimized and charged zeolite-slabs coming from Materials Studio library. Balancing the cationic charge was done by deprotonation of an external silanol group (ZeO) or the substitution of a silicon atom by aluminum (ZeAl) followed by manual charge adjustment. Slabs with two deprotonated silanol groups (2ZeO) and one deprotonated silanol group and aluminum substitution (Ze(O+Al)) were also made. Silanol deprotonation was always done at the channel entrance next to the template. ZSM-5 containing 1,6-diaminohexane was kept neutral. The reference zeolites to calculate the destabilization energy consisted of similar systems with the aim to rule out the influence of deprotonation and Al substitution. An *exchange* system in the case of $C_{16}H_{33}$-[N^+-methylpiperidine] was made to analyze the influence of the conformation of the template in the SSZ-13 cavity.

6. Catalytic activity measurements

The proton form of the zeolite was pressed into pellets, and then crushed and sieved to obtain particles ranging in size from 250 to 500 μm. Catalytic activity measurements were carried out in a quartz tubular fixed-bed reactor with 50 mg catalyst loading. The inner diameter of the quartz tube reactor was 4 mm. Before reaction, the catalysts were activated at 550 °C in synthetic air (30 ml min^{-1}) for 2 h. The methanol-to-olefins reaction was performed at 350 °C. Methanol

(Merck, 99 %) was introduced to the reactor by leading a flow of 30 ml min^{-1} of He through a saturator kept at −17.2 °C. This resulted in a WHSV of 0.8 g g^{-1} h^{-1}. The product effluent was analysed online by gas chromatography (Compact GC Interscience equipped with TCD and FID detectors with RT-Q-Bond and Al_2O_3/KCl columns). The reaction was followed for 24 h. Methanol conversion is based on the inlet and outlet concentrations of methanol as determined by GC analysis of the reactor feed before and after the reaction and the reactor effluent during reaction. Dimethylether was considered as a reactant in these calculations.

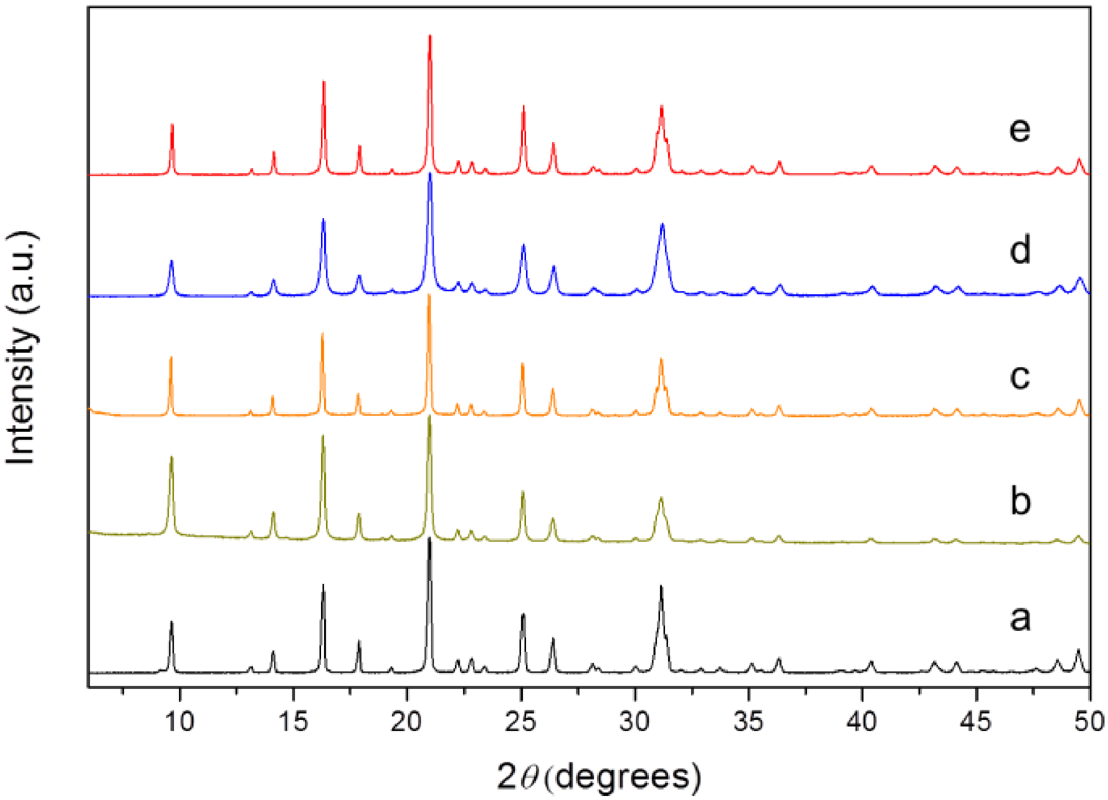


Fig. S1 XRD patterns of as-synthesized SSZ-13-bulk (a), SSZ-13-$C_{16}N_1$ (b), SSZ-13-$C_{16}N_2$ (c), SSZ-13-C_{16}MP (d) and SSZ-13-C_{16}MP(5%) (e).

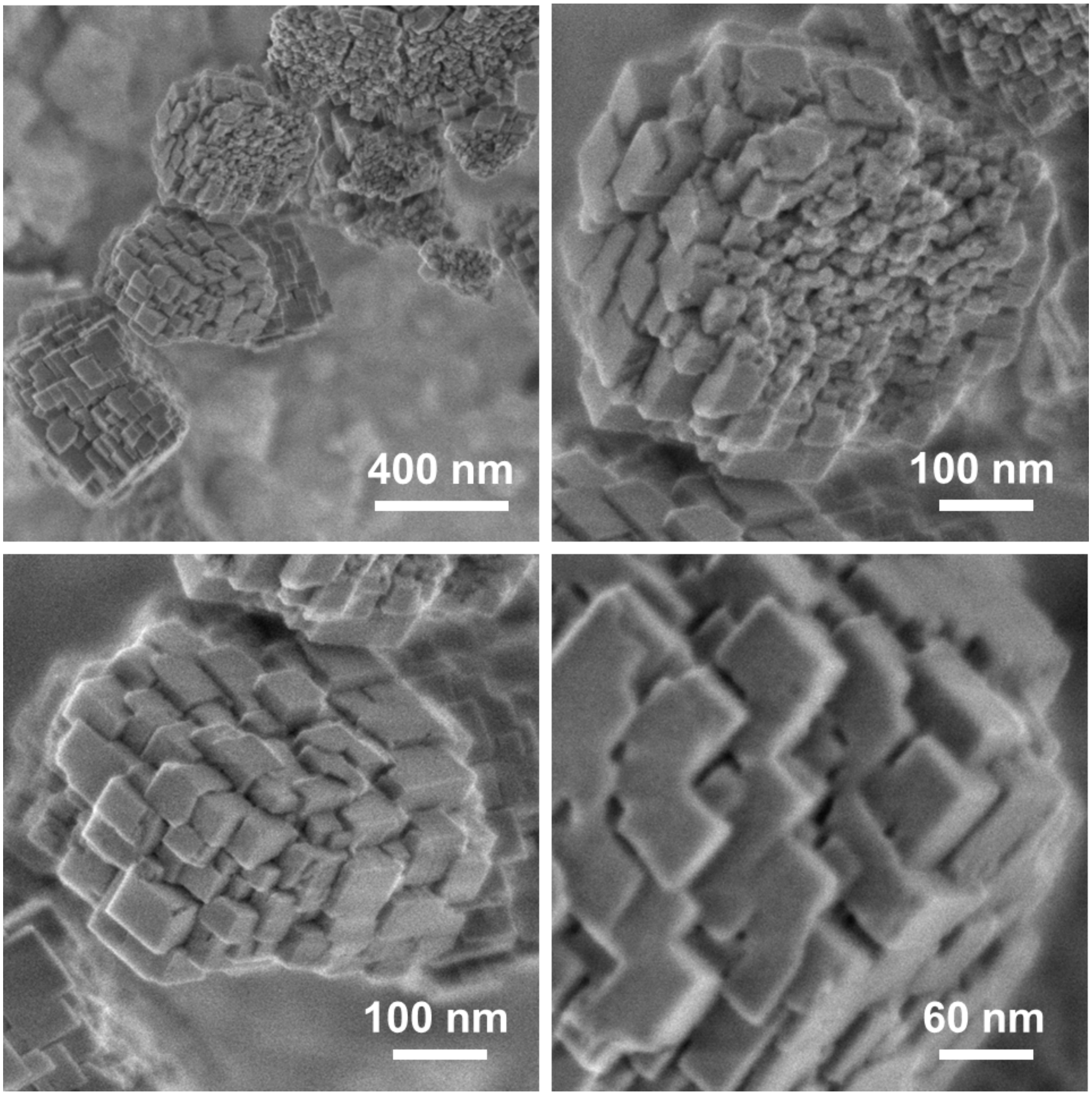
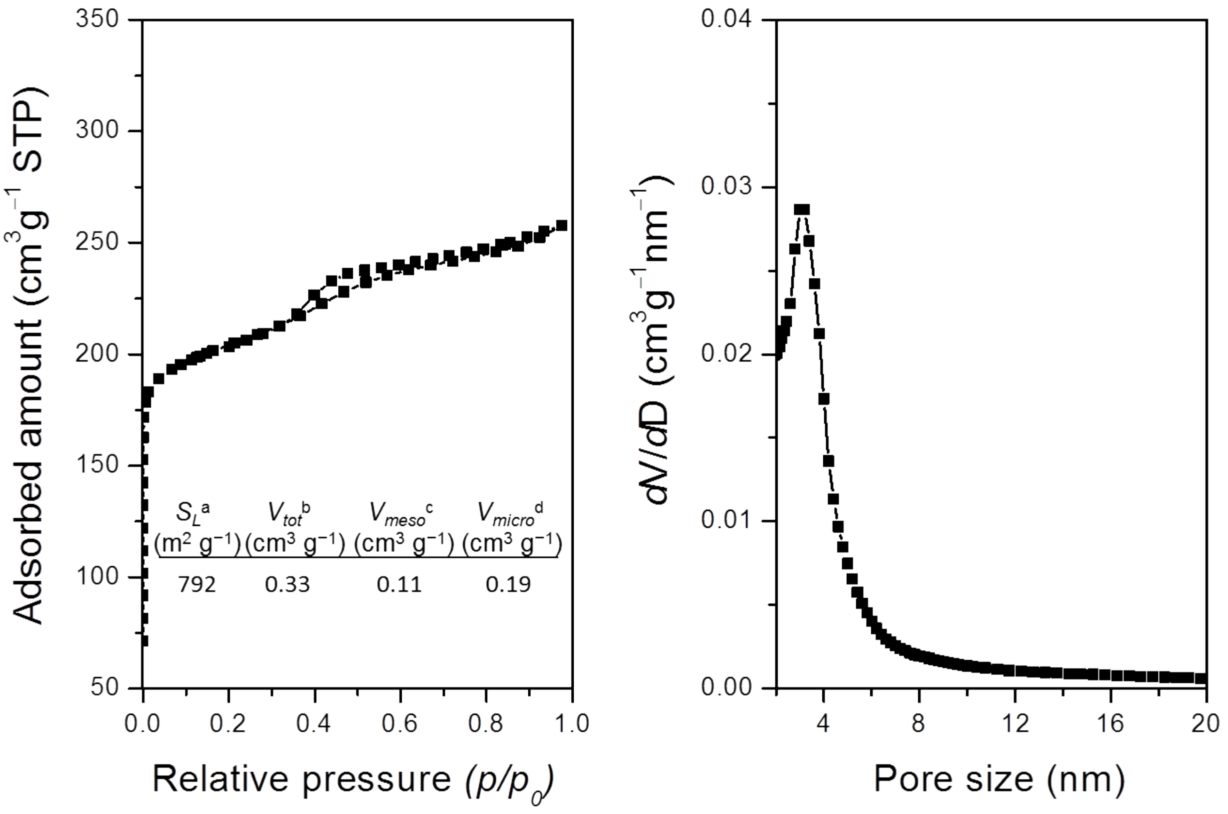


Fig. S2 LV-SEM images taken at different magnifications of SSZ-13-C_{16}MP.



S_L^a (m^2 g^{-1})	V_{tot}^b (cm^3 g^{-1})	V_{meso}^c (cm^3 g^{-1})	V_{micro}^d (cm^3 g^{-1})
792	0.33	0.11	0.19

Fig. S3 Ar physisorption isotherm (left) and mesopore size distribution (right) of SSZ-13-C_{16}MP(5%). [a] S_L is the Langmuir surface area obtained in the relative pressure range (p/p_0) of 0.05–0.20; [b] V_{tot} is the total pore volume calculated at p/p_0= 0.97; [c] V_{meso} and [d] V_{micro} are the mesopore volume and the micropore volume calculated from the *BJH* method and the *t*-plot method, respectively.

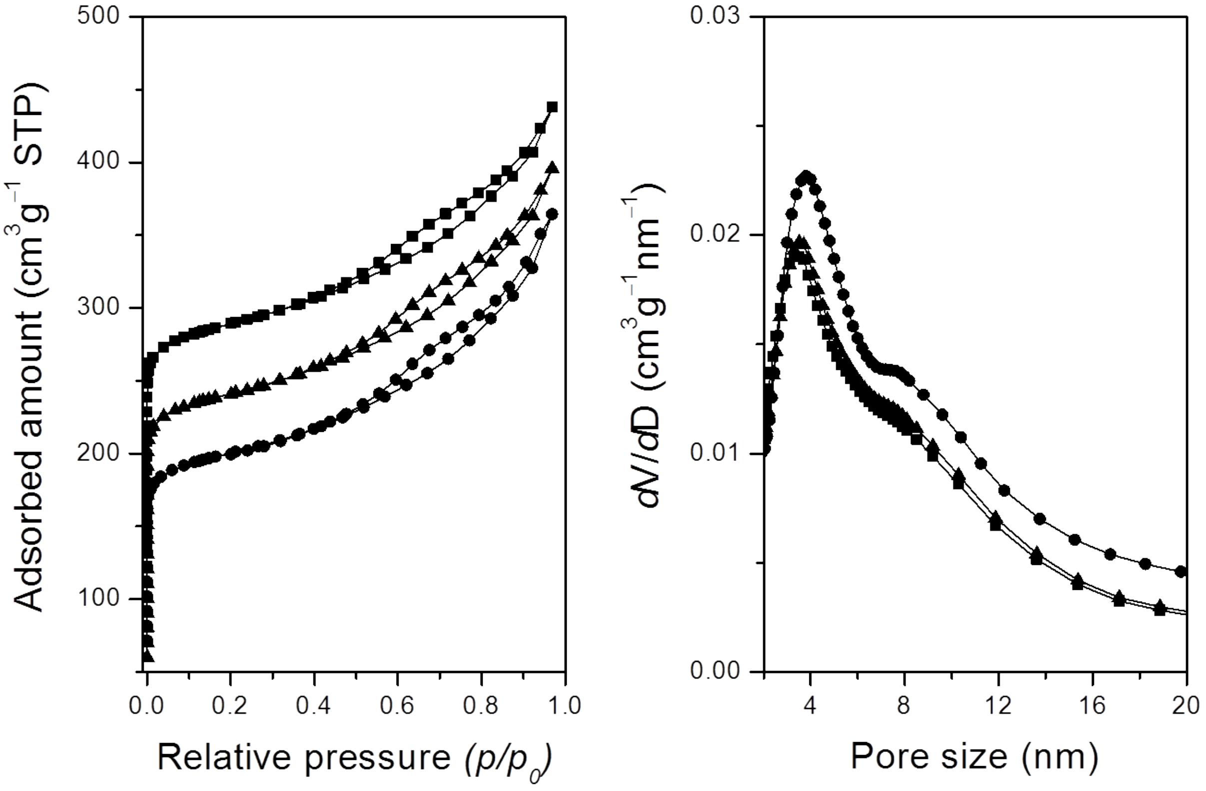


Fig. S4 Ar physisorption isotherms (left) and mesopore size distributions (right) of SSZ-13-C_{16}MP compressed at increasing external pressure: 0 MPa (●), 150 MPa (▲), and 300 MPa (■). The isotherms were vertically offset by equal intervals of 50 cm^3 g^{-1}.

Table S1 Textural properties of the calcined zeolites.

Zeolite	S_L[a] (m^2g^{-1})	V_{total} (cm^3g^{-1})	V_{meso} (cm^3g^{-1})	V_{micro} (cm^3g^{-1})
SSZ-13-bulk	723	0.25	0.01	0.22
SSZ-13-$C_{16}N_2$	778	0.37	0.12	0.22
SSZ-13-C_{16}MP-0 MPa	777	0.47	0.25	0.18
- 150 MPa	745	0.44	0.23	0.17
- 300 MPa	737	0.43	0.22	0.17
ZSM-5-bulk	377[b]	0.21	0.06	0.12
ZSM-5-C_{16}MP-DAH	418[b]	0.37	0.22	0.11
ZSM-5-C_{16}MP-DEA	395[b]	0.37	0.24	0.09

[a] Langmuir surface area obtained for $p/p_0 = 0.05–0.20$. [b] BET surface area obtained for $p/p_0 = 0.10–0.20$.

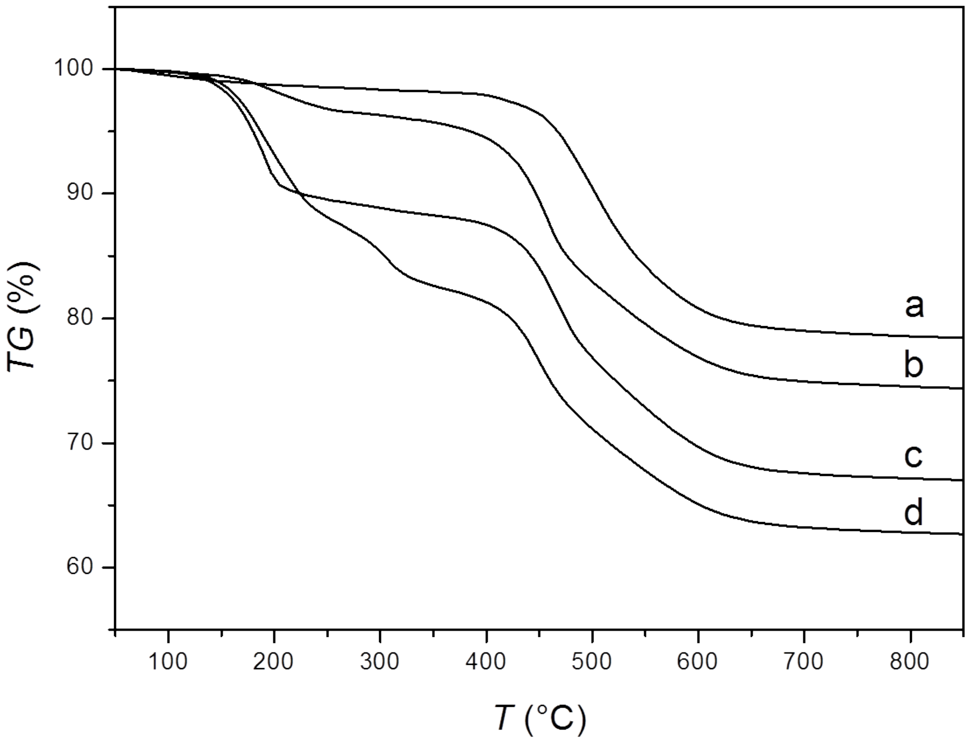


Fig. S5 Thermogravimetric analysis (TGA) of as-synthesized zeolites. The weight losses for SSZ-13-bulk (a), SSZ-13-$C_{16}N_1$ (b), SSZ-13-$C_{16}N_2$ (c) and SSZ-13-C_{16}MP (d) are 22 %, 25 %, 33 %, and 37 %, respectively.

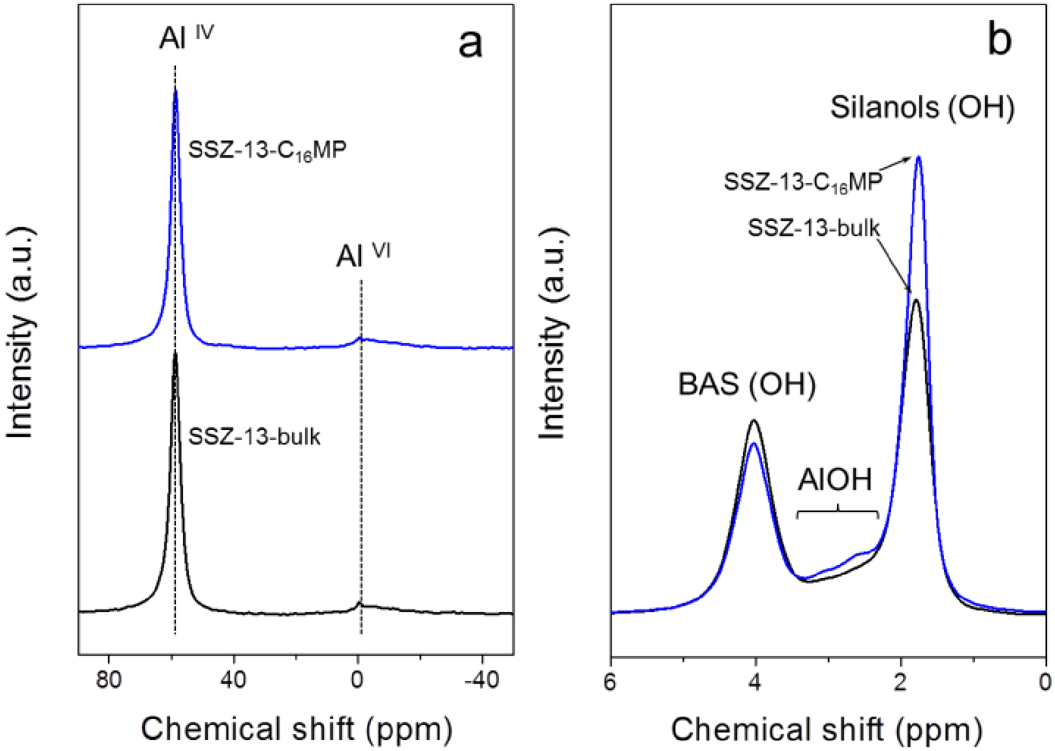


Fig. S6 ^{27}Al MAS (a) and ^{1}H MAS NMR spectra (b) of the proton forms of SSZ-13-bulk and SSZ-13-C_{16}MP.

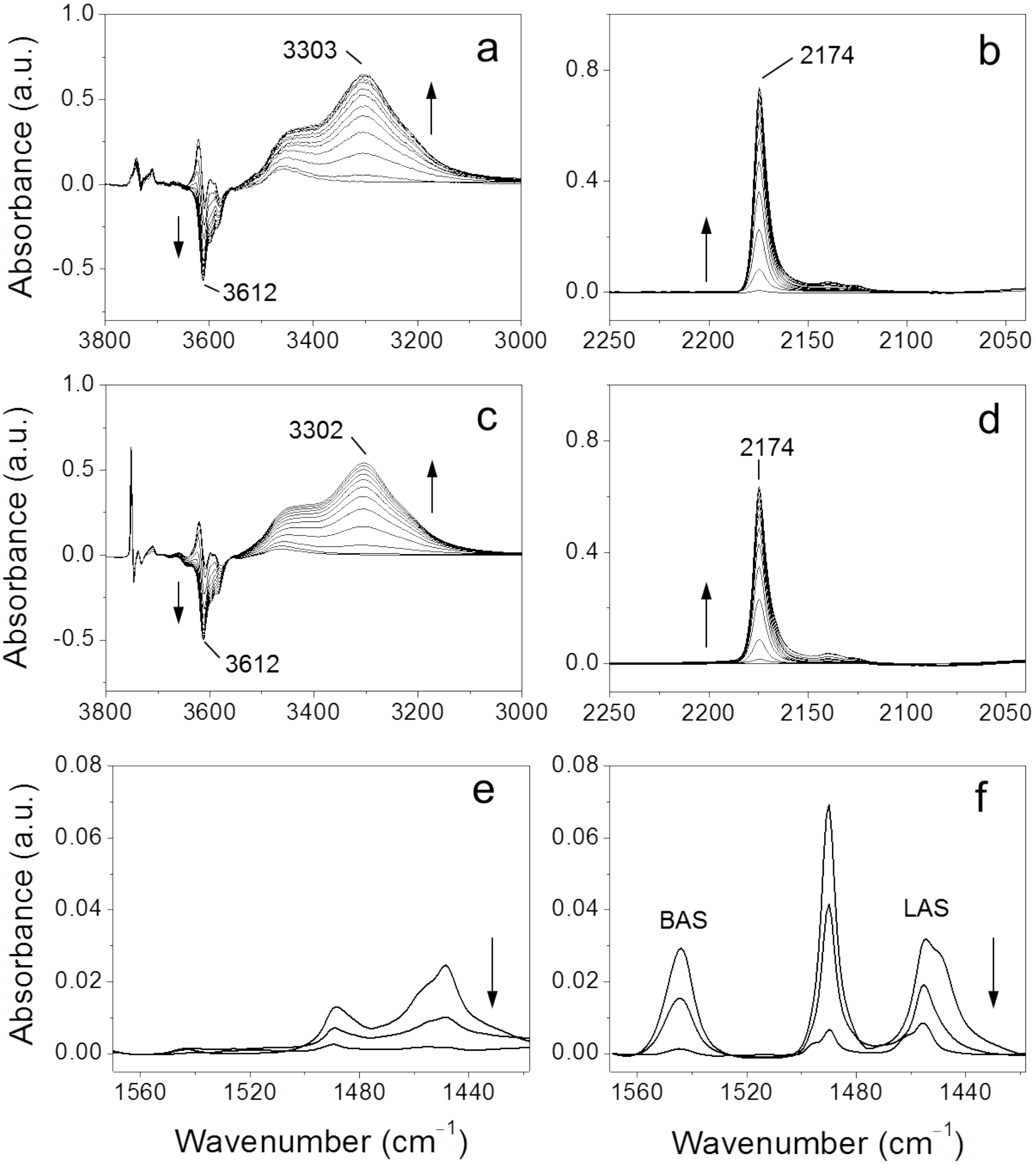


Fig. S7 (a-d) Infrared spectra of OH and CO stretching regions with increasing CO coverage (arrow indicates increasing CO coverage) at 80 K of the proton forms of SSZ-13-bulk (a, b) and SSZ-13-C_{16}MP (c, d). (e, f) Infrared spectra of pyridine adsorbed on the proton forms of SSZ-13-bulk (e) and SSZ-13-C_{16}MP (f) after evacuation at 150, 300 and 500 °C (arrow indicates increasing evacuation temperature), IR spectra were recorded at 150 °C.

Table S2 Si/Al ratio and acidity properties of the proton forms of SSZ-13-bulk and SSZ-13-C_{16}MP.

Zeolite	Si/Al	Al ^{IV} (%)	Al ^{VI} (%)	BAS[a] (mmol g^{-1})	extBAS[b] (mmol g^{-1})
SSZ-13-bulk	21	89	11	0.65	0.00
SSZ-13-C_{16}MP	23	88	12	0.50	0.07

[a] density of Brønsted acid sites calculated from ^{1}H MAS NMR spectra. [b] density of BAS at external crystal surface determined by IR spectroscopy of adsorbed pyridine after evacuation at 150 °C.

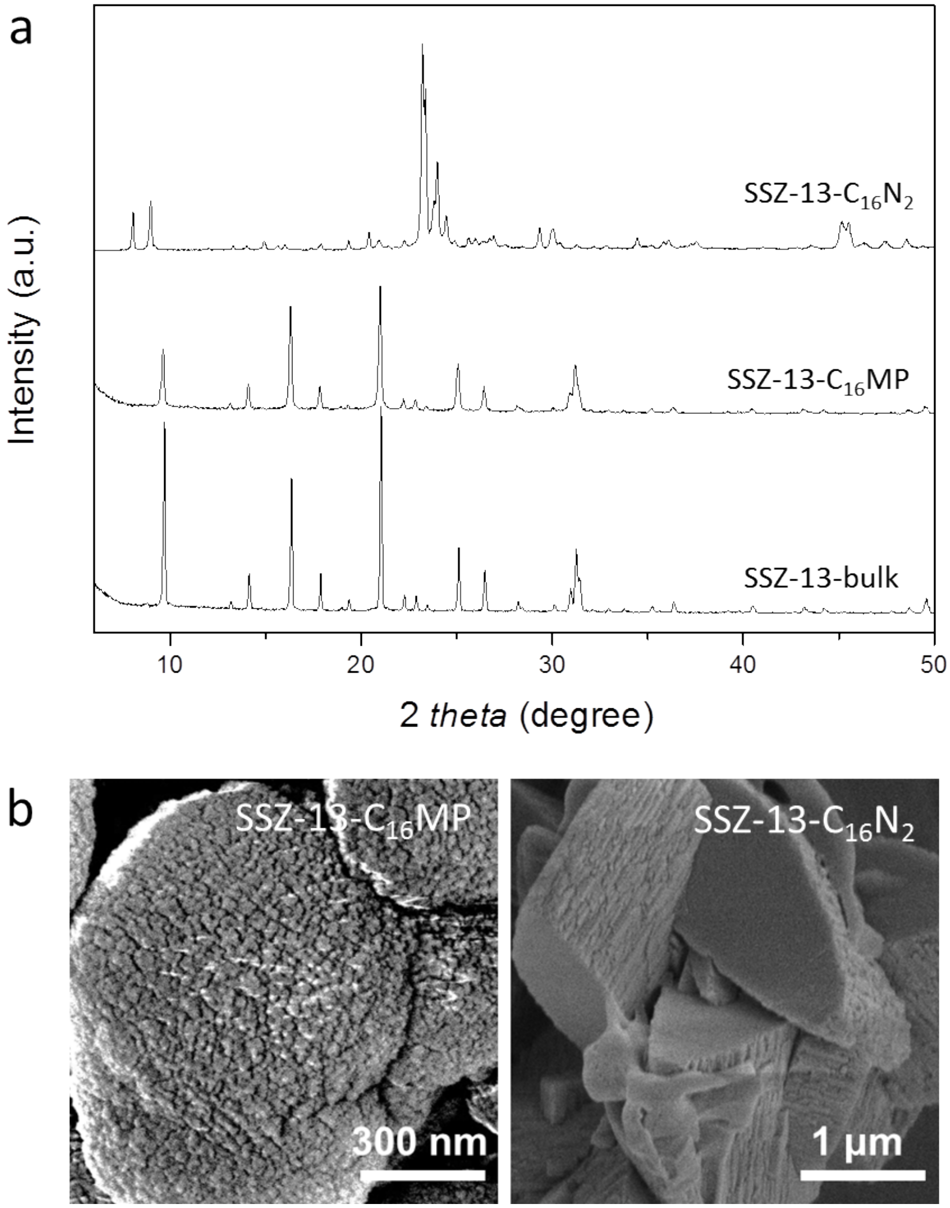
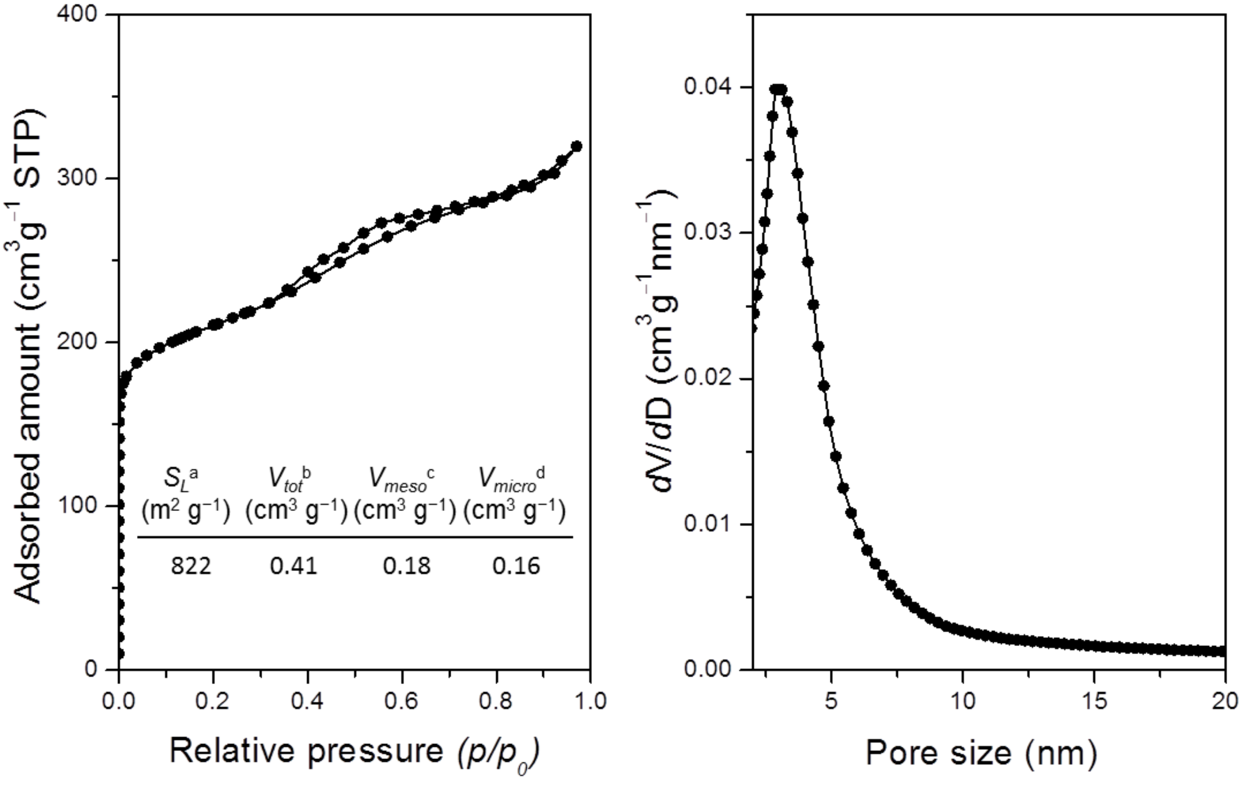


Fig. S8 XRD patterns (a) and SEM images (b) of as-synthesized SSZ-13-bulk (SEM image not shown), SSZ-13-C_{16}MP, and SSZ-13-$C_{16}N_2$ synthesized at initial gel Si/Al ratio of 50. The XRD pattern of SSZ-13-$C_{16}N_2$ shows that predominantly MFI formed.



S_L^{a} (m^2 g^{-1})	V_{tot}^{b} (cm^3 g^{-1})	V_{meso}^{c} (cm^3 g^{-1})	V_{micro}^{d} (cm^3 g^{-1})
822	0.41	0.18	0.16

Fig. S9 Ar physisorption isotherms (left) and mesopore size distributions (right) of SSZ-13-C_{16}MP synthesized at a Si/Al ratio of 50 ($^a S_L$ is the Langmuir surface area obtained in the relative pressure range (p/p_0) of 0.05–0.20; $^b V_{tot}$ is the total pore volume calculated at p/p_0= 0.97; $^c V_{meso}$ and $^d V_{micro}$ are the mesopore volume and the micropore volume calculated from the *BJH* method and the *t*-plot method, respectively).

Table S3 Interaction energies of SDA and mesoporogens in CHA zeolite. The cationic charge is balanced by deprotonation of external silanol group(s) (ZeO) or by substitution of framework Si by Al (ZeAl).

Template	Interaction energy (kJ mol^{-1})	Electrostatic energy (kJ mol^{-1})	Van der Waals energy (kJ mol^{-1})	CHA destabilization energy (kJ mol^{-1})
TMAda$^+$ ZeO	–373	–228	–146	12
TMAda$^+$ ZeAl	–539	–402	–137	–23
$C_{16}MP^+$ ZeO	–496	–316	–180	13
$C_{16}MP^+$ ZeAl	–457	–280	–176	–24
$C_{16}MP^+$ exchanged	–494	–313	–182	–
$C_{16}N_1^+$ ZeO	–478	–270	–208	0
$C_{16}N_1^+$ ZeAl	–525	–311	–214	–36
$C_{16}N_2^{2+}$ (I)[a] 2ZeO	–1365	–1238	–127	85
$C_{16}N_2^{2+}$ (I) Ze(O+Al)	–1309	–1172	–137	99
$C_{16}N_2^{2+}$ (II)[b] 2ZeO	–1015	–807	–208	54
$C_{16}N_2^{2+}$ (II) Ze(O+Al	–1398	–1167	–231	66

[a] $C_{16}N_2^{2+}$ (I): one ammonium center at the surface and another one in the subjacent zeolite cage;

[b] $C_{16}N_2^{2+}$(II): two ammonium groups placed in two adjacent zeolite cages.

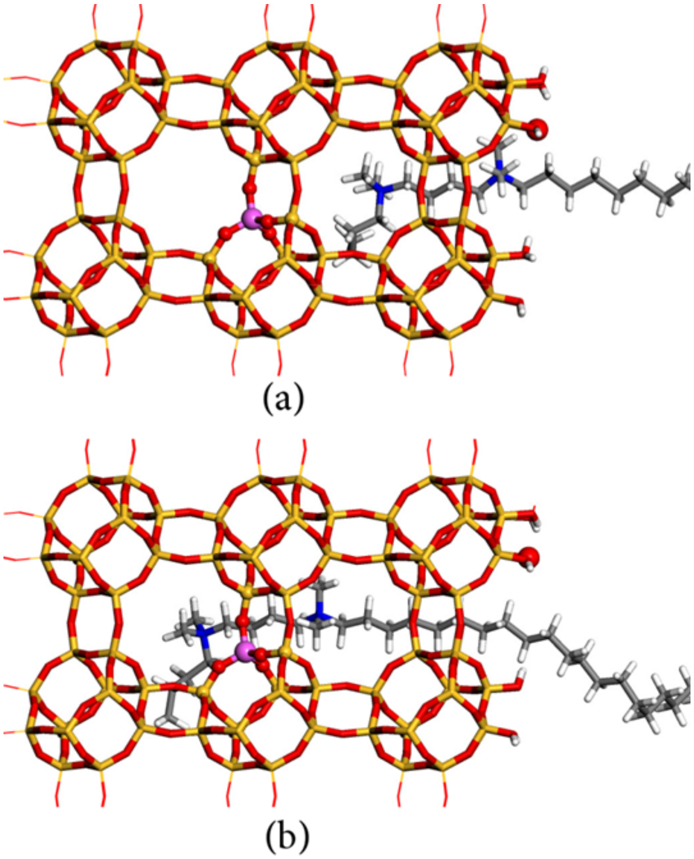

(a)
(b)

Fig. S10 Example of two configuration of the $C_{16}N_2$ template in configure I (a) and configuration II (b) for the models involving one Al substition and one deprotonated silanol group.

Table S4 Interaction energies of several templates in the MFI zeolite. Templates are given in their cationic form (except DAH). The cationic charge is balanced by deprotonation of external silanol group (ZeO) or by Al substitution of framework Si (ZeAl).

Template	Interaction energy (kJ mol^{-1})	Electrostatic energy (kJ mol^{-1})	Van der Waals energy (kJ mol^{-1})
2TPA$^+$ 2ZeO	−1047	−719	−328
2TPA$^+$ 2ZeAl	−1458	−1135	−323
2C$_{16}$MP$^+$ 2ZeO	−1095	−739	−356
2C$_{16}$MP$^+$ 2ZeAl	−1463	−1138	−326
DAH ZeO	−120	−4	−115

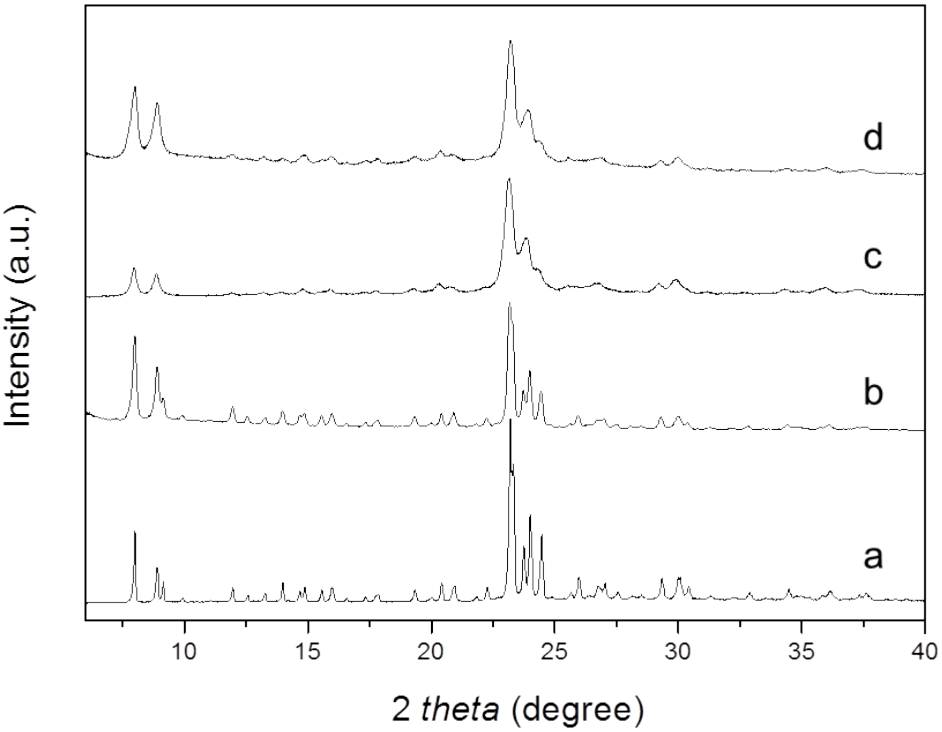


Fig. S11 XRD patterns of as-synthesized zeolites ZSM-5-bulk (a), ZSM-5-C_{16}MP-TPAOH (b), ZSM-5-C_{16}MP-DAH (c) and ZSM-5-C_{16}MP-DEA (d).

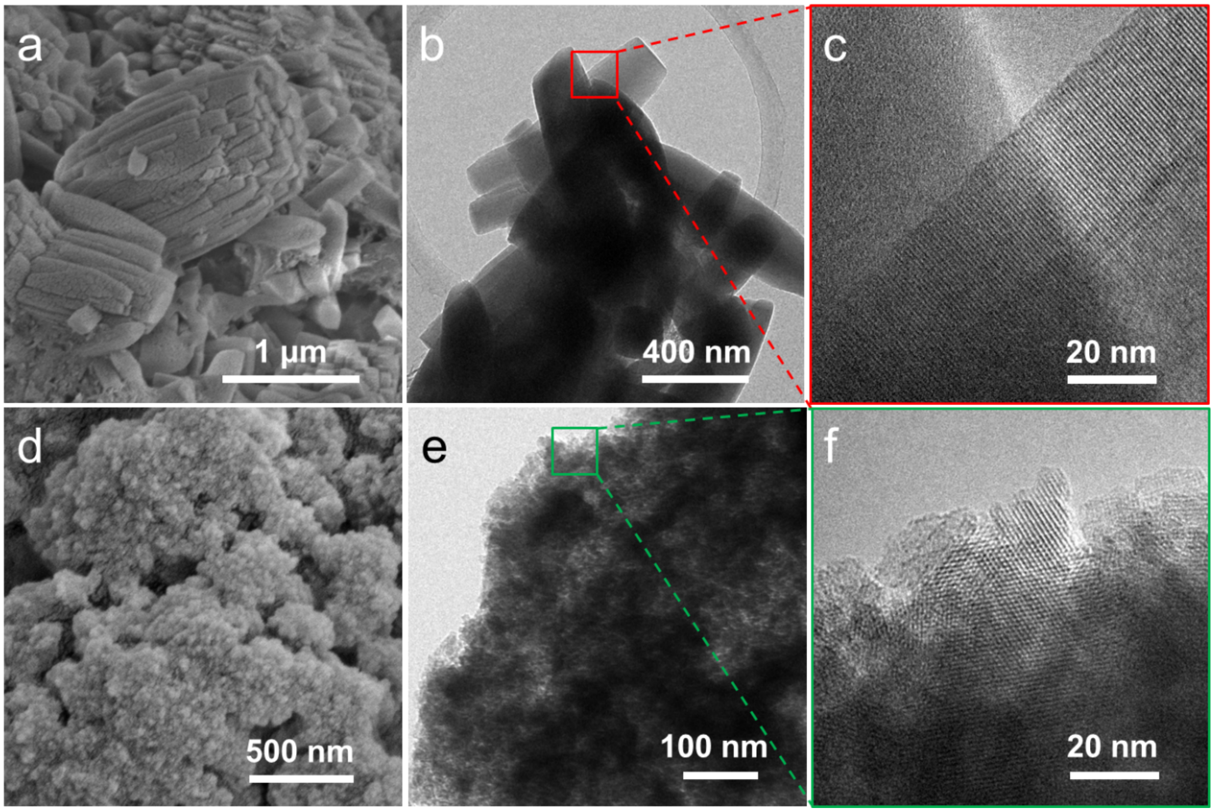


Fig. S12 EM images of as-synthesized ZSM-5-C_{16}MP-TPAOH (a, b, and c), and ZSM-5-C_{16}MP-DEA (d, e, and f).

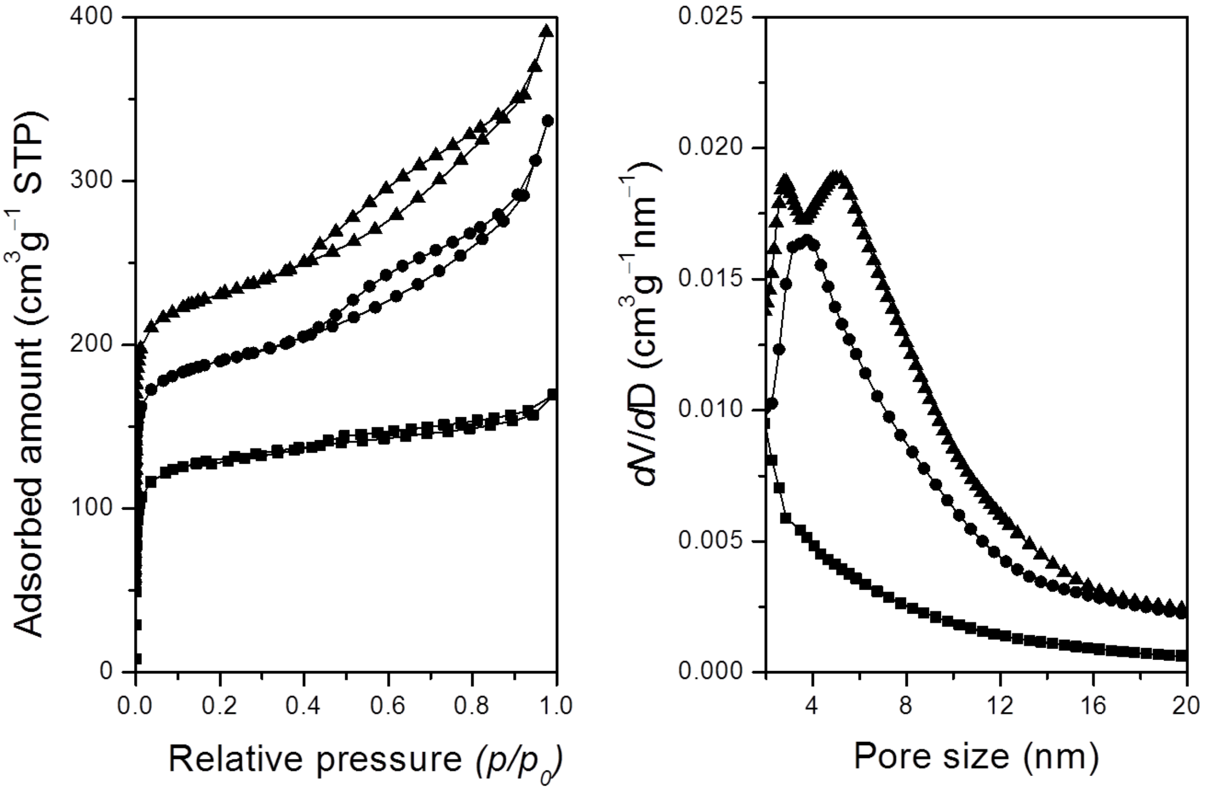


Fig. S13 Ar physisorption isotherms (left) and mesopore size distributions (right) of ZSM-5-bulk (■), ZSM-5-C_{16}MP-DAH (●), and ZSM-5-C_{16}MP-DEA (▲). The isotherms were vertically offset by equal intervals of 50 cm^3 g^{-1}.

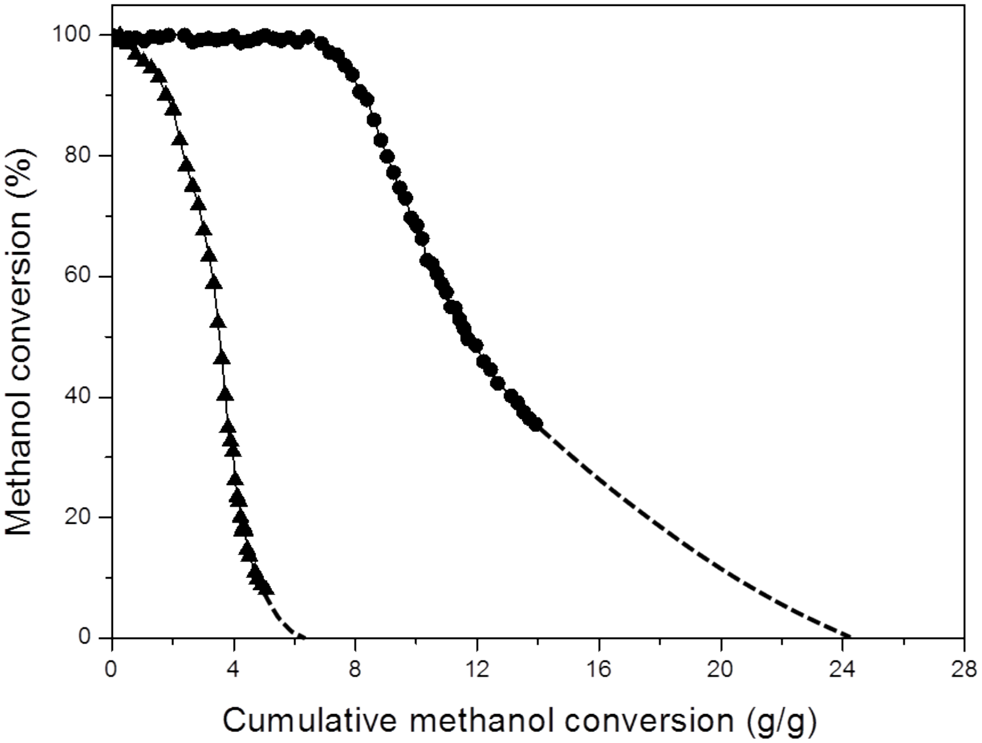


Fig. S14 Methanol conversion versus cumulative amount of methanol that has been converted to hydrocarbons. Extrapolation to zero methanol conversion gives the total methanol conversion capacity for SSZ-13-bulk (▲), SSZ-13-C_{16}MP (●).