Electronic Supplementary Material (ESI) for Dalton Transactions

Electronic Supplementary Information

Optimal topotactic conversion of layered octosilicate to RWR-type zeolite by separating the formation stages of interlayer condensation and elimination of organic guest molecules

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Details of the experimental procedure

Preparation of layered silicate (Na-Oct) and protonated layered silicate (H-Oct).

Layered octosilicate (Na-Oct) was prepared according to a literature (D. Mochizuki *et al.*, *Chem. Mater.*, 2006, **18**, 5223). Fumed silica (99.8 % SiO_2, Aldrich), NaOH (97.0 %, Wako Pure Chemical Ltd.) and deionized water were mixed in the composition of SiO_2:Na_2O:H_2O = 4:1:25.8. The mixture was treated hydrothermally at 100 °C for 4 weeks in a sealed Teflon-sealed vessel. The XRD pattern and ^{29}Si MAS NMR spectrum of the obtained sample are the same as those of Na-Oct reported previously (D. Mochizuki *et al.*, *Chem. Mater.*, 2006, **18**, 5223), indicating the formation of Na-Oct. Protonated layered octosilicate (H-Oct) was obtained from Na-Oct by the treatment with 0.1 M HCl (Wako Pure Chemical Ltd.) for 2d according to a literature (S. Kiba *et al.*, *J. Mater. Chem.*, 2010, **20**, 3202).

Interlayer condensation of H-Oct by refluxing in N-methylformamide and the subsequent calcination (synthesis of Reflux-NMF-Oct and Cal-Reflux-NMF-Oct, respectively).

H-Oct was refluxed in N-methylformamide (NMF; Aldrich) at 180 °C for 1 h. After refluxing, the mixture was centrifuged and dried under vacuum to obtain Reflux-NMF-Oct. In order to eliminate organic compounds in Reflux-NMF-Oct, Reflux-NMF-Oct was calcined at 550 °C for 6 h with a heating rate of 2.5 °C/min. The calcined sample is denoted as Cal-Reflux-NMF-Oct.

Intercalation of NMF into H-Oct at r.t. and the subsequent calcination (synthesis of NMF-Oct and Cal-NMF-Oct).

H-Oct was dispersed in NMF and stirred at r.t. for 1 h. The mixture was centrifuged and dried under vacuum. The obtained sample is denoted as NMF-Oct. NMF-Oct was calcined at 550 °C for 6 h with a heating rate of 2.5 °C/min. The calcined sample is denoted as Cal-NMF-Oct.

Investigation of thermal stabilities of Cal-Reflux-NMF-Oct and Cal-NMF-Oct.

Cal-Reflux-NMF-Oct and Cal-NMF-Oct were heated at 900 °C for 6 h with a heating rate of 2.5 °C/min. The obtained samples are denoted as Cal-Reflux-NMF-Oct_900 and Cal-NMF-Oct_900, respectively.

Characterization

Powder XRD measurements were performed on a Rigaku Rint-Ultima III powder diffractometer with CuKα radiation ($\lambda = 0.15406$ nm) by using a parallel beam geometry equipped with a parabolic multilayer mirror. Solid-state ^{13}C CP/MAS NMR spectra were recorded on a JEOL JNM-ECX-400 spectrometer at a resonance frequency of 99.5 MHz and a recycle delay of 5 s. The samples were put into a 4 or 6 mm zirconia rotor and spun at 10 kHz. Solid-state ^{29}Si MAS NMR spectra were also recorded on the same spectrometer at a resonance frequency of 78.65 MHz with a 90° pulse and a recycle delay of 200 s by using a 4 or 6 mm zirconia rotor and spinning at 6 kHz. The ^{13}C and ^{29}Si chemical shifts were externally referenced to hexamethylbenzene at 17.4ppm ($-CH_3$) and poly(dimethylsilane) at -33.8 ppm, respectively. The amounts of organic constituents were determined by CHN analysis (Perkin-Elmer, 2400 Series II). Thermogravimetry (TG) measurements were carried out with a Rigaku Thermo Plus 2 instrument under a dry air flow at a heating rate of 10 °C/min. The scanning electron microscopy (SEM) images were obtained by using a Hitachi S5500 scanning electron microscope. Nitrogen adsorption/desorption isotherms were measured with a Quantachrome Autosorb-1 instrument at 77 K. The samples were outgassed under vacuum at 350 °C for 48 h prior to the measurement. Brunauer-Emmett-Teller (BET) surface area was calculated from adsorption branch in the relative pressure range from 0.02 to 0.10.

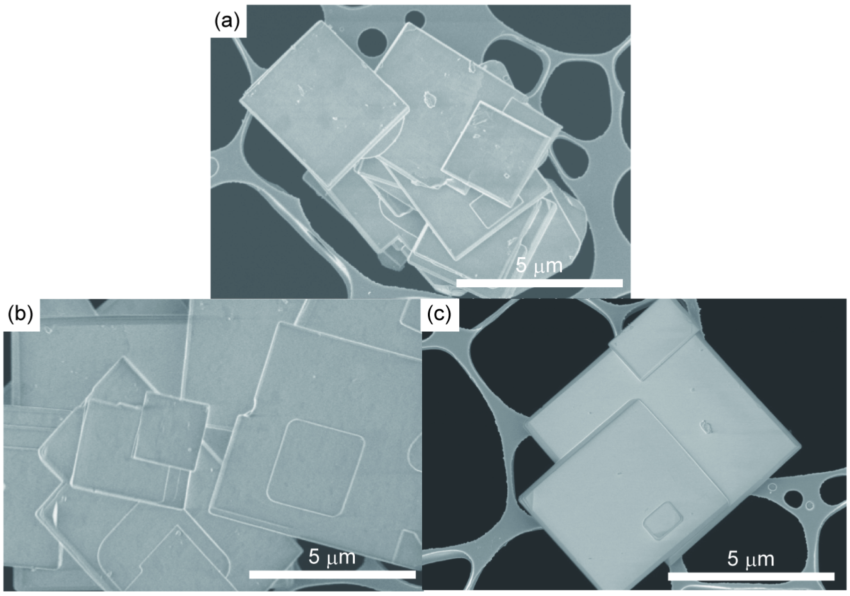

Fig. S1 SEM images of (a) H-Oct, (b) Reflux-NMF-Oct, and (c) Cal-Reflux-NMF-Oct.

Table S1 CHN data of the samples.

	C / mass %	H / mass %	N / mass %	C/N
Reflux-NMF-Oct	1.9	0.1	0.9	2.5
Cal-Reflux-NMF-Oct	0.1	0.0	0.0	-
NMF-Oct	15.3	3.8	7.9	2.3
Cal-NMF-Oct	0.2	0.0	0.0	-

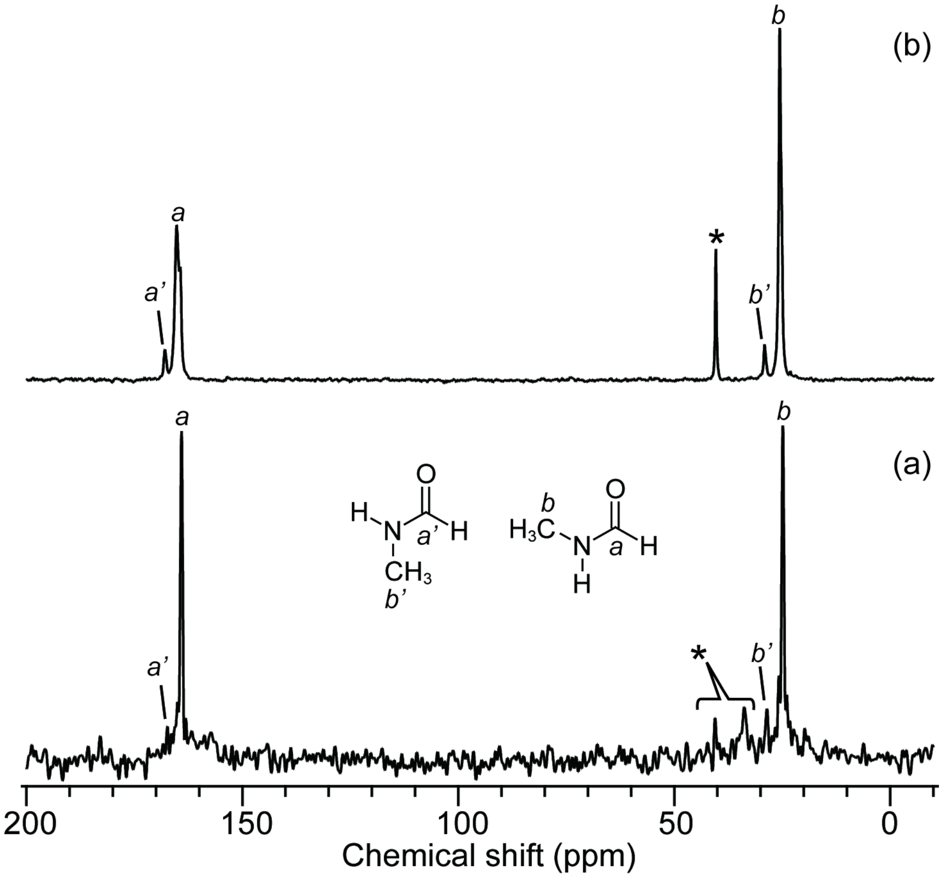

Fig. S2 ^{13}C CP/MAS NMR spectra of (a) Reflux-NMF-Oct and (b) NMF-Oct.
(The signals marked by asterisk are not assigned though they may be due to decomposed products of NMF.)

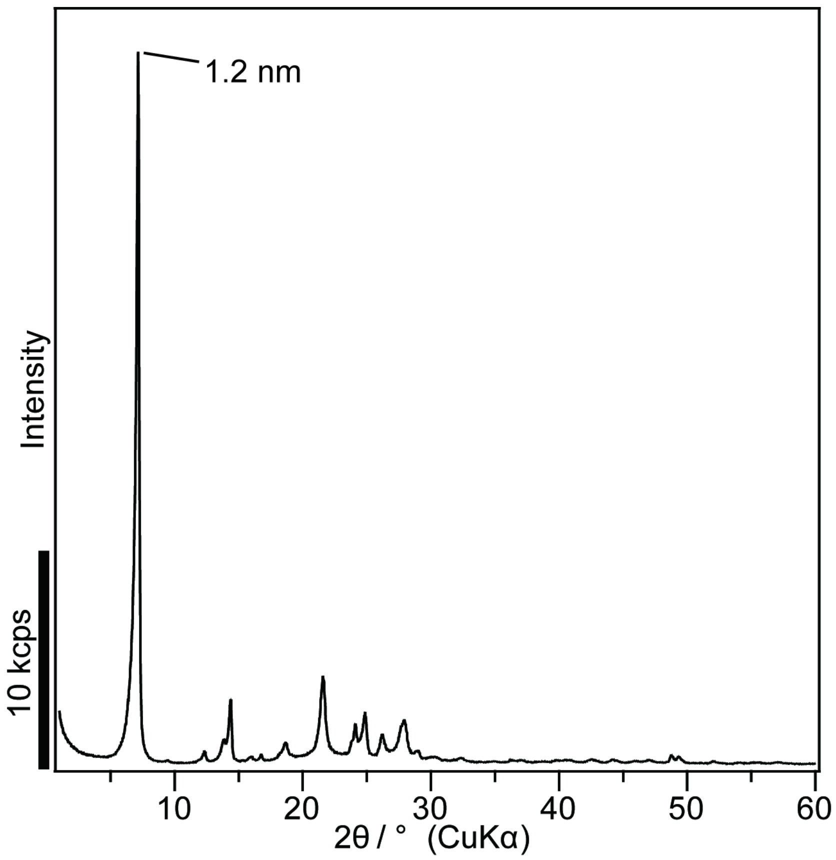

Fig. S3 XRD pattern of NMF-Oct.

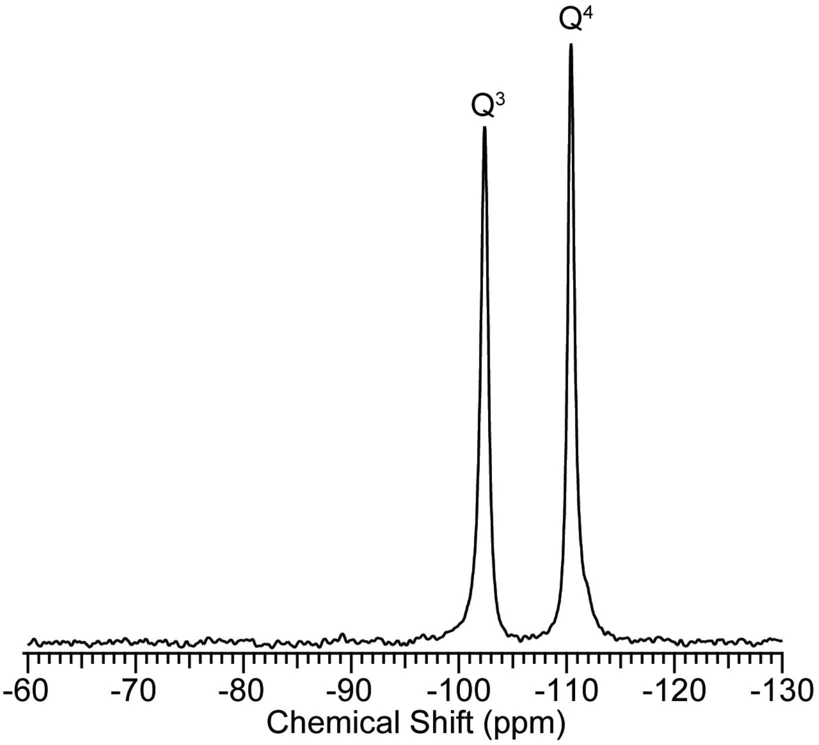

Fig. S4 ^{29}Si MAS NMR spectrum of NMF-Oct. The Q^3/Q^4 ratio is 1.

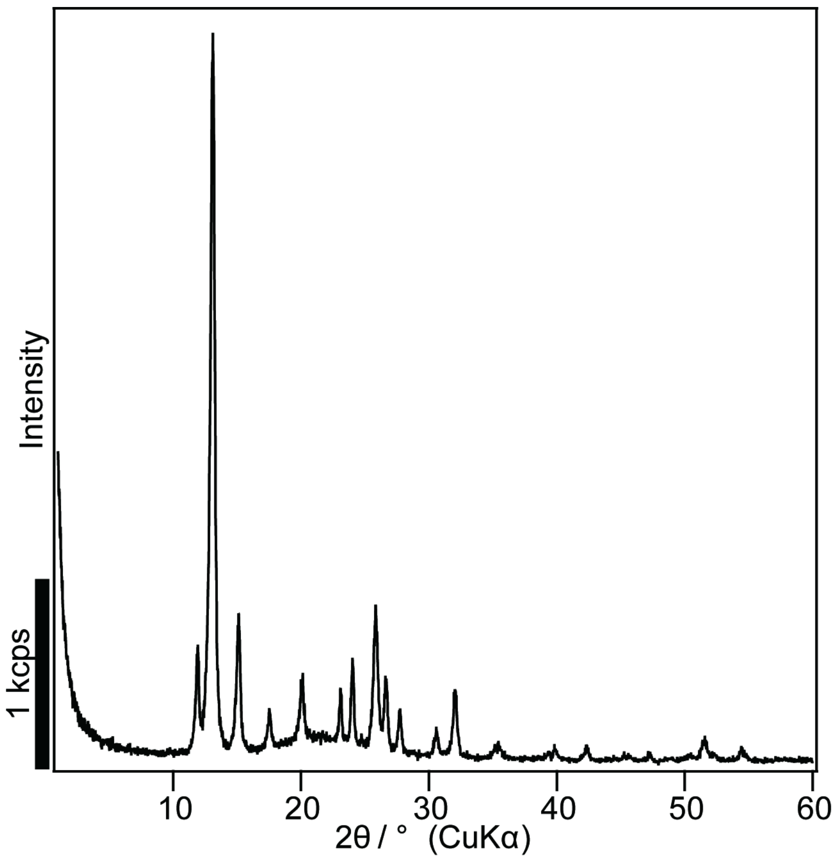

Fig. S5 XRD pattern of Cal-Reflux-NMF-Oct after TG-DTA measurement.

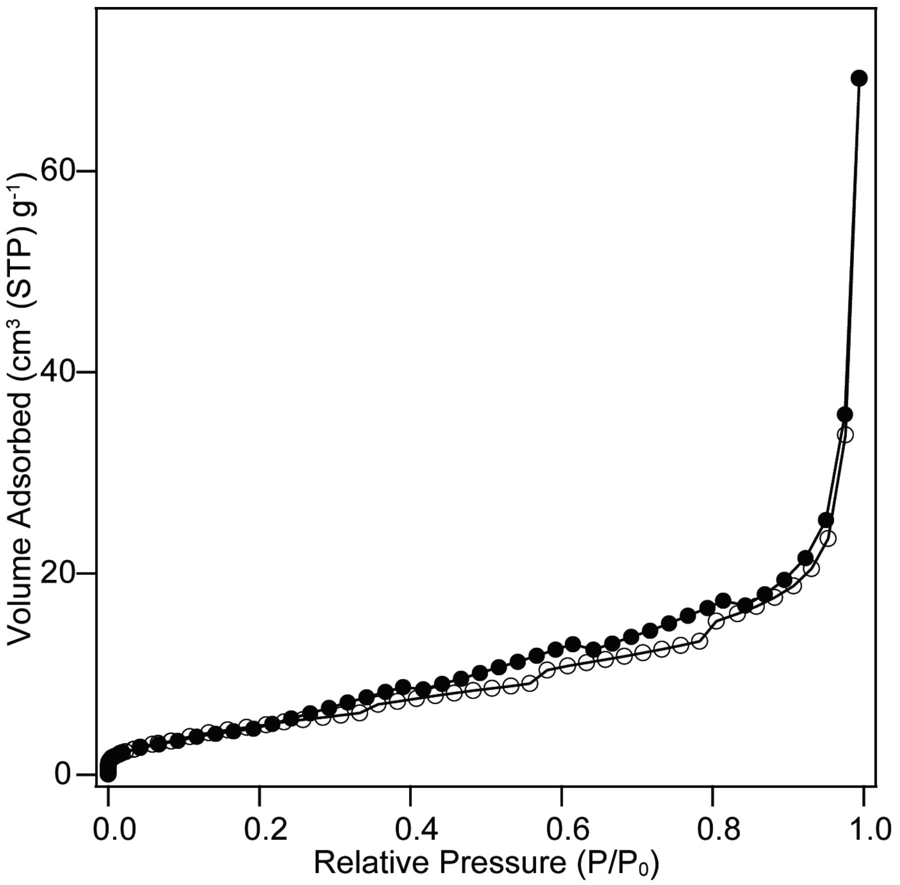

Fig. S6 N_2 adsorption/desorption isotherms of Cal-Reflux-NMF-Oct. The BET surface area is calculated to be 16 $m^2 \cdot g^{-1}$