Supplementary Information
for
Unseeded Hydroxide-Mediated Synthesis and CO_2 Adsorption Properties of an Aluminosilicate Zeolite with the RTH Topology

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Structural Characterization

The synchrotron powder X-ray diffraction (XRD) data were recorded on the beamline 9B at the Pohang Acceleration Laboratory (Pohang, Korea) using monochromated radiation with λ = 1.4865 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 20º. Data were collected at room temperature in flat plate mode, with a step size of 0.01º and overlaps of 2º to the next detector bank over the 2θ range 5.0 - 125.5º. The pattern was successfully indexed as monoclinic, with a = 9.744, b = 20.744, c = 9.883 Å, β = 96.64º, using the program NTREOR,[S1] as implemented in EXPO2009,[S2] and the systematic absences were compatible with the *C*2/*m* space group. Rietveld refinement was performed in GSAS[S3] using the EXPGUI interface[S4] with a model consistent with the RTH structure type but with the above cell parameters and starting with only Si and O. Initially, a fixed shifted Chebyshev function with 20 terms was used to model the background. After refining the scale factor, unit cell, zero shift and profile terms (pseudo-Voigt function type 4),[S3] the Si and O positions were refined under soft distance restrains (Si-O 1.61 Å and nonbonding O-O 2.61 Å distances within tetrahedra, initially with a relatively heavy weight). Difference Fourier analysis revealed at this point an interesting feature with the shape of a quadrangular torus inside the cavity. Then, a rigid-body cation (centered on a dummy H at the gravity center) was introduced to model the organic structure-directing agent (OSDA). No real hydrogen atom was included and, instead, the occupancy factors of CH and CH_3 groups were adjusted to account for the total number of electrons.[S5] This approach produced high atomic displacement parameters in the final model to compensate for the more spread electronic density of the CH and CH_3 groups. The starting position was close to but a little off the center of the cavity in the *xy* plane, and the occupancy was halved to account for the two cations per cavity (four per unit cell) found by elemental analysis. Upon refining its position, the cation moved away from the described position and took a conformation that, considering the four symmetric cations, closely matched the above mentioned torus. Attempts to refine the structure in space groups *Cm* or *C*2 failed (in *Cm* the two cations formed a corner of the referred quadrangular torus, implying collision (because of the full occupancy of sites), and leaving the opposite side of the cavity deficient in electronic density; in *C*2 the cations have a more logical parallel arrangement, similar to that found in *C/2m*, but the refinement could not be made to converge). Then, the distance restrains were gradually relaxed. Al was introduced at the same positions as Si with fractional occupancies of 0.0909 and 0.9091, respectively, to account for the overall Si/Al ratio of 10, determined by elemental analysis. Al and Si at each position were forced to move together. The restrains were further relaxed and the background was also refined, before the isotropic atomic displacement parameters were also introduced in the refinement (for the OSDA cation these parameters were refined in groups: CH_3, CH, and N1-C2-

N3). Finally, the restrains were completely eliminated. No preferential occupation by Al could be proven or disproven. Crystallographic data are collected in Table S1 and atomic parameters in Table S2. While the values of the residuals are reasonably good, the reduced χ^2 is uncomfortably high (8.882) and the Rietveld plot shows relatively large discrepancies between the calculated and experimental patterns (Figure S4). The disagreements are related to the shape of the peaks which have very long tails and narrow full-widths at half-maximums (fwhm), together with a strong asymmetry, and could not be modelled any better using other profile functions available in GSAS. Thus, a model independent Le Bail type whole profile fitting was undertaken in GSAS, refining the same number and type of non-structural parameters, plus the cell parameters. The resulting χ^2 was also relatively high (5.508) and, furthermore, exactly the same type of disagreement between the calculated and experimental patterns were observed (Figure S5), suggesting the relatively high χ^2 values are actually due to the difficulty in modelling the peak shape (long tails and asymmetry) of the high quality synchrotron data.[S6]

References

(S1) A. Altomare, C. Giacovazzo, A. Guagliardi, A. Moliterni, R. Rizzi and P.-E. Werner, *J. Appl. Crystallogr.*, 2000, **33**, 1180.
(S2) A. Altomare, M. Camalli, C. Cuocci, C. Giacovazzo, A. Moliterni and R. Rizzi, *J. Appl. Crystallogr.*, 2009, **42**, 1197.
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Table S1 Crystallographic and experimental parameters for the Rietveld refinement of as-made 123TMI-RTH.

wavelength (Å)	1.4865
temperature (K)	293
2θ range	5.00-125.50
no. of data points	12051
no. of reflections	1844
space group	*C2/m*
unit cell parameters (Å)	
a	9.74697(25)
b	20.7517(5)
c	9.88360(23)
β	96.6492(12)
cell volume (Å^3)	1985.67(13)
residuals	
R_{wp}	8.95
R_p	6.98
R_F^2	6.391
reduced χ^2	8.882

Table S2 Fractional atomic coordinates, isotropic displacement parameters, and fractional occupancies for as-made 123TMI-RTH in space group *C*2/*m*.

atom	*x*	*y*	*z*	U_{iso}(×100)	occupancy[a]
Si1	0.25527	0.23487	0.71954	1.83	0.90910
Al1	0.25527	0.23487	0.71954	1.83	0.09090
Si2	0.08587	0.07630	0.37912	2.08	0.90910
Al2	0.08587	0.07630	0.37912	2.08	0.09090
Si3	0.34613	0.15409	0.48912	2.11	0.90910
Al3	0.34613	0.15409	0.48912	2.11	0.09090
Si4	0.49993	0.31974	0.83947	1.67	0.90910
Al4	0.49993	0.31974	0.83947	1.67	0.09090
O1	0.30069	0.17557	0.62818	1.37	1.00000
O2	0.50000	0.33399	1.00000	0.76	1.00000
O3	0.09392	0.00000	0.32384	3.42	1.00000
O4	0.25729	0.09493	0.43283	2.43	1.00000
O5	0.50000	0.12735	0.50000	3.44	1.00000
O6	0.37524	0.26811	0.80525	3.91	1.00000
O7	0.14462	0.21240	0.82294	2.93	1.00000
O8	0.17174	0.28534	0.61129	2.75	1.00000
O9	0.47451	0.38305	0.75681	3.80	1.00000
O10	0.00000	0.08903	0.50000	1.48	1.00000
N1	0.01254	0.41493	0.11548	10.62	0.50000
C5	0.04181	0.37827	0.00411	28.50	0.58333
C4	0.16232	0.39948	-0.03071	28.50	0.58333
N3	0.20630	0.44904	0.05955	10.62	0.50000
C2	0.11367	0.45737	0.14692	10.62	0.50000
C6	-0.11312	0.40596	0.18408	24.03	0.75000
C7	0.33716	0.48431	0.05185	24.03	0.75000
C8	0.11829	0.50498	0.26080	24.03	0.75000

[a] Not refined.

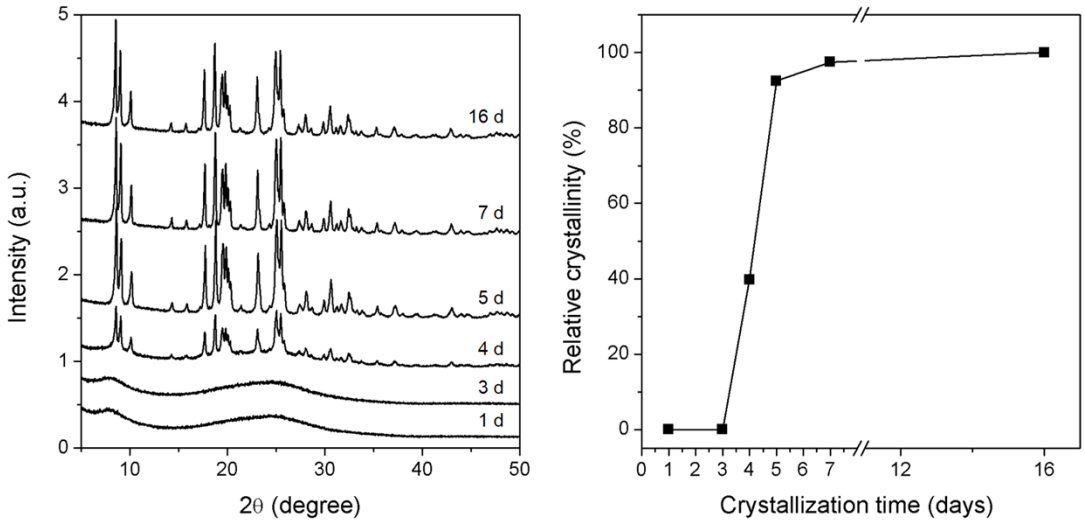

Fig. S1 Powder XRD patterns (left) and relative crystallinities (right) for a series of solid products obtained after crystallization using $123TMI^{+}$ and Na^{+} ions at Si/Al = 10 for different times.

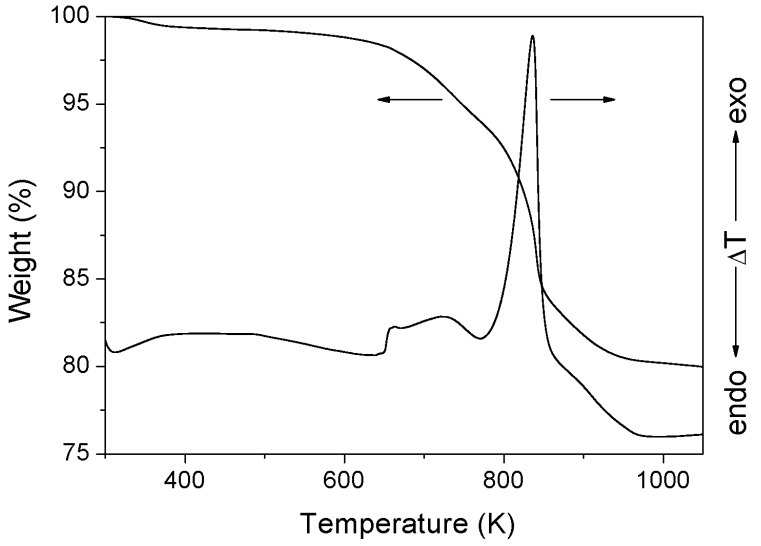

Fig. S2 TGA/DTA curves of as-made RTH.

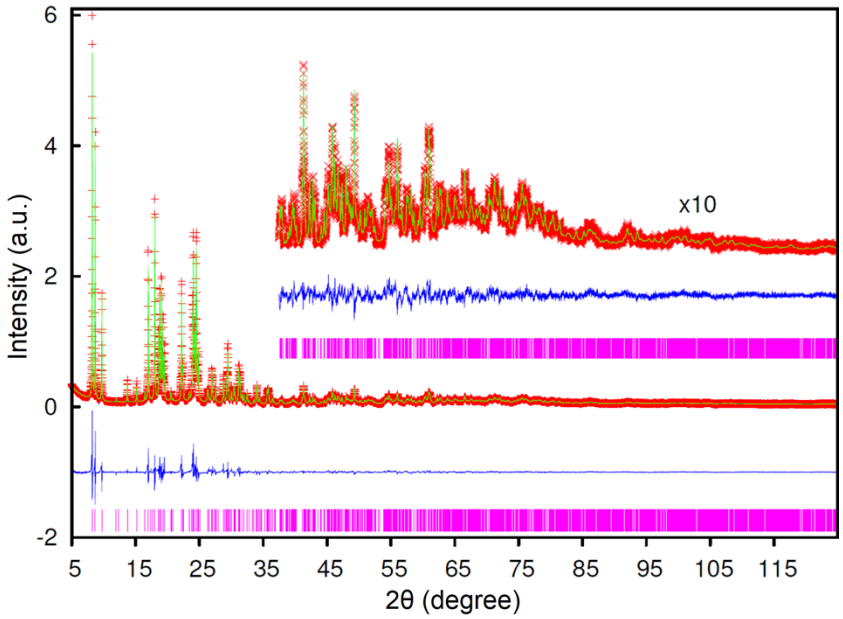

Fig. S3 Rietveld plot for as-made 123TMI-RTH. Experimental (crosses), calculated (solid line), and difference plot (lower trace). The tick marks represent the positions of allowed reflections (λ = 1.48650 Å).

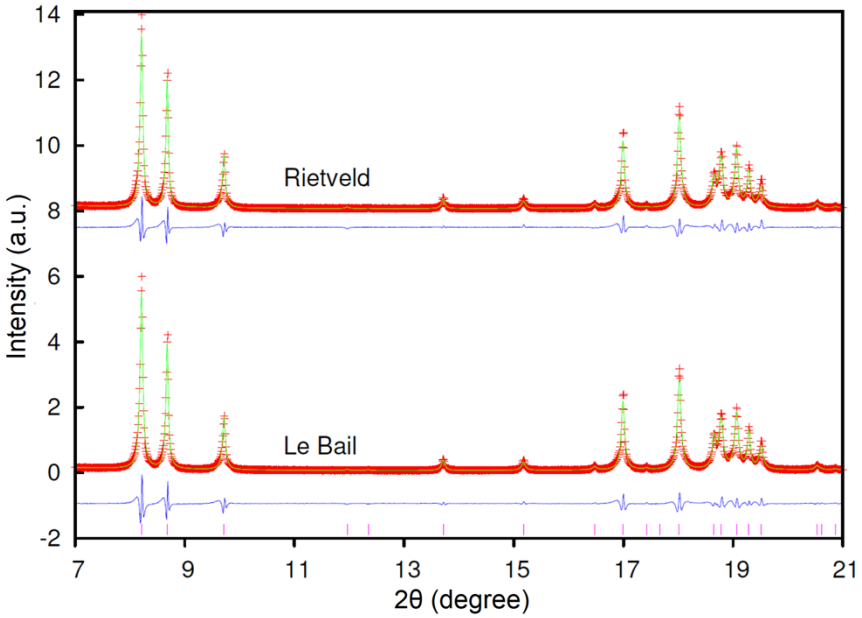

Fig. S4 Comparison between Rietveld and Le Bail plots for as-made 123TMI-RTH. Experimental (crosses), calculated (solid line), and difference plot (lower trace). The tick marks represent the positions of allowed reflections (λ = 1.48650 Å).

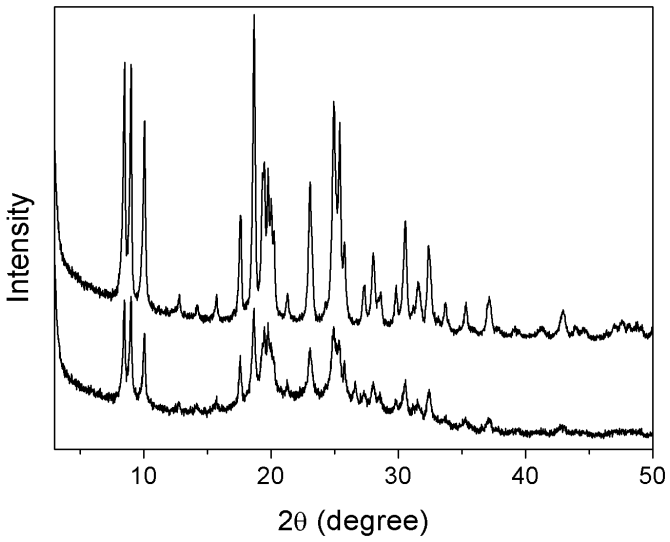

Fig. S5 XRD patterns of fresh (top) and hydrothermally aged (bottom; at 1023 K for 24 h with flowing air containing 10% H_2O) Cu-RTH.

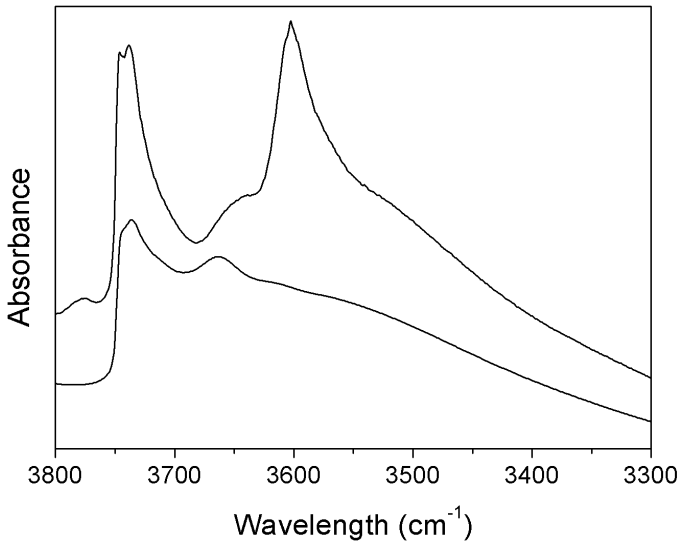

Fig. S6 IR spectra in the OH stretching region of H-RTH (top) and Na-RTH (bottom).

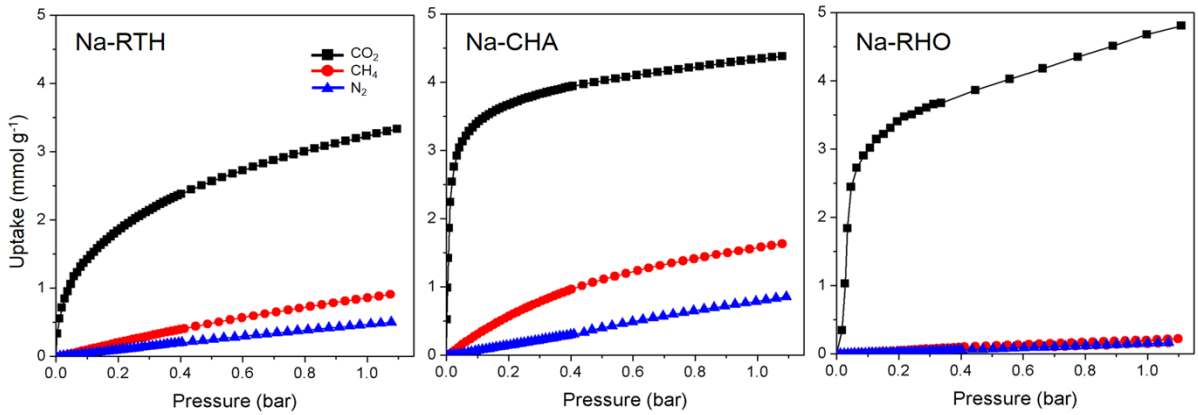

Fig. S7 CO_2, CH_4, and N_2 adsorption isotherms at 298 K of Na-RTH, Na-CHA, and Na-RHO (from left to right).

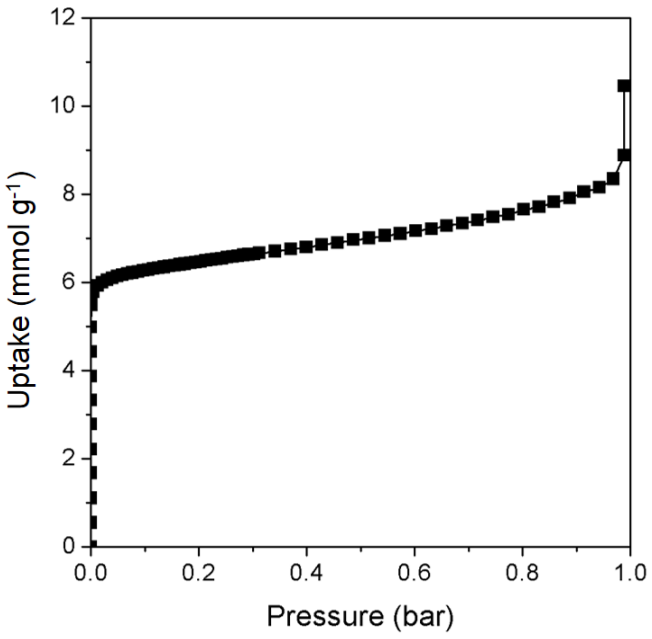

Fig. S8 N_2 adsorption isotherm of Na-RTH at 77 K.