Supporting Information for

Facile and selective synthesis of zeolites L and W from a single-source heptanuclear aluminosilicate precursor

Akira Imaizumi,[a] *Akinobu Nakada,*[a] *Takeshi Matsumoto,*[b] *and Ho-Chol Chang* [a, *]

[a] Department of Applied Chemistry, Faculty of Science and Engineering, Chuo University, 1-13-27 Kasuga, Bunkyo-ku, Tokyo 112-8551, Japan.

[b] Precursory Research for Embryonic Science and Technology (PRESTO), Japan Science and Technology Agency (JST), 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan.

* To whom correspondence should be addressed. E-mail: chang@kc.chuo-u.ac.jp

Phone: +81-3-3817-1897. Fax: +81-3-3817-1895.

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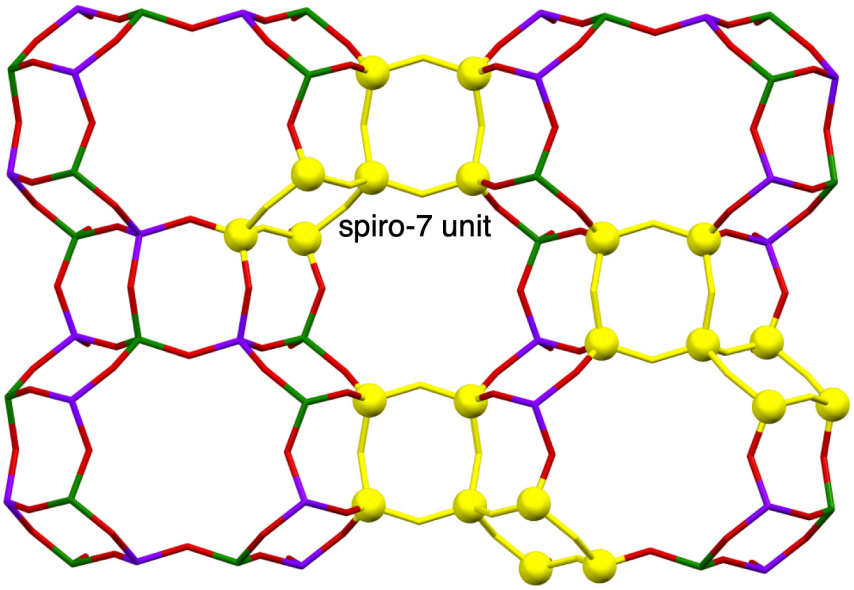

Fig. S1 Spiro-7 unit (yellow) in the MER-type structure. Color code: red = O; purple = Al; green = Si. The Si/Al ratio of the structure equals 1, and K^+ ions are omitted for clarity.

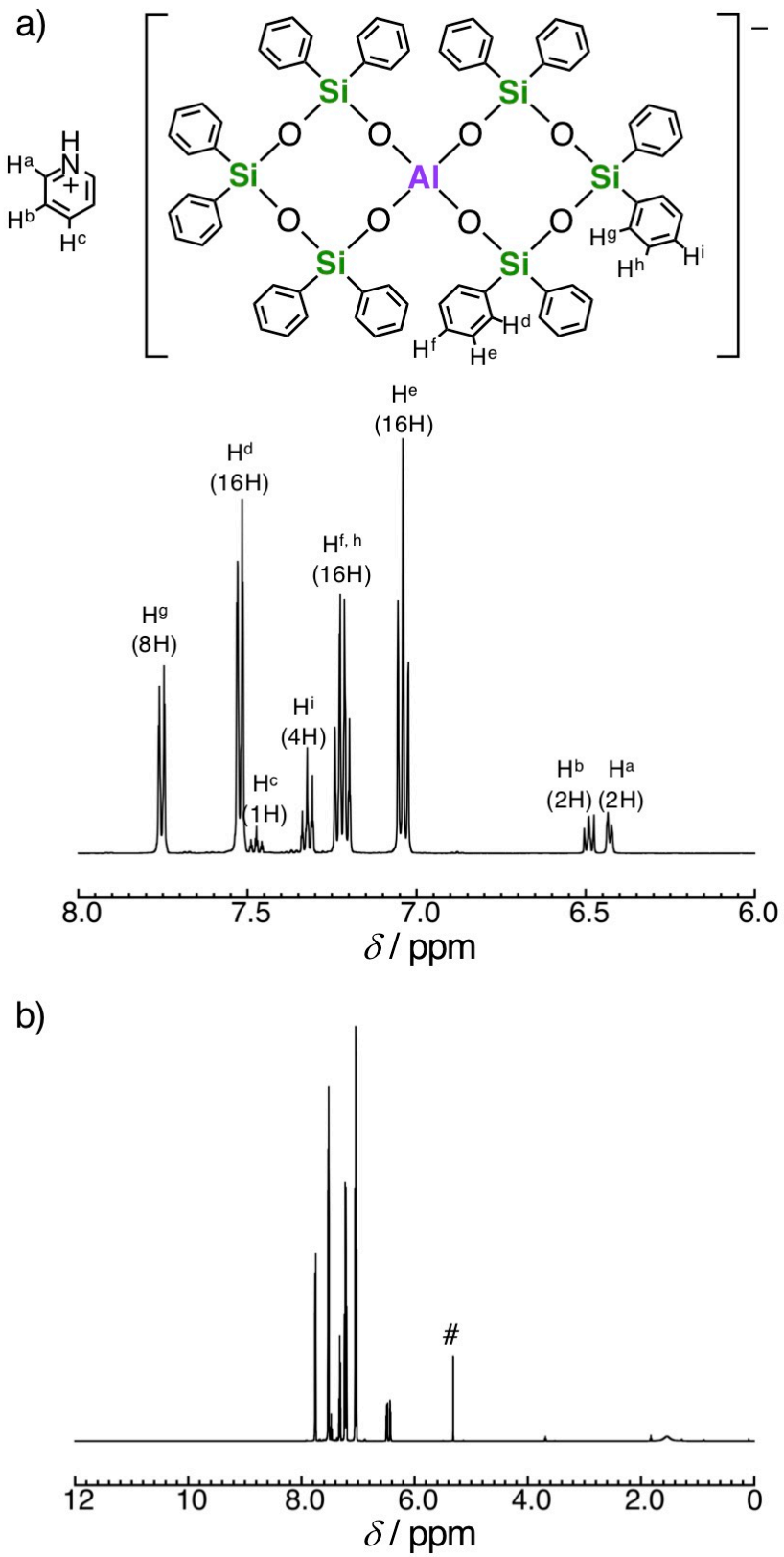

Fig. S2 a) Aromatic region and b) full range of the ^{1}H NMR (500 MHz, CD_2Cl_2) spectra of **AlSi$_6$**. A symbol "#" denotes the residual proton of dichloromethane.

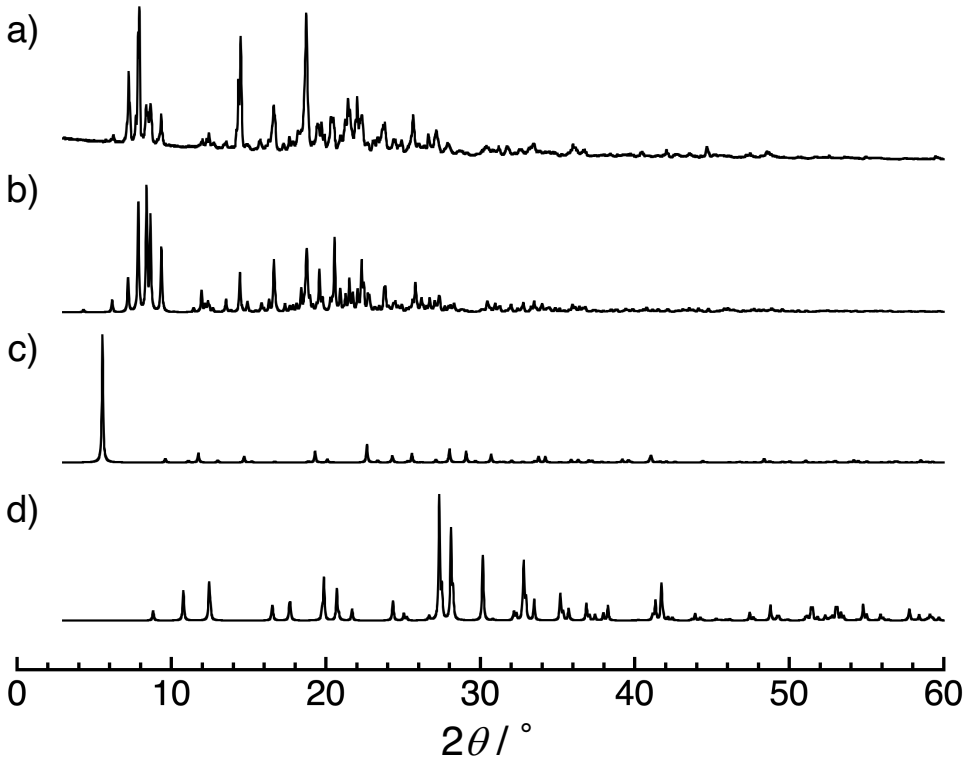

Fig. S3 PXRD pattern of a) the synthesized **AlSi$_6$** and the simulated patterns for b) **AlSi$_6$**, c) zeolite L[S1], and d) W.[S2]

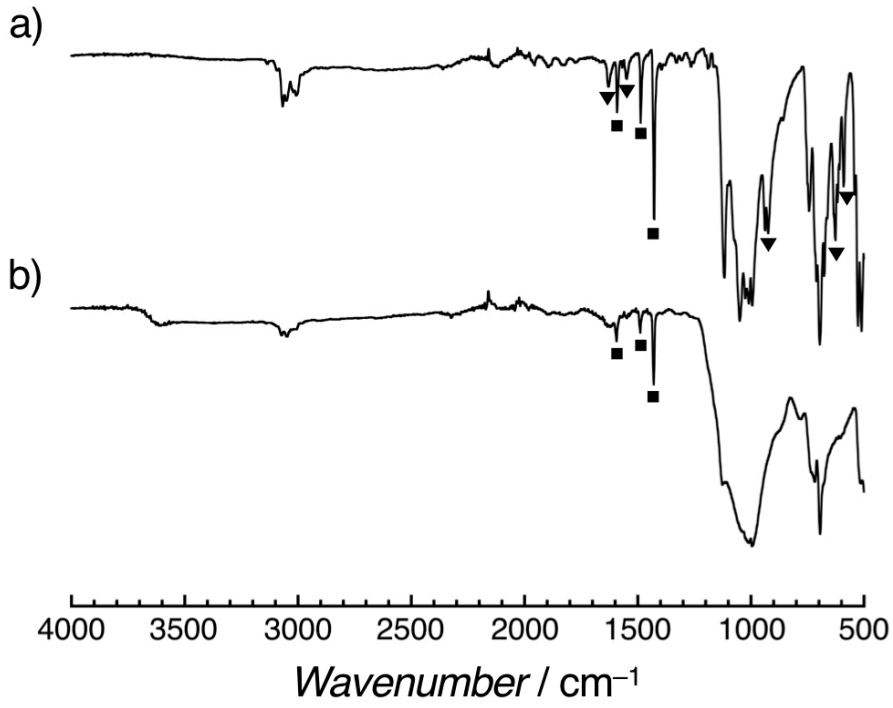

Fig. S4 IR spectra of a) **AlSi$_6$** and b) the samples obtained from TG measurements at 180 °C. The symbols "▼" and "■" mark absorption bands assignable to pyridinium and phenyl group, respectively.

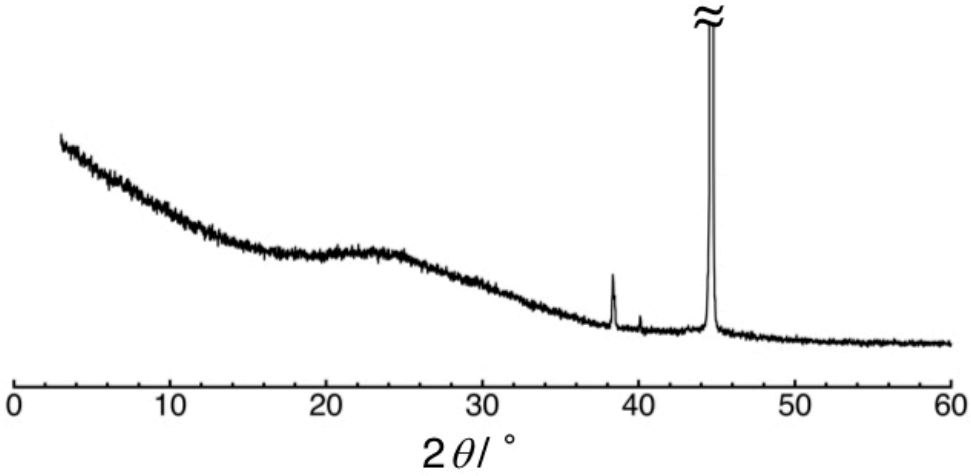

Fig. S5 PXRD pattern of the sample obtained from the heating **$AlSi_6$** to 800 °C under an N_2 atmosphere. The diffractions peaks at 38.3, 40.1, and 44.6° are originated from the Al pan used as a sample holder.

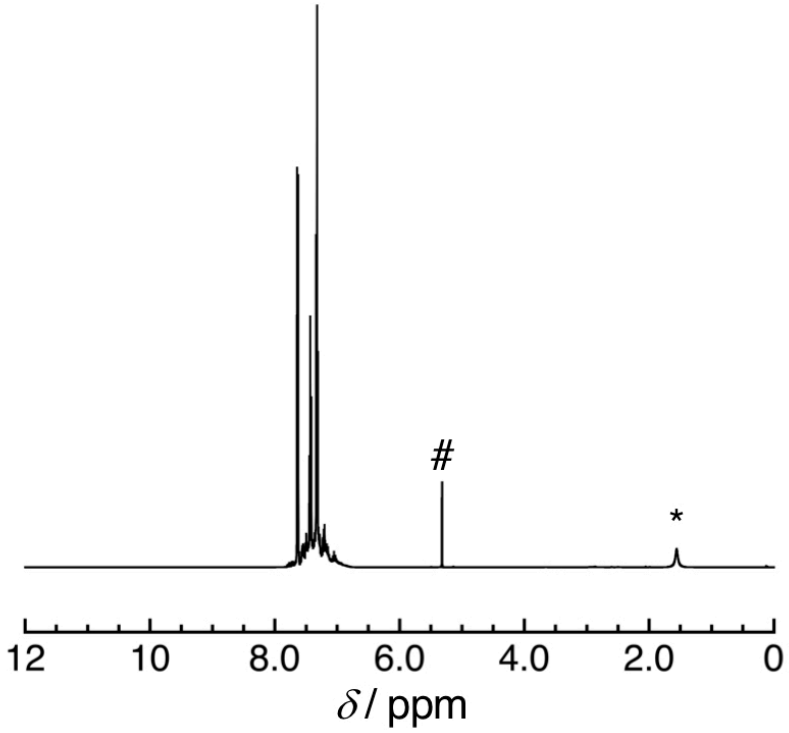

Fig. S6 ^{1}H NMR (500 MHz, CD_2Cl_2) spectrum of the product in the solution phase obtained from refluxing **AlSi$_6$** in aqueous HCl (12 eq.) for 12 h. The symbols "#" and "*" denote the residual proton of dichloromethane and protons of *Si*–OH and/or H_2O, respectively.

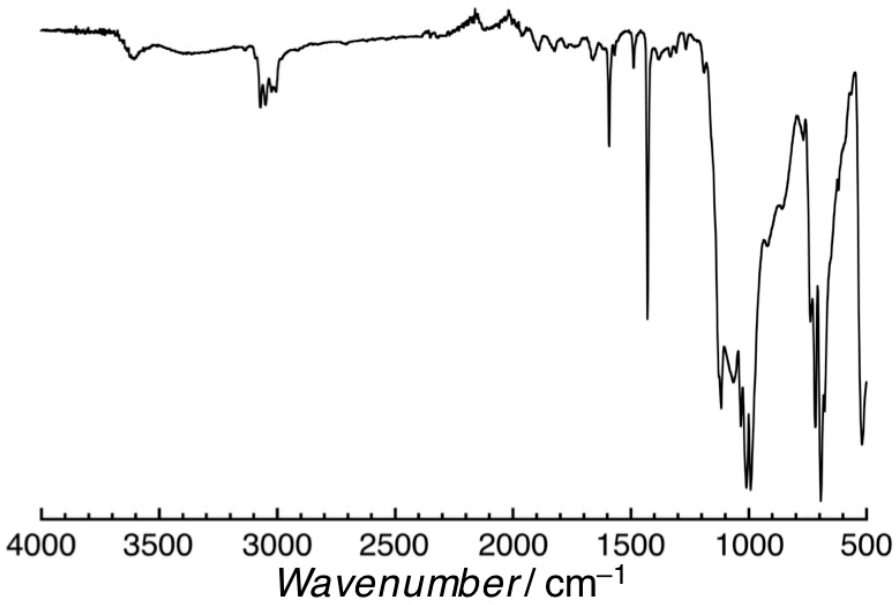

Fig. S7 IR spectrum of the products in the solution phase obtained from the hydrothermal treatment of **AlSi$_6$** at 150 °C for 12 h in the presence of HCl (12 eq.).

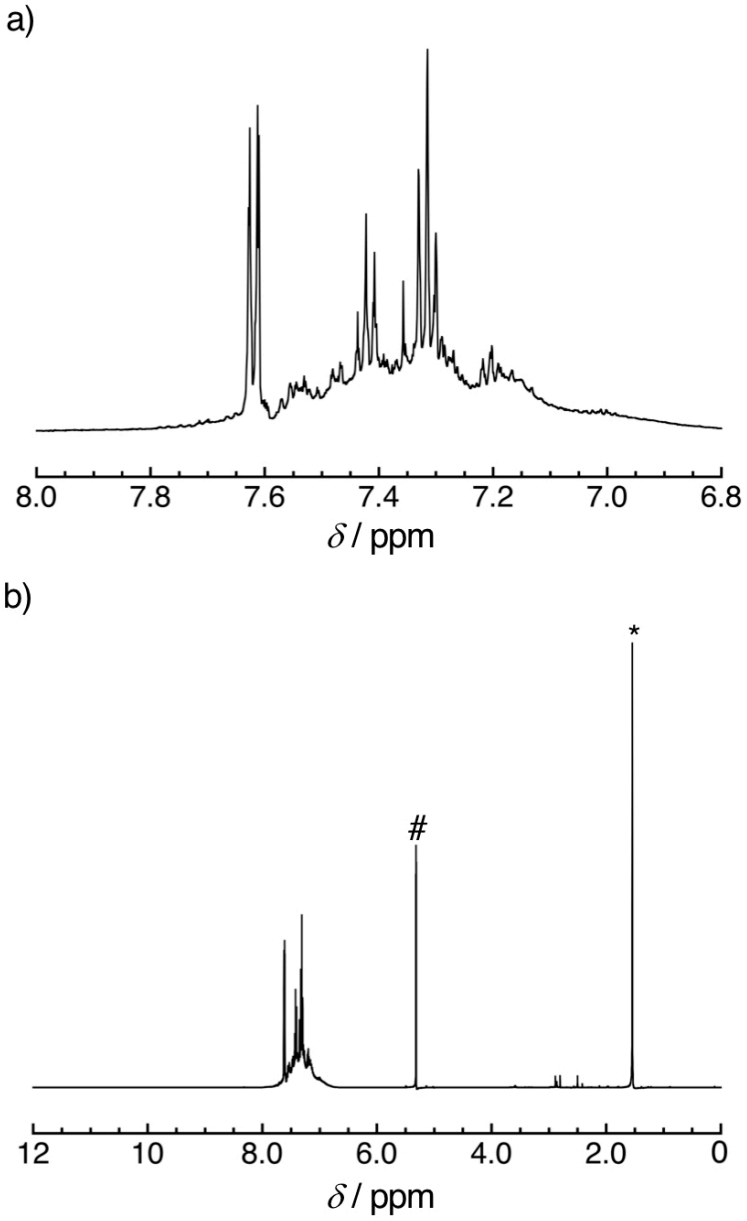

Fig. S8 a) Aromatic region and b) full range of the ^{1}H NMR (500 MHz, CD_2Cl_2) spectrum of the product in the solution phase obtained from the hydrothermal treatment of **AlSi$_6$** at 150 °C for 12 h in aqueous HCl (12 eq.). The symbol # denote the residual proton of dichloromethane and protons, and the signal ***** denotes *Si*–OH and/or H_2O.

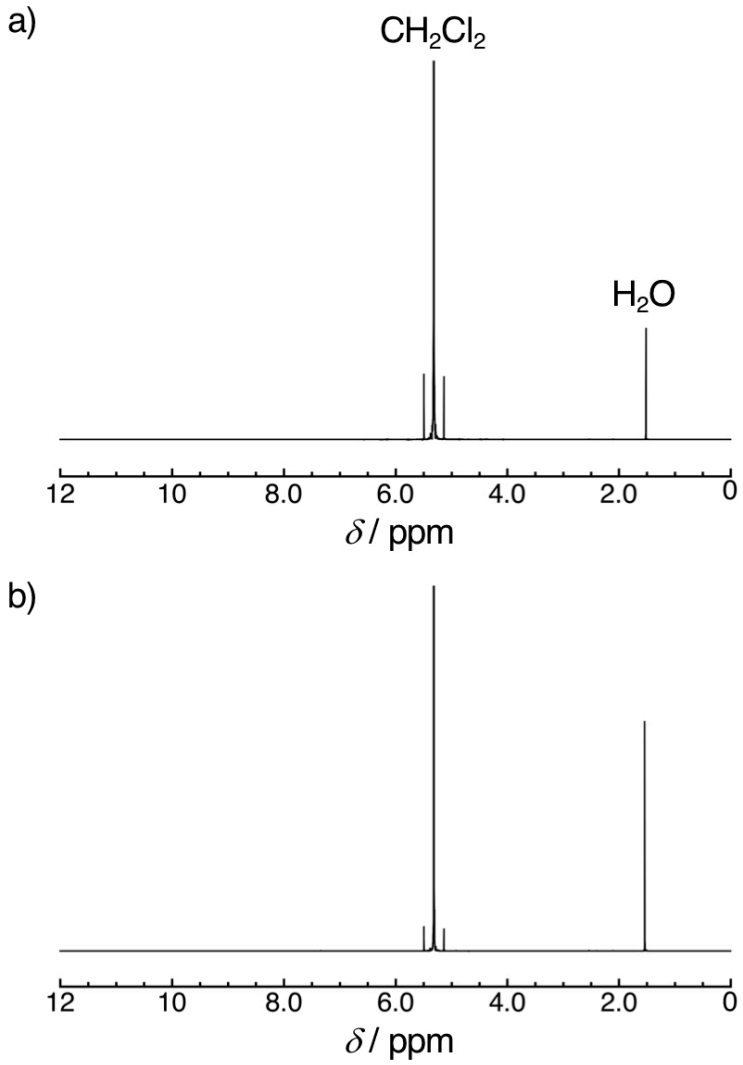

Fig. S9 ^{1}H NMR spectra (500 MHz, CD_2Cl_2) of the products in the solution phase obtained from a) refluxing and b) the hydrothermal treatment of **AlSi$_6$** at 150 °C for 12 h in the presence of HCl (12 eq.).

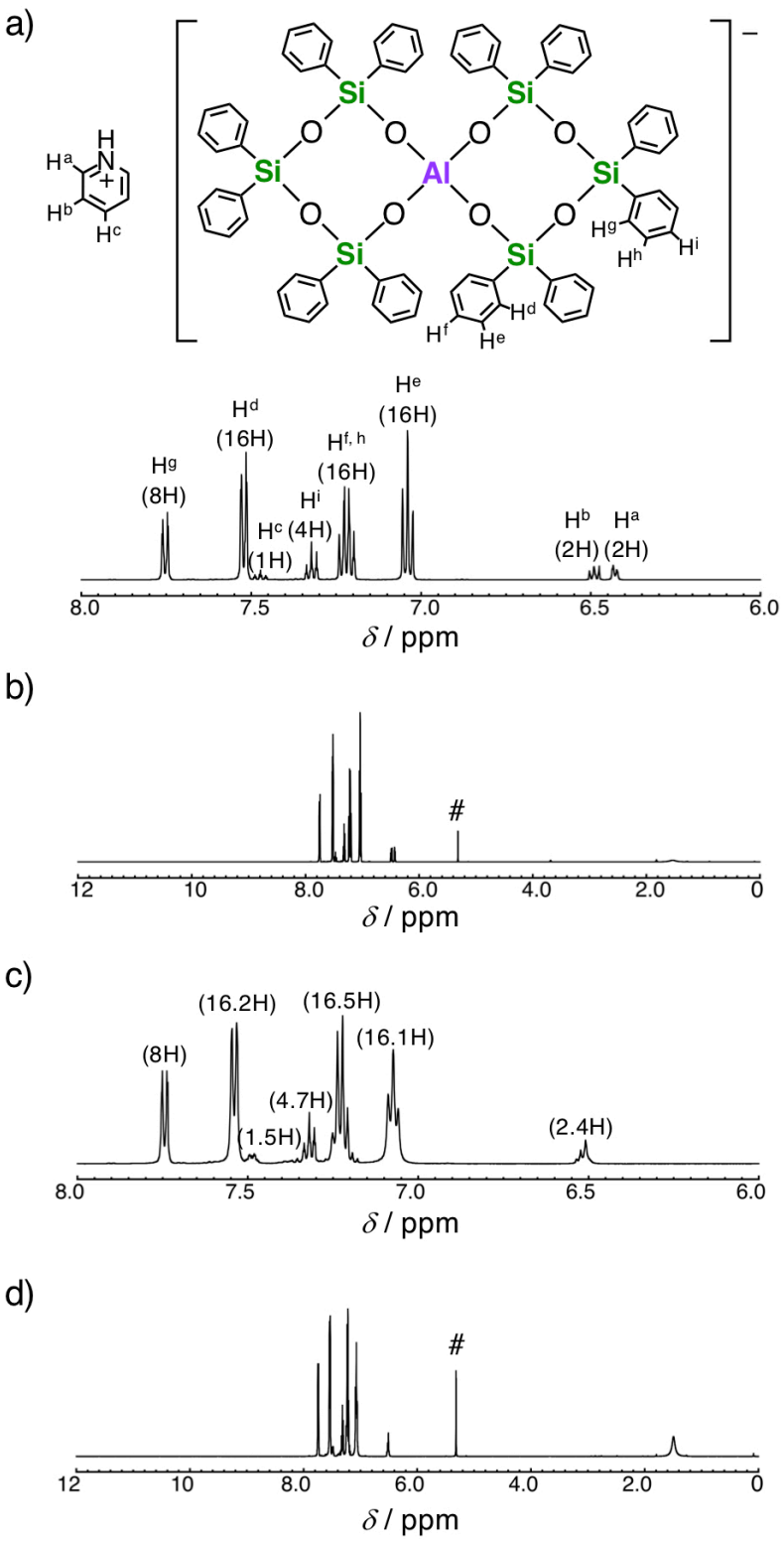

Fig. S10 Aromatic region and full range of the ^{1}H NMR spectra (500 MHz, CD_2Cl_2) of a, b) **AlSi$_6$** and c, d) the soluble products obtained from the refluxing of **AlSi$_6$** for 12 h in aqueous KOH (12 eq.). The symbol "#" denotes the residual proton of dichloromethane.

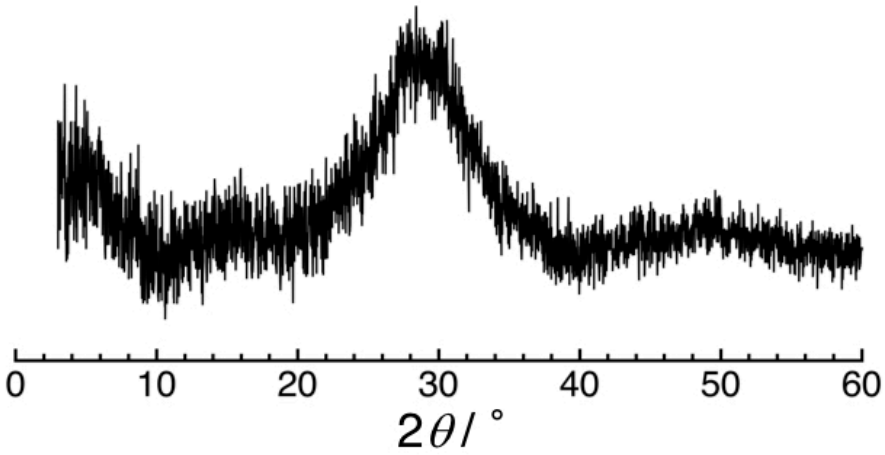

Fig. S11 PXRD pattern of the product obtained from the refluxing of **AlSi$_6$** in aqueous KOH (12 eq.) for 12 h.

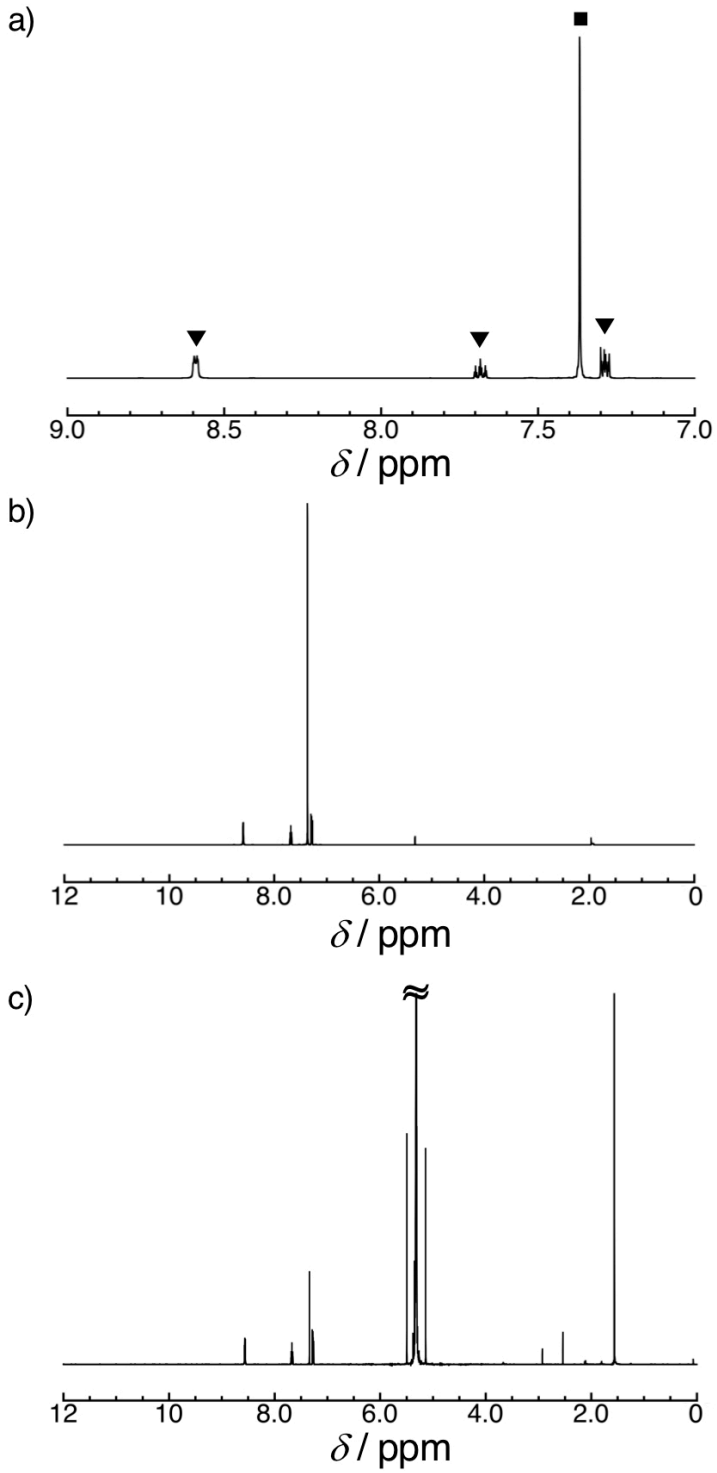

Fig. S12 a) Aromatic region and b) full range of the ^{1}H NMR (500 MHz, CD_2Cl_2) spectrum of a mixture of pyridine and benzene for reference, and c) full range spectrum of the soluble product in CD_2Cl_2 obtained from hydrothermal treatment of **AlSi$_6$** in the presence of KOH (12 eq.) at 150 °C for 12 h. The symbols ▼ and ■ denote signals from pyridine and benzene, respectively.

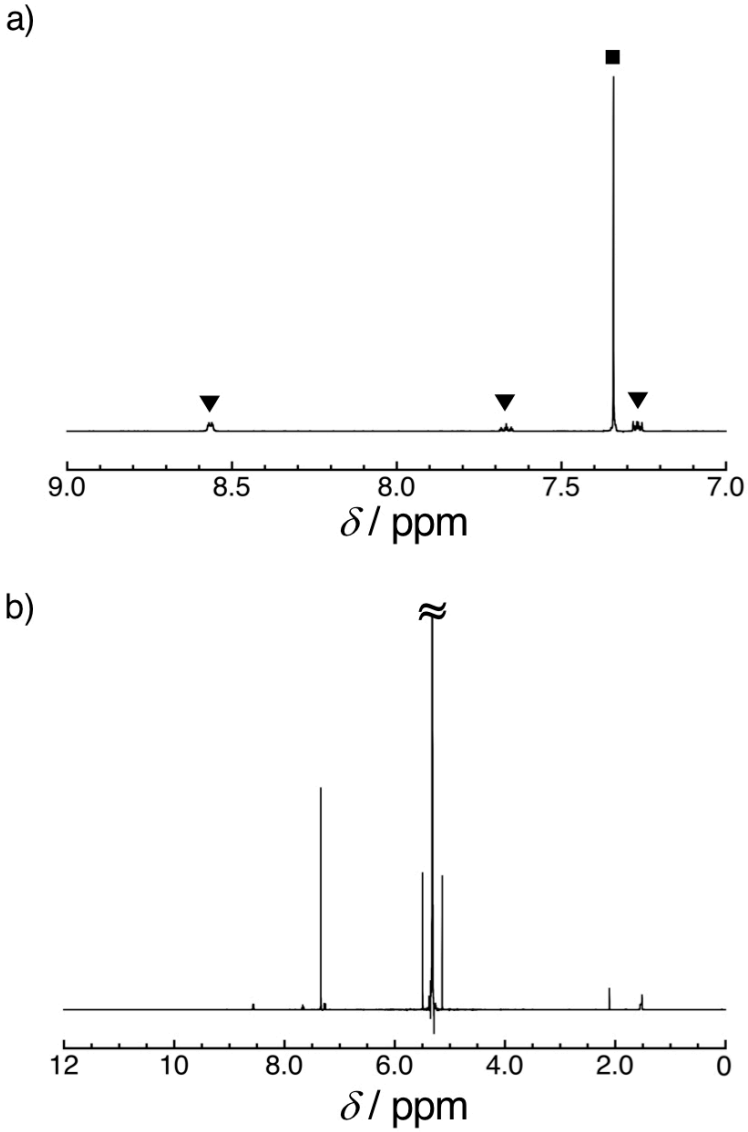

Fig. S13 a) Aromatic region and b) full range of the ^{1}H NMR (500 MHz) spectrum of the soluble product in CD_2Cl_2 obtained from the hydrothermal treatment of **AlSi$_6$** in the presence of KOH (12 eq.) at 160 ˚C for 12 h. The symbols ▼ and ■ denote signals from pyridine and benzene, respectively.

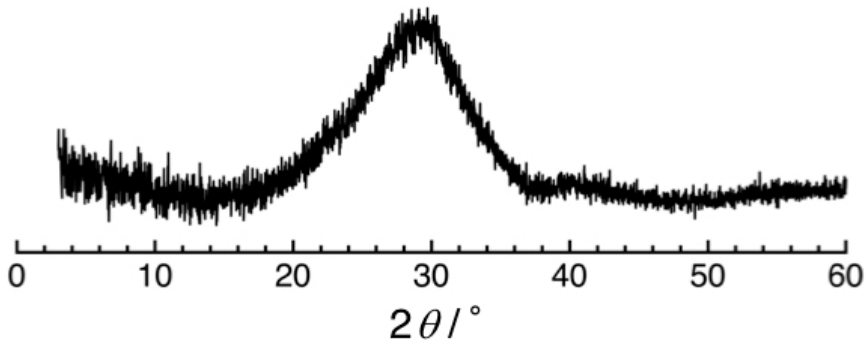

Fig. S14 PXRD pattern of the amorphous solid obtained from the hydrothermal treatment of **AlSi$_6$** in the presence of KOH (24 eq.) at 160 °C.

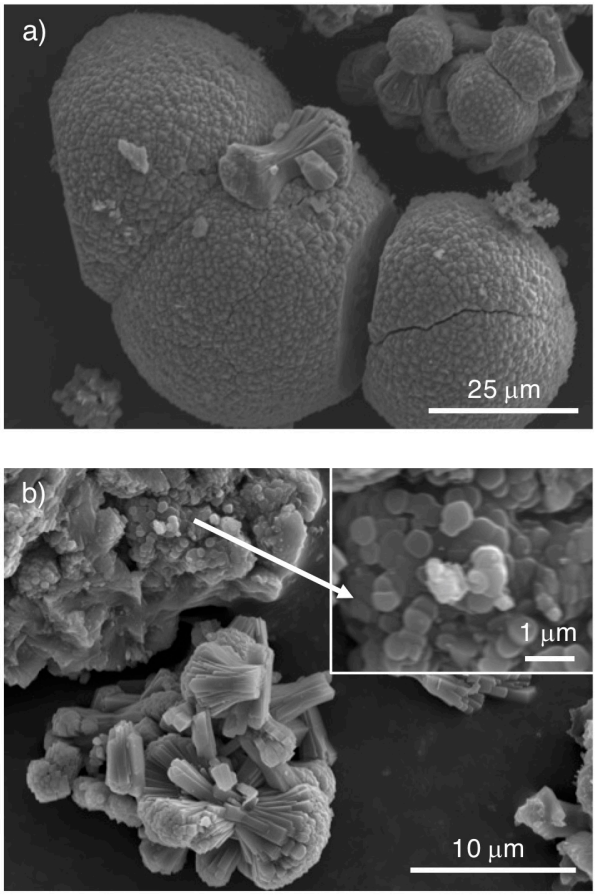

Fig. S15 SEM images of a) zeolite W and b) a mixture of zeolite W and L obtained from the hydrothermal treatment of **AlSi$_6$** in the presence of KOH (*x* eq.) at 160 °C (a) *x* = 9 and b) *x* = 6). Inset in b) shows closed up image of disk-shaped crystals of zeolite L.

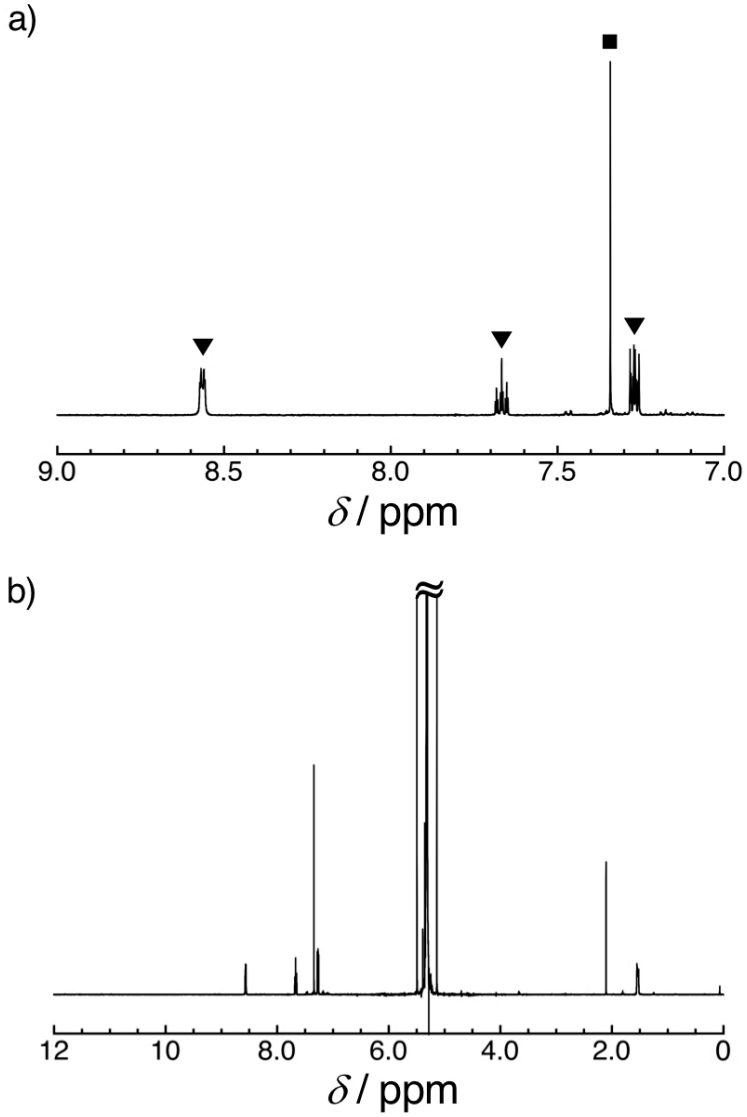

Fig. S16 a) Aromatic region and b) full range of the ^{1}H NMR (500 MHz) spectrum of the soluble product in CD_2Cl_2 obtained from the hydrothermal treatment of **AlSi$_6$** in the presence of KOH (3 eq.) at 160 °C for 12 h. The symbols ▼ and ■ denote signals from pyridine and benzene, respectively.

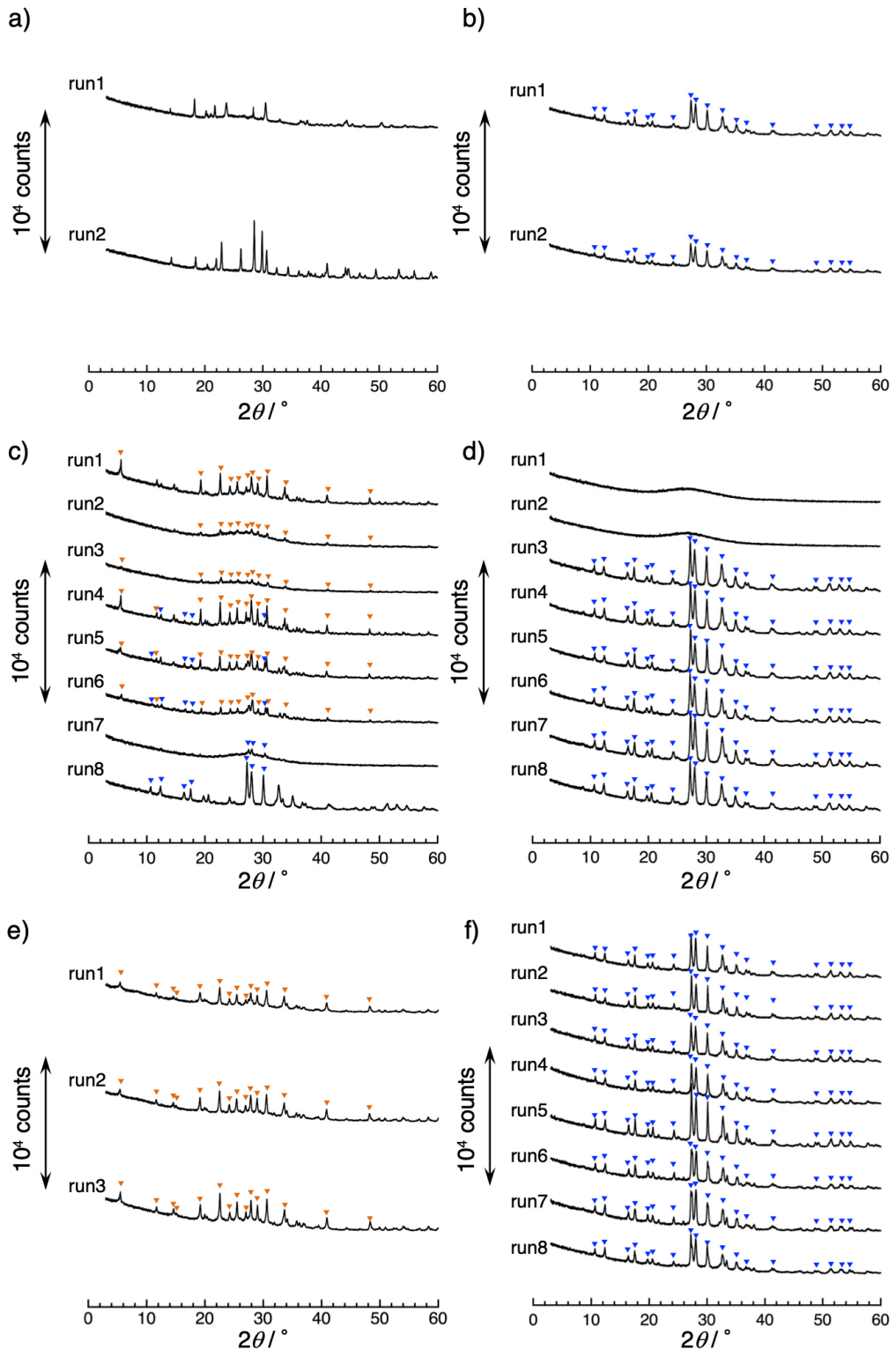

Fig. S17 PXRD patterns of powders synthesized from a) $Al(OH)_3$, SiO_2, and 3 eq. KOH; b) $Al(OH)_3$, SiO_2, and 12 eq. KOH; c) Al, SiO_2, and 3 eq. KOH; d) Al, SiO_2 and 12 eq. KOH; e) **AlSi$_6$** and 3 eq. KOH; f) **AlSi$_6$** and 12 eq. KOH. All reactions were carried out for 12 h at 160 ˚C. All measurements were performed using the following conditions: scan rate = 5 °/min; step = 0.02 °; at room temperature. The symbols "▼" and "▼" indicate peaks derived from zeolites L and W, respectively.

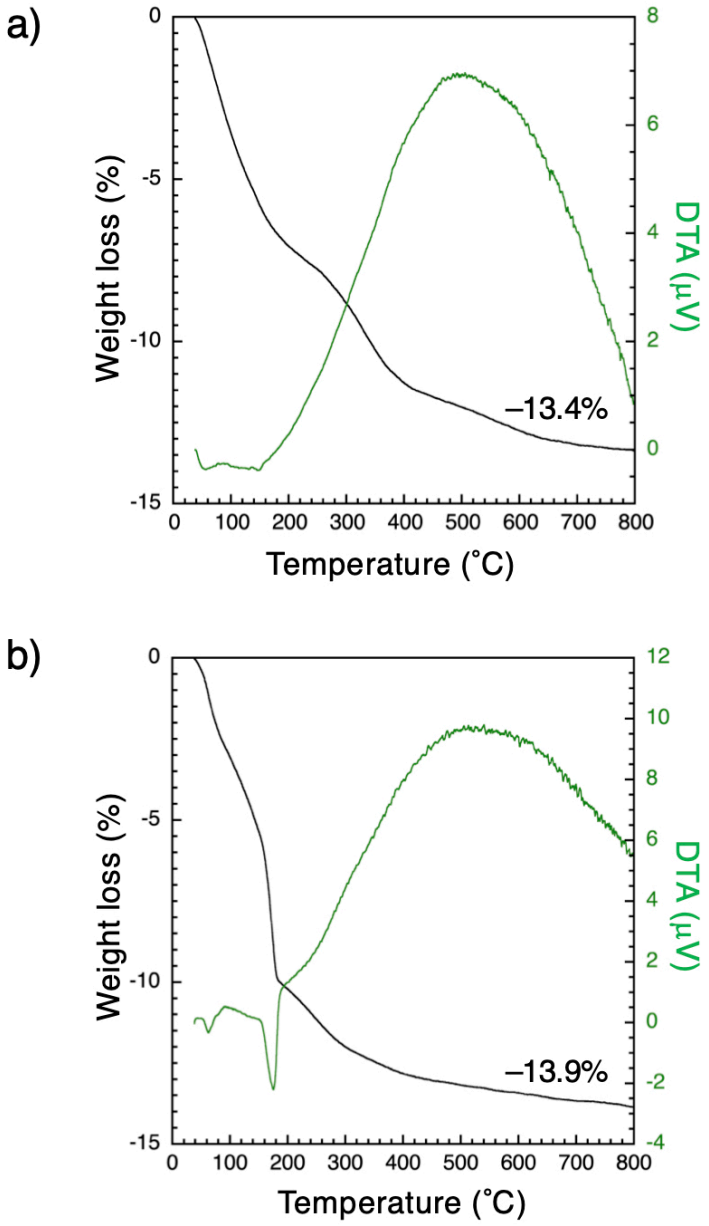

Fig. S18 TG (black line)-DTA (green line) diagrams of a) zeolites L and b) W synthesized from **AlSi$_6$** in the presence of 3 or 12 eq. of KOH at 160 °C for 12 h, respectively.

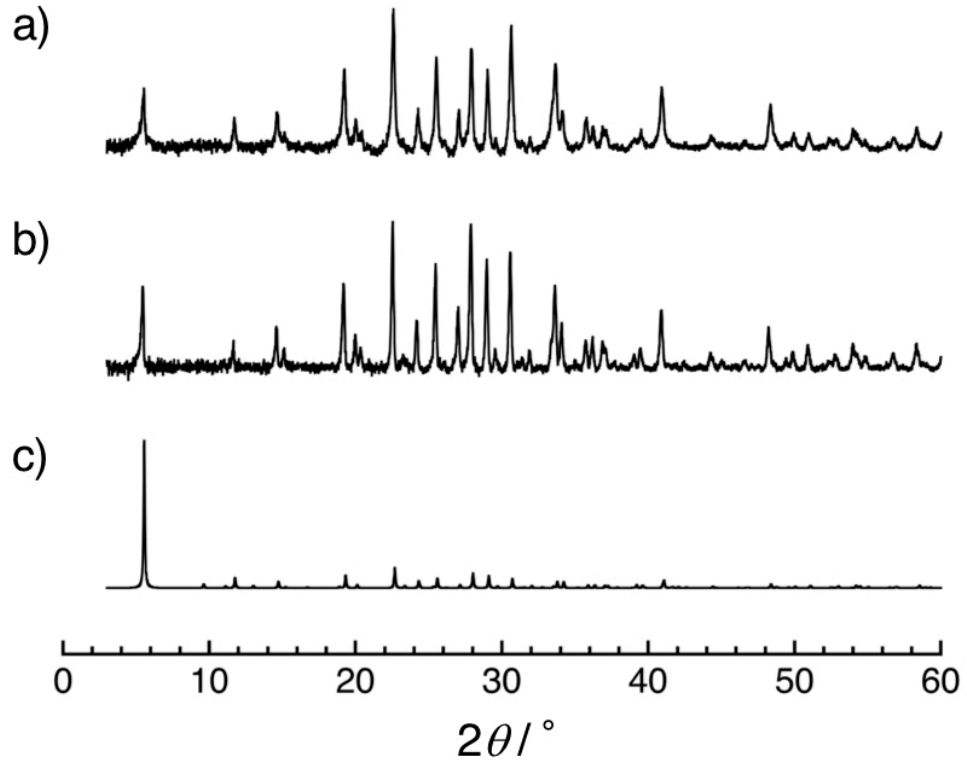

Fig. S19 PXRD patterns of the zeolite L obtained from the hydrothermal treatment of **AlSi$_6$** in the presence of KOH (3 eq.) at a) 180 and b) 200 °C. c) The simulated PXRD pattern of zeolite L.[S1]

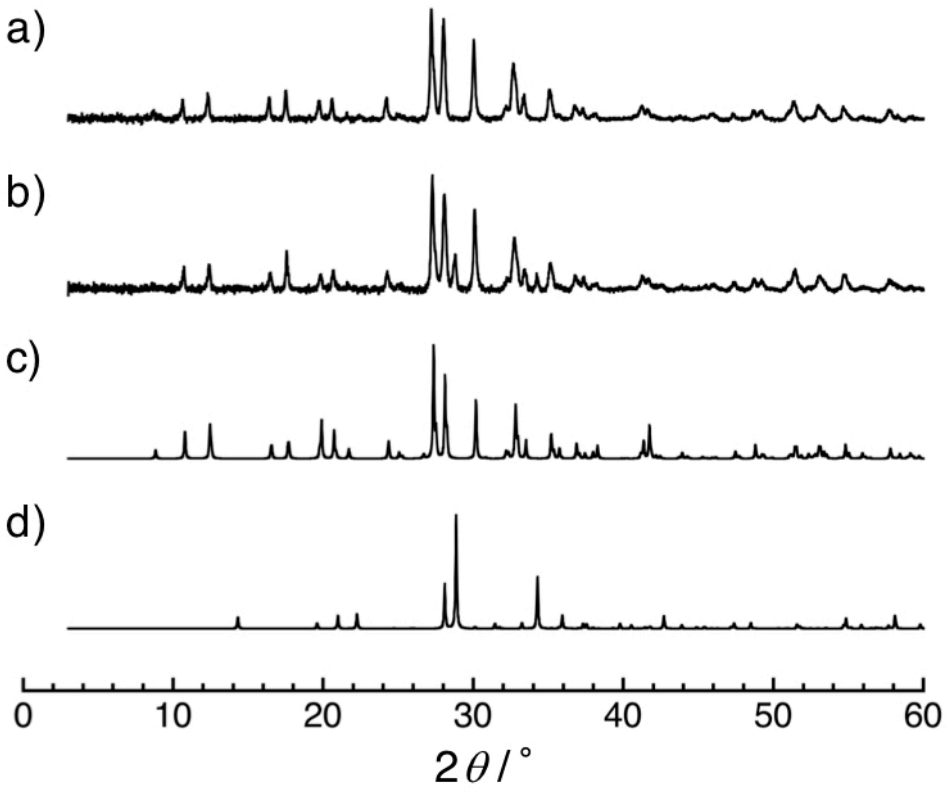

Fig. S20 PXRD patterns of the mixture of zeolite W and megakalsilite obtained from the hydrothermal treatments of **AlSi$_6$** in the presence of KOH (x eq.) at 180 °C (a) x = 6 and b) x = 9). Simulated PXRD patterns for c) zeolite W[S2] and d) megakalsilite.[S3]

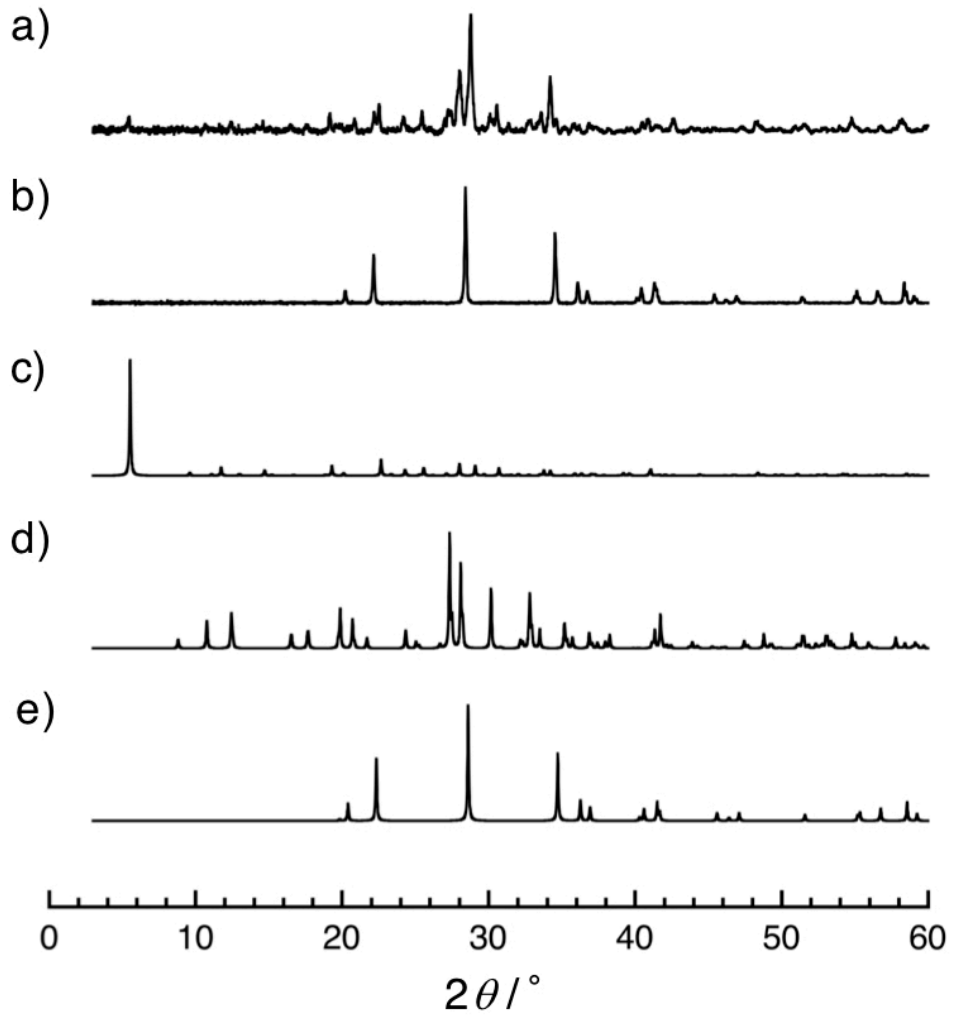

Fig. S21 PXRD patterns of zeolites L, W, and kalsilite obtained from the hydrothermal treatments of **AlSi$_6$** in the presence of KOH (*x* eq.) at 200 °C (a) *x* = 6 and b) *x* = 9). Simulated PXRD patterns for c) zeolite L,[S1] d) zeolite W,[S2] and e) kalsilite.[S4]

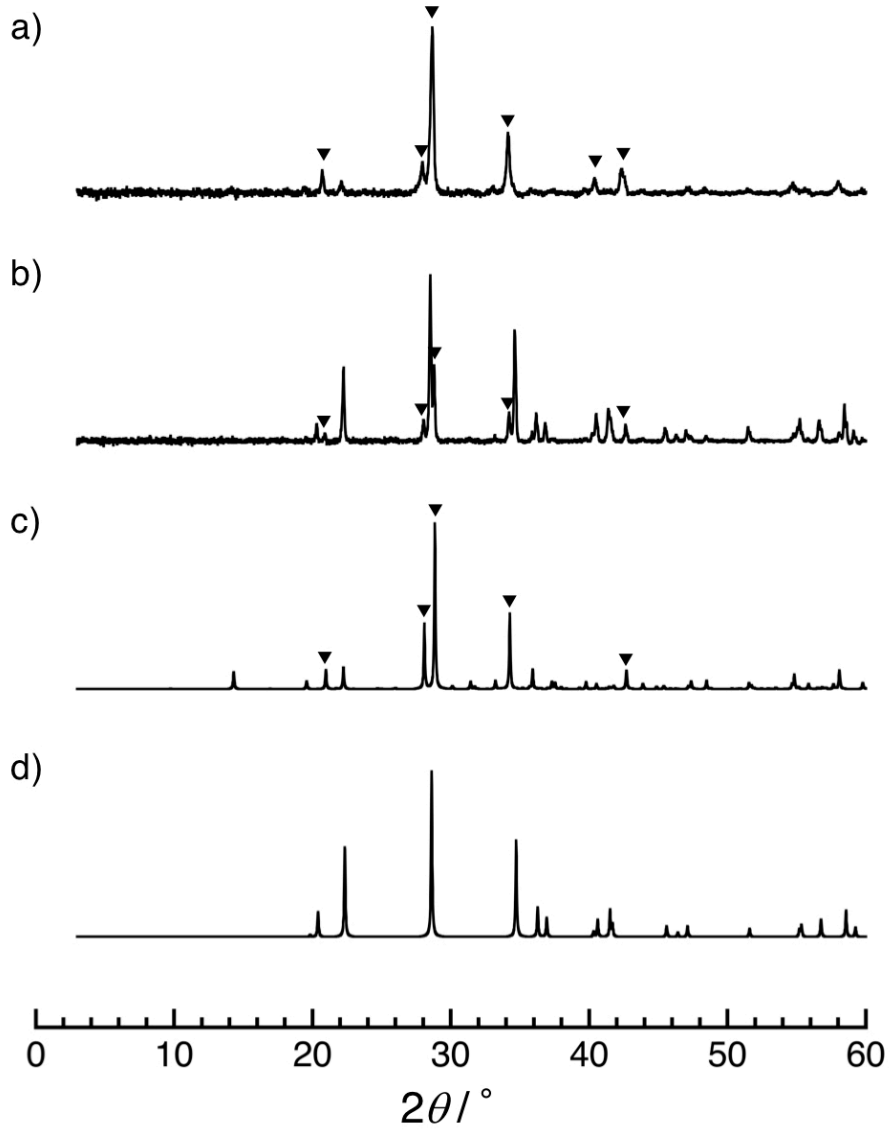

Fig. S22 PXRD patterns of the megakalsilite and kalsilite obtained frmo the hydrothermal treatment of **AlSi$_6$** in the presence of KOH 12 eq. at a) 180 and b) 200 °C. Simulated PXRD patterns for c) megakalsilite[S3] and d) kalsilite.[S4] The signal "▼" denotes characteristic diffraction peaks for megakalsilite.

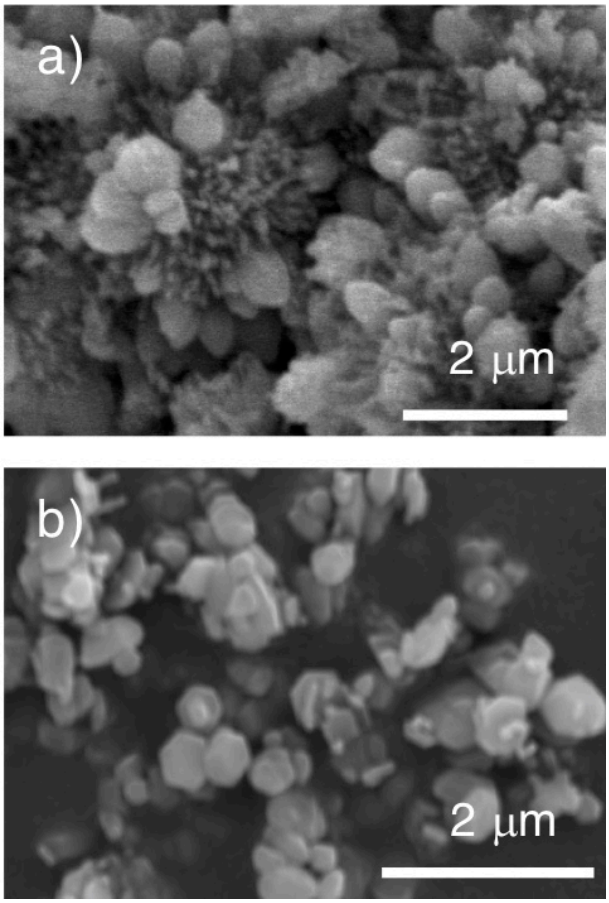

Fig. S23 SEM images of a) kalsilite and b) megakalsilite obtained from the hydrothermal treatments of **AlSi$_6$** in the presence of KOH (12 eq.) at a) 180 and b) 200 °C.

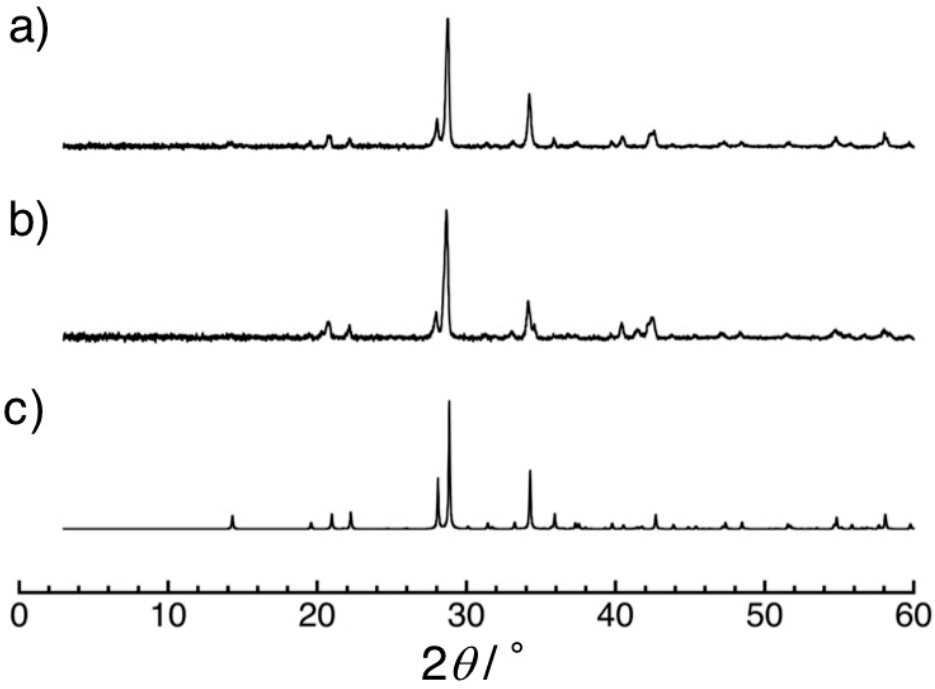

Fig. S24 PXRD patterns of the megakalsilite obtained from the hydrothermal treatments of **AlSi$_6$** in the presence of KOH (24 eq.) at a) 180 and b) 200 °C. c) Simulated PXRD patterns for megakalsilite.[S3]

References

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S3. A. P. Khomyakov, G. N. Nechelyustov, E. Sokolova, E. Bonaccorsi, S. Merlino and M. Pasero, *Can. Mineral*., 2002, **40**, 961–970.

S4. A. J. Perrotta and J. V. Smith, *Mineral. Mag*., 1965, **35**, 588–595.