Electronic Supporting Information

First Preparation of Microporous AFY-type MeAPO by Topotactic Pillaring of Lamellar Aluminophosphate Precursor

Kazuyuki Maeda,* Kentaro Wakui, Kyosuke Arakawa and Atsushi Kondo

Department of Applied Chemistry, Tokyo University of Agriculture and Technology,

2-24-16 Naka-cho, Koganei, Tokyo 184-8588, Japan.

TEL/Fax: +81-42-388-7040 E-mail: k-maeda@cc.tuat.ac.jp

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Experimental details

Materials: Aluminium isopropoxide was supplied by Kawaken Fine Chemicals Co. Ltd.   Zinc nitrate hexahydrate of 99.0 % purity and zinc acetate dihydrate of 99.0 % purity were purchased from Wako Chemicals Co. Ltd.   n-Butylamine were purchased from TCI, acetonitrile and methanol from Kanto Chemicals.   Anhydrous methanol and acetonitrile were also obtained from Kanto Chemicals.   The chemicals were used as purchased without further purification.   Milli-Q filtered water with resistivity >18 MΩ·cm was used throughout the experiments.

Preparation of PreAFY and ion exchange with alkali metal cations: The layered ALPO precursor $[BuNH_3]_3[Al_3P_4O_{16}]$ (PreAFY) was prepared according to the literature[1] in a slightly modified procedure.   A typical preparation procedure of K-PreAFY is as follows: PreAFY (700 mg) was treated with solutions of $K(O_2CCH_3)$ (8.7 mmol) in a 1:1 (v/v) methanol/acetonitrile mixed solvent (10 mL) at an ambient temperature for 24 h.   The obtained precipitate was filtrated and thoroughly washed with methanol to give K-PreAFY.   Dryness of the solid was avoided throughout the procedure except the samples used for laboratory XRD and TG-DTA measurement.   K-PreAFY dispersed in the solution was used for further treatment.   Similar preparations using alkali metal acetate (AO_2CCH_3: A = Li, Na, K, Cs) gave A-PreAFY.

Preparation of K-ZnAFY: A typical preparation procedure of K-ZnAFY is as follows: A mixed solution of $Zn(O_2CCH_3)_2·2H_2O$ (2.5 mmol) and $Zn(NO_3)_2·6H_2O$ (2.5 mmol) dissolved in a 1:1 (v/v) methanol/acetonitrile mixed solvent (10 mL) was added to the above methanol-dispersed K-PreAFY, and the mixture was heated in a Teflon-lined autoclave at 60 °C for 5 d.   The precipitate was filtrated and thoroughly washed with the same solvent.   Preparation with other combinations of A and pillaring metal cations Me (Me =Zn, Mg, Mn, and Co) were also attempted in similar ways to give A-MeAFY samples shown in Fig S8.

Preparation of K-ZnAFY-ah: A modified procedure based on the above K-ZnAFY preparation with removal of water from the system as far as possible throughout the reaction was used to obtain K-ZnAFY-ah.   A typical preparation procedure is as follows: Potassium acetate (2.0 mmol) was dried under vacuum in a Schlenk flask, and anhydrous

methanol (5 mL) and anhydrous acetonitrile (5 mL) were added under nitrogen. After dissolution of potassium acetate, PreAFY (200 mg) was added and reacted at 60 °C for 1 d. The resulting solid were washed with anhydrous methanol under nitrogen to obtain K-PreAFY-ah (in methanol). A mixture of zinc nitrate hexahydrate (0.57 mmol) and zinc acetate dihydrate (0.57 mmol) was heated at 130 °C for 12 h under nitrogen in another Schlenk flask. Anhydrous methanol (5 mL) and anhydrous acetonitrile (5 mL) were added to this mixture, and the salts were dissolved at 60 °C for 1 h. This solution was added to the methanol-dispersed K-PreAFY-ah, the mixture was heated at 60 °C for 5 d under nitrogen. The resulting solid was filtrated and air-dried to obtain K-ZnAFY-ah.

Characterization: Energy-dispersive X-ray (EDX) spectrometry was measured on a PHILIPS EDAX-DX-4. TG-DTA was measured on a Rigaku Thermo Plus 2 at a heating rate of 10 K min^{-1} under an air flow at 100 ml min^{-1}. Laboratory Powder X-ray diffraction (XRD) patterns except high resolution data were measured on a Rigaku RINT-2100S using monochromated Cu-Kα radiation. The high resolution synchrotron diffraction data were collected on the diffractometer of the BL02B2 ($\lambda \approx 0.8$ Å, exact values are shown at each respective data) at SPring-8 (Hyogo, Japan) using a powder sample loaded in a 0.5 mm glass capillary for dry powder samples or in a 0.5-1.0 mm glass capillary for wet samples sealed with the mother liquor. SEM images were obtained on a JEOL JSM-6510 scanning electron microscope. CHN elemental analysis was performed on a Perkin-Elmer Series II CHNS/O analyzer 2400. The nitrogen adsorption measurements at 77 K were performed on BELSORP 28 (Bell Japan).

Crystal Structure Determination of K-PreAFY: The high-resolution synchrotron diffraction data of *A*-PreAFY and related samples were collected using a powder sample with the mother liquor loaded in a 0.5-1.0 mm glass capillary and sealed with the liquid. The diffraction data of K-PreAFY was successfully indexed with a hexagonal unit cell using the NTREOR module in EXPO2014 software.[2] The extinction rule suggested the space group $P\overline{3}$, which is the same as PreAFY. The intensities extracted in the Le Bail method using EXPO2014 was used for the direct method. No reasonable framework model was obtained for K-PreAFY in the direct method. However, as for the similarly measured XRD data of Cs-PreAFY, a framework model retaining the original PreAFY

framework topology with an interlayer Cs site was obtained, which gave a reasonable simulated XRD pattern. This framework model was used as an initial model for K-PreAFY, and a potassium site and three additional sites, which can be assigned to solvent molecules, were found in the 12MR channels by the difference Fourier synthesis. The solvent molecules should be disordered in the channels, which can be a mixture of methanol, acetonitrile, and water. It is difficult to know even the approximate composition of the extra-framework species because the sample is in the solvent mixture. In order to simplify the system, the solvent mixture was represented by three virtual atoms Ow7, Ow8 and Ow9 simulating water molecules (1O + 2H) located at the two sites found in the channels. The model was refined in the Rietveld method using RIETAN-FP[3] with soft geometrical restraints [prescribed distances/Å: Al-O 1.73(3), P-O 1.52(3); prescribed angles/°: C-C-C(H) 120.0(9), O-Al(P)-O 109(3), Al-O-P 145(13)]. To stabilize the refinement, the displacement parameters for all the framework atoms (Al, P and framework O) were constrained to be the same. In spite of the simple treatment of the disordered solvent molecules, the refinement finally resulted in reasonable convergence (R_{wp} = 0.0707, R_F = 0.0086). The structure models are drawn using VESTA.[4]

Distance Least Squares (DLS) analysis of K-ZnAFY: The lattice parameters of K-ZnAFY were refined on a synchrotron diffraction data (λ = 0.79964 Å, 3.2 – 23.0°) in the Pawley method by using the Reflex module in Materials Studio software. The obtained lattice parameters a = 12.442(1) Å and c = 8.826(2) Å (R_{wp} = 0.0344) were used in the DLS analysis to verify geometrical validity as an AFY topology and to obtain geometrically ideal atomic coordinates of the framework. The imposed geometrical restraints were as follows; bond distances/Å Al-O: 1.73(1) Å, P-O: 1.52(1) Å, Zn-O: 1.95(1) Å, and bond angles/° O–T–O: 109.47(200), T–O–T: 145(8). The refinement converged to R = 0.0048 to support the geometrical validity as an AFY-type framework. The obtained atomic coordinates were used to simulate the XRD pattern shown in Fig. 2b.

References

1) A. M. Chippindale *et al., J. Chem. Soc., Dalton Trans*., 1997, **16**, 2639–2644.

2) A. Altomare, C. Cuocci, C. Giacovazzo, A. Moliterni, R. Rizzi, N. Corriero and A. Falcicchio, *J. Appl. Cryst.,* 2014, **46**, 1231–1235.

3) F. Izumi and K. Momma, *Solid State Phenom.*, 2007, **130**, 15–20.

4) K. Momma and F. Izumi, *J. Appl. Crystallogr.*, 2011, **44**, 1272–1276.

5) Ch. Baerlocher, A. Hepp, and W. M. Meier., *DLS-76, A distance least squares refinement program*, ETH, Zurich, 1976.

Table S1 Crystallographic information for K-PreAFY.

Crystal system	trigonal
Space group	$P\bar{3}$
a/Å	12.9251(13)
c/Å	7.9339(7)
R_{wp}	0.0707
R_F	0.0086
R_e	0.0109

Table S2 Comparison of cell parameters of AFY-related phases indexed in trigonal systems.[§]

Sample	a /Å	c /Å
K-ZnAFY[*]	12.44	8.825
Na-ZnAFY	13.02	8.438
Na-MnAFY	13.01	16.83[†]
ZnAPO-50[**]	12.73	9.006
MnAPO-50[***]	12.75	9.140
Li-PreAFY	12.73	8.540
Na-PreAFY	13.00	16.80[†]
K-PreAFY	12.91	7.948
Cs-PreAFY	13.04	8.622
PreAFY	13.15	9.908

[§]The cell parameters were obtained by Le Bail refinement (EXPO2014) unless otherwise stated.   [*]Pawley refinement (Materials Studio)
[**]From Ref. 21 (Rietveld)   [***]From Ref. 20 (Single crystal)
[†]Indexed with double length for c

Table S3 Interlayer distances of K-ZnAFY prepared with various solvents.

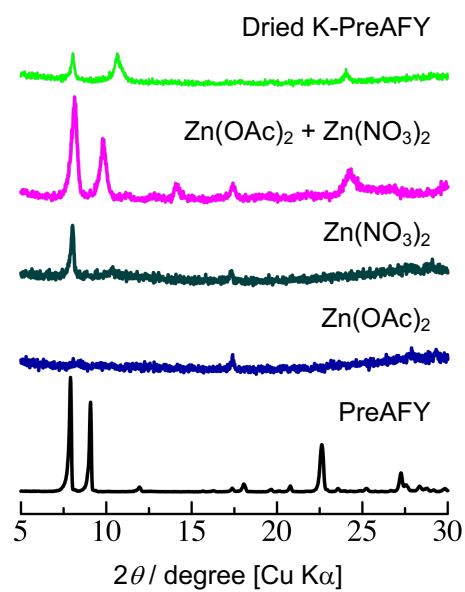| Solvent	Interlayer distance /Å
CH_3CN/CH_3OH	9.04
$CHCl_3/CH_3OH$	8.49
THF/CH_3OH	8.46
$DMSO/CH_3OH$	8.33
CH_3OH	8.46
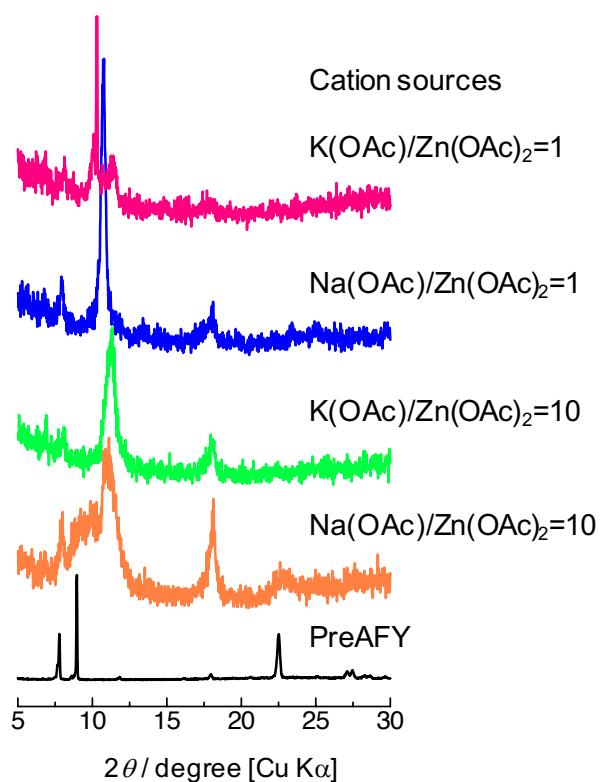
Fig. S1 XRD patterns of Na-ZnAFY and K-ZnAFY prepared in a single-step cation exchange at an ambient temperature for 5 d.
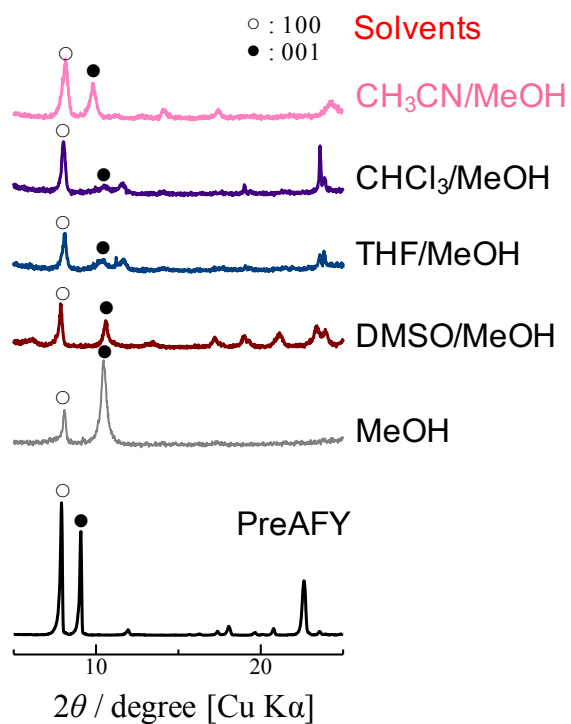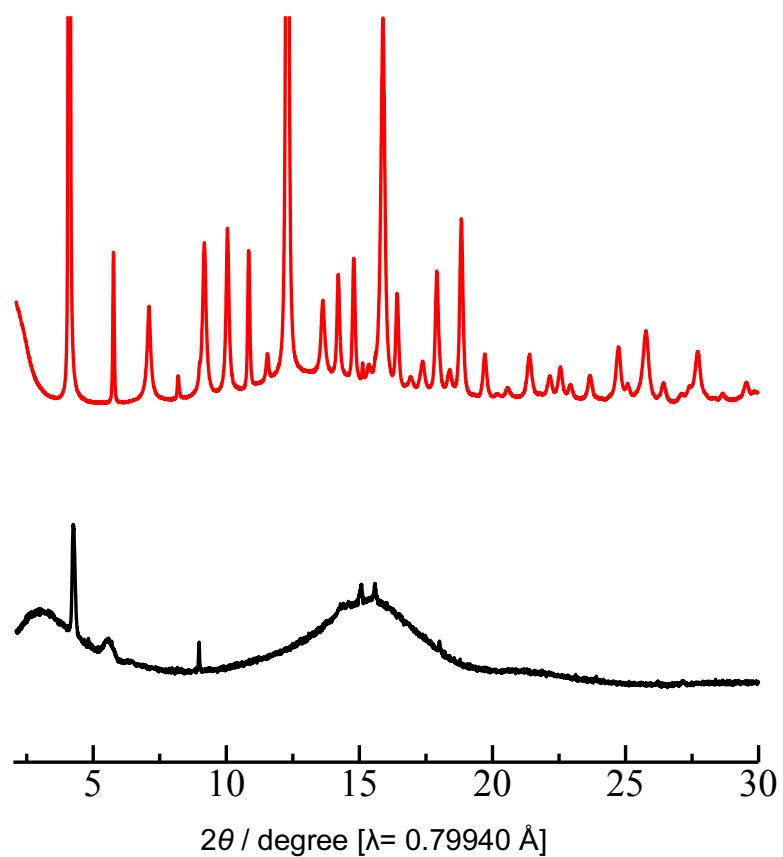

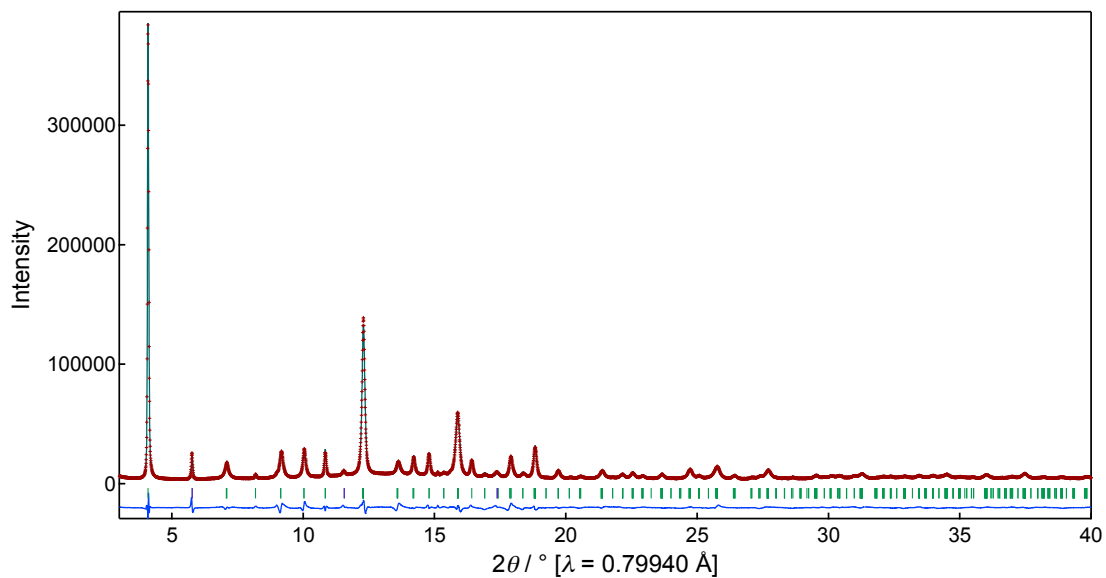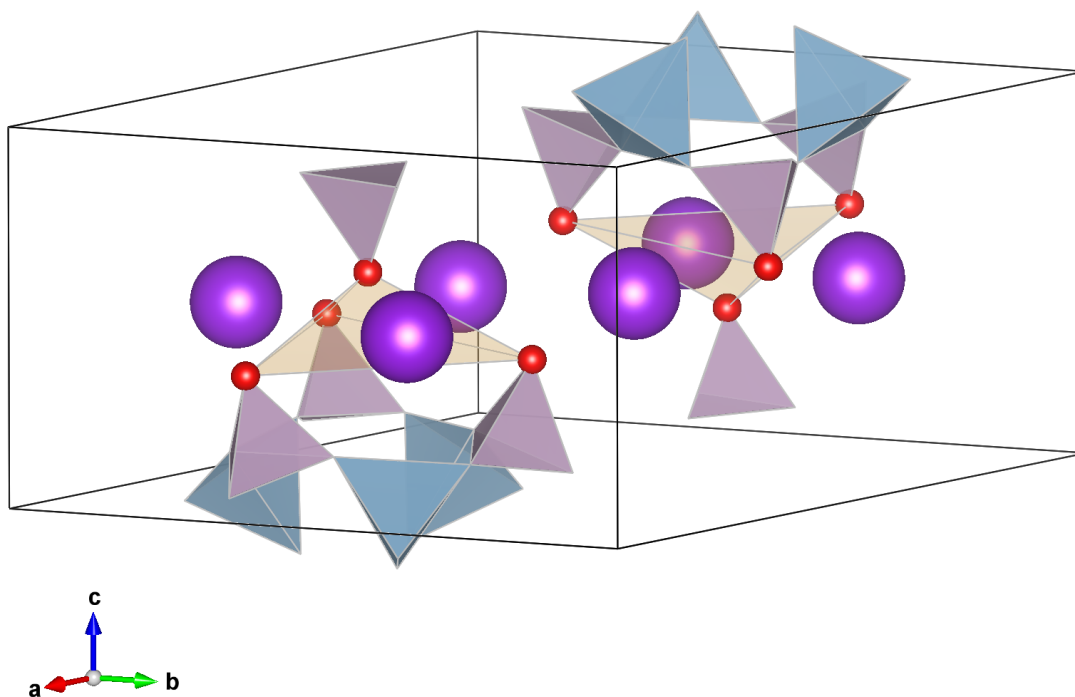**Fig. S2** XRD patterns of K-ZnAFY prepared with various solvents.

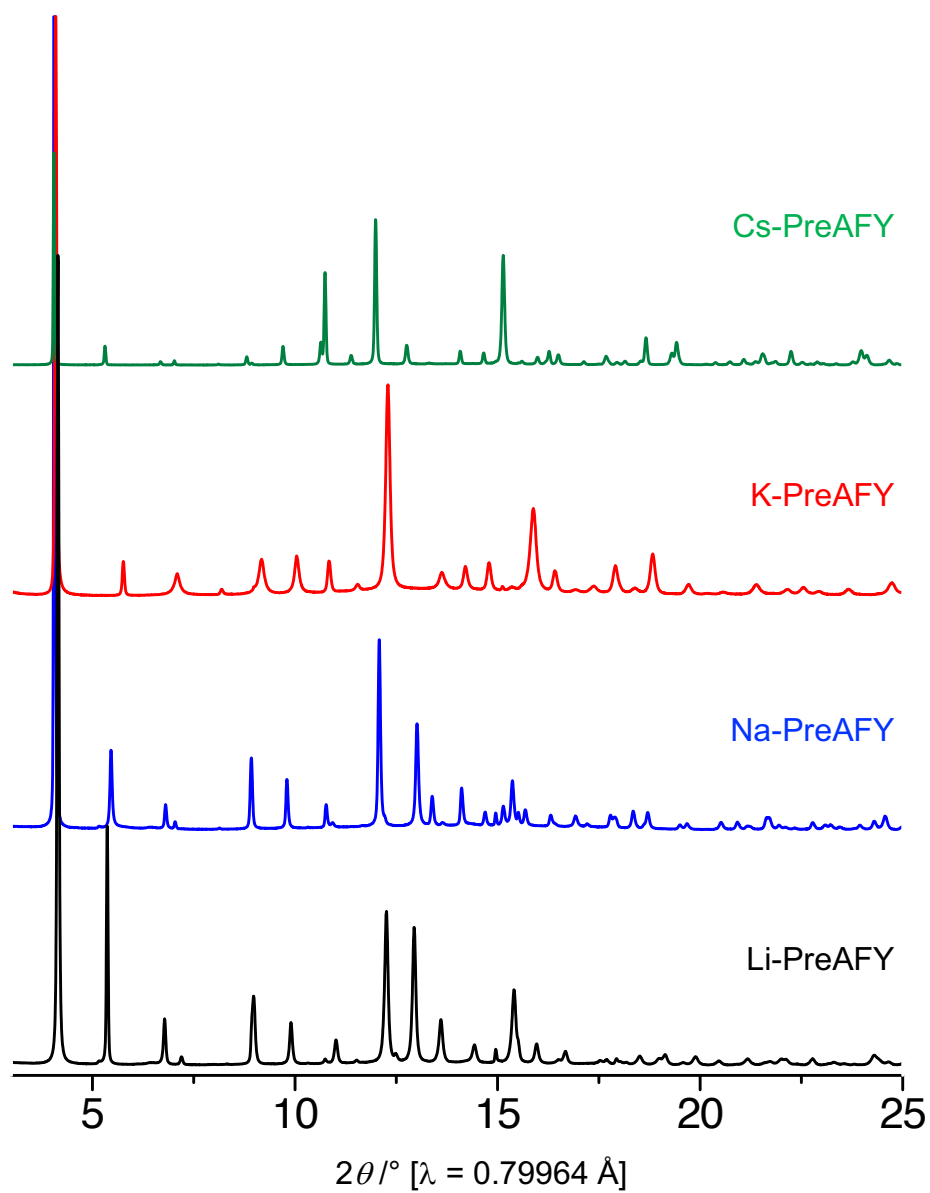**Fig. S3** XRD patterns of K-ZnAFY prepared from various zinc sources.

Fig. S4 XRD patterns of K-PreAFY sealed with the solvent (upper) and dried in air (lower).

Fig. S5 Rietveld plot of K-PreAFY.

Fig. S6 Structure around the virtual tetrahedral vacancies in K-PreAFY. Blueish grey tetrahedra: AlO_4, pale purple tetrahedra: PO_4, Purple spheres: K atoms. The virtual vacancies are indicated as pale orange distorted tetrahedra topped with red spheres (oxygen atoms).
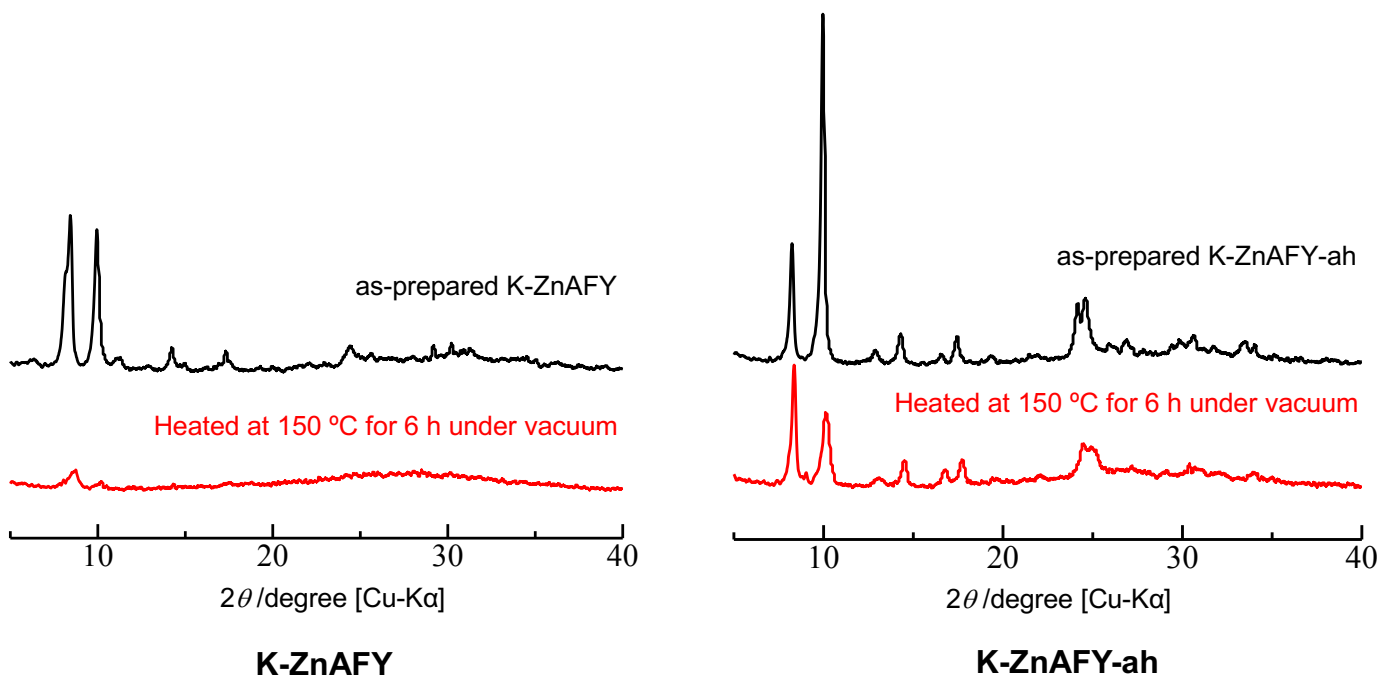
Fig. S7 XRD patterns of *A*-PreAFY prepared with various alkali metal cations (A) measured using capillaries sealed with the solvent.
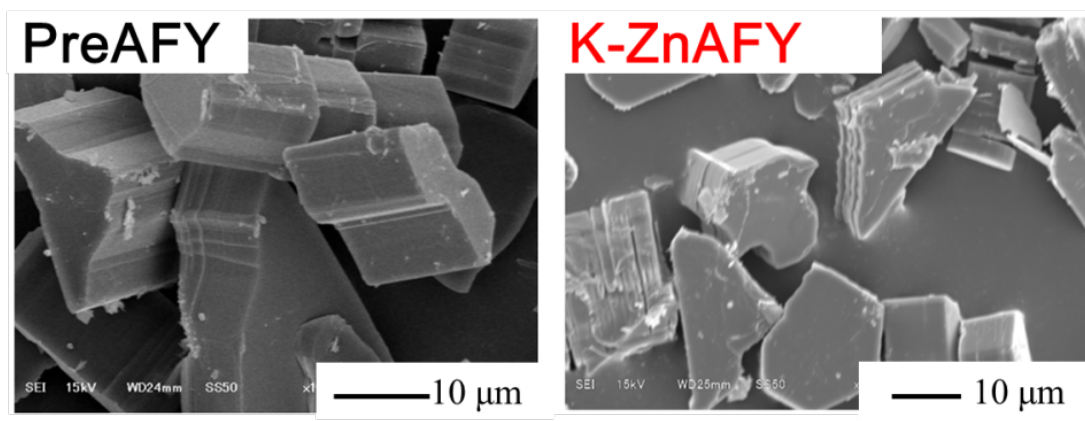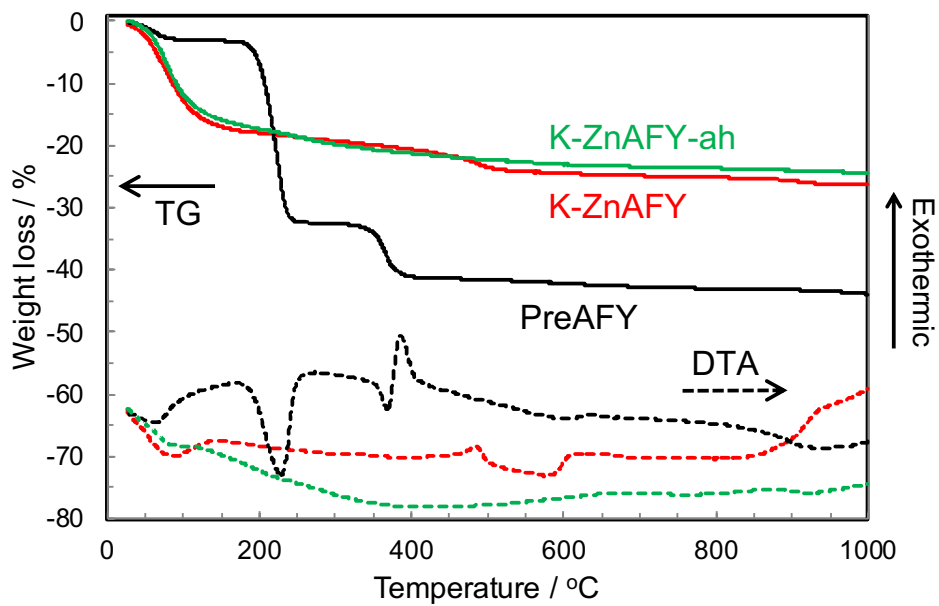
Fig. S8 SEM images of PreAFY and K-ZnAFY.
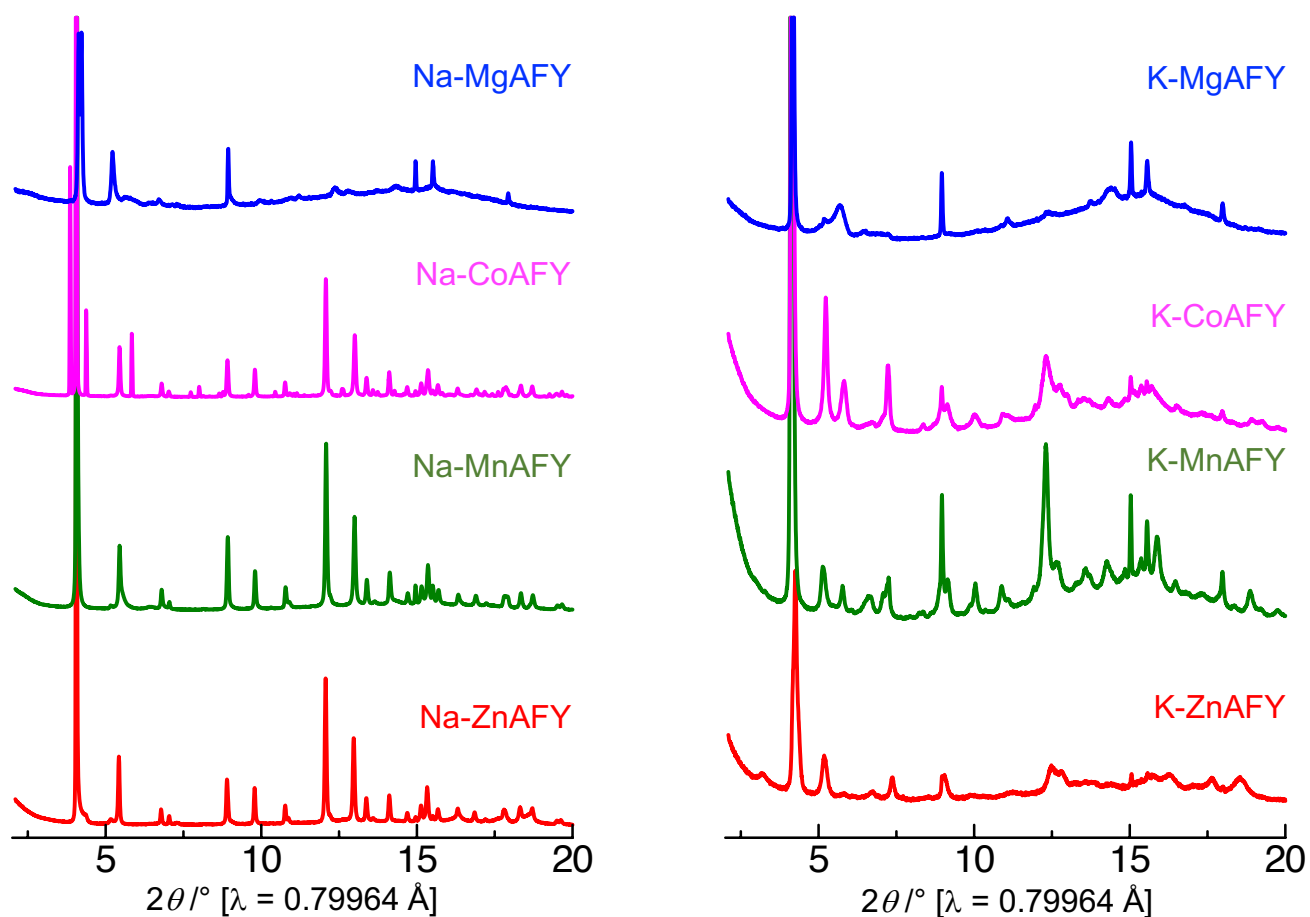
Fig. S9 XRD patterns of Na-*Me*AFY (left) and K-*Me*AFY (right) reacted with various pillaring metal cations (*Me*).   Na-*Me*AFY (Me = Co, Mn, and Zn) samples were measured using capillaries sealed with the solvent.

Fig. S10 XRD patterns of as-prepared and heat-treated K-ZnAFY (left) and K-ZnAFY-ah (right).

Fig. S11 TG-DTA curves of K-ZnAFY and K-ZnAFY-ah.