

Electronic Supplementary Information

Solvent-Free Synthesis of FAU Zeolite from Coal Fly Ash

Pei Liu, ^a Qinming Wu, ^{*a,b} Keping Yan, ^{a,b} Liang Wang, ^{a,b} and Feng-Shou Xiao ^{*a,b}

^a College of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310027, China.

^b Shanxi-Zheda Institute of Advanced Materials and Chemical Engineering, Taiyuan, 030032, China.

* Corresponding author. E-mail: qinmingwu@zju.edu.cn; fsxiao@zju.edu.cn

Experimental Section

Materials

Coal fly ash (CFA) used in the present study was obtained from an electric power plant in Henan, China. The chemical composition of the CFA has been listed in Table S1. Sodium hydroxide (NaOH, AR, 96%, Sinopharm Chemical Reagent Co., Ltd.), sodium aluminate (NaAlO₂, CP, Sinopharm Chemical Reagent Co., Ltd.), colloidal silica (30 wt.% SiO₂ in water, Zhejiang Yuda Chemical Co., Ltd.), hydrochloric acid (HCl, AR, 36.5%, Sinopharm Chemical Reagent Co., Ltd.), magnesium chloride hexahydrate (MgCl₂·6H₂O, AR, 98%, Sinopharm Chemical Reagent Co., Ltd.), and calcium nitrate tetrahydrate [Ca(NO₃)₂·4H₂O, ACS, Aladdin Chemistry Co., Ltd.] were employed without further purification.

Preparation of FAU zeolite from conventional route

NaAlO₂, NaOH, and water were mixed and then stirred for 30 min, followed by the addition of colloidal silica. After stirring for 2 h, the homogeneous gel with molar ratios of 4.5 SiO₂ : 1 Al₂O₃ : 1.80 Na₂O : 120 H₂O was obtained, then transferred into a Teflon-lined autoclave at 80 °C for 24 h.¹ The solid product was obtained by centrifugating, washing with deionized water, and drying overnight at 60 °C, which was designated as C-FAU. ICP-OES analysis displayed the Si/Al of C-FAU zeolite at about 1.53.

Solvent-free synthesis of FAU zeolite from coal fly ash

CFA was activated at high-temperature alkali fusion before solvent-free synthesis of FAU zeolite. As a typical run, CFA was mixed with NaOH powder at a mass ratio of 1:1.2 and then calcined at 800 °C for 2 h. After high temperature treatment, the obtained mixture was cooled to room temperature and then ground into a fine powder.

As a typical run for the solvent-free synthesis of FAU zeolite, 2.2 g fine powder, 2.2 g HCl, and 0.1 g C-FAU zeolite as seed were mixed, grinding for 10 min. After treatment at 80 °C for 24 h in an autoclave, the crystallization was complete. The solid product was obtained by filtrating, washing with deionized water, and drying overnight at 60 °C, which was designated as S-FAU. Notably, a substantial amount of NaCl would be generated with addition of HCl, but NaCl can be removed by filtrating and washing with deionized water after the crystallization.

Characterization

Structure and crystallinity of the samples were determined by X-ray diffraction (XRD) analysis conducted on a Rigaku Ultimate VI X-ray diffractometer (40 kV, 40 mA) using Cu_{Kα} (λ=1.5406 Å) radiation from 5 to 40°. Scanning electron microscopy (SEM) images were taken on Hitachi SU-1510 electron microscopes. Chemical composition of the CFA was analyzed by X-ray fluorescence (XRF) on a Bruker S8

TIGER instrument. Nitrogen adsorption-desorption isotherms were measured with a Micromeritics ASAP 2020M and a Tristar system at -196 °C. Solid-state ^{29}Si and ^{27}Al magic angle-spinning (MAS) NMR spectra were performed on a Bruker AVANCE III HD spectrometer. The solid sample composition was analyzed on inductively coupled plasma (ICP) with a Perkin-Elmer 3300DV emission spectrometer. The Fourier transform infrared (FT-IR) spectra were recorded by a FT-IR spectrophotometer (Nicolet iS10) using a KBr method.

Performance tests

CO₂ adsorption

CO₂ adsorption experiments were carried out using high-purity CO₂ (99.999%) at 0 °C over a pressure range of 0-101.325 KPa by Micromeritics Tristar II 3020 for C-FAU and S-FAU. Each sample was placed inside the balance and outgassed prior the experiment at 300 °C under vacuum condition for 12 h. Afterwards, the sample was cooled down to the experiment temperature while the gas pressure was increased stepwise until 101.325 KPa. The mass variation was recorded constantly for each pressure level until achieving the equilibrium condition.

Ion-exchange tests

Ca²⁺ exchange capacity (CEC) of C-FAU and S-FAU zeolites were carried out by stirring 0.0670 g of sample in 250 mL of Ca(NO₃)₂ aqueous solution (0.08 mol L⁻¹) at room temperature. After stirring for 15 min, the concentration of Ca²⁺ in the solution was measured by calcium ion selective electrode. The CEC was expressed in meq/g.

Mg²⁺ exchange capacity (MEC) of C-FAU and S-FAU zeolites were carried out by stirring 0.0670 g of sample in 250 mL of MgCl₂ aqueous solution (0.08 mol L⁻¹) at room temperature. After stirring for 15 min, the concentration of Mg²⁺ in the solution was analyzed by ICP-OES. The MEC were expressed in meq/g.

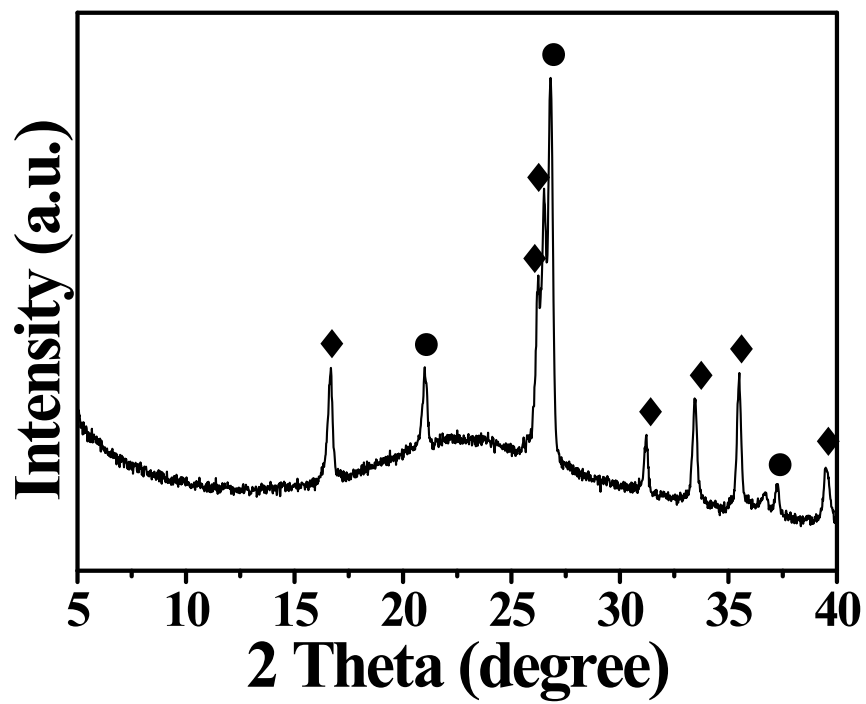


Figure S1. XRD pattern of coal fly ash (●: quartz, ◆: mullite.).

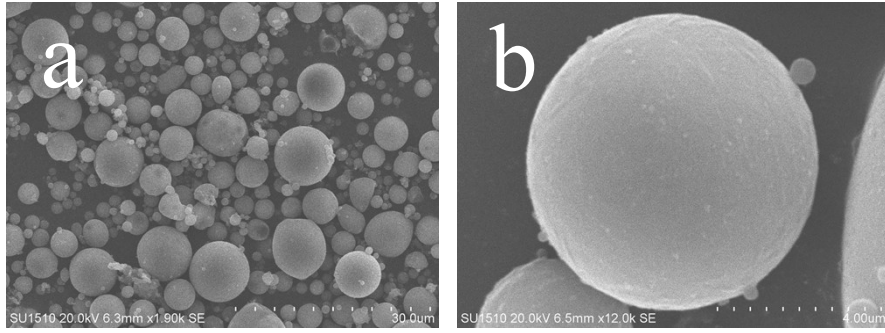


Figure S2. (a) and (b) SEM images of coal fly ash.

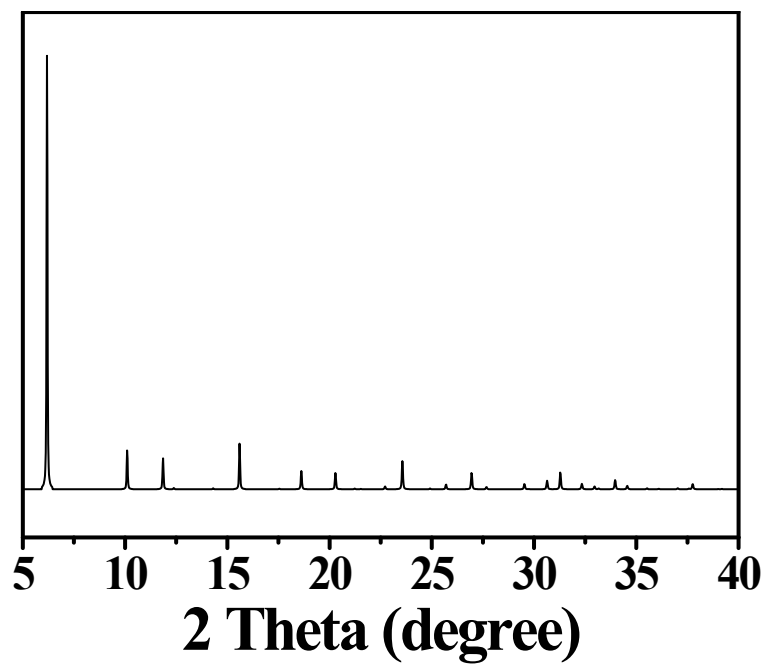


Figure S3. Simulated XRD pattern of FAU zeolite.

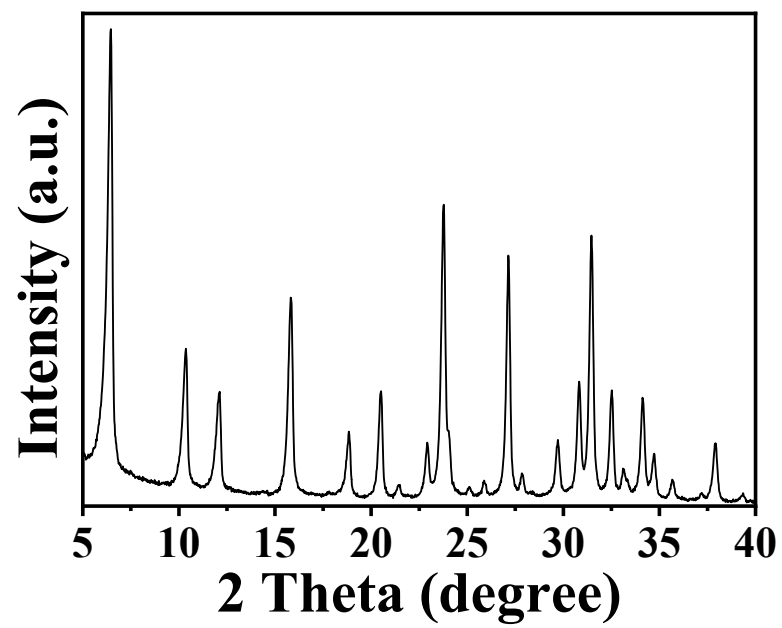


Figure S4. XRD pattern of C-FAU zeolite.

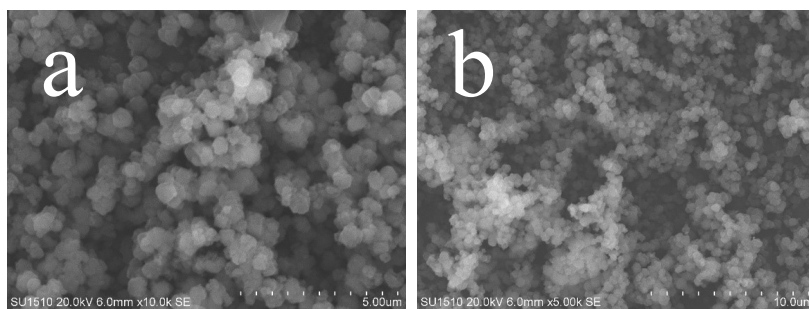


Figure S5. (a) and (b) SEM images of C-FAU zeolite.

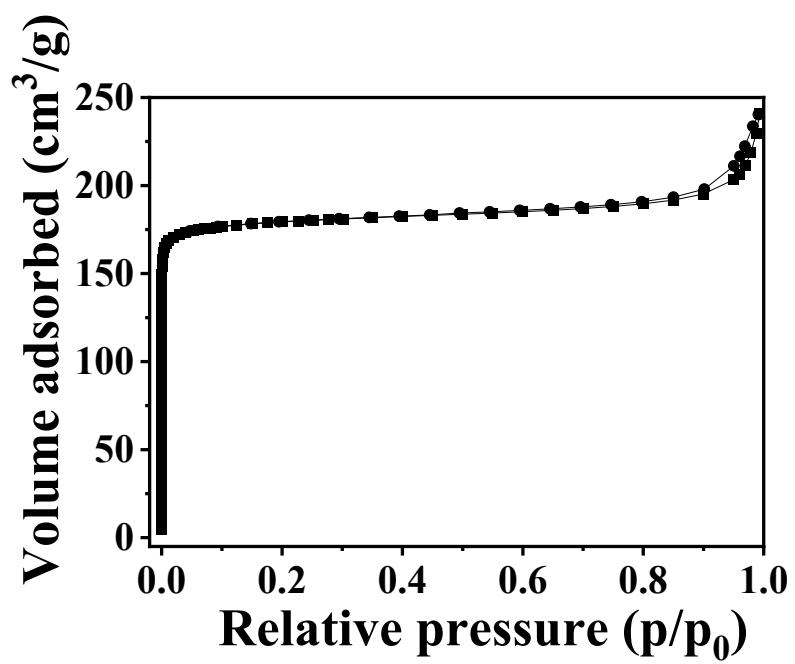


Figure S6. N₂ sorption isotherms of C-FAU zeolite.

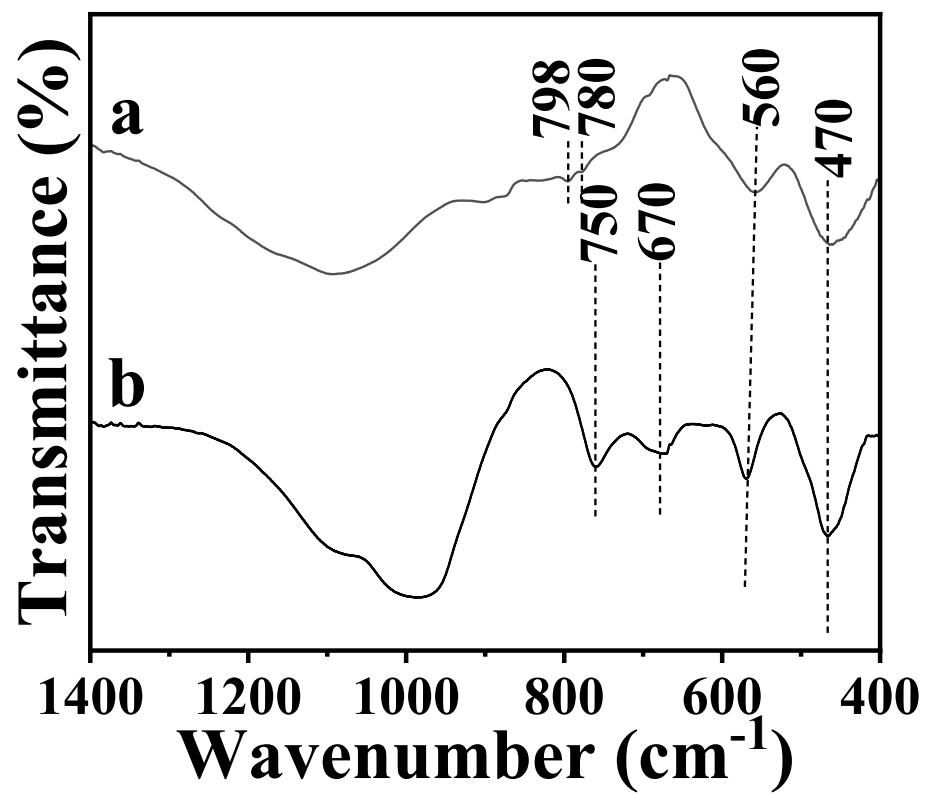


Figure S7. FT-IR spectra of (a) CFA and (b) S-FAU zeolite.

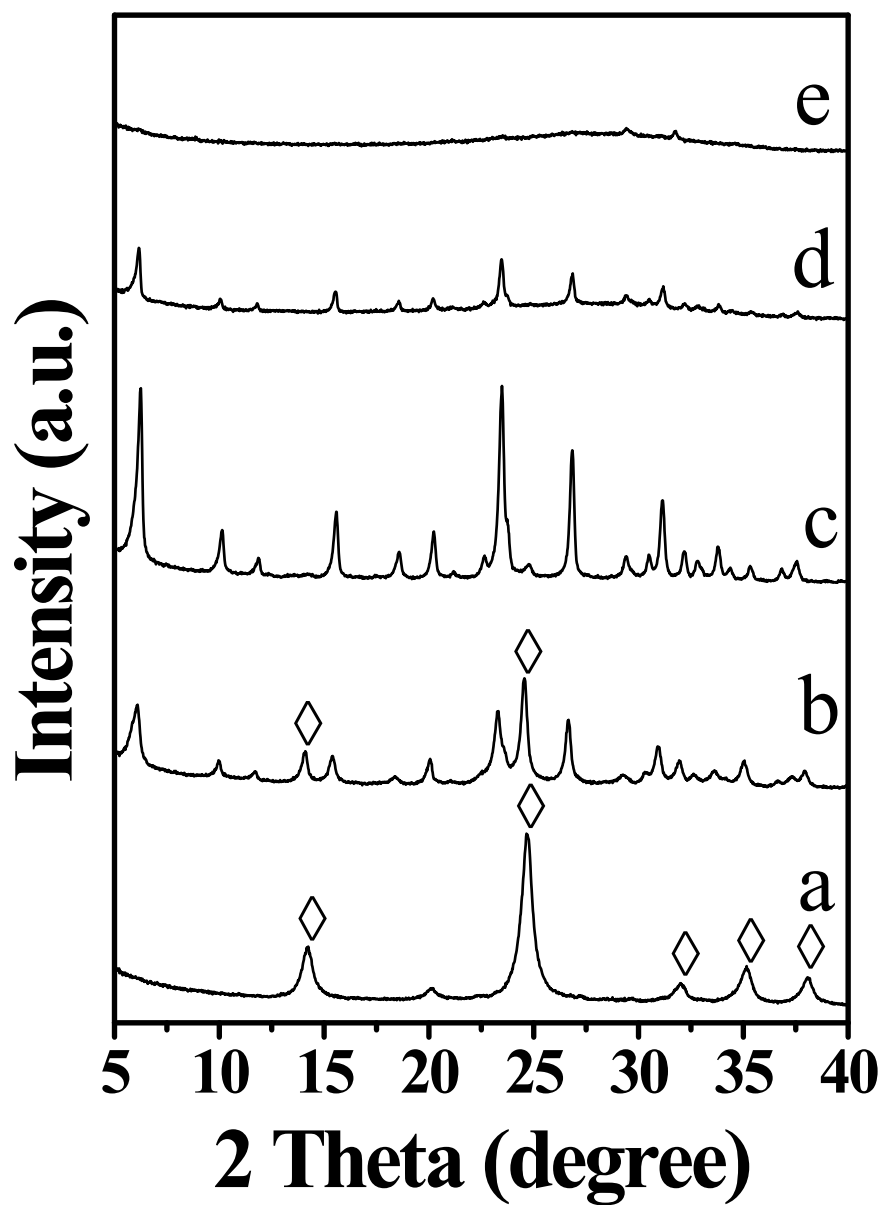


Figure S8. XRD patterns of the samples synthesized with HCl/SiO₂ ratio of (a) 2.16, (b) 2.40, (c) 2.64, (d) 2.88, and (e) 3.12, respectively (\diamond : SOD zeolite).

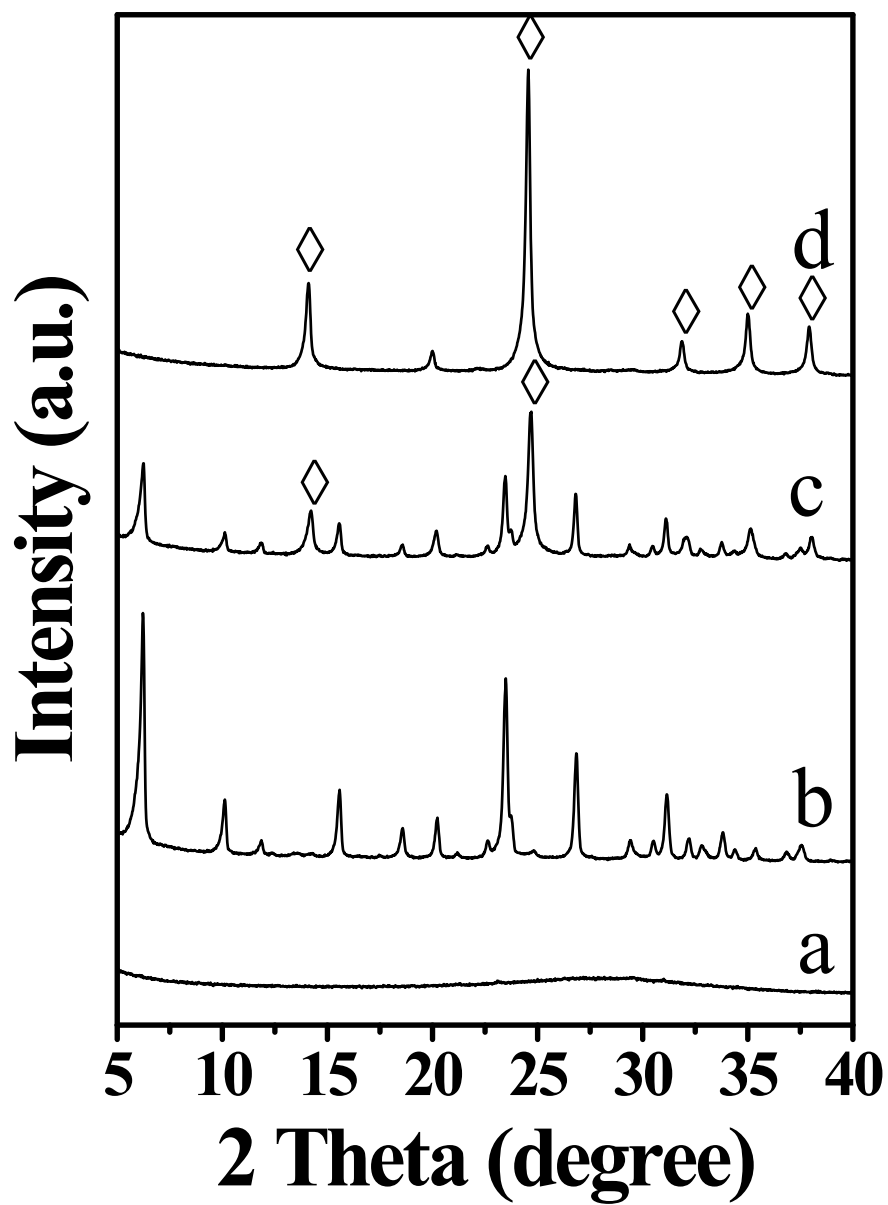


Figure S9. XRD patterns of the samples synthesized with crystallization temperature of (a) 60 °C, (b) 80 °C, (c) 100 °C, and (d) 120 °C, respectively (\diamond : SOD zeolite).

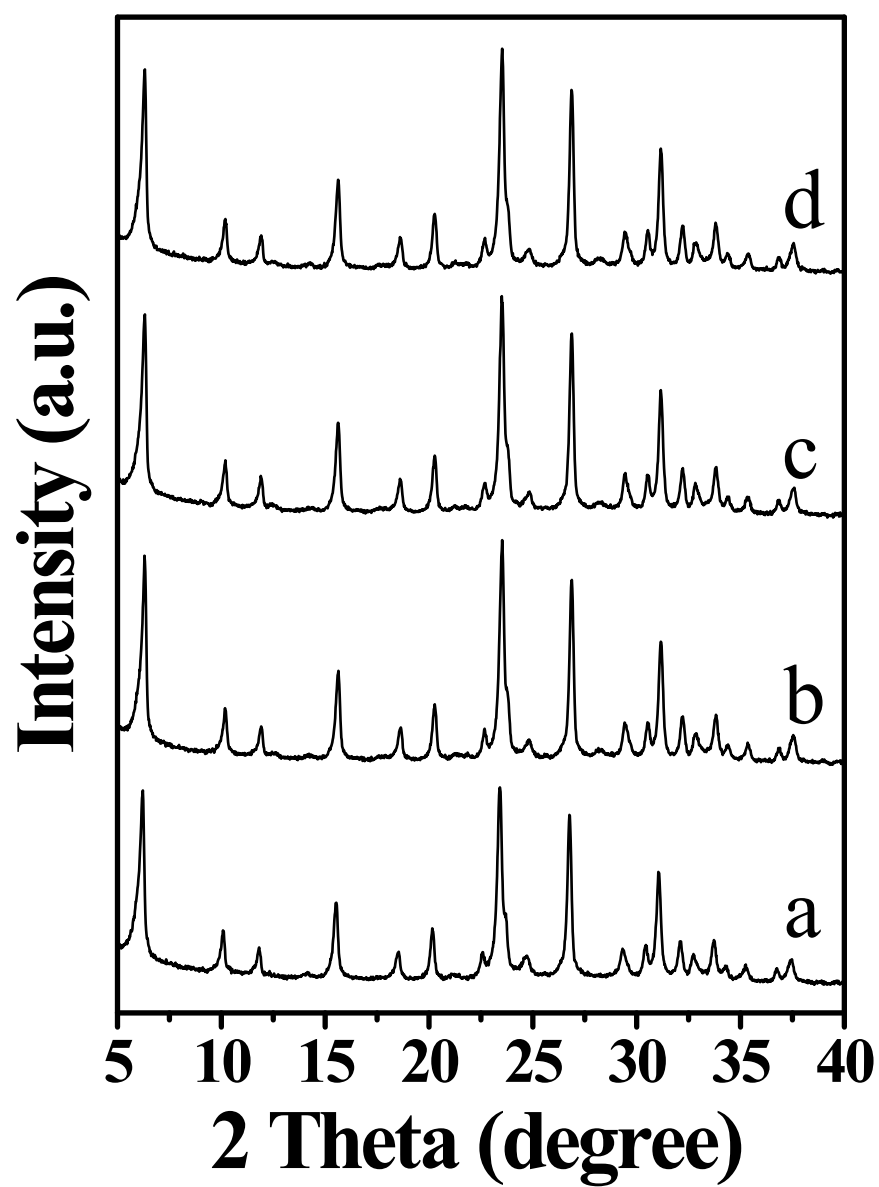


Figure S10. XRD patterns of the samples synthesized with the seed content of (a) 0 %, (b) 5 %, (c) 10 %, and (d) 20 %, respectively.

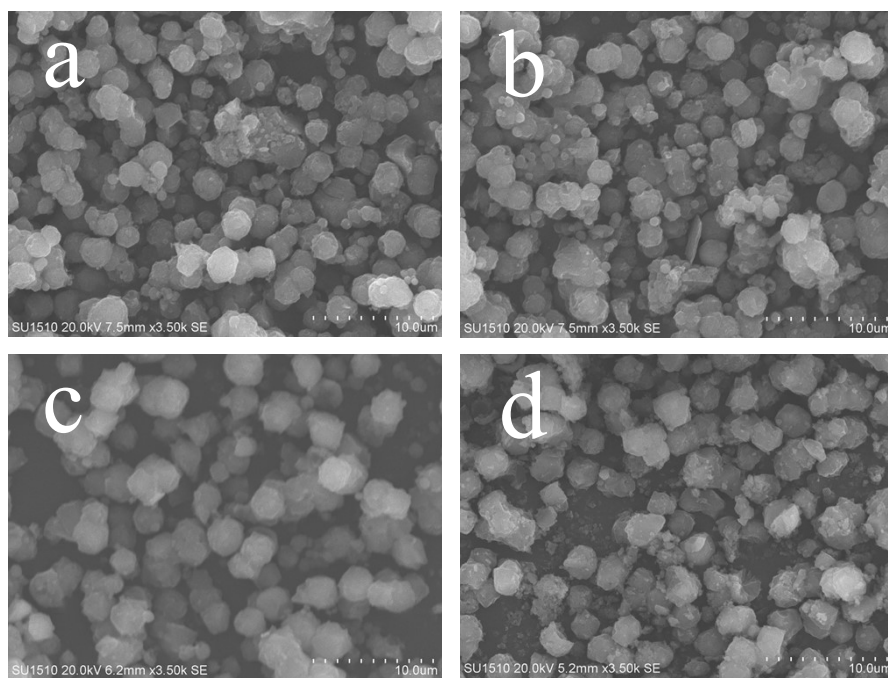


Figure S11. SEM images of the samples synthesized with the seed content of (a) 0 %, (b) 5 %, (c) 10 %, and (d) 20 %, respectively.

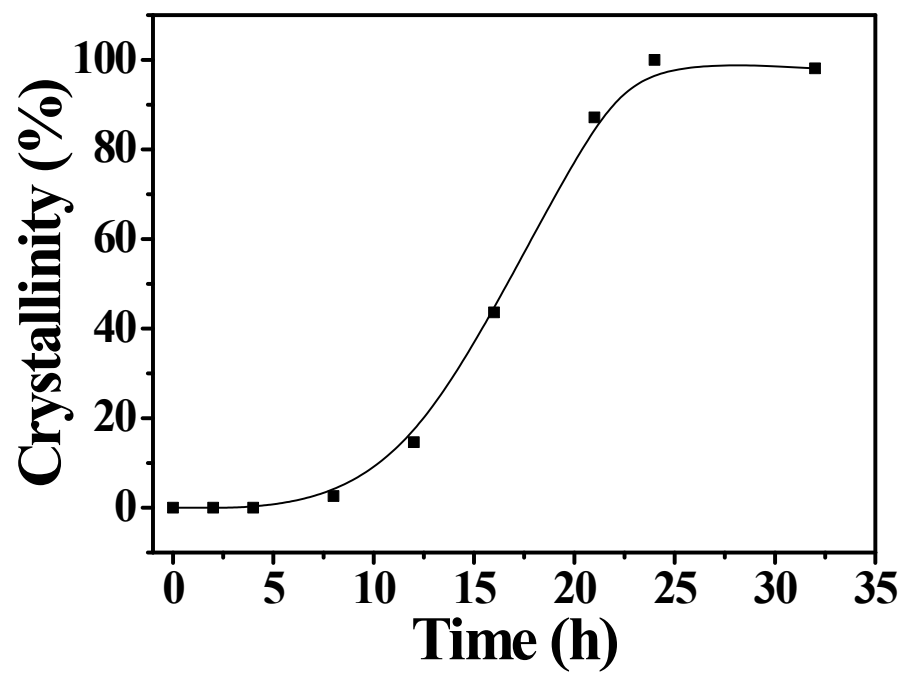


Figure S12. Dependence of the S-FAU zeolite crystallinity on crystallization time.

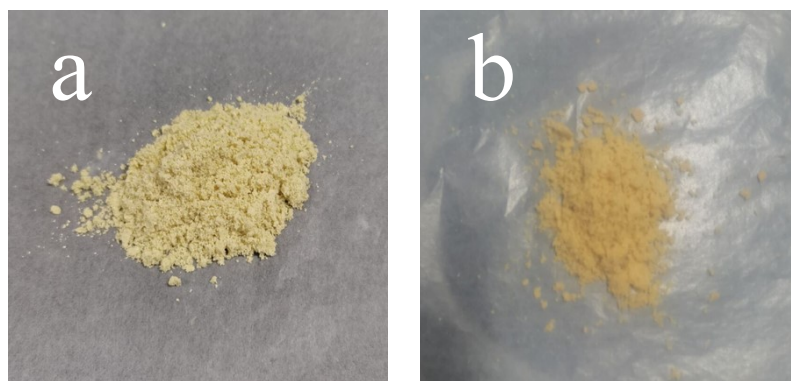
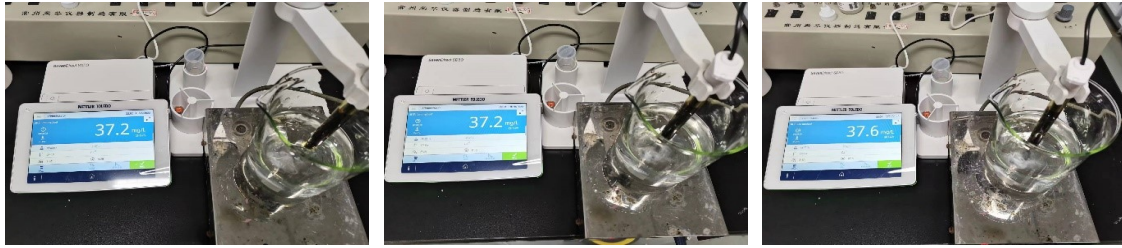
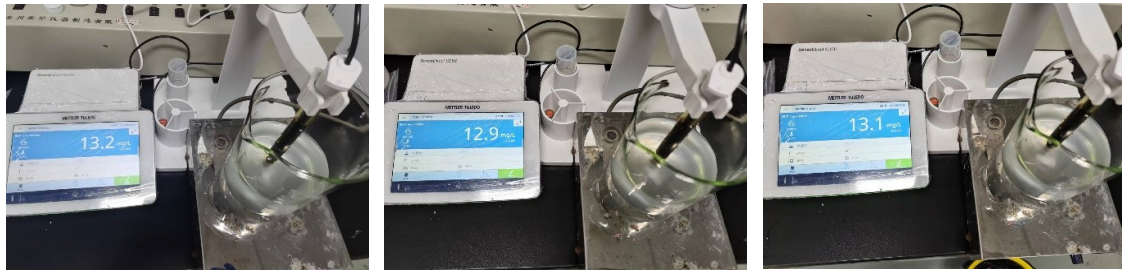


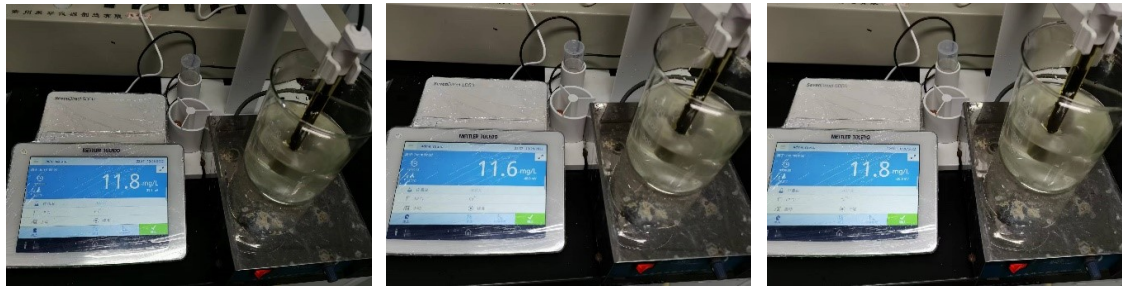
Figure S13. The photographs of (a) the starting mixtures before crystallization and (b) the product after crystallization.



(a) the concentration of Ca²⁺ solution before ion exchange.



(b) the concentration of Ca²⁺ solution after ion exchange with C-FAU zeolite.



(c) the concentration of Ca²⁺ solution after ion exchange with S-FAU zeolite.

Figure S14. Tests of Ca²⁺ concentration in the solution by calcium ion selective electrode.

Mean Data: Sample062							
Analyte	Mean Corrected Intensity	Calib. Conc. Units	Std.Dev.	Sample Conc. Units	Std.Dev.	RSD	
Mg 285.213	4524524.7	26.60 mg/L	0.265	26.60 mg/L	0.265	1.00%	

Mean Data: Sample063							
Analyte	Mean Corrected Intensity	Calib. Conc. Units	Std.Dev.	Sample Conc. Units	Std.Dev.	RSD	
Mg 285.213	4505226.0	26.49 mg/L	0.108	26.49 mg/L	0.108	0.41%	

Mean Data: Sample003							
Analyte	Mean Corrected Intensity	Calib. Conc. Units	Std.Dev.	Sample Conc. Units	Std.Dev.	RSD	
Mg 285.213	4102268.2	26.36 mg/L	0.352	26.36 mg/L	0.352	1.34%	

(a) the concentration of Mg^{2+} solution before ion exchange.

Mean Data: Sample050							
Analyte	Mean Corrected Intensity	Calib. Conc. Units	Std.Dev.	Sample Conc. Units	Std.Dev.	RSD	
Mg 285.213	448427.8	10.96 mg/L	0.560	10.96 mg/L	0.560	5.11%	

Mean Data: Sample050							
Analyte	Mean Corrected Intensity	Calib. Conc. Units	Std.Dev.	Sample Conc. Units	Std.Dev.	RSD	
Mg 285.213	2427765.8	13.48 mg/L	0.618	13.48 mg/L	0.618	4.59%	

Mean Data: Sample049							
Analyte	Mean Corrected Intensity	Calib. Conc. Units	Std.Dev.	Sample Conc. Units	Std.Dev.	RSD	
Mg 285.213	460664.3	11.26 mg/L	0.035	11.26 mg/L	0.035	0.31%	

(b) the concentration of Mg^{2+} solution after ion exchange with C-FAU zeolite.

Mean Data: Sample046							
Analyte	Mean Corrected Intensity	Calib. Conc. Units	Std.Dev.	Sample Conc. Units	Std.Dev.	RSD	
Mg 285.213	497310.1	12.15 mg/L	0.244	12.15 mg/L	0.244	2.01%	

Mean Data: Sample051							
Analyte	Mean Corrected Intensity	Calib. Conc. Units	Std.Dev.	Sample Conc. Units	Std.Dev.	RSD	
Mg 285.213	412626.0	10.08 mg/L	0.160	10.08 mg/L	0.160	1.59%	

Mean Data: Sample047							
Analyte	Mean Corrected Intensity	Calib. Conc. Units	Std.Dev.	Sample Conc. Units	Std.Dev.	RSD	
Mg 285.213	464172.2	11.34 mg/L	0.180	11.34 mg/L	0.180	1.59%	

(c) the concentration of Mg^{2+} solution after ion exchange with S-FAU zeolite.

Figure S15. Tests of Mg^{2+} concentration in the solution by ICP-OES.

Reference

1. Q. Wang, Q. Zhang, H. Yu, *Chinese J. Chem.*, 2020, 41(04), 616-622.