Supplementary material

Eco-friendly synthesis of zeolite A from synthesis cakes prepared by removing the liquid phase of aged synthesis mixtures

Soon Hee Park, Jae-Kyung Yang, Jong-Ho Kim, Chang-Bock Chung and Gon Seo*

School of Applied Chemical Engineering and the Research Institute for Catalysis, Chonnam National University, 77 Yongbong-Ro, Buk-Gu, Gwangju 500-757, Republic of Korea

*To whom correspondence should be addressed

Tel: +82-62-530-1876

Fax: +82-62-530-1899

E-mail: gseo@chonnam.ac.kr.

Experimental

Preparation of synthesis mixture and cake

Sodium silicate (Daejung, 30 wt% SiO_2), sodium aluminate (Junsei, 56 wt%), and sodium hydroxide (Daejung, 98%) were dissolved in distilled water in order to prepare a synthesis mixture with composition of 1.0 Al_2O_3 : 1.9 SiO_2 : 3.2 Na_2O : 125 H_2O according to a verified synthesis of zeolite A.[14] The synthesis mixture was stirred with a mechanical stirrer at 250 rpm and 15 ^oC for 24 h. The liquid phase of the synthesis mixture was partially removed by simple filtering with filter paper (Whatman filter papers No. 1) to obtain a synthesis cake. The synthesis mixture and cake were named SM-SF and SC-SF, respectively, with SF standing for simple filtering. A filter press (Hwaseng) was used in the preparation of a synthesis cake named SC-FF under forced filtering, with FF standing for forced filtering. The water contents of SC-SF and SC-FF were determined by using a moisture analyzer (Precisa Gravimetrics AG Dietikon, CXM50).

Hydrothermal reaction of synthesis mixture and cake

For the hydrothermal reaction, 20 g of the synthesis mixture of zeolite A was charged in a 45 mL autoclave (Parr Teflon-lined stainless steel bomb) and placed in an oven controlled at a preset synthesis temperature. After hydrothermal reaction for a given time, the autoclave was removed and immediately cooled with tap water. The solid phase contained in the autoclave was collected by filtering, followed by washing with deionized water until the filtrate pH reached 10. The solid phase was put in an oven controlled at 100 ^oC and dried for 12 h. The hydrothermal reaction of the synthesis cake was also performed following the same procedure, except that 10 g of the synthesis

cake was charged in a 23 mL autoclave to obtain similar amounts of zeolite A from both synthesis mixture and cake. Ten autoclaves were used in each synthesis run to determine the variation of the zeolite content with reaction time.

Characterization of zeolite A

The XRD patterns of the solid phases collected in the crystallization of zeolite A from the synthesis mixtures and cakes were recorded on a high resolution X-ray diffractometer (HR-XRD, PANalytical, X'Pert Pro Multi Purpose) using a Cu-Kα X-ray filtered with a nickel filter under 40 kV and 20 mA. The crystallinity of zeolite A was calculated from the sum of the heights of the peaks observed at $2\theta = 7.2^{o}$, 10.2^{o}, 24.0^{o}, 27.1^{o}, and 29.9° attributed to zeolite A.[17] The sum of the peak heights of the solid phase was divided by that of a standard zeolite A sample that was synthesized for a sufficient time and composed of perfect cubic crystals of 1 μm without any appreciable impurity in its XRD pattern and SEM image. ^{29}Si magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectra of silicon atoms in the framework of zeolite A were recorded on an NMR spectrometer (Varian, Unity Solid Inova WB 200MHz system) at a resonance frequency of 39.79 MHz after a π/2 single-pulse excitation for 2 μs. The spinning rate of sample was 5 kHz. The shape and size of zeolite A were examined using scanning electron microscope (SEM, Shimadzu SS-550). The average particle size of zeolite A was determined from the measured sizes of more than 100 zeolite particles. The chemical compositions of the synthesis mixtures, cakes, and filtrates were analyzed using an induced coupled plasma-atomic emission spectrometer (ICP-AES, Perkin-Elmer, OPTIMA 8300). Adsorption isotherms of nitrogen and carbon dioxide were obtained using an automatic volumetric adsorption system (Mirae SI, NanoPorosity-XQ). The samples were evacuated at 200 ^{o}C for 5 h prior to the exposure to adsorption gas, and the adsorption temperatures for nitrogen and carbon dioxide were set at 77 K and 273 K, respectively.

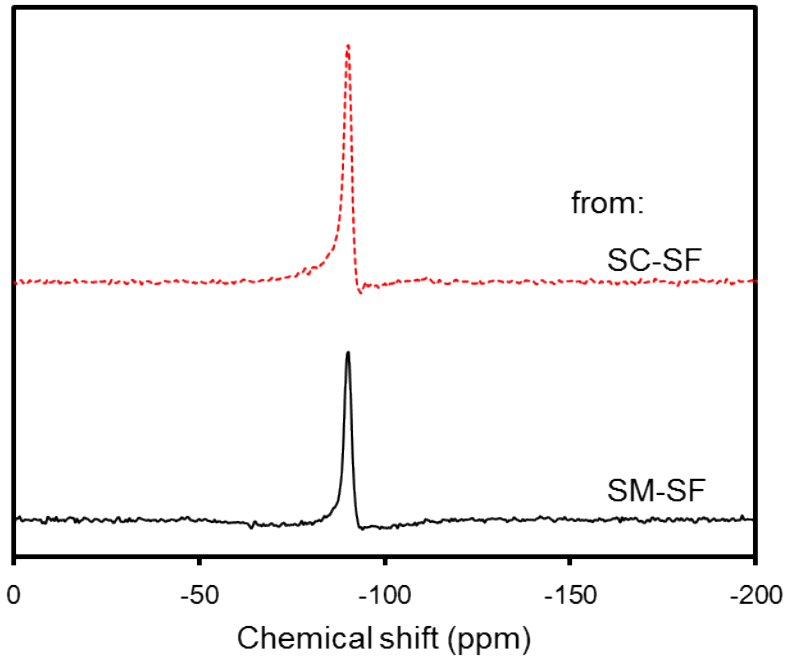


Fig. S1. ^{29}Si MAS NMR spectra of zeolite A synthesized from SM-SF (solid line) and SC-SF (dotted line) at 70 °C for 5 h.

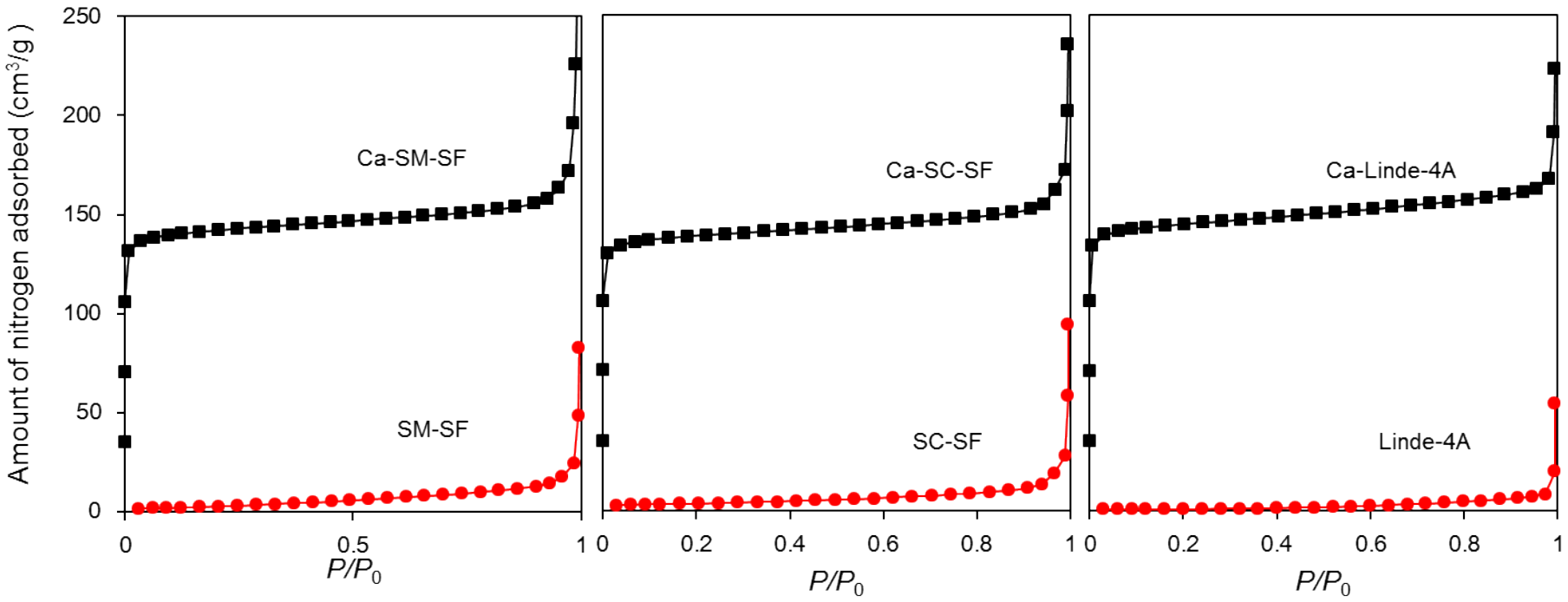


Fig. S2. Adsorption isotherms of nitrogen on LTA zeolites (A) SM-SF, (B) SC-SF, and (C) Linde-4A at 77 K. Calcium ion-exchanged LTA zeolites were denoted by adding "Ca" in front of their names.

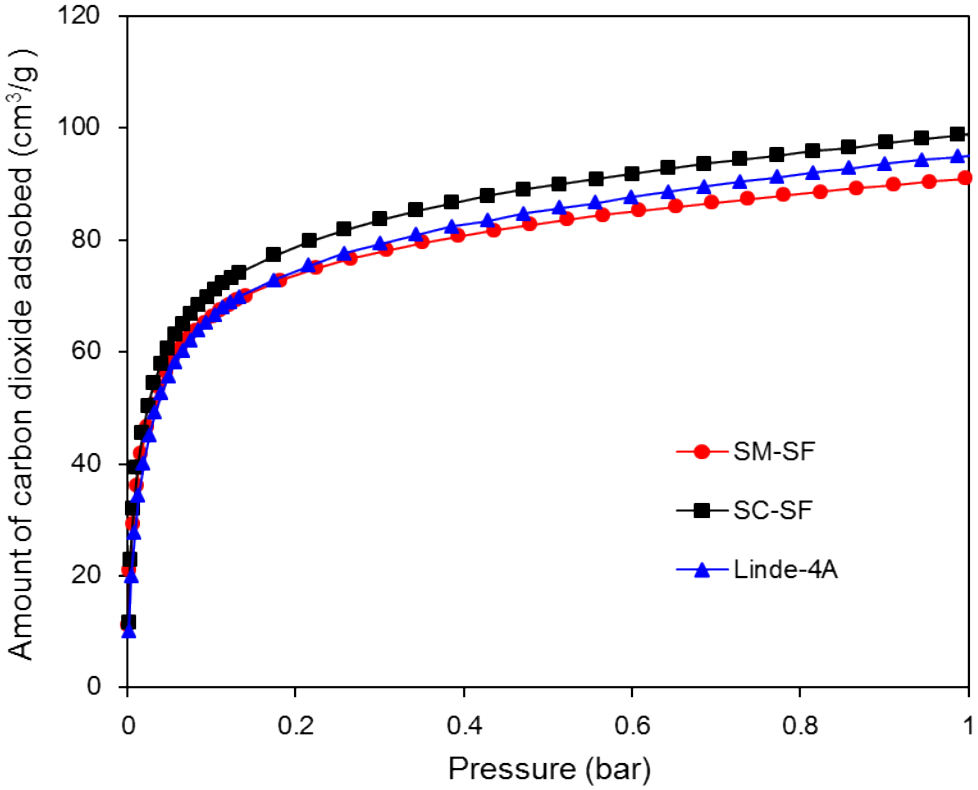


Fig. S3. Adsorption isotherms of carbon dioxide on LTA zeolites at 273 K.

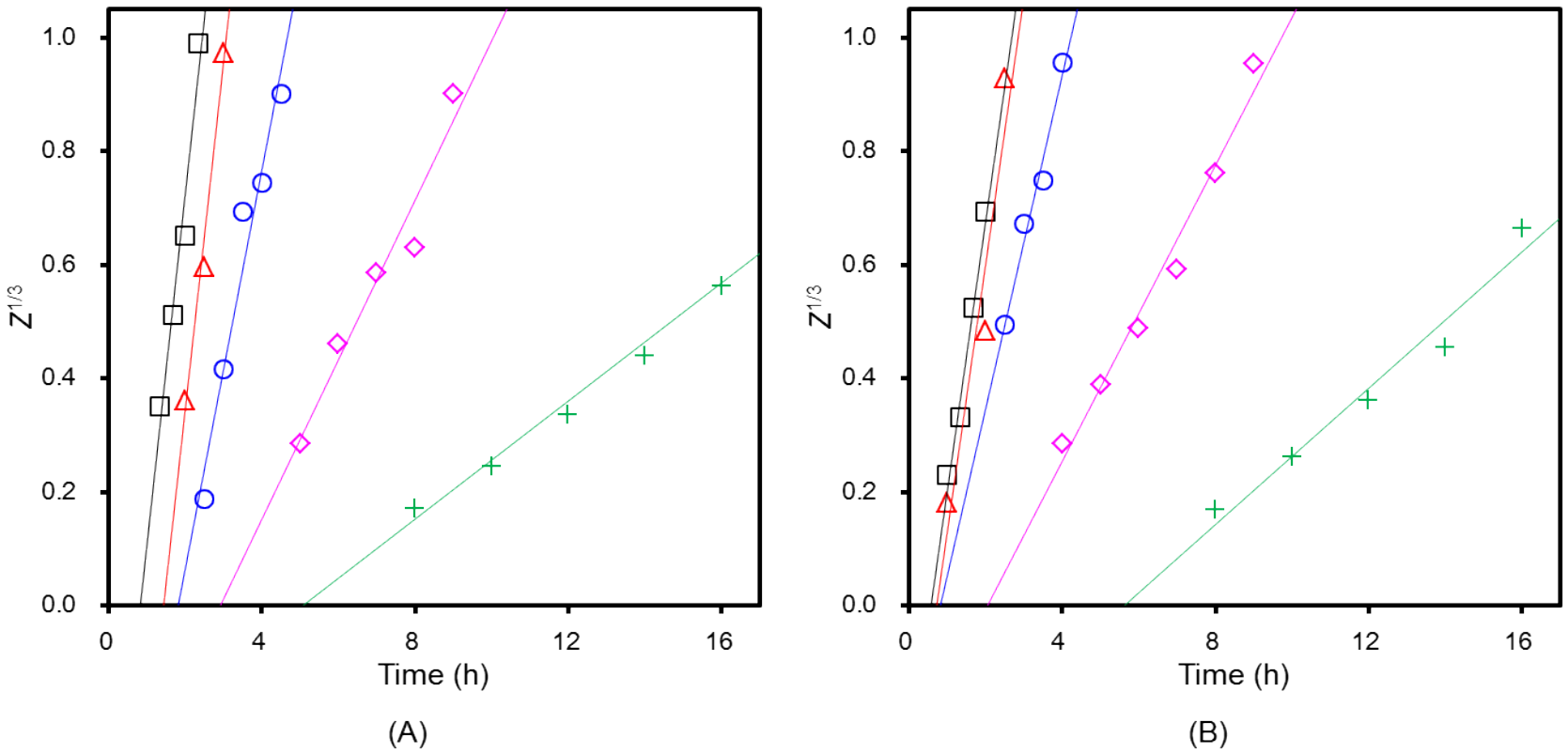


Fig. S4. Plot of $Z^{1/3}$ vs time in the crystallization of zeolite A from (A) SM-SF and (B) SC-SF at different temperatures: (+) 50 °C, (◇) 60 °C, (○) 70 °C, (Δ) 80 °C and (□) 90 °C.

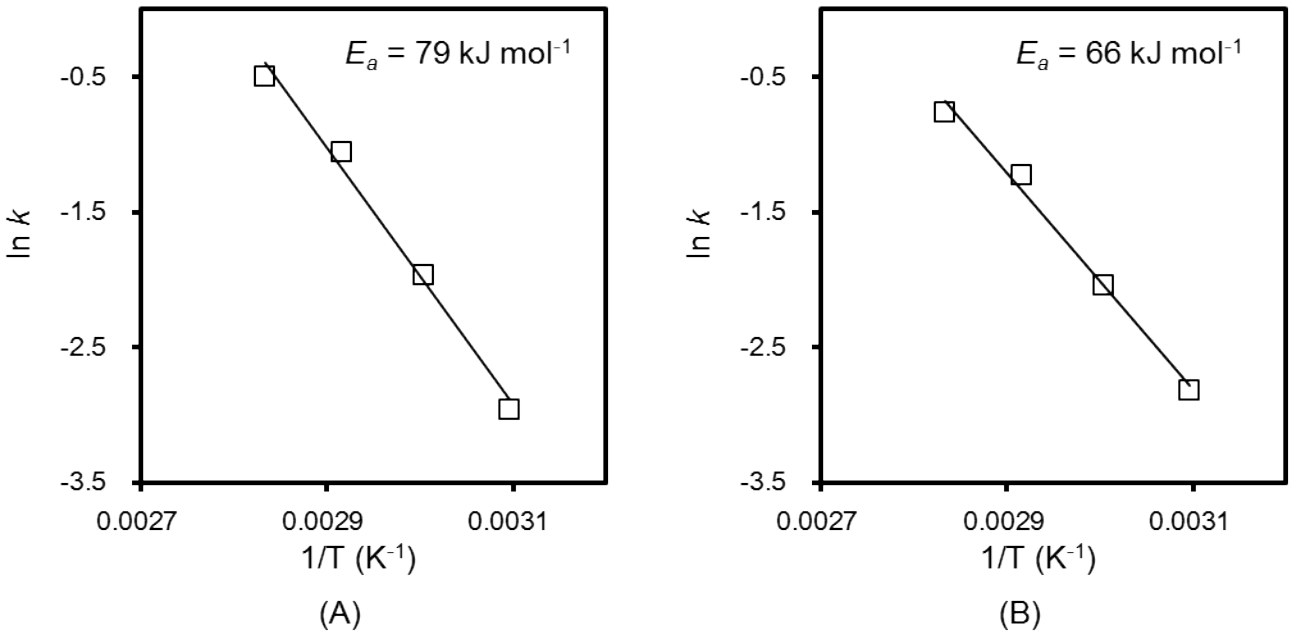
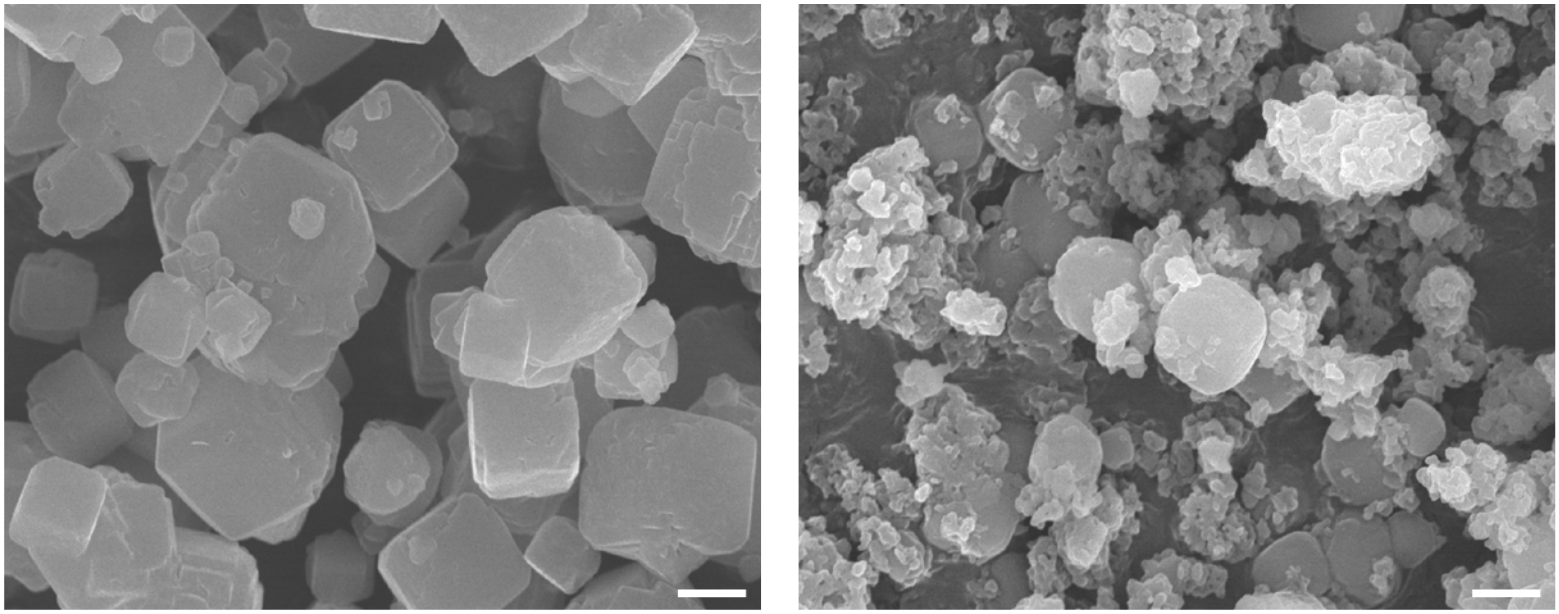


Fig. S5. Arrhenius plots for the crystallization of zeolite A from (A) SM-SF and (B) SC-SF.



(A) (B)

Fig. S6. SEM photos of zeolite A from (A) SM-HC and (B) SC-HC through hydrothermal reaction at 70 °C for 6 h. The inserted scale bars represent 1.0 μm.

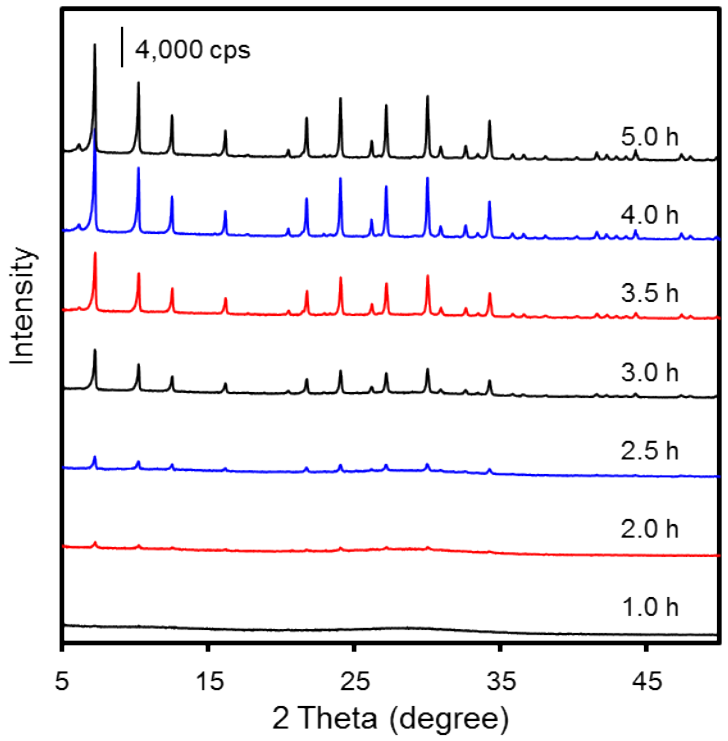


Fig. S7. XRD patterns of solid phases obtained in the crystallization of zeolite A from SC-FF1 at 70 ºC