Electronic Supplementary Information

Organotemplate-Free Synthesis of Al-Rich ZSM-35 and ZSM-22 Zeolites with Addition of ZSM-57 Zeolite Seeds

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Characterization

X-ray diffraction (XRD) data of the samples were collected with a Rigaku Ultimate VI X-ray diffractometer (40 kV, 40 mA) using $CuK_{\alpha 1}$ radiation (λ=1.5406 Å) using a flat plate sample holder. Scanning electron microscopy (SEM) images of the samples were performed on Hitachi SU-1510 electron microscope and Hitachi S-4800 field emission scanning electron microscope. N_2 sorption experiments of the samples were performed on a BELSORP-max and Tristar system. The pore volume and surface area were calculated from using the t-plot and BET methods. The compositions of the samples were determined by Perkin-Elmer 3300DV inductively coupled plasma optical emission spectrometer (ICP-OES). Solid-state NMR spectra of the samples were recorded on a Varian Inifity Plus 400 spectrometer. The acidity of the samples was measured by MicroActive for AutoChem II 2920 Version NH_3-temperature-programmed desorption (NH_3-TPD). 100 mg of the sample (40-80 mesh) was placed into a quartz tube and pretreated in He flow at 500 °C for 30 min, and the temperature was reduced to 100 °C for the adsorption of NH_3 in 10% NH_3/He gas mixture flow (30–50 mL/min) about 1 h. After saturation, the catalyst was purged by He gas flow (30–50 mL/min) for 1 h to remove the physically adsorbed NH_3 on the surface. Finally, the signal of NH_3 desorption was monitored by the thermal conductivity detector (TCD) in He flow at a heating rate of 10 °C/min from 100 to 600 °C.

Catalytic tests

Catalytic reaction of *n*-dodecane hydroisomerization was carried out in a continuously flowing fixed-bed reactor installed with a stainless-steel tube. The reaction pressure was 45 bar, the H_2/*n*-dodecane molar ratio was 15, and the weight hourly space velocity (WHSV) was 1.5 h^{-1}, and the reaction temperature was controlled from 260 °C to 320 °C. Prior to the test, a quantity of 1.5 g of each catalyst was pressed, crushed, and sifted with 20–40 mesh followed by mixing with quartz sand (20–50 mesh) to a constant volume of 5.0 mL before loading into the isothermal zone of the reactor tube. The catalyst was then reduced for 4 h at atmospheric pressure with a

heating rate of 5 °C/min and a H_2 flow rate of 80 mL/min at the temperature of 400 °C. The liquid products were detected using a gas chromatograph (Agilent 7820A) equipped with a flame ionization detector (FID) with a DB-1HT capillary column (30 m × 0.25 mm × 0.1 μm). The component distributions of the obtained product were analyzed on a gas chromatograph-mass spectrometer (Thermo Scientific ISQ 7000). The *n*-dodecane conversion, *iso*-dodecane selectivity and isomer yield were calculated as follows:

$$conversion\ (\%) = \frac{n-dodecane\ consumption}{n-dodecane\ feed} \times 100$$

$$isomerization\ selectivity\ (\%) = \frac{iso-dodecane\ formed}{n-dodecane\ consumption} \times 100$$

$$isomer\ yield\ (\%) = \frac{iso-dodecane\ formed}{n-dodecane\ feed} \times 100$$

Quantitative Calculation

1. Calculation formula of yield of the target zeolite product

$$Yield\ (\%) = \frac{m_{product}}{m_{Al_2O_3} + m_{SiO_2} + m_{seeds}} \times 100$$

2. The crystallinity of Al-rich S-ZSM-35 is based on its peak intensity at 25.19° and 25.64° in XRD pattern, and fully crystallized Al-rich S-ZSM-35 synthesized at 160 °C for 12 h is designated as 100% crystallinity; The crystallinity of Al-rich S-ZSM-22 is based on its peak intensity at 20.35° and 24.26° in XRD pattern, and fully crystallized Al-rich S-ZSM-22 synthesized at 160 °C for 15 h is designated as 100% crystallinity.

Supporting Figure Captions

Figure S1 (a) XRD pattern and (b) SEM image of the ZSM-57 zeolite seeds.

Figure S2 (a) XRD pattern, (b) SEM image and (c) ^{27}Al MAS NMR spectrum of the H-S-ZSM-35 zeolite.

Figure S3 The dependence of S-ZSM-35 crystallinity on the crystallization time.

Figure S4 XRD patterns of the products synthesized from the starting mixture with the molar ratio of 1.0 SiO_2: 0.03 Al_2O_3: 0.34 Na_2O: 35 H_2O by adding different mass of ZSM-57 zeolite seeds at 160 °C for 12 h. The mass ratios of zeolite seeds to silica source were (a) 0%, (b) 1%, (c) 3%, (d) 5%, (e) 7% and (f) 11%, respectively.

Figure S5 XRD patterns of the products synthesized from the starting mixture with the molar ratio of 1.0 SiO_2: 0.03 Al_2O_3: 0.27–0.42 Na_2O: 35 H_2O with addition of ZSM-57 zeolite seeds (5%) at 160 °C for 12 h. Na_2O/SiO_2 ratios were (a) 0.27, (b) 0.31, (c) 0.34, (d) 0.38, and (e) 0.42, respectively.

Figure S6 XRD patterns of the products synthesized from the starting mixture with the molar ratio of 1.0 SiO_2: 0.1–0.005 Al_2O_3: 0.34 Na_2O: 35 H_2O with addition of ZSM-57 zeolite seeds (5%) at 160 °C for 12 h. SiO_2/Al_2O_3 ratios were (a) 10, (b) 20, (c) 32, (d) 65 and (e) 200, respectively.

Figure S7 XRD patterns of the products synthesized from the starting mixture with the molar ratio of 1.0 SiO_2: 0.03 Al_2O_3: 0.34 Na_2O: 15–55 H_2O with addition of ZSM-57 zeolite seeds (5%) at 160 °C for 12 h. H_2O/SiO_2 ratios were (a) 15, (b) 25, (c) 35, (d) 45, and (e) 55, respectively.

Figure S8 XRD patterns of products synthesized from the starting mixture with the molar ratio of 1.0 SiO_2: 0.03 Al_2O_3: 0.34 Na_2O: 35 H_2O with addition of ZSM-57 zeolite seeds (5%) at different temperatures for 12 h. The crystallization temperatures were (a) 140 °C, (b) 160 °C, and (c) 180 °C, respectively.

Figure S9 (a) XRD pattern, (b) SEM image and (c) ^{27}Al MAS NMR spectrum of the H-S-ZSM-22 zeolite.

Figure S10 The dependence of S-ZSM-22 crystallinity on the crystallization time.

Figure S11 XRD patterns of the products synthesized from the starting mixture with the molar ratio of 1.0 SiO_2: 0.0025 Al_2O_3: 0.27 Na_2O: 35 H_2O by adding different mass of ZSM-57 zeolite seeds at 160 °C for 15 h. The mass ratios of zeolite seeds to the silica source were (a) 0%, (b) 1%, (c) 3%, (d) 5%, (e) 7% and (f) 11%, respectively.

Figure S12 XRD patterns of the products synthesized from the starting mixture with the molar ratio of 1.0 SiO_2: 0.0025 Al_2O_3: 0.19–0.34 Na_2O: 35 H_2O with addition of ZSM-57 zeolite seeds (5%) at 160 °C for 15 h. Na_2O/SiO_2 ratios were (a) 0.19, (b) 0.23, (c) 0.27, (d) 0.31, and (e) 0.34, respectively.

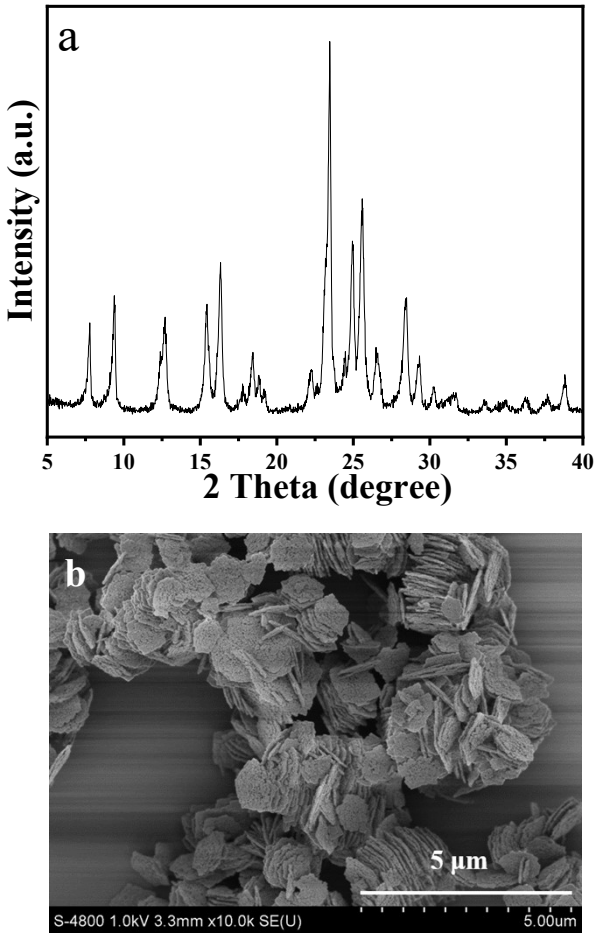
Figure S13 XRD patterns of the products synthesized from the starting mixture with the molar ratio of 1.0 SiO_2: 0.03–0.0017 Al_2O_3: 0.27 Na_2O: 35 H_2O with addition of ZSM-57 zeolite seeds (5%) at 160 °C for 15 h. SiO_2/Al_2O_3 ratios were (a) 32, (b) 200, (c) 400, (d) 500, and (d) 600, respectively.

Figure S14 XRD patterns of the products synthesized from the starting mixture with the molar ratio of 1.0 SiO_2: 0.0025 Al_2O_3: 0.27 Na_2O: 15–55 H_2O with addition of ZSM-57 zeolite seeds (5%) at 160 °C for 15 h. H_2O/SiO_2 ratios were (a) 15, (b) 25, (c) 35, (d) 40, and (e) 55, respectively.

Figure S15 XRD patterns of the products synthesized from the starting mixture with the molar ratio of 1.0 SiO_2: 0.0025 Al_2O_3: 0.27 Na_2O: 35 H_2O with addition of ZSM-57 zeolite seeds (5%) zeolite crystals at different temperatures for 15 h. The crystallization temperatures were (a) 140 °C, (b) 160 °C, and (c) 180 °C, respectively.

Figure S16 NH_3-TPD curves of the (a) H-S-ZSM-22 and (b) H-C-ZSM-22.

Figure S17 (a) XRD pattern and (b) SEM image of the conventional ZSM-22 zeolite.



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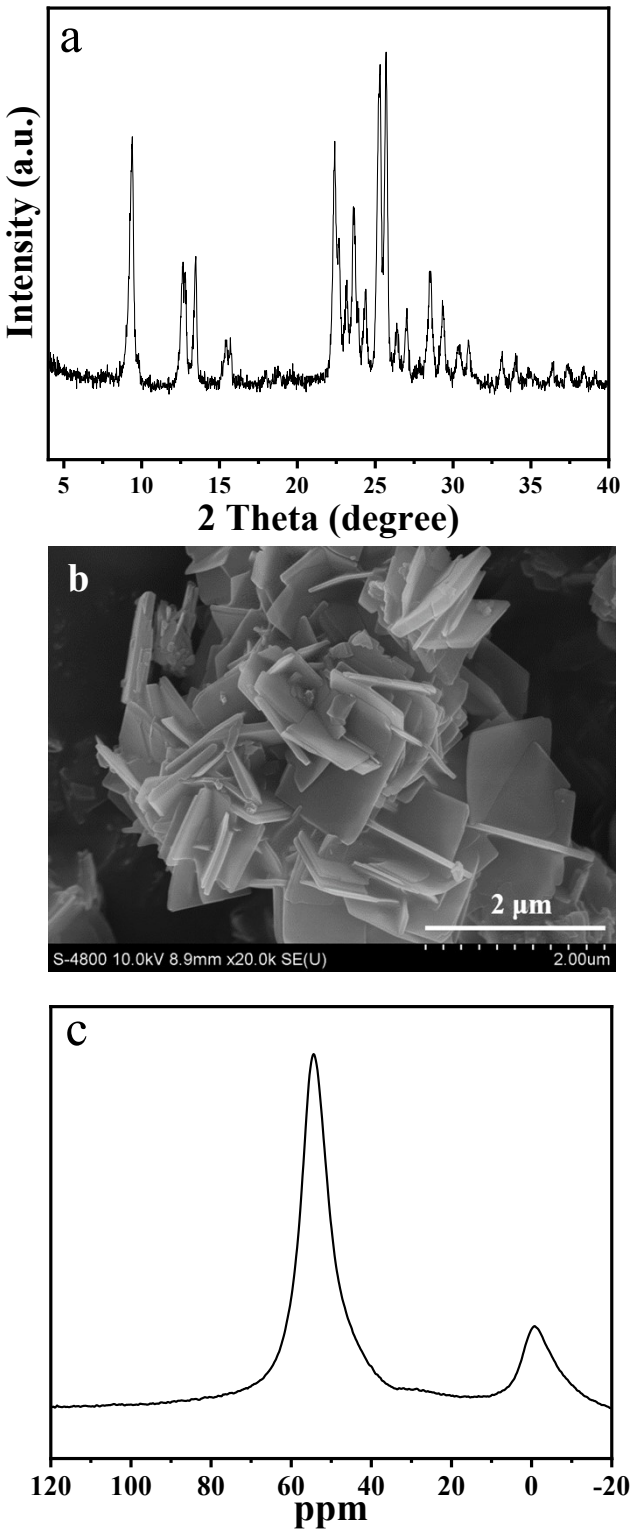
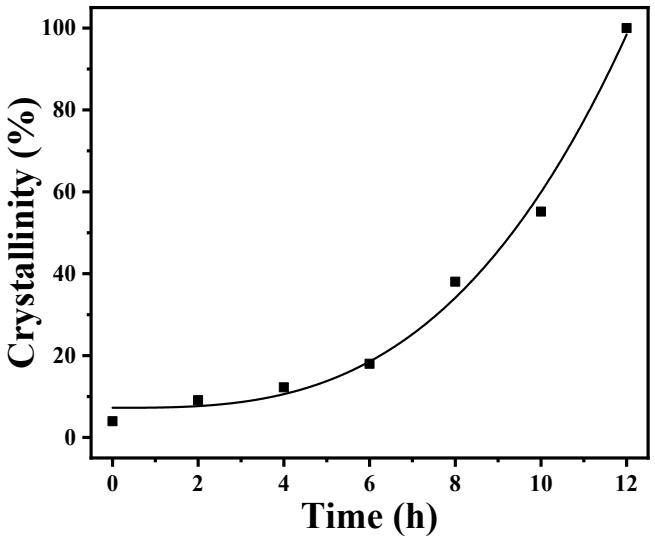


Figure S2 (a) XRD pattern, (b) SEM image and (c) ^{27}Al MAS NMR spectrum of the H-S-ZSM-35 zeolite.



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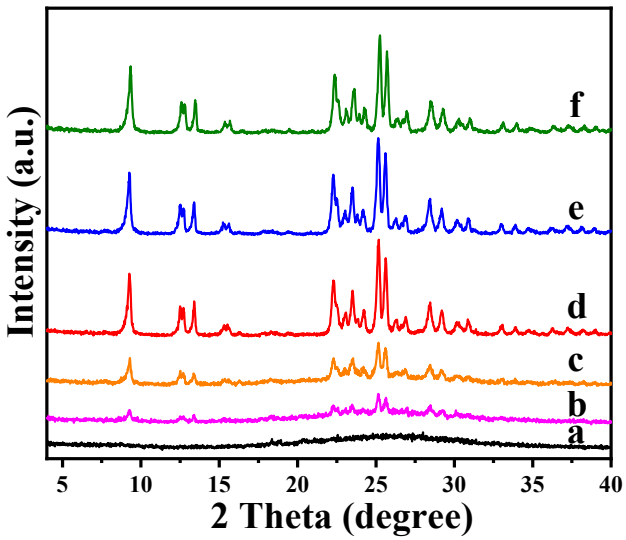

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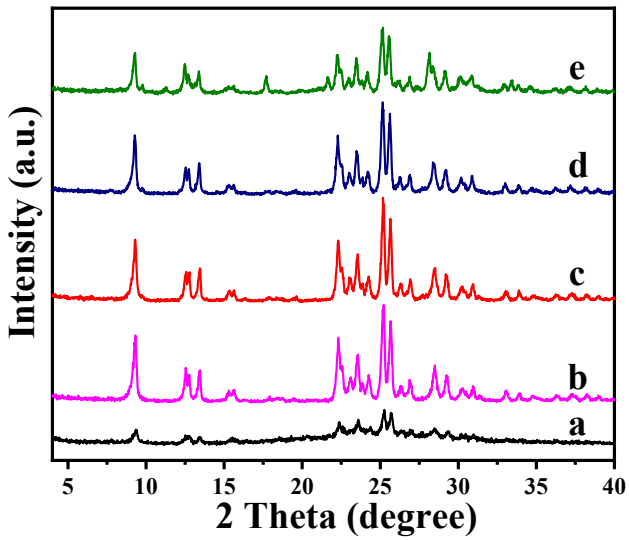

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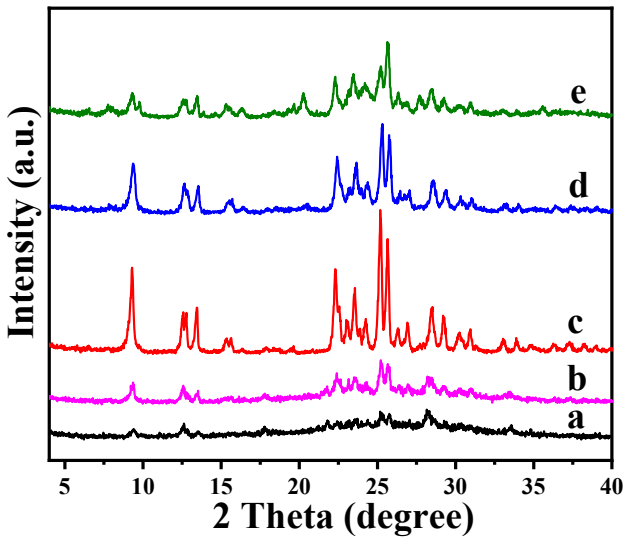

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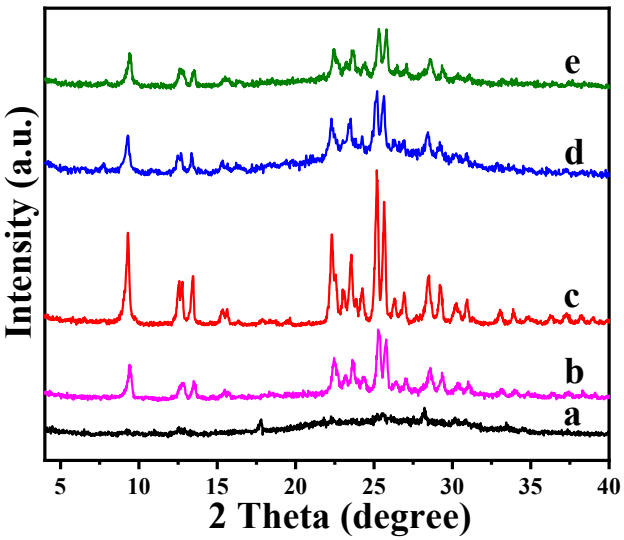

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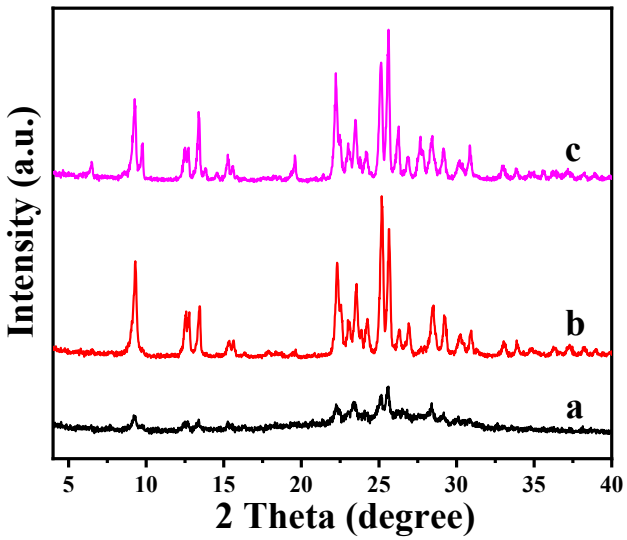

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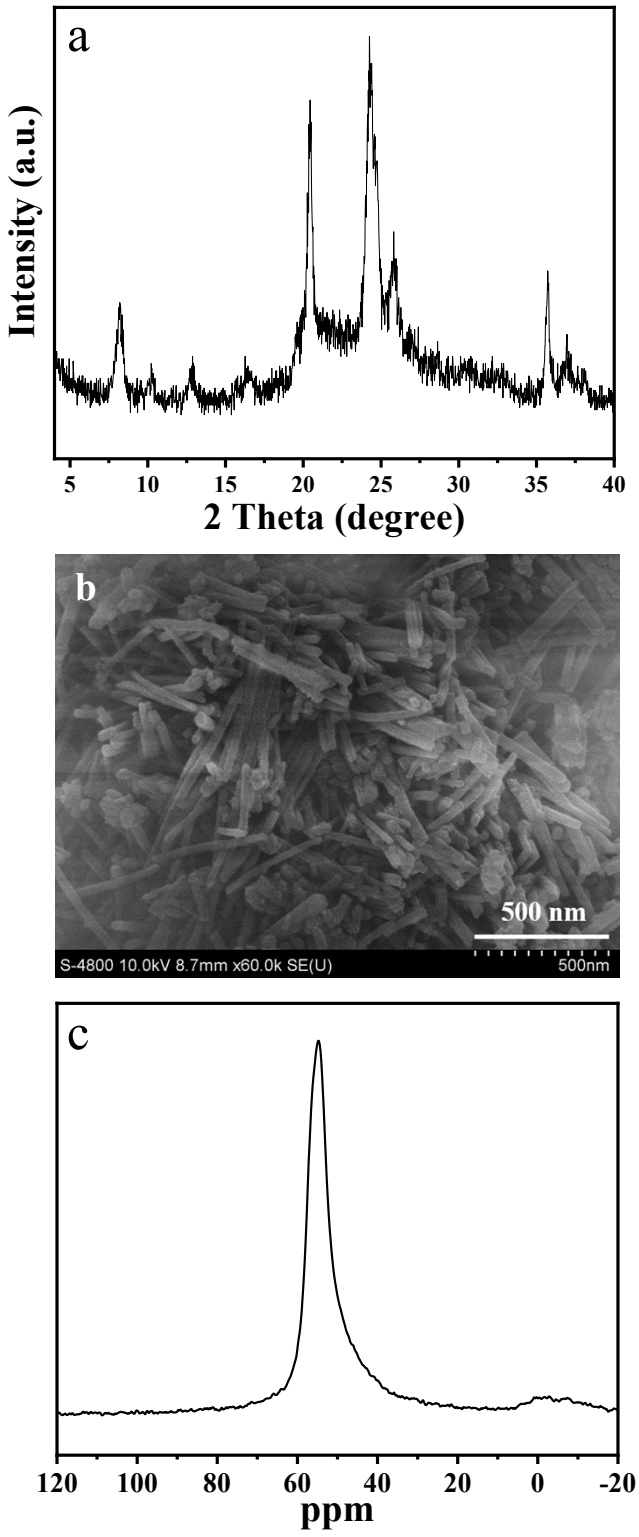

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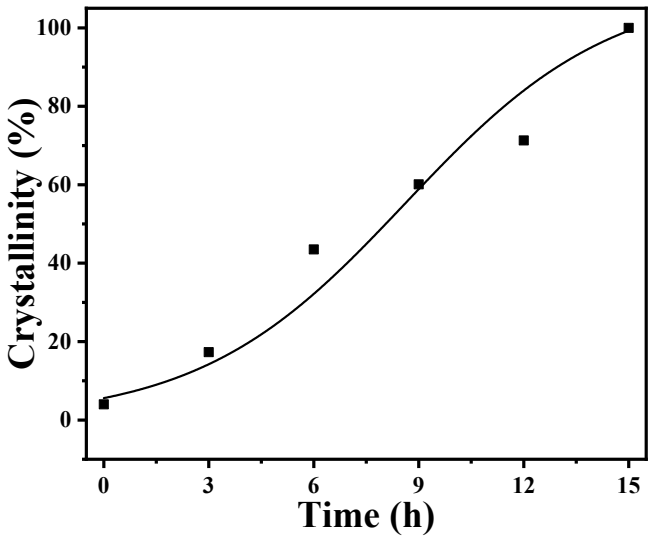

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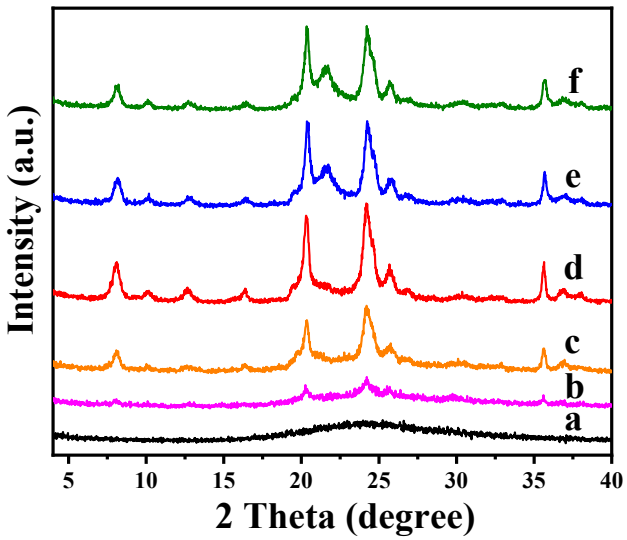

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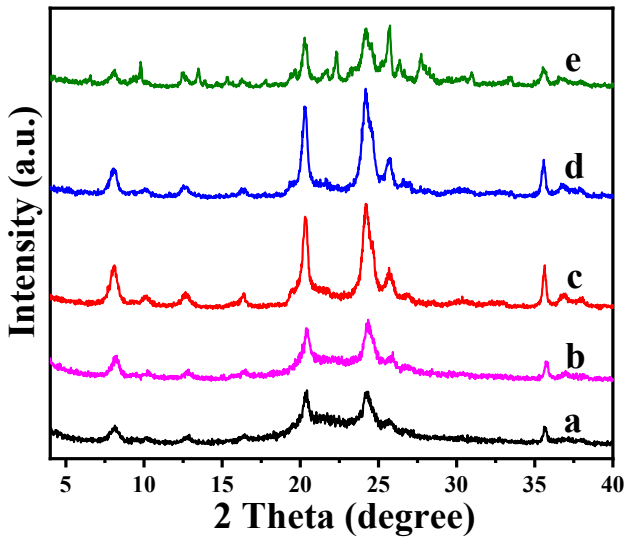

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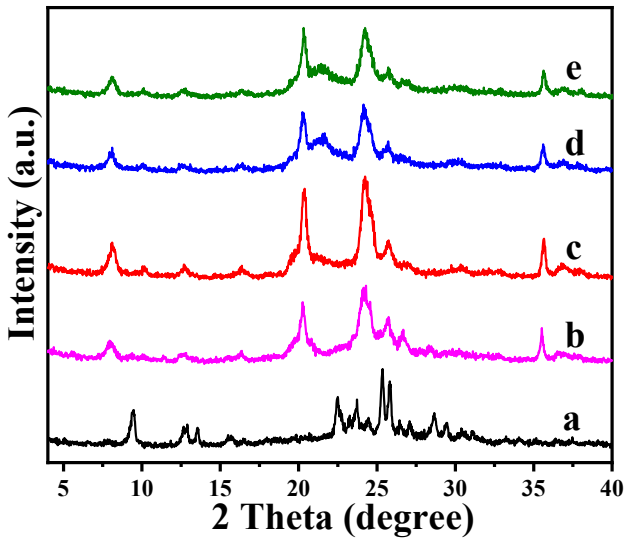

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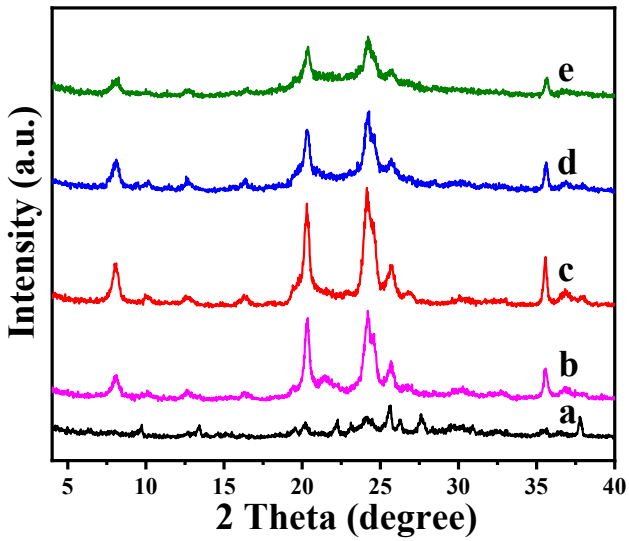

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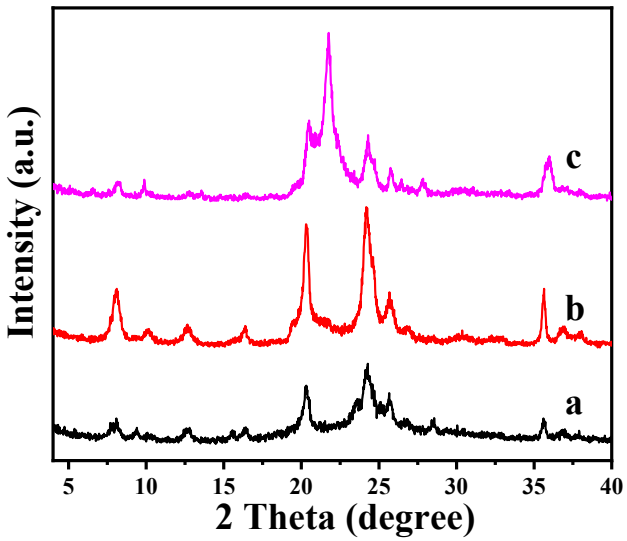

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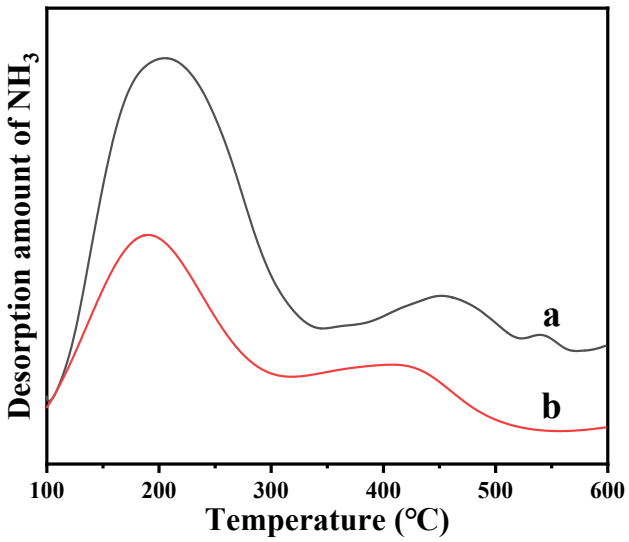

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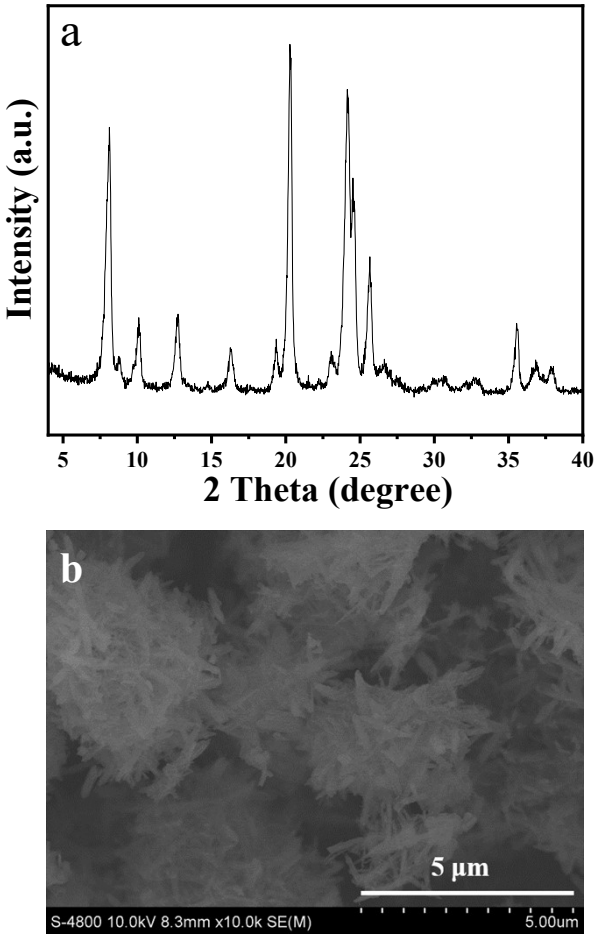

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