Electronic Supplementary Information (ESI)

Identification of the key factor promoting the enrichment of chiral polymorph A in zeolite beta and the synthesis of chiral polymorph A highly enriched zeolite beta

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1. Experimental Details

1.1 Materials

Tetraethyl orthosilicate (TEOS, 98 wt%) and ammonium fluoride (NH_4F) were obtained from the Tianjin Fuchen Chemical Reagent Factory. Tetraethylammonium hydroxide (TEAOH, 35% aqueous solution) was purchased from Alfa Aesar Company. Hydrogen fluoride (HF, 40% aqueous solution), oxalic acid dihydrate ($H_2C_2O_4{\cdot}2H_2O$), citric acid monohydrate ($C_6H_8O_7{\cdot}H_2O$), acetic acid (CH_3COOH, 98 wt%) and phosphoric acid (H_3PO_4, 85% aqueous solution) were supplied by the Beijing Chemical Reagent Factory. Phosphorus pentoxide (P_2O_5) was obtained from the Tianjin sixth chemical reagent factory. All reagents were used without purification.

1.2 Synthesis of zeolite beta with different fluorides

The synthetic procedure of zeolite beta is based on the previous synthesis route with slight modifications. Typically, 4.5 g of TEOS, 5.0 g of deionized water (DI), and 2.21 g of TEAOH were added to a plastic beaker. After the hydrolysis of TEOS for 6 h, the resulting mixture was stirred for a further 6 h and then dried in a freeze drier for 2 d until the weight of the mixture reached 2.4 g, H_2O/SiO_2 ratio reached approximately 1 by calculation (After the complete hydrolysis of TEOS and the evaporation of ethanol and most of the water, the weight of the mixture then includes 1.26 g silica, 0.774 g TEAOH and a small amount of water. The weight of H_2O could be estimated and the H_2O/SiO_2 ratio could be calculated). The dehydrated mixture was ground into fine powder. Subsequently, an appropriate amount of HF or NH_4F was added and mixed homogeneously. The molar composition of the final mixture is SiO_2: 0.25 TEAOH: x F^-, where the x=0.15, 0.25 and 0.5. The final mixture was then loaded into an autoclave and heated at 150 °C for 7 days. The solid product (denoted as HF-beta-x or NH_4F-beta-x) was washed thoroughly with deionized water via filtration and dried at 80 °C overnight.

1.3 Acidic synthesis route

The synthetic procedure of polymorph A-enriched zeolite beta with different acid additives is described as follows. First, 4.5 g of TEOS, 5.0 g of deionized water, and 2.21 g of TEAOH were added to a plastic beaker, the mixture was then stirred at ambient temperature in condition of seal for 6 h. After the hydrolysis of TEOS, the resulting mixture was stirred for a further 6 h in the open system at ambient temperature to evaporate generated ethanol and most of the water to form a thick gel and then freeze-dried for 2 d until the weight of the mixture reached 2.4 g, H_2O/SiO_2 ratio reached approximately 1 by calculation. (After the complete hydrolysis of TEOS and the evaporation of ethanol and most of the water, the weight of the mixture then includes 1.26 g silica, 0.774 g TEAOH and a small amount of water. The weight of H_2O could be estimated and the H_2O/SiO_2 ratio could be calculated). Subsequently, 0.19 g of NH_4F was added to the dehydrated mixture and the mixture was ground into fine powder. An appropriate amount of acid additive was subsequently added while grinding. Acid additive were oxalic citric acid monohydrate, phosphorus pentoxide, acetic acid, acid dehydrate, or phosphoric acid. The optimal molar composition of the synthesis mixture was SiO_2: 0.25 TEAOH: 0.25 NH_4F: y acid, where the y acid=0.12 $C_6H_8O_7$, 0.12 P_2O_5, 0.1 CH_3COOH, 0.15 $H_2C_2O_4$, or 0.06 H_3PO_4. The resulting mixture was then loaded into an autoclave and heated at 150 °C for 10 days. The solid product (denoted as acid-beta-y) was washed thoroughly with deionized water via filtration and dried at 80 °C overnight. The as-synthesized materials were calcined at 550 °C for 8 h to remove the OSDAs.

1.4 Characterization

Powder XRD patterns were recorded on a Rigaku D/MAX-2550 diffractometer equipped with a graphite monochromator using Cu Kα radiation (λ = 1.5418 Å) and operated at 50 kV and 200 mA. The samples were scanned in the 2θ range from 4° to 40° with step size of 0.02°. SEM images were collected on a JEOL JSM-6510 microscope. Thermogravimetric analysis (TGA) with a heating rate of 10 °C/min was performed in air using a TGA Q500 analyser from TA Instruments. Nitrogen adsorption–desorption measurements were carried out on a Micromeritics 2020 analyser at 77.35 K after the sample had degassed at 300 °C under vacuum. High resolution transmission electron microscopy (HRTEM) images were collected on a JEM-2100F transmission electron microscope (spherical aberration constant Cs = 0.6mm) operated at 300 kV. A typical experiment was as follows: a small amount of the sample was crushed and dispersed in ethanol, forming a particle/ethanol mixture. A few drops of the mixture were transferred to copper nets supported on hollow carbon films for the TEM experiments. A bottom-mounted CCD camera (Gatan Multi Scan Camera Model 832) was used to record images and a double tilt holder was used to tile the crystal to the desired orientation. The ^{19}F MAS NMR spectra were recorded on a Bruker AVANCE III 400 WB spectrometer equipped with a 2.5 mm standard bore CP MAS probe head whose X channel was tuned to 376.55 MHz for ^{19}F, using a magnetic field of 9.39 T at 297 K. The dried and finely powdered samples were packed in the ZrO_2 rotor closed with Kel-F cap which were spun at 20 kHz rate. A total of 500 scans were recorded with 3 s recycle delay for each sample. All ^{19}F MAS chemical shifts are referenced to the resonances of trichlorofluoromethane ($CFCl_3$) standard (δ=0.00).

1.5 Simulation of powder X-ray diffraction (XRD) patterns

The powder XRD patterns of zeolite betas with different polymorph compositions were simulated using the program DIFFaX_v1813 in detail. The unit cell parameters and planar translations of the building layer of zeolite beta were extracted from the database of international zeolite association (IZA) as the starting model. The simulation was based on the random stacking of layers in the structure of zeolite beta. The instrumental broadening was shaped by the pseudo-Voigt peak shape function wherein the parameters were set as 0.89, −0.32, 0.08 and 0.6 for u, v, w and σ respectively.

2. Results

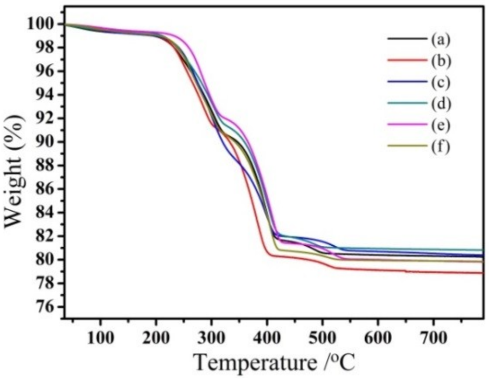

Fig. S1 TGA curves of $C_6H_8O_7$-beta-0.12 (a), P_2O_5-beta-0.12 (b), CH_3COOH-beta-0.1 (c), $H_2C_2O_4$-beta-0.15 (d), experiment 4-HF-beta-0.5 (e), and H_3PO_4-beta-0.06 (f).

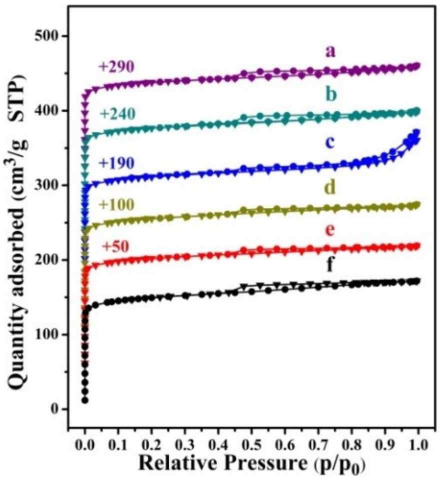

Fig. S2 Nitrogen adsorption-desorption isotherms of $C_6H_8O_7$-beta-0.12 (a), P_2O_5-beta-0.12 (b), CH_3COOH-beta-0.1 (c), $H_2C_2O_4$-beta-0.15 (d), experiment 4-HF-beta-0.5 (e), and H_3PO_4-beta-0.06 (f).

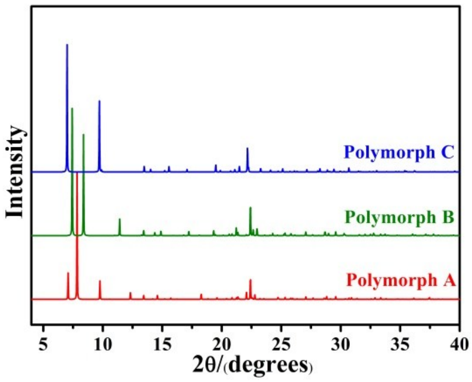

Fig. S3 Simulated XRD patterns of pure zeolite beta polymorph A, B, and C.