# Supporting information

## A green route for the crystallization of chiral polymorph A-enriched zeolite beta

Tingting Lu[a†], Liangkui Zhu[a†], Xiaohe Wang[a], Wenfu Yan[a]*, Wei Shi[b], Ruren Xu[a]

[a]State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, 2699 Qianjin Street, Changchun 130012, P. R. China

*Corresponding author: yanw@jlu.edu.cn

[b]Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education), Nankai University, Tianjin 300071, China

### 1. Experimental Details

#### 1.1 Materials

Tetraethyl orthosilicate (TEOS, 99 wt%, Tianjin Fuchen Chemical Reagents Factory), tetraethylammonium hydroxide (TEAOH, 35 wt%, Alfa Aesar), ammonium fluoride ($NH_4F$, Tianjin Fuchen Chemical Reagents Factory), methanol ($CH_3OH$, Beijing Chemical Works), ethanol ($C_2H_5OH$, Beijing Chemical Works) and polyethylene glycol (PEG-400, 2000, 4000, 10000, Tianjin kwangfu Fine Chemical Industry Research Institute) were used in the preparation of zeolite Beta. All reagents were used without purification.

#### 1.2 Synthesis of zeolite beta in the presence of alcohol additive

The synthetic procedure of zeolite beta with different alcohol additives is described as follows. In a typical synthesis, 4.5 g TEOS and 4 g deionized water were added to 2.21 g aqueous TEAOH solution (35 wt%), the mixture was then stirred at ambient temperature in condition of seal for 4 hours. After the hydrolysis of TEOS, the resulting mixture was stirred for a further 8 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 three days until the weight of the mixture reached 2.2 g, $H_2O/SiO_2$ ratio reached approximately 0.5 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, 0.77 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 mixed with 0.19 g ammonium fluoride solid and ground into uniform fine powder. Subsequently, an appropriate amount of the alcohol additives were added while stirring. It is worth mentioning that the solid alcohol additives (i.e., PEG-2000, 4000, 10000) could be added to the dehydrated mixture and grounded simultaneously. Finally, the uniform mixture was transferred into an autoclave and heated at 150 °C for 7 days. The solid product was washed thoroughly with water via filtration and dried at 80 °C overnight. The template was removed by calcination in air at 550 °C for 6-8 h.

The molar composition of the final mixture is $SiO_2$: 0.25TEAOH: 0.5$H_2O$: 0.25$NH_4F$: nR (R=alcohol additives). A summary of optimal amount of alcohol additives is listed in Table S1 respectively. The products are denoted as R-Beta-n, where the n value represents the $R/SiO_2$ mole ratio.

**Table S1** Summary of optimal amount of respective alcohol additives

| Alcohol(R) | EtOH | MeOH | PEG-400 | PEG-2000 | PEG-4000 | PEG-10000 |
|---|---|---|---|---|---|---|
| n=R/$SiO_2$ | 0.6 | 0.65 | 0.045 | 0.04 | 0.05 | 0.03 |

### 1.3 Characterization

The powder X-ray diffraction (XRD) patterns were recorded on a Rigaku D/MAX-2550 instrument operating at 50 kV and 200 mA using Cu Kα radiation (λ=0.15418 nm). The samples were scanned in the 2θ range of 4–40°, with a step size of 0.02°. Scanning electron microscopy (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 isotherms were measured with 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 dry-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.

### 1.4 Simulation of powder X-ray diffraction (XRD) patterns

The powder XRD patterns of the intergrowth structure 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 beta zeolites were extracted from the database of international zeolite association as the starting model. The simulation was based on the random stacking of layers in the zeolite structure.

## 2. Results

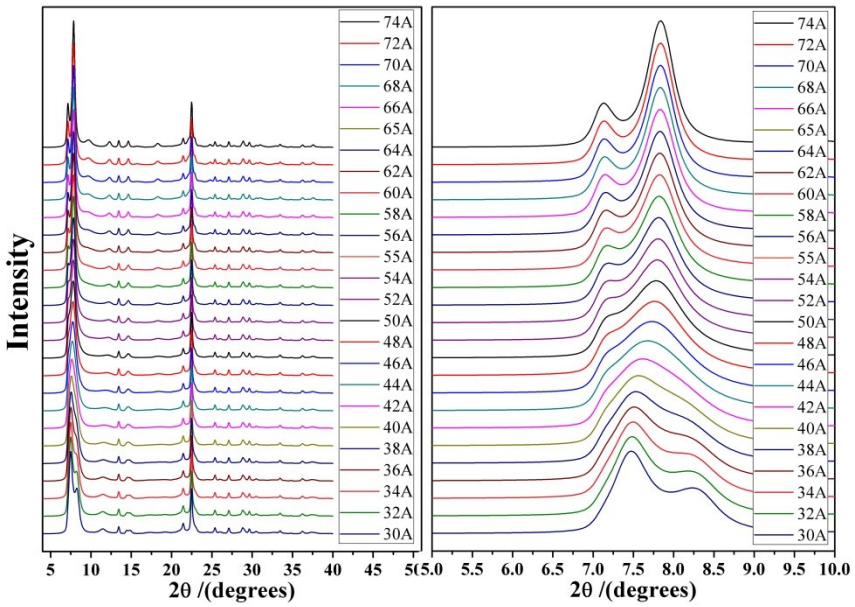


**Fig.S1** The simulated powder XRD patterns of zeolite beta with different portions of polymorph A (74 A represents the composition of zeolite beta is 74% polymorph A and 26% polymorph B).

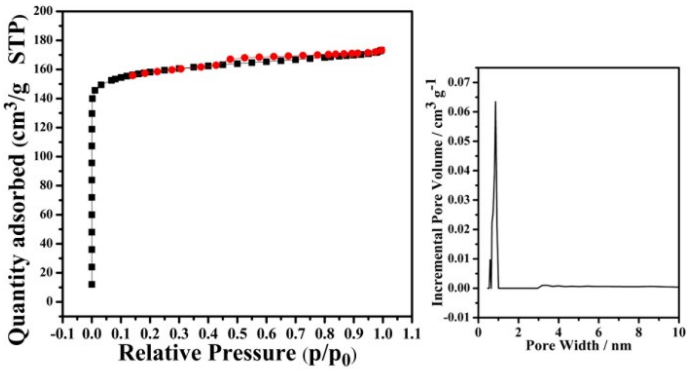


**Fig.S2** $N_2$ adsorption-desorption isotherms and pore size distribution curves of EtOH-Beta-0.6.

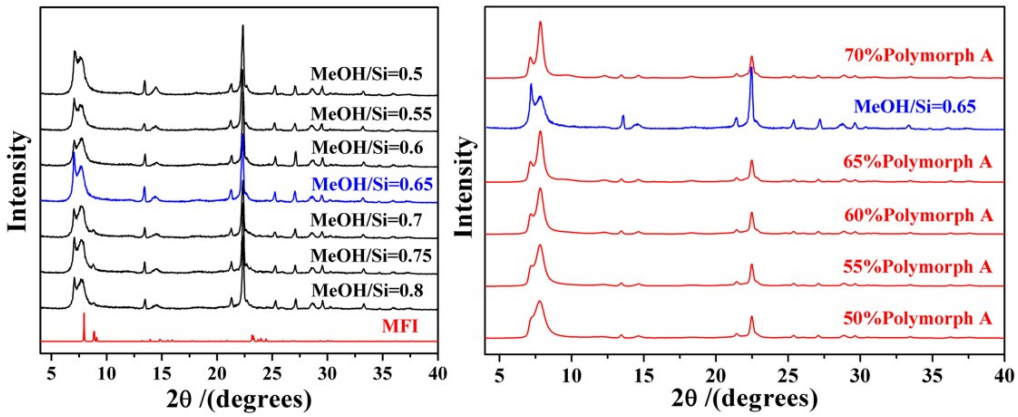


**Fig.S3** XRD patterns of the calcined samples prepared with different MeOH/$SiO_2$ ratios.

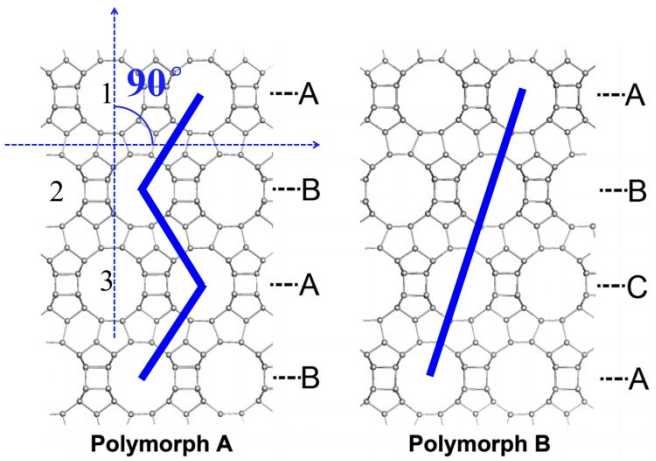


**Fig.S4** Structures of polymorph A and polymorph B of zeolite beta that show the different stacking sequences of the 12-ring channels as ABAB… and ABCABC… types, respectively.

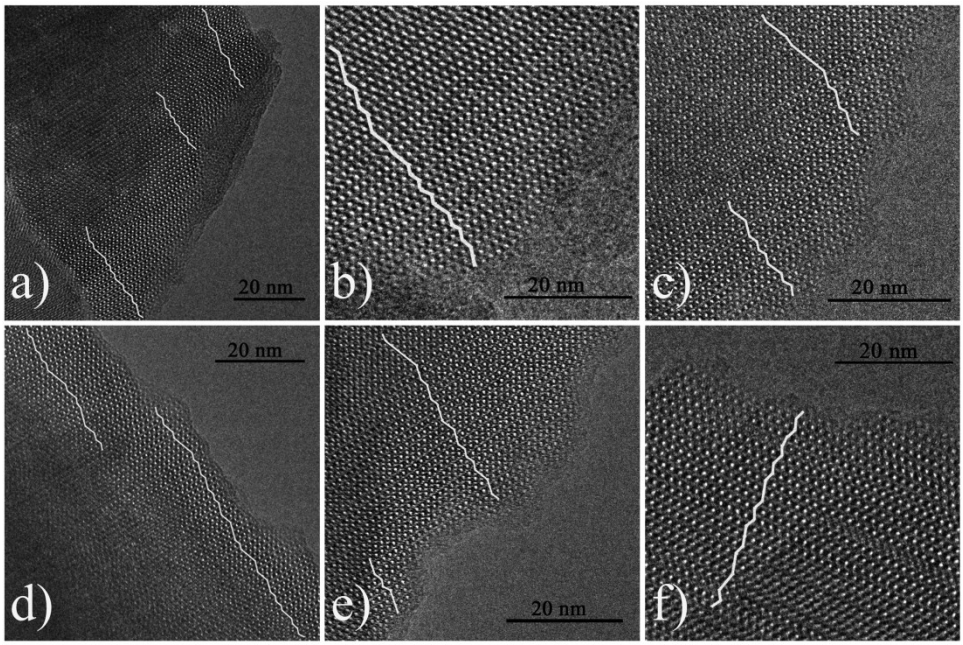


**Fig.S5** HRTEM images of PEG10000-Beta-0.03 aligned along the [100] direction. A fold line is added in the image to mark the stacking sequences of the 12-ring channels.

**Table S2** Statistical results of the 12-ring channel layers in polymorph A and polymorph B from the HRTEM images

| HRTEM images | Polymorph A (layers) | Polymorph B (layers) | Polymorph A proportion % |
|---|---|---|---|
| Fig.4-a | 29 | 18 | 61.70 |
| Fig.4-b | 60 | 28 | 68.18 |
| Fig.4-c | 19 | 7 | 73.08 |
| Fig.4-d | 21 | 7 | 75.00 |
| Fig.S4-a | 32 | 17 | 65.30 |
| Fig.S4-b | 19 | 8 | 70.37 |
| Fig.S4-c | 19 | 12 | 61.29 |
| Fig.S4-d | 48 | 24 | 66.67 |
| Fig.S4-e | 20 | 13 | 60.61 |
| Fig.S4-f | 17 | 4 | 80.95 |

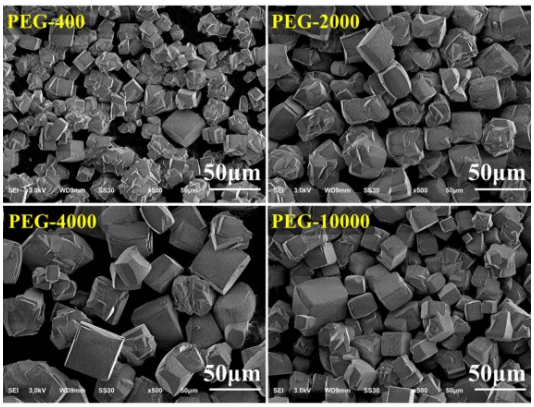

**Fig.S6** SEM images of calcined polymorph A-enriched zeolite beta prepared with different molecular weight PEG

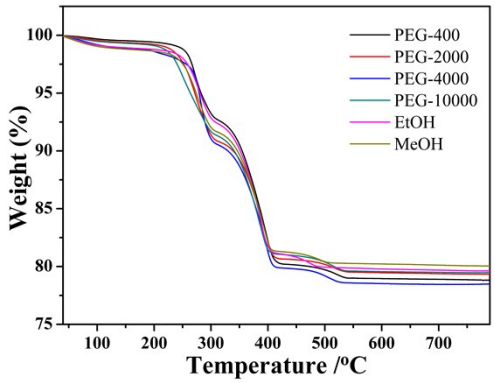


**Fig.S7** TGA curves of polymorph A-enriched zeolite beta prepared in the presence of different alcohol additives.

**Table S3** Summary of the results in the TGA analyses of the polymorph A-enriched zeolite beta prepared in the presence of different alcohol additives.

| alcohol additives | First step | | Second step | | Third step | | Fourth step | | Total weight loss% |
|---|---|---|---|---|---|---|---|---|---|
| | $T_1$/°C | Loss% | $T_2$/°C | Loss% | $T_3$/°C | Loss% | $T_4$/°C | Loss% | |
| PEG-400 | 250 | 1.2 | 310 | 6.1 | 422 | 12.5 | 542 | 1.3 | 21.1 |
| PEG-2000 | 216 | 1.0 | 310 | 8.2 | 418 | 10.2 | 540 | 1.3 | 20.7 |
| PEG-4000 | 248 | 2.2 | 310 | 7.2 | 415 | 10.7 | 531 | 1.4 | 21.5 |
| PEG-10000 | 210 | 1.1 | 306 | 7.5 | 407 | 10.3 | 540 | 1.5 | 20.4 |
| EtOH | 231 | 1.4 | 304 | 6.0 | 409 | 11.4 | 491 | 1.4 | 20.2 |
| MeOH | 227 | 1.6 | 308 | 6.7 | 440 | 10.4 | 550 | 1.2 | 19.9 |

Tn represents the end temperature of each step.

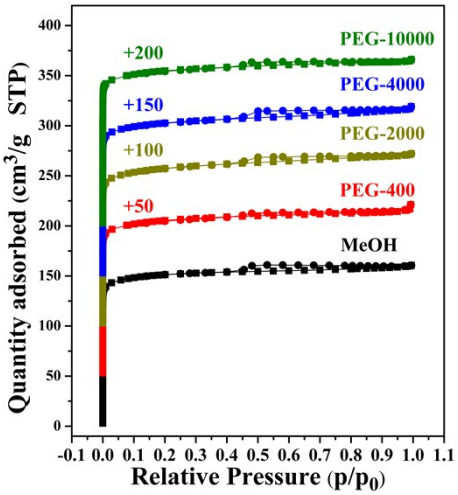


**Fig.S8** $N_2$ adsorption-desorption isotherms of polymorph A-enriched zeolite beta prepared in the presence of different alcohol additives.