

Controllable synthesis of obvious core-shell structured Y/Beta composite zeolite through a stepwise-induced method

Bo Ren, Shiyang Bai, Jihong Sun*, Faqian Zhang, Minghui Fan

College of Environmental and Energy Engineering, Beijing University of Technology,

Beijing 100124, P. R. China

Supplementary information

1. The detail experimental procedures

As a typical run, the core-Y zeolite was carried out in aluminosilicate gel with molar ratio of $\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 : \text{SiO}_2 : \text{H}_2\text{O} : \text{H}_2\text{SO}_4$ was 4.7 : 1 : 10.8 : 200 : 0.67. The mixture was stirred 4 h and the feedstock gel was aged at room temperature for another 24 h prior to crystallization, then the mixture was transferred into an autoclave and keep at 100 °C for 48 h without stirring. The reacted mixture containing the presynthesized NaY-zeolite (unfiltered) was used in the second-step synthesis. The TEAOH (35%) was added to the reacted mixture and stirred for 12 h at room temperature, the silica (about 50 nm) was added into the mixture and stirred for 6 h, at last a quantity of sulfured was added and the new mixture became stickier because of the pH value decrease, some silica precipitation. The new mixture with the molar composition of the gel : $\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 : \text{SiO}_2 : \text{TEAOH} : \text{H}_2\text{O} : \text{H}_2\text{SO}_4 = 4.7 : 1 : 15 : 3.9 : 260 : 4.7$, and loaded into an autoclave for hydrothermal treatment at 140 °C for 0~84 h. The solid product was collect by filtrating, drying at 80 °C for 10 h.

The powder X-ray diffractive (XRD) patterns were collected on the XD-3 of the Beijing Purkinje General Instrument Co., with graphite monochromatized Cu-K α ($\lambda=0.154056$ nm) radiation at 36 kV, 20 mA. All the samples were collected in the range of 5-50 ° with continuous scanning mode, and the scanning speed was 2 °/min. The scanning electron microscopy (SEM) images were captured on a Hitachi field-emission scanning electron microscope (S-4300) operated at an accelerating voltage of 15 kV. Thermogravimetric analyses (TGA) were carried out between 25 and 800 °C using a Perkin-Elmer Pyris1 TG analyzer under 20 mL/min N₂ flow with a heating rate of 10 °C/min. The transmittance electron microscopy (TEM) and energy dispersive X-ray (EDX) analyses were performed using a Hitachi HT7700 microscope and Phoenix 30T (EDAX Co.), EDX data was averaged from multiple overscans and spot analysis.

2. Relationship between the weight percent of zeolite Y and corresponding peak-areas amount of zeolite Y in the mixture of zeolite Y and Beta

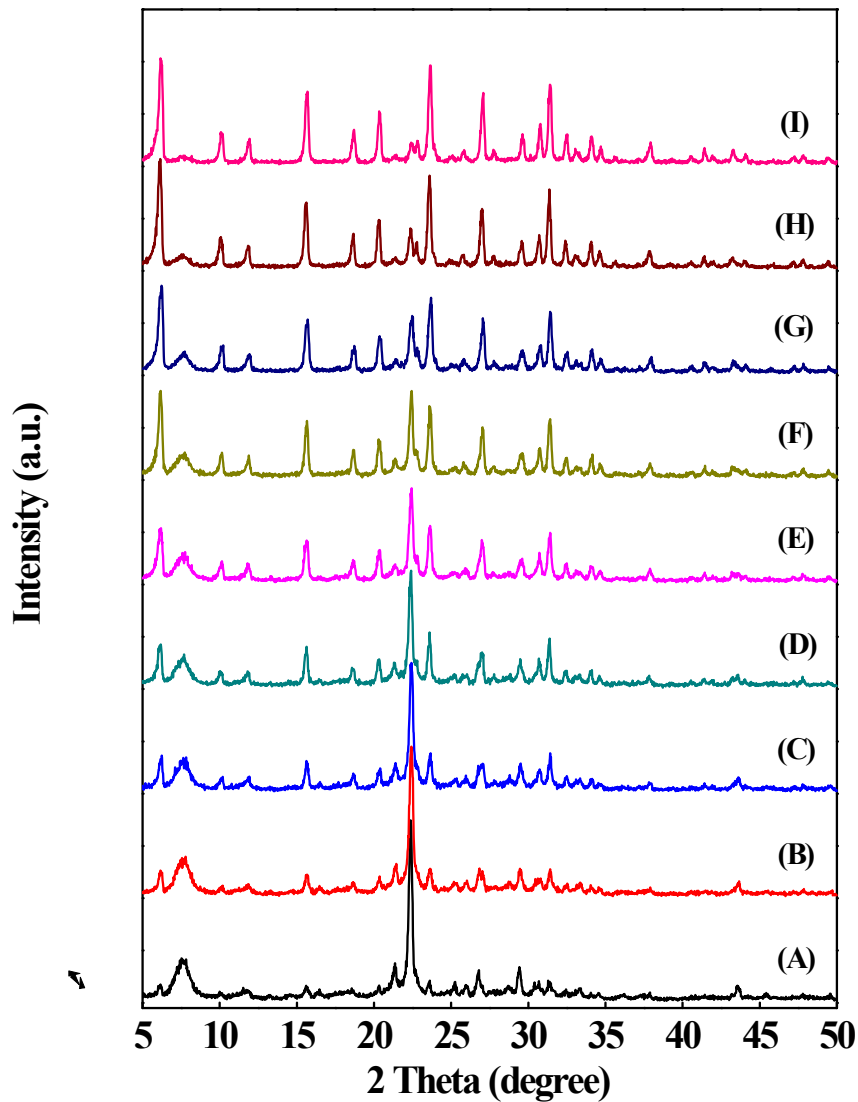


Figure 1S. The XRD patterns of Y and Beta mechanical mixture
 The weight percent of zeolite Y in the mixture of zeolite Y and Beta is as following:
 (A) 10 %; (B) 20 %; (C) 30 %; (D) 40 %; (E) 50 %; (F) 60 %; (G) 70 %; (H) 80 %
 and (I) 90 %

According to XRD patterns in Figure 1S, the peak areas were calculated by using the selected diffraction peaks of (111), (331), (642), (555) for zeolite Y and that of (101), (300) and (302) for zeolite Beta, then, the peak-areas amount of zeolite Y in total peak-areas of zeolite Y and Beta was obtained. Thereafter, the relationship between the weight percent of zeolite Y (shown in X-axis) and corresponding peak-areas amount of zeolite Y (shown in Y-axis) in the mixture of zeolite Y and Beta was shown in Figure 2S (the relative coefficient (R^2) is around 0.9991), which can be used to estimate the relative amounts of zeolite Y in the Y/Beta composite zeolites.

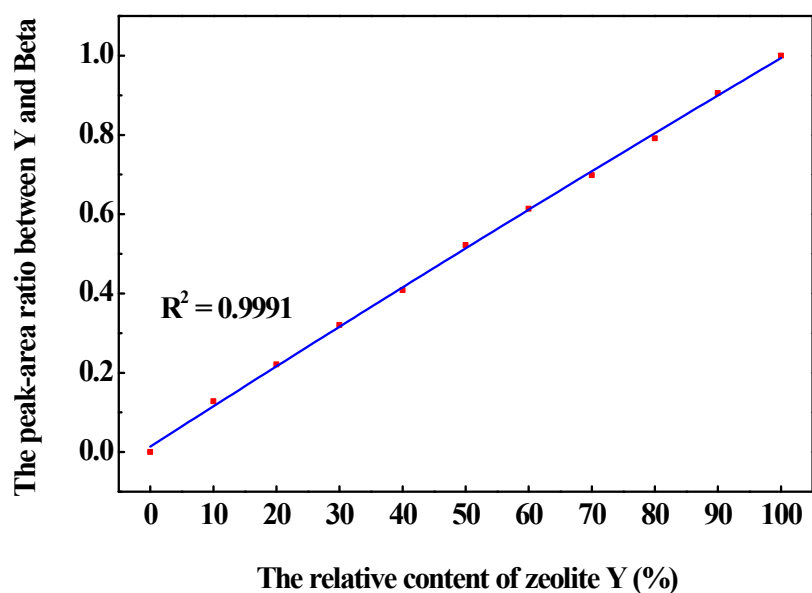


Figure 2S. Relationship between the weight percent of zeolite Y and corresponding peak-areas amount of zeolite Y in the mixture of zeolite Y and Beta

3. The thermal stability of the composite zeolite

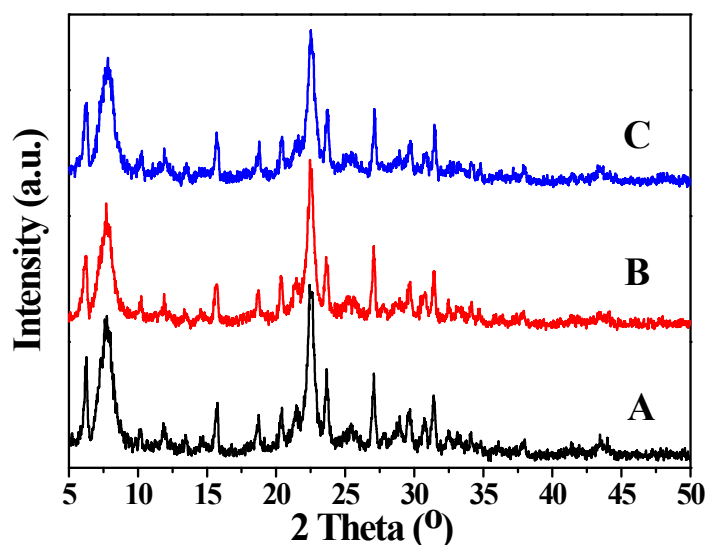


Figure 3S. XRD patterns of the calcined samples (crystallization time is 74 h) calcined at (A) 650 °C; (B) 750 °C; (C) 850 °C

Taking sample (crystallization time is 74 h) as an example, the thermal stability of the composite zeolite sample was evaluated. After calcined at 650 °C, 750 °C, and 850 °C, respectively, the XRD patterns in Figure 3S indicated that their diffractive intensity of the characteristic peaks with higher relative crystallinity could be almost unchanged.

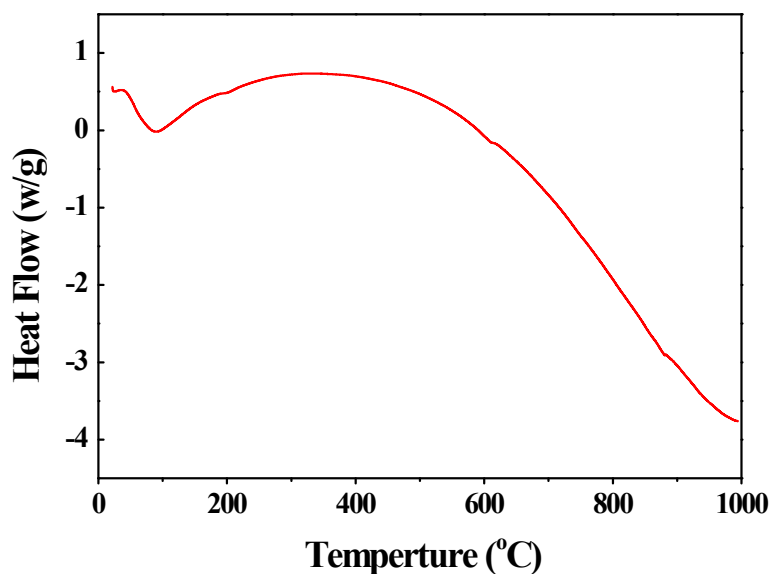


Figure 4S. DSC thermogram curve of composite zeolite

Besides that, the stability analysis was also demonstrated by DSC illustration (Figure 4S), the result showed not obvious phase transition exothermic peak below 1000 °C.

Obviously, these observations suggest that the composite zeolite had a high thermal stability.

4. Preparation of H-type catalysts and Catalytic testing

The sodium form of Y/Beta composite zeolites were converted to the hydrogen form by ammonium ion exchange method. The 1.0 g of composite zeolite was firstly treated with 100 mL of 1 M ammonium chloride solution at 80 °C for 2 h. After filtered and washed with distilled water, the obtained residue was then dried at a temperature of 120 °C for 4 h. The above cycle was repeated three times to get complete exchange of sodium. Finally, the samples were heated at 550 °C for 5 h to decompose to H-zeolite.

The cracking activities of H- type composite zeolite were determined with cumene as the probe molecules, using a flow-type apparatus equipped with a fixed-bed reactor. Nitrogen was used as carrier gas at flows of 3.0 L/h. The catalysts were pressed binder-free and crushed to a particle size of 60-80 mesh and the catalyst amount was around 0.26 g. In the case of cumene cracking, nitrogen saturated with vaporized cumene at 300 °C was passed through the reactor (the flow rate of liquid state cumene = 6.0 mL/h), and the reaction temperature was about 300 °C. Reaction products were analyzed by an online gas chromatograph with flame ionization detector.