



Structural features of binary microporous zeolite composite Y-Beta and its hydrocracking performance

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ABSTRACT

Y-Beta zeolite composites denoted as HS-FBZ (High-Silica-Faujasite-Beta-Zeolite) were synthesized hydrothermally using high silica Y as precursor and characterized by XRD, N₂ adsorption, SEM, HRTEM, NH₃-TPD and FT-IR spectra of pyridine. The results reveal that the different ratios of Y and Beta zeolites in the composites induced the change of surface areas, pore diameters and acid properties of HS-FBZ, and the extended Beta layers on the zeolite Y surface were observed. The composite exhibited an excellent hydrocracking activity for heavy oil. Compared with the corresponding physical mixture of Y and Beta zeolites, the zeolite composite as a hydrocracking catalyst for vacuum gas oil increased the heavy naphtha yield by 5.61 wt% and the jet fuel yield by 11.52 wt%.

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Zeolite Y as a catalytic material was widely studied because of its appropriate pore structure, acidity, thermal and hydrothermal stability in petroleum refining [1–6]. On the other hand, the high acid density of zeolite Y facilitates the deposition of carbon in its channels, especially on its external surface, which causes a blockage of the channels and an untimely deactivation of the catalyst in the catalytic cracking. Many studies have been conducted to modify zeolite Y, which gives rise to improved surface property of the zeolite so as to obtain a reasonable distribution of acidity [7–9]. Similarly, significant attentions had been focused on zeolite Beta as a result of its high Si/Al ratio and hydroisomerization activity, low hydrogen-transfer capacity and catalytic deactivation, and easy availability in petrochemical processing [10–12]. Previous studies focused mainly on properties and applications of the two zeolites in hydrocracking [5,12–14]. Recently, with the appearance of zeolite composites, such as ZSM-5/Y [15,16], MCM-41-Beta [17], and MCM-41/Y [18], many researchers had paid attention to the study of the composites in hydrocracking and FCC processes [15,16], in which the composites show the advantage over single component because of the combination of two kinds of molecular sieves. Li and his co-workers synthesized a High-Silica-Faujasite-Beta-Zeolite composite (HS-FBZ) using high silica Y as precursor [19,20]. However, the understanding on the structure and property of the zeolite composite is still very limited. In the present paper, the zeolite composite HS-FBZ was synthesized in the same way and further

investigated to reveal its physico-chemical and hydrocracking properties, as well as the correlation between them. The hydrocracking activity of HS-FBZ was investigated and compared with that of physical mixture of Y and Beta zeolites.

1. Experimental

1.1. Synthesis of HS-FBZ composite

The HS-FBZ composite zeolite was prepared hydrothermally in a Teflon-lined autoclave under static condition. Typically, 7.2 g of Y zeolite powder was treated in 35 mL of 0.1 mol/L NaOH aqueous solution at 80 °C for 12 h [21], then 5.8 g of tetraethylammonium bromide (TEABr) and 2 mL of NH₄OH were added to the mixture, and the pH value of the system was adjusted to 13 by adding 1 mol/L H₂SO₄. The resultant mixture was stirred at room temperature for 0.5 h, subsequently 21 mL of silica sol was added slowly under vigorous stirring. Finally, the mixture was heated at 140 °C for 5–9 days. The synthesized product was filtered, washed with distilled water to pH < 8.0, and dried at 100 °C overnight. The as-synthesized sample was calcined at 500 °C for 5 h under air atmosphere to remove the organic template. The heating rate was controlled at 2 °C/min. By the same procedure, three HS-FBZ zeolite composites with different amounts of Beta and Y zeolites were obtained, of which the composites including 20 wt%, 40 wt% and 60 wt% Beta zeolite are denoted as HS-FBZ-20, HS-FBZ-40, HS-FBZ-60, respectively. The three composite zeolites have almost the same Si/Al ratios, as determined by chemical analysis, which are 10.91, 10.89, 10.63, respectively. The calcined samples were treated repeatedly three times with 1 mol/L NH₄NO₃ solution at

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80 °C for 1 h, filtered and washed with deionized water, and finally calcined at 500 °C for 5 h under air atmosphere to give the H-form of HS-FBZ.

1.2. Catalyst preparation

For hydrocracking reaction, a bifunctional catalyst was prepared, in which the H-form zeolite composite HS-FBZ was used as the support, Ni–Mo as the active components, pseudo-boehmite and amorphous silica–alumina as the binders. The catalyst preparation procedure was as follows: HS-FBZ, pseudo-boehmite and amorphous silica–alumina (10–20 wt%) were mixed by grinding, blended by adding distilled water, and extruded to get the catalyst carrier. The bifunctional catalyst was prepared by stepwise impregnation of the carrier with the solution of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ (Beijing Chemical Co., PR China) and $\text{Ni}(\text{NO}_3)_2$ (Beijing Chemical Co., PR China). After every carrier impregnation step, the resulting solids were dried at 110 °C for 3 h. The final solid samples were then calcined at 500 °C for 4 h.

1.3. Characterization of HS-FBZ composite

XRD patterns of the samples were recorded using a Rigaku Dmax X-ray diffractometer, Ni-filtered $\text{Cu K}\alpha$, 40 kV and 80 mA. A working plot was obtained by plotting the intensity of the diffraction peak at $2\theta = 6.16$ versus the mass fraction of Y zeolite by measuring a series of physical mixtures with known mass fractions of Y zeolite. The mass fraction of Y zeolite in the composite HS-FBZ can be estimated from the intensity of the XRD diffraction peak at $2\theta = 6.16$, which is the characteristic peak of Y zeolite. N_2 adsorption–desorption isotherms were obtained at liquid nitrogen temperature on a Micromeritics ASAP2400 apparatus. The mesoporous structure was analyzed from desorption branch of the isotherm by the Barrett–Joyner–Halenda (BJH) method, and the microporous structure was obtained from the t -plot analysis of the adsorption branch of the isotherm. Infrared spectra were obtained on a Bio-Rad spectrometer in KBr pellets in the range of 400–1600 cm^{-1} . Crystal morphology and size were determined using a JSM-6301F scanning electron microscope (SEM). X-ray energy dispersive spectroscopy was carried out on Oxford-Link ISIS. TEM images of the prepared materials were captured in a Tecnai G220 field emission electron microscope. Samples were prepared by dispersing the powder in methanol via sonication for about 20 min followed by evaporation on a 300 mesh continuous carbon film TEM grid. The acidity of H-form HS-FBZ was measured by ammonia temperature-programmed desorption technique (NH_3 -TPD) on a chemical adsorption instrument Micromeritics 2910. The sample was outgassed at 500 °C for 1 h under He flow and then NH_3 was adsorbed at 100 °C until saturation. Desorption of the adsorbed ammonia began from 100 °C to 500 °C by 10 °C/min after the sample was purged by He. The acid types (i.e. Brønsted or Lewis type) were recorded on an FT-IR spectrometer by in situ pyridine adsorption.

1.4. Catalytic test

The catalytic experiments were carried out on a standard micro-activity test unit (MAT). Iranian vacuum gas oil (VGO) was employed as the feedstock. Reaction conditions were as follows: total pressure = 15.7 MPa, $\text{WHSV} = 1.5 \text{ h}^{-1}$, and $\text{H}_2/\text{hydrocarbon}$ molar ratio = 1500/1. Two temperatures were adopted, 385 °C and 382.5 °C. The product was distilled to produce the following fractions: light naphtha, heavy naphtha, gasoline, diesel oil, and tail oil. The product distribution, gasoline group and octane number were off-line analyzed on a gas chromatograph. The coke on catalyst was measured with a coke analyzer.

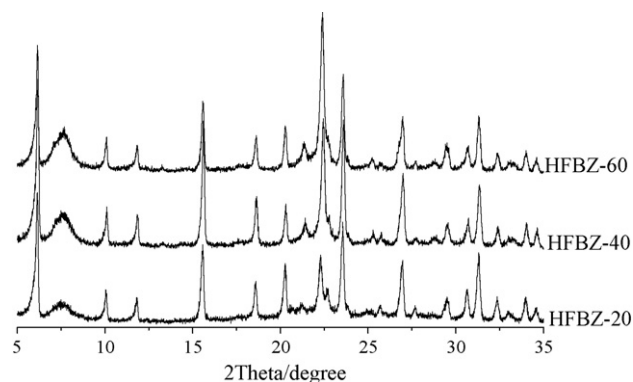


Fig. 1. XRD patterns of HS-FBZ composites.

2. Results and discussion

Fig. 1 shows the XRD patterns of the zeolite composites HS-FBZ. The characteristic peaks corresponding to zeolites Y and Beta can be observed together, indicating the co-existence of Y and Beta zeolite phases in the composite HS-FBZ. The analysis by XRD also shows that the zeolite composite HS-FBZ resulting from the intergrowth of zeolites Y and Beta was obtained with high crystallinity. It is interesting that the peak intensities of high silica Y zeolite phase in the three composites changed only slightly, the peak intensities of Beta zeolite phase at 7.5 and 22.4° increased gradually with the increasing crystallization time. As a result an extended Beta layer overgrew on zeolite Y surface protecting the precursor from being further corroded in the reaction solution [22].

N_2 adsorption–desorption results are shown in Table 1. The total surface area of the composites is lower than that of Y zeolite. However, the external surface area of the composites is in the range of 81 and 89 m^2/g , nearly two times that of Y zeolite. The composites also possess larger pore size and considerable pore volume. As shown in Fig. 2, the pore size distributions are centered

Table 1
The structure parameters of HS-FBZ composites.

Sample	S_{BET} (m^2/g)	S_{micro} (m^2/g)	S_{external} (m^2/g) ^a	V_{total} (cc/g)	Average pore size (Å)
Y	845	796	48	0.36	16.8
HS-FBZ-20	692	604	88	0.39	22.5
HS-FBZ-40	703	623	81	0.35	20.1
HS-FBZ-60	715	627	89	0.34	19.0

^a t -plot method.

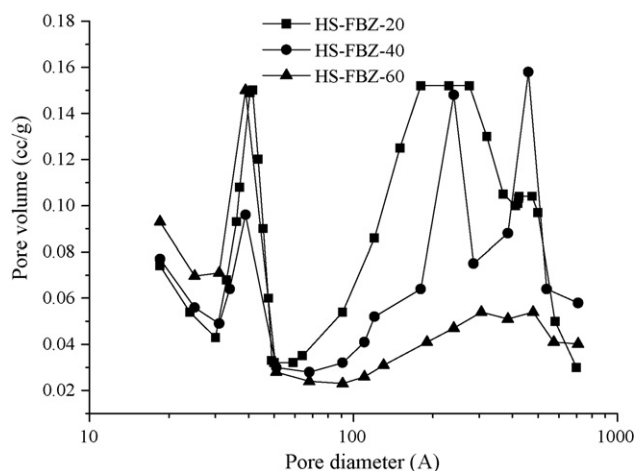


Fig. 2. Pore size distribution of HS-FBZ composites.

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