Electronic Supplementary Information

High-efficiency hydrocracking of phenanthrene into BTX aromatics over a Ni-modified lamellar-crystal HY zeolite

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Table of content

S1. Experimental

S2. Diffusivities in Y crystal

S3. The computational process of effective factors

S4. Table S2. The results of phenanthrene hydrocracking over the regenerative 10%

Ni-C/HY and 10% Ni-C/HY samples

Supporting References

S1. Experimental

Catalyst preparation

The lamellar-crystal Y zeolite with a Si/Al molar ratio of 4.47 was synthesized by hydrothermal method. Both aluminium sulfate and sodium aluminate were used as the initial Al sources, and sodium silicate was used as the initial Si sources. The mixture was dissolved in distilled water, then sodium hydroxide, cetyltrimethylammonium bromide (as a synthesis aid) and directing agent were also added and stirred well. The molar composition of the gel system was 6.3 Na₂O: Al₂O₃: 10 SiO₂: 220 H₂O, and the molar ratio of cetyltrimethylammonium bromide to Al₂O₃ was 0.8. After an aging treatment for 16.0 h at 318 K, the gel mixture was packed into a stainless steel autoclave, and the crystallization was performed for 16.0 h at 373 K with stirring speed of 90 r/min. Then the autoclave was cooled to room temperature, and the synthetic product was discharged, washed, separated and dried to obtain lamellar-crystal NaY zeolite. The above-mentioned lamellar-crystal NaY zeolite (L/NaY) and a conventional-morphology NaY zeolite (C/NaY) were respectively converted to NH₄-type by ion-exchange with aqueous NH₄NO₃ solution. Subsequently, they were dried in an oven at 393 K and then calcined at 813 K with a ramp of 3 K/min for 1.0 h. The obtained HY zeolites were denoted to L/HY and C/HY, respectively. The Ni-modification (10 wt%, calculated by Ni-element weight) of HY zeolites was performed by first impregnation in Ni(NO₃)₂·6H₂O solution, subsequent drying at 393 K for 6.0 h, and finally calcining at 813 K for 1.0 h. The

modified samples were labeled as 10% Ni-C/HY and 10% Ni-L/HY, respectively. All prepared Ni-containing samples were reduced in a high purity H_2 flow at 773K for 1.0 h for subsequent characterization and catalytic evaluation (except those for XRD).

Characterization

The X-ray diffraction patterns of zeolite samples were collected on a force D8 powder diffractometer operating at 40 kV and 30 mA (using Cu-K α radiation). Scanning electron microscope (SEM, JSM-6610LV) and transmission electron microscope (TEM, JEM-2100) were used to observe the crystal morphology, crystal size and surface Ni-species of the prepared samples. The specific surface area and pore volume were calculated, based on the adsorption-desorption of N₂ at 77 K (NOVA 2200e, Quantachrome). The acidity of samples was determined by ammonia temperature programmed desorption (NH₃-TPD, Altmira-100 Characterization System, Zeolton) and pyridine infrared spectroscopy (Py-IR, Bruker IFS-88). The coke on the used catalyst was analyzed by using thermogravimetric analysis (Netzsch STA 449 C, Germany).

Catalytic reaction

The prepared catalyst (5.0 g) was packed into a stainless steel tubular fixed-bed reactor with an inner diameter of 1.5 cm, and pretreated at 773 K for 1 h in high purity hydrogen flow. When the temperature was cooled to 698 K, the reactive material consisted of 75 wt% toluene and 25 wt% phenanthrene was pumped into the reactor by using a metering pump. Hydrocracking was carried out at the condition of 1.0 h⁻¹

WHSV, 4.0 MPa and H_2 /phenanthrene = 2.0 mol/mol. The tail gas was analyzed by a HP-5890 gas chromatograph equipped with a FID detector and a 50 m HP-PLOT/Al₂O₃ "S" capillary column. Oil-phase analysis was carried out by using an HP-5890 gas chromatograph with a FID detector and a 50 m HP-FFAP capability column. The conversion and product distribution & BTX yield etc. were calculated according to the total volume/weight (except H₂) and the chromatographic analysis results of gas and oil products, combining the chromatographic normalization, etc.

S2. Diffusivities in Y crystal

Molecular diffusion coefficient D_{AB} can be calculated by the Fuller-Schettler-Giddings semi-empirical formula:

$$D_{AB} = \frac{0.001T^{1.75} (1/M_A + 1/M_B)^{0.5}}{p[(\Sigma V_A)^{1/3} + (\Sigma V_B)^{1/3}]^2}$$
(S1)

 D_{AB} is the relative diffusivity in the mixture of components A and B; M_A and M_B are the relative molecular weights of components A and B, respectively; (ΣV_A) and (ΣV_B) are the diffusion volumes of components A and B, respectively; calculated according to common atomic diffusion volume tables. As the reaction temperature and pressure remain the same, the relative diffusivity of the two different-shape crystals should also remain the same.

When the pore size of the catalyst is very small, Knudson diffusion is the main consideration for micropore diffusion because more gas molecules collide with the solid surface. The Knudson diffusion coefficient for component A can be calculated as follows:

$$D_{K,A} = 9.7 \times 10^3 r \sqrt{T/M_A} \quad (cm^2/s)$$
 (S2)

where, r is the pore radius (cm); T is the temperature (K); M_A is the relative molecular weights of components A.

In fact, the diffusion in micropores includes both molecular diffusion and Knudson diffusion, both of which cannot be ignored. The comprehensive diffusion coefficient D_A can be expressed by:

$$\frac{1}{D_A} = \frac{1}{D_{AB}} + \frac{1}{D_{K,A}}$$
(S3)

The comprehensive diffusion coefficient calculated above needs to be corrected to obtain the effective diffusion coefficient D_{eA} :

$$D_{eA} = \frac{\theta}{\tau} D_A \tag{S4}$$

where, $\boldsymbol{\theta}$ is the porosity of solid catalyst; τ is the bending factor.

Parameter	Unit	Value
Effective diffusion coefficient (De)	cm ² /s	9.18×10 ⁻⁴
Molecular diffusion coefficient (D_{AB})	cm ² /s	2.6×10 ⁻³
Knudson diffusion coefficient (D _K)	cm ² /s	1.42×10 ⁻³

Table S1. Parameters for diffusion in Y zeolite

S3. The computational process of effective factors

In order to describe the effect of internal diffusion on reaction rate more directly, the effective factor (η) was introduced and calculated as Eq. (S5). Due to the high surplus of hydrogen,^{1,2} the reaction rate was calculated by first-order kinetics.

$$\eta = \frac{R_A}{R_{As}} \tag{S5}$$

where, R_A is the rate of the reaction affected by internal diffusion, R_{As} is the rate of the reaction without internal-diffusion effect.

The morphologies of the two catalysts were different, and the corresponding calculation procedures were also different. The L/HY crystal was treated as an infinite plate, the area of the plate was set as S, the thickness was 2L = 20 nm, and the material balance of reactant A can be carried out:z

$$\frac{d^2 C_A}{dl^2} - \frac{k_v}{D_e} C_A = 0 \tag{S6}$$

where, k_v is the reaction rate constant calculated per unit volume of catalyst. with the boundary condition:

$$l = 0, dC_A/dl = 0 \tag{S7}$$

$$l = L, C_A = C_{As} \tag{S8}$$

The actual reaction rate in the entire crystal plate can be calculated by integrating Eq. (S6), Eq. (S7) and Eq. (S8):

$$R_A = 2 \int_0^L k_V C_A S dl = \frac{th(\lambda L)}{\lambda} 2Sk_V C_{AS}$$
(S9)

When there was no internal diffusion effect,

$$C_A = C_{As} \tag{S10}$$

The intrinsic reaction rate of the plate without the influence of internal diffusion can be calculated by

$$R_{As} = 2SLk_V C_{As} \tag{S11}$$

Substitute Eq. (S9) and Eq. (S11) into Eq. (S5) to calculate

$$\eta = \frac{th(\phi_L)}{\phi_L} = \frac{th(10\lambda)}{10\lambda}$$
(S12)

The Thiele modulus of the L/HY catalyst can be denoted by $\Phi_{\rm L}$

$$\phi_L = \lambda L = L \sqrt{k_V / D_e} = 10\lambda \tag{S13}$$

C/HY crystal was treated as a sphericity, where the average radius was 375 nm, reactant concentration distribution differential equation can be calculated by:

$$\frac{d^2 C_A}{dl^2} + \frac{2dC_A}{l \ dl} = \lambda^2 C_A \tag{S14}$$

with the boundary condition:

$$l = 0, dC_A/dl = 0 \tag{S15}$$

$$l = R, C_A = C_{As} \tag{S16}$$

According to L/HY calculation method, η can be obtained

$$\eta = \frac{1}{\phi_c} \left[\frac{1}{th(3\phi_c)} - \frac{1}{3\phi_c} \right] = \frac{1}{125\lambda} \left[\frac{1}{th(375\lambda)} - \frac{1}{375\lambda} \right]$$
(S17)

Where, the thiele modulus of the C/HY catalyst can be denoted by $\Phi_{\rm C}$

$$\phi_C = \frac{R}{3} \sqrt{k_V / D_e} = \frac{R}{3} \lambda = 125\lambda \tag{S19}$$

S4. Table S2. The results of phenanthrene hydrocracking over the regenerative 10%

Ni-C/HY and 10% Ni-C/HY samples.

Catalyst	Conversion (%)	BTX selectivity (%)	BTX yield (%)
Regenerative 10% Ni-C/HY	79.6	54.5	43.4
Regenerative 10% Ni-L/HY	96.8	73.1	70.8

Conversion: Phenanthrene conversion; BTX: BTX aromatics. The reaction data were

obtained at the time-on-stream of 1.0 h.

Supporting References

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