Electronic Supplementary Material

Catalyst particle shapes and pore structure engineering for hydrodesulfurization and hydrodenitrogenation reactions

Yao Shi[1]*, Zhao Li[1]*, Changfeng Yang[1], Zhanlin Yang[2], Zhenhui Lv[2], Chong Peng[2], Baolian Su[3],Weikang Yuan[1], Xinggui Zhou[1], Xuezhi Duan (✉)[1]

1 State Key Laboratory of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, China

2 Dalian Research Institute of Petroleum and Petrochemicals, SINOPEC, Dalian 116045, China

3 Laboratory of Inorganic Materials Chemistry, University of Namur, B-5000 Namur, Belgium

E-mail: xzduan@ecust.edu.cn

* These authors contributed equally to this work.

Table S1 Variables of simulation for HDS and HDN process

Variable	Symbol	Formula
Temperature dependence of liquid density	$\Delta\rho_P$	$\Delta\rho_p=\left(0.167+16.181\times10^{-0.0425\rho_0}\right)\frac{P}{1000}-0.01\left(0.229+263\times10^{-0.0603\rho_0}\right)\left(\frac{P}{1000}\right)^2$
Pressure dependence of liquid density	$\Delta\rho_T$	$\Delta\rho_T=\left[0.0133+152.4(\rho_0+\Delta\rho_p)^{-2.45}\right](T-520)-\left[8.1\times10^{-6}-0.0622\times10^{-0.764(\rho_0+\Delta\rho_p)}\right](T-520)^2$
Density of gas oil	ρ_L	$\rho_L=\rho_0+\Delta\rho_p-\Delta\rho_T$
Dimensionless number of Glaso's correlation	a	$a=10.313\left[\log_{10}(T-460)\right]-36.447$
API gravity	API	$API=\frac{141.5}{\rho_{15.6}}-131.5$
Viscosity of gas oil	μ_L	$\mu_L=3.141\times10^{10}(T-460)^{-3.444}\left[\log_{10}(API)\right]^a$

Diffusion Coefficient	De_i	$De_i = \frac{\varepsilon}{\tau}\left(\frac{1}{(1/D_i^L)+(1/D_{K,i})}\right)$
Catalyst tortuosity	τ	$\tau = 1 - \frac{1}{2}\log\varepsilon$
Catalyst porosity	ε	$\varepsilon = \exp\left(-\frac{4}{3}\pi n_1 a_1^3\right)$
Surface area per unit volume	σ	$\sigma = 4\pi\varepsilon n_1 a_1^2$
Surface area per unit mass	S	$S = \frac{\sigma}{\rho_{cat}}$
Pore diameter	d_{pore}	$d_{pore} = \frac{1}{\pi n_1 a_1^2}$
Knudsen diffusion coefficient	$D_{K,i}$	$D_{K,i} = 48.5 d_{pore}\left(\frac{T}{M_W}\right)^{0.5}$
Molecular diffusion coefficient	D_i^L	$D_i^L = 8.93\times10^{-12}\frac{\upsilon_L^{0.267}T}{\upsilon_i^{0.433}\mu_L}$
Liquid molar volume	υ_L	$\upsilon_L = 0.285\left(\upsilon_c^L\right)^{1.048}$
Critical molar volume of liquid	υ_c^L	$\upsilon_c^L = 7.5214\times10^{-3}T_{MeABP}^{0.2896}\rho_{15.6}^{-0.7666}M_w$
Molar volume of gas	υ_i	$\upsilon_i = 0.285\upsilon_c^{1.048}$ （i=H_2, H_2S）
Density of catalyst	ρ_{cat}	$\rho_{cat} = \rho_s(1-\varepsilon)$

Mesh sensitivity analysis

Unstructured tetrahedral meshes are employed to mesh fluid and solid domains of single catalyst particle model. Two boundary layers are added to the inner and outer surfaces of the particle and reactor. The stretch factor and thickness adjustment factor are set as 1.2 and 5, respectively. In order to ensure the accuracy of the model, the mesh sensitivity analysis based on the trilobe catalyst particle was performed as shown in Table S2 and Fig. S1.

Table S2 Mesh sensitivity analysis

Mesh	Number of elements*10^{-5}	Average reaction rate (mol/m^3/s)
Mesh1	6.2	41.59
Mesh2	7.2	41.23
Mesh3	8.0	41.09
Mesh4	9.2	40.96
Mesh5	11.3	40.79
Mesh6	13.0	40.73
Mesh7	15.4	40.69
Mesh8	16.2	40.66
Mesh9	25.8	40.60

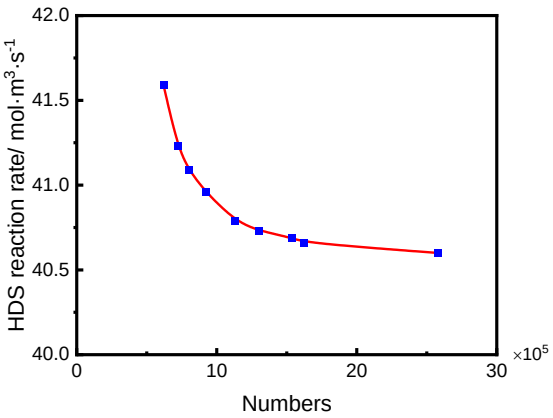

Fig. S1 HDS reaction rate as a function of number of elements

Two-dimensional (2-D) reactor model

The scheme diagram of 2-D reactor model is illustrated in Fig. S2. The height of the reactor is 25.2 cm, and the diameter of the reactor is 2.54 cm. The particle parameter is shown in Table 1. The particle model is coupled to the reactor model by particle-reactor interface. The momentum, mass and energy conservation equations are applied in the fluid domain, and the mass and energy conservation equations as well as HDS/HDN reactions are applied in the particle domain. The detailed equations and corresponding boundary conditions are the same as that applied in single-particle model as described in paragraph 2.3 (Governing equations) in the manuscript.

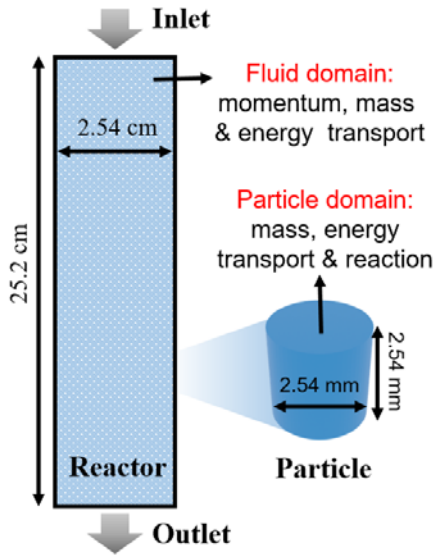

Fig. S2 Scheme diagram of 2-D reactor model

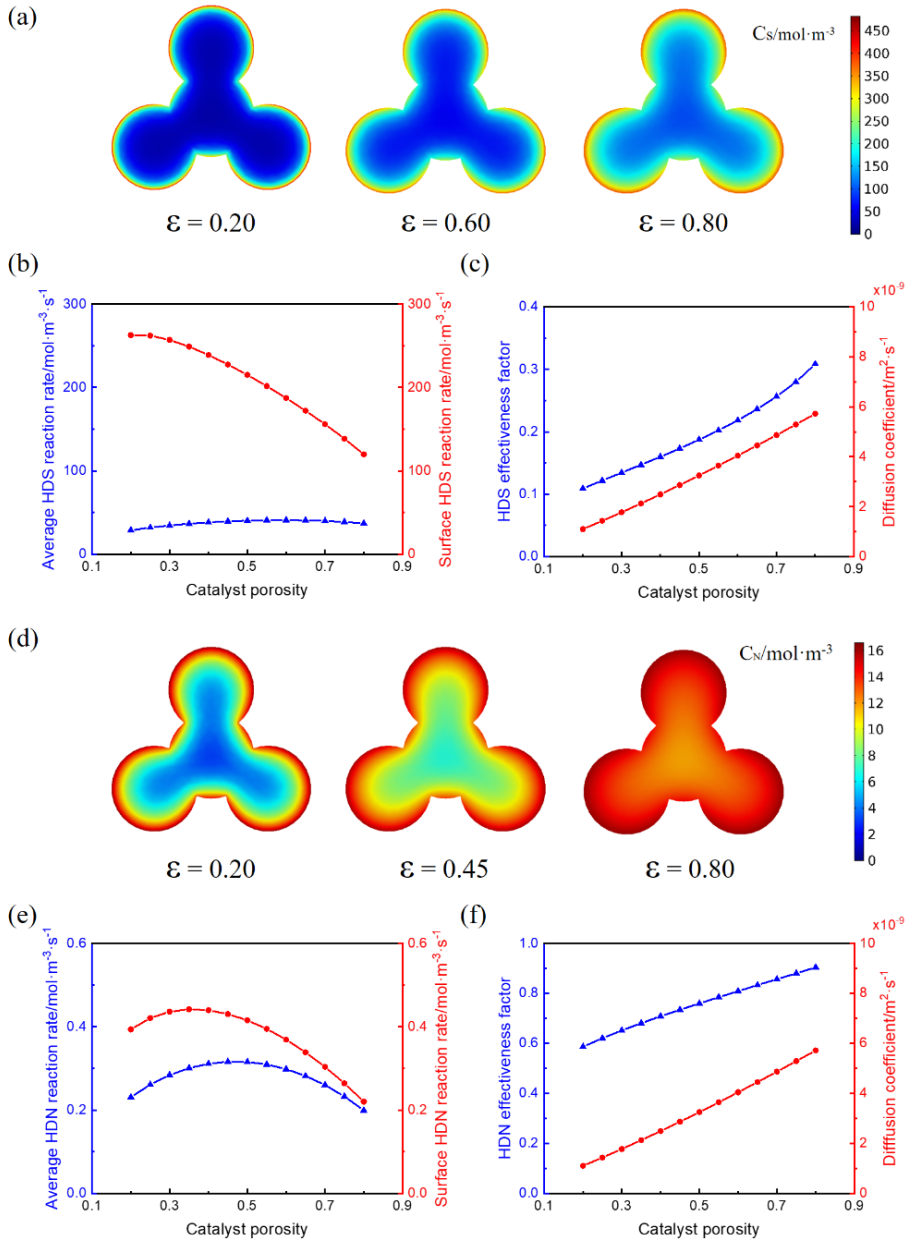

Fig. S3 (a) Concentration distribution of sulfur-containing compounds within trilobe catalyst particle with different porosity, (b) Average and surface HDS reaction rate, and (c) HDS effectiveness factor and diffusion coefficient with respect to porosity, (d) Concentration distribution of nitrogen-containing compounds within trilobe catalyst particle with different porosity (e) Average and surface HDN reaction rate, and (f) HDN effectiveness factor and diffusion coefficient with respect to porosity