Supplementary Information

Single event kinetic modeling for paraffin hydrocracking over an industrial Ni-W silica-aluminum catalyst

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(1) The elimination of the external diffusion

The method of eliminating the external diffusion[1] is as following:

We checked the reactant conversion by varying the catalyst loading (1.55g and 2.33g, respectively), in which H_2/C_8 ratio changed from 200 to 1000. The external diffusion experiments were performed at 654K (the highest temperature in the whole experimental points). The conversion of C_8 was higher than 90% at this condition, and the conversion decreased slightly with the increasing H_2/C_8 ratio. When the H_2/C_8 ratio $\geqq 400$, the two conversion lines overlapped (see in Fig. S1). We assumed that the influence of external diffusion could be eliminated at H_2/C_8 ratio ≥ 400 and the kinetic experimental data were collected accordingly.
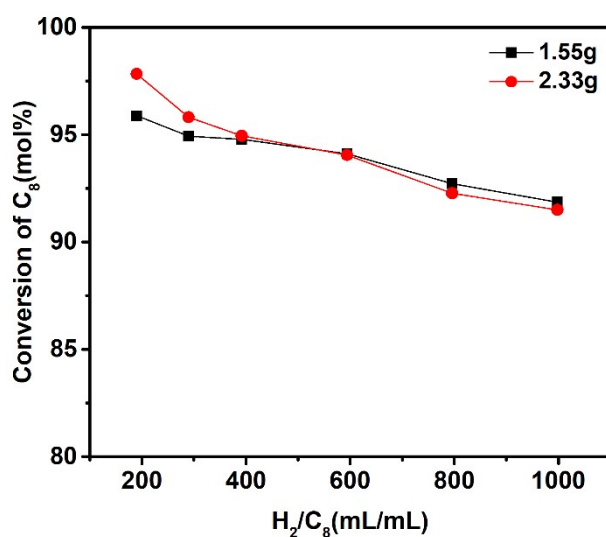

Fig. S1. C_8 Conversion as a function of H_2/C_8 ratio with two different catalyst loadings (reaction condition: T=654K, p=5.0MPa, LHSV=3.0h^{-1})

(2) The internal diffusion estimation

The internal diffusion limitation was checked by the Weisz−Prater criterion (C_{WP}).[2,3]

$$C_{WP} = \frac{r_{obs}\rho_c R_p^{\,2}}{D_e C_s} < 1$$

Where r_{obs} = observed reaction rate, mol/kg cat./s

ρ_c = density of the catalyst, kg/m³

R_p = radius of the catalyst particle, m

D_e = effective diffusivity, m²/s

C_s = concentration of the component at the external surface of catalyst, mol/m³

C_s was calculated in terms of the following equation:

$$C_s = C_0 = \frac{N_{oct}}{V} = \frac{P_{oct}}{RT}$$

Where P_{oct} = the pressure of n-octane, Pa

T= reaction temperature, K

R= universal gas constant, 8.314 J/mol/K

The effective diffusion coefficient D_e is calculated as following:

$$D_e = \frac{1}{\dfrac{1}{D_k} + \dfrac{1}{D_{AB}}}$$

D_k is the Knudsen diffusivity, m²/s and D_{AB} is the molecular diffusivity, m²/s

$$D_k = \frac{\overline{v}l}{3}$$

$$D_{AB} = \frac{0.001T^{1.75}(\dfrac{1}{M_A} + \dfrac{1}{M_B})^{0.5}}{(P/0.101325)\left[(\sum V)_A^{1/3} + (\sum V)_B^{1/3}\right]^2}$$

Where l = the pore diameter of the catalyst (6 nm, from BJH desorption branch).

$\overline{v}$ = the average velocity of the molecular, m/s

P = reaction pressure, MPa;

$(\sum V)_A$ and $(\sum V)_B$ = molecular diffusion volumes of components A and B, cm^3, respectively.[4]

M_A and M_B = molecular weights of components A and B, respectively, g/mol.

Here, components A and B stand for H_2 and n-octane, respectively.

D_{AB} and D_k are of the same magnitude by calculation, pore diffusion belongs to the transition zone diffusion.

The average velocity of the molecule can be calculated as following:

$$\overline{v} = \sqrt{\frac{8k_bT}{\pi m}} = \sqrt{\frac{8RT}{\pi M}}$$

Where M = The molecular weight of the molecule, kg/mol

In hydrocracking of n-octane, the maximum observed reaction rate is 6.20×10^{-3} mol/kg cat./s at reaction temperature 654K.

ρ_c =950kg/m^3

R_p =1.25×10^{-4}m

D_e =5.3×10^{-7} m^2/s

C_s =134.65mol/m^3

Therefore, $C_{WP} = \dfrac{r_{obs}\rho_c R_p^{\ 2}}{D_e C_s}$ = [(6.20×10^{-3}mol/kg   cat./s)×(950kg/m^3)×(1.25×10^{-4}m)^2]/[(5.3×10^{-7} m^2/s)×134.65mol/m^3]=1.29×10^{-3} << 1

C_{WP} value is far less than 1 at current experimental situations. The effect of internal diffusion is negligible.

(3) β-scission reaction of various carbenium ions

We obeyed the carbenium ion reaction principles developed over the last few decades in our computer-aided reaction network generation. The proposed β-scission mechanism suggested that linear paraffins may undergo several steps of isomerization until a configuration is attained that is favorable to β-scission.

As early as 1985, Planelles et.al. confirmed that the energy barrier in β-scission of a linear secondary carbenium ion (form a primary carbenium ion and an olefin species) was at least 50 kcal/mol, but the value of β-scission of a branched carbenium ion was only 30 kcal/mol.[5] Guillaume in IFP reported that the relative rate in β-scission of a linear secondary carbenium ion to form a primary carbenium ion is nearly 0, compared with the rates in forming secondary and tertiary carbenium ions by β-scission of branched carbenium ions.[6] Therefore, the linear secondary carbenium ions were not considered in β-scission, viz type D in Fig. S2. All the other possible mono-, di- and tri- branched carbenium ions were considered in β-scission, viz examples like type A, B and C Fig. S2.
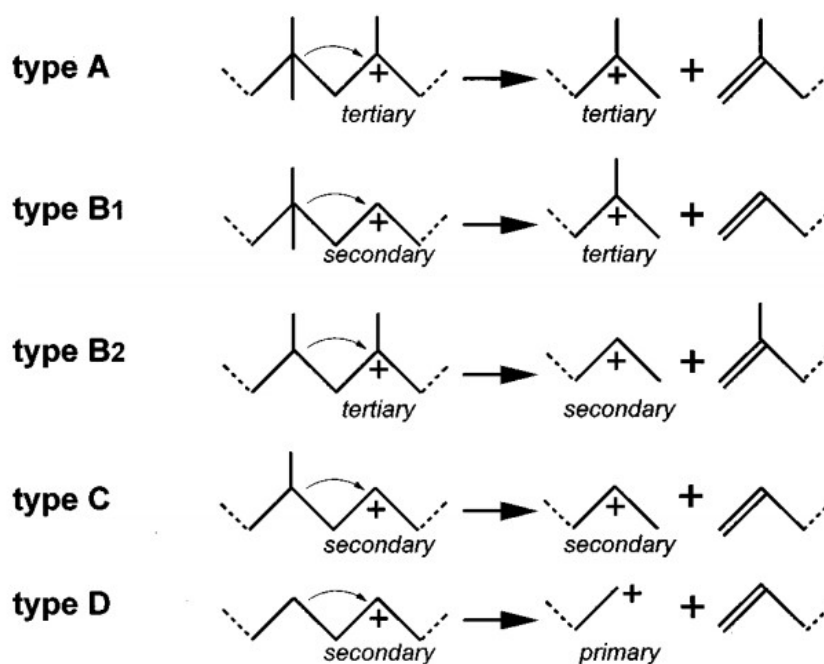

Fig. S2. β-scission of various carbenium ions

(4) Mass balance of the experimental points

The detailed experimental condition, conversion and mass balance information of the experimental data used for kinetic parameter estimation were listed in Table S1.

Table S1. Information of the experimental points used for parameter estimation

Exp. points	T (K)	Pressure (MPa)	LHSV (h⁻¹)	Inlet C_8 (ml/h)	Inlet H_2 (ml/h)	H_2/oil (v./v.)	Conv. (%)	Mass balance (%)
1	573	5.0	3.0	9.0	7200.0	800	5.9	96
2	603	5.0	3.0	9.0	7200.0	800	17.9	96
3	611	5.0	3.0	9.0	7200.0	800	25.1	96
4	618	5.0	3.0	9.0	7200.0	800	29.3	97
5	627	5.0	3.0	9.0	7200.0	800	52.1	95
6	636	5.0	3.0	9.0	10800.0	1200	69.1	93
7	636	5.0	4.0	12.0	9600.0	800	55.1	98
8	636	5.0	3.0	9.0	7200.0	800	71.2	94
9	636	5.0	2.0	6.0	4800.0	800	82.2	96
10	636	5.0	1.0	3.0	2400.0	800	93.7	93
11	636	5.0	3.0	9.0	5400.0	600	72.4	96
12	636	5.0	3.0	9.0	3600.0	400	76.4	95
13	636	8.0	3.0	9.0	7200.0	800	58.6	98
14	636	6.5	3.0	9.0	7200.0	800	66.1	96
15	636	5.0	3.0	9.0	9000.0	1000	68.4	94
16	636	3.5	3.0	9.0	7200.0	800	78.5	96
17	636	2.0	3.0	9.0	7200.0	800	83.7	96
18	645	5.0	3.0	9.0	7200.0	800	84.5	94
19	654	5.0	3.0	9.0	10800.0	1200	89.8	90
20	654	5.0	3.0	9.0	9000.0	1000	91.5	92
21	654	5.0	3.0	9.0	7200.0	800	92.3	92
22	654	5.0	3.0	9.0	5400.0	600	94.1	88
23	654	5.0	3.0	9.0	3600.0	400	94.9	90

(5) Peclet number calculation in fixed-bed reactor

The axial dispersion coefficient and dimensionless Peclet number in the tubular fixed-bed reactor were estimated in terms of the new empirical correlations developed by Rastegar and Gu, in which both molecular diffusion coefficient and bed voidage were considered in the axial dispersion coefficient estimation.[7] The bed-length-based Peclet number and the axial dispersion coefficient are as follows:

$$Pe_L = \frac{Lu}{\varepsilon_b D_b}$$

$$D_b = 0.7 D_m + \frac{2 R_p v \varepsilon_b}{0.18 + 0.008 \, \mathrm{Re}^{0.59}}$$

Where ε_b = bed voidage;

L= length of the catalyst bed, m;

R_p = catalyst particle radius, m;

u = superficial velocity at reaction conditions, m/s;

D_b= axial dispersion coefficient, m²/s;

D_m= molecular diffusivity, m²/s;

The Reynolds number is calculated as following:

$$\mathrm{Re}_p = \frac{u d_p \rho}{(1 - \varepsilon_b) \mu}$$

Where ρ = density of the fluid, kg/m³;

d_p = catalyst particle diameter, m;

μ = viscosity of the fluid, Pa.s;

The molecular diffusion coefficent D_m can be determined by the following equations:

$$D_m = \frac{1}{3} \bar{v} \lambda$$

$$\bar{v} = \sqrt{\frac{8 k_b T}{\pi m}} = \sqrt{\frac{8 R T}{\pi M}}$$

$$\lambda = \frac{1}{\sqrt{2} \pi d^2 n} = \frac{R T}{\sqrt{2} \pi d^2 P N_A}$$

Where $\bar{v}$ = the average velocity, m/s;

λ = the mean free path in the gas phase;

M = the molecular weight of the species, kg/mol;

d = molecular dynamics diameter, e.g., octane with 4.9×10^{-10} m.[8]

P = reaction pressure, MPa;

In this study, the catalyst bed voidage ε_b is around 0.35, the catalyst bed length L is 30 mm, the catalyst particle diameter d_p is about 0.25 mm. The values of the Peclet number at current reaction conditions (the experimental points in Table S1) were estimated and the results were shown in Fig.S3. The values of the Peclet number at current conditions ranged from 113 to 162. We assumed that the flow regime at current situations could be approximately regarded as ideal plug flow.
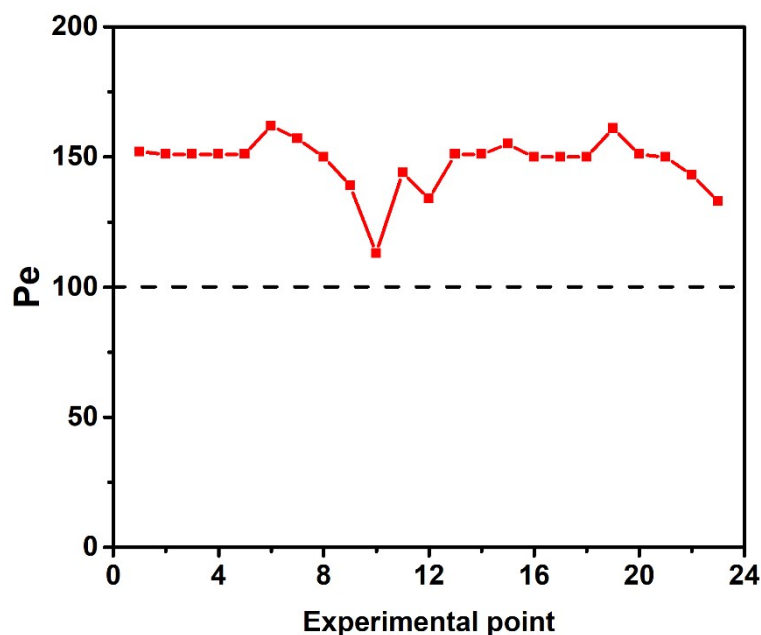

Fig.S3 The values of the Peclet number at current reaction conditions

Reference

1. C. Perego and S. Peratello, *Catal. Today*, 1999, **52**, 133-145.
2. Y. Wang, H.-H. Liu, S.-Y. Wang, M.-F. Luo and J.-Q. Lu, *J.Catal.*, 2014, **311**, 314-324.
3. W.-S. Lee, Z. Wang, R. J. Wu and A. Bhan, *J.Catal.*, 2014, **319**, 44-53.
4. E. N. Fuller, P. D. Schettler and J. C. Giddings, *Ind. Eng. Chem. Res.*, 1996, **58**, 18–27.
5. J. Planelles, J. Sánchez-Marin, F. Tomás and A. Corma, *J. Chem. Soc.*, 1985, 333-340.
6. D. Guillaume, *Ind. Eng. Chem. Res.*, 2006, **45**, 4554-4557.
7. S. O. Rastegar and T. Gu, *J. Chromatogr A*, 2017, **1490**, 133-137.
8. F. Jiménez-Cruz and G. C. Laredo, *Fuel*, 2004, **83**, 2183-2188.