

Temperature Sensitive Synthesis of γ -Al₂O₃ Support with different Morphologies for CoMo/ γ -Al₂O₃ Catalysts towards Hydrodesulfurization of Thiophene and 4,6-Dimethyldibenzothiophene

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SUPPORTING INFORMATION

Captions

SI 1. Test for external mass transport limitation.

SI 2. Figure S1. Relationships between conversion and H₂/oil ratio.

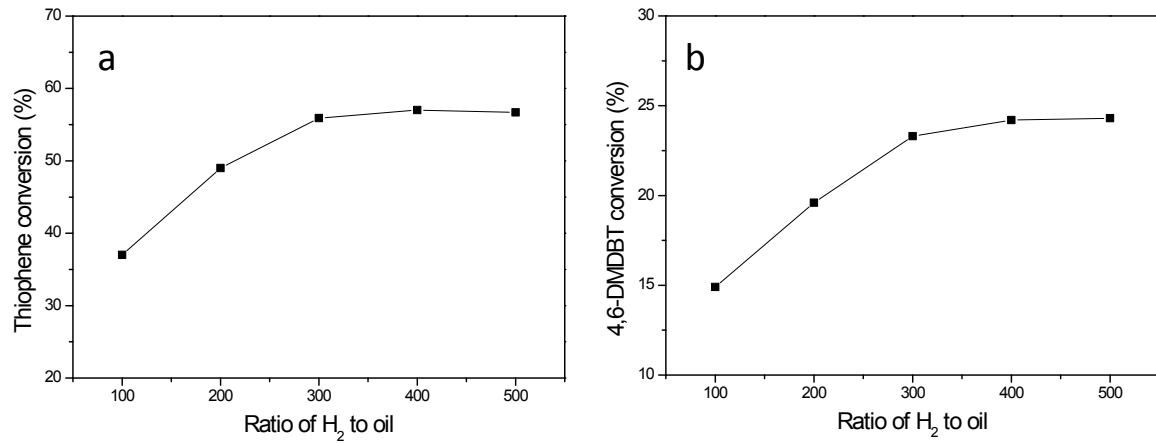
SI 3. Weisz-Prater Criterion for Internal Diffusion.

SI 4. Calculation of the crystalline aggregation ratio.

SI 5. Analysis of products from the conversion of 1-hexene.

SI 1. Test for external mass transport limitation:

To evaluate the external mass transport limitation during HDS reaction, the HDS reaction using CoMo/CA as catalyst with different H₂/oil ratios were tested (Fig. S1). Finally, we found that once the H₂/oil ratio was higher than 300, the conversions of thiophene and 4,6-DMDBT did not have a obvious difference (Fig. S1). Considering this, we chose 400 as the H₂/oil ratio for the formal HDS reaction, it could be concluded that the external mass transport limitation could be neglected.



SI 2. Figure S1 Relationships between conversion and H₂/oil ratio: (a) HDS of a mixture of thiophene and n-hexene-1 (220 °C); (b) HDS of 4,6-DMDBT (300 °C)

SI 3. Weisz-Prater Criterion for Internal Diffusion:

If
$$C_{WP} = \frac{-r_{(obs)}\rho_c R^2}{D_e C_s} < 1$$
, then internal mass transfer effects can be neglected.

$-r_{(obs)}$ = observed HDS reaction rate, kmol/kg-cat·s

R = catalyst particle radius, m

ρ_c = solid catalyst density, kg/m³

D_e = effective liquid-phase diffusivity of H₂, m²/s

= 0.1D (according to the calculation method of Crezee et al.), where

D = liquid-phase diffusivity of H₂, m²/s

C_s = concentration of H₂ at the catalyst surface, kmol /m³

For HDS of a mixture of thiophene and n-hexene-1:

$$C_{WP} = \frac{-r_{(obs)}\rho_c R^2}{D_e C_s} = (1.57 \times 10^{-8} \text{ kmol/kg-cat}\cdot\text{s}) \times (500 \text{ kg/m}^3) \times (4.25 \times 10^{-4} \text{ m})^2 / [(3.23 \times 10^{-10} \text{ m}^2/\text{s}) \times (0.478 \text{ kmol/m}^3)] = 9.2 \times 10^{-3} < 1$$

So, it can be concluded that the internal mass transfer effects in HDS of a mixture of thiophene and n-hexene-1 can be neglected.

For HDS of 4,6-DMDBT:

$$C_{WP} = \frac{-r_{(obs)}\rho_c R^2}{D_e C_s} = (1.18 \times 10^{-8} \text{ kmol/kg-cat}\cdot\text{s}) \times (500 \text{ kg/m}^3) \times (4.25 \times 10^{-4} \text{ m})^2 / [(45.84 \times 10^{-10} \text{ m}^2/\text{s}) \times (0.406 \text{ kmol/m}^3)] = 5.7 \times 10^{-4} < 1$$

So, it can be concluded that the internal mass transfer effects in HDS of 4,6-DMDBT can be neglected.

To avoid the influence of internal diffusion, the Weisz-Prater criterion was calculated with the “worst-case”, which made a largest C_{WP} value (we assumed that all thiophene/4,6-DMDBT were converted).

SI 4. Calculation of the crystalline aggregation ratio.

The crystalline aggregation ratios of the γ -Al₂O₃ products are calculated according to the following equation [1]:

$$\text{crystalline aggregation ratio} = \frac{SA_{theor}}{SA_{BET}}$$

where SA is surface area ($\text{m}^2 \text{g}^{-1}$) and $SA_{theor} = 6000/(\rho_{\gamma\text{-Al}_2\text{O}_3} \times D)$ ($\rho_{\gamma\text{-Al}_2\text{O}_3} = 3.65 \text{ g cm}^{-3}$, the theoretical density of the $\gamma\text{-Al}_2\text{O}_3$ phase, and D is the average crystalline size (nm) derived from the X-ray diffraction data by the Debye-Scherrer formula).

SI 5. Analysis of products from the conversion of 1-hexene.

Detailed analysis of products from the hydrogenation and isomerization of 1-hexene over CoMo/ACH catalyst with the heptane solution containing 10 % 1-hexene and 1000 ppm thiophene by using GC-MS Instrument ^a.

product	Content (%)
1-hexene	8.11
2-hexene	0.07
3-hexene	0.14
n-hexane	1.62
2-methyl-pentane	0.06
3-methyl-pentane	0.05
n-heptane (solvent)	89.95

a Reaction conditions: P = 2.0 Mpa, T = 220 °C, LHSV = 4.76h⁻¹, and H₂/feed ratio=400/1 (v/v).

To verify the main reaction for 1-hexene conversion, GC-MS instrument was used to analyze the product. The result showed that more than 85 % product were n-hexane and more than 91 % product were alkane, which indicated that hydrogenation was the mainly reaction. So the conversion of 1-hexene could be regarded as the hydrogenation (HYD) conversion of 1-hexene.

1. R. Vidruk, M. V. Landau, M. Herskowitz, V. Ezersky and A. Goldbourt, *J. Catal.*, 2011, **282**, 215-227.