Temperature Sensitive Synthesis of $\gamma$-Al$_2$O$_3$ Support with different Morphologies for CoMo/$\gamma$-Al$_2$O$_3$ 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 H$_2$/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 H$_2$/oil ratios were tested (Fig. S1). Finally, we found that once the H$_2$/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 H$_2$/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 H$_2$/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:

\[ C_{WP} = \frac{-r_{(obs)} \rho_c R^2}{D_e C_s} < 1 \]

If \( C_{WP} < 1 \), then internal mass transfer effects can be neglected.

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

\( R \) = catalyst particle radius, m

\( \rho_c \) = solid catalyst density, kg/m$^3$

\( D_e \) = effective liquid-phase diffusivity of H$_2$, m$^2$/s

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

\( D \) = liquid-phase diffusivity of H$_2$, m$^2$/s

\( C_s \) = concentration of H$_2$ at the catalyst surface, kmol/m$^3$
For HDS of a mixture of thiophene and n-hexene-1:

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

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:

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

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 \(\gamma\)-Al\(_2\)O\(_3\) products are calculated according to the following equation [1]:
crystalline aggregation ratio = \frac{SA_{theor}}{SA_{BET}},

where SA is surface area (m\(^2\) g\(^{-1}\)) and SA_{theor} = \frac{6000}{(\rho_{\gamma-Al_2O_3} \times D)} (\rho_{\gamma-Al_2O_3} = 3.65 \text{ g cm}^{-3}, the theoretical density of the \gamma-Al_2O_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.

<table>
<thead>
<tr>
<th>product</th>
<th>Content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-hexene</td>
<td>8.11</td>
</tr>
<tr>
<td>2-hexene</td>
<td>0.07</td>
</tr>
<tr>
<td>3-hexene</td>
<td>0.14</td>
</tr>
<tr>
<td>n-hexane</td>
<td>1.62</td>
</tr>
<tr>
<td>2-methyl-pentane</td>
<td>0.06</td>
</tr>
<tr>
<td>3-methyl-pentane</td>
<td>0.05</td>
</tr>
<tr>
<td>n-heptane (solvent)</td>
<td>89.95</td>
</tr>
</tbody>
</table>

a Reaction conditions: P = 2.0 Mpa, T = 220 °C, LHSV = 4.76 h\(^{-1}\), and H\(_2/\text{feed}\) 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.