Pore size effect of mesoporous support on metal particle size of Co/SiO2 catalyst in Fischer-Tropsch synthesis

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ABSTRACT
Fischer Tropsch (FT) synthesis is an alternative route to produce ultrahigh pure hydrocarbon fuels. The length of hydrocarbon chain produced from FT synthesis taking place over the cobalt supported catalysts is depended upon the reactant and product diffusion as well as the metal particle size of the catalyst. Some works were reported that the pore size diameter of the support can control the metal dispersion. Therefore, the pore size can be considered as an important parameter for supported FT catalysts. This work aims to study the effect of pore size of mesoporous silica on metal particle size of cobalt-based catalysts and FT performance. The synthesized silica with the average pore size diameter of 7.2 nm and the commercial silica with the average diameter of 6.7 nm were used as supports to prepare CS catalyst samples. The cobalt supported on synthesized SiO2 shows larger cobalt oxide particle with lower dispersion compared to the results of the catalyst prepared using the commercial silica. Large cobalt oxide particle of supported catalyst decreases the interaction between metal and support which results in the increasing reducibility of cobalt oxide species and provides large cobalt metal particle after the reduction process. The FT tests were carried out under atmospheric pressure at 220 °C, GHSV of 300 h⁻¹ and H2/CO feed ratio of 2. The enhancement of selectivity towards long chain hydrocarbons (C₇⁺) and FT activity were obtained from the catalyst with larger cobalt particle size. The growth of hydrocarbon chain during polymerization can be facilitated by the large surface of active site formed in the large pore size of support. Thus, the pore size diameter of support is an important key for the FT catalytic performance of cobalt catalyst supported on mesoporous silica materials.

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1. Introduction

Among the textural properties, the pore size diameter of the support is one of the key factors that affect the size of the cobalt oxide particles (also the cobalt metal particle after activation), the mass transfer of reactants and products, the re-adsorption of the α-alkene, and the chemisorption ratio of H₂ and CO on the surface of active sites. The different adsorption properties of metal particles located in narrow and wide pores are often employed to explain the effect of pore sizes diameter on reaction rates and selectivity of Fischer-Tropsch (FT) synthesis.

Consequently, the pore size diameter of the support influences the performance of the cobalt catalyst in the FT reaction.

The supports for cobalt-based catalysts have been normally used in FT reaction, including silica, alumina, titanium magnesia and carbon etc. (Sathyamoorthy et al., 2013; Yang et al., 2011). These materials have been considered as candidate supports for cobalt-based catalyst in FT reaction due to their desirable properties such as surface area, and pore size distributions (Cheng et al., 2015; Guo et al., 2009). The support with a smaller pore size diameter enhances the dispersion of cobalt in cobalt-based catalysts but limits the diffusion of syngas and products, thus providing light hydrocarbons. In contrast, the support with a larger pore size
diameter improves the reducibility, favors the diffusion of syngas and products, and thus produces heavy hydrocarbons (Li et al., 2017). Mesoporous silica materials have attracted as supports for metal supported catalysts for FT synthesis because of their high surface area. This property is beneficial to increase the cobalt dispersion, and to enhance pore size distribution from narrow to large pore size, which can well control the cobalt particle size, improve the diffusion of reactants and products in the mesoporous channel, and improve the distributions of hydrocarbon products from the FTS (Liu et al., 2007). For example, the cobalt supported catalyst on mesoporous alumino-silicate with a pore size of 3.4 nm exhibits a selectivity for the C10-C20 fraction as high as 38.5% (Wei et al., 2002).

Thus, the present work has been elucidated the effect of pore size diameter of mesoporous silica support on metal particle size of cobalt based catalysts for FT synthesis. Cobalt supported on two different mesoporous silica materials (synthesized silica and commercial silica) were prepared. The pore structure of the supports and the catalysts were characterized using N2 adsorption measurement. The cobalt particle size and dispersion were identified by X-ray diffraction (XRD), Transmission electron microscopy (TEM) and hydrogen temperature programmed desorption (H2-TPD) techniques. The surface interaction and reducibility of the catalysts were evaluated in hydrogen temperature-programmed reduction (H2-TPR) measurement. The FT tests were carried out in the down-flow fixed bed reactor. The catalytic performance was studied in terms of activity and selectivity toward gasoline-diesel range of hydrocarbon products.

2. Methodology

2.1. Catalyst preparation

The solution of Co(NO3)2·6H2O was added onto the synthesized SiO2 (Ssyn) and commercial SiO2 support (Scom, Davasil Grade 636) using the incipient wetness impregnation method (IWI). The catalyst was dried and calcined in followings. 20% loading of Co supported SiO2 namely, 20%Co/synthesized SiO2 (CSSyn) and 20%Co/commercial SiO2 (CSScom) catalyst was then prepared for the investigation.

2.2. Catalyst characterization

N2 adsorption-desorption of samples were measured to determine total surface area, pore volume and pore size diameter by volumetric sorption instrument (BEL-Japan, BELSORP-mini II). Prior to the analysis, 0.2 g of sample was pretreated by degassing under N2 flow at 350°C for 4 h. The N2 adsorption-desorption measurement was performed under liquid N2 at -196°C.

XRD was applied to identify the cobalt crystallite size and phase of cobalt based catalyst via X-ray powder diffractometer (Bruker, D8 Discover) with monochromatized Cu Kα radiation (40 kV, 40 mA) at 2θ = 0.5 - 80°. The average Co3O4 crystallite size (DCo3O4 XRD) was calculated using the Scherrer equation (Eq. 1). The spherical cobalt crystallites of uniform diameter (dCo) with a site density of 14.6 at/nm2 can be determined using the formula (Eq. 2) reported by Jones and Bartholomew (de la Osa et al., 2016; Jones and Bartholomew, 1988); and the metal dispersion (Dm, XRD) was calculated by Eq. 3 as follows:

\[ D_{\text{Co3O4,XRD}} = \frac{k\lambda}{B \cos \theta} \] (1)

\[ d\text{Co} = 0.75D_{\text{Co3O4,XRD}} \] (2)

\[ D_{\text{m,XRD}} = \frac{96}{d\text{Co}} \] (3)

where k is a dimensionless shape factor, λ is X-Ray wavelength, B is line broadening at half the maximum intensity in radians, and θ is Bragg angle.

TEM images were obtained from a TEM instrument (Jeol JEM-2010) operated at 200 kV. The sample was deposited as a dry powder on a thin carbon film mounted on a copper grid.

H2-TPD was employed to determine the metal dispersion and metal size on the support surface. In the H2-TPD experiment, 0.05 g of calcined catalyst was pre-reduced in H2 flow. The sample was then cooled down to 100°C in Ar flow. Subsequently, the hydrogen chemisorption was performed for 0.5 h at 100°C. Finally, H2 desorption was measured in the temperature range of 40°C to 500°C under Ar flow using TCD detector installed in chemisorption analyzer (BEL-Japan, BELCAT-B). Metal dispersion and metal particle size were calculated using Eq. 4 and Eq. 5:

\[ \%D_{\text{m}} = \frac{[V_{\text{chem}}/22414xSFxMW(/[m\text{x}p]/100)]\times100}{(Am x \rho x 10^6)} \] (4)

\[ \text{Size of metal particle} = 6/(Am \times \rho \times 10^6) \times 10^{-9} \] (5)

where %Dm is percent of metal dispersion, Vchem is amount of adsorption (cm3), m is sample weight (g), p is weight percent of supported metal content (wt%), MW is molar mass of metal, SF is stoichiometry factor (number of metal atom per molecule of adsorbed hydrogen) which the Co atom/molecule of H2 is 2 and Am, is area per gram of active metal and ρ is density of active metal.

The reducibility and the reduction temperature of catalyst were evaluated by H2-TPR technique. Prior to the H2-TPR test, 0.2 g of sample was pretreated at 220°C in the flow of inert gas. Then, 5%H2/Ar gas was introduced to the catalyst before the temperature was programmed from room temperature to 900°C. H2 consumption due to the reduction was investigated by gas chromatograph (Agilent, GC 6820) equipped with a TCD detector.

2.3. Catalytic tests

FT reaction was carried out in a down-flow fixed-bed reactor employed 1.0 g of the calcined catalyst
(diluted with silica powder). Before the reaction operation, the catalyst was reduced in-situ in H₂ flow at 500°C for overnight. Subsequently, the catalyst bed was cooled down to the reaction temperature of 220°C in a flow of inert gas. Then, the FT reaction was performed for 24h under atmospheric pressure in a flow of syngas at GHSV 300 h⁻¹ using H₂/CO feed ratio of 2. Effluent gases were detected by on-line gas chromatograph (Bruker, GC 450-valve) using FID and TCD detector. The liquid product was collected in a cold trap and analyzed by gas chromatograph (Bruker, GC430). The activity, selectivity and CO conversion of FT catalyst have been determined.

3. Results and discussion

Total surface area (Sₜᵉᵗ), total pore volume (TPV) and mean pore diameter (MPD) of silica supports and cobalt supported catalysts are summarized in Table 1. The total surface area of S_syn is not significantly different with S_com.

Table 1: Physical properties of SiO₂ supports and cobalt supported catalysts

<table>
<thead>
<tr>
<th>Sample</th>
<th>S_BET (m²/g)</th>
<th>TPV (cm³/g)</th>
<th>MPD (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S_syn</td>
<td>474</td>
<td>0.85</td>
<td>7.17</td>
</tr>
<tr>
<td>C_Syn</td>
<td>327</td>
<td>0.61</td>
<td>7.53</td>
</tr>
<tr>
<td>S_com</td>
<td>481</td>
<td>0.80</td>
<td>6.72</td>
</tr>
<tr>
<td>C_Scom</td>
<td>362</td>
<td>0.57</td>
<td>6.34</td>
</tr>
</tbody>
</table>

The total surface area and total pore volume of C_Syn and C_Scom catalysts decrease compared to the support. This is due to the pores blocking by cobalt species during catalyst impregnation (Khodakov et al., 2002).

The N₂ adsorption and desorption isotherms and the pore size distribution (PSD) of silica supports and cobalt supported catalysts are displayed in Fig. 1. All isotherms represent a type IV according to IUPAC classification (Brunauer et al., 1940) with H1 type of hysteresis loop indicating a mesoporous material (Khodakov et al., 2002; Yang et al., 2011). PSD of supports and catalysts were calculated by BJH method. The PSD curve of S_syn support shows broad peak in the wide range of pore diameter from 2 nm to 25 nm which indicates a non-uniform mesopore structure. The S_com support has a narrow pore diameter distribution in the range of 2-10 nm which refers to a more uniform mesopore structure with smaller pore size compared to S_syn.

XRD patterns of C_Syn and C_Scom (Fig. 2) indicate the presence of Co₃O₄ phase. The cobalt oxide average crystalline size (D_co3o4_XRD), cobalt crystalline size (d_Co₀) and cobalt crystalline dispersion (D_m_XRD) examined by XRD technique are reported in Table 2. The Co₃O₄ average crystalline and cobalt crystalline size of C_Syn catalyst are slightly larger than that of C_Scom catalyst, leading to low metal dispersion of C_Syn catalyst. These results disclose that larger Co₃O₄ crystallites are formed in wider pores of synthesized silica support (Khodakov et al., 2002).

Table 2: Particle size of cobalt metal and cobalt oxide calculated by XRD, H₂-TPD and TEM technique

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>D_co3o4_XRD (nm)</th>
<th>d_Co₀ (nm)</th>
<th>D_m_XRD (%D)</th>
<th>Co₀ particle size (nm)</th>
<th>Co dispersion (%)</th>
<th>D_co3o4_TEM (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_Syn</td>
<td>18.0</td>
<td>13.5</td>
<td>7.11</td>
<td>26.47</td>
<td>3.77</td>
<td>5.6</td>
</tr>
<tr>
<td>C_Scom</td>
<td>14.4</td>
<td>10.8</td>
<td>8.89</td>
<td>14.06</td>
<td>7.09</td>
<td>6.0</td>
</tr>
</tbody>
</table>

* Calculated by XRD using equations, D_co3o4_XRD = (kλ/B cos θ), d(Co₀) = 0.75D and %D = 96/d(Co₀); * Estimated by H₂-TPD technique; * Determined from randomly selected particle in the TEM images

Fig. 1: Nitrogen adsorption-desorption isotherms and pore size distribution (BJH) curves of SiO₂ supports and cobalt supported catalysts
The cobalt particle size and cobalt dispersion determined by H\textsubscript{2}-TPD technique. The results, reported in Table 2, are in agreement with the XRD results. The CS\textsubscript{syn} catalyst shows the larger cobalt particle size with lower cobalt dispersion compared to CS\textsubscript{com} catalyst.

![Fig. 2: The XRD pattern of cobalt supported catalyst](image)

![Fig. 3: TEM images and particle distribution of cobalt oxide of cobalt supported catalysts](image)

TEM images and particle size distribution (PSD) of CS\textsubscript{syn} and CS\textsubscript{com} catalysts are shown in Fig. 3. The average particle size of CS\textsubscript{syn} and CS\textsubscript{com} catalyst is not significant different, which the values are 5.6 and 6.0 nm, respectively. The TEM images reveal that Co\textsubscript{3}O\textsubscript{4} particles favor to aggregate into Co\textsubscript{3}O\textsubscript{4} cluster. The Co\textsubscript{3}O\textsubscript{4} cluster size of CS\textsubscript{syn} is larger than that in CS\textsubscript{com}. The result was found in the same trend as XRD result. Moreover, the aggregation of Co\textsubscript{3}O\textsubscript{4} particle occurs on the catalyst surface and partly penetrates through inner pores of the support resulting in the decrease of surface area and pore size distribution. This is also confirmed by the results obtained from N\textsubscript{2} adsorption-desorption isotherms and pore size distribution from BJH curves in Fig. 1.

H\textsubscript{2}-TPR profiles of cobalt supported catalysts (CS\textsubscript{syn} and CS\textsubscript{com}) are illustrated in Fig. 4. The profiles exhibit several hydrogen consumption peaks for the reduction. Overlapping peaks observed could be corresponded to the different cobalt oxide reduction steps. The deconvolution of overlapping peaks was performed to separate the reduction peak assigned to Co\textsubscript{3}O\textsubscript{4}, CoO\textsubscript{x} (including CoO) and Co-SiO\textsubscript{2} as α, β, and γ species, respectively. The first sharp peak observed in the temperature range from 200-320 °C could be assigned to the partial reduction of Co\textsubscript{3}O\textsubscript{4} to CoO\textsubscript{x}, and the second broad reduction peak found in the temperature higher than 320 °C could be ascribed to the reduction of CoO\textsubscript{x} to Co\textsubscript{0}. The third broad peak at temperatures above 650 °C could be probably assigned to cobalt silicate species, which is more difficult to be reduced.

![Fig. 4: H\textsubscript{2}-TPR profiles of cobalt supported catalysts](image)

H\textsubscript{2}-TPR results show that the first peak of both catalysts presents a similar profile. However, the second peak of CoO\textsubscript{x} species reduction shows the different figure. The second peak profile of CS\textsubscript{com} shown as overlapped peak is wider than that of CS\textsubscript{syn} catalyst. It could be suggested that there are many different CoO\textsubscript{x} species, which are reduced at different temperature region. Moreover, the third peak obviously appears for CS\textsubscript{com} catalyst but it is almost negligible for CS\textsubscript{syn}.

These results could be due to the effect of particle size of cobalt species. The smaller particles, which form in the smaller pore diameter in CS\textsubscript{com}, strongly interact with the support, leading to more difficult to be reduced. In contrast, larger particles which form in the larger pore size in CS\textsubscript{syn} can be more easily reduced. Consequently, the reducibility of cobalt oxide in the catalyst is depended on the pore size of catalyst support (Riva et al., 2000; Sun et al., 2017).

3.1 Fischer-Tropsch synthesis

The catalytic performances of CS\textsubscript{syn} and CS\textsubscript{com} catalysts were investigated via Fisher-Tropsch reaction and the results are reported in Table 3. It was found that CO conversion and chain growth probability (α) of CS\textsubscript{syn} are higher than those of CS\textsubscript{com} catalyst. Moreover, the slightly higher hydrocarbon selectivity toward liquid product (C\textsubscript{5+} including gasoline (C\textsubscript{5}-C\textsubscript{9}), kerosene (C\textsubscript{10}-C\textsubscript{15}) and diesel (C\textsubscript{16}-C\textsubscript{24})) with the lower methane selectivity and olefin to paraffin (O/P) ratio were obtained from CS\textsubscript{syn}.

The Co/SiO\textsubscript{2} catalyst is well known that it posts a strong tendency for secondary reactions involving re-adsorption. These reactions not only lead to a decrease in olefin and LPG products but also cause the formation of high molecular weight products. In addition, high methane selectivity has been favored

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for cobalt-based catalysts with low reducibility and high dispersion.

**Table 3:** The catalytic performance and product distribution of cobalt supported catalysts

<table>
<thead>
<tr>
<th>Sample</th>
<th>CO Conversion (%)</th>
<th>α</th>
<th>O/P ratio</th>
<th>Hydrocarbon selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CSsyn</td>
<td>15.58</td>
<td>0.78</td>
<td>0.37</td>
<td>CH₄</td>
</tr>
<tr>
<td>CScom</td>
<td>12.19</td>
<td>0.62</td>
<td>0.47</td>
<td>0.02</td>
</tr>
</tbody>
</table>

CSsyn catalyst with larger cobalt particle size and higher reducibility provides more surface active sites to produce higher hydrocarbons (C₅+), compared to CScom catalyst. A similar result is that C₅+ selectivity increases with increasing cobalt particle sizes, was also reported by Bezemer et al. (2006).

Furthermore, the C₅+ selectivity of the cobalt supported catalysts in FT synthesis also relates to the pore size of supported catalysts. It is often described in terms of the mass transfer limitation of the product (Okabe et al., 2004). For small pore diameter, the heavier hydrocarbon product is considered to be hydro-cracked into lighter hydrocarbons, resulting in the increasing lighter gas hydrocarbons and lower chain growth probability (α). Corresponding to Ghampson and co-worker, they studied the effect of pore diameter (3 to 22 nm) on the size of cobalt oxide and FT performance. The correlation between pore diameter and turnover frequency (TOF) of the catalyst was reported. The maximum TOF was obtained from the catalyst with a pore diameter around 13 nm (Ghampson et al., 2010).

The catalytic performance in FT reaction of CSsyn and CScom catalysts is presented in Fig. 5. The product activity and selectivity towards C₅+ obtained from CSsyn catalyst are apparently higher than those obtained from CScom catalyst. This could be attributed to the effect of pore size of support on metal particle size of cobalt supported catalyst. The correlation between physical and chemical properties of catalyst and the activity of product distribution could be explained in the same manner as mention above.

**Fig. 5:** Activity of hydrocarbon product distribution in FT reaction over cobalt supported catalysts at 220 °C for 24h

4. Conclusion

Characterization and catalytic testing results exhibit strong influence of porosity of silica support on the cobalt oxide size, cobalt metal size, reducibility, and FT catalytic performance of cobalt catalyst supported on silica.

Characterization results reveals that larger pore size of silica support allows larger cobalt oxide cluster to form. The larger particle size of cobalt oxide enhances the reducibility of cobalt oxide species in the catalyst with lowering the interaction between cobalt and support. Catalytic activity and product selectivity results present that the catalyst with larger cobalt particle provides higher FT activity for all hydrocarbon products with higher chain growth probability and greater C₅+ selectivity due to the improvement of the tendency for secondary reactions including re-adsorption. This reason also leads to the decrease in O/P ratio of the product compared to the catalyst with smaller cobalt particle.

Thus, FT performance, cobalt particle size and reducibility of cobalt supported catalysts are strongly impacted by pore sizes of support.

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