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 (C₅⁺) 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 C_{10}-C_{20} 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, Davislil 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 (CScom) 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 (Bukker, D8 Discover) with monochromatized Cu Kα radiation (40 kV, 40 mA) at 2θ = 0.5 - 80°. The average Co₃O₄ crystallite size (D_{Co₃O₄ XRD}) was calculated using the Scherrer equation (Eq. 1). The spherical cobalt crystallites of uniform diameter (dCo⁴) 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:

\[ D_{Co₃O₄ XRD} = \frac{kl}{B \cos \theta} \]  
\[ dCo⁴ = 0.75D_{Co₃O₄ XRD} \]  
\[ Dₘ XRD = \frac{96}{dCo⁴} \]

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:

\[ %Dₘ = \frac{[V_{chem}/22414xSFxMw/([mₓp]/100)]x100}{\rho x 10^9} \]  
\[ Size of metal particle = 6/(Am x ρ x 10^9) x 10^9 \]

where %Dₘ is percent of metal dispersion, V_{chem} 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 A_m 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 24 h 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 (SBET), total pore volume (TPV) and mean pore diameter (MPV) of silica supports and cobalt supported catalysts are summarized in Table 1. The total surface area of Ssyn is not significantly different with Scom.

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

| Sample | SBET (m²/g) | TPV (cm³/g) | MPD (nm) |
|--------|-------------|-------------|----------|
| Ssyn   | 474         | 0.85        | 7.17     |
| CSsyn  | 327         | 0.61        | 7.53     |
| Scom   | 481         | 0.80        | 6.72     |
| CScom  | 362         | 0.57        | 6.34     |

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

| Catalyst | X-Ray Diffractiona | H₂-TPDb | TEMc |
|----------|-------------------|---------|------|
| D Co₃O₄ (nm) | d Co⁰ (nm) | Dm XRD (%D) | Co⁰ particle size (nm) | Co dispersion (%) | D Co₃O₄ TEM (nm) |
| CSyn     | 18.0             | 13.5    | 7.11  | 26.47 | 3.77 | 5.6 |
| CSCom    | 14.4             | 10.8    | 8.99  | 14.06 | 7.09 | 6.0 |

a Calculated by XRD using equations, D Co₃O₄ XRD = (kλ/B cos θ), d(Co⁰) = 0.75D and %D = 96/d(Co⁰); b Estimated by H₂-TPD technique; c Determined from randomly selected particle in the TEM images.

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

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$_2$-TPD technique. The results, reported in Table 2, are in agreement with the XRD results. The CSsyn catalyst shows the larger cobalt particle size with lower cobalt dispersion compared to CScom catalyst.

**Fig. 2:** The XRD pattern of cobalt supported catalyst

**Fig. 3:** TEM images and particle distribution of cobalt oxide of cobalt supported catalysts

TEM images and particle size distribution (PSD) of CSsyn and CScom catalysts are shown in Fig. 3. The average particle size of CSsyn and CScom catalyst is not significant different, which the values are 5.6 and 6.0 nm, respectively. The TEM images reveal that Co$_3$O$_4$ particles favor to aggregate into Co$_3$O$_4$ cluster. The Co$_3$O$_4$ cluster size of CSsyn is larger than that in CScom. The result was found in the same trend as XRD result. Moreover, the aggregation of Co$_3$O$_4$ 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$_2$ adsorption-desorption isotherms and pore size distribution from BJH curves in Fig. 1.

H$_2$-TPR profiles of cobalt supported catalysts (CSsyn and CScom) 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$_3$O$_4$, CoO$_x$ (including CoO) and Co-SiO$_2$ as $\alpha$, $\beta$, and $\gamma$ species, respectively. The first sharp peak observed in the temperature range from 200-320 °C could be assigned to the partial reduction of Co$_3$O$_4$ to CoO$_x$ and the second broad reduction peak found in the temperature higher than 320 °C could be ascribed to the reduction of CoO$_x$ to Co$^0$. 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$_2$-TPR profiles of cobalt supported catalysts

H$_2$-TPR results show that the first peak of both catalysts presents a similar profile. However, the second peak of CoO$_x$ species reduction shows the different figure. The second peak profile of CScom shown as overlapped peak is wider than that of CSsyn catalyst. It could be suggested that there are many different CoO$_x$ species, which are reduced at different temperature region. Moreover, the third peak obviously appears for CScom catalyst but it is almost negligible for CSsyn.

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 CScom, strongly interact with the support, leading to more difficult to be reduced. In contrast, larger particles which form in the larger pore size in CSsyn 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 CSsyn and CScom 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 ($\alpha$) of CSsyn are higher than those of CScom catalyst. Moreover, the slightly higher hydrocarbon selectivity toward liquid product (C$_5^+$ including gasoline (C$_5$-C$_9$), kerosene (C$_10$-C$_15$) and diesel (C$_16$-C$_24$)) with the lower methane selectivity and olefin to paraffin (O/P) ratio were obtained from CSsyn.

The Co/SiO$_2$ 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...
for cobalt-based catalysts with low reducibility and high dispersion.

| Sample | CO Conversion (%) | α | O/P ratio | LPG | Gasoline | Kerosene | Diesel |
|--------|-------------------|---|-----------|-----|----------|----------|--------|
| CSsyn  | 15.58             | 0.78 | 0.37 | 0.02 | 52.18    | 45.51    | 2.28   |
| CScom  | 12.19             | 0.62 | 0.47 | 36.10| 13.75    | 11.88    | 36.35  | 1.92   |

CSyn catalyst with larger cobalt particle size and higher reducibility provides more surface active sites to produce higher hydrocarbons (C$_6^+$), compared to CScom catalyst. A similar result is that C$_5^+$ selectivity increases with increasing cobalt particle sizes, was also reported by Bezemer et al. (2006).

Furthermore, the C$_5^+$ 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 C$_5^+$ 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](image)

### 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 C$_5^+$ 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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