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Effects Of Cu On The Modified Co-Based Catalyst Activity For Fischer-Tropsch Synthesis

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Future fuel scarcity issue has become major concern for many energy security policies. As a very potential process to produce fuel, Fischer-Tropsch synthesis (FTS) with cobalt-based catalyst has been developed to produce wax as feedstock for further catalytic cracking. Therefore, this research was conducted to observe Co/Al_2O_3 catalyst properties enhancement through support pre-treatment using NH_4NO_3 and Cu promoter addition toward higher activity and selectivity. Catalysts were prepared by dry impregnation method. XRD, BET and TPR analyses were performed to characterize catalysts properties. Activity tests showed CO conversion, H_2 conversion and selectivity of C_{5+} were in the range of 25.1% to 96.2%, 24.2% to 83.7% and 53.5% to 75.9% respectively. Crystallography measurements exhibited 8.6-9.8 nm cobalt particles size. In this study, FTS was evaluated by using fixed-bed reactor at 20 bar, 250 C, and WHSV of 1500 ml/g.cat/h^{-1}. Support pre-treatment increased the pore size of γ-Al_2O_3 and slightly enlarged cobalt diameter. While addition of Cu improved the reducibility of the catalyst.

Keywords : Fischer-tropsch, Support pre-treatment, Cu promoter, Modified Co-based catalyst, Reducibility, Particle size

INTRODUCTION

The Fischer-Tropsch Synthesis (FTS) to produce fuel through conversion of natural gas, coal and biomass into syngas, is one of potential process to solve future fuel scarcity issue. However, according to Anderson-Schulz-Flory (ASF) distribution, FTS products are spread on wide range of hydrocarbon from methane to waxy products (Dry 1981). To obtain a higher selective product, intensive effort needs to be performed by modifying catalyst.

The cobalt-based catalyst has been long known as a well-performing type of catalyst comprising higher conversion per pass, higher long chain hydrocarbon product (C_{5+}) selectivity, and higher stability (Wang and Chen 1991). Some of the problems that are often encountered in this type of catalyst are reduction-activity problems and products selectivity enhancement problems (Surisetty et al. 2010).

The reduction of the catalyst can be increased by the addition of group 11 promoter (Cu, Ag, Au) (Jacobs et al. 2009). This promoter plays a role by modifying the character of the support-active metal formation through structural surface engineering and electronic density so that the reduction temperature can be decreased by a two-stage reduction mechanism simultaneously, and as a consequences an improved catalytic activity obtained (Jacobs et al. 2014). Another factor affecting the activity of the catalyst is the cobalt particle size. Large cobalt particle size tends to be readily available on catalysts with large pore sizes (Li et al. 2007). Good activity is obtained on cobalt particle size above 9 nm (Bezemer et al. 2006). In addition, high selectivity product towards C_{5+} also tends to be obtained for large pore size and large cobalt particles (Shimura et al. 2014). The pre-treatment process of the support using ammonium nitrate (NH_4NO_3) can be used to modify the pore size by reducing the content of the impurities compound (Na_2O) in the support and the partly dissolution of Al_2O_3 (Zhang et al. 2003).

In this research, we studied the Co/Al_2O_3 catalyst properties enhancement systems toward higher activity using Cu promoter addition on γ-Al_2O_3 support pre-treated with NH_4NO_3 aqueous solution (100P) from our previous studies.

EXPERIMENTAL

Materials

The active phase and promoter materials used are cobalt ($Co(NO_3)_2.6H_2O$) and copper nitrate ($Cu(NO_3)_2.3H_2O$) precursor. The materials used for support pre-treatment media are ammonium nitrate (NH_4NO_3). Those materials was obtained from Merck™. Commercial γ-Al_2O_3 support (This Support has an average pore size (d_{pore}) of 8.5 nm, surface area (SA) of 227.3 m2/gr, and pore volume (V_{pore}) 0.46 cc/g). Synthesis gas with composition of N_2 = 10,2%, CO = 31,1%, and H_2 = 58,7% from MESA Int. Tech.

Catalyst Preparation

The modified-catalyst was prepared by conventional incipient – wetness impregnation method of required composition using γ-Al_2O_3 pre-treated with NH_4NO_3 aqueous solution (100P) as the modified-support from our previous study with a cobalt and copper nitrate precursor in deionized water.

Table 1. The nomenclature of prepared catalyst composition

Catalyst	Cons. Co (%w-w)	Cons. Cu (%w-w)
Co-Cu(0)	15	0
Co-Cu(0.6)	15	0.6
Co-Cu(1.2)	15	1.2
Co-Cu(2.76)	15	2.76

The impregnation was conducted by continuous stirring of the slurry at ambient temperature. After impregnation, the sample was dried at 110°C and calcined at 350°C. Preparation of the promoted catalyst were performed by co-impregnation of cobalt nitrate precursor and copper nitrate as the promoter. Drying and calcination steps were carried out as described procedures above. The prepared catalyst composition were listed in **Table 1**.

Catalyst Characterizations

The surface properties of samples (BET surface area, average pore diameter and pore volume) were determined by nitrogen adsorption at 77 K using NOVA 3200e instrument. Pore volume and pore size distributions were calculated using BJH method.

X-ray diffractograms were performed using Bruker 8D Advance diffractometer with monochromatic Cu-Kα radiation. The diffraction spectrum was recorded at a range of angles between 2θ = 20° and 2θ = 90°. The average size of the Co_3O_4 crystallites of the samples were calculated according to the Scherrer equation (from the line width of the most intense reflection at 2θ = 36.9°, referring to its [311] crystal face). The exhibited Co_3O_4 particle size could be used to calculate Co particle diameter (dp Co) after reduction by hydrogen according to the Schanke equation.

The temperature programmed reduction with hydrogen (H_2-TPR) was performed using Micrometrics Auto Chem II 2920 apparatus to determine the catalyst reduction properties. As stated in H_2-TPR standard operating procedure, the samples were initially pre-treated in helium flow and heated simultaneously up to 400°C then held for 2 h in order to remove adsorbed water and other contaminate substances followed by cooling to 50°C. The mixture gas containing of 5% H_2/Ar as reducing agent was passed through the catalyst samples at a flow rate of 58 cm^3/min with heating rate of 5°C min^{-1} up to 850°C.

Catalytic Activity Measurements

Catalytic activity test was conducted using tubular fixed-bed reactor (I.D. = 10 mm) loaded with 1 g catalyst. Prior to the FT reaction, H_2 gas with flow rate of 90 NTP ml/min at 400°C was passed over the sample to reduce the catalyst. After the reduction was completed, the sample was cooling down to 250°C in flowing H_2. The pressure then, was slowly increased up to 20 bars as the flowing gas switched to syngas (molar ratio of H_2/CO = 2 : 1), then the syngas feed flow rate was adjusted to 25 ml/min. The gas phase sample were taken every 1 hour at input and output points and analyzed using a gas chromatograph (GC) equipped by molsieve packed column and Thermal Conductivity Detector (TCD) detector. The liquid phase sample was taken at the end of the reaction and analyzed using a GC equipped with an Rtx-1 packed column and used detector was Flame Ionization Detector (FID).

RESULTS AND DISCUSSION

In our previous experiments, we point out the influence of γ-Al_2O_3 pre-treatment with NH_4NO_3 aqueous solution on the physical properties of support. At 100 g/L NH_4NO_3 aqueous solution, the average pore diameter, the pore volume were observed to be higher, and the surface acidity of support was decreased, thus expected to be beneficial for obtaining large cobalt particles size (dp Co) and for high yields of C_{5+} hydrocarbon due to suppression of cracking properties. In this study, therefore, we used γ-Al_2O_3 pre-treated with 100gr/L NH_4NO_3 aqueous solution (100P) as the support.

Physical Properties of Cu Promoted Modified-Catalysts

The surface properties of modified catalyst are summarized in **Table 2**. and **Figure 3**. As shown in **Figure 3**. the pores of all characterized catalyst samples are falling in the mesopore range with pore size of 6 - 10 nm.

Table 2. Physical properties of Cu promoted modified-catalysts

Samples	Average pore diameter (nm)	Pore Volume (mL/g)	BET surface area (m^2/g)
100P	10.5	0.48	184.7
Co-Cu(0)	9.81	0.64	273.1
Co-Cu(0.6)	9.95	0.59	228.9
Co-Cu(1.2)	10.5	0.8	292.8

The intensity of dV/dlog(D) for these catalysts have similarity except for Co-Cu(1.2) catalyst. However, surface area of the modified catalyst increased relative to 100P support.

Cobalt Particle Size (dp Co) of Cu Promoted Modified-Catalysts by XRD

The XRD diffractograms of catalysts were collected and stacked as shown in (**Figure 1**.) indicated that Co species in calcinated Cu modified cobalt-based catalysts surface all existed in the form of Co_3O_4 crystalline phase, no diffraction peak of CoO, Cobalt aluminate or other Co species were found.

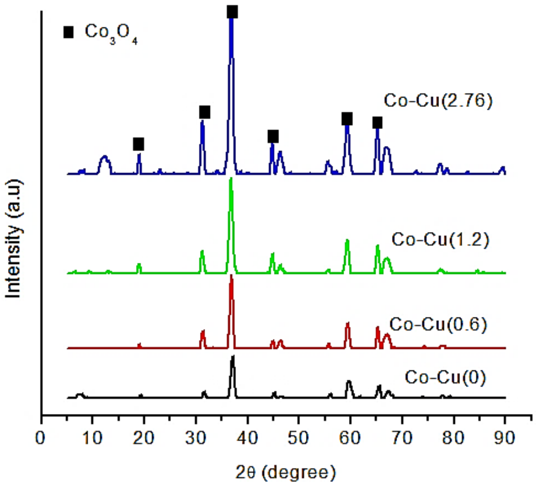

Fig. 1: XRD pattern of Cu promoted modified-catalyst

The strongest diffraction peak of Co_3O_4 crystalline phase was at 36.9°, which was corresponding to the ([311]) crystal phase of Co_3O_4 crystalline phase (Schanke et al 1995). Debye-Scherrer equation was used to calculate the particle size of Co_3O_4 from each samples diffractogram peak. While the particle size of cobalt, is estimated using Schanke equation with consideration of changes in molar volume occurring during Co_3O_4 transition to Co°.

The cobalt particle size calculation results are shown in **Table 3**. It shows that the average cobalt particle size (dp Co) obtained is in the range of 8.6-9.8 nm.

Table 3. Average Co_3O_4 and Co^o crystallite diameter on catalyst surface

Samples	dp Co_3O_4 (nm)	dp Co (nm)
Co-Cu(0)	16.3	9.2
Co-Cu(0.6)	12.7	9.5
Co-Cu(1.2)	11.5	8.6
Co-Cu(2.76)	13.5	9.8

Effects of Cu promoter on the Modified Catalysts

TPR analysis was conducted to understand the reduction behaviour of cobalt oxide to its active phase as it is responsible for FTS activity. **Table 4** shows the H_2-TPR profile temperature of the modified catalyst with different concentration of Cu promoter.

The process of cobalt oxide reduction is a two-stage process that occurs simultaneously starting from the reduction of Co_3O_4 to CoO and CoO to Co^o. To produce a catalyst of good performance, all cobalt oxide fractions must be reduced to their active phase. Cobalt-alumina oxide in the form of spinel ($CoO*Al_2O_3$ or Co_3O_4* Al_2O_3) is an extremely difficult oxide to be reduced. This compound maybe formed by the substitution of Co^{3+} ions with Al^{3+} ions on the support surface, so this compound should be avoided. (Borg 2007).

According to (Schanke et al. 1995), the Co_3O_4 reduction process to CoO is represented by a peak generally between a temperature of 100°C - 350°C. While CoO reduction process to Co^o is represented by peak with temperature range between 350°C - 600°C. The peak that appears at temperatures above 600°C represents the reduction of the cobalt alumina compound which is hard to reduce.

From **Table 4**, it can be seen that addition of Cu promoters is able to increase reduction process of catalyst. As more Cu is added, the probability formation of the cobalt alumina spinel compound is getting smaller. According to (Morales and Weckhuysen 2006), Cu metals may act as electronic promoters through the formation of alloys / sandwiches with the Co-active metal which leads to weaken the interaction between the cobalt active phase and the alumina support surface.

Table 4. H_2-TPR of Cu promoted modified catalyst

Samples	Cons. Cu (%)	Peak 1 (°C)	Peak 2 (°C)	Peak 3 (°C)
Co-Cu(0)	0	-	405	730
Co-Cu(0.6)	0.6	326	395.7	675.5
Co-Cu(1.2)	1.2	309	377.8	-
Co-Cu(2.76)	2.76	-	324	-

Activity and Selectivity of the Cu Promoted Modified-Catalysts

The catalytic performance of the Cu promoted modified-catalyst was carried out at 250°C, 20 bar, 1500 ml/g.cat.h^{-1} in a tubular fixed-bed reactor. The reaction performance was evaluated on the basis of the average calculation of syngas conversion and C_{5+} selectivity as shown in **Table 5**. It shows that when the standard catalyst Co/γ-Al_2O_3 are compared with modified Co-Cu (0) catalyst, modification using γ-Al_2O_3 pre-treated with 100 g/L NH_4NO_3 aqueous solution, it increases CO and H_2 conversion from 25.1% and 24.2 % to 85.2% and 77.3%.

Pre-treatment of support with NH_4NO_3 solution will bring about the change of γ-Al_2O_3 surface acidity. The surface acidic strength and acidic amount decreased with increasing concentration of pre-treatment media. The effect of adjusting support surface acidity will bring the interaction between cobalt species and the supports become much lower. Thus improved the reducibility, which improved the activity and the selectivity for heavy hydrocarbon (Li et al. 2007).

CO conversion increases with addition of Cu and particle size of cobalt active phase and its reducibility as shown in **Fig. 2** and **Table 4**. As already well known, the large pores on FTS catalyst having a large surface area is beneficial for obtaining a large cobalt crystallite size and for the facile transport of heavy hydrocarbons formed during FTS reaction. These large pores also have been suggested to be linked to less coking formation from wax deposition (Catita 2014). However, the addition of the promoter has a maxima value in which the addition of excess promoter concentration will actually give a negative effect (Jacobs et al. 2014).

Table 5. Catalytic activity and hydrocarbon distribution over the Cu promoted modified-catalyst

Samples	Co/γ-Al_2O_3	Co-Cu(0)	Co-Cu(0.6)	Co-Cu(1.2)	Co-Cu(2.76)
XCO (%)	25.1	85.2%	96.2%	89.5%	28.9%
XH_2 (%)	24.2	77.3%	83.7%	78.5%	28.4%
C_1	-	8.8	5.2	3.6	4.0
C_2-C_4	-	37.7	26.7	20.4	22.1
C_{5+}	-	53.5	68.1	75.9	73.9
Yield (%) C_{5+}	-	45.5	66.7	67.9	21.3

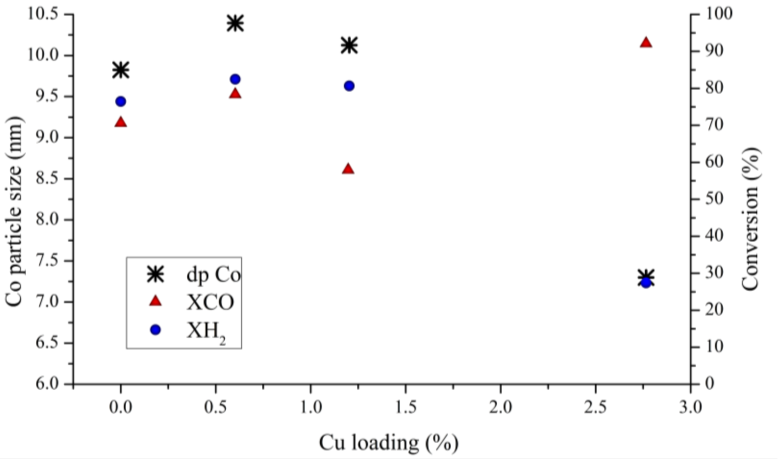

Fig. 2: Correlation between cobalt particle size, concentration of promoter and catalytic activity

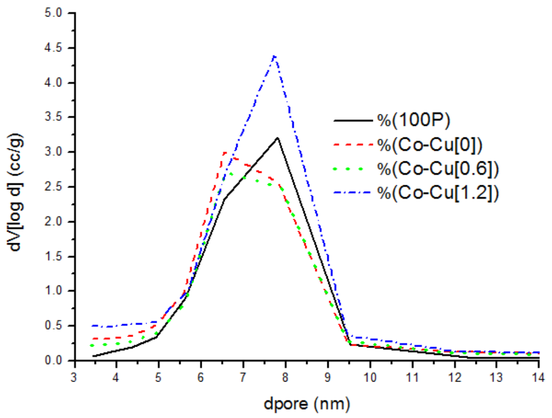

Fig. 3: Pore size distribution of promoted modified Co-based Catalysts

CONCLUSION

Addition of Cu promoter on the modified Co-based catalyst can improve the reducibility and activity of catalyst. The Co-Cu(0.6) catalyst obtained from our experiments is the best catalyst that offers higher CO conversion and C_{5+} selectivity. The larger pore size of the support affects the size of the cobalt particles formed. The particle size of Co then affects conversion and selectivity. High conversion values and selectivity of C_{5+} formation were obtained at a minimum Co particle size of 8 nm.

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