STUDIES ON FISCHER-TROPSCH SYNTHESIS OVER Co-BASED CATALYSTS

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Introduction

The conversion of natural gas to hydrocarbons by Fischer-Tropsch synthesis (FTS) is currently one of the most promising research topics in the energy industry, due to the limited petroleum reservoirs and global warming problems [1]. Also FTS is considered as an effective method for the production of wide range liquid hydrocarbon fuels and value added chemicals using synthesis gas [2-3]. Synthesis gas (syngas) can be obtained from relatively abundant resources such as natural gas, coal, petroleum, biomass and even organic waste [4]. The products of FTS can be used as feedstock of the chemical industry and the transportation fuels market due to the economic utilization of natural gas to clean fuels, valuable chemicals and waxes.

Recently, the development of catalysts with high activity and desired selectivity in the middle distillate range was the focus of the most of the workers [5-8]. Many researchers [1,8-10] have studied several combinations of FT active metals such as Co, Fe, Ni, Ru with different supports with acidic function. The fundamental research is essential to achieve a new and improved catalyst in establishing reaction mechanism, understanding the surface science of catalysis.

The cobalt-based catalyst shows the highest yield, longest life-time and produces linear alkanes [11] and became the standard catalyst for commercial industry in FTS [12]. Cobalt catalysts are good for natural-gas based FTS for the production of mainly middle distillates and long chain products (wax) [13-15]. Disadvantages of cobalt catalyst are the high costs of cobalt, low water gas shift activity as compared to iron catalyst and also it needs to have high metal dispersion.

The FT reaction mechanism and the large number of species produced during FTS is the major problem for development of new and potential kinetic expressions. However, most FTS researches have focused on catalyst improvement. It was reported [15] that the design of FTS reactor is a key technology for commercialization of GTL process. However none of the available models is accurate enough for a reliable reactor design. The lack of reliable kinetic studies for products and reactants based on the proper reaction mechanism seems to be the main problem. Until now, none of the available literature models obtain enough details to describe the complete product distribution of the Fischer-Tropsch synthesis.

In this study, we have investigated studies on the FTS reaction over Co(20%)/SiO_2 catalyst in a slurry bed FT synthesis reactor system. The FT products are monitored by on-line GC systems and the catalyst was characterized using different analytical techniques such as XRD, low temperature (77K) nitrogen physisorption, FT-IR, TPR and TEM techniques.

Experimental

The cobalt (20%) supported silica catalyst was prepared by conventional incipient wetness impregnation method using cobalt nitrate and silica gel as support. The Physico-chemical properties were analyzed by XRD, TEM, N_2 adsorption and by TPR method.
The characteristics of prepared catalysts were compared to Co/Al_2O_3 and $Co\text{-}Ru/Al_2O_3$ catalysts.

Catalyst Preparation

The Co/SiO_2 catalyst with total metallic loading of 20% was prepared by an incipient wetness impregnation method. The cobalt nitrate (Yakuri Chemicals, Japan) was used as the precursor of cobalt and silica gel (Aldrich, Davisil) with BET surface area 489 m^2/g, pore size 60 Å, pore volume 0.75 cc/g and particle size 35-75 μm (200-425 mesh) was used as a support. The requisite amount of cobalt nitrate solution and silica support was well mixed with stirring by incipient impregnation method. Silica gel was heated at 500 ^{o}C for 5h before the impregnation step. Then the sample was dried at 115 ^{o}C for 5h and calcined in a muffle furnace at 300 ^{o}C for 2h. The catalyst was pre-sieved to 35-75 μm particle size before carrying out the reduction for FTS reaction.

Characterization of Catalyst

An X-ray Diffractometer (XRD-6000, Shimadzu Co., Japan) monochromatized CuKα radiation (λ=1.5404 Å) was used for recording the XRD profiles of all calcined samples over the scan range 2θ = 20 to 80° with a scan rate of 2^{o} min^{-1}. The average Co_3O_4 particle sizes of all the catalysts were calculated using Debye-Scherrer equation. Then from the diameter of a given Co_3O_4 particle, the diameter of metallic Co crystallite was calculated by the formula (1) [16-17] and compared to TEM images which were obtained by Philips CM-30 microscope.

$$d_v(Co^{o}) = 0.75\ d\ (Co_3O_4) \qquad (1)$$

Textural properties of the samples such as BET surface area, total pore volume and pore size distribution were studied using low temperature (77K) nitrogen adsorption using Autosorb-1, (Quanta-chrome Co.). Prior to the determination of adsorption isotherm, the sample was evacuated at 10^{-2} torr and at 453 K to remove all physisorbed species from the surface of the adsorbent. The temperature programmed reduction (TPR) study was performed by Micromeritics, Autochem II, Chemisorption analyzer for all samples. The catalyst (0.05 g) was heated and purged with He, and was then reduced in a flow of 5%H_2/95% Ar from 323 to 1373 K at a rate of 10 K/min. Hydrogen consumed for the reduction was determined by TCD GC.

FT reaction in Slurry Type Reactor System

The FT synthesis was carried out in 250 ml stainless steel high pressure Parr reactor. The mixture of H_2 and CO (99.999% purity) with a H_2 /CO molar ratio of 2 was used as syngas reactant. For a typical procedure, the catalyst of 1 g was activated ex situ at 400 ^{o}C for 14 h in H_2 gas with a flow rate of 70 ml min^{-1}. The reduced catalyst was then transferred to the reactor containing 80 ml of squalane ($C_{30}H_{62}$) solvent in an inert atmosphere. Then the reactor was fixed up with a cover equipped with a motor driven flat blade impeller, the reaction system was purged with syngas. The flow rate of syngas was controlled and monitored using a massflow controller (FM-20A, Chunma Data System Co., Ltd). The operation conditions for kinetic studies were Temperature = 210 ~ 250 ^{o}C, Pressure 15 ~ 25 bar, H_2/CO feed ratio of 1.3 ~ 3.0, Feed rate 5 g_{cat} h mol^{-1} and stirring speed was maintained at 900 rpm. Effluent gas was passed through two consecutive traps to condense remaining liquid products. The effluent gas flow was measured with a wet gas flow meter.

Products in the effluent gas were analyzed by two consecutive online gas chromatograph (GC). CO, H_2, CO_2 and CH_4 were analyzed with carbosphere packed column with TCD detector and gaseous hydrocarbons < C10) were analysed with GS GasPro column using FID detector equipped to the same GC. Higher hydrocarbons were analysed using separate GC equipped with HP-1 column and FID detector. The yield of hydrocarbons was calculated on the basis of carbon number. The wax product was analyzed using GC-mass spectroscopy equipped with HP-1 column.

Results and Discussion

Characterization of Catalyst

XRD : The XRD spectrum of Co/SiO_2 sample was recorded in its oxide state and is shown in Figure 1 The prominent XRD lines at 2θ ~ 31^o, 37^o, 45^o, 55^o, 59^o and 65^o are those of Co_3O_4, marked by '*' correspond to Co_3O_4 (JCPDS No.42-1467) for Co/SiO_2 sample. The pattern (all indexed peaks) clearly indicates the spinel phase of Co_3O_4 (cubic symmetry, space group: Fd3m, lattice constant a_0 = 0.8084 nm; JCPDS file no. 43-1003). Table 1 shows the characteristics of Co-based catalysts. The average particle size of the catalysts was calculated using the full width at half maximum (FWHM) of the most intense peak [311] of the X-ray diffraction pattern using Debye-Scherrer equation. The broadening of the peaks reveal the small crystallite size and was found to be in nanometer scale (5.47 ~ 9.5 nm) range. The diameter of metallic Co crystallite in Co/SiO_2 sample was calculated by the formula (1), from the diameter of a given Co_3O_4 particle and was found to be 4.3 ~ 7.1 nm. Co-Ru/Al_2O_3 catalyst shows larger crystal size compared to the other catalysts. It's from a high calcination temperature to stabilize Ru contents in the catalyst.

Table 1. Physical characterization of prepared catalyst

Sample	Catalyst Composition (wt%)	Crystallite size, (nm)	BET, S.A (m^2/g)	Total pore volume (cc/g)
Co/SiO_2	$Co:SiO_2$=20:80	5.47	331.6	0.51
Co/Al_2O_3	$Co:Al_2O_3$=20:80	5.90	151.1	0.31
Co-Ru/ Al_2O_3	$Ru:Co:Al_2O_3$=1:19.8:79.2	9.5	-	-

TPR study

Figure 2 show TPR profile of Co/SiO_2 catalyst. It shows two peaks in between 243 °C ~ 348 °C and 348 °C ~ 500 °C corresponding to the reduction of Co^{3+} to Co^{2+} and Co^{2+} to Co^o respectively.

TEM images

Figure 3 shows the TEM micrographs of Co/SiO_2 catalyst. It can be seen that the average crystallite size is very small, nanosized. The catalyst has almost all cobalt particles of round shape with size less than 5 nm. These results are nearer to the values calculated from Scherrer equation as listed in Table 1. Figure 4 depicts the electron diffraction pattern of Co/SiO_2 catalyst. The pattern shows continuous rings representating very large number of small nanosized, randomly distributed crystals. White spots represent the presence of metal Co in the sample. The pattern reveals that the sample is highly crystalline.

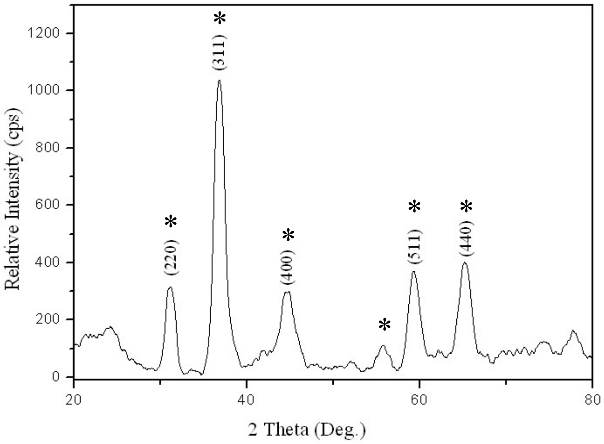

Figure 1. XRD spectrum of Co/SiO_2 catalyst.

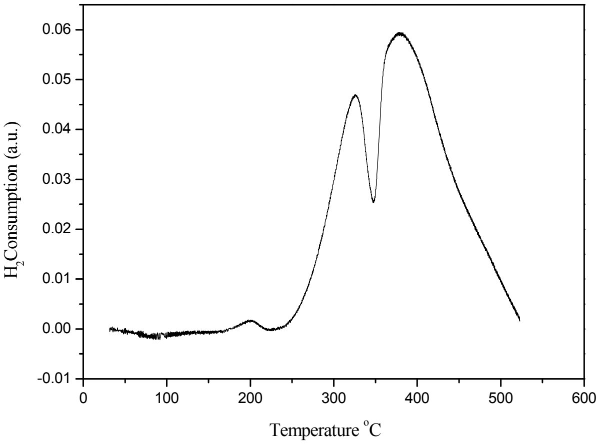

Figure 2. TPR profile of Co/SiO_2 catalyst.

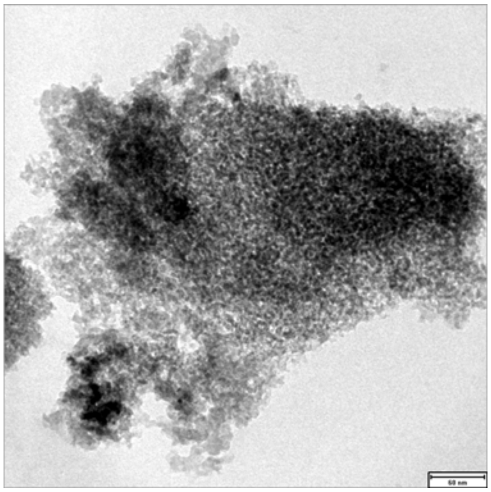

Figure 3. TEM micrographs of Co/SiO_2 catalyst.

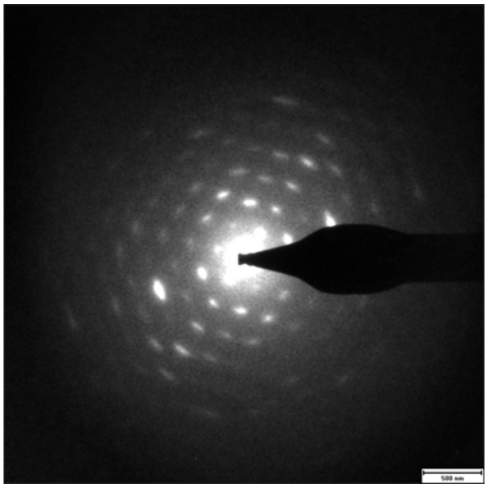

Figure 4. Diffraction pattern of Co/SiO_2 catalyst.

Nitrogen physisorption : Figure 5 shows adsorption-desorption isotherm of nitrogen of Co/SiO_2 catalyst. The isotherm can be classified as type IV according to the IUPAC convention [18] and is typical of mesoporous material. The isotherm shows a linear increase at low relative pressure of nitrogen upto P/P_o=0.4 indicates monolayer nitrogen adsorption in the mesoporous pores. At higher relative pressure > 0.4, a steep rise in nitrogen uptake was observed due to capillary condensation inside the mesoporous pores [19]. BET surface area was found to be 331.6 m^2/g and the pore volume was 0.50946 cc/g (Table 1). The pore size distribution curve (Fig. 6) shows pore of ~ 59.8 Å.

FT reaction in Slurry Type Reactor System

The operation conditions were T= 210 ~ 250 °C, Pressure 15 ~ 20 bar, Feed rate 5 g_{cat} h mol^{-1} and stirring speed was maintained at 900 rpm. The outgas flow was measured with a wet gas flow meter for product analysis. The products in the outgas were analyzed by two consecutive on-line GC and off-line one. The yield of hydrocarbons and the chain growgth probalility was calculated on the basis of carbon number using reaction kinetics data.

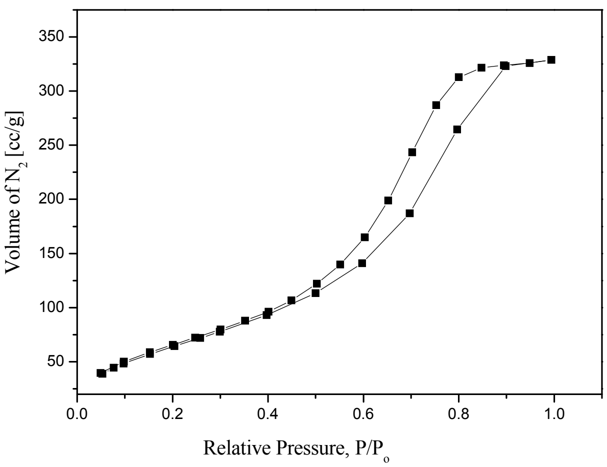

Figure 5. Low temperature (77K) Nitrogen sorption isotherms for Co/SiO_2 catalyst.

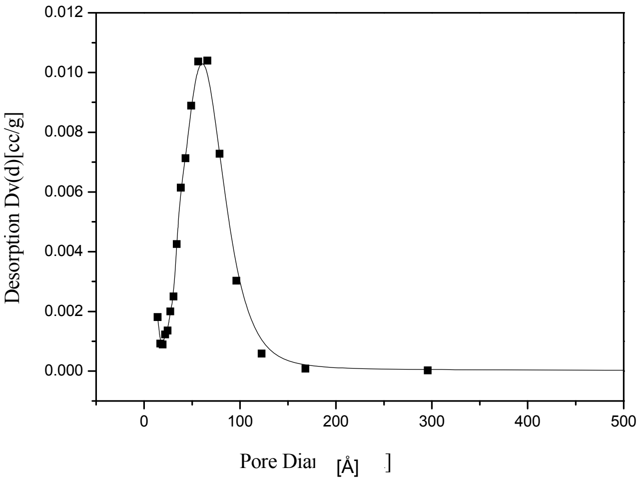

Figure 6. Low temperature (77K) Nitrogen Pore size distribution curve for Co/SiO_2 catalyst.

Table 2. Effect of temperature on selectivity and chain growth probability for FTS reation over Co/SiO_2 catalyst in slurry bed reactor systme under 25bar and $H_2/CO=2$.

Temperature (^oC)	**CO Conversion (%)**	**CH_4 Selectivity (%)**	**Chain Growth Probability (α)**	
			(C_3~C_8)	**(C_9~C_{20})**
230	52	42	0.69	0.78
250	48	38	0.71	0.82

Table 2 shows the performance of Co/SiO_2 catalyst for FTS at different temperature (210 ~ 230 ^oC) at 25bar pressure of H_2/CO feed ratio of 2. CO conversion and CH_4 selectivity was found to increase with increase in temperature from 210 to 250 ^oC Hence from the result, we can optimize the proper reactor temperature fro FTS. The influence of temperature on the ASF chain growth probability was investigated. It is found that the ASF chain growth probability increase with increse in temperature from 210 to 250 ^oC in (C_3-C_8) and (C_9-C_{20}) range, when all other conditions are kept constant. The increasing trend is mainly due to the decrease of desorption rates of FTS species on the catalyst surface, which increase the probability of surface polymerization process [20-21].

Table 3 shows the performance of different Co catalysts for FTS in temperature range of 230 ~ 250 ^oC, 20bar, H_2/CO feed ratio of 2. CO conversion for Co/SiO_2 and $Co\text{-}Ru/Al_2O_3$ catalysts were 28 and 22 % with CH_4 selectivity 18.7 and 14.6 %, respectivly. Co/Al_2O_3 catalyst at high temperature of 250 ^oC, however showed increase in CO conversion (47 %) with increase in methane selectivity

(39.8 %). Chain growth probability of Co/SiO$_2$ catalyst was higher for (C$_3$ ~ C$_8$) and (C$_9$ ~ C$_{20}$) hydrocarbon than Co-Ru/Al$_2$O$_3$ catalyst.

Table 3. Performance of Co-based catalysts in FTS

Catalyst	**CO Conversion (%)**	**CH$_4$ Selectivity (%)**	**Chain Growth Probability (α)**	
			(C$_3$~C$_8$)	**(C$_9$~C$_{20}$)**
Co/SiO$_2$	28	18.7	0.82	0.96
Co/Al$_2$O$_3$	47	39.8	-	-
Ru-Co/Al$_2$O$_3$	22	14.6	0.79	0.92

Reaction conditions ; 230 °C, 20bar, H$_2$/CO feed ratio of 2.
for Co/Al$_2$O$_3$ catalsyst at 250°C, 20bar and feed ratio of 2.

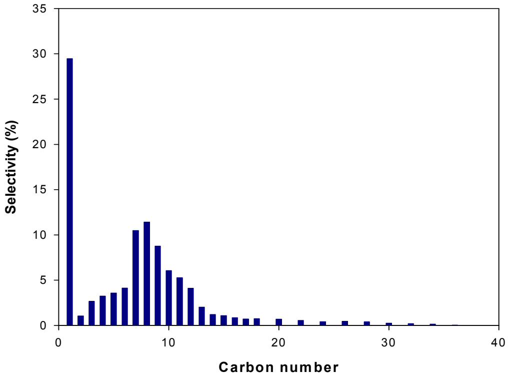

Figure 7 shows the carbon product distribution of FTS over Co/SiO$_2$ catalyst. CH$_4$ selectivity was 28% where a C$_2$ selectivity was less than 3%. The major FTS product over Co/SiO$_2$ catalyst was liquid fuel consists of C$_7$ to C$_{13}$. The results concluded that 250 °C temperature and pressure in the range of 20 ~ 25 bar is suitable for producing liquid fuel less than C$_{20}$ [22].

Figure 7. product distribution for FTS over Co/SiO$_2$ catalyst (250°C, 25bar H$_2$/CO=2).

Conclusions

The particle size of the catalyst calculated from XRD was found to be 5.47 nm and it was good match with TEM results. The effect of temperature on FT reaction was increasing conversion of CO and selectivity of CH$_4$. However, it do not affect on the chin growth probability. The reaction pressure increases a reaction rate in initial time of FTS reaction but it decreased dramatically. In this study, the formation of less than C$_{20}$ were preferred and the proper conditions for the producing liquid fuel was above 250°C in temperature range and between 20 ~ 25 bar in reaction pressure.

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