Effects of Pressure on the Performance of CNTs-Supported Catalyst in a Fischer-Tropsch Reaction

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Abstract: Fischer-Tropsch (FT) reaction involves conversion of syngas (a mixture of carbon monoxide and hydrogen) into higher hydrocarbons in the presence of an active catalyst. The syngas can be derived from non-petroleum feedstocks such as coal, biomass and natural gas, thus the FT reaction provides an alternative route for production of clean fuels. The FT process has received growing interest in recent years due to uncertainty in the Middle East, fast depletion of fossil fuel and environmental concern. This paper reports the synthesis, physicochemical properties and catalytic performance of cobalt-based catalyst in the FT reaction. The catalysts comprised metal nanoparticles supported on carbon nanotubes (CNTs) which were synthesized via a wet impregnation method. The catalysts were characterized using transmission electron microscopy (TEM), temperature-programmed reduction/desorption (TPR/TPD) and X-ray photoelectron spectroscopy (XPS). The performance of the cobalt-based catalysts in a FT reaction was evaluated in a fixed bed microreactor equipped with an on-line gas chromatograph for analyses of hydrocarbon products. The catalysts investigated in this work were Co/CNTs, 70Co30Mn/CNTs, 0.06%K/70Co30Fe/CNTs and 0.04%Nb/70Co30Fe/CNTs. TEM analyses revealed that the average sizes of the metal nanoparticles were 4-5 nm. Based on TPD analyses, the dispersion of these nanoparticles on CNTs were greater than 90%. The presence of both Co^{2+} and Co^{3+} ions were confirmed by XPS analysis. The 0.04%Nb/70Co30Fe/CNTs catalyst performed better than other catalysts in the FT reaction where it resulted in CO conversion of 35% and 16% C_{5+} selectivity at pressure of 1 bar, 220 °C and H_2 :CO of 2:1. Using the same catalyst, the CO conversion and C_{5+} selectivity increased to 60% and 57%, respectively when the pressure was increased to 20 bar.

Key word: Fischer-Tropsch, catalyst, cobalt, fuels.

1. Introduction

Fischer-Tropsch (FT) synthesis is a process which deals with the chemical conversion of syngas (a mixture of carbon monoxide and hydrogen) derived from coal, biomass and natural gas into hydrocarbons consisting of paraffins, olefins, alcohols and aldehydes [1]. Due to uncertainty in the Middle East, limited petroleum reserves and environmental restrictions, FT reaction is gaining more attention nowadays than ever. Fischer-Tropsch synthesis is

considered as a surface-catalyzed polymerization reaction which provides an alternative route for production of clean fuels from non-petroleum source. Cobalt and iron-based catalysts are the most widely used catalysts in the FT reaction. Tavasoli et. al. [2] discovered that the combination of the two most active catalysts, Fe and Co, enhanced the selectivity to alcohols and olefins. It has also been reported that TiO_2 -supported Co-Mn catalyst enhanced the selectivity to higher olefins and middle distillate [3]. Arsalanfar and co-workers [1] recently reported the kinetics and mechanism of Fe-Co-Mn system at temperature range of 290-320 °C and reaction pressure of 1-10 bar. Their findings show that the C_{5+}

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selectivity was enhanced with increasing reaction pressure. They also derived kinetic expressions based on the Langmuir-Hinshelwood-Hougen-Watson mechanism where one of the possibility involved associative CO adsorption on the surface of the transition metal and then hydrogenated producing CH_x monomers which consequently propagate to produce hydrocarbons and oxygenates with a broad range of functionalities and chain lengths.

Gaubas and Klein [4] reported that promoters such as Na, Li, K and Cs increased alkene selectivity and chain growth probability on the iron and cobalt FT catalysts. The application of K as a promoter was found to inhibit the FTS activity drastically while Zr promoter improved the FTS activity significantly due to increase in the surface acidity and heat of adsorption of H_2 on Co catalyst [5]. The effect of Nb as a promoter on CNTs-supported Co-based catalyst has not been reported in the literature. This paper reports the characterization and performance studies of cobalt-based catalyst in a FT reaction. The catalysts tested include monometallic Co and bimetallic Co catalysts promoted with Nb and K. The effects of operating pressure on the CO conversion, CH_4 selectivity and C_{5+} hydrocarbons selectivity over various Co-based catalysts are presented.

2. Experiments

Prior to metal loading carbon nanotubes (CNTs), (purity >95%, length: 10-50 μm , diameter: 10-25 nm, ILJIN Nanotech Co., Ltd) were functionalized and activated. In this process, required amount of CNTs were treated with 35 vol% HNO_3 (65vol%, Merck) for 16 h at 110 $^\circ\text{C}$ followed by washing with deionized water until the pH was neutral and drying overnight at 120 $^\circ\text{C}$. Catalysts were prepared using a wet impregnation method with 5 wt% metal loading on CNTs. For each catalyst, required amounts of the precursor salts i.e. $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ($\geq 98\%$, Fluka) and $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ($\geq 99.0\%$, Merck) were dissolved in deionized water and added to the support drop-wise

with constant stirring followed by drying at 120 $^\circ\text{C}$ overnight and calcining at 500 $^\circ\text{C}$ in nitrogen atmosphere for 6 hours. Bimetallic catalysts, namely Co-Fe and Co-Mn systems were prepared via co-impregnation method. The catalysts were promoted by adding solutions of niobium nitrate or potassium nitrate to the dried catalysts.

The TPR/TPO/TPD profiles of the catalysts were investigated using TPDRO1100 MS (CE Instruments) equipped with a thermal conductivity detector and a mass spectrometer. Typically 20 mg catalyst was placed in the U-shaped quartz tube. Catalyst samples were degassed in a flow of nitrogen at 200 $^\circ\text{C}$. H_2 -TPR was performed using 5% H_2/N_2 with a flow rate of 20 $\text{cm}^3 \cdot \text{min}^{-1}$ and heating from 40 $^\circ\text{C}$ to 800 $^\circ\text{C}$ at 10 $^\circ\text{C} \cdot \text{min}^{-1}$. For H_2 -TPD, the sample was reduced under H_2 flow at 370 $^\circ\text{C}$ for 6 h, cooled to 40 $^\circ\text{C}$ under H_2 flow, flushed with He to remove physisorbed H_2 and then heated to 400 $^\circ\text{C}$ under He flow at 10 $^\circ\text{C} \cdot \text{min}^{-1}$ for 3 h. H_2 -TPD analysis was used to calculate the degree of dispersion of the catalysts and results of TPO analyses were used to calculate the degree of reduction of the catalyst. The CO chemisorption was conducted after the H_2 -TPD by introducing pulses of CO at 250 $^\circ\text{C}$ until the TCD signal was constant.

Morphology of the catalyst samples was characterized using transmission electron microscopy (Zeiss LIBRA 200 TEM at 200 kV). X-ray photoelectron spectra were obtained from K-Alpha spectrometer (Thermo Scientific) at 50 eV pass energy. Fischer-Tropsch reaction was performed in a fixed-bed microreactor (Microactivity-Reference, PID, Eng & Tech) at $T = 220$ $^\circ\text{C}$, $P = 1$ and 20 bar, and $\text{H}_2/\text{CO} = 2$ v/v. Catalyst sample (40 mg) was reduced *in-situ* at 653 K for 5 h in 30 $\text{ml} \cdot \text{min}^{-1}$ of pure hydrogen. On-line gas analysis was performed using Agilent 6890 Hewlett Packard (HP) gas chromatograph (GC) equipped with TCD and FID detectors. Hydrocarbons were separated by the GC-Al/KCl column while other gases were separated

by the serially connected HP-Plot U and HP-Molesieve columns.

3. Experimental Results

3.1 Physicochemical Properties

Fig. 1 shows the TEM of the 70Co30Mn catalyst on CNTs support. Most of the nanoparticles were deposited in the inner walls of the CNTs. The average size of the nanoparticles was 5 ± 2 nm.

The properties of the catalysts are revealed in Table 1. The incorporation of Fe and Mn into Co increased the reducibility, dispersion and CO adsorption capacity of the Co catalyst. However, both K and Nb promoters were found to decrease the reducibility of Co possibly due to electronic modification of the Co which resulted in an increase in CoO phase, as revealed by the XPS studies. The presence of CoO could also contribute to the lower degree of reduction for the promoted 70Co30Fe catalyst. Nevertheless, the presence of both K and Nb promoters enhanced the dispersion and the CO adsorption capacity of the Co-based catalyst.

Fig. 2 shows the XPS spectrum of Co2p region of the un-promoted and Nb-promoted Co-Fe catalyst and the detailed results of XPS are shown in Table 2.

The F30 sample shows an asymmetric main peak of Co2p_{3/2} at 780.4 eV and a satellite peak at 788.3 eV. The Co₃O₄ compound contains Co³⁺ in octahedral symmetry and Co²⁺ in tetrahedral symmetry with binding energy at 779.5 and 780.3 eV, respectively [6]. It has been reported that the presence of a satellite peak at binding energy (BE) around 6 eV above the main peak Co2p_{3/2} is a characteristic of the

octahedrally-coordinated high-spin Co²⁺ oxides (CoO) [7]. In this work, the satellite peak was detected at BE higher than 6 eV, presumably due to difference in support material and electronic modification due to incorporation of a second metal into the Co-based catalyst. The octahedral Co³⁺ and tetrahedral Co²⁺ peaks were not completely resolved in the XPS spectra due to small difference in BE between Co³⁺ (octahedral) and Co²⁺ (tetrahedral) ions. However, the asymmetric Co2p_{3/2} peak suggests that the main peak was due to presence of both Co³⁺ (octahedral) and Co²⁺ (tetrahedral) ions. Results of XPS show that the monometallic Co only contained Co₃O₄ phase whereas the bimetallic Co-Fe and the promoted catalysts also contained CoO phase, as evidenced by the presence of the satellite peak. The ratios of satellite peak (Co²⁺) to the main Co2p_{3/2} peak (Co³⁺) varied with incorporation of a second metal and a promoter. The highest Co²⁺/Co³⁺ ratio was obtained from Nb-promoted 70Co30Fe catalyst which also showed the highest catalytic activity.

Fig. 1 TEM image of 70Co30Mn/CNTs.

Table 1 Results of chemisorption studies on CNTs-supported catalysts.

Code	Catalyst	R* (%)	D* (%)	CO ads (μmol/ gcat)
Co	Co	56.2	73.5	9.0
F30	70Co30Fe	62.2	90.4	13.2
F30K1	0.06%K/ 70Co30Fe	44.1	96.7	15.6
F30Nb2	0.04%Nb/ 70Co30Fe	42.8	96.3	20.7
N30	70Co30Mn	62.2	94.8	17.8

R* is the reduction (%) and D* is the dispersion.

Fig. 2 XPS Co2p spectra (a) F30 (b) F30Nb2.

Table 2 Results of XPS analyses.

Code	BE (eV) Co2p _{3/2}	BE (eV) Fe2p _{3/2}	Peak ratio Co ²⁺ / Co ³⁺
Co	780.6	-	0.19
F30	780.4	711.3	0.83
F30K1	780.6	711.3	0.76
F30Nb2	780.2	711.6	2.4
N30	780.1	-	0.7

3.2 Catalytic Activities

Figs. 3-5 show the effects of pressure on the CO conversion, CH₄ and C₅₊ selectivities, respectively.

The CO conversion over Co, F30K1 (0.06%K/70Co30Fe), F30Nb2 (0.04%Nb/70Co30Fe) and N30 (70Co30Mn) catalysts at 20 bar operating pressure was increased by 27.3%, 55.9%, 59.6% and 38.5%, respectively, compared to those of at 1 bar. This trend agreed with those reported in the literature where it has been suggested that increase in operating pressure increased the concentration of the reactant species over the active sites of the catalysts and hence CO conversion increased. This could also be attributed to increase in adsorption of CO molecules on the surface of the catalysts and improved collision probability of reactants and catalyst [7]. The CO conversion correlated well with the catalyst properties.

Fig. 3 Effects of operating pressure on CO conversions.

Fig. 4 Effects of operating pressure on CH₄ selectivity.

Fig. 5 Effects of operating pressure on C₅₊ selectivity.

Amongst the catalysts tested, the Nb-promoted Fe-Co bimetallic system (F30Nb2) exhibited high dispersion, largest CO adsorption capacity and highest ratio of $\text{Co}^{2+}/\text{Co}^{3+}$ thus exhibited highest catalytic activity.

Fig. 4 shows that selectivity to CH_4 (undesired product) was suppressed at higher operating pressure while Fig. 5 revealed that increasing the pressure to 20 bar increased the selectivity of C_{5+} hydrocarbons (desired products). This effect was more pronounced for the Nb-promoted catalyst (F30Nb2) where C_{5+} selectivity increased from 16.1% to 57.3%. It has been proposed that with increase in the operating pressure the chain growth probability increased which consequently favored selectivities to higher hydrocarbons [8]. Fernandes and Sousa [9] has also reported that an increase in operating pressure would generally increase the chain propagation of CH_x monomers onto the active surfaces of the catalysts and hence increase selectivities for higher hydrocarbons. The values for CO conversion and C_{5+} selectivity were lower than those reported by Tavasoli et al. [2] where they have reported CO conversion of 47% and C_{5+} selectivity of 85.1% using 10%Co/CNTs catalyst under similar operating conditions. However, the CH_4 selectivity obtained from this work was similar to value reported by them, which was 9.3%. The higher CO conversion and C_{5+} selectivity could be due to higher Co loading than the one used in this work.

4. Conclusions

Co-based catalysts with different formulations were supported on CNTs. The incorporation of a second metal improved the degrees of reducibility and dispersion of the catalysts. Results of XPS confirmed that promoters (K and Nb) caused electronic modification in the Co-based catalyst. The performance of the catalysts was evaluated in a Fischer-Tropsch reaction. Amongst the catalysts tested, the Nb-promoted Co-Fe catalyst showed the highest catalytic activity and selectivity of C_{5+} hydrocarbons (desired products). Increasing the

pressure from 1 to 20 bar enhanced both the CO conversion and C_{5+} hydrocarbon selectivity (desired products) while the CH_4 selectivity (undesired product) was suppressed.

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