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$_5$+...
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 CH₃ monomers which consequently propagate to produce hydrocarbons and oxygenates with a broad range of functionalities and chain lengths.

Gauba 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 H₂ 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, CH₄ selectivity and C₅+ 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% HNO₃ (65vol%, Merck) for 16 h at 110 °C followed by washing with deionized water until the pH was neutral and drying overnight at 120 °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. Co(NO₃)₂·6H₂O (≥98%, Fluka) and Mn(NO₃)₂·4H₂O (≥99.0%, Merck) were dissolved in deionized water and added to the support drop-wise with constant stirring followed by drying at 120 °C overnight and calcining at 500 °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 °C. H₂-TPR was performed using 5% H₂/N₂ with a flow rate of 20 cm³·min⁻¹ and heating from 40 °C to 800 °C at 10 °C·min⁻¹. For H₂-TPD, the sample was reduced under H₂ flow at 370 °C for 6 h, cooled to 40 °C under H₂ flow, flushed with He to remove physisorbed H₂ and then heated to 400 °C under He flow at 10 °C·min⁻¹ for 3 h. H₂-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 H₂-TPD by introducing pulses of CO at 250 °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 (Microreactivity-Reference, PID, Eng &Tech) at T = 220 °C, P = 1 and 20 bar, and H₂/CO = 2 v/v. Catalyst sample (40 mg) was reduced in-situ at 653 K for 5 h in 30 ml·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-AI/KCl column while other gases were separated
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 Co2p3/2 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 Co2p3/2 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 Co2p3/2 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 Co2p3/2 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.](image)

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

Table 2  Results of XPS analyses.

| Code | BE (eV) Co2p3/2 | BE (eV) Fe2p3/2 | Peak ratio Co2+ / Co3+ |
|------|-----------------|-----------------|----------------------|
| 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 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.
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Amongst the catalysts tested, the Nb-promoted Fe-Co bimetallic system (F30Nb2) exhibited high dispersion, largest CO adsorption capacity and highest ratio of Co²⁺/Co³⁺ thus exhibited highest catalytic activity.

Fig. 4 shows that selectivity to CH₄ (undesired product) was suppressed at higher operating pressure while Fig. 5 revealed that increasing the pressure to 20 bar increased the selectivity of C₅⁺ hydrocarbons (desired products). This effect was more pronounced for the Nb-promoted catalyst (F30Nb2) where C₅⁺ 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 CH₅ monomers onto the active surfaces of the catalysts and hence increase selectivities for higher hydrocarbons. The values for CO conversion and C₅⁺ selectivity were lower than those reported by Tavasoli et al. [2] where they have reported CO conversion of 47% and C₅⁺ selectivity of 85.1% using 10%Co/CNTs catalyst under similar operating conditions. However, the CH₄ selectivity obtained from this work was similar to value reported by them, which was 9.3%. The higher CO conversion and C₅⁺ 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 C₅⁺ hydrocarbons (desired products). Increasing the pressure from 1 to 20 bar enhanced both the CO conversion and C₅⁺ hydrocarbon selectivity (desired products) while the CH₄ selectivity (undesired product) was suppressed.

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