Development of Cobalt-Niobium Bimetallic catalysts for Fischer-Tropsch reaction

Mohammad Tazli Azizan, Mir Muhammad Sohaib, Noorasmawati Mohd Zabidi

ABSTRACT

The synthesis, characterization and performance evaluation in Fischer-Tropsch reaction of silica supported cobalt and niobium bimetallic catalysts prepared through the reverse microemulsion method are discussed here. The physiochemical properties of the catalyst were analysed using transmission electron microscopy (TEM), and N2 physical adsorption. Fischer-Tropsch synthesis was carried out in a fixed-bed microreactor at 493 K, 1 atm, H2:CO molar ratio of 2:1 and space velocity, SV = 20 mL/min. TEM analysis indicated that addition of niobium changes the structure of cobalt particles from spherical to hexagonal in structure. CO conversion for all the catalysts were between 10 -11% only. The lowest CH4 selectivity and highest C5+ selectivity were 6.58% and 8.79% respectively as shown by 95Co5Nb/SiO2. All synthesized catalyst produce high olefin content with the highest being 88.74% (90Co10Nb/SiO2). In general all the synthesized catalysts are found to be more suitable to make olefin rather than paraffin, which needs to be further hydrogenated for alkane production. The low production of C5+ however is also subjected to low reaction pressure and Nb is suitable to be the catalyst promoter instead as a bimetallic couple to Co.

INTRODUCTION

The manifestation on world sustainability for the future generation has encouraged the interest to find new ways of doing things to preserve the environment, among which, to seek for the alternatives to hydrocarbon feedstock. The discovery on appropriate ways to utilize world’s abundant hydrocarbon resources other than crude oil has attracted considerable interest in recent years. Biogas, biomass, coal, coal-bed gas and natural gas are all hydrocarbon feedstock which can be converted into liquid fuels. However, direct transformation of these non-petroleum hydrocarbon resources into synthetic liquid fuels is relatively complex. One of the most practical ways of transforming these non-petroleum based hydrocarbon feedstock into synthetic liquid fuels is through the Fischer-Tropsch synthesis. Liquid fuels derived from the FTS are of high quality and do not contain sulphur or aromatics (Zhang, Qet. et al., 2013). Generally, there are three main steps of FTS; production of syngas (a mixture of CO + H2), liquefaction of syn gas and products up grading (Masters, C., 1979). The following stoichiometric reactions (equation 1-4) illustrate the different possibilities of products being formed during FTS (Xu, J, 2003):

- Methanation: $CO + 3H_2 \rightarrow CH_4 + H_2O$ (1)
- Paraffin formation: $nCO + (2n + 2)H_2 \rightarrow C_nH_{2n+2} + nH_2O$ (2)
- Olefin formation: $nCO + 2nH_2 \rightarrow C_nH_{2n} + nH_2O$ (3)
- Oxygenate formation: $nCO + 2nH_2 \rightarrow C_nH_{2n+1}OH + (n - 1)H_2O$ (4)

The catalyst is the key for further improvement in the efficiency of FTS. The development of catalyst with high activity, selectivity and stability are the areas of focus in the field of FTS research. All the elements of group VIII of the periodic table display considerable activity towards FTS (Ali S. et al., 2011). Among them, cobalt is the most preferred catalyst due to its low cost, high activity, stability and hydrocarbon productivity. The incorporation of second metal component in cobalt based catalyst enhances the activity and stability compared to its monometallic counterpart. Examples of such...
bimetallic cobalt catalysts include combinations such as Co-Fe, Co-Mn and Co-Ru. These bimetallic catalysts are dispersed on supports which act as a carrier and contribute to the catalytic activity. Among the most commonly used supports for Co based catalysts are SiO$_2$, Al$_2$O$_3$ and TiO$_2$ (Ali S et. al., 2011, Khodakov, A.Y. et. al., 2007, Diehl & Khodakov A.Y., 2009). The summary of works carried out by other researchers on Cobalt catalyst for FTS is highlighted in Table 1. From Table 1, three main catalysts system can be grouped together which consisted of Fe bimetallic couple to Co/Al$_2$O$_3$ catalysts (Ali S. et. al., 2011), Co-based catalysts in the presence of Re as the bimetallic couple with different support such as Al$_2$O$_3$, TiO$_2$ and SiO$_2$ (Diehl,F and A.Y Khodakov, 2009) and finally Nb doped Co/CNT catalysts system (Ali, S et. al., 2011b). The findings from Diehl, F and A.Y Khodakov (2009), suggested that at high reaction pressure i.e. at 20 bar, and relatively low reaction temperature, the CO conversion is high as well as the selectivity of C5+. Among all the catalysts synthesized by Diehl and A.Y Khodakov (2009), Re paired with Co over TiO$_2$ catalysts gave high selectivity of C5+. However, with respect Co/SiO$_2$ catalyst, the conversion was lower, though in the presence of Re as bimetallic pair.

In this paper, a preliminary study on synthesis of silica supported monometallic and bimetallic cobalt and niobium catalysts is presented. It is the main interest to see if Co/SiO$_2$ catalytic activities can be improved in the presence of niobium. The effects of incorporating different loadings of niobium into cobalt on the physiochemical properties and Fischer Tropsch synthesis activity of the silica supported catalysts are discussed.

### Table 1: Summary of the catalysts prepared and evaluated in Fischer-Tropsch reaction by various researchers.

<table>
<thead>
<tr>
<th>Author</th>
<th>Catalyst</th>
<th>Reaction Conditions</th>
<th>CO conversion (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ali S et. al. (2011)</td>
<td>Co/Al$_2$O$_3$</td>
<td>T = 543 K P = 1 bar H$_2$/CO = 2</td>
<td>6.3</td>
<td>15.6 CH$_4$ 3.5 C$_5$</td>
</tr>
<tr>
<td>Ali S et. al. (2011)</td>
<td>70Co30Fe/Al$_2$O$_3$</td>
<td>T = 543 K P = 1 bar H$_2$/CO = 2</td>
<td>8.1</td>
<td>16.1 CH$_4$ 3.2 C$_5$</td>
</tr>
<tr>
<td>Ali S et. al. (2011)</td>
<td>50Co50Fe/Al$_2$O$_3$</td>
<td>T = 543 K P = 1 bar H$_2$/CO = 2</td>
<td>7.5</td>
<td>18.4 CH$_4$ 2.2 C$_5$</td>
</tr>
<tr>
<td>Ali S et. al. (2011)</td>
<td>30Co70Fe/Al$_2$O$_3$</td>
<td>T = 543 K P = 1 bar H$_2$/CO = 2</td>
<td>4.2</td>
<td>19.0 CH$_4$ 1.0 C$_5$</td>
</tr>
<tr>
<td>Diehl, F. and A.Y. Khodakov (2009)</td>
<td>10%Co/Al$_2$O$_3$</td>
<td>T = 483 K P = 20 bar H$_2$/CO = 2</td>
<td>42.6</td>
<td>9.7 CH$_4$ 80.2</td>
</tr>
<tr>
<td>Diehl, F. and A.Y. Khodakov (2009)</td>
<td>10%Co-0.5%Re/Al$_2$O$_3$</td>
<td>T = 483 K P = 20 bar H$_2$/CO = 2</td>
<td>42.8</td>
<td>8.8 CH$_4$ 80.8</td>
</tr>
<tr>
<td>Diehl, F. and A.Y. Khodakov (2009)</td>
<td>10%Co/SiO$_2$</td>
<td>T = 483 K P = 20 bar H$_2$/CO = 2</td>
<td>40.4</td>
<td>9.1 CH$_4$ 81.7</td>
</tr>
<tr>
<td>Diehl, F. and A.Y. Khodakov (2009)</td>
<td>10%Co-0.5%Re/SiO$_2$</td>
<td>T = 483 K P = 20 bar H$_2$/CO = 2</td>
<td>40.3</td>
<td>8.7 CH$_4$ 83.4</td>
</tr>
<tr>
<td>Diehl, F. and A.Y. Khodakov (2009)</td>
<td>10%Co/TiO$_2$</td>
<td>T = 483 K P = 20 bar H$_2$/CO = 2</td>
<td>39.8</td>
<td>10.2 CH$_4$ 81.6</td>
</tr>
<tr>
<td>Diehl, F. and A.Y. Khodakov (2009)</td>
<td>10%Co-0.5%Re/TiO$_2$</td>
<td>T = 483 K P = 20 bar H$_2$/CO = 2</td>
<td>42.6</td>
<td>8.9 CH$_4$ 84.8</td>
</tr>
<tr>
<td>Ali, S et. al. (2011b)</td>
<td>Co/CNT</td>
<td>T = 543 K P = 1 bar H$_2$/CO = 2</td>
<td>15.7</td>
<td>17.4 CH$_4$ 14.0</td>
</tr>
<tr>
<td>Ali, S et. al. (2011b)</td>
<td>0.02%Nb/Co/CNT</td>
<td>T = 543 K P = 1 bar H$_2$/CO = 2</td>
<td>21.6</td>
<td>12.6 CH$_4$ 15.1</td>
</tr>
<tr>
<td>Ali, S et. al. (2011b)</td>
<td>0.04%Nb/Co/CNT</td>
<td>T = 543 K P = 1 bar H$_2$/CO = 2</td>
<td>25.5</td>
<td>7.1 CH$_4$ 19.5</td>
</tr>
<tr>
<td>Ali, S et. al. (2011b)</td>
<td>0.06%Nb/Co/CNT</td>
<td>T = 543 K P = 1 bar H$_2$/CO = 2</td>
<td>22.2</td>
<td>7.8 CH$_4$ 14.3</td>
</tr>
</tbody>
</table>

**Methodology:**

**Preparation of catalysts:**
Three catalysts were synthesized and characterized, denoted as 100Co/SiO2, 95Co5Nb/SiO2, and 90Co10Nb/SiO2. Silica (silica dioxide, 99.8%, Evonik) was used as a support for the catalyst. Prior to the deposition of metal particles it was dried at 350°C for 3 h and then allowed to cool at room temperature. Two separate microemulsions were prepared prior to mixing them together. Microemulsion A was prepared using triton X-114 (98.0%, ACROS Chemicals) and cyclohexane (98.0%, Aldrich). Microemulsion B was prepared using catalyst precursor cobalt (cobalt nitrate, 99.0%, Merck) and niobium (ammonium niobium oxalate, 99.9%, Aldrich). The two microemulsions were mixed together until a microemulsion mixture was formed. Hydrazine (98%, Aldrich) was then added to the microemulsion mixture in a 10 fold molar excess to the metal content. The silica support was then straight away added to the microemulsion and the mixture was stirred continuously for 3 h with drop wise addition of THF (99.5%, J.T Baker) at a rate of 1mL/min. The mixture was then left overnight for sedimentation. The solid catalyst was collected using vacuum filtration, washed several times with ethanol and left for overnight drying. Finally, the catalyst was calcined at 500°C for 3 h to remove traces of surfactant and nitrate precursor.

**Characterization of catalysts:**

\[
\text{CO conversion (\%) = } \frac{CO_{in} - CO_{out}}{CO_{in}} \times 100
\]

\[
\text{CH4 selectivity (\%) = } \frac{\eta_{\text{CH}_4}}{\sum \eta_{\text{hydrocarbons}}} \times 100
\]

\[
\text{C}_2-\text{C}_4 \text{ selectivity (\%) = } \frac{\sum \eta_{\text{C}_2-\text{C}_4}}{\sum \eta_{\text{hydrocarbons}}} \times 100
\]

\[
\text{C}_5+ \text{ selectivity (\%) = } \frac{\sum \eta_{\text{C}_5+}}{\sum \eta_{\text{hydrocarbons}}} \times 100
\]

\[
\text{Olefin (\%) = } \frac{\sum \eta_{\text{olefin}}}{\sum \eta_{\text{hydrocarbons}}} \times 100
\]

\(\eta\) represents the number of moles of the respective component.

**RESULTS & DISCUSSIONS**

**Morphology of the catalysts:**

TEM analysis revealed the morphology of the sample catalysts. TEM images of the catalyst samples at 50 nm magnification are shown in Figure 1. The addition of niobium changed the structure of cobalt particles from spherical to hexagonal in structure (Figure 1D). Furthermore, from the FESEM observation, it can be demonstrated that the addition of niobium to the catalyst led to a better dispersion of particles and they are more homogenous. 90Co10Nb/SiO2 shows the most well dispersed particles (Figure 2).

The morphology of the catalyst samples was analysed using transmission electron microscope (Carl Zeiss Libra 200 FE) at 200 KV accelerating voltage. TEM sample was prepared in iso-propanol and the suspension was then deposited on a carbon coated copper grid. Field Emission Scanning Electron Microscopy (Carl Zeiss AG Supra 55 VP) was also used to observe the morphology of the catalysts and the homogeneity of the metals over the support. The samples were mounted on aluminium stubs using carbon tape and the images were taken at 5kV of the beam voltages. Meanwhile, the textural properties of the catalyst samples such as surface area, average pore size distribution and pore volume, were measured using N2-adsorption (Micromeritics ASAP 2000).

**Catalytic activity:**

The performance of the catalyst in Fischer-Tropsch synthesis was studied using a fixed bed microreactor at 493 K and 1 atm, H2:CO molar ratio of 2:1 and space velocity, SV = 20 mL/min. Generally, 0.2 g of catalyst sample was fed into the reactor and reduced at 673 K for 5 h under pure H2 flow. The product was analyzed via on-line gas chromatography (GC) to identify the products obtained from the reactor. The CO conversion, different hydrocarbons selectivity and olefin selectivity were calculated using equations (1), (2), (3), (4) and (5):  

\[
N2-adsorption revealed the surface area, average pore size distribution and pore volume of the sample catalysts. Table 2 illustrates the textural properties of the catalyst. The addition of niobium to the catalyst decreased the pore volume and pore size. The BET surface area was strongly dependent on the ratio of cobalt and niobium. The largest surface area of 4.0061m²/g was obtained when the cobalt and niobium ratio was 90:10. Based on desorption pore volume plot by BJH method, Figure 3B and 3C illustrate that multiple kinds of pores existed in sample 95Co5Nb/SiO2 and 90Co10Nb/SiO2 whereas only one kind of pore was obtained from sample 100Co/SiO2 (Figure 3A).
These indicate that the textural properties of catalyst changed from nonporous to porous upon addition of niobium. Furthermore, sample 100Co/SiO2 follows type III isotherm which indicates weak interaction between adsorbate and adsorbent while the other two samples with niobium addition follow type II isotherm, indicating macroporous adsorbent and unrestricted multilayer adsorption.

<table>
<thead>
<tr>
<th>Co:NB</th>
<th>BET Surface Area (m²/g)</th>
<th>Pore Volume (cm³/g)</th>
<th>Pore Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100:0</td>
<td>2.4135</td>
<td>0.008340</td>
<td>16.35850</td>
</tr>
<tr>
<td>95:5</td>
<td>1.8483</td>
<td>0.003253</td>
<td>11.77000</td>
</tr>
<tr>
<td>90:10</td>
<td>4.0061</td>
<td>0.006123</td>
<td>6.11356</td>
</tr>
</tbody>
</table>

**Fig. 1:** Representative TEM images for sample A) 100Co/SiO2, B) 95Co5Nb/SiO2, C) 90Co10Nb/SiO2 and D) Hexagonal structure of Co particle after addition of niobium

**Catalytic Activity:**

The FTS performance of sample catalysts was evaluated after 5 h of time on stream. The CO conversion and product selectivity of the sample catalysts are summarized in Table 3. The highest CO conversion was 11% exhibited by 100Co/SiO2 whereas the lowest was 10.23% exhibited by 95Co5Nb/SiO2. In general, the CO conversion was quite low for all catalysts prepared, but generally they are better than Ali S et. al. (2011) on Co-Fe/Al₂O₃ catalysts. CH₄ selectivity for all the catalyst samples is quite low compared to C₂-C₄ selectivity. The highest C5+ selectivity is given by 95Co5Nb/SiO2 which is 8.79%. The reason for low selectivity towards C5+ hydrocarbons is that, the Fischer Tropsch reactions favor high pressure conditions (15-20 bar). Since the experiment was conducted under atmospheric pressure, high C5+ selectivity could not be achieved. In addition, 90Co10Nb/SiO2 gives the highest olefin selectivity. High olefin production indicate that all the catalysts are suitable to make olefin rather than paraffin. This suggests that more hydrogenation reaction is required in the reactor to hydrogenate all alkenes to alkanes, following the stepwise F-T reaction (Dry, M.E, 2002).

It is interesting to note that, the findings obtained here can be used as a good guidance in order to synthesize Nb promoted Co supported catalysts in the future. The findings from Ali S. et. al. (2011b) on Nb and Co catalysts suggested that Nb can be used as a promoter to Co, at a very low weight percentage over CNT catalyst. This finding defined the limit of to what extent would Nb weight percentage should be coupled with Co over SiO2 support, which is not more than 5 wt%. This again, emphasized that Nb is not suitable to be the bimetallic couple for Co, but instead becoming a promoter to Co catalysts.

According to the time on stream of CO conversion over all the three catalysts as shown in Figure 4, it can clearly be seen that, though the...
catalysts’ conversions are relatively low, these catalysts, which were synthesized via reverse microemulsion method can be considered as stable. For the total duration of 5 hours of continuous reaction, the conversion of CO remained stable and no sign of deactivation had been detected.

Fig. 2: FESEM images at magnification of 1.00 KX and 10.00 KX.

Fig. 3: Desorption pore volume plot by BJH method for A) 100Co/SiO2, B) 95Co5Nb/SiO2 and C) 90Co10Nb/SiO2.
Table 3: Activity and product distribution of catalyst samples.

<table>
<thead>
<tr>
<th>Co:Nb</th>
<th>CO conversion (%)</th>
<th>CH₄</th>
<th>C₂-C₄</th>
<th>C₅+</th>
<th>Olefins</th>
</tr>
</thead>
<tbody>
<tr>
<td>100:0</td>
<td>11.00</td>
<td>7.64</td>
<td>91.89</td>
<td>0.49</td>
<td>86.51</td>
</tr>
<tr>
<td>95:5</td>
<td>10.23</td>
<td>6.58</td>
<td>84.85</td>
<td>8.79</td>
<td>86.32</td>
</tr>
<tr>
<td>90:10</td>
<td>10.31</td>
<td>7.74</td>
<td>91.80</td>
<td>0.46</td>
<td>88.74</td>
</tr>
</tbody>
</table>

Fig. 4: Time on stream studies of CO conversion over all three catalysts.

Conclusion:
The addition of niobium changes the structure of cobalt particles from spherical to hexagonal in structure and decreases the pore size and pore volume of particles. The CO conversion is relatively low, but the synthesized catalysts are relatively stable. CH₄ selectivity for all sample catalysts is relatively low compared to C₂-C₄ selectivity with the highest C₅+ selectivity is obtained by the FTS reaction over 95Co5Nb/SiO₂. All prepared catalysts demonstrated high olefin productivity thus the catalysts synthesized are more suitable to produce olefin rather than paraffin. The finding shows that Nb is more suitable to be used as a promoter, rather than as a bimetallic couple to Co, and the weight percentage of Nb should not be more than 5wt%.

ACKNOWLEDGEMENT

This work was financially supported by Ministry of Education (Higher Education Department) under MyRA Incentive Grant Program.

REFERENCES