CHAPTER SIX

This chapter deals with discussion on the results of the Fischer-Tropsch evaluation of the iron and cobalt catalysts.

6.1 Iron catalysts

Comparison of Table 4.1.1 and 5.1.2 shows that surface area of Fe-Zn-Ca catalyst is higher than that of Fe-Zn catalyst which accounts for the higher reaction rate for liquid & wax production for the Fe-Zn-Ca catalyst however an increase in reaction rate of liquid & wax production for Fe-Zn-Cu catalyst is due to higher hydrogenation activity (Fig 4.1.4). The commercial precipitated Fe-SiO$_2$ based F-T catalysts are water gas shift (WGS) active. The WGS is often considered as desired complementary activity which accounts for H$_2$/CO usage ratio flexibility of the Fe-based F-T catalysts [192]. However, the WGS activity is at the expense of expelling part of the CO as CO$_2$ resulting in lower carbon utilization. Also it has been a long held general view that CO$_2$ hydrogenation over iron based FT catalysts occurs via reverse water gas shift reaction (r-WGS) mechanism [192, 193]. When used as promoter, K enhances WGS activity in iron based FT catalysts. Hence, K has become ubiquitous promoter in commercial iron based FT catalysts. Based on the principle of microscopic reversibility, K is also generally considered relevant for H$_2$ and CO$_2$ management including achieving low CO$_2$ selectivity via the WGS equilibrium (CO + H$_2$O $\rightleftharpoons$ CO$_2$ + H$_2$) [95].

Normally the WGS equilibrium can be constrained to favour low CO$_2$ selectivity by removal of water and high by imposing CO$_2$ partial pressure. Dominik et al. [194] have proposed use of a membrane to facility in situ removal of water from the catalyst bed. This approach suffers the disadvantage of complex reactor system [195]. However, in this study low CO$_2$ selectivity is achieved without imposition of the water removal and high CO$_2$ partial pressure. Therefore the CO$_2$ selectivity of the Fe-Zn based catalysts in this study did not occur via WGS equilibrium. Wensheng et al [196] have investigated FT synthesis using CO$_2$ containing syngas of H$_2$/CO ratio 2 over Fe$_2$O$_3$ promoted with Zn, Cu and K. The
catalyst has been prepared by impregnating with a solution containing Zn(NO$_3$)$_2$, K$_2$CO$_3$, and Cu(NO$_3$)$_2$. They have reported that the Zn catalyst display lower CO$_2$ selectivity than unpromoted and other Zn-free promoted catalysts. They have also observed that effect of Zn on CO$_2$ selectivity is suppressed in the presence of the other promoters, but the authors did not probe further on why the effect is suppressed.

Ni et al. [46] have proposed that r-WGS is not an indispensable step in FT reaction with CO$_2$. Similar studies [47, 48] on CO$_2$ hydrogenation over Zr promoted and unpromoted Fe-Zn catalysts indicate that hydrocarbon formation from CO$_2$ proceeds largely via methanol intermediate. The reports have implicated ZnFe$_2$O$_4$ as an active phase for the methanol formation. This suggests that lower CO$_2$ selectivity observed in the Zn impregnated Fe$_2$O$_3$ reported by Wensheng et al [196] can be attributed to ZnFe$_2$O$_4$ phase. However, formation of ZnFe$_2$O$_4$ becomes suppressed in the presence of other promoters when the Zn/Fe ratio in the catalyst is very small (≈ 0.05) and the impregnation method used for adding Zn to the catalyst favours interaction of Zn with the other promoters over Fe$_2$O$_3$. Similarly, it can also be said that ZnFe$_2$O$_4$ phase is not only a textural promoter as suggested by Li et al [160] but plays an important role in lowering CO$_2$ selectivity obtained in the Fe-Zn (Zn/Fe = 0.1). They have introduced Zn by co-precipitation with Fe but the effect on CO$_2$ selectivity of Zn becomes suppressed when the catalyst is promoted by Cu and K, which are introduced by impregnation.

The above highlights suggest that sufficient amount of ZnFe$_2$O$_4$ phase formation is required to minimise CO$_2$ selectivity and subsequent introduction of other promoters will not affect the CO$_2$ selectivity. The Zn/Fe ratio of 0.25 and co-precipitation method used in this study produce sufficient ZnFe$_2$O$_4$ phase and it influences the product selectivity which is not inhibited by other promoters. As shown in Table 5.1.2, the catalysts display very low CO$_2$ selectivity. This low CO$_2$ selectivity can be attributed to in-situ utilization of the CO$_2$ generated for hydrocarbon formation via the reaction [48]:

\[
\text{CO}_2 + 3\text{H}_2 \rightarrow \text{[CH}_3\text{OH]} + \text{H}_2\text{O} \rightarrow \text{CO} + 2\text{H}_2 \rightarrow \text{-CH}_2\text{-} + \text{H}_2\text{O}.
\]
Surface acidity and basicity are important catalyst properties which influence FT product selectivity. NH$_3$- and CO$_2$-TPD studies of the catalysts indicate that unpromoted Fe-Zn oxide possesses major and fairly distributed weak and medium strength acid-base sites. Incorporation of the promoters alters the sites distributions. Cu incorporation in Fe-Zn decreases total sites densities but the distributions are less affected. Presence of Ca in Fe-Zn introduces strong basic sites in the catalyst. Effect of the promoters is evident on the product selectivity of the catalysts (Tables 5.1.1, 5.1.2 and Figure 5.1.3). Copper promoted catalysts produce little or no wax product and display lower olefins/paraffins ratio compared to the copper free catalysts (Figure 5.1.3). This may be due to increase in hydrogenation activity of the catalysts with copper promotion. It also accounts for their lower α-values relative to those without copper. The difference in the product selectivity of Fe-Zn-Ca and Fe-Zn may be due to the presence of strong basic sites on the Fe-Zn-Ca catalyst, which promotes alternative chain termination step (Aldol condensation route). However, it appears that the influence of Cu dominates Ca as indicated by the similar selectivities obtained in the Cu containing catalysts.

![Figure 6.1.1: Olefins/parafins ratios of the oil portion of the liquid product of the iron catalysts](image-url)
Besides the low CO$_2$ selectivity, the composition of reactor exit gas from the unpromoted catalyst (Fe-Zn) has some interesting features. First, cumulative selectivities of undesired products (CO$_2$ and CH$_4$) in the exit gas are very low. Second, C$_2$/C$_3$ ratio is only slightly greater than unity. This is contrary to the popular anomaly in C$_2$ selectivity in most reported FT product spectrum (Figure 6.1.2).

Figure 6.1.2: Anomaly in C$_2$ selectivity in typical FT product spectrum

C$_2$/C$_3$ ratio in conventional LTFT product spectrum is usually less than unity. C$_2$/C$_3$ ratio greater than unity have only been reported for LTFT using H$_2$/CO/CO$_2$ feed [197-199]. Third, C$_4$ selectivity is about half that of C$_2$, and selectivity of C$_2$ is also about half that of C$_1$. Similar results are observed in the promoted catalysts except in Fe-Zn-Ca which displays twice the value of C$_1$/C$_2$ ratio compared to other catalysts. The outlier behaviour may be due to higher propensity of C$_2$ to reactivity on Fe-Zn-Ca. This may be attributed to synergistic effect of high hydrogenation activity and presence of strong basic sites on Fe-Zn-Ca.
While it is too difficult to draw mechanistic information from the observed selectivity of the exit gas composition of the catalysts, it is believed that the trends can give insights to C-C coupling pathway on the catalysts. A mini ASF plot (Figure 6.1.4) using C₁ to C₄ data in the Table 5.1.1 suggests that same monomer and/or C-C coupling mechanism in the four catalysts. Also, the ratios C₃̅/C₃, C₂̅/C₂ and C₁ selectivity (Figure 6.1.2) mirrored the order of hydrogenation activity of the catalysts.
The analysis of the liquid products reveals the C₅⁺ product selectivity. The carbon number distribution of hydrocarbons for each of the Fe-based catalyst has been presented in Figure 5.1.3 and product selectivities follow a non-ASF distribution (Figure 6.1.5). A line of best fit to the data at carbon number ≥ 8 is used to obtain chain growth probability, ‘α’, for the catalysts (Table 6.1.1).

![Figure 6.1.5: ASF plot of liquid hydrocarbons products of the iron catalysts](image)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>C₅-C₇</th>
<th>C₈-C₁₈</th>
<th>C₉-C₁₉</th>
<th>α-values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-Zn</td>
<td>1.1</td>
<td>53.6</td>
<td>44.6</td>
<td>0.8</td>
</tr>
<tr>
<td>Fe-Zn-Ca</td>
<td>5.4</td>
<td>67.4</td>
<td>27.1</td>
<td>0.8</td>
</tr>
<tr>
<td>Fe-Zn-Cu</td>
<td>1.7</td>
<td>96.1</td>
<td>2.4</td>
<td>0.7</td>
</tr>
<tr>
<td>Fe-Zn-Cu-Ca</td>
<td>6.1</td>
<td>84.0</td>
<td>9.9</td>
<td>0.7</td>
</tr>
</tbody>
</table>

Table 6.1.1: Summary of carbon number range product selectivity of the iron catalysts

A summary of the carbon number range product selectivity of the catalysts in Figure 5.1.3 is presented in Table 6.1.1. The Table shows that presence of calcium increased the proportion of C₅-C₇ at the expense of those of > C₁₉ while retaining the same proportion of
C₈-C₁₈ as it in calcium free counterpart. Copper and calcium promotion increased the proportion of C₈-C₁₈. Copper promotion tends to cut off the hydrocarbon chain at C₁₈; while Ca merely shrunk the distribution in favour of C₈-C₁₈ range. Cu-Ca co-promoted catalyst displays about average of the distribution of respective separately promoted catalysts. Taking into consideration that Fe-Zn-Cu produced no wax product (Table 6.1.1), it is worthwhile observing that copper promoted catalyst displays an unprecedented high selectivity to C₈-C₁₈ portion (Table 5.1.2). With the exception of core-shell catalysts (zeolite encapsulated FT catalysts) [200], no such observation on LTFT Fe-catalyst with such a narrow carbon number product selectivity has been reported before.

The C₅⁺ hydrocarbon distribution of the iron catalysts in terms of fuel classification is presented in Table 6.1.2. Ca promotion increases gasoline fractions with a proportionate decrease of wax fraction. With respect to unpromoted catalyst, both diesel and gasoline fractions increased in the Cu promoted catalysts at the expense wax selectivity. Fe-Zn-Cu and Fe-Zn-Cu-Ca catalysts show similar selectivity to gasoline and diesel fractions, but kerosene fraction in Fe-Zn-Cu catalyst is higher than that of Fe-Zn-Cu-Ca catalyst. Refining of the FT-products derived from the present study (Table 6.1.2) is required to meet the fuels specification for different end uses.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Gasoline (C₇-C₁₁)</th>
<th>Kerosene (C₉-C₁₅)</th>
<th>Diesel (C₁₂-C₂₂)</th>
<th>Wax &gt; C₂₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-Zn</td>
<td>15.5</td>
<td>38.1</td>
<td>51.4</td>
<td>32.6.</td>
</tr>
<tr>
<td>Fe-Zn-Ca</td>
<td>31.3</td>
<td>48.8</td>
<td>49.9</td>
<td>16.3</td>
</tr>
<tr>
<td>Fe-Zn-Cu</td>
<td>40.1</td>
<td>73.4</td>
<td>58.2</td>
<td>1.1</td>
</tr>
<tr>
<td>Fe-Zn-Cu-Ca</td>
<td>39.6</td>
<td>60.7</td>
<td>57.4</td>
<td>1.4</td>
</tr>
</tbody>
</table>

Table 6.1.2: C₅⁺ hydrocarbon distribution of the iron catalysts in terms of fuel classification.
6.2 Cobalt catalysts

As shown in Table 4.2.1, BET surface area of the cobalt catalysts decrease with increasing metal loadings. However, the adsorption behaviour of the catalysts depends on the nature of phases or surface species on the catalysts. Adsorption of reactants on the catalysts surface is a key elementary step in the reaction; hence CO and H\(_2\) adsorption are examined to gain insight about the performance of the catalysts. Although CO adsorption on substrates (metals, oxides etc) has been a subject of many theoretical and experimental studies, interpretation of CO desorption profiles require cautions. CO can behave as a Lewis acid or a Lewis base depending on the nature of surface and reaction conditions. Based on electronegativity of carbon and oxygen, C=O bond is expected to be partially polar molecule with \(\delta^+\) and \(\delta^-\) charges on carbon and oxygen respectively. This implies that CO should adsorb on positive centres (or anion vacant sites) through the oxygen atom and on negative centres (cation vacant sites) through the carbon atom. However, molecular orbital theory denotes neutral ground state CO molecules as \(\delta^-\text{C}=\text{O}^+\delta\), as opposed to what is expected based on normal electronegativity values of carbon and oxygen. It is explained that the situation is because the centre of the 5\(\sigma\) orbital lies not along the molecular axis but outside the inter-nuclear distance [201]. Thus, a reverse situation is likely for adsorption of CO on surface defects. Similarly, according to valence bond theory, CO has lone pairs of electrons on its oxygen atom and a vacant p-orbital on its carbon atom. This implies that CO can be adsorbed on a substrate through the carbon atom as a Lewis base or as a Lewis acid. Another aspect of interpretation of results of CO desorption studies is the possibility of molecular or dissociative adsorption [202-205]. Comparison of site distributions in CO-TPD and NH\(_3\)-TPD profiles of the catalysts indicates that CO behaves as base, although weaker base than NH\(_3\). The CO-TPD profiles (Figure 4.2.12) of the supports show higher and very broad desorption temperatures compared to those of NH\(_3\)-TPD profiles. It indicates that CO adsorption on \(\gamma\)-alumina is an activated process and that acid-base behaviour of CO coupled with acid-base sites on the \(\gamma\)-alumina.

Amount of CO adsorbed on metal sites is a function of adsorption stoichiometry and metal dispersion. The amounts of desorbed CO of copper promoted catalysts are lower than those
of copper-free catalysts (Figure 4.2.15). The lower CO adsorption capacities of the copper containing catalysts may be due to the decoration effect of copper clusters on cobalt nanoparticles. However, higher adsorption strength of the copper containing catalysts is not consistent with normal Cu-CO interaction explanation. Similar decrease in CO adsorption capacity is reported for Pd-Cu/SiO$_2$ catalyst [206]. Resasco and co-workers showed through density functional theory (DFT) calculation that furfural adsorbed on Cu/SiO$_2$ through carbonyl O in a g1(O)-aldehyde configuration. Copper alloy of Pd, Ni and Co are found to exhibit higher hydrogenation activity and selectivity for conversion of furfural to furfuryl alcohol [207,208]. The performance of the catalysts is explained in terms of synergistic adsorption of the carbonyl compound through O atom by copper and through the C atom by the alloy metals (Pd, Ni, Co). Strong molecular CO adsorption on Co$^{2+}$ species have been proposed to account for alcohol selectivity in Co-Cu catalyst [209-212]. In the present study copper containing catalyst show higher reducibility than the copper-free counter, hence, stronger CO adsorption on the catalyst will be inconsistent with presence of non-reducible cobalt species. A plausible explanation for the observed CO adsorption strength in the copper containing catalysts is a synergistic interaction of CO with cobalt and copper through its carbon and oxygen atoms respectively. This adsorption behaviour of CO on the Co-Cu based catalysts is strongly connected with the observed oxygenates selectivity of Co-Cu/Al$_2$O$_3$.

The H$_2$-TPD experiments are carried out for catalysts and the unloaded supports under the same condition. Co shows higher H$_2$ chemisorption capacity compared to Cu. But the adsorption capacity of the metals (Co, Cu) is an order magnitude lower than that of γ-alumina. It is inferred that the H$_2$ adsorption capacities of the catalysts are to a large extent due to the supports. Cu-support interface appears to promote H$_2$ adsorption. It is worthy of note that in spite of the separate facile adsorption of CO and H$_2$ on the supports, they are not active for CO hydrogenation or C-C coupling. This may suggests that CO and H$_2$ adsorptions on the supports are mutually exclusive or because the phases of the support (Al and Ca) are not redox active. CO adsorption requires either an acidic or a basic site; H$_2$ chemisorption requires a pair of acid-base sites. A recent report have identified Al–O–CO
units in the transition state involved in CO activation step of Fischer-Tropsch synthesis over γ-alumina supported cobalt catalyst [213]. CO hydrogenation is not a facile process on γ-alumina because CO adsorption on γ-alumina surface may impairs H₂ adsorption. However, γ-alumina may serve as hydrogen and CO reservoir for metal sites in γ-alumina supported metal catalysts for syngas conversions.

The TCD and FID analysis of the reactor exit gas is presented in Table 5.2.1. Exit H₂/CO ratio of the promoted catalysts are lower than that of the unpromoted catalyst. This implies that the promoted catalysts display higher H₂/CO usage ratio compared to the unpromoted catalyst. Usually high H₂/CO usage ratio is an indication of high hydrogenation activity and high selectivity to methane and gaseous products. However, the result presented in Table 5.2.1 shows that the H₂/CO usage ratio of the promoted catalysts does not reflect in their C₁-C₄ selectivities. It is observed that characteristic deviation in C₂ selectivity from ASF distribution that is typical of FTS production spectrum is less apparent in the catalysts; especially the Ca-containing catalysts (Figure 6.2.1). It is also worth of note that CO₂ and CH₄ selectivities of the promoted catalysts are very low compared to that of the unpromoted catalyst. Promotion of Ca and Cu virtually suppresses CO₂ selectivity, but presence Cu appears to have higher influence in decreasing methane selectivity. This is contrary to the observation of Jacobs et al. [214], whose report indicates increased methane and decreased C₅+ selectivities in a copper promoted Co/Al₂O₃ catalyst.
The carbon number distribution of oil portions of the products is shown in Figure 5.2.3. All the Co-based catalysts show similar positively skewed unimodal product distribution of hydrocarbons with modes occurring around C₉ – C₁₃ for Co/Al₂O₃, Co/CaO-Al₂O₃ and Co-Cu/CaO-Al₂O₃ catalysts whereas mode occurs at C₁₁ – C₁₅ for Co-Cu/Al₂O₃ catalyst. The carbon number distribution of hydrocarbons from the catalysts followed ASF distribution up till about C₂₅ after which the data curve deviates from its straight line nature. This kind of deviation for ASF distribution model has been widely reported. It is believed that such deviation is due to natural low diffusivity of the FTS products with increasing carbon number which contribute to decreasing tendency of desorption from the active sites of the catalysts. Calculated chain growth probabilities (‘α’ values) of the catalysts from ASF plot and a summary of the carbon number range product selectivity of the catalysts are presented in Table 6.2.1. The ‘α’ values of product distribution for the catalysts decrease with increasing metal loading on the γ-alumina. This coincides with increase of C₅-C₇ and decrease of > C₁₉ selectivities of the catalysts (except Co-Cu/Al₂O₃) with increasing metal loading on the γ-alumina. From Table 4.2.4, it is observed that the surface concentration of cobalt in presence of the promoters suggests that the promoters inhibit or block the chain growth sites. The Cu promotion leads to increase in > C₁₉ selectivity and decrease in C₅-C₇.
selectivity as evident from the product distribution for the catalysts Co/Al₂O₃ and Co-Cu/Al₂O₃ in Table 6.2.1. But the C₈-C₁₈ selectivity increases with increasing metal loading on the γ-alumina.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>C₅-C₇</th>
<th>C₈-C₁₈</th>
<th>&gt; C₁₉</th>
<th>α-values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co/Al₂O₃</td>
<td>9.9</td>
<td>66.6</td>
<td>22.6</td>
<td>0.84</td>
</tr>
<tr>
<td>Co-Cu/Al₂O₃</td>
<td>2.2</td>
<td>69.8</td>
<td>27.7</td>
<td>0.82</td>
</tr>
<tr>
<td>Co/CaO-Al₂O₃</td>
<td>12.3</td>
<td>70.5</td>
<td>16.5</td>
<td>0.81</td>
</tr>
<tr>
<td>Co-Cu/CaO-Al₂O₃</td>
<td>17.7</td>
<td>72.5</td>
<td>9.5</td>
<td>0.80</td>
</tr>
</tbody>
</table>

Table 6.2.1: Summary of carbon number range product selectivity of the cobalt catalysts

Figure 6.2.2: ASF plot of liquid hydrocarbons products of the cobalt catalysts

The C₅⁺ hydrocarbon distribution of the cobalt catalysts in terms of fuel classification is presented in Table 6.2.2. Co-Cu/Al₂O₃ shows increase in diesel and decrease in gasoline fractions compared to Co/Al₂O₃. The Ca-containing cobalt catalysts display decrease in wax selectivity and increase in gasoline and diesel fractions. While the four catalysts produced fairly similar distribution of kerosene fraction.
Despite the similar carbon number distributions of hydrocarbons discussed above, the catalysts display different activity and dissimilarities in terms of gross product selectivity (Table 5.2.2). Co-Cu/Al₂O₃ has lowest activity and hydrocarbon selectivity among the cobalt catalysts. More than > 98.7% of non-gaseous product is oxygenate rich aqueous products. Pictures of the used catalysts are shown in Figure 6.2.3. The two catalysts namely Co-Cu/Al₂O₃ and Co-Cu/CaO-Al₂O₃ are wax free. Cobalt fine contamination of FT wax has been reported in commercial GTL plant in which alumina supported cobalt catalyst is used. Recently, Bui and de Klerk [215] have also drawn attention to cobalt leaching via carboxylic acids produced during FT synthesis. They have explained that there is high tendency of cobalt leaching if these carboxylates are produced in substantial amount during FT synthesis. Because the decomposition temperatures of C₁-C₅ carboxylates of cobalt (>250 °C) are higher than the operating temperature for a typical cobalt-based low-temperature FT process (~220 °C). However, ICPOES analysis of the aqueous products obtained from the Co-Cu/Al₂O₃ shows no clear evidence of cobalt leaching.

Recent reports by de la Osa et al. indicate that Ca promoted cobalt catalysts increase FT synthesis rate and C₅⁺ selectivity in favour of C₁₆-C₁₆ hydrocarbons [141]. A contrary result is obtained in the present study. The difference may be due to effect of catalyst preparation condition. After cobalt impregnation de la Osa et al., calcined their catalysts at 550 °C, in this study the catalysts are calcined at 350 °C.
Figure 6.2.3: Pictures of the cobalt catalysts after reaction

Co/Al₂O₃  
Co/Ca-Al₂O₃  
Co-Cu/Al₂O₃  
Co-Cu/CaO-Al₂O₃