

CHAPTER II

LITERATURE REVIEWS

There have been a number of researchers studying alumina-supported Co and Fe catalysts in Fischer-Tropsch synthesis. Many researchers have improved these catalysts by changing the compositions of alumina supports or by adding small amounts of metal to modify the alumina supports.

2.1 Alumina synthesis by the solvothermal method

Inoue *et al.* (1988-1996) have developed a technique to synthesize inorganic materials by using organic media at elevated temperature (200-300°C) under autogeneous pressure of organic for many years. It has been found that many oxides and mixed oxides can be crystallized in organic media at temperature lower than that required by the hydrothermal reaction. In 1988, they have reported that the glycothermal treatment (the use of glycol instead of water for hydrothermal treatment) of gibbsite at 250°C yielded glycol derivative of boehmite. In 1992, they have found that the reaction of aluminum isopropoxide (AIP) in toluene at 300°C resulted in χ -alumina. In 1995, they have prepared silica-modified alumina by the reaction of AIP and tetraethyl orthosilicate (TEOS) in 1,4-butanediol at 300°C. The products were found to maintain large surface areas after calcination at high temperature.

Mekasuwandumrong *et al.* (2000-2004) synthesized nanocrystalline transition alumina with micro spherical particles and high thermal stability by decomposition of aluminum isopropoxide (AIP) under solvothermal conditions. It have been reported that thermal decomposition of aluminum isopropoxide in mineral oil at 250-300°C over 2 h resulted in χ -alumina powder having high thermal stability that could be transformed directly to α -alumina at temperature higher than 1000°.

2.2 Effect of support for cobalt catalysts in FTS

R. Riva *et al.* (2000) studied the interaction of cobalt with two different kinds of support: silica and titania and their effect on the dispersion and reducibility by XPS, TPR, TPO, XRD and TEM. They also showed that the interaction is much stronger in the case of titania. The different reactivity of cobalt with silica and titania explains why reducing and reoxidizing treatments have opposite effects on the dispersion of cobalt depending on whether it is supported on SiO₂ or TiO₂. The low reactivity of cobalt with silica favors sintering effects. Conversely, due to the high reactivity of cobalt with titania, the coverage of TiO₂ by cobalt tends to increase after the same treatments.

R. Bechara *et al.* (2001) studied the Co/Al₂O₃ catalysts, prepared from four commercial aluminas, with different cobalt loading have been studied for the carbonmonoxide hydrogenation. The activity of the powder catalyst at 15 wt% cobalt on alumina follows a logarithmic decrease with the time on stream, as for the paraffin/olefin ratio. This behavior can be explained by the evolution of the catalyst surface (partial reoxidation, site blocking). On the other hand, the product distribution does not significantly change with the time on stream. The selectivity follows the Schulz-Flory model; secondary reactions, are not significant. An increase in the reduction temperature generally improves the CO transformation rate and favours the production of higher hydrocarbons. The activity and selectivity on heavy product improvements result from the increases, respectively in the number of active sites and in the coordination number of metallic cobalt atoms. It seems that the increase of cobalt loading affect the specific rate of reaction or/and the selectivity only through its influence on the reducibility of the active phase. For higher cobalt loading, high site density leads to secondary, which modifies the product distribution. The study of the influence of the support has shown the importance of the porosity of pellet catalysts after impregnation on the activity and the selectivity. The evolution of the chain growth probability α is closely related to the degree of reduction, increasing the more reduced the cobalt is. Nevertheless, the chain growth probability α seems to be limited at a maximum value, which is around 0.89 at our conditions.

J. Zhang *et al.* (2003) studied the cobalt supported on different γ -alumina carries prepared by incipient wetness impregnation are used to investigate the effect of support on the performance of cobalt catalysts for FTS. It is found that the acidity of the support has a great influence on the interaction with metallic cobalt and the reducibility of cobalt. The support with low acidity leads to the higher active FTS catalysts. Furthermore, the high reducibility and more bridged type Co which is favored by γ -alumina with low acidity appears to be responsible for high C_5^+ hydrocarbon selectivity and low methane selectivity.

B. Jongsomjit *et al.* (2003) studied Zirconia (Zr)-modified alumina-supported Co catalysts by the sequential impregnation method. They have studied the impact of Zr loading on the reducibility of Co in the absence and presence of water vapor. They reported that Zr modification of the alumina support had a significant impact on the catalyst properties: the overall activity during FT synthesis increased significantly upon Zr modification due to an increase in reducibility during standard reduction. Furthermore, the increase in reducibility appeared to have been caused by a decrease in the amount of Co-SCF. They also suggested that Zr modification may have caused: (i) a stabilization of the alumina support by blocking Co “aluminate” formation and/or (ii) a minimization of the impact of water vapor in modifying the surface properties of alumina, thereby decreasing the ease of Co reaction with the alumina.

H. Xiong *et al.* (2005) studied Al_2O_3 that was calcined at different temperatures to get supports with different pore size. Co/ Al_2O_3 catalysts with different pore size were prepared by incipient wetness impregnation technique. The pore size of support Al_2O_3 was found to have a significant effect on Co_3O_4 crystallite diameter, catalyst reducibility and FTS activity. The larger pore size enhanced the formation of bigger crystallite diameter Co_3O_4 on the catalyst and the occurrence of larger pore size catalyst decreased the number of cobalt active sites on the surface of the catalyst and the reducibility of the catalyst, resulting in the decrease in FTS activity.

B. Jongsomjit *et al.* (2005) studied the dependence of crystalline phases in titania on the catalytic properties of Co/ TiO_2 catalysts during CO hydrogenation. They suggested that the presence of rutile phase (19 mol%) in titania resulted in significant

increases in the catalytic activities during CO hydrogenation. This is mostly due to an increase in stability of the titania support with the presence of rutile phase. They proposed that the presence of rutile phase in titania stabilized the catalysts, probably due to two reasons: (i) blockage of the formation of Co species strongly interacts with the titania support or Co-SCF; and (ii) inhibition of the impact of water vapor produced during reduction.

B. Jongsomjit *et al.* (2006) studied the catalytic behaviors of mixed TiO_2 - SiO_2 -supported cobalt catalyst. It was found that both initial and steady-state rates during CO hydrogenation dramatically decreased with the amounts of titania present in the mixed supports. The decreased activities had to be attributed to the lower number of reduced cobalt metal surface atoms for catalyzing the reaction. At the specified conditions, the selectivity of the longer chain hydrocarbons (C_2 - C_5) was more pronounced with the presence of titania in the mixed supports. It can be concluded that the presence of titania apparently inhibited the chain growth probability during CO hydrogenation.

2.3 Effect of Cu for iron catalysts in FTS

S. Li *et al.* (2001) studied the Zn, K, and Cu effects on the structure and surface area and on the reduction, carburization, and catalytic behavior of Fe-Zn and Fe oxides used as precursors to Fischer-Tropsch synthesis (FTS) catalysts. It is found that Fe_2O_3 precursors initially reduce to Fe_3O_4 and then to metallic Fe (in H_2) or to a mixture of $\text{Fe}_{2.5}\text{C}$ and Fe_3C (in CO). Zn, present as ZnFe_2O_4 , increases the surface area of precipitated oxide precursors by inhibiting sintering during thermal treatment and during activation in H_2/CO reactant mixtures, leading to higher FTS rates than on ZnO-free precursors. ZnFe_2O_4 species do not reduce to active FTS structures, but lead instead to the loss of active components; as a result, maximum FTS rates are achieved at intermediate Zn/Fe atomic ratios. Cu increases the rate of Fe_2O_3 reduction to Fe_3O_4 by providing H_2 dissociation sites. Potassium increases CO activation rates and increases the rate of carburization of Fe_3O_4 . In this manner, Cu and K promote the nucleation of oxygen-deficient FeO_x species involved as intermediate inorganic structures in reduction and carburization of Fe_2O_3 and decrease the ultimate size of the Fe oxide and carbide structures formed during activation in synthesis gas. As a

result, Cu and K increase FTS rates on catalysts formed from Fe–Zn oxide precursors. Cu increases CH₄ and the paraffin content in FTS products, but the additional presence of K inhibits these effects.

R.J. O'Brien *et al.* (2004) studied the impact of copper on an alkali promoted iron Fischer–Tropsch catalyst. It is found that the FTS rate increased with increasing copper loading in the range of 0–2 atomic ratio per 100 Fe. According to a proposed kinetic expression, the FT reaction rate is dependent on a rate constant, k , and an adsorption parameter, b . Copper has been found to increase the rate constant and decrease the adsorption parameter, both of which cause an increase in FT rate. They also reported that copper increased the water gas shift rate; however, it did not increase CO₂ selectivity when comparisons were made at similar conversion. The water gas shift reaction quotient only approaches the equilibrium constant at high conversion; furthermore, copper did not increase the reaction quotient. The effect of copper on product selectivity has been determined over a wide range of conversions. It is found that copper had a similar effect on product selectivity as potassium. Methane selectivity decreased and products heavier than C₁₁ increased with increasing copper loading. Copper did not effect alkene selectivity or the isomerization of 1-alkenes to 2-alkenes.

V. Zyl *et al.* (2004) invented an iron-based FTS catalyst composition wherein the main iron phase is ferrihydrite, where the catalyst composition includes a high amount of copper. Typically, the composition includes 15% to 20% (by mass) copper, replacing manganese and zinc in the composition. It was found that the catalyst compositions according to the invention having high amounts of copper show good productivity and selectivity towards alcohol and olefins in the Fischer-Tropsch reaction, and are comparable to catalysts containing manganese and zinc.

C.H. Zhang *et al.* (2006) studied the metal–silica interaction and catalytic behavior of Cu-promoted Fe-Mn-K/SiO₂ catalysts in FTS reaction. The characterization results indicate that several kinds of metal oxide–silica interactions are present on Fe-Mn-K/SiO₂ catalysts with or without copper, which include iron–silica, copper–silica, and potassium–silica interactions. In addition to the well-known effect of Cu promoter on easing the reduction of iron-based FTS catalysts, it is found

that Cu promoter can increase the rate of carburization, but does not vary the extent of carburization during the steady-state FTS reaction. The basicity of the Cu and K co-promoted catalyst is greatly enhanced, as demonstrated by CO₂-TPD results. In the FTS reaction, Cu improves the rate of catalyst activation and shortens the induction period, whereas the addition of Cu has no apparent influence on the steady-state activity of the catalyst. Promotion of Cu strongly affects hydrocarbon selectivity. The product distribution shifts to heavy hydrocarbons, and the olefin/paraffin ratio is enhanced on the catalyst due to the indirect enhancement of surface basicity by the copper promotion effect.