CHAPTER I

INTRODUCTION

Depleting oil reserves make it necessary to develop alternative methods for synthesizing hydrocarbon fuels. The Fischer-Tropsch synthesis (FTS), first developed in Germany in 1923, is an important technology in the production of liquid fuels and chemicals from syngas derived from coal, natural gas, and other carbon-containing materials (Zhang *et al.*, 2006). Today, this procedure is again of great interest, because it is a method of obtaining "Clean" fuels and chemicals. However, the cost of its production is higher than fuels from oil refineries. Therefore, much research has been performed in order to bring the production cost down by attempting to develop better catalysts.

Several metals are active for the FTS, however, only cobalt and iron catalysts appear economically feasible on an industrial scale (Rao *et al.*, 1992). Cobalt catalysts are known to be attractive due to their high activity, selectivity for linear hydrocarbons (Steynberg *et al.*, 2004; Iglesia, 1997). Iron catalysts are more versatile than cobalt catalysts, produce less methane and can be geared for the production of alkenes, oxygenates and branched hydrocarbons, depending on promoters and the process conditions employed (O'Brien *et al.*, 1997; Mills, 1988). Many inorganic supports such as SiO_2 (Martinez *et al.*, 2003; Kusama *et al.*, 1997), Al_2O_3 (Jongsomjit *et al.*, 2003; Das *et al.*, 2003; Cubeiro *et al.*, 1999), TiO_2 (Rothaemel *et al.*, 1997; Jongsomjit *et al.*, 2005) and zeolites (Li *et al.*, 2003) have been extensively studied for supported Co and Fe catalysts for years.

It is well known that Al_2O_3 is usually adopted as the support to prepare cobalt catalysts due to its excellent texture. Its amphoteric nature also provides a variety of interesting features (Adesina, 1996). Various alumina phases (α, γ, χ, δ, η and θ) has been prepared by different methods such as, sol-gel synthesis (Brinker and Scherrer, 1990), hydrothermal synthesis (Dawson, 1988), microwave synthesis (Deng and Lin, 1997), emulsion evaporation (Sarikaya *et al.*, 2001; Sevinc *et al.*, 1991), plasma technique (Scott and Matijevic, 1978), and solvothermal synthesis (Inoue *et al.*, 1995; Inoue *et al.*, 1996). Among these methods, solvothermal synthesis attracts the most attention because it gives the products with small uniform morphology, well-controlled chemical composition, and narrow size distribution. Furthermore, desired shape and size of particles can be produced by controlling process conditions such as solute concentration, reaction temperature, reaction time, and the type of solvent (Deng *et al.*, 2003).

For alumina supported cobalt catalysts, it is reported that γ-Al_2O_3 is usually used as the support because it provides a better dispersion of catalytically active metals due to its higher surface area. Only a few publications have reported the effect of other crystalline phases of alumina on the properties of alumina-supported catalysts. To our knowledge, the effect of mixed γ- and χ-Al_2O_3 phases on the properties of Al_2O_3 as a catalyst support has never been reported.

For alumina supported iron catalysts, it is found that Fe can easily react with alumina support to form compounds (Zhang *et al.*, 2006; Wan, Articles in press) and is often difficult to reduce when highly dispersed on the support. Development of highly active supported Fe catalysts could reduce the catalyst density making catalyst application in fluidized/slurry reactors easier. Most of the studies reported methods used for improving these catalysts performance by promoting with the additives such as K (Duvenhage and Coville, 2005), Mn (Li *et al.*, 2007; Li *et al.*, 2002), Cr (Duvenhage and Coville, 2005), Ru (Li *et al.*, 2002), and Pd (Luo *et al.*, 2004). Cu is usually present in bulk Fe catalysts as a reduction promoter (Li *et al.*, 2002; Storch *et al.*, 1951; Xu and Bartholomew, 2005). It facilitates reduction of iron oxide to metallic iron during hydrogen activations by lowering the reduction temperature which, in turn, reduces sintering of the metallic iron that is formed (Dry *et al.*, 1981). However, little work has been done for using Cu to modify the metal oxide support for supported iron catalyst. Cu is more interesting than many other transition metals since it does not alloy with Fe. This means there is less chance that desired Fe catalytic properties would be modified.

This thesis focuses on investigation of various factors affecting characteristics and catalytic properties of alumina-supported Co and Fe FTS catalysts, which are the effect of concentration of aluminum isopropoxide (AIP) in 1-butanol used in the preparation of nanocrystalline alumina by solvothermal method for alumina and alumina-supported Co catalysts, the effect of mixed γ and χ crystalline phases in alumina support for alumina-supported Co catalysts, and the effect of Cu as an Al_2O_3-modifier for alumina-supported Fe catalysts. The study was scoped as follows:

Topic 1: To investigate the influence of concentration of aluminum isopropoxide in 1-butanol used in the preparation of nanocrystalline alumina by solvothermal method on the properties of alumina powders and alumina supported-cobalt catalysts during CO hydrogenation reaction.

1. Preparation of nanocrystalline Al_2O_3 with different amount of aluminum isopropoxide (10, 15, 25, and 35 g) in 1-butanol by solvothermal method.
2. Preparation of Al_2O_3-supported Co catalysts (10 wt% Co) using the incipient wetness impregnation method.
3. Characterization of alumina and the catalyst samples using X-ray diffraction (XRD), BET surface area, transmission electron microscopy (TEM), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), H_2 chemisorption, and temperature programmed reduction (TPR).
4. Reaction study of the catalyst samples in CO hydrogenation at 220°C and 1 atm and a H_2/CO ratio of 10.

Topic 2: To investigate the effect of mixed γ and χ crystalline phases in Al_2O_3 on the characteristics and catalytic activities of alumina-supported cobalt catalysts during CO hydrogenation reaction.

1. Preparation of nanocrystalline Al_2O_3 with different amount of aluminum isopropoxide (10, 15, 25, and 35 g) in 1-butanol by solvothermal method.
2. Preparation of Al_2O_3-supported Co catalysts with different Co loadings (5, 10, 15, and 20 wt% Co) using the incipient wetness impregnation method.

3. Characterization of alumina and the catalyst samples using X-ray diffraction (XRD), BET surface area, transmission electron microscopy (TEM), and H_2 chemisorption.
4. Reaction study of the catalyst samples in CO hydrogenation at 220°C and 1 atm and a H_2/CO ratio of 10.

Topic 3: To investigate the effect of Cu as an Al_2O_3-modifier on the characteristics and catalytic activities of alumina-supported iron catalysts during FTS reaction.

1. Preparation of Cu-modified alumina supported Fe catalysts (10 wt% Cu, 20 wt% Fe) using the sequential incipient wetness impregnation method (Use the commercial γ-alumina support).
2. Characterization of the catalyst samples using X-ray diffraction (XRD), BET surface area, scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), and CO chemisorption.
3. Reaction study of the catalyst samples in FTS reaction at 280°C and 1.8 atm and a H_2/CO ratio of 2.