CHAPTER II

LITERATURE REVIEWS

This chapter reviews the work about alumina-silica composites supported Co catalyst that is also of great interest in the field of heterogeneous catalysis, while it has been used for catalytic application. The last section of this review shows a few research investigate supported metal catalyst in CO and CO_2 hydrogenation system.

2.1 The silica supported metals

Kogelbauer et al. [1995] studied the formation of cobalt silicates on Co/SiO_2 under hydrothermal conditions. Hydrothermal treatment at 220°C led to a catalyst with lower reducibility due to the formation of both reducible and nonreducible (at temperature < 900°C) Co silicates. They also showed that silicate was formed in catalysts which had been used for FT synthesis. No significant change occurred upon hydrothermal treatment of calcined catalyst. The presence of air during the hydrothermal treatment inhibited the formation of silicate and they proposed that the formation of silicate was linked to the presence of metallic cobalt.

Choi [1995] investigated the reduction of cobalt catalysts supported on Al_2O_3, SiO_2, and TiO_2 and the effect of metal loading on the reduction. The activation energy of reduction increased in following order: $Co/SiO_2 > Co/Al_2O_3 > Co/TiO_2$. For different metal loading, the catalyst with the higher loading is more readily reducible than with the lower metal loading.

Jacobs et al. [2002] investigated the effect of support, loading and promoter on the reducibility of cobalt catalysts. They have reported that significant support interactions on the reduction of cobalt oxide species were observed in the order $Al_2O_3 > TiO_2 > SiO_2$. Addition of Ru and Pt exhibited a similar catalytic effect by decreasing the reduction temperature of cobalt oxide species, and for Co species where a significant surface interaction with the support was present, while Re impacted mainly the reduction of Co species interaction with the support. They also suggested that, for catalysts prepared with a noble metal promoter and reduced at the same temperature, the increase in the number of active sites was due to mainly to improvements in the percentage reduction rather than the actual dispersion (cluster size). Increasing the cobalt loading, and therefore the average Co cluster size, was found to exhibit improved reducibility by decreasing interactions with the support.

Okabe et al. [2004] investigated Fischer-Tropsch synthesis was carried out in slurry phase over uniformly dispersed Co-SiO_2 catalysts prepared by the sol-gel method. When 0.01-1 wt% of noble metals were added to the Co-SiO_2 catalysts, a high and stable catalytic activity was obtained over 60 h of the reaction at 503 K and 1 MPa. The addition of noble metals increased the reducibility of surface Co on the catalysts, without changing the particle size of Co metal significantly. High dispersion of metallic Co species stabilized on SiO_2 was responsible for stable activity. The uniform pore size of the catalysts was enlarged by varying the preparation conditions and by adding organic compounds such as *N,N*-dimethylformamide and formamide. Increased pore size resulted in decrease in CO conversion and selectivity for CO_2, a byproduct, and an increase in the olefin/paraffin ratio of the products. By modifying the surface of wide pore silica with Co-SiO_2 prepared by the sol-gel method, a bimodal pore structure catalyst was prepared. The bimodal catalyst showed high catalytic performance with reducing the amounts of the expensive.

2.2 The alumina-silica composites supported metals

The research has emphasized that the supports such as Al_2O_3, SiO_2, and TiO_2 can significantly enhanced the activity, selectivity and catalytic properties as well [Storsaeter et al., 2005]. SiO_2 has been considered to be very attractive because of high surface area, thermal stability and improving the reduction degree of supported cobalt [Khodakov et al., 1997; Backman et al., 1998]

Nowadays, the alumina-silica composites supported metal catalysts have attracted the scientists attention in the catalyst filed. Recently, it was reported that alumina-silica modified supports exhibited better catalysic properties than classical oxides such as alumina or silica.

Daniell et al. [2000] investigated the modification of g-alumina with silica led to the creation of both highly acidic Lewis and Brönsted acid sites (BASs); the former through isomorphous substitution of Si^{4+} ions by Al^{3+} ions at tetrahedral lattice sites; and the latter through formation of bridged hydroxy groups, similar to those found in zeolites. The relative strength and quantity of these sites reached a maximum with 40 wt.% silica content, above which the surface of the samples became silica coated and exhibited acidity approximating that of pure silica.

Baca et al. [2008] synthesized multiple grafting of Al isopropoxide, the mesoporous aluminas of controlled pore sizes, in organic solvents on mesoporous silica SBA-15. The results show that the chemical nature of the Al-grafted materials varies continuously with the number of grafting from pure silica to pure alumina. Typically, after three graftings, this original method of synthesis allows one to prepare ordered mesoporous alumina with specific surface areas above 300 m^2 g^{-1} and a narrow pore size distribution centered on ca. 60 A^o.

Gu et al. [2009] studied the mesoporous silica with modified alumina through one-pot synthesis, solvent-free solid grinding and gel-mixing methods, in order to optimize the adsorptive capability of mesoporous composite. Modification with alumina significantly increased the ability of MCM-41 to trap NPYR, and among various preparations the solvent-free solid grinding method was able to disperse alumina guest with high accessibility and to reserve surface silanol groups on MCM-41. Typically, the Al_2O_3/MCM-41 composite synthesized by solvent-free method with 12 wt.% alumina exhibited a capacity comparable to zeolite NaY for trapping NPYR in airflow but four times superior to NaY for adsorbing bulky nitrosamine NNN in solution.

Marie et al. [2009] studied the structure and catalytic performance in fixed bed reactor at 20 bars of cobalt FischereTropsch catalysts supported by commercial alumina (Puralox) and silica-doped alumina (Siralox) by varied cobalt loading between 8 and 15 wt.%; both alumina and silica-doped alumina supports had similar textural properties. The presence of small amounts of silica in alumina (5 wt.% SiO_2) enhanced cobalt reducibility and hindered formation of hardly reducible cobalt aluminate species. Higher FischereTropsch reaction rate over cobalt catalysts supported on silica-doped alumina was attributed to better cobalt reducibility.

Sun et al. [2010] studied the reversible promotional effect of SiO2 modification to Co/Al_2O_3 catalyst for Fischer–Tropsch synthesis. The addition of a small amount of SiO_2- to Al_2O_3-supported cobalt catalyst significantly increased the reduction degree of the supported cobalt oxides and the metallic cobalt surface area. Compared with the Al_2O_3-promoted Co/SiO_2 catalyst, the present catalyst exhibited a reversible promotional effect in slurry-phase FTS. Either Al_2O_3 modification to Co/SiO_2 or SiO_2 addition to Co/Al_2O_3 exhibited highest CO conversion at 10 wt.% extra addition amount, indicating the precise balance among dispersion, reduction degree, BET surface area and metallic Co surface area.

2.3 The supported metal catalysts in CO and CO_2 hydrogenation system

Development of catalyst for CO and CO_2 hydrogenation is the key technology of gas to liquid (GTL) process. The catalytic hydrogenation of carbon monoxide and carbon dioxide produces a large variety of products ranging from methane and methanol to higher molecular weight alkanes, alkenes and alcohols. [Somorjai, 1994; Dry, 1996; Adesina, 1996; Iglesia, 1997].

Frohlich et al. [1996] investigated the activation and deactivation of Co foils during hydrogenation of carbon dioxide in dependence on pretreatment of the catalyst and time on stream, temperature and composition of the educt gas by means of a combination of various methods. Both oxidation/reduction of the surface and incorporation of oxygen and carbon in the bulk lead to marked changes in the surface structure and a considerable increase in surface area. The catalytic activity of the oxidized surface concerning the hydrogenation of CO_2 is small, but increases strongly with reduction. Deactivation is accompanied with structural changes and proved to be reversible. Chemical poisoning was only observed after addition of hydrogen sulfide to the educt gas.

Lahtinen et al. [1994] investigated C, CO and CO_2 hydrogenation on cobalt foil model catalysts. It was found that the reactions produce mainly methan, but with selectiveities of 98, 80, and 99 wt% at 525 K for C, CO and CO_2, respectively. The rate of methane formation on cobalt foil shows zero order partial pressure dependence on CO_2 and first order partial pressure dependence on H_2. The reaction proceeds via dissociation of C-O bonds and formation of CoO on the surface. The reduction of CoO is the rate limiting step in the CO and CO_2 hydrogenation reaction. These authors also proposed the reaction mechanisms for C, CO and CO_2 hydrogenation.

The reaction mechanisms proposed for C, CO and CO_2 hydrogenation.

C HYDROGENATION	**CO HYDROGENATION**	**CO_2 HYDROGENATION**
	$CO + {}^{*} \leftrightarrow CO^{*}$	$CO_2 + {}^{*} \leftrightarrow CO_2^{*}$
$H_2 + 2^{*} \leftrightarrow 2H^{*}$	$H_2 + 2^{*} \leftrightarrow 2H^{*}$	$H_2 + 2^{*} \leftrightarrow 2H^{*}$
		$CO_2^{*} + Co \leftrightarrow CO^{*} + CoO$
	$CO^{*} + Co \leftrightarrow C^{*} + CoO$	$CO^{*} + Co \leftrightarrow C^{*} + CoO$
$C^{*} + H^{*} \leftrightarrow CH^{*} + {}^{*}$	$C^{*} + H^{*} \leftrightarrow CH^{*} + {}^{*}$	$C^{*} + H^{*} \leftrightarrow CH^{*} + {}^{*}$
$CH^{*} + H^{*} \leftrightarrow CH_2^{*} + {}^{*}$	$CH^{*} + H^{*} \leftrightarrow CH_2^{*} + {}^{*}$	$CH^{*} + H^{*} \leftrightarrow CH_2^{*} + {}^{*}$
$CH_2^{*} + H^{*} \leftrightarrow CH_3^{*} + {}^{*}$	$CH_2^{*} + H^{*} \leftrightarrow CH_3^{*} + {}^{*}$	$CH_2^{*} + H^{*} \leftrightarrow CH_3^{*} + {}^{*}$
$CH_3^{*} + H^{*} \leftrightarrow CH_4 + 2^{*}$	$CH_3^{*} + H^{*} \leftrightarrow CH_4 + 2^{*}$	$CH_3^{*} + H^{*} \leftrightarrow CH_4 + 2^{*}$
	$CoO + H^{*} \rightarrow OH^{*} + Co$	$CoO + H^{*} \rightarrow OH^{*} + Co$
	$OH^{*} + H^{*} \leftrightarrow H_2O + 2^{*}$	$OH^{*} + H^{*} \leftrightarrow H_2O + 2^{*}$
		or
		$CO^{*} + H^{*} \leftrightarrow COH^{*} + {}^{*}$
		$COH^{*} + H^{*} \leftrightarrow H_2CO^{*} + {}^{*}$
		$H_2CO^{*} + Co \leftrightarrow CH_2^{*} + CoO$

Yongqing et al. [2002] investigated CO and CO_2 hydrogenation on silica and alumina supported cobalt Fischer-Tropsch synthesis catalysts. It found that CO and CO_2 hydrogenation obtained similar catalytic activity but the selectivity was very different, FTS product distributions were observed with an $\propto$ of about 0.8; in contrast, the CO_2 hydrogenation products contained about 70% or more of methane and propose reaction pathway for CO and CO_2 hydrogenation.

Okabe et al. [2004] investigated the Fischer-Tropsch synthesis that was carried out in slurry phase over uniformly dispersed Co/SiO_2 catalysts prepared by sol-gel method. When 0.01-1 wt% of noble metals were added to the Co/SiO_2 catalysts, a high and stable catalytic activity was obtained over 60 h of the reaction at 503 K and 1 MPa. The addition of noble metals increased the reducibility of surface Co on the catalysts, without changing the particle size of Co metal. The uniform pore size of the catalysts was enlarged by varying the preparation conditions. Increase pore size resulted in decreased CO conversion and selectivity for CO_2 and increased olefin/paraffin ration of the products.

Panagiotopoulou et al. [2008] investigated that the catalytic performance of Al_2O_3 supported noble metal catalysts for the methanation of CO, CO_2 and their mixture with respect to nature of the dispersed metallic phase (Ru, Rh, Pt, Pd). It has been found that, for all experimental conditions investigated, Ru and Rh are significantly more active than Pt and Pd. Selectivity towards hydrogenation products depends strongly on the noble metal catalyst employed as on whether solo- or co-methanation of CO/CO_2 is occurring. In present of water in the feed, catalytic activity of Ru is not affected, while that of Rh is reduced. On the other hand, the performance of pt and Pd is poor since they promote the undesired water-gas shift reaction.