CHAPTER II

REVIEW OF METHANOL SYNTHESIS

Methanol can be produced from almost any hydrocarbon or carbon materials. At present virtually all synthetic methanol is produced by the catalytic reaction of carbon monoxide and hydrogen made either by reforming natural gas, or from petroleum-derived heavy-hydrogen mixtures.

The first industrial catalyst for the synthesis of methanol from CO and H_2 was zinc/chromium (chromite) catalyst, introduced by BASF in 1923. Its main drawback was a low activity. In order to reach a profitable yield of methanol, the process had to be carried out at high temperature and pressure (573-653 K, up to 25 MPa). The conversion achievable may be greatly limited by thermodynamic equilibrium. Since the reaction are all exothermic, maximum equilibrium conversion is a achievable at the low temperature. With a mixture of carbon monoxide and hydrogen a large charity of products are thermodynamically more stable than methanol. The methanol synthesis catalyst must therefore be highly selectivity as well as active.

To produce a relatively pure methanol product directly requires care in catalyst manufacture, and producers to avoid catalyst contamination iron and nickel in the metallic form are good catalysts for formation of methanol and these metals cannot be allowed to come in contact with synthesis gas under reaction conditions

R,G. Herman, et al. [1] studied the formation, electronic structure and surface composition of catalyst Cu /ZnO/Al$_2$O$_3$ and Cu/ZnO/Cr$_2$O$_3$ in low pressure methanol synthesis in 1979, and reported that, the surface of the working catalyst is free of carbon, both in the presence and absence of CO$_2$ in the feed gas. A synthesis methanol is proposed whereby the Cu^I centers nondissociatively chemisorb and active carbon monoxide and the ZnO surface active hydrogen. Catalyst deactivation in CO/H$_2$ mixture is explained as the reduction of Cu to inactive copper metal, while the rate enhancing effect of O$_2$, water and CO$_2$ in due to the maintenance of an oxidation potential high enough to keep the copper in the active Cu^I state. No special pore distribution are presence of crystalline phase such as spinals is necessary for selectively of the Cu/ZnO catalyst to the formation of methanol.

They also pointed out that the Cu$^+$ dissolved in the ZnO phase is an active site in the methanol synthesis reaction. An active site of the catalyst derived from an amorphous Cu-Zr alloy might be Cu$^+$ similar to the Cu/ZnO catalyst.

The effect of carbon dioxide on the catalytic synthesis of methanol over the copper-zinc oxide catalyst were investigated for CO$_2$/CO/H$_2$ ratios between 0/30/70 in 1982 [2]. A maximum synthesis rate were observed at CO$_2$/CO/H$_2$ = 2/28/70. At lower concentration of CO$_2$ the catalyst is deactivated by over reduction and at higher concentration of CO$_2$ the synthesis is retarded by a strong adsorption of this gas.

A kinetic model is presented which quantitatively describes the observed pattern in the indicated range of synthesis gas compositions and at temperatures between 225 and 250 °C. This model is consistent with all physical characteristics of the Cu/ZnO catalysts and corroborates earlier

finding that an intermediate oxidation state of the reactants indicated that, carbon dioxide is strongly bound and immobile while carbon monoxide and hydrogen are chemisorbed with intermediate strength and experience a considerable mobility in the adsorbed layer. At concentrations of CO_2 greater than 10%, methane is a side product. Mechanistic implications of this finding are that there is a nonselective pathway parallel to the CO hydrogenation ; this pathway many involve formate and methoxy intermediates.

J.B. Friedrich et al.[3] presented in 1983 about the activities and surface properties of a partially leached alloy in the synthesis of methanol over Raney copper-zinc catalysts. The catalysts prepared by the caustic leaching of an alloy containing 36 wt.% Cu, 15 wt.% Zn, 49 wt.% Al. For various period of time have been shown to have high activities for methanol synthesis. The activity passes through a maximum with time of leaching and is related to both increased surface are and concentration of ZnO on the catalyst surface. It has been established that the presence of ZnO increased the activity of Raney copper for the methanol synthesis reaction.

For the study of fully extracted [4] Raney copper-zinc catalysts and the associated physical and chemical properties of these catalyst, have been examined. The catalyst was prepared by leaching a series of Al-Cu-Zn alloys containing approximately 50 wt.% Al and of differency Cu/Zn ratios with aqueous NaOH until complete reaction had taken place. Hydrogenation of a mixture of carbon monoxide and carbon dioxide shown that Raney catalysts prepared from alloys containing approximately 50 wt.% Al, 30-36 wt.% Cu and 14-20 wt.% Zn had the greatest activity for methanol synthesis.

The activity component for those Raney catalysts was found to be metallic copper and the activity exhibited a maximum for catalysts

containing approximately 97 wt.% copper. The residual zinc in these catalysts was found to provide a promotional effect to catalytic activity. The surface areas of catalysts increased from 17 to 39 m^2g^{-1} with increasing zinc content of the precursor alloy. The catalysts exhibited a narrow pore size distribution with the pore radius decreasing with increasing alloy zinc level. Carbon monoxide and hydrogen adsorption were used to determine the nature of the catalyst surface.

In 1985, Yokoyama et al.[5] have studied the activation process of the,amorphous $Pd_{35}Zr_{65}$ alloy and the methanol synthesis reaction over copper-group IV metal amorphous alloy as catalyst precursor, pure copper (99.9%) were arc-melted together in argon atmosphere. The crystalline phase in the catalyst was identified by X-ray diffraction and the average size of copper particles formed in the crystallined sample was estimated from the half-value width of X-ray diffraction peaks. DTA measurement under various gas atmosphere of 1.0 MPa. The reaction.was carried out under a gas pressure of 6.0 MPa and gas mixture of CO, H_2 and Ar (CO/H_2/Ar = 31/64/5, O_2 < 1 ppm.) was used without further purification.

It had been reported that, the surface of amorphous alloys containing zirconium are covered with thin ZrO_2 layer. At the initial state of the reaction the amorphous Cu-Zr phase swells due to the adsorption of hydrogen, and then cracked are formed in the surface ZrO_2 layer. CO and H_2 penetrate into these cracks, and the methanation reaction take place on the amorphous Cu-Zr phase. Then zirconium is oxidized by water or oxygen produced during the mathanation or by trace amount of impurity oxygen in the mixed gas. Due to the oxidation of zirconium, zirconium content in the amorphous phase decreases. This makes the same time, new cracks may formed ZrO_2 layer beneath the original ZrO_2 layer. This process makes the catalyst have a large surface area which contains fine Cu particles dispersed in ZrO_2.

G.C. Chinchen et al. studied in 1987 [6] on the mechanism of methanol synthesis from $CO_2/CO/H_2$ mixture over copper/ zinc oxide/ alumina catalyst by using ^{14}C-labeled reactants. From P_{CO2}/P_{CO} ratio from ~ 0.02 to 1 the fraction of methanol made from carbon dioxide rised from ~0.7 to 1, so carbon dioxide is the major reactant under industrial conditions. These is no carbon-containing surface intermediate common to methanol synthesis and the water gas shift reaction.

Roger M. et al. [7] has been reported the activation of NdCu, $NdCu_2$, $NdCu_5$ and $CeCu_2$ alloy precursors for methanol synthesis catalyst using in-situ XRD to observe and measure the activity of methanol. Pressure of 2-30 bar and temperatures in the range of 300-573 K were employed. It was shown that the formation of certain intermediate hydride phases is crucial to the eventual production of highly active catalysts and the methanol activity does not correlate with Cu crystallite size. CO_2 is a very effective poison which does not visibly effect the morphology of the metal phase. These findings strongly suggest that, the reaction mechanism which obtains here is quite different from that which operates on conventional $Cu-ZnO/Al_2O_3$ methanol synthesis catalysts.

In 1989, Daniel Gasser and Alfons Baiker [8] presented the hydrogenation of carbon dioxide over copper-zirconium catalysis prepared by in-situ activation of the precursor in CO_2/H_2 and CO/H_2 reactant gas mixtures. During this activation, the initially low activity of the amorphous alloy increased largely and reached finally a steady state. Structural and chemical changes of the amorphous precursor during its transition to the active stable catalysts were investigated using gas adsorption, X-ray diffraction, N_2O-titration, Auger electron spectroscopy and scanning electron microscopy. The as prepared catalysts consisted of copper pre-dominantly present as metal particles and stabilized by amorphous zirconium dioxide. XRD indicated that the metallic copper particles existed in two forms, as

small, probably disordered particles and as larger crystalline particles. The most important changes the amorphous Cu-Zr alloy underwent during in-situ activation were: (i) oxidation of zirconium to zirconium oxides; (ii) segregation of copper from the bulk onto the surface; and, (iii) partial crystallization. The activity and the selectivity behavior of the Cu/ZrO_2 derived from the amorphous Cu_7Zr_3 alloy were found to be similar as those of Cu/ZrO_2 prepared by coprecipitation of the corresponding metal nitrates. This suggests that the copper sites active for carbon dioxide hydrogenation are in both preparations of similar nature.

J.R. Jennings et al. [9] suggested the effect of carbon dioxide on the methanol synthesis activity of catalysts derived from binary rare earth/Cu precursors and from ternary rare earth/Cu/Ti, Zr or Al precursors used to investigate by microreactor studies and radiochemical tracer techniques. In the former case, carbon dioxide causes strong irreversible deactivation. However, the inclusion of a third metal component significantly enhances poisoning resistance without undue loss of the very high activity exhibited by the binary materials. Results obtained with $^{14}CO_2$ indicated clearly that the methanol product is derived principally from carbon monoxide : the catalytic mechanism which operates on this novel class of materials must therefore be quite different from that which is characteristic of conventional $Cu/ZnO/Al_2O_3$ catalysts.

In 1993 H. Edward Curry-Hyde et al. [10] studied the improvements of Raney copper methanol synthesis catalyst through impregnation in term of pore structure and the influence on activity and reported that, the high activity for a Raney $Cu-ZnO-Al_2O_3$. produced by leaching Cu-Al-Zn (43.2-39-17.8 wt.%) alloy pellets in a sodium zincate rich sodium hydroxide solution, has been compared with an industrial coprecipitated $Cu-ZnO-Al_2O_3$ catalyst. The carbon monoxide and carbon dioxide conversions for gas hourly space velocities between 11 000 h^{-1} and 80 000 h^{-1} were considerably higher for

the pelleted Raney catalyst than for the coprecipitated catalyst pellets. This has been attributed to a large difference in the intra-particle mass transfer resistances of the two types of catalyst. The unique pore structureof the Raney catalyst which exhibits a well developed bimodal macro and meso pore size distribution results in low mass transfer resistances in the Raney catalyst pellets. By comparison, the coprecipitated catalyst pellets have only a small volume fraction of macro pores

Tomoyuki Inui et al. [11] had presented the hydrogenation of carbon dioxide to C_1-C_7 hydrocarbons via methanol on composite catalysts compared with syngas. It markedly effected the rate of syngas conversions. Since the equilibrium between syngas and methanol was shift. The rate of hydrogenation was not affected. For this reason , it was considered that methanol was formed via CO as the intermediate in CO_2 hydrogenation on the composite catalyst and consequently the selectivity to methanol was considerably low. Therefore, the effect of H-ZSM-5 was reduced. Nevertheless, hydrocarbons containing 71.8% C_2-C_7 in addition to 28.2% methane could be obtained on a catalyst of mixed Pd-Na modified Cu-Cr-Zn oxides and H-ZSM-5

C.J. Jiang et al.[12] studied kinetic of steam reforming of methanol over copper based catalysts at temperatures from 443 to 533 K. Screening experiments shows that, a coprecipitated CuO-ZnO-Al_2O_3 low-temperature methanol synthesis catalyst had the highest activity and did not deactivate with time on line. It also exhibited 100% selectivity to carbon dioxide and hydrogen (the desired reaction products). Kinetic measurements made over the coprecipitated CuO-ZnO-Al_2O_3 were found to fit the power law expression

$$r_{SR} = k_0 e^{-105kl\,/\,mol\,/\,RT} P^{0.26}_{MeOH} P^{0.03}_{H2O} P^{-0.2}_{H2}$$

Carbon dioxide was found to have no effect on the kinetics of steam reforming of methanol . When carbon monoxide as added to the feed there was negligible influence on the steam reforming reaction with an order of 0.016 being observed.

A. Coteron and A.N. Hayhurst [13] studied methanol synthesis by amorphous copper-based catalysts, with compositions: $Cu_{70}Zr_{30}$, $Cu_{70}Zn_{30}$ and $Cu_{70}Zn_{15}Al_{15}$ prepares by spark-erosion technique, using kerosene as the dielectric. Two of them, viz. $Cu_{70}Zr_{30}$ and $Cu_{70}Zn_{15}Al_{15}$, were obtained in a fully amorphous state, whereas some crystalline copper was detected in the $Cu_{70}Zn_{30}$ sample. Specific surface areas were measured for these spark-eroded powders and were several orders of magnitude higher than those of traditional amorphous ribbons prepared by melt-spinning. SEM analysis indicated that the powders were in fact very small, spherical, metallic particles(<1.5 μm diameter),highly dispersed in a carbon matrix of large surface area. These powders were found to be active for the synthesis of methanol from both $CO+H_2$ and CO_2+H_2. The steady-state rate of methanol production from CO_2+H_2 was greater than that measured from $CO+H_2$. This indicates that methanol is produced preferentially from carbon dioxide. Steady-state selectivities to methanol of over 99 mol-% were observed for CO_2+H_2, whereas only 75-90 mol-% of methanol was formed from $CO+H_2$ as reactants.

Hiroaki Sakurai et al. [14] presented the hydrogenation of CO_2 over gold supported on metal oxides by coprecipitaion and deposition precipitation method. The reaction was investigated at temperature between 150 and 400 °C and a pressure of 8 atm. The methanol yields reached a maximum at temperatures between 200 and 300 °C, depending on the support oxides. The highest yield and selectivity toward methanol was obtained on Au/ZnO at 200°C Au/Fe_2O_3 was the most active for methanol synthesis, exhibiting activity almost comparable to that of the conventional

Cu/ZnO catalyst with the same metal content. Gold supported on TiO_2 was so active in reducing CO_2 to CO that the conversion was close to equilibrium. Over Au/ZnO as well as over Cu/ZnO, CO_2 could be hydrogenated to methanol at lower temperature than CO.

Li Fan and Kaoru Fujimoto [15] reported that A Pd/CeO$_2$ catalyst reduced by flowing hydrogen at 500°C for 1h was found to be an excellent catalyst for the hydrogenation of CO_2 to methanol. At 230° C and 30 bar, the CO_2 conversion was 3% while methanol selectivity reached 90% even the composition of reactant gas was $CO_2 : H_2 = 1 : 3$. The durability of this catalyst was also extremely high. The effect of the reaction temperature, the contact time of the reactants as well as the CO_2/H_2 ratio on the reaction performance were investigated.

In 1994, Ana Terlecki-Baricevic et al. [16] investigated the effect of mixed sulfur oxides pretreatment on the surface state and carbon monoxide oxidation activity of $Cu_xZn_{1-x} Cr_2O_4$ mixed oxides, using X-ray photoelectron spectroscopy (XPS) and kinetic measurements. The results obtained indicate that, SO_X species bind prefer entially to the surface zinc ions, which thus protect from poisoning the surface copper ions which are the active species for carbon monoxide oxidation.

T. Fujitani et al.[17] studied the role of metal oxides in promoting a copper based catalyst for methanol synthesis using reactive frontal chromatography method (RFC).An excellent correlation between the specific activity for methanol synthesis and oxygen coverage (θ) was obtained, where the activity increased linearly with oxygen coverage (θ) at~ <0.16 and then decreased at~>0.18. The results strongly indicate that support effect or addition of metal oxides revealed in methanol synthesis over copper catalysts is ascribed to the ratio of Cu^+ to Cu^0 an the surface of copper particles.

Y. Kanai et al. [18] presented the evidence for the migration of ZnO_X in a CuO/ZnO methaol synthesis catalystby using XRD, TEM coupled with EDX, TPD and FT-IR. As the reduction temperature increased, the specific activity for the hydrogenation of CO_2 increased, whereas the activity for the hydrogenation of CO decreased. The EDX and XRD results definitely showed that ZnO_X (x = 0-1) moieties migrate onto the Cu/ZnO catalysts were reduced at high temperature above 600 K. The content of Zn dissolved in the Cu particles increased with reduction temperature and reached ~18% at a reduction temperature of 723 K. The CO-TPD and FT-IR results suggested the presence of Cu^+ sites formed in the vicnity of ZnO_X on the Cu surface, where the Cu^+ species were regarded as an active catalytic component for methanol synthesis.

In 1995 S. Bailey et al. [19] studied the nature of the species adsorbed on a $Cu/ZnO/Al_2O_3$ catalyst while it was producing methanol has been elucidated in this study using DRIFTS The species are carbon carbonates, formate, CO, oxygen atoms (~2% of a monolayer) and methoxy on the Cu and methoxy on the ZnO.The frequencies observed for the C-O stretch on Cu, 2076, 2092, 2105 and 2132 cm^{-1}, have revealed the morphology of the copper component of the operating catalyst. The surface of the copper is predominantly the (111) face (65%)(the 2076 cm^{-1} peak) with the (755)(the 2092 cm^{-1} peak) and the (311)(the 2105 cm^{-1} peak) faces occupying roughly 20% and 15%, respectively, of the copper areas. The 2132 cm^{-1} peak derives from CO adsorbed on Cu^+ site on the copper which is ~2% of a monolayer.

The main advantage expected from the use of mixed-metal cluster compounds as precursors of heterogeneous catalysts is the possibility of tailoring highly dispersed bimatallic particles with uniform mixed-metal phases

The relationship between the copper surface area and the activity of $CuO/ZnO/Al_2O_3$ water-gas shift catalysts was reported by R.A. Hadden et al. [20] that, there is no single function which can describe the above relationship. However, discrete copper area-activity relationships one evident within groups of catalyst whose precursor species were formed under indential preparation conditions. Within these groups simple, linear, area-activity relationships are discovered

M.S. Wainwright et al. [21] presented the used of Raney copper to catalyst the synthesis of methanol and the water-gas shift reaction is reviewed. The preparation of Raney copper and Raney copper-zinc alloys together with their leaching to form active catalyst is first considered. The production of methanol is promoted by copper and the major- but not the only-role of zinc oxide involves the production of higher and more stable copper surface areas. There is some evidence that the catalytic activity of both methanol synthesis and water-gas shift may be improved by events occurring at the Cu-ZnO interface. It is now clear that carbon dioxide is the major reactant forming methanol under industrial conditions. Both in the water-gas shift and synthesis reactions, formates appear to be the main intermediates. Raney catalysts have the advantages of high mechanical strength, of regenerability and producing less side products during methanol synthesis-an important partial consideration. Their applicability to industrial operations would seem advantageous.

M. Fujiwara et al. [22] studied the hydrogenation of carbon dioxide using a Cu-Zn-Cr oxide/zeolite composite catalyst system. The change in the structure of the oxide catalyst during the reaction was found to be very significant, with the catalytic activity decreasing rapidly at temperature over 350°C. Measurement of metallic copper surface areas revealed a sharp decrease in exposed metallic copper caused by the sintering of the catalyst. The reaction of methanol over various composite catalyst was also

examined. The results indicated that composite catalysts with low metallic copper surface areas promoted the methanol to gasoline reaction, while high surface areas caused the decomposition of methanol to carbon monoxide. These results suggested that hydrocarbon synthesis and the decomposition of methanol are competitive.

Rinaldo Psaro et al.[23] reported that, cluster-derived FeIr/MgO catalysts prepared from $[Et_4N]_2 [Fe_2Ir_4(CO)]_{16}$ and $[Et_4N]_2 [Fe_2Ir_2(CO)]_{12}$ exhibit high activity in methanol synthesis from $CO+H_2$. The catalyst performance improves significantly upon raising the Fe:Ir ratio in the precursor from 2:4 to 2:2 with the letter sample, at 488-523 K and 6.1 MPa, methanol productivities up to 100 $mol/mol_{Ir}h$ are obtained with selectivity around 90%. Preliminary extended X-ray absorption fine structure characterization suggests that the formation of active sites upon activation in hydrogenation at 623 K is related to the presence of highly dispersed particles stabilized on the surface by interfacial iron.

B.B. Breman et al [24] was presented the kinetic results of the gas-slurry methanol-higher alcohol synthesis from $CO/CO_2/H_2$ (syngas) over a $Cu_{0.44} Zn_{0.43} Al_{0.12} Cs_{0.031}$ catalyst (particles size : 50-75 μm), slurried in n-octacosane. Experimental conditions varied as follows : pressure = 20-80 bar, temperature = 473-573 K, H_2/CO ratio in the feed = 0.53-3.38, mole fraction CO_2 in the feed = 0.026-0.037 and space velocity = 0.065×10^{-3}-1.395×10^{-3} $Nm^3 s^{-1} kg^{-1}$ cat. Methanol was the major product. Further, higher 1-alcohol, 2-methyl-1-alcohols, methyl esters, n-paraffins, CO_2 and H_2O were formed. In contrast to observations in a gas-solid system, the product distributions of the alcohols, the paraffins and methyl esterd could be predicted with average relative deviations of 5.9%, 7.8% and 1.6%, respectively. The prersence of n-octacosane as a slurry liquid appeared to affect substantially both the product distributions and the values of the model parameters relative to the corresponding gas-solid system.

A methanol-higher alcohol mixture can replace tetraethyl leach as an octane booster in gasoline. Alternatively, it may subsitute gasoline to the benefit of a country. The higher alcohols are required to present separation of methanol from gasoline in cold weather. With a suitable catalyst, methanol and higher alcohols can be produced simulataneously from a $CO/CO_2/H_2$ mixture (syngas) via similar processes as in use for the methanol synthesis. The following overall reaction play a role :

methanol synthesis : $CO + 2H_2 \rightarrow CH_3OH$

$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$

water-gas-shift reaction : $CO + H_2O \rightarrow CO + H_2$

Higher alcohol synthesis $nCO + 2nH_2 \rightarrow C_nH_{2n+1}OH + (n-1)H_2O$