



CHAPTER 2

LITERATURE SURVEY

2.1 Introduction

In general when we mention about alcohol, we usually refer to ethanol or ethyl alcohol. Ethanol is one of the earliest chemical known as the constituent of alcoholic beverage since antiquity. In this chapter we will briefly introduce previous work on ethanol synthesis with respect to petrochemical technique or catalytic reaction. Also mentioned will be methanol synthesis from synthesis gas. These will then lead to new developments on the synthesis of mixed alcohols from synthesis gas, with emphasis on the ethanol synthesis catalysts.

2.2 Ethanol Synthesis

At present in Thailand ethanol is produced by the fermentation process. But in the U.S.A. and Europe, the industrial grade ethanol is mainly produced via chemical synthesis. The first synthesis of ethanol was carried out by Bethelot in 1855, and until 1930 his method, generally known as the ethyl sulphate or sulfation hydrolysis process, had been applied industrially. In the above indirect hydration process, sulfuric acid is incorporated in the synthesis reaction route. Dilute acid is obtained, which corrodes the reactor, so the material of construction is costly. Also it may pollute the environment. In 1943, the vapour-phase direct hydration of ethylene was introduced. Ethylene gas and steam were fed through a bed of catalyst composed of phosphoric acid impregnated on

supporting material. This process is a good example of heterogeneous catalytic reaction. Since ethylene is a valuable feedstock to the Thai petrochemical industry, direct synthesis of ethanol from syngas or from methanol and syngas will be more advantageous. The process of ethanol synthesis from syngas will be competitive with the fermentation process, As the rise in world population will gradually outstrip world food production.

2.2.1 Ethanol Synthesis from Methanol and Syngas

Ethanol synthesis from methanol and syngas is generally known as homologation reaction. In this process, hydrogen and carbon monoxide are reacted with methanol to produce ethanol in the presence of catalysts. The molar ratio of hydrogen to carbon monoxide varies from 10:1 to 1:10, especially from 3:1 to 1:3. However conventional synthesis gas typically consists of hydrogen and carbon monoxide at a ratio of about 1:1. The pressure which is favorable to the process generally exceeds 1000 psig (6.83 MPa or 68.04 atg), but should be less than 10,000 psig (68.30 MPa or 680.4 atg). An especially desirable pressure range is from about 2,000 psig (13.66 MPa or 136.08 atg) to about 5,000 psig (34.15 MPa or 340.20 atg). The temperature which is suitable is one that is high enough to initiate a reaction between the reactants herein to produce ethanol, typically from about 150°C to about 250°C. The reaction is conducted for a time period sufficient to convert methanol to ethanol, normally from about 0.5 hour to about 10 hours, especially from about 1 hour to about 5 hours. The following are some previous works on ethanol synthesis via the homologation process.

Pretzer et al.(1977) developed a process for the selective formation of ethanol which involved contacting methanol, hydrogen and carbon monoxide with a catalyst system comprising

cobalt acetylacetonate, a tertiary organo Group 5A compound of the Periodic Table (i.e. phosphorous, arsenic, osmium), a first promoter comprising an iodine compound and a second promoter comprising a ruthenium compound. Two years later, they invented a new process for the selective homologation of methanol to ethanol which comprised introducing into a reaction zone methanol, hydrogen, carbon monoxide, a cobalt tricarbonyl complex and an iodine promoter and then subjecting the contents of the reaction zone to an elevated temperature and an elevated pressure for a time period sufficient to convert methanol to ethanol.

Fiato and Charleston (1979) used a phosphine-iodine promoted cobalt-ruthenium catalyst for selectively producing ethanol from methanol, hydrogen and carbon monoxide. The cobalt component of the catalyst came from a number of sources, such as certain known cobalt carboxylates, cobalt carbonyls, cobalt oxides, etc. A convenient source of cobalt was cobalt acetate. The other components came from a number of compounds that can ionize to form the required components. In their work, they also investigated the suitable amounts of phosphine ligand to enhance catalyst stability and to increase selectivity to ethanol and higher activity. Doyle (1980) of Exxon Research & Engineering Co., Ltd. developed an iron-cobalt carbonyl complex and an iodide promoter for a homogeneous catalytic process for the selective conversion of methanol to ethanol or acetaldehyde.

It should be noted that cobalt carbonyl complexes are generally used as homologation catalyst and at least one promoter is used.

2.2.2. Heterogeneous Catalysis of Ethanol Synthesis

In the homologation process, the major disadvantage is the high separation costs of products, reactants and catalyst. In addition, some amount of catalyst may be lost during the separation process. Hence heterogeneous catalysis merits close study. Furthermore, the working pressure of the homologation process is very high, although the reaction temperature is not high, ca. $175-250^{\circ}\text{C}$. Such a high working pressure and the long reaction time required are not satisfactory for production on an industrial scale, because the reactor investment cost and the running cost of compression are very expensive. On the other hand, a heterogeneous process requires much less investment costs than the homologation process. In the heterogeneous catalytic hydrogenation of carbon monoxide to obtain the alcohols, the crucial question is how to prepare a highly effective catalyst.

In fact since studies on the practical applications of carbon monoxide and hydrogen synthesis were carried out in Germany during world War II, considerable attention has been given to Fischer-Tropsch and related synthesis. Bright predictions have been made of their enormous potential in the production of alcohols, oxygenated compounds and fuels. Many details have been mentioned in a book called "Source Book of Industrial Solvent," vol.3. The book describes how ethanol was synthesized either via the fermentation process or from ethylene, consequently leading to the study of ethanol synthesis from syngas.

In the following paragraph are some recent studies on the synthesis of ethanol from syngas. Some investigators employed Fischer-Tropsch type catalysts or their modifications. Others used catalysts containing such rare earth elements as rhodium

(Rh), ruthenium (Ru), and rhenium (Re), as well as their combinations with other metals.

In their studies, Bartley et al. (1979), Ichikawa et al. (1982), etc. used rhodium catalysts prepared by dispersing rhodium on a support, such as titanium oxide, zirconium dioxide, etc., to produce ethanol via the hydrogenation of carbon monoxide. SiO_2 support doping with alkali metal, eg. Na, or with other metal like metal oxide of group 4B and 5B in the Periodic Table, eg. Hf, Th, V, Nb, and Ta etc. were used by Naito, et al. (1982) and Ichikawa et al. (1982), respectively. Also bimetal catalysts such as Cd-Rh/ SiO_2 , and a polycomponent system, Rh-Mn-Zn-X, were used for methanol and ethanol synthesis from synthesis gas (Naito et al., 1982, Agency of industrial Science and technology). Other noble metal catalysts containing rhodium were prepared in complex form as mono and bimetal catalysts. These catalyst systems are usually promoted with halides and phosphonium salt, e.g. $\text{Ru}(\text{CO})_5\text{I}_3$, $\text{Ru}_3(\text{CO})_{12}-\text{CO}_2(\text{CO})_8/\text{Bu}_4\text{PBr}$ (Dombek, 1983, Knifton, 1984). Rhodium is well-known catalyst for hydrogenation of olefins and other unsaturated substances.

Both rhodium and ruthenium are scarce and expensive. So it should pay to find certain more common elements to substitute for these elements in the hydrogenation of carbon monoxide. From the Periodic Table, by focusing on the transition elements as shown below,

24	Cr	25	Mn	26	Fe	27	Co	28	Ni	29	Cu	30	Zn
42	Mo	43	Tc	44	Ru	45	Rh	46	Pd	47	Ag	48	Cd
74	W	75	Re	76	Os	77	Ir	78	Pt	79	Au	80	Hg

It is seen that cobalt and iron are in the same column as rhodium and ruthenium. Addition of another element is also often attempted. Hachenberg et al. (1979) prepared catalysts containing

Co along with at least one of the elements Au, Ag, Re, as carrier for ethanol synthesis from H_2 and CO. They reported 60 % selectivity of ethanol based on the CO converted. A modified methanol synthesis catalyst, namely, copper/zinc oxide promoted with potassium carbonate has also been used to produce higher alcohols (Smith et al., 1984). The latter work led to the study on synthesis of higher alcohols for use as fuel grade and an octane number enhancing substance.

2.3 Methanol Synthesis

Methanol is the smallest molecule of alcohols. It is a clean synthetic fuel and chemical feed stock that can be made from a wide variety of material and energy sources and applied to an equally wide variety of uses. Today methanol is produced in large plants and the technology is considered fairly standard. The reaction of methanol synthesis is



$$G^\circ = 25,100 + 56.8T \text{ kcal/mol}$$

Since the thermodynamic limitation of methanol is particularly severe. High pressures are required in methanol synthesis to achieve reasonable conversion. The methanol-synthesis catalyst must therefore be highly selective as well as active. There are two types of processes in methanol synthesis. One is high-pressure types. The other is low-pressure types (Satterfield, 1980).

2.3.1 High-Pressure Process

In the high pressure process, the original catalyst is zinc hydroxychromates, which is made by combining chromium trioxide with an excess of zinc oxide in the presence of water.

Commercially an high quality catalyst is $\text{ZnO-Cr}_2\text{O}_3$. The catalyst is reduced with hydrogen or synthesis gas at 309 to 338°C. In operation, the pressure is typically about 24 to 30 MPa. The operating temperature is in the range of 350 to 400°C, and an adiabatic temperature rise of 20 to 25°C is taken along each bed. The catalyst is typically in the form of pellets about 6 x 6 mm. or rings of OD x ID x h of 10 x 4 x 8 mm. The superficial contact time is 0.1 to 0.2 s, calculated at STP. Normal catalyst life is about 2 years.

2.3.2 Low-Pressure Process

A more active catalyst than the above can be made from a combination of copper and zinc together with a textural promoter such as chromia or alumina. This permits the use of a lower pressure, in the range of about 5 to 10 MPa, and a temperature of about 240 to 260°C. The Lurgi low-pressure process, a commercial process, operates at about 250 to 260°C, and 4 to 5.5 MPa. A low-pressure methanol synthesis process is advantageously combined with production of synthesis gas by partial oxidation since the latter can be carried out at the methanol synthesis pressure, thus avoiding the necessity of intermediate gas compression. The low-pressure process is usually the process of choice in a new installation.

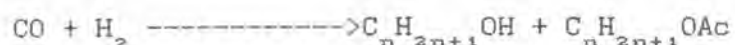
2.4 Alcohols Synthesis from Synthesis Gas or Fuel Alcohol Synthesis from Synthesis Gas

In 2.2 most of the catalysts for hydrogenation of carbon monoxide to ethanol have limited selectivity for ethanol. Thus a wide range of alcohol product distribution is obtained. This makes these catalysts uncompetitive to those of the

conventional processes (ethylene hydration and fermentation). Fortunately, blending of either pure or mixed alcohols with gasoline could enhance its octane number. Nowadays in Europe and North America demands for unleaded and low-lead gasoline are increasing. Therefore a number of the researches on alcohol synthesis in recent years are aimed at synthesis of mixed alcohols from syngas. A. Sugier & E. Freund (1977) of Institut Francais du Petrole invented a process for manufacturing linear alcohols from synthesis gas. They prepared a series of catalysts. The catalysts which are prepared contain at least 4 essential elements, i.e. copper, cobalt, a third metal M selected from chromium, iron, vanadium and manganese and a fourth metal A which is an alkaline metal, preferably lithium, sodium or potassium. Zinc is optional. These elements are in the following atomic proportion : $Cu_x Co_y M_z A_v$. When zinc is present, it is in the atomic proportion Zn_u . In a preferred catalytic formula, $x = 1$, $y = 0.2$ to 1.2 , $z = 0.1$ to 1 and $v = 0.02$ to 0.2 where $u = 0$ to $0.5y$. The Cu, Co, M and eventually Zn metals are usually present as oxides, such as CuO , CoO , CrO_3 , or as thermally decomposable salts, such as carbonate, sulfate, nitrate, oxalate, tartrate, citrate, acetate or succinate, or in the form of complexes, for example, a chromate or vanadate. The coprecipitation technique were employed to prepare homogeneous metal oxide catalysts. Using multiple adiabatic reactors Courty et al. (1984) of the same institute synthesized C_1-C_6 alcohol is in the present of a mixed-oxide catalyst system containing copper and cobalt as key components. These metals were associated to at least one of the metals M of the following list : Al, Ce, Cr, Fe, La, Mn, Pr, Nd, Y, Zn as well as, to at least one alkali and/or alkalai earth metal compound. The high flexibility of performance allows the varying of product alcohols.

Knifton et.al. (1984) of Texaco Chemical Co., Ltd.

prepared a process for producing C_1-C_9 alcohols and acetate esters directly from syngas according to the equation below.



The catalysts were ruthenium complex, dispersed in a molten salt, e.g. a triruthenium dodecacarbonyl-tert-butyl-phosphonium iodide combination. The catalyst precursor generally comprises of ruthenium (IV) oxides, a tetrabutyl phosphonium halide and optionally, one or more co-catalyst species selected from the group indicating halogen-free titanium or zirconium compounds, a cobalt derivative and a halogen-free manganese or rhenium compound. The hydrogenation of carbon monoxide to synthesis alcohols usually need an elevated temperature (typically 200-250°C) and pressure above 6 Mpa ca. 60 atg (Sugier, 1979, Courty, 1984, Knifton, 1984) and the ratio of $CO:H_2$ is 1:2 to 1:2.5 (Courty, 1984).