



CHAPTER II

LITERATURE REVIEW

2.1 Background

Nowadays, global energy requirements are mostly dependent on fossil fuels (about 80% of the present world energy demand). This will eventually lead to the foreseeable depletion of limited fossil energy resource. Presently, the utilization of fossil fuels are causing global climate change mainly due to the emission of pollutants, including CO_x , NO_x , SO_x , C_xH_x , soot, ash, droplets of tars, and other organic compounds, which are released into the atmosphere as a result of their combustion. In order to remedy the depletion of fossil fuels and their environmental misdeeds, fuel cell has been suggested as the alternative energy that can replace the fossil based energy in the future.

2.2 Fuel Cells

Fuel cells are electrochemical devices that directly convert a fuel's energy to electrical energy without combustion. They provide a very clean energy, high reliability, very little noise, high quality electricity, highly efficient source of electrical energy and potentially to power electric vehicles. Their goals are cost reduction and pollutant minimization keeping a high efficiency.

In theory a fuel cell uses hydrogen as a fuel to produce electrons, protons, heat, water and electricity. The basic design of a fuel cell involves two electrodes on either side of an electrolyte. Hydrogen fuel is supplied to the anode (negative terminal) of the fuel cell while oxygen is supplied to the cathode (positive terminal) of the fuel cell. Through a chemical reaction, the hydrogen is split into an electron and proton. Each takes a different path to the cathode. The electrons are capable of taking a part other than through the electrolyte, when harnessed correctly can produce electricity for a given load. The proton passed through the electrolyte and both are reunited at the cathode. The electron, proton and oxygen combine to form the harmless byproduct of water. The diagram of fuel cell unit is shown in Figure 2.1.

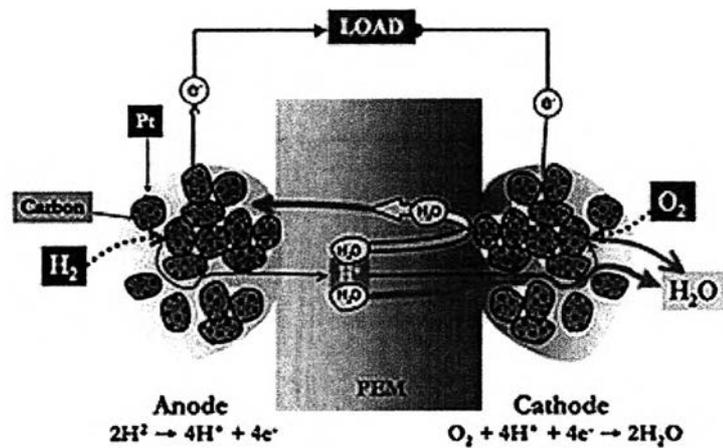
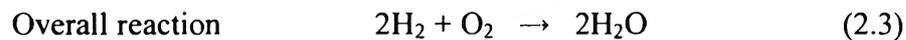
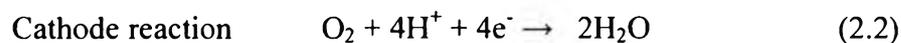


Figure 2.1 Diagram of fuel cell unit (Polymer Electrolyte Membrane fuel cell).

Fuel cell technology is based upon the simple combustion reactions which given below.



The fuel cell producing electricity through a chemical reaction therefore, there are significantly cleaner emissions than from a fuel combustion process. The hydrogen fuel can be supplied from a variety of substances if a “fuel reformer” is added to the fuel cell system. Therefore, hydrogen can be obtained from hydrocarbon fuel such as natural gas, diesel fuel, kerosene or methanol.

Fuel cells are primary classified by a kind of electrolyte they employed, which also determines the kind of chemical reactions that take place in the cell, the kind of catalysts required, the temperature range in which the cell operates, the fuel required and other factors. These characteristics also affect the applications for which these fuel cells are most suitable. There are several types of fuel cells currently under development, each with their own advantages, limitations, and potential applications. A few of the most promising types are included Polymer Electrolyte Membrane

(PEM), Phosphoric Acid (PA), Molten Carbonate (MC) and Solid Oxide (SO) as shown in Table 2.1.

Table 2.1 Comparison of the system of fuel cells (Naknam, 2006)

Fuel Cell System	PEMFC	MCFC	PAFC	SOFC
Electrolyte	Ion exchange Membrane	Molten Carbonate salt	Liquid phosphoric acid	Solid metal oxide
Operating Temp (°C)	60-100	600-1000	150-200	600-1000
Oxidant	O ₂ /Air	CO ₂ /O ₂ /Air	O ₂ /Air	O ₂ /Air
Maximum Efficiency (%)	60	85	80	85
Maximum Power Output Range (size)	250 kW	2 MW	1 MW	220 kW
Waste heat uses	Space heating or water heating	Excess heat can produce high-pressure steam	Space heating or water heating	Excess heat can be used to heat water or produce steam
Applications	Vehicle applications, medium to large scale stationary power generation	Large-scale power generation	Medium to large scale power generation	Medium to large scale power generation

In the mobile applications, the suitable type of fuel cell that meet the requirement is PEMFC. The advantages of using PEMFC are fast startup time, low

sensitivity to orientation and favorable power to weight ratio. PEMFC is particularly suitable for using in passenger vehicles, such as cars and buses.

PEMFC operates at relatively low temperature of around 60-100 °C. Low temperature operation allows them to quickly start (less warm-up time) resulting in less wear on system components and better durability. However, a requirement of noble-metal catalyst (typically Pt) for separating the hydrogen's electrons and protons at the anode cell also increase the system cost. Moreover, the Pt catalyst is also extremely sensitive to CO poisoning. Thus, it requires an additional reactor to abate CO in H₂ stream, particularly for the derived from alcohols or hydrocarbon fuels (commercial gasoline), before feeding to PEMFC. The effect of CO contaminant is shown in Figure 2.2.

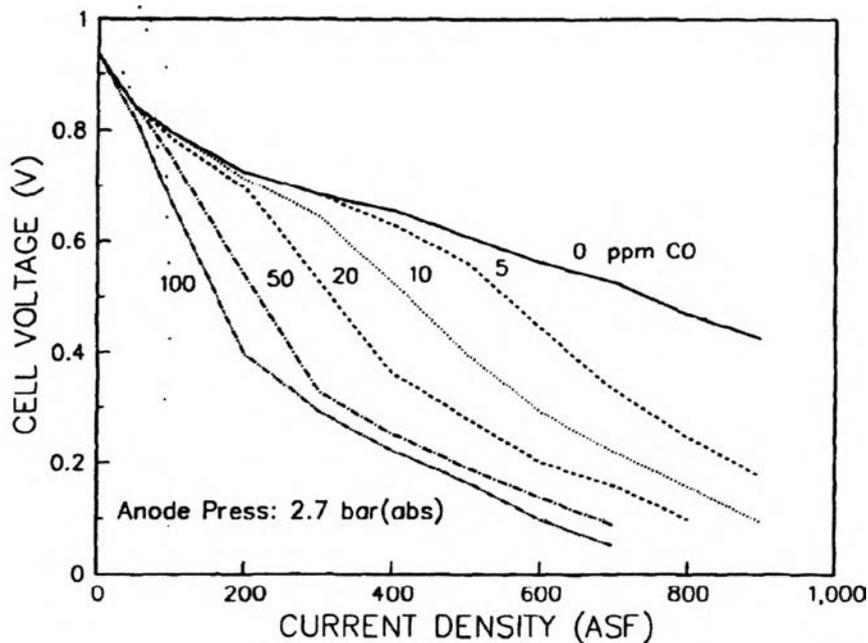


Figure 2.2 Effect of CO contamination on PEMFC electrolyte performance (Amphlett *et al.*, 1996).

2.3 Hydrogen Production from Methanol

Hydrogen is the most common base material in the universe. On earth, practically all hydrogen is in a compound formed with other elements. It reacts very readily with oxygen to create H_2O . Under hydrogen production processes, the water molecule and the raw material are split, and the results are H_2 , CO and CO_2 . In other words, the hydrogen gas comes from both steam and hydrocarbon compounds. Hydrogen supply for the on-board application can be compressed hydrogen, store in a metal hydride or reforming of high hydrogen content material. And reforming of high content hydrogen material is preferred due to its no more safety consideration, appropriate weight and can use biomass as a fuel.

Among the high content hydrogen material, methanol is regard as one of the most promising candidates for the on-board reforming to hydrogen. The advantages of using methanol are: (Maela *et al.*, 2004)

- high hydrogen/carbon ratio
- convert in to hydrogen at moderate temperature
- reducing the risk coke formation
- can be produced from plants (renewable source)
- clean fuel no addition of CO_2 to the atmosphere

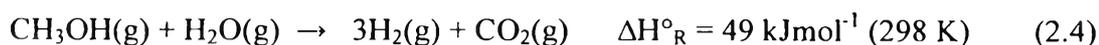
In Table 2.2, Ahmed *et al.* (1997) calculated the hydrogen concentration which may be attained when using different fuels and then compared these values with experimental results. From this table, it can be concluded that methanol have the highest hydrogen concentration when compare with others.

Table 2.2 Concentration of hydrogen in the product gas obtained with different hydrocarbons (Ahmed *et al.*, 1997)

Fuel	H ₂ concentration, % (dry)		H ₂	Temperature
	Theoretical	Experimental	Selectivity(%)	(°C)
Methanol	70	64	91	450
Ethanol	71	62	88	580
i-Octane	68	60	88	630
Cyclohexane	67	61	91	700
2-Pentene	67	58	88	670
Toluene	61	50	82	660

2.3.1 Steam Reforming of Methanol

Steam reforming is a reaction between hydrocarbon fuel and water to create hydrogen. Steam reforming is a highly efficient conversion process, which has received much attention due to the ability to produce a gas with high hydrogen concentration (75% when using methanol as a feedstock) while maintaining a high carbon dioxide selectivity. The main drawback of steam reforming is that the reaction is moderately endothermic. The use of surplus heat from the effluent of the catalytic burner could satisfy the energy demand. However, the addition of oxygen to the steam reforming process speeds up the conversion, due to the occurrence of exothermic oxidation reactions. The reaction of steam reforming process is shown in Equation 2.4.



The steam reforming process is usually operated with excess steam, to induce the water gas shift (WGS) reaction (Equation 2.5) in the reformer in order to lower the CO concentration in the product gas.



The WGS reaction reduces the CO content while increasing the hydrogen content in the product stream. At equilibrium conditions, the forward reaction is favored by low temperatures. It is important to have an efficient reformer including a WGS step, since this reduces the volume of the subsequent CO removal step. The diagram of steam reforming process are shown in Figure 2.3

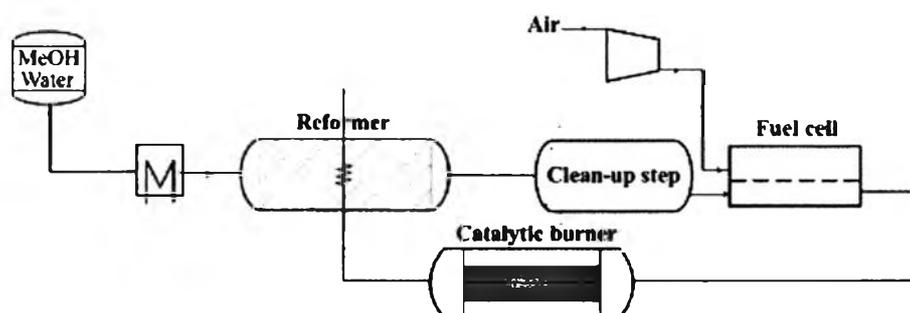


Figure 2.3 Methanol Reforming System (Lindstrom *et al.*, 2002).

2.3.1.1 Reactor for Methanol Steam Reforming

A microchannel reactor system has been developed for methanol steam reforming. This application is especially important to keep isothermal conditions in the catalyst bed for highly endothermic reactions. This reactor provides high heat transfer efficiency, incorporating a built-in preheating zone, and accurate catalyst bed temperature measurement. Figure 2.4 shows schematics of the reactor assembly. The catalytic portion of the reactor is a microchannel slot with the gap width of 0.508 mm. The catalyst is located in the lower portion of the channel so that the reactants can be preheated to a desired temperature in the upper portion of the channel before entering the catalyst bed. The microchannel is “sandwiched” by two separated oil-heating channels, which are designed to allow oil to circulate at a high rate and maintain a high heat transfer coefficient at the same time.

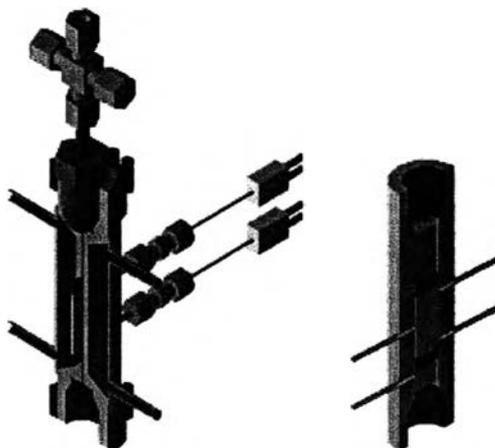


Figure 2.4 Microchannel reactor assembly (Cao *et al.*, 2004).

2.3.1.2 Experimental Condition

The effect of reaction conditions for steam reforming of methanol (SRM) over the G-66 MR Cu/ZnO/Al₂O₃ catalyst from Sud-Chemie are as follows: (Agrell *et al.*, 2002)

- Effect of reaction temperature is shown in Figure 2.5. The result showed that the methanol conversion increased when increasing the reaction temperature until the maximum attainable value of 100% at 320°C.

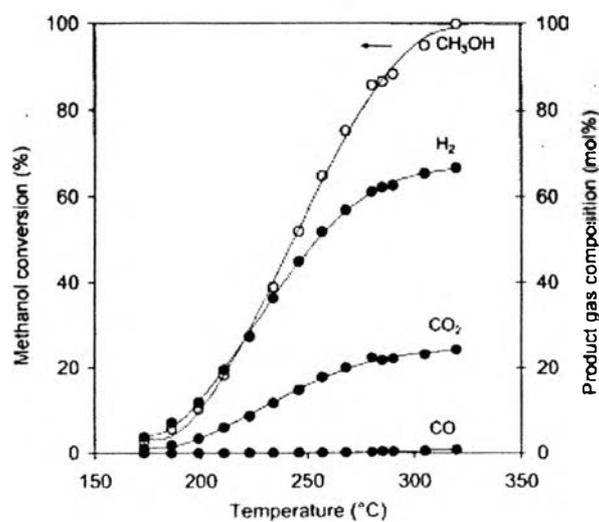


Figure 2.5 Effect of reaction temperature in methanol steam reforming reaction (Agrell *et al.*, 2002).

- Effect of $\text{H}_2\text{O}/\text{CH}_3\text{OH}$ ratio on CO formation in the methanol stream reforming reaction is shown in Figure 2.6. The CO selectivity at 320°C was increased from 3% to 11% when the molar ratio of $\text{H}_2\text{O}/\text{CH}_3\text{OH}$ was changed from 1.3 to 1.0. Clearly, an excess amount of steam required by stoichiometry effectively suppresses CO formation.

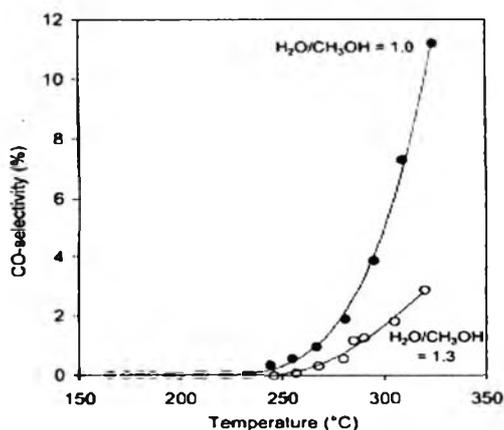


Figure 2.6 Effect of $\text{H}_2\text{O}/\text{CH}_3\text{OH}$ ratio on CO formation in the methanol stream reforming (Agrell *et al.*, 2002).

- Effect of methanol feed rate on H_2 and CO_2 production rates are shown in Figure 2.7. This result showed that the hydrogen production rate are increased when increasing the methanol feed rate from $30 \text{ mmol}/\text{kg}(\text{cat})\cdot\text{s}$ to $270 \text{ mmol}/\text{kg}(\text{cat})\cdot\text{s}$.

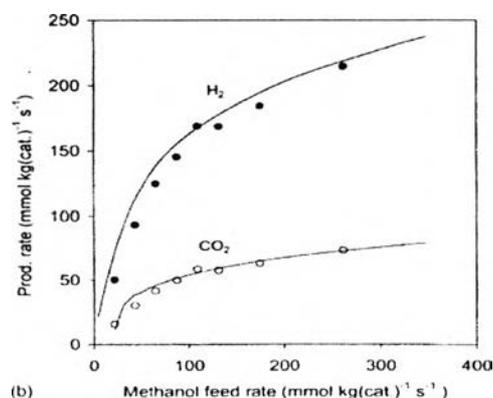


Figure 2.7 Effect of methanol feed rate on the hydrogen production rate in the methanol stream reforming (Agrell *et al.*, 2002).

2.3.1.3 Mechanism of Methanol Steam Reforming

Some researchers (Takahashi *et al.*, 1982; Takezawa *et al.*, 1997) suggested the methanol steam reforming process via methyl formate formation, in which no CO takes part in the reaction. The steam reforming of methanol proceeded through the following sequence of steps.



According to the study performed by Takahashi *et al.* (1982), the WGS reaction was found to be blocked in the presence of methanol on Cu/SiO₂. Another argument for methanol steam reforming reaction has been raised by Takezawa *et al.* (1997), they found that HCHO and CH₃OCH are involved in the reaction.

By introducing HCHO to the feed of methanol-water mixture, the complete conversion of HCOH to CO₂ and H₂ was observed. The reaction of HCHO and water occurred more rapidly as compared to the steam reforming of methanol. Based on these results, they concluded that the production of hydrogen and carbon dioxide over copper-based catalysts includes the formation of formaldehyde and HCOOH as intermediate products that can be described as follows:



Furthermore, the reaction rate of methyl formate from the reaction of HCHO in both the absence and in the presence of methanol was determined. The rate of methyl formate formation was found to be more enhanced in the presence of methanol at the temperature range from 77 to 177°C. The rate in the presence of methanol was estimated to be (at 120°C) 20 times higher than in the absence of methanol. This indicates that the formation of methyl formate from the mixture of HCHO and CH₃OH is much more rapid than the dehydrogenation of metha-

nol to methyl formate. They concluded that the formation of methyl formate over copper-based catalysts occurs through a pathway:



2.3.1.4 Kinetic of Methanol Steam Reforming

A semi-empirical model of the kinetics of the catalyst steam reforming of methanol over CuO/ZnO/Al₂O₃ catalyst has been developed by Amphlett *et al.* (1994) using the reaction schemes of irreversible reaction of SRM and decomposition reaction. They found that the water gas-shift reaction could be neglected without substantial loss in accuracy. The rate equations for both reactions can be written as follows:

$$r_{CH_3OH} = -k_1 C_{CH_3OH} - k_2$$

$$r_{H_2O} = -k_1 C_{CH_3OH}$$

$$r_{CO_2} = k_1 C_{CH_3OH}$$

$$r_{CO} = k_2$$

$$r_{H_2} = 3k_1 C_{CH_3OH} + 2k_2$$

The reaction rate of methanol and water consumption is depending only on the concentration of methanol and not on water concentration. Furthermore, the reaction rate of CO formation is a zero-order rate which means that the formation of CO is not affected by the concentration of methanol or the concentration of water.

2.3.1.5 Methanol Steam Reforming reaction in fuel cell

Hydrogen production based on methanol steam reforming reaction for fuel cell drive system consists of the following main devices: a methanol steam reformer, a catalytic burner which provides heat for the reformer and converts all burnable gases in the flue gas into water and carbon dioxide, a gas cleaning unit which reduces CO concentration of the hydrogen-rich product and feeds to the PEMFC. A gas storage system is also integrated in the fuel cell system in order to

feed the fuel cell during the start-up and speed-up phases. A scheme of the fuel cell drive system based on SRM is shown in Figure 2.8.

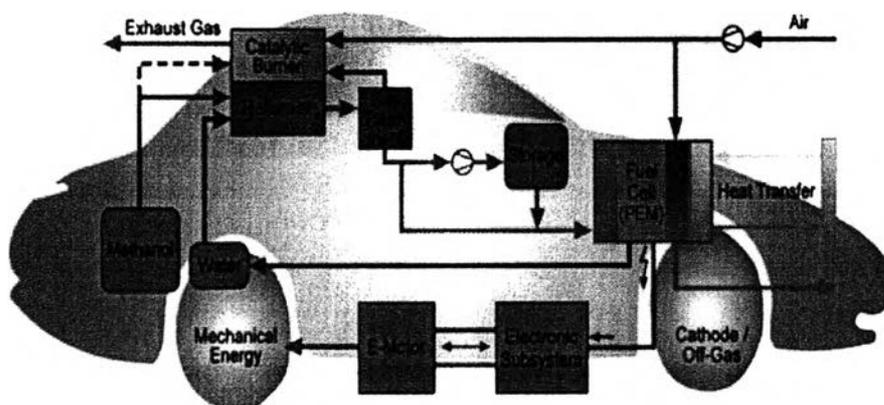
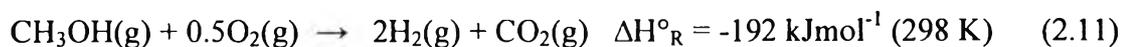


Figure 2.8 Fuel cell drive system (Wiese *et al.*, 1999).

2.3.2 Partial Oxidation of Methanol

Partial oxidation reaction is a process that partially oxidizes the fuel to CO and H₂ rather than fully oxidizes to CO₂ and H₂O. This is accomplished by injecting air with the fuel steam prior to the reformer. The advantage of partial oxidation over steam reforming is that it is an exothermic reaction rather than an endothermic reaction and therefore generates its own heat. The reaction of partial oxidation of methanol process is shown in Equation 2.11.



Cu–Zn has been investigated as a catalyst in several papers, either unsupported or supported on $\gamma\text{-Al}_2\text{O}_3$. Huang and Wang (1986), and Alejo *et al.* (1997) have investigated hydrogen generation via partial oxidation of methanol. Cu–ZnO is the active form, which means that to avoid deactivation nitrogen has to be used during purge when the system is shut down. If the catalyst (Fe–Cr-oxide, Cu–Zn-oxide) is oxidized by air during shutdown, it can be reduced by hydrogen in-situ in order to recreate its initial activity. Care must be taken not to superheat the catalyst during reduction, since the process is exothermic. Excessive heating can cause the

copper particles to sinter and a loss of metal surface area will thus occur. One possibility is to use low concentrations of hydrogen in nitrogen (5–10%) during the reduction process.

2.3.3 Decomposition of Methanol

Decomposition is the process to produce hydrogen from hydrocarbon such as methanol. This process has to be coupled with efficient water-gas shift steps to convert CO. The process is strongly endothermic and the reaction is shown in Equation 2.12. The advantage of this decomposition reaction with methanol is not suitable due to the risk of coking.



An extensive review on hydrogen generation by methanol decomposition can be found in Choi and Stenger (2002). They studied the methanol decomposition reaction catalyzed by a commercial Cu/ZnO/Al₂O₃ in the presence and absence of water. The result of this study showed that water addition to the feed increased the yield of hydrogen and reduced the formation of: dimethyl ether; methyl formate and methane. And the mechanism of methanol decomposition is shown in Figure 2.9.

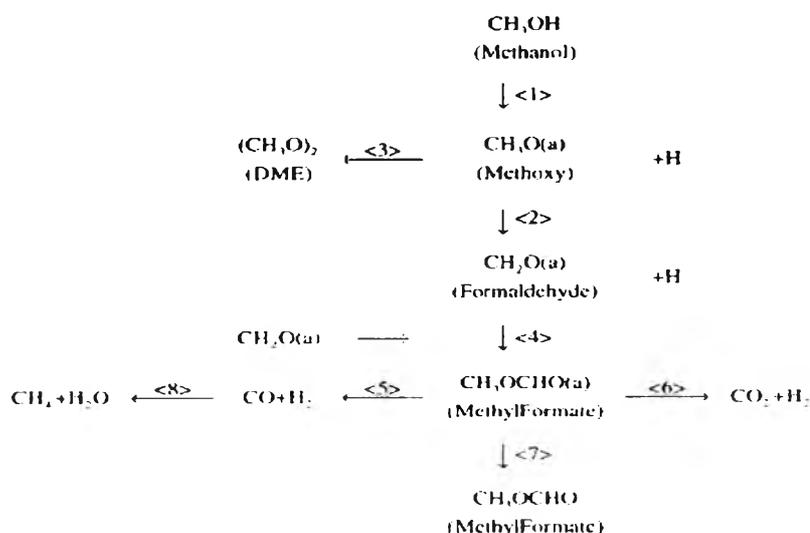
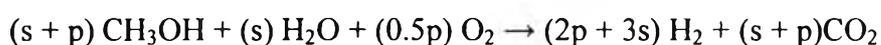


Figure 2.9 Schematic diagram of the mechanism of methanol decomposition.

2.3.4 Autothermal (Oxidative steam reforming of methanol)

Autothermal is a combination of partial oxidation and steam reforming. The term reflects the heat exchanging between the endothermic steam reforming process and the exothermic partial oxidation, which also creates a sufficient heat to drive itself and generates more hydrogen than only partial oxidation alone. The reaction of oxidative steam reforming of methanol are shown in Eq. 2.13



Where s and p are stoichiometric coefficient for steam reforming and partial oxidative respectively. In this process methanol are reacted with a mixture of O_2 and steam in a “thermo reactor” over a catalyst surface.

2.4 Catalysts Development for Steam Reforming of Methanol

The potential of steam reforming of methanol for hydrogen production in PEMFC applications make researchers try to develop the catalysts for satisfactory performance. The Cu-based catalysts for methanol synthesis, are major used for the first generation of catalyst; however, they have the disadvantages of fast deactivation and pyrophoric characteristics. Hence, the non-copper catalysts have been investigated for the hope that the better performance might be found. Oxide supported precious metals including Pd, Pt and Rh have received a great deal of attention. These materials are very active; however, unlike Cu-based catalysts, precious metals-based catalysts have poor CO_2 selectivity, yielding primary CO and H_2 during the methanol steam reforming (Iwasa *et al.*, 2004).

2.4.1 Copper-based catalysts

In Cu-based catalyst, the Cu/ZnO/ Al_2O_3 catalyst, which is traditionally used for low-temperature water-gas shift and methanol synthesis. has been widely used in methanol steam reforming reaction. Many researchers studied the method of preparation, characterization and evaluation of Cu/ZnO/ Al_2O_3 catalysts. Shishido *et al.* (2004) studied Cu/ZnO and Cu/ZnO/ Al_2O_3 catalysts prepared by ho-

mogeneous precipitation (HP) using urea hydrolysis and they found that the catalysts showed higher activities than those prepared by coprecipitation (CP). It is suggested that the good catalytic performances of HP-Cu/ZnO and HP-Cu/ZnO/Al₂O₃ are due to both highly dispersed Cu metal species and to high accessibility of the Cu metal species to methanol and steam. In 2002, Kumari *et al.* studied the effect of Cu/Zn ratio of the surface and sub-surface on the activity and stability of methanol steam reforming catalysts. The result showed that surface and sub-surface Cu/Zn composition in the range of 1.2-1.5 may produce catalysts with stable activity. The introduction of zinc into Cu/Al₂O₃ catalysts is known to limit the sintering and improving the dispersion of copper (Fierro *et al.*, 1995). Therefore, Houteit *et al.* (1996) interested to study the copper oxide supported on alumina (Cu/Al₂O₃) and promoted with cesium (Cu-Cs/Al₂O₃) and they found that cesium prevents the reduction of copper oxide into metallic Cu, by the hydrogen produced, and inhibited the formation of CuAl₂O₄ spinel upon thermal treatment. Bichon *et al.* (2006) studied the Pd promoter for Cu-based catalysts and the result showed that the addition of Pd also lead to poorer selectivity, due to a significant increase in the selectivity to CO. Furthermore, many researchers studied Cu-based catalysts in other supports. Men *et al.* (2004) studied Cu/CeO₂/γ-Al₂O₃ thin film catalyst on the 10 microchannels of a microreactor. Ritzkopt *et al.* (2006) studied Cu/ZrO₂ catalysts and the result show that Cu/ZrO₂ can reduce CO formation at high methanol conversions compared to the commercial Cu/ZnO catalyst.

2.4.2 Paladium-based catalysts

Iwasa *et al.* (1995) first discovered that when supporting the Pd on ZnO, the catalytic function of Pd can be greatly modified, resulting in highly active and selective catalyst for methanol steam reforming, which was not found previously on precious metal catalysts. Under steam reforming conditions, the Pd/ZnO catalyst produces mainly CO₂ and H₂ along with minimal amount of CO. Pd-based catalysts are more stable than Cu-based catalysts and can operate at a wider temperature range. Chin *et al.* (2002) studied the characterization of Pd/ZnO catalysts in steam reforming of methanol, it was found that Pd-Zn alloy can be formed under reducing environment at moderate temperature (<300°C). This specie is highly selective for

the steam reforming of methanol, which is not normally observed on precious metal-based catalysts. In 2006, Karim *et al.* studied the effect of pretreatment on the Pd-Zn alloy formation; they found that even without pretreatment, Pd-Zn alloy particles were formed after reaction at 250°C, due to the facile reduction of ZnO in the presence of Pd and H₂. Samples treated at low temperatures in H₂ showed the coexistence of monometallic Pd and Pd-Zn alloy particles. Higher-temperature reduction led to complete transformation of Pd into Pd-Zn alloy and elimination of the small particles, leading to improved selectivity. Chin *et al.* (2003) studied the effect of preparation technique to Pd/ZnO catalytic properties. The results showed that during impregnation of Pd, the use of highly acidic Pd nitrate aqueous precursor has shown to alter the textural properties such as porosities and crystalline structures of ZnO, where dissolution of ZnO is evident. The dissolution of ZnO into Zn²⁺ not only modified the physical properties of support, but also affected the extent of mixing between Zn²⁺ and Pd²⁺ in the subsequent pretreatment. Furthermore, Liu *et al.* (2006) studied the deactivation of Pd/ZnO catalysts; they suggested that the deactivation of Pd/ZnO is due mainly to two phenomena: surface fouling by deposited carbon, reducing the activity and increasing CO formation, and surface oxidation of the Pd-Zn alloy through reactions and resulting mainly in higher CO formation. After deactivation, the Pd/ZnO catalyst can be regenerated by oxidative removal of the carbon deposits in an oxygen containing atmosphere at relatively low temperatures and by reducing treatment in a hydrogen-containing atmosphere at higher temperatures.

2.5 Gold Catalyst

Gold (Z=79) has the atomic configuration as [Xe]4f¹⁴5d¹⁰6s¹, and therefore lies in Group 11(IB) of the periodic classification of elements. It is a congener of Cu and Ag, which often being referred to as the “coinage metals”, and lies between Pt in group 10 and mercury in group 12. The physical properties of Au are shown in Table 2.3.

Table 2.3 Physical Properties of Au (Bond *et al.*, 2006)

Property	Gold (Au)
Atomic number	79
Atomic mass	196.9665
Electronic configuration	[Xe]4f ¹⁴ 5d ¹⁰ 6s ¹
Structure	FCC
Lattice constant (nm)	0.408
Metallic radius (nm)	0.14420
Density (g/cm ³)	19.32
Melting temp. (K)	1337
Boiling temp. (K)	3081

Gold catalysis is a rapidly developing topic of both academic and industrial research and significant advances have been made within the last decade. In particular, it is interesting to note the increasing number of patents related to gold catalysts in polymer electrolyte membrane (PEM) fuel cell technology, including some from major original equipment manufacturers. The justification for developing the gold catalyst technologies described is not only based on their promising technical performance, but also the relatively low stable price and greater availability of gold compared with the platinum group metals.

Furthermore, it has already been demonstrated that gold can have the highest catalyst activity for some reactions, including the oxidation of carbon monoxide and the hydrochlorination of ethyne and it is believed that in a number of specific areas, gold catalysts will be used in commercial applications, including pollution control. The reactions for which gold has already been demonstrated to be a strong catalyst include: (Cameron *et al.*, 2003)

- oxidation of CO and hydrocarbons
- water gas shift (WGS)
- reduction of NO with propene, CO or H₂
- reactions with halogenated compounds
- water or H₂O production from H₂ and O₂

- removal of CO from hydrogen streams
- hydrochlorination of ethyne
- selective oxidation, e.g. epoxidation of olefins
- selective hydrogenation
- hydrogenation of CO and CO₂

Haruta's work (1997) showed that nanoparticulate gold particle (less than 5 nm) is very active for many reactions. For preferential oxidation of CO (PROX) in hydrogen-rich reformer gas Kahlich *et al.* (1999) mentioned that Au/ α -Fe₂O₃ is significantly more active than the commercial PROX catalysts, i.e. Pt/ γ -Al₂O₃. It was founded that Au/CeO₂ and Au/ α -Fe₂O₃ catalysts, made using a deposition precipitation technique, are effective in PROX reaction. For water gas shift reaction, both Au/ α -Fe₂O₃ (Andreeva *et al.*, 1998) and Au/TiO₂ (Sakurai *et al.*, 1997) are active at low temperatures and the preparation of Au/ α -Fe₂O₃ and Au/TiO₂ by deposition-precipitation produces more active catalysts than those prepared by co-precipitation.

Furthermore, in Molten carbonate fuel cells (MCFCs), specific areas requiring gas and electrolyte seals, as well as improved electrical contact, could benefit from the use of gold since it is the only material shown to be immune to corrosion from the molten electrolyte. For the corrosion test results, Cameron *et al.* (2003) showed that gold was not affected by immersion in molten carbonate electrolytes over periods exceeding 90 h.

2.6 ZnO and ZnO-Fe₂O₃ Support

Zinc oxide occurs naturally as the mineral zincite. Zinc oxide is for the most part insoluble in water, but is soluble in acids and alkalis. It exhibits piezoelectric characteristics in thin film form. Such thin films can be deposited by process like sputter deposition. Zinc oxide is also luminescent and light sensitive. The structures of ZnO are shown in Figure 2.10, the left picture shows the SEM-image of ZnO powder particles. the center shows the typical shape of ZnO powder particles, a hexagonal column with the top-face corresponding to the Zn-terminated Zn-ZnO surface

and the bottom to the O-terminated O-ZnO surface. The six side faces are all equivalent and correspond to the mixed terminated ZnO (1010) surface. And the right picture shows the atomic model of a hexagonal column of a ZnO particle. (Chemie and Bochum, 2007)

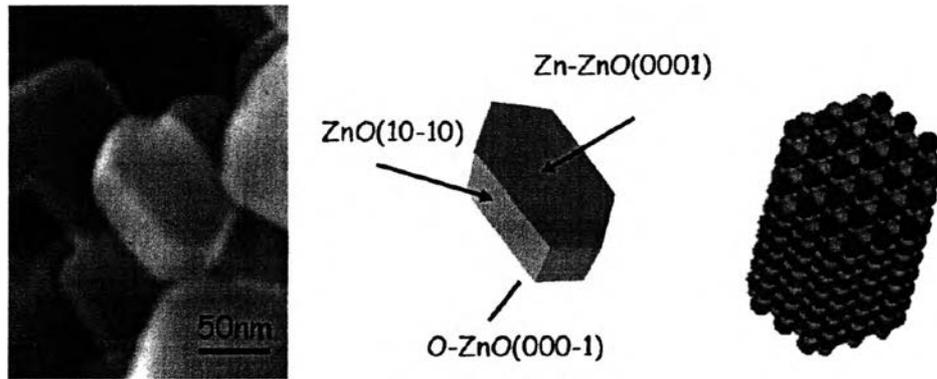


Figure 2.10 The structure of ZnO (Chemie and Bochum, 2007).

Today, in terms of industrial added value, the chemical properties of ZnO surfaces are the most important ones. Many different chemicals are produced using ZnO or ZnO-based compounds as a heterogeneous catalyst. The most prominent example is methanol, which until 1960 the catalysts containing ZnO as the active component have been produced. In 1998, Fujitani *et al.* studied the effect of ZnO in methanol synthesis catalysts and they found that ZnO in Cu/ZnO based catalysts is ascribed to both increases in the Cu dispersion and the specific activity. Moreover, Iwasa *et al.* (2005) studied the steam reforming of methanol over ZnO-supported transition metal catalysts and they found that Pd/ZnO catalyst is more active than Cu/ZnO catalyst at high temperatures because Pd/ZnO can form PdZn alloy at mild temperature and PdZn alloy catalyst can maintain its activity without deactivation, while the Cu/ZnO catalyst loses its activity.

Nowaday, many researchers are interested in using Fe₂O₃-supported with Au metal (Au/Fe₂O₃) for WGS reaction. Silberova *et al.* (2006) mentioned that at elevated temperature, the Fe₂O₃ support, in the presence of Au particles is easily reduced and contributes the catalytic performance for WGS reaction. The water to

Fe_2O_3 does not contribute to reoxidation to a large extent and, consequently, to high CO_2 production as observed over $\text{Au}/\text{Fe}_2\text{O}_3$. Furthermore, H_2 is evolved only in the presence of Au particles and when a certain degree of Fe oxide reduction is achieved.

For the composite oxide (Fe_2O_3 -ZnO Support), Sakurai *et al.* (1996) studied the methanol synthesis over gold catalysts supported on metal oxides and they found that the addition of oxides like Fe_2O_3 and TiO_2 on Au/ZnO , methanol conversion can be enhanced, maintaining high selectivity exceeding that for commercial $\text{Cu}/\text{ZnO}-\text{Fe}_2\text{O}_3$ catalyst. The methanol selectivity over gold catalysts supported on metal oxides is shown in Figure 2.11.

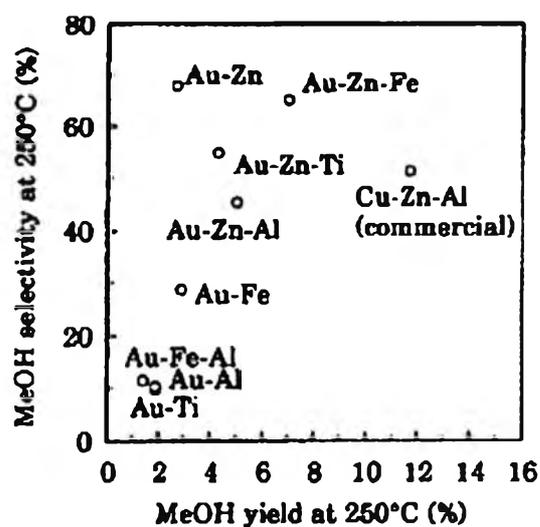


Figure 2.11 Relationship between methanol yield and selectivity over $\text{Au}/\text{MO}_x/\text{M}'\text{O}_y$ (Sakurai *et al.*, 1996).