

CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Fuel Cells

Fuel cells are energy devices that use hydrogen as a fuel to produce electrons, protons, heat and water. Fuel cell technology is based upon the simple combustion reaction given in Equation 2.1.



A fuel cell does not require recharging the same as a battery. In theory a fuel cell will produce electricity as long as fuel is constantly supplied. The basic design of a fuel cell involves two electrodes on either side of an electrolyte. Hydrogen and oxygen pass over each of the electrodes and through means of a chemical reaction, electricity, heat and water are produced as shown in Figure 2.1.

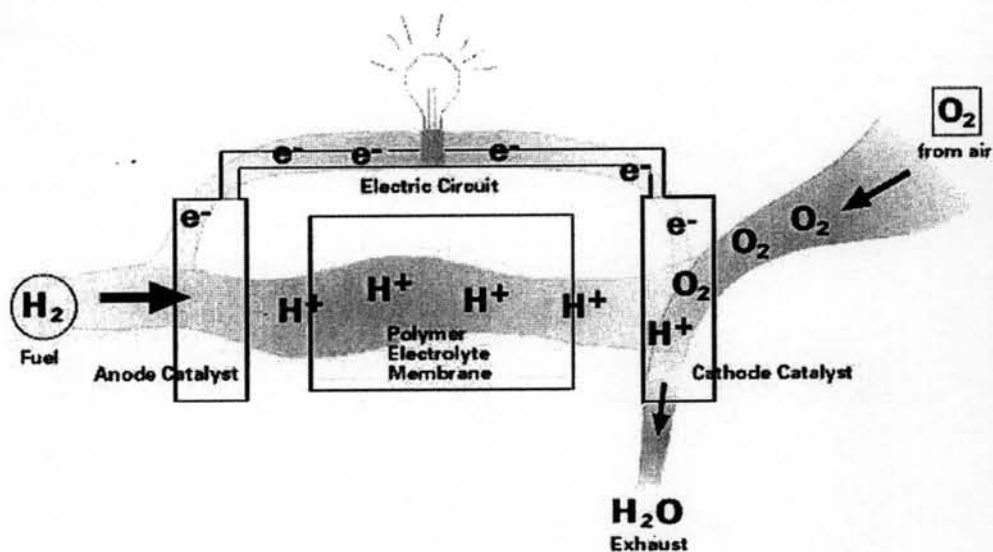


Figure 2.1 Fuel cell unit.

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 a proton. Each takes a different path to the cathode. The electrons are capable of taking a path other than through the electrolyte, which, when harnessed correctly can produce electricity for a given load. The proton passes through the electrolyte and both are reunited at the cathode. The electron, proton, and oxygen combine to form the harmless byproduct of water.

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 or methanol. The fuel cell's means for producing electricity is through a chemical reaction, therefore, there are significantly cleaner emissions than from a fuel combustion process.

The fuel cell can be classified by the type of electrolyte used and the following names and abbreviations are now frequently used in publications: Alkaline Fuel Cell (AFC), Phosphoric Acid Fuel Cell (PAFC), Molten Carbonate Fuel Cell (MCFC), Solid Oxide Fuel Cell (SOFC) and Proton Exchange Membrane Fuel Cell (PEMFC).

Table 2.1 Applications for H₂/O₂ fuel cell system (Kordesch and Simader, 1996)

Fuel Cell System	Temperature Range	Efficiency (Cell)	Electrolyte	Application area
AFC	60-90°C	50-60%	35-50% KOH	Traction application/ space application
PEMFC	50-80°C	50-60%	Polymer Membrane (Nafion/Dow)	Traction application/ space application
PAFC	160-220°C	55%	Concentrated Phosphoric Acid	Predominantly dispersed, power application (50-500 kW, 1MW, 5MW, 11MW)
MCFC	620-660°C	60-65%	Molten Carbonate Melts (Li ₂ CO ₃ /Na ₂ CO ₃)	Power generation
SOFC	800-1000°C	55-65%	Yttrium-stabilized Zirkondioxide (ZrO ₂ /Y ₂ O ₃)	Power generation

In the mobile applications, the suitable type of fuel cell that meet the requirement is PEMFC. The advantages of using PEMFC (Kordesch and Simader, 1996) are as follows:

- There is no free corrosive liquid in the cell
- Simple fabrication
- High pressure differential tolerance
- Long life time

But there are some disadvantages of using PEMFC, which are

- The high cost of fluorinated polymer electrolyte
- The water management in membrane
- Poor CO tolerance (Figure 2.2)

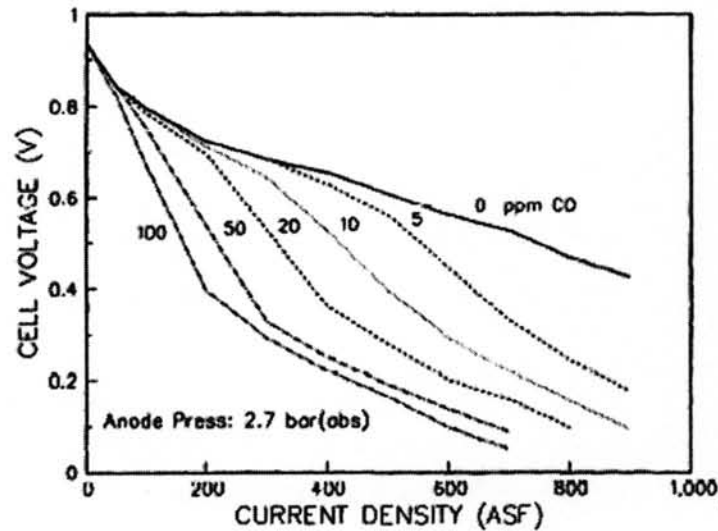


Figure 2.2 Effect of CO contamination on PEMFC electrolyte performance (Amplett *et al.*, 1996).

Table 2.2 PEMFC anode feed gas specification (Amplett *et al.*, 1996)

Components	Specifications	Comments
Hydrogen	50-100%	Cell performance not adversely effected by moderate dilution
CO	Max. 10-100 ppm	Severe poison to electrocatalyst (partly reversible) Tolerance level dependent on cell design and operating conditions
N ₂ , CO ₂	0-50%	Relatively inert
Water	Variable	Humidification necessary. Requirements very with electrode design.
Methane	0% desirable	Relatively inert
Formic acid	0%	Severe poison (irreversible)
Methanol	0% desirable	Reversible performance loss at 5000 ppm
Formaldehyde	0% desirable	Reversible performance loss at 5000 ppm
Methyl formate	0% desirable	Reversible performance loss at 5000 ppm

The hydrogen stream that can enter the anode of the fuel cell for a good performance are described in Table 2.2.

2.2 Hydrogen Production

The crucial problem in utilization of fuel cell is hydrogen supply. Hydrogen can be produced by various methods as shown in Figure 2.3.

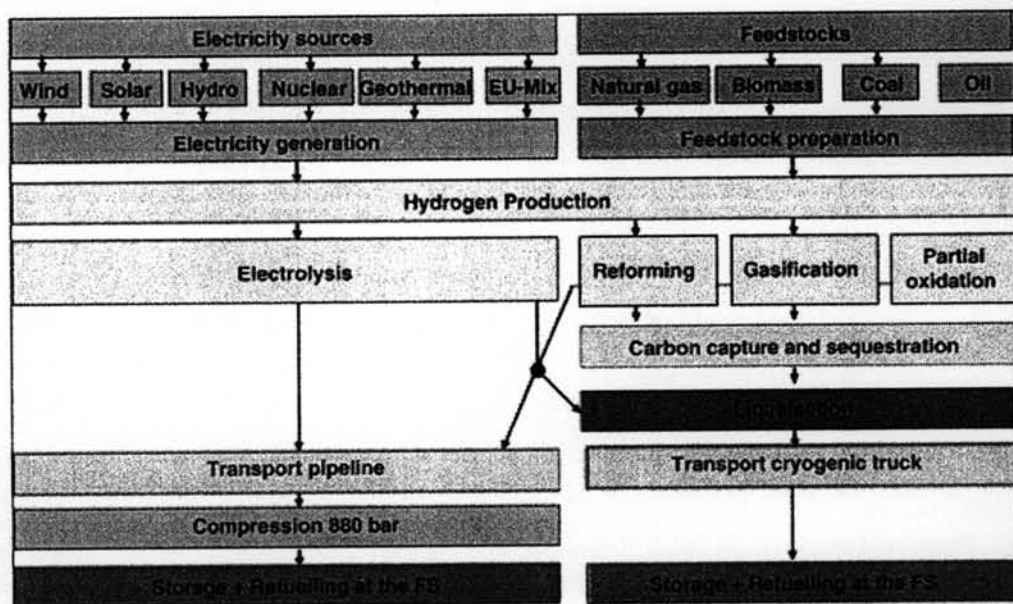
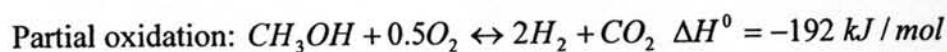
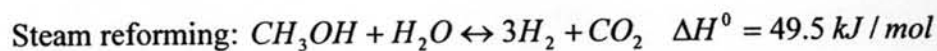
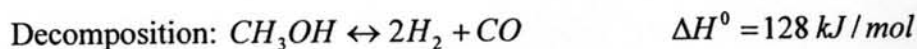


Figure 2.3 Sub-systems of hydrogen pathways (Wietdchel *et al.*, 2006).

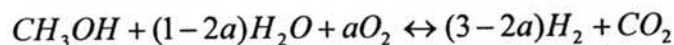
Hydrogen supply for the on-board application can be compressed hydrogen, store in a metal hydride or reforming of high hydrogen content material. And reforming of high content hydrogen material is preferred due to its no more safety consideration, appropriate weight and can use biomass as a fuel.

2.2.1 Hydrogen Production from Methanol

Among liquid hydrocarbon fuels, methanol is regarded as one of the most promising candidates for the on-board reforming to hydrogen. Four processes are feasible as follows:



Oxidative steam reforming:



$$\Delta H^0 = 49.5 - a * 241.8 \text{ kJ/mol}$$

where a is an oxygen to methanol (O/M) molar ratio.

In contrast to the decomposition and the steam reforming of methanol (SRM), the partial oxidation is an exothermic reaction, but the generation of heat could cause sintering of the particles and hence the deactivation of the catalyst. In addition, a maximum yield of hydrogen (66% by volume) can only be achieved by using pure oxygen for the reaction. As for automobile fuel cell technology normally air would be used, the less amount of hydrogen could be produced, because the product stream will be diluted with nitrogen. Moreover, deactivation of the catalyst must be considered when using air as a reactant, because sulfur and chlorine compounds could lead to a poisoning of the material. (Moore *et al.*, 2000)

The decomposition as well as the steam reforming is endothermic reactions and therefore addition energy supply is necessary. (Agrell *et al.*, 2003a) One idea to solve this problem is the use of the heat of exhaust gas. Although the decomposition reaction is simple reaction by using solely methanol as a starting feedstock, the production of carbon monoxide makes it very inappropriate for PEMFC applications.

By combining partial oxidation and steam reforming of methanol, a system is called oxidative steam reforming, which is dynamic, forms a relatively high hydrogen concentration and avoids critical hot spots in the reactor. The heat for steam reforming of methanol could be provided by the partial oxidation reaction.

The high concentration of hydrogen (75% by volume), and the high selective to carbon dioxide make the steam reforming of methanol to a very favorable process for the mobile applications. Additionally, it was recently shown that the potential of methanol as feed stock for making hydrogen production in the on-board

applications such as the automobiles (e.g. Honda, Ford, Mitsubishi and Daimler-Chrysler) as well as the fuel cell unit for laptop computer of Ultacell® Company.

2.2.2 Steam reforming of methanol

The general reaction conditions of steam reforming of methanol (SRM) are as follows:

- reaction temperature: 200-300°C (Agrell *et al.*, 2003)
- atmospheric pressure
- 1 to 1.5 molar ratio of steam to methanol

The main products of SRM are hydrogen, carbon dioxide and a low content of carbon monoxide is produced in this process (up to 2 volume % in dry product stream when using a copper-based catalyst). Hydrogen production based on SRM 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 2.4.

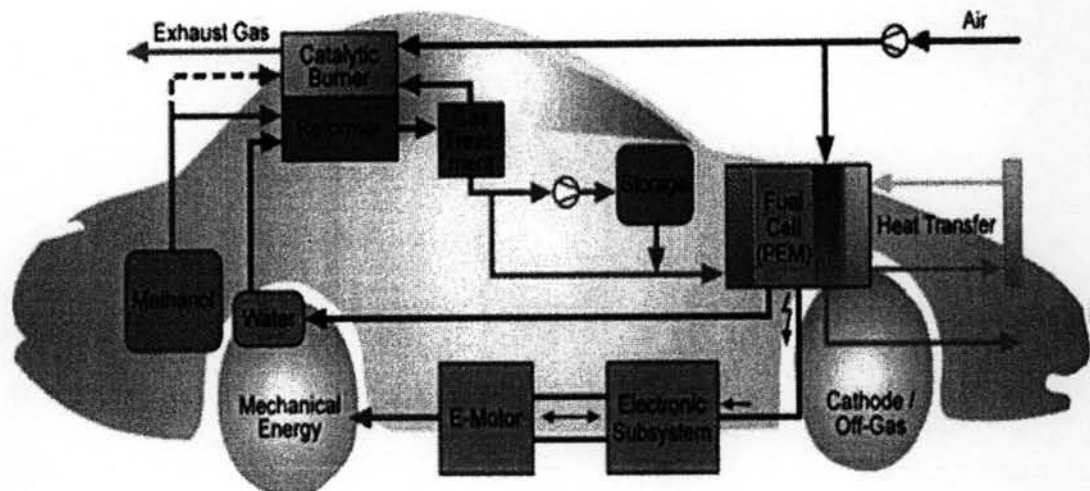


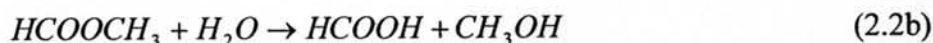
Figure 2.4 Fuel cell drive system. (Wiese *et al.*, 1999).

2.2.3 Mechanisms of steam reforming of methanol

There have been some controversies in the literature concerning the mechanisms for production of hydrogen and carbon dioxide by SRM. The study of the mechanism of the formation of CO as a by-product has received much attention. There are several schemes suggested in the literature.

2.2.3.1 No formation of CO in the reaction route

(Breen *et al.*, 1999; Takahashi *et al.*, 1982; Jiang *et al.*, 1993a; Jiang *et al.*, 1993b) Some researchers (Takahashi *et al.*, 1982; Takezawa *et al.*, 1997) suggested the SRM 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.



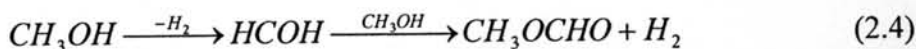
According to the study performed by Takahashi *et al.* (1982), the WGS reaction was found to be blocked in the presence of methanol on Cu/SiO₂. Another argument for excluding WGS in the reaction scheme is that the equilibrium constant $K_p = \frac{P_{\text{CO}_2} P_{\text{H}_2}}{P_{\text{CO}} P_{\text{H}_2\text{O}}}$ determined in the experiment greatly exceeded those obtained for the WGS reaction (Takezawa *et al.*, 1997). A detailed study of the reaction scheme on the Cu/SiO₂ catalyst has been performed by Takezawa *et al.* (1997). They found that HCHO and CH₃OOCH 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 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 methanol to methyl formate. They concluded that the formation of methyl formate over copper-based catalysts occurs through a pathway:



2.2.3.2 The decomposition of methanol and water gas shift reaction

(Santacesaria and carrá., 1983; Amphlett *et al.*, 1985)



These schemes were suggested by Santacesaria and carrá (1983) who studied the SRM kinetics over a commercial low-temperature Cu/ZnO/Al₂O₃ shift catalyst in a continuous stirred-tank reactor. They found that CO concentration was negligible in the product. Based on this result, they assumed that CO is produced from decomposition of methanol and followed by water gas-shift reaction, where the decomposition reaction was found to be the rate-determining step. According to this scheme, CO is an intermediate product.

2.2.3.3 The steam reforming of methanol and decomposition of methanol



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:

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

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

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

$$r_{CO} = k_2$$

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

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.

2.2.3.4 The steam reforming of methanol, decomposition of methanol and water gas-shift reaction



The scheme of SRM process which includes SRM, WGS and decomposition is proposed by Peppley *et al.* (1999) and Amphlett *et al.* (1994). They studied the reaction network for SRM over a Cu/ZnO/Al₂O₃ catalyst. They claim that in order to fully understand the reaction network, all three reactions must be included in the model. They found that there are two types of catalyst sites that are responsible for the catalyst activity and selectivity, one for the SRM and WGS reactions and another for the decomposition reaction.

2.2.3.5 Steam reforming of methanol and reverse water gas shift reaction (Reuse *et al.*, 2004)



A kinetic study of steam reforming of methanol on a commercial CuO/ZnO/Al₂O₃ catalyst has been performed by Purnama *et al.* (2004). The experimental results of CO partial pressure as a function of contact time at different temperatures showed very clearly that CO was formed as a consecutive product. The reaction scheme used is the direct formation of CO₂ and hydrogen by SR reaction

and formation of CO as consecutive product by reverse WGS reaction. A simulation employing this scheme is able to fit the experimental data well over a wide temperature range (230-300° C). In the work of Breen *et al.* (1999), they observed that CO is formed at high methanol conversions and long contact times. No CO was formed at all at low contact times. This indicates that CO is a secondary product, formed by reverse WGS reaction. This result agrees well with the work of Agrell *et. al* (2002). They found that the level of CO decreases with decreasing contact time.

2.3 Catalysts 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 copper-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 are also investigated for the hope that the better performance might be found. The summary of the various catalysts studied are listed in Table 2.3.

Table 2.3 Selected data for SRM of copper-based catalysts development

References	Catalysts	Reaction Temperature (°C)	H ₂ O/CH ₃ OH molar ratio	CH ₃ OH conversion, H ₂ information, CO and CO ₂ in formations
Copper based catalysts				
Tanabe <i>et al.</i> , (2006)	Al-Cu-Fe Quasicrystalline	300	1.5	677 ml.min ⁻¹ g-cat ⁻¹ (H ₂)
Fukanori <i>et al.</i> , (2006)	Cu/ZnO	300	1.5	~81% CH ₃ OH conversion ~0.9% CO content ~13 mmol.min ⁻¹ g-cat ⁻¹ (H ₂)
Agrell <i>et al.</i> , (2003)	Cu/ZnO	300	1.0	99% CH ₃ OH conversion ~1% CO content
Ritzkopf <i>et al.</i> , (2006)	Cu/ZrO ₂	300	1.0	90% CH ₃ OH conversion 0.5% CO content
Yao <i>et al.</i> , (2006)	Cu/ZrO ₂	260	-	100% CH ₃ OH conversion 4.5% CO content 0.32 mol.hr ⁻¹ g-cat ⁻¹ (H ₂)
Takezawa and Iwasa (1997)	Cu/SiO ₂	220	1.0	345 μmol.min ⁻¹ g-cat ⁻¹ (H ₂)

Table 2.3 Selected data for SRM of copper-based catalysts development (Continue)

Lui <i>et al.</i> , (2001)	Cu/CeO ₂	260	1.0	90.7% conversion 97.7% CO ₂ selectivity 2.3% CO selectivity 90.5 cm ³ .min ⁻¹ g _{-cat} ⁻¹ (H ₂)
Ma <i>et al.</i> , (2000)	Cu-CrO ₃	260	1.0	~230 mmol.min ⁻¹ g _{-Cu} ⁻¹ (H ₂)
Papavasiliou <i>et al.</i> , (2005)	Cu-Mn-O	280	1.5	100% CH ₃ OH conversion 92% H ₂ selectivity
Suwa <i>et al.</i> , (2004)	Zn-Pd/C	255	1.4	98% CH ₃ OH conversion 95% CO ₂ selectivity
Yong-Feng <i>et al.</i> , (2004)	CuZn(Zr)AlO	250	1.3	61.1% CH ₃ OH conversion 0.067% CO content 99.6% CO ₂ selectivity
Mastalir <i>et al.</i> , (2005)	Cu/ZrO ₂ /CeO ₂	250	1.0	30% CH ₃ OH conversion 0.05% CO content
Zhang and Shi (2003)	Cu/CeO ₂ /Al ₂ O ₃	250	1.0	95.5% conversion 0.2944 mol.hr ⁻¹ g _{-cat} ⁻¹ (H ₂) 0.14% CO content

Table 2.3 Selected data for SRM of copper-based catalysts development (Continue)

Takahashi <i>et al.</i> , (2001)	Cu-Zr-Au amorphous alloy	250	1.0	100% CH ₃ OH conversion 60% CO ₂ selectivity
Yu <i>et al.</i> , (2006)	Cu/Zn/Ce	272	1.3	85% CH ₃ OH conversion 1.1% CO dry content
Shen and Song (2002)	Cu/Zn/Al	230	1.43	100% CH ₃ OH conversion 0.2% CO content
Kumari <i>et al.</i> , (2002)	CuO/ZnO/Al ₂ O ₃	250	1.3	100% CH ₃ OH conversion ~10 L.hr ⁻¹ g _{-cat} ⁻¹ (H ₂)
Won <i>et al.</i> , (2006)	CuO/ZnO/Al ₂ O ₃	270	1.5	99.5% conversion 1.5 L/hr (H ₂) 1.4% CO content
Wild and Verhaak (2000)	Commercial copper	280	1.5-2.0	100% CH ₃ OH conversion 2500 ppm CO
Agrell <i>et al.</i> , (2002)	Cu/ZnO/Al ₂ O ₃	~300	1.3	95% CH ₃ OH conversion 1% CO content

Table 2.4 Selected data for SRM of non-copper catalysts development

Non-copper based catalysts				
Chin <i>et al.</i> , (2003)	Pd/ZnO	254	1.8	30% CH ₃ OH conversion 10% CO selectivity
Cao <i>et al.</i> , (2004)	Pd/ZnO	240	1.0	100% CH ₃ OH conversion
Ranganathan <i>et al.</i> , (2005)	Pd/ZnO	230°C	1.0	TOF = 0.8 ± 0.3 s ⁻¹
	Pd/CeO ₂	230°C	1.0	TOF = 0.4 ± 0.2 s ⁻¹
Gómez-Sainero <i>et al.</i> , (2005)	Pd/CeO ₂ -Sm ₂ O ₃	400	1.2	80% CH ₃ OH conversion 0.46 mol.hr ⁻¹ g-cat ⁻¹ (H ₂) 0.22 mol.hr ⁻¹ g-cat ⁻¹ (CO) 97.5% CO selectivity
Pinzari <i>et al.</i> , (2006)	Zn/TiO	400	1.1	2.7mol.Carbonmole ⁻¹ (H ₂)

The classical work done by Takezawa and Iwasa (1997), they studied the comparison of Ni, Rh, Pt, Pd and Cu supported on SiO₂ for steam reforming of methanol and they reported that the best performance among these catalysts was Cu/SiO₂. Besides, they also investigated the effect of supports (such as SiO₂, Al₂O₃, Nb₂O₅, La₂O₃, ZrO₂ and ZnO) for Pd loading. It was found that the Pd/ZnO showed the best performance in their work.

A series of copper catalysts, (Cu/CeO₂, Cu/ZnO, Cu/Zn(Al)O, CuAl₂O₃), was tested for steam reforming of methanol (Lui *et al.*, 2001). The highest methanol conversion was obtained by using Cu/CeO₂ prepared by co-precipitation. From these results give a hint that for copper catalysts, the CeO₂ support may give higher methanol conversion than ZnO support.

2.4 Gold Catalysts

Gold normally is considered to be inert in the ambient condition but it is incredible that gold particle size with the less than 5 nm particle size (Haruta, 1997) is very active for many reactions.

The reactions that gold shown the good performance are as follows: (Cameron *et al.*, 2003)

- Oxidation of CO and hydrocarbons,
- Water gas shift (WGS),
- Reduction of NO with propane, CO or H₂,
- Reactions with halogenated compounds,
- Water or H₂O₂ production from H₂ and O₂,
- Removal of CO from hydrogen streams,
- Hydrochlorination of ethylene,
- Selective oxidation, e.g. epoxydation of olefins,
- Selective hydrogenation,
- Hydrogenation of CO and CO₂

In the PEMFC application the removal of CO is needed, the selective oxidation of the CO in the hydrogen stream (Luengnaruemitchai *et al.*, 2004) over gold supported on ceria showed reliable results with a proper catalyst preparation.

That comes up with the motivation of this work, hydrogen production via steam reforming of methanol for PEMFC applications. The catalysts for this work are Au/CeO₂ and Au/ZnO. The synergism of the gold metal and the supports is expected to have a good production rate of hydrogen and low CO content.