



CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Background

In the present, most of energy that we use is depended on fossil fuel base but increasing of crude oil price and environmental concern are the motivation to searching for alternative energy which are not base on fossil fuel. Inexhaustible and non-polluting, hydrogen is described by many as the fuel to our future energy needs. One of the most plentiful elements on Earth and in the cosmos, and use it as a clean-burning fuel or in fuel cells to power cars, heat houses and offices, generate electricity, etc. it produces only water as a byproduct and none of the CO₂ and other pollutants obtained by burning fossil fuels and in the current carbon (fossil fuel)-base economy. 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.

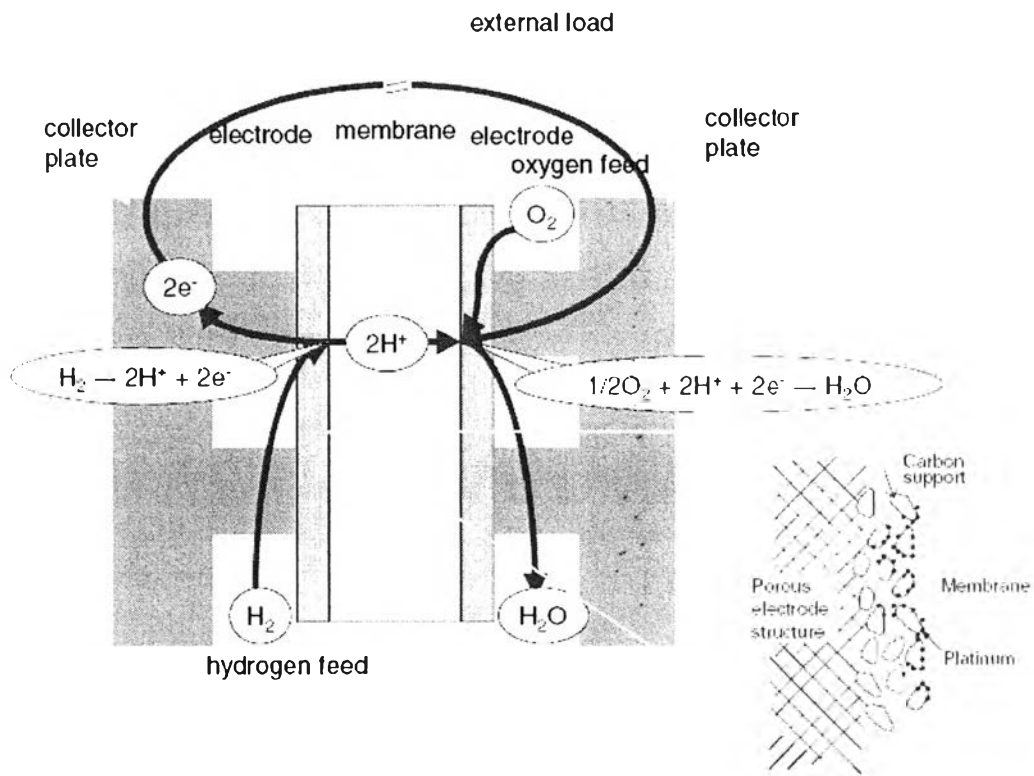
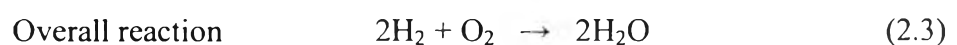
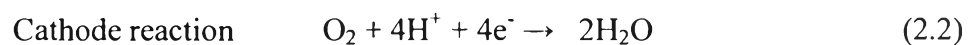
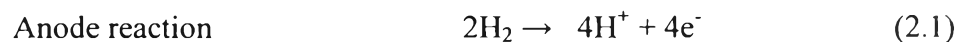


Figure 2.1 Diagram of fuel cell unit (Polymer Electrolyte Membrane fuel cell) (Barbir, 2006).

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



Fuel cells produce electricity through a chemical reaction; therefore, it is a clean energy generator. 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.

In the mobile applications, the suitable type of fuel cell that meets the requirement is PEMFC. The advantages of using PEMFC are fast startup time, low sensitivity to orientation, and favorable power to weight ratio. It is particularly suitable for using in passenger vehicles, such as cars and buses.

PEMFC operates at relatively low temperature of around 60 to 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. In addition, because carbon monoxide molecules are easily adsorbed on the Pt surface through irreversible chemisorptions at low temperatures (27 to 80°C), the formation of carbon monoxide can significantly deactivate the catalyst layer of PEMFC. 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.

Table 2.1 Comparison of the system of fuel cells

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

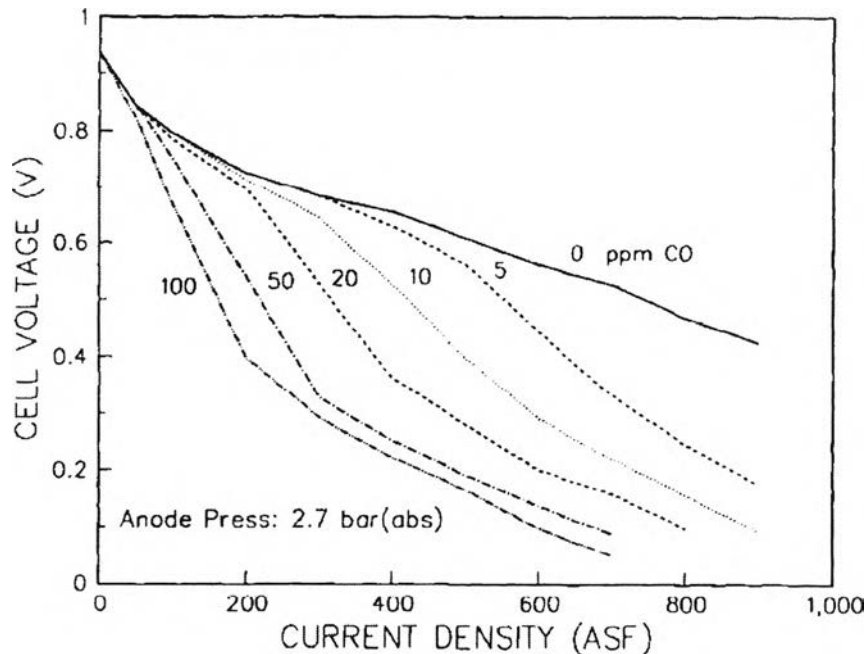


Figure 2.2 Effect of CO contamination on PEMFC electrolyte performance (Amphlett *et al.*, 1996).

2.3 Hydrogen Production form Methanol

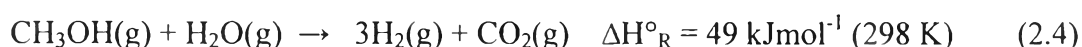
Methanol (CH_3OH) is the simplest, safest, and easiest to store and transport liquid oxygenated hydrocarbon. At present, it is prepared almost exclusively from synthesis gas (syn-gas, a mixture of CO and H_2) obtained from the incomplete combustion of fossil fuels (mainly natural gas or coal). Methanol can also be prepared from biomass (wood, agricultural byproducts, municipal waste, etc.), but these play only a minor role. The production of methanol is also possible by the oxidative conversion of methane, avoiding the initial preparation of syn-gas, or by reductive hydrogenative conversion of CO_2 (from industrial exhausts of fossil fuel burning power plants, cement plants, etc. and eventually the atmosphere itself). The hydrogen required (which is eventually generated from water using non-fossil fuel-based energy) is thus stored in the form of a safe and easily transportable liquid. The

chemical recycling of excess CO₂ would, at the same time, also help to mitigate climate changes caused in a significant part by the excessive burning of fossil fuels.

Methanol or its derivatives can already be used as substitutes for gasoline and diesel fuel in today's internal combustion engine-powered cars and it can convert to hydrogen, which 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 H₂O. Under hydrogen production processes, the water molecule and the raw material are split, and the results are H₂, CO and CO₂. 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. Conventionally, hydrogen can be extracted from methanol via the following processes: decomposition, steam reforming, partial oxidation, and auto-thermal reforming.

2.3.1 Methanol Steam Reforming

Steam reforming is a reaction between hydrocarbon fuel and water and also is the most extensively studied process due to its high hydrogen yield and high composition toward carbon dioxide. The overall reaction for SRM is shown in Eq. 2.4.



When using stoichiometric feedstock, the steam reforming of methanol ideally produces only hydrogen and carbon dioxide. However, methane and carbon monoxide are usually found in the product stream, depending upon the type of catalyst and the operating conditions. The formation of methane consumes hydrogen from methanol and steam, suppressing the production of hydrogen gas as a result.

The observation of these undesired byproducts suggests a complicated mechanism for methanol steam reforming. Although the mechanism of carbon

monoxide formation during SRM is currently not clear, the decomposition of methanol (Eq.2.5) is believed to be one possible pathway of producing carbon monoxide. Under methanol steam reforming conditions, this carbon monoxide can be either transformed to carbon dioxide via the water-gas shift (WGS) reaction (Eq.2.6) or to methane via the hydrogenation of carbon monoxide (Eq.2.7) (Breen *et al.*, 1999).



The steam reforming process is usually operated with excess steam, to induce the water gas shift (WGS) reaction (Eq. 2.6) in the reformer in order to lower the CO concentration in the product gas. The diagram of steam reforming process is shown in Figure 2.3.

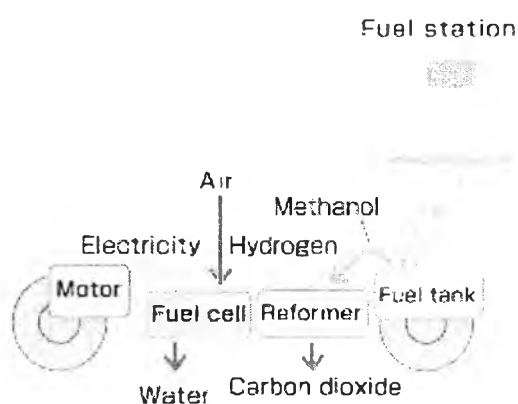


Figure 2.3 On-board methanol reforming system (jcwinnie.biz/wordpress/p=1676).

2.3.1.1 Experimental Condition

The effect of reaction temperature on the catalytic performance is shown in Figure 2.4. Zhang *et al.*, 2002 found that the methanol conversion increased with increasing the reaction temperature, while methanol is converted almost completely into H₂, CO₂ and CO up to 280°C.

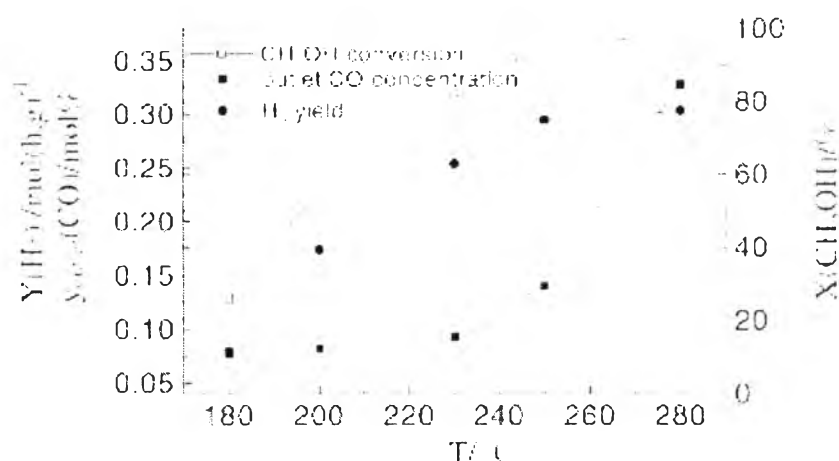


Figure 2.4 Effect of reaction temperature in methanol steam reforming reaction (Zhang *et al.*, 2002).

2.3.1.2 Mechanism of Methanol Steam Reforming

There are limited kinetic studies and reaction mechanisms data available for the steam reforming of methanol process in the literature. The individual reactions Eqs. (2.8)–(2.10) to be included in the kinetic model are still under debate.

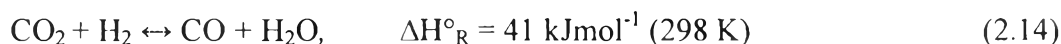


Santacesaria and Carra (1983) have proposed the reaction sequence of methanol decomposition (Eq. 2.9) followed by WGS reaction (Eq. 2.10). The CO is produced first in the reaction sequence; therefore, its concentration in the product stream must be equal to or greater than the concentration of CO at the WGS reaction equilibrium. Jiang *et al.* (1993) have proposed the elementary surface reaction mechanisms and

derived the Langmuir–Hinshelwood (LH) expression. They suggested CO formation via decomposition of methyl formate (Eqs. 2.11–2.13).



The kinetic expression from this predicts the rates of methanol conversion and carbon dioxide formation. They neglect the CO formation that cannot be neglected as even very low CO concentration can poison the Pt anode of PEM FC. Peppley *et al.* (1999) developed a LH rate expression considering SRM, decomposition of methanol (DM) and WGS reactions with dual site mechanism. It can be seen that in all the reaction mechanisms the route of CO formation is different. Breen and Ross *et al.* (1999) studied CO formation mechanism through DRIFT analysis and confirmed that the CO formation over CuO/ZnO/ZrO₂/Al₂O₃ catalyst for steam reforming of methanol occurs via (RWGS) reaction (Eq. 2.10). After that, many researchers have also proposed the CO formation via RWGS (Agrell *et al.*, 2001; Reuse *et al.*, 2004) that uses the products of the reforming reaction i.e. H₂ and CO₂.



Patel and Pant., (2007) study a kinetic of steam reforming of methanol, it was carried out over Cu/ZnO/Al₂O₃ catalyst with composition Cu/ZnO/Al₂O₃:10/5/85 (wt%). The concentration of CO in the product gas was less than 1% and was always well below the equilibrium CO concentration of the WGS. This supports the reaction sequence of methanol steam reforming followed by the RWGS.

Henderson *et al.* (2002) studied the activation of water, surface defects have been long believed to be the most active sites for water dissociation on oxide surfaces. During hydrogen prereduction in this study, ceria is highly reduced and more oxygen anion vacancies are created on the ceria surface. Trimm *et al.* (1994) reported that Ce₂O₃ is such a strong reducing reagent that it can decompose water into hydrogen. Therefore, water can be activated by the reduced ceria. It is

noted that the production of CO_2 consumes one surface oxygen. Men *et al.* (2004) depicted schematically in Figure 2.5 involving four distinct steps: (i) the adsorption of methanol and water at the Cu/CeO₂ interface; (ii) the surface reaction and the desorption of gaseous products; (iii) the migration of surface oxygen from CeO₂ to the reduced Cu (oxygen reverse spillover); (iv) the regeneration of partially oxidized copper and oxygen vacancies.

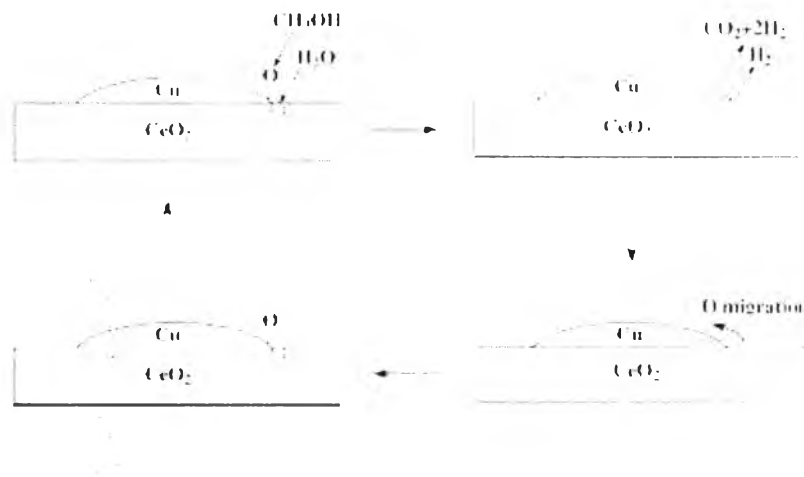


Figure 2.5 Proposed reaction mechanism for SRM at the Cu/Ce interface (Men *et al.*, 2004).

2.3.1.3 Kinetic of Methanol Steam Reforming

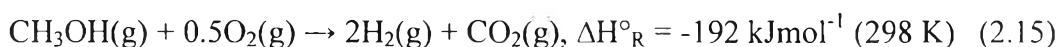
A semi-empirical model of the kinetics of the steam reforming of methanol over CuO/ZnO/Al₂O₃ catalyst has been developed by Amphlett *et al.* (1994) using the reaction schemes of irreversible reaction of SRM and decomposition reaction. They found that the WGS could be neglected without substantial loss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

$$\begin{aligned}
 r_{\text{CH}_3\text{OH}} &= -k_1 C_{\text{CH}_3\text{OH}} - k_2 \\
 r_{\text{H}_2\text{O}} &= -k_1 C_{\text{CH}_3\text{OH}} \\
 r_{\text{CO}_2} &= k_1 C_{\text{CH}_3\text{OH}} \\
 r_{\text{CO}} &= k_2 \\
 r_{\text{H}_2} &= 3k_1 C_{\text{CH}_3\text{OH}} + 2k_2
 \end{aligned}$$

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.

2.3.1.4 Partial Oxidation of Methanol

Partial oxidation reaction is a reaction that partially oxidizes the fuel to CO and H₂ rather than fully oxidizes to CO₂ and H₂O. Although, the partial oxidation reaction produces less favourable H₂/CO₂ ratios, there are several advantages over steam reforming. For instance, the partial oxidation reaction is exothermic, no steam generation is required and the reaction rate is higher. The reaction of partial oxidation of methanol is shown in Eq.2.11.



Copper-zinc catalyst has been found to be very active for the partial oxidation of methanol. The onset of the partial oxidation reaction is 488°C and the rates of methanol and oxygen conversion increase strongly with temperature to selectivity produce H₂ and CO₂ (Figure 2.6). The rate of CO formation was very low throughout the temperature range explored (200 to 225°C) and H₂O formation decreased for temperature above 488°C. As a general rule, methanol conversion to H₂ and CO₂ increased with copper content, reaching a maximum with Cu₄₀Zn₆₀ catalyst and decreasing for higher copper loadings. The Cu₄₀Zn₆₀ catalyst with the highest copper metal surface area was the most active and selective for the partial oxidation of methanol. Non-reduced catalysts prior to the reaction displayed very low activity, mainly producing CO₂ and H₂O and only traces of H₂. From the reaction rates and copper areas, TOF values were calculated as a function of copper content at constant temperature (497°C). It was found that both the apparent activation energy and the TOF were higher for the low-copper catalysts and they decreased slightly, tending to a constant value at Cu-loadings above 50%(atom). The simultaneous variation of E_a and TOF suggests that the enhancement in reactivity is a consequence of a change in the nature of the active sites rather than being induced by a simple spillover type synergy. The activity data in the partial oxidation reaction of methanol to hydrogen

and CO_2 over Cu/ZnO catalysts obtained with different catalyst compositions and different Cu^0 metal surface areas revealed that the reaction depend on the presence of both phases: ZnO and Cu^0 . On the other hand, for catalysts with Cu concentrations in the range of 40-60 wt%, the copper metal surface area seems to be the main factor determining the reaction rate (Fierro *et al.*, 2000).

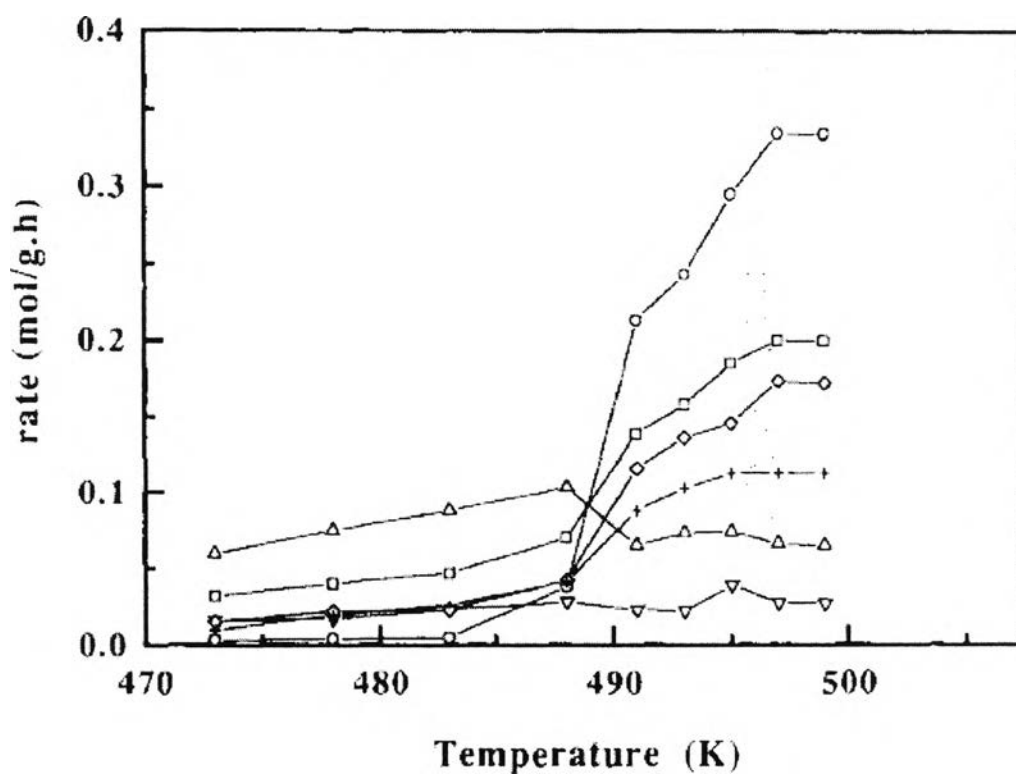


Figure 2.6. Partial oxidation of methanol over the catalyst $\text{Cu}_{40}\text{Zn}_{60}$: (□), CH_3OH conversion; (+), O_2 conversion; (○), H_2 ; (◇), CO_2 ; (Δ), H_2O ; (▽), CO. (Alejo *et al.*, 1997).

2.3.1.5 Decomposition of Methanol

Methanol decomposition is an on-board source of H_2 and CO for chemical process and fuel cell. The decomposition reaction is endothermic with a 90.7 kJ/mol heat of reaction (Eq. 2.12).

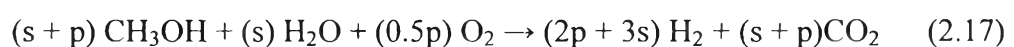


Consequently, heat must be provided to maintain the reaction. Apart from being harmful to health, CO produced is an atmospheric pollutant and a poison for the fuel cell. Therefore, some downstream processing must be done to eliminate the CO from the system before releasing the product stream to the fuel cell. The decomposition can also produce undesired byproducts such as di-methylether and methane (Brown *et al.*, 2004).

This reaction can be performed over metals from Group 10, among which Ni and Pd have been those most widely studied. The metals have been supported on different oxide substrates such as Al₂O₃, TiO₂, SiO₂, CeO₂, ZrO₂ and Pr₂O₃ were studied. Pd seems to be the most effective for methanol decomposition and in the case of Pd supported on CeO₂, it was observed that the decomposition reaction of methanol is sensitive to the metal structure of the catalyst. Usami *et al.* (1998) tested a number of metal oxide-supported Pd catalysts and found that Pd/CeO₂, Pd/Pr₂O₂, and Pd/ZrO₂ catalysts prepared by a deposition-precipitation procedure were active for the selective decomposition of methanol to H₂ and CO at temperature below 523°C. It was observed that the interaction of the Pd phase and the ZrO₂ influences the performance of Pd/ZrO₂ catalyst to a large extent in which smaller metal particles and a stronger contact with the support should be favorable for the decomposition reaction.

2.1.3.6 Autothermal (Oxidative Steam Reforming of Methanol)

Autothermal is the combination of partial oxidation and steam reforming. This 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 H₂ than only partial oxidation alone. The reaction of oxidative steam reforming of methanol is shown in Eq. 2.13.



Where s and p are stoichiometric coefficient for steam reforming and partial oxidative, respectively. In this process, methanol is 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.

2.4.1 Copper-based Catalysts

A large variety of catalysts for the methanol steam reforming including copper in their composition have been reported. Shen *et al.* (1997) found that the Cu/ZnO catalysts showed the activity of steam reforming of methanol to vary with composition. The commercial Cu/ZnO water gas-shift and methanol synthesis catalyst have also been found to be active for the steam reforming reaction (Amphlett *et al.*, 1995). Methanol steam reforming over these Cu/ZrO₂ materials results in substantially reduced CO formation at high methanol conversions compared to the commercial Cu/ZnO catalyst (Ritzkopf *et al.*, 2006). Jeong *et al.* (2006) found that ZrO₂ added to the Cu/Zn-based catalyst enhances copper dispersion on the catalyst surface. Among the catalysts tested, Cu/ZnO/ZrO₂/Al₂O₃ exhibits the highest methanol conversion and the lowest CO concentration in the outlet gas. Men *et al.* (2004) studied the activity of Cu/CeO₂ and they purposed that the rationalized correlation of the catalytic activity dependence with the characteristics is in line with a reaction mechanism, which supposes that the copper/ceria boundary is the active site for steam reforming of methanol and the oxygen reverse spillover from ceria to copper is involved in the catalysis cycle. Patel *et al.* (2006) studied the activity and stability enhancement of copper-alumina catalyst using cerium and zinc promoters and reported that the cerium promoted Cu–Zn–Ce–Al-oxide catalysts greatly improved the activity and hydrogen selectivity and also kept the CO formation very low. Using cerium in the SRM could be carried out at lower temperature with high

methanol conversion, resulting in suppression of methanol decomposition and RWGS reaction eventually end-up with the low CO and H₂ rich product stream. Cerium also stabilizes the copper–alumina catalysts effectively that was confirmed by deactivation studies in which cerium promoted Cu–Zn–Ce–Al-oxide catalysts gave the consistent performance for a long run-time compared to catalysts containing only zinc promoter. Liu *et al.* (2001) found that a 3.9 wt.% Cu/CeO₂ (cop) catalyst showed 53.9% conversion for the steam reforming of methanol at 240°C, which was higher than the conversions over Cu/ZnO (37.9%), Cu/Zn(Al)O (32.3%), and Cu/Al₂O₃ (11.2%) with the same Cu loading under the same reaction conditions.

2.4.2 Non Copper-based Catalysts

Metals from Group 8, 9, and 10, especially palladium, are highly active in the partial oxidation of methanol (Cubeiro *et al.*, 1998). Iwasa *et al.* (1995) found that the catalytic performance of Pd/ZnO for MSR was greatly improved by previously reducing the catalysts at higher temperatures. The original catalytic functions of metallic palladium were greatly modified as a result of the formation of PdZn alloys. Over the catalysts containing alloys, formaldehyde species formed in the reaction were suggested to be effectively attacked by water, being transformed into CO₂ and H₂. Chin *et al.* (2002) studied MSR over a highly active Pd/ZnO catalyst and reported that the Pd/ZnO catalysts not only exhibited high activity, but more importantly very low selectivity to CO for MSR. Under the conditions examined, the decomposition activity is minimal. Easwar *et al.* (2005) studied the activity and selectivity pattern of ZnO and CeO₂ supported Pd catalysts in MSR and it turned out that the Pd/ZnO catalysts had lower MSR rates but were more selective for the production of CO₂ than the Pd/CeO₂ catalysts. The methanol conversion rates were proportional to the H₂ chemisorption uptake, suggesting that the rate determining step was catalyzed by Pd. Yunhua *et al.* (2006) studied the interaction between Pd and ZnO during reduction of Pd/ZnO catalyst for MSR and the result showed that metallic Pd is highly dispersed on ZnO. The strong interaction between Pd and ZnO during the catalyst reduction with hydrogen leads to hydrogen spillover from Pd to ZnO, which causes the reduction of ZnO close to the metallic Pd and the formation of PdZn alloy. And the methanol conversion and CO₂ selectivity reach maxima. Recently, Dagle *et al.* (2008) studied PdZnAl catalysts for the reactions of

WGS, MSR, and RWGS and found that the CO selectivities were observed to be lower than the calculated equilibrium values over a range of temperatures and steam/carbon ratios studied while the reaction rate constants were approximately of the same magnitude for both WGS and methanol steam reforming. These results indicated that although Pd/ZnO/Al₂O₃ are active WGS catalysts, WGS is not involved in methanol steam reforming. RWGS rate constants are on the order of about 20 times lower than that of methanol steam reforming, suggesting that RWGS reaction could be one of the sources for small amount of CO formation in methanol steam reforming.

2.5 Gold Catalyst

Gold has long been regarded as a poorly active catalyst. Recently, Gold catalysts have been attracting rapidly growing interests due to their potential applicabilities to many reactions of both industrial and environmental importance. It has atomic number 79 and atomic weight 196.967. The physical properties of Au are shown in Table 2.2.

Table 2.2 Physical properties of Au (<http://en.wikipedia.org/wiki/Gold>)

Phase	solid
Density (near r.t.)	19.3 g cm ⁻³
Liquid density at m.p.	17.31 g cm ⁻³
Melting point	1337.33 K (1064.18°C, 1947.52°F)
Boiling point	3129 K (2856°C, 5173°F)
Heat of fusion	12.55 kJ mol ⁻¹
Heat of vaporization	324 kJ mol ⁻¹
Specific heat capacity	25°C 25.418 J mol ⁻¹ K ⁻¹

Cameron *et al.* (2003) concluded that 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:

- oxidation of CO and hydrocarbons,
- water gas shift (WGS),
- reduction of NO with propene, CO or H₂,
- reactions with halogenated compounds,
- water or H₂O₂ 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.

However, Haruta *et al.* (2001) studied the deposited Au as nanoparticles on metal oxides by means of co-precipitation and deposition–precipitation techniques. It exhibited surprisingly high catalytic activity for CO oxidation at temperature as low as 200°C. Goodman and coworkers (2003) have reported an inspiring result obtained by using a model Au/TiO₂ catalyst. As shown in Figure 2.7, turn over frequency (TOF) for CO oxidation reaches a maximum at a diameter of Au islands of 3.5 nm (3 atoms thick) where Au partially loses its metallic nature. They suggested that this transition might be correlated to the high catalytic activity. Since the sample used for catalytic activity measurements was composed of the Au islands with a certain size distribution.

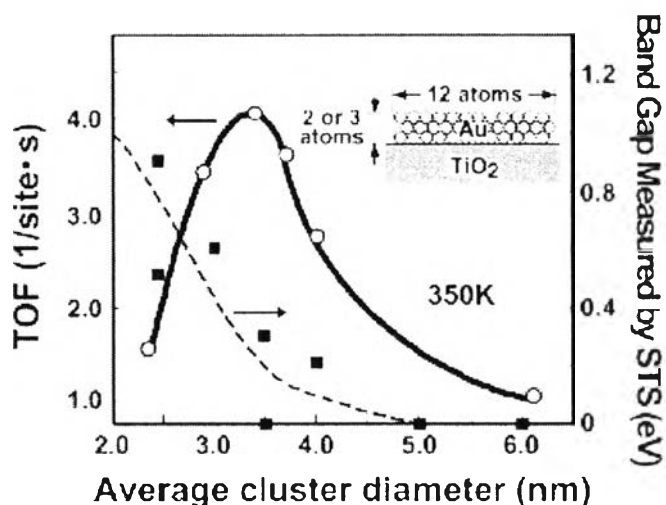


Figure 2.7 Turn over frequencies and band-gap measured by STM as a function of the diameter of Au islands deposited on TiO_2 (Haruta *et al.*, 2001).

Andreeva *et al.* (1996) reported that the $\text{Au}/\alpha\text{-Fe}_2\text{O}_3$ sample exhibited high catalytic activity at low temperatures in the WGS reaction. This activity is even higher than that of the most efficient catalyst for the same reaction, namely, the industrial copper–zinc–aluminium ($\text{CuO}/\text{ZnO}/\text{Al}_2\text{O}_3$) catalyst under the same conditions. It was shown that ceria plays the role of an active support capable of producing oxygen. The high and stable activity of Au/CeO_2 catalysts could arise from the high and stable gold dispersion present during the catalytic operation (Andreeva *et al.*, 2002). Sakurai *et al.* (2005) found that the Au/CeO_2 catalysts prepared by the deposition–precipitation method was the most active catalyst at temperatures between 100 and 250°C without producing methane below 623°C. It is deduced that the WGS reaction proceeds over the perimeter interfaces of small gold particles on a reduced cerium oxide surface. Mareau *et al.* (2006) studied the activity of gold catalyst supported on various oxides in CO oxidation reaction and their improvement by inclusion of an iron component. they found that addition of iron in the preparation lowered the rate of deactivation when TiO_2 , SnO_2 and CeO_2 were used as supports. Paopo (2007) studied the methanol steam reforming by using Au/CeO_2 catalyst and studied the effect of catalyst preparation, Incipient Wetness Impregnation (IWI), Co-

precipitation (CP), and Deposition-precipitation (DP) on the catalytic activities. The results showed that the DP exhibited the smallest gold particle size and the highest methanol conversion.

There are many type of catalysts currently in use and under study in the steam reforming of methanol. However, two main factors; active site and support, which significantly affect to the catalytic performance. CeO_2 always uses as a support because the functions of CeO_2 and its composite catalyst have attracted numerous investigations. The cations Ce^{4+} is quite easily reduced, and the surface lattice oxide ions are readily mobilized, so that cation vacancies are common. Oxide ions inside the lattice are also removable, and a whole rage of nonstoichiometric oxides between CeO_2 and Ce_2O_3 . It is well known that the lattice oxygen mobility and concomitant oxide ion conductivity in cerium oxide can be increased by the substitution of another metal ion for cerium. Because the ceria shows much improved properties under doping, a lot of ceria-based systems have been investigated. It has been proved that the lower valence ions in ceria influence the energetic properties by lowering the activation energy for oxygen migration (Vidmar *et al.*, 1997). Kongzhai *et al.* (2007) studied the catalytic activity for methane selective oxidation by using $\text{Ce}_{1-x}\text{Fe}_x\text{O}_2$ complex oxides. The characteristic results revealed that the combination of Ce and Fe oxide in the catalysts could lower the temperature necessary to reduce the cerium oxide. The catalytic activity for selective CH_4 oxidation was strongly influenced by dropped Fe species. Adding the appropriate amount of Fe_2O_3 to CeO_2 could promote the action between CH_4 and CeO_2 . Hongyan *et al.* (2008) studied the catalytic properties for ethanol steam reforming by using $\text{Ce}_x\text{Fe}_{1-x}\text{O}_2$ solid solution catalyst and the results showed that the $\text{Ce}_x\text{Fe}_{1-x}\text{O}_2$ solid solutions have superior catalytic activity and selectivity for hydrogen in the ethanol steam reforming compared with the CeO_2 and $\alpha\text{-Fe}_2\text{O}_3$ catalysts, as shown in Figure 2.8 and 2.9. In methanol steam reforming, the activity of CeO_2 catalyst is higher than the commercial catalyst. Another one support, which is easily reduced like ceria, is ferric oxide which is found to be most effective catalyst in WGS reaction when used as supports for Au. All of these are the motivation in this work to study effect of composite support ($\text{CeO}_2\text{-Fe}_2\text{O}_3$) on the catalytic activity for the methanol reforming. In particular, the

physical and electronic properties of a gold catalyst are greatly affected by using $\text{CeO}_2\text{-Fe}_2\text{O}_3$.

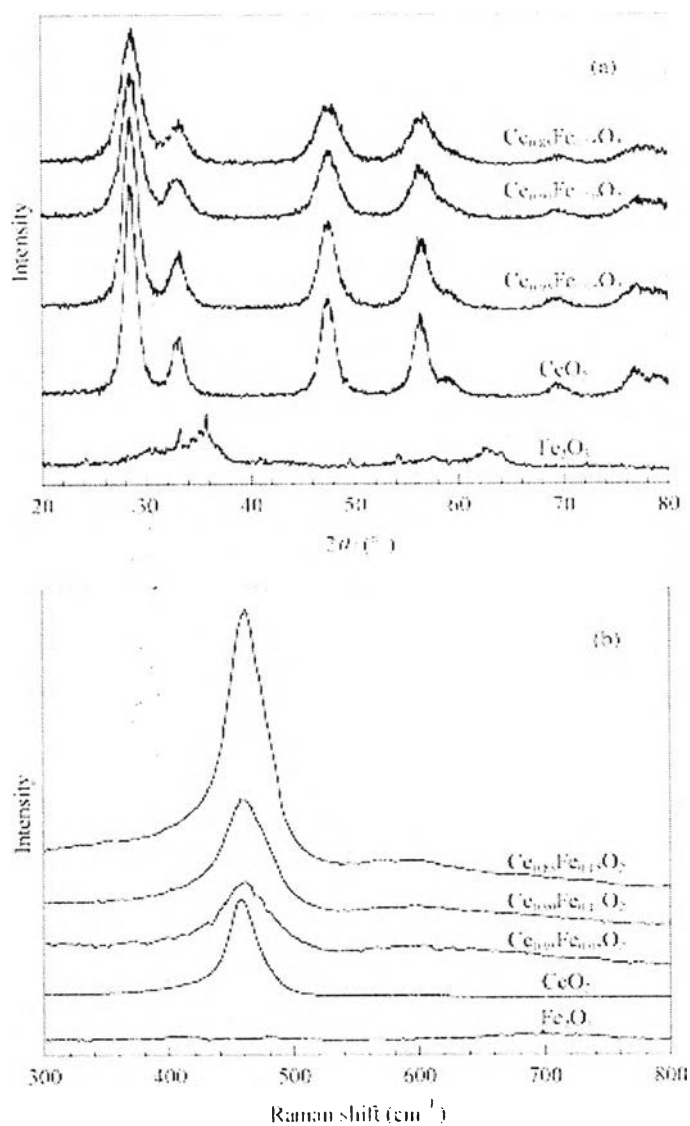


Figure 2.8 XRD patterns (a) and Raman spectra (b) of different samples of composited oxide catalysts (Hongyan *et al.*, 2008).

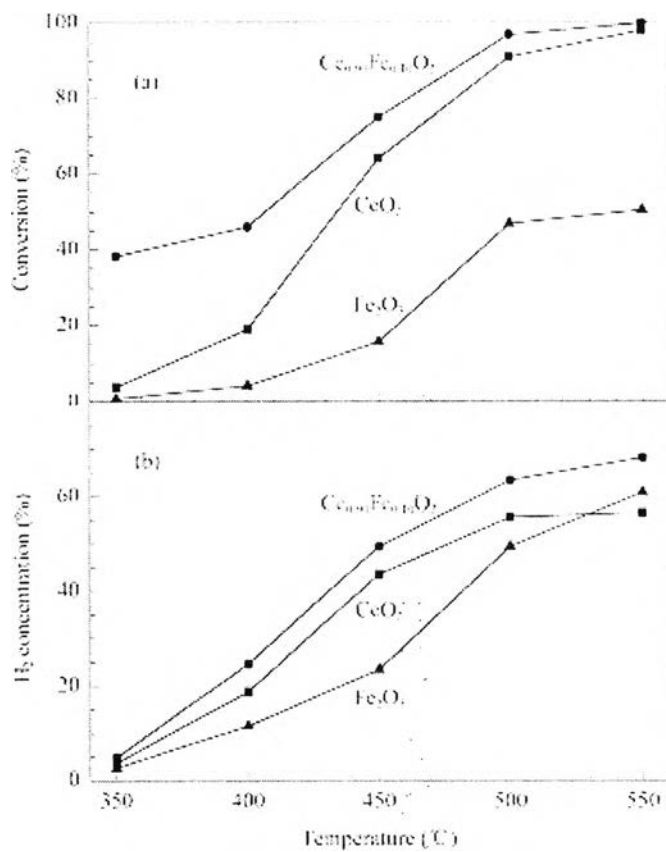


Figure 2.9 Ethanol conversion (a) and hydrogen concentration (b) in the effluent of steam reforming of ethanol as a function of reaction temperature over different samples (Hongyan *et al.*, 2008).