CHAPTER II
LITERATURE REVIEW

2.1 Fuel Cells

Fuel cell is an electrochemical energy conversion device directly converting chemical energy into electrical energy with high efficiency and low or zero emissions. Electrical energy is produced by electrochemical oxidation of the fuel forming only water and heat as by-products. Fuel cells can be divided into different categories with respect to their operating temperature range, as shown in Table 2.1 (EG&G Tech. Serv. 2004).

Table 2.1 Fuel cell categorization (EG&G Tech. Serv. 2004)

Fuel cell type	Abbreviation	Electrolyte	Operating Temp. (°C)
Solid oxide	SOFC	Perovskites (Ceramics)	600–1000
Molten carbonate	MCFC	Immobilized liquid molten carbonate in LiAlO$_2$	650
Phosphoric acid	PAFC	Immobilized liquid phosphoric acid in SiC	190–220
Proton exchange membrane	PEMFC	Hydrated polymeric ion exchange membranes	40–80
Direct methanol	DMFC	Hydrated polymeric ion exchange membranes	40–80
Alkaline	AFC	Potassium hydroxide in Asbestos matrix	65–220

The solid oxide and molten carbonate fuel cells require high temperature to operate. Both of them are suitable for large-scale stationary applications owing to the time consumption to reach the required temperature. The phosphoric acid fuel cell is

another one which is suitable for stationary and medium-sized utility applications because of their low power density and the corrosive liquid electrolyte. The alkaline fuel cell is a very efficient fuel cell; however, it can be impractical in mass transportation as it is the most expensive fuel cell used in the NASA's space program. The proton exchange membrane and the direct-methanol fuel cells are highly suitable for mobile application due to low operation temperature and a compact format. They are similar in term of electrolyte type, polymer membrane, but they are different in term of fuel source. The whole system of the direct-methanol fuel cell can be much more compact by using methanol as fuel and eliminate the need for a fuel reformer. However, the problem of methanol crossover in the electrolyte is still the main trouble, leading to loss of cell voltage. Moreover, the power density of the direct-methanol fuel cell is lower than a conventional hydrogen-fuelled PEM fuel cell. Figure 2.1 shows the schematic of proton exchange membrane fuel cell system (EG&G Tech. Serv. 2004; Agrell 2003).
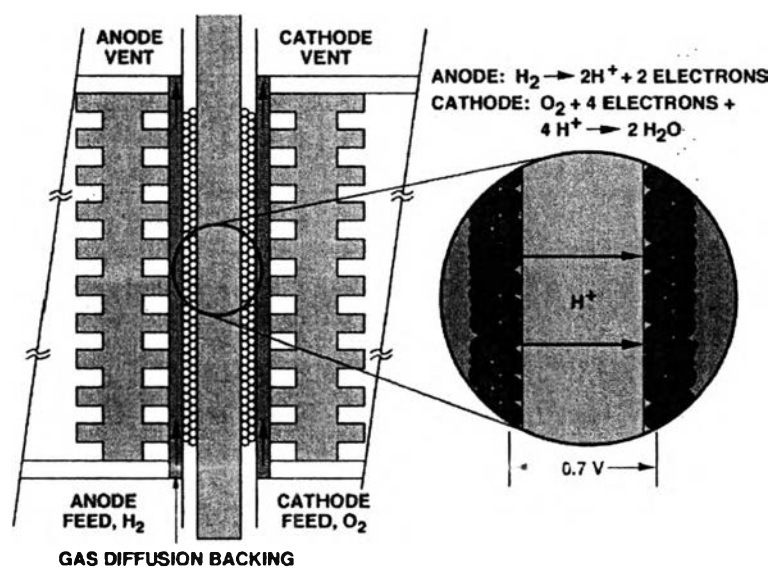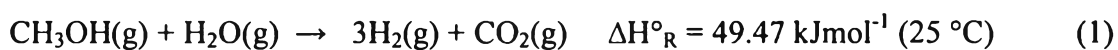

Figure 2.1 Schematic of proton exchange membrane fuel cell system (EG&G Tech Serv. 2004).

2.2 Hydrogen Production from Methanol

Methanol is the best source for hydrogen fuel because it has high hydrogen-to-carbon ratio (4:1), low soot formation, low sulfur contamination and can be produced from a variety of sources (natural gas, coal, and biomass). Moreover, it is easy handling, and has low cost, low boiling point (65 °C), and no carbon-carbon bonds. Methanol can be converted to hydrogen at lower temperatures (150–350 °C) than most other fuels (>500 °C). In terms of environmental impact, methanol is readily metabolized by ambient organisms in the environment. Because it is miscible with water, methanol spills do not spread over wide areas of open water as the way that oil and gasoline spills do. However, it is relatively high toxicity and the optimal conditions are still required for methanol reforming process (Palo *et al.*, 2007; Cheekatamarla *et al.*, 2006). Hydrogen can be produced from methanol by three traditional techniques: steam reforming (SR), partial oxidation (POx), and autothermal reforming (ATR). Considering the route of steam reforming, the steam reforming of methanol is an endothermic reaction, typically performed at 200–300 °C over a reforming catalyst, thus, an external source of heat is need (Wilson *et al.*, 2009; Cheekatamarla *et al.*, 2006). The overall reaction for SR is expressed in Eq. 1. This steam reforming reaction is the sequence of two processes, methanol decomposition (Eq. 2) and the water–gas-shift (WGS) reaction (Eq. 3) (Wilson *et al.*, 2009; Dokmaingam *et al.*, 2006).

$$CH_3OH(g) + H_2O(g) \rightarrow 3H_2(g) + CO_2(g) \quad \Delta H°_R = 49.47 \text{ kJmol}^{-1} \text{ (25 °C)} \quad (1)$$

$$CH_3OH(g) \rightarrow 2H_2(g) + CO(g) \quad \Delta H°_R = 90.64 \text{ kJmol}^{-1} \text{ (25 °C)} \quad (2)$$

$$CO(g) + H_2O(g) \rightarrow H_2(g) + CO_2(g) \quad \Delta H°_R = -41.17 \text{ kJmol}^{-1} \text{ (25 °C)} \quad (3)$$

The SR is considered to be the most favorable process of hydrogen production in comparison to the other methods. The main reason is the ability to produce gas with high hydrogen concentration. Under favorable conditions, the H_2

concentration can reach up to 75 % by volume on a dry basis. Moreover, high selectivity for carbon dioxide and the least carbon monoxide formation (high CO concentration can deteriorate the catalytic electrode) are advantages. (Palo *et al.*, 2007; Weiss *et al.*, 2005; Avgouropoulos *et al.*, 2001; Agrell *et al.*, 2002).

2.3 Catalyst Development for Methanol Steam Reforming

Hydrogen production by SR of methanol has been successfully demonstrated and a large variety of catalysts have been reported to be active for methanol SR. The majority of these catalysts have been focused on Cu-based materials. Nevertheless, copper has some significant drawbacks, such as fast deactivation, pyrophoricity, and high temperature sintering. Thus, other based catalysts of group VIII metals such as Pd, Pt, and Ni have been investigated to overcome the drawbacks (Palo *et al.*, 2007; Cheekatamarla *et al.*, 2006; Agrell *et al.*, 2002).

2.3.1 Copper-based Catalysts

Generally, catalysts with high copper content show higher conversion and selectivity. However, good catalyst formulations contain well dispersed copper, high surface area, and small particle size (Matsumura *et al.*, 2009; Oguchi *et al.*, 2005: Liu *et al.*, 2002). The most interesting catalysts for methanol SR are the type of $CuO/ZnO/Al_2O_3$ based catalysts. ZnO-based materials have been reported as effective Cu supports for the SR of methanol (Liu *et al.*, 2002). They are often with addition of alumina (Al_2O_3) to improve their surface area and mechanical strength, and to prevent catalyst sintering (Huang *et al.*, 2009). A kinetic study of methanol SR over commercial catalyst $CuO/ZnO/Al_2O_3$ has been reported by Purnama *et al.* (2004a). The reaction is the direct formation of CO_2 and hydrogen by the SR reaction and the formation of CO as a sequential product by the reverse WGS reaction.

A number of copper based catalysts promoted with different promoters have been investigated. Lindstrom *et al.* (2002) reported that Zn-promoted Cu/Al_2O_3 was more active than Zr or Cr-promoted samples. The promotional effects of zirconia (ZrO_2) have also been interested in many researchers. Purnama *et al.* (2004b) used zirconia as the support for CuO. Using the zirconia support, the copper

was found to be more active, and gave less CO. This catalyst was more stable compared to a commercial $CuO/ZnO/Al_2O_3$ catalyst. Ritzkopf *et al.* (2006) also reported higher methanol conversion and reduced CO formation over Cu/ZrO_2 catalysts. Yong-Feng *et al.* (2004) reported ZrO_2 promotion to increase conversion and to improve selectivity. ZrO_2 promotion was shown to increase copper dispersion and to weaken the interaction between CuO and Al_2O_3 to avoid the generation of a $CuAl_2O_4$ spinel type compound.

Recently, Matsumura *et al.* (2009b) studied high temperature (400 °C) methanol SR over $Cu/ZnO/ZrO_2$ catalysts. The result showed that the activity of $Cu/ZnO/ZrO_2$ was more stable than Cu/ZnO, Cu/ZrO_2, and a commercial $Cu/ZnO/Al_2O_3$ catalysts prepared by the same method. Steam reforming of methanol over silica-supported copper catalyst prepared by sol-gel method was also stuied by the same group (Matsumura *et al.*, 2009a). The activity of a commercial $Cu/ZnO/Al_2O_3$ catalyst at 250 °C was significantly lower than that of 40 wt% Cu/SiO_2, and the selectivity to carbon monoxide was higher. Furthermore, the addition of zinc ions to 40 wt% Cu/SiO_2 resulted in the suppression of CO formation in the reaction (Matsumura *et al.*, 2009c). Beside the use of ZnO, ZrO_2, and Al_2O_3 as supports or promoters, Ceria (CeO_2) is another one which has been found in SR of methanol.

Liu *et al.* (2002) compared Cu/CeO_2 with Cu/ZnO, $Cu/Zn(Al)O$, and Cu/Al_2O_3 catalysts, and found that the Cu/CeO_2 catalyst showed a higher activity than Cu/ZnO, $Cu/Zn(Al)O$, and Cu/Al_2O_3 catalysts with the same Cu loading under the same reaction conditions. Huang *et al.*, 2009 found that CeO_2 could increase the Cu dispersion, the thermal stability of the catalysts and reduce the CO concentration. Liu *et al.* (2003) and Papavasiliou *et al.* (2004) reported that CuO/CeO_2 was effective for methanol SR. Effect of dopant (La, Zr, Zn, Sm, Mg, Gd, Y, and Ca) on the performance of $CuO-CeO_2$ catalysts prepared via the urea-nitrate combustion method was investigated by Papavasiliou *et al.* (2007). All doped catalysts produced less CO than $CuO-CeO_2$. However, the activity of $CuO-CeO_2$ catalysts was not improved by doping.

2.3.2 Group VIII metals-based Catalysts

The catalytic performance of group VIII metals is greatly different from that of copper in the SR of methanol. Group VIII metals predominantly catalyze methanol decomposition, transforming methanol to CO and H_2, and tend not to be selective for the reforming reaction (Eq. 1). In the presence of water, the WGS can convert some of the CO to CO_2 (Palo et al., 2007). Thus, the catalysts being active to hydrogen production and high carbon dioxide selectivity are attractive. Iwasa et al. (1995) discovered that Pd/ZnO based catalysts appearred to be the most interesting. In contrast to the Ni, Co, and Pt on ZnO support, the Pd on ZnO support, the catalytic function of Pd can be greatly modified, resulting in a highly active and selective catalyst for methanol SR. No reaction occurred over ZnO or Zn alone. They (Iwasa et al., 2003) expanded their work on various supports, ZnO, In_2O_3; Ga_2O_3; SiO_2; MgO; ZrO_2; CeO_2; Al_2O_3, by loading group VIII metals, such as Co, Ni, Ru, Ir, and Pt, and found that both Pd and Pt formed alloys with In, Ga, and Zn. When alloys were formed, improvement in the selectivity for methanol reforming was found. Chin et al. (2002) studied methanol steam reforming (MSR) over highly active Pd/ZnO catalyst and reportedthat the Pd/ZnO catalyst not only exhibited high activity, but also low selectivity to CO due to Pd–Zn alloy formation. Ranganathan et al. (2005) studied MSR over Pd/ZnO and Pd/CeO_2 catalysts, and observed that the Pd/ZnO catalyst had lower SR rates, but were more selective for the production of CO_2 than the Pd/CeO_2 catalyst. They suggested (Ranganathan et al., 2005) that a Pd/ZnO catalyst favored the reforming reaction due to its higher density of acidic sites. Comparatively, a Pd/CeO_2 catalyst, which produced a high amount of CO, had a higher density of basic sites, which favors the decomposition reaction. Recently, mesoporous SBA-15 was used as support of Pd-Zn catalyst in partial oxidation and SR of methanol (Eswaramoorthi et al., 2009). It was found that 4.5 wt% Pd–6.75 wt% Zn/SBA-15 showed better performance in SR than in partial oxidation of methanol in terms of H_2 and CO_2 selectivities.

The SR on Ni catalyst was studied by Kikuchi et al. (2003). They tested the activities, stabilities and selectivities of Cu/ZnO, Ni/Al_2O_3, and Ru/Al_2O_3 catalysts, and the result showed that the Ni/Al_2O_3 catalyst was the most stable

activity at 723 K, but gave relatively low hydrogen yield because of methanation (Eq. 6).

$$CO(g) + 3H_2(g) \rightarrow CH_4(g) + H_2O(g) \tag{6}$$

Dokmaingam et al. (2005) reported that the thermal stablility and carbon deposition resistivity, causing the catalyst deactivation on the surface, of Ni/CeO_2 were better than Ni/Al_2O_3. Catalytic acitivity in SR of Ni–Cu alloys supported on carbon nanotubes (CNTs) was studied by Liao et al. (2008). The result showed that the catalytic activity of 20 %wt Ni_{20}–Cu_{80}/CNTs was much higher than that of Ni_{20}–Cu_{80}/C and Ni_{20}/Cu_{80}/CNTs due to less aggregation of metal particles and the formation of Ni–Cu alloys interfering with adsorption of hydrogen on Ni.

2.4 Synthesis Route

Ceria-base catalysts can be prepared or synthesized by many methods. However, most methods requires either high reaction temperature or special equipment (Trovarelli et al., 2002). Sol-gel technology is one of the best methods, providing many advantages, such as low temperature operation, high purity of product, various physical-form products, compositional homogeneity and ultrafine product (Trovarelli et al., 2002, Ksapabutr 2004, Chalermnontakarn 2007).

Metal alkoxides are popular precursors for the sol-gel technique due to their sensitivity to water, and they can undergo a slow condensation to build larger and larger molecules by polymerization process (Brinker et al., 1990, Ksapabutr 2004). The reactions involving in the sol-gel process are hydrolysis (Eq. 7) and condensation (Eqs.8 and 9 representing by either dehydration (oxolation) or dealcoholation (alcoxolation), respectively (Brinker et al., 1990, Kakihana 1996).

$$M(OR)_n + xH_2O \rightarrow M(OH)_x(OR)_{n-x} + xROH \tag{7}$$

$$—M—OH + HO—M— \rightarrow —M—O—M— + H_2O \tag{8}$$

$$—M—OH + RO—M— \rightarrow —M—O—M— + ROH \tag{9}$$

2.5 Gadolinium doped Ceria (GDC)

The active form of cerium is CeO_2. The doped CeO_2 materials can be used in many applications, such as electrodes (Chalermnontakarn 2007) and electrolytes (Inaba *et al.*, 1996) for solid oxide fuel cell, and catalysis (Trovarelli *et al.*, 2002). One of dopants that is wildly interesting in the properties is gadolinium (Gd), an element in Lantanide series and having atomic number of 64. Since the ionic radii of Gd^{3+} are nearly the same as Ce^{4+}, Gd incorporation in ceria lattice can create more oxygen ion vacancies to produce less distortion in host lattices thereby to avoid phase instability. These excess oxygen vacancies created often lead to higher ionic conductivity than un-doped ceria (Jadhav *et al.*, 2009).

Huang *et al.*, (2008) studied the SR of methane over Ni/GDC catalysts, and found that 5 % Ni/GDC led to the highest formation rates of both hydrogen and CO_2. They (Huang *et al.*, 2003) also studied the CO oxidation over GDC and CuO/GDC, and observed that CO oxidation activities of the CuO/GDC catalysts, which the support hold at 260 °C for 2 h during calcinations, increased at a much faster rate than that of the CuO/CeO$_2$ catalyst. 5 mole% Gd doping showed the best CO oxidation activities at temperature over 200 °C.