

CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Background of Hydrogen

According to the use of burning fuel and/or hydrocarbon liquid fuel, the greenhouse gas emission is being still the topic of environmental concern. In order to remedy the depletion of fossil fuels and their environmental misdeeds, the tracing of new interested technology is currently focused on the fuel cell application, which becomes promising candidates as alternative sources of energy for mobile electronics and zero-emission automobile applications (Manzoli *et al.*, 2004). Compared with burning fossil fuel, the fuel cell produces only water as a by-product, none of the CO₂ or other pollutants, and also the electrical work. Among the types of fuel cells, the proton exchange membrane fuel cells (PEMFCs) received much attention in worldwide due to its high efficiency with clean exhaust gas by consuming hydrogen and oxygen (Faungnawakij *et al.*, 2006). Consequently, the PEM fuel cell is expected to be one of the green technologies that can replace the fossil based energy in the future. However, the feed reactants of the PEMFCs is required as the high H₂ purity that limits the CO contamination less than 10 ppm since CO acts as the poison for deteriorating the Pt electrode in the fuel cell (Pojanavaraphan *et al.*, 2012). To provide the suitable reactants for the PEMFCs usage, the H₂ production must be evaluated for the best process and the best condition.

2.2 Fuel Cells

Fuel cells are defined as the electrochemical devices that convert the chemical energy of a chemical reaction directly into electrical energy and heat. Electrochemical reactions are the most efficient means to convert chemical energy to electrical energy. In principle, a fuel cell operates like a battery, but does not run down or require recharging as long as a fuel, such as hydrogen, and an oxidant, such as air are supplied. Unlike the typical batteries, the energy density of the fuel cell is not constant but approaches that of the fuel used as the duration of the mission

increases. Hence, it is received much attention for the longer duration missions. Especially for the transportation applications, the fuel cell on hydrogen has a much longer distance between refueling or recharging than current batteries.

The basic physical structure of most fuel cells consists of an electrolyte layer in contact with porous anode and cathode electrodes on either side. Starting with the fuel and an oxidant entering the anode and cathode electrodes, respectively, these reactants are separated by a selectively conductive electrolyte. Conduction through the electrolyte can occur in either direction—anode to cathode or cathode to anode—depending on the designing of fuel cell. After that, both fuel and oxidant are transformed at the particular electrodes into the charge carrier species, which include H^+ , CO_3^{2-} , O^{2-} , OH^- , etc (Shekhawat *et al.*, 2011). As mentioned previously, the classification of the fuel cell has been developed using organic fuels and various charge carriers and summarised into Table 2.1. Besides, the schematic representation of the fuel cell with the reactant/product gases and the ion conduct flow directions through the cell is also shown in Figure 2.1. However, the deep details what each fuel cell type work are not discussed in this section.

Table 2.1 Electrochemical Reactions and Charge Carriers in Fuel Cells (Shekhawat *et al.*, 2011)

Fuel cell	Charge carrier through electrolyte	Anode reaction	Cathode reaction
Direct carbon (DCFC–SOFC-based)	O^{2-}	$C + O^{2-} \rightarrow CO_2 + 2e^-$	$1/2O_2 + 2e^- \rightarrow O^{2-}$
Polymer electrolyte (PEFC or PEM)	H^+	$H_2 \rightarrow 2H^+ + 2e^-$	$1/2O_2 + 2H^+ + 2e^- \rightarrow H_2O$
Phosphoric acid (PAFC)	H^+	$H_2 \rightarrow 2H^+ + 2e^-$	$1/2O_2 + 2H^+ + 2e^- \rightarrow H_2O$
Alkaline (AFC)	OH^-	$H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$	$1/2O_2 + H_2O + 2e^- \rightarrow 2OH^-$
Molten carbonate (MCFC)	CO_3^{2-}	$H_2 + CO_3^{2-} \rightarrow H_2O + CO_2 + 2e^-$ $CO + CO_3^{2-} \rightarrow 2CO_2 + 2e^-$	$1/2O_2 + CO_2 + 2e^- \rightarrow CO_3^{2-}$
Solid oxide (SOFC)	O^{2-}	$H_2 + O^{2-} \rightarrow H_2O + 2e^-$ $CO + O^{2-} \rightarrow CO_2 + 2e^-$ $CH_4 + 4O^{2-} \rightarrow 2H_2O + CO_2 + 8e^-$	$1/2O_2 + 2e^- \rightarrow O^{2-}$

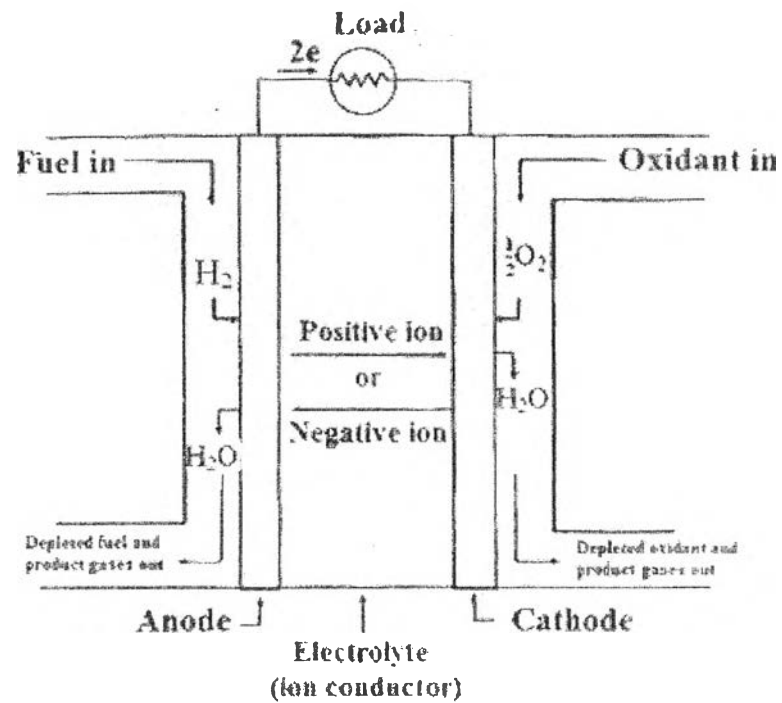


Figure 2.1 Schematic representation of an individual fuel cell (Shekhawat *et al.*, 2011).

It is clearly seen that each type of fuel cell is designed to meet the different application. When compared to other fuel cells, the PEM fuel cell is favorable in many companies because of its low operating temperature, response to transients, and compact size, which make it desirable for a number of residential, commercial, and military applications using pure hydrogen. Nonetheless, the main disadvantage of the PEM fuel cell is that the carbon monoxide (CO)-containing fuel streams from reformed hydrocarbon or oxygenated compounds will attack or poison the platinum (Pt) electrode, resulting in lowering the cell performance. As a result, the CO removal unit is essential to approach the high H₂ purity with CO-free gas (or CO < 10 ppm) in the stream before entering the PEM fuel cell.

2.3 Fuel Processors

The purpose of a fuel processor is to convert a commonly available fuel, such as gasoline, diesel, or natural gas, into a gas stream containing primarily, or

only, the compound(s) required by the fuel cell (Shekhawat *et al.*, 2011). A representative process diagram for a fuel processor designed to convert a liquid fuel (with added water to maximize H₂ yield and prevent catalysts deactivation) into a CO-free gas stream containing essentially only H₂ and CO₂ is shown in Figure 2.2. The fuel processor may consist of three steps, depending on the type of fuel cell (high or low temperature); (i) reforming of the liquid fuel into syngas, (ii) water-gas shift (WGS), and (iii) preferential CO oxidation (PROX).

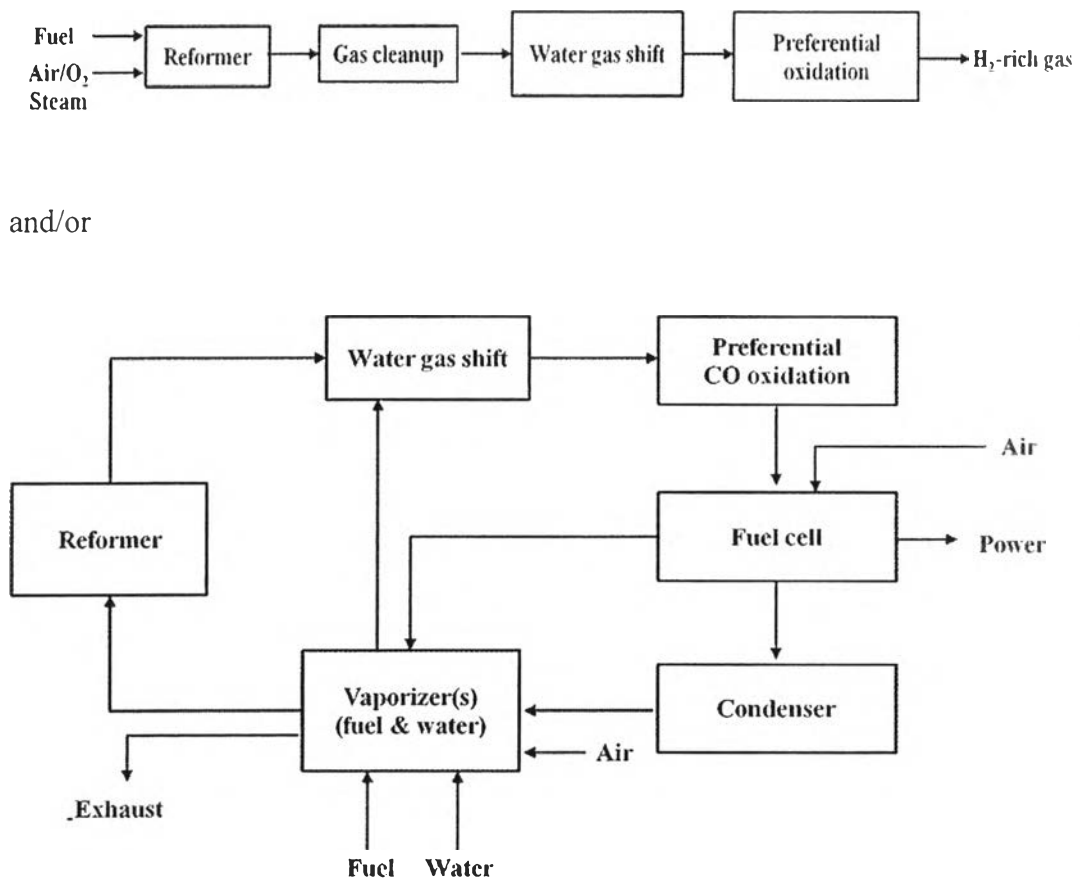


Figure 2.2 Generic fuel processor (Shekhawat *et al.*, 2011).

Since each type of fuel cell requires a different fuel, the fuel processor must be designed to match the fuel cell. For example, the low-temperature PEM fuel cell requires pure H₂ and cannot operate in the presence of CO concentrations greater than 10–20 ppm for any significant time.

According to the abundant type of the fuel processor, the conventional fuels are widely used to produce the H₂-rich reformat for powering the fuel cell, such as natural gas (methane) (Enger *et al.*, 2008), methanol (Breen *et al.*, 1999), ethanol (Vaidya *et al.*, 2006), dimethyl ether (Semelsberger *et al.*, 2006), propane (Zeng *et al.*, 2010), butane (Ferrandon *et al.*, 2010), gasoline (Qi *et al.*, 2006), kerosene (Yoon *et al.*, 2009), and biodiesel (Kang *et al.*, 2006). Among the fuel sources, alcohol-based fuels are widely attractive because they can be reformed at relatively low temperatures and are free of sulfur compounds. The comparison of the thermodynamically operating temperatures of oxygenated compounds and hydrocarbons in the partial oxidation was summarized into Table 2.2.

Table 2.2 Comparison of thermodynamic properties for oxygenated hydrocarbons to alkanes: O/C = 1.2 (Calculations using HSC chemistry 5.0) (Roin, A. (2002)).

Fuel	T _{c=0} * (°C)
CH ₄	706
C ₂ H ₆	711
C ₁₄ H ₃₀	713
C ₁₈ H ₃₈	713
CH ₃ OH	512
C ₂ H ₅ OH	612
C ₂ H ₆ O	612
C ₁₉ H ₃₆ O ₂	684

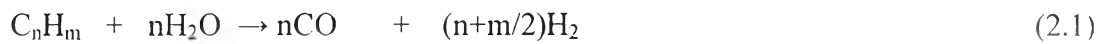
*T_{c=0} is defined as the operating temperature for achieving “zero carbon or coke” in the partial oxidation reaction.

From the given information, it would; therefore, be beneficial for the reformer unit to apply alcohol as the reactant fuel in producing high H₂ purity at low temperature as the first step, and then optimize the CO removal unit at the last step.

2.3.1 Reforming

The hydrogen production based on the hydrocarbon fuels is a well-established process for the petrochemical industry and for refineries, especially for the reforming process or reformer that are classified into three processes; the steam reforming (SR), partial oxidation (POX), and oxidative steam reforming (OSR) processes (Joyeux *et al.*, 2007) for light and heavy hydrocarbons (i.g. paraffins and aromatic compounds), as shown in below equations (Shekhawat *et al.*, 2011):

Steam Reforming (SR)



Partial Oxidation (POX)



Oxidative Steam reforming (OSR)



where n and m are the stoichiometry of carbon and hydrogen atoms, respectively.

These reactions can also produce the H₂O and CO₂ as the final products, depending on the operating reaction temperature, and the fuel types. However, the operating temperature of this reforming process is typically in the high-temperature range from 600 °C to 1000 °C, even including the help of catalyst (Jamal *et al.*, 1994). The large temperature difference between the fuel cell (~90–100 °C) and the hydrocarbon reformer can lower the system efficiency. This high temperature also leads to the formation of unwanted oxides of nitrogen (NO_x), oxides of sulfur (SO_x), coke formation, and sintering of an active metal catalyst (Nielsen *et al.*, 2011). For these reasons, they are not suitable to produce hydrogen via this thermal process.

2.3.2 Water-gas Shift (WGS)

During the hydrogen production in the reformer unit, the CO gas is possibly formed as the side product that can be the rich amounts (> 10 ppm). Not only this side product, but the remained fuel and the steam also come out from the reformer unit. In order to minimize the problems of rich-CO contents and remaining reactants in the reformat stream, the additional unit, known as water-gas shift reaction, is taken place before entering to the PEM fuel cell since this reaction helps

both CO reduction and H₂ production by interacting the CO and the remained steam in the reformat to form CO₂ and H₂ as the final products, as shown in Eq. (2.4).



The WGS reaction is an exothermic reaction, which is favorable at low temperature. It means that the operating temperature of this unit requires less than that of reformer unit, approximately 150–250 °C (Dagle *et al.*, 2011). Sometimes, the reforming process is usually operated with an excess steam to induce the WGS reaction in order to lower the CO concentration within the H₂ production in the product gas altogether. However, the efficiency of this unit still depends on the type of catalyst selection and the operating conditions, as illustrated in the Table 2.3.

Table 2.3 Summary of the Different WGS Catalyst Types (Dagle *et al.*, 2011)

Catalyst	Temperature (°C)	GHSV ($\times 10^3 \text{ h}^{-1}$)	Stability	Advantages	Limitations
Fe-based	300–500	10–15	Acceptable for industrial use	<ul style="list-style-type: none"> • Low cost 	<ul style="list-style-type: none"> • Sensitive to gas composition • Pyrophoric • Special activation procedure
Cu-based	180–260	5–15	Good	<ul style="list-style-type: none"> • Low cost • Highest activity and stability among all catalysts below 240 °C 	<ul style="list-style-type: none"> • Pyrophoric • Special activation procedure • Sensitive to high temperature and water condensation
Pt	220–350	10–25	Still an issue, however, Pt–Re showed promising stability	<ul style="list-style-type: none"> • Non pyrophoric • Highly active above 250 °C • Could replace HTS Fe catalysts • No special activation procedure required 	<ul style="list-style-type: none"> • Deactivation • Low activity compared to Cu below 250 °C • High cost
Au	150–260	5–10	Still an issue	<ul style="list-style-type: none"> • Non pyrophoric • Highly active 150–240 °C • No special activation procedure required 	<ul style="list-style-type: none"> • Deactivation • Sensitive to high temperature • High cost

*HTS = High temperature water gas shift reaction

Eventhough this efficient unit facilitates the rich-H₂ with less CO amount, the unexpected side reactions might occur simultaneously to form many side products, resulting in fluctuating the CO selectivity towards H₂. For example, Breen *et al.* (1999) have studied CO formation mechanism over CuO/ZnO/ZrO₂/Al₂O₃ catalyst for steam reforming of methanol through DRIFT analysis, and confirmed that the CO was formed via reverse water gas shift (RWGS) reaction (Eq. (2.5)), which occurred at high temperature due to its endothermic reaction. Similary, many researchers also reported the same mechanism pathway (Agrell *et al.*, 2001; Patel and Pant, 2007) that consumed the products of the reforming reaction i.e. H₂ and CO₂. Taking into account the improvement of selective CO reduction, the pros and cons of the WGS system must be significantly concerned to approach the optimum conditions.



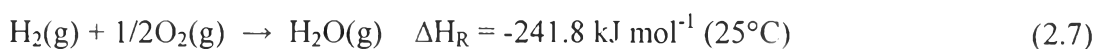
2.3.3 Preferential CO oxidation (PROX)

The PROX unit is received much attention in many fuel processor, when compared to the WGS unit, due to its abundant advantages, such as the simplest, most straightforward, and cost-effective approach to CO minimization (Park *et al.*, 2009; Lemons R.A., 1990). This can be also assigned as the remedy unit for the fuel processor because it is specifically used for CO reduction, where the rich-CO in the reformat can totally react with the oxygen fed in the PROX unit to form CO₂ as the final product. In the other words, the aim of the PROX is to selectively oxidize CO, reducing its concentration to acceptable ppm levels without simultaneous oxidation of the hydrogen present in the shift reformat, which is closely to the syngas condition for PEM fuel cell. The following reactions can be involved in the PROX unit;

Carbon monoxide Oxidation



Hydrogen Oxidation



Carbon monoxide Methanation



Carbon dioxide Methanation



All of these reactions are highly exothermic reaction, so they appeared simultaneously at very low temperature (~90–150 °C). The primary oxidation pathways are mostly occurred in Eqs. (2.6) and (2.7), where the selective CO oxidation can be the desirable outcome and H₂ oxidation can be avoided if the limiting of oxygen fed is approached. This results in the CO minimization. Although CO methanation is known as the “self-limiting reaction” in the absence of CO₂, if it occurs, it can lead to significant hydrogen loss. Likewise, the potential of CO₂ methanation, as described above, especially when large quantities of CO₂ are presented in the reformat, can be the significant concern in the realistic situation (Dagle *et al.*, 2011).

As the simplest way to avoid the existences of undesired reactions (H₂ oxidation and methanation), one of the most important keys for the selective toward CO oxidation in the PROX in practical application is the controlling appropriate level of O₂ (air) fed into the reactor. Too little air results in too high concentration of residual CO and anode poisoning. Too much air results in excess H₂ consumption since all O₂ fed to the PROX reactor is generally consumed (Dagle *et al.*, 2011). In addition, greater demands are placed on developing selective PROX catalyst to test with feedstocks that contain realistic concentrations of H₂, CO, and CO₂ under the low-temperature operation, as exemplified in Table 2.4. Some catalysts are highly selective CO oxidation in the presence of H₂, but they are frequently active over a fairly narrow temperature range. It has been reported the catalytic activity of the catalyst could be easily changes, depending on the total amounts of feed components in the PROX, not only H₂, CO, and CO₂ (Dagle *et al.*, 2011). In some experiments, the thermal management and temperature control seemed to be the important consideration for the PROX reactor (Dagle *et al.*, 2011). For the alternative choices as follow, all of them become the challenge topics for many reserchers in this field. Therefore, the effective parameters for optimizing the PROX performance are being still elucidated until present.

Table 2.4 Comparison of promoted and unpromoted Pt/Al₂O₃ for PROX reaction (Particle size 40–60 μm, 1000 ppm CO, 20 vol% H₂, 10 vol% H₂O, VHSV = 120,000 h⁻¹, WHSV = 150,000 Lg⁻¹h⁻¹) (Korotkikh *et al.*, 2000)

Reaction conditions		Promoted Pt catalyst		Pt/Al ₂ O ₃	
Temperature (°C)	O ₂ /CO ratio	X _{CO} (%)	Selectivity (%)	X _{CO} (%)	Selectivity (%)
90	0.5	68	78	13.2	82
90	0.75	90	65	12.7	66
150	0.5	62 ^a	60 ^a	26.8	57

^aData were obtained with the monolith catalyst at VHSV at 80,000 h⁻¹, WHSV at 923,000 L g⁻¹ h⁻¹

2.4 Hydrogen Production from Methanol

According to many drawbacks of using hydrocarbons as the feeding reactants in the reformer unit, the oxygenated compounds proven better energy saving since they require the heat of reaction less than the steam reforming of hydrocarbons, resulting in operating lower temperature. Among the oxygenated compounds, methyl alcohol or methanol (CH₃OH) is attractive for fuel-cell engines in transportation applications due to its self handling, low cost, and ease of synthesis from a variety of feedstocks (biomass, coal and natural gas) (Shishido *et al.*, 2007). In general, methanol is prepared exclusively from synthesis gas (CO and H₂) obtained from the incomplete combustion of fossil fuels (mainly natural gas or coal). The production of methanol is also possible by passing through the oxidative conversion of methane, avoiding the initial preparation of syn-gas, or by passing through reductive hydrogenative conversion of CO₂ (from industrial exhausts of fossil fuel burning power plants, cement plants, etc. and eventually the atmosphere itself). According to its overall attractive properties, methanol or its derivatives can be widely used as substitutes for gasoline and diesel fuel in today's internal combustion engine-powered cars, and it can be converted to hydrogen, which is the most common based material in the universal transportation.

Moreover, methanol has been recommended as the best source for hydrogen fuel among the high energy density liquid fuels, due to the presence of high hydrogen/carbon ratio—having a lower soot formation than other hydrocarbons and

being converted into hydrogen at moderate temperatures (200–400 °C)—relatively low boiling point, easy storage, low cost (Pinzari *et al.*, 2006), and no carbon-carbon bond, which are difficult to break, greatly in minimizing the risk for coke formation (Perez *et al.*, 2008), and efficiently operated at low temperature when compared to other oxygenated compounds.

To better understand the correlation between the performance of hydrogen production and the alcohol type, the study of the hydrogen production via partial oxidation of alcohols (Figure 2.3) has been done by Wanat and coworkers (Wanat *et al.*, 2005), who examined methanol, ethanol, 1-propanol, and 2-propanol. The significant information was provided in this effort, where the comparison among all four alcohols over one catalyst (Rh–Ce on a foam monolith) indicated that the temperature trends were similar for all alcohols when increasing the mole carbon-to-mole oxygen ratio at the feed input. However, the methanol had the lowest operating temperature, while the full conversion and the high H₂ and CO selectivities were observed in the same C/O ratio. The decreasing in product selectivity and the increasing in operating temperature were pronounced when using the heavy and bulky alcohol compounds (C₂–C₃). This suggested that the size and the structure of the alcohol influenced the product distributions significantly. The difference in performance between 1-propanol and 2-propanol is an excellent example of how the structure can change the overall conversion and selectivity.

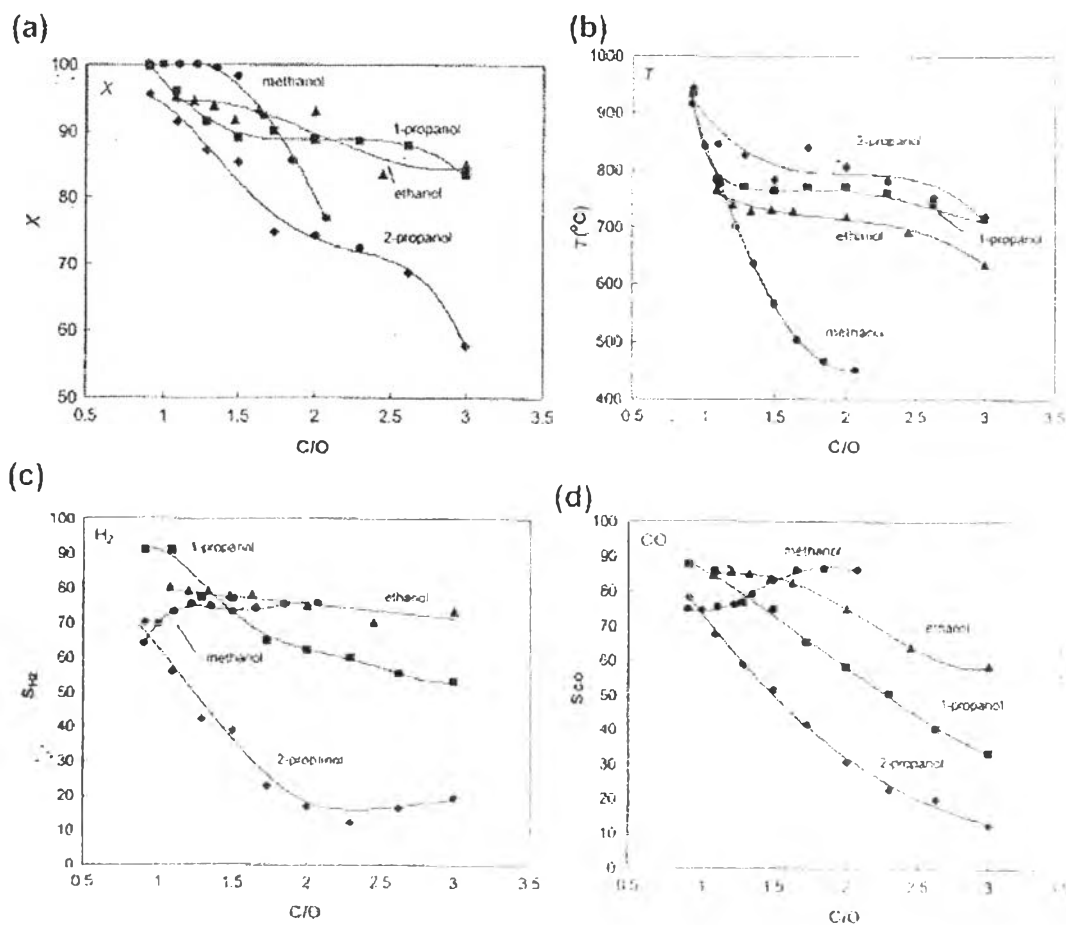


Figure 2.3 Partial oxidation of different alcohols as various C/O ratios with Rn-Ce catalyst on a foam monolith; (a) conversion, (b) operating temperature, (c) H₂ selectivity, and (d) CO selectivity (Wanat *et al.*, 2005).

Additionally, it has been reported that the heavy oxygenated compounds, such as ethanol (C₂H₅OH), have ability to form abundant side products via many side reactions after breaking the C-C bond; therefore, the H₂ selectivity can be less favorable, as illustrated in Figure 2.4 (Haryanto *et al.*, 2005).

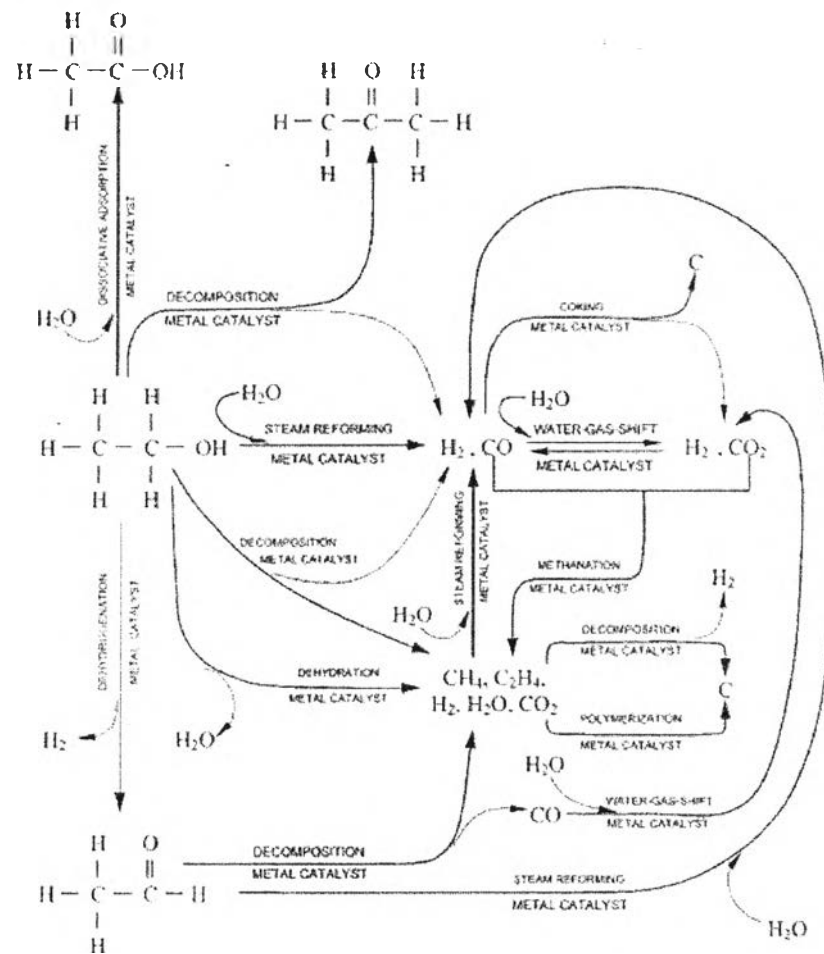


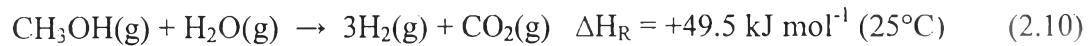
Figure 2.4 A review of mechanism pathways of the steam reforming of ethanol over metal catalysts (Haryanto *et al.*, 2005).

All of all, the selection of methanol as the fuel in reformer seems to be the promising way for high H_2 production. The hydrogen production routes from methanol can be achieved by three main catalytic processes; steam reforming of methanol (SRM), partial oxidation of methanol (POM), and oxidative steam reforming of methanol (OSRM).

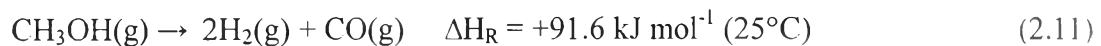
2.4.1 Steam Reforming of Methanol (SRM)

Steam reforming is an endothermic reaction, which is favorable at high temperature (250–350 °C), and low pressure (Armor *et al.*, 2008). Thus, the reaction requires energy input, which makes transient operation difficult when bursts of energy are needed (Perez *et al.*, 2007). This reaction reacts between oxygenated fuel

and water, and also is the most extensively studied process due to its highest hydrogen yield (3 moles of H₂ per mole of CH₃OH) (Pinzari *et al.*, 2006). The overall reaction for SRM is shown in Eq. (2.10).



When using stoichiometric feedstock, the SRM ideally produces only H₂ and CO₂. However, this reaction has a slow start up. SRM is the combination of the decomposition of methanol (DCM, Eq. (2.11)) and the WGS reactions (Pinzari *et al.*, 2006), which probably are the side reactions occurring during the SRM simultaneously.

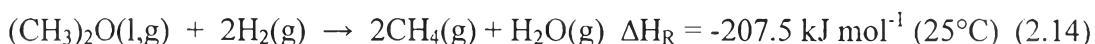


Therefore, DCM is believed to be one possible pathway of CO formation, which can be continually transformed to either CO₂ via the WGS reaction or CH₄ via the CO hydrogenation (Breen *et al.*, 1999). As described in the fuel processor, the SRM process is sometimes operated with an excess steam to induce the WGS reaction in order to lower the CO concentration within the H₂ production in the product gas altogether. However, the type of catalyst selection and the operating conditions are also dependent. Some authors reported the formation of CH₄ in the SRM that originated from the consumption of the hydrogen in the product gas and the steam (Eq. 2.12), possibly suppressing the H₂ production as well. Nonetheless, the origins of these undesired by-product gases are still unclear and elucidated until present.

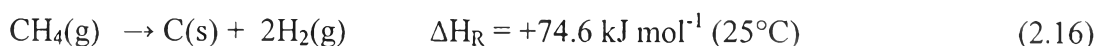
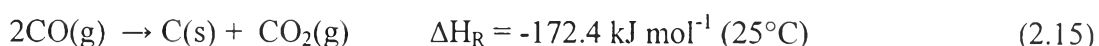


In term of liquid products (condensates), the formation of toxic constituents, including formic acid (HCOOH), formaldehyde (CH₂O), and dimethylether (DME, CH₃OCH₃) has been observed in the SRM (Houteit *et al.*, 2006). The methanol dehydration (DEH) reaction could produce DME under the use of solid-acid or titania (TiO₂) catalysts in the temperature range of 250–350 °C (Pinzari *et al.*, 2006),

as shown in Eq. (2.13). Likewise, Hussein *et al.* (1991) found that at higher temperature than 350 °C, DME could react over titania surface in the presence of H₂ to form CH₄ and water (Eq. (2.14)).



Although there are many researchers improving the hydrogen production rate on the SRM by using the commercial Cu/Zn/Al catalysts, the significant amount of CO (> 100 ppm) was still approached as an unsuitable feed for PEMFCs. In addition, the coke or carbon species can be formed or deposited the catalysts packed in the SRM reactor; hence, its activity can be severely deactivated (Pojanavaraphan *et al.*, 2012). The regeneration of catalyst section might be required and taken more utility cost. It is strongly noted that the coke formation may take place by different routes (whisker carbon, gum formation, pyrolytic coke, etc.). For instance, Faungnawakij *et al.* (2006) proposed that one possibility might come from the CO, and Armor *et al.* (2008) also indicated two major pathways (Eqs. (2.15) and (2.16)) for coke formation as following:



Based on these observations, it is necessary to avoid the risk of coke formation, high content of CO, and other by-products which might affect the SRM activity. In some cases, the studies of experimental conditions, kinetic models, and additional catalyst components are widely investigated for the SRM improvement as well.

2.4.1.1 Experimental Condition

According to our recent work (Pojanavaraphan *et al.*, 2012), the effects of reaction temperature and H₂O/CH₃OH molar ratio on SRM activity have been studied over 1 wt% Au/CeO₂ catalyst in the range of 200–400 °C, as shown in Figure 2.5. The results revealed that both CH₃OH conversion and H₂ yield increased with reaction temperature, and approached the highest values at 400 °C.

For the steam variation, the H₂O/CH₃OH at 2/1 was the optimum condition for achieving the highest SRM activity. The best conclusion was that the reaction temperature, steam content, and the catalyst selection were responsible for the SRM performance.

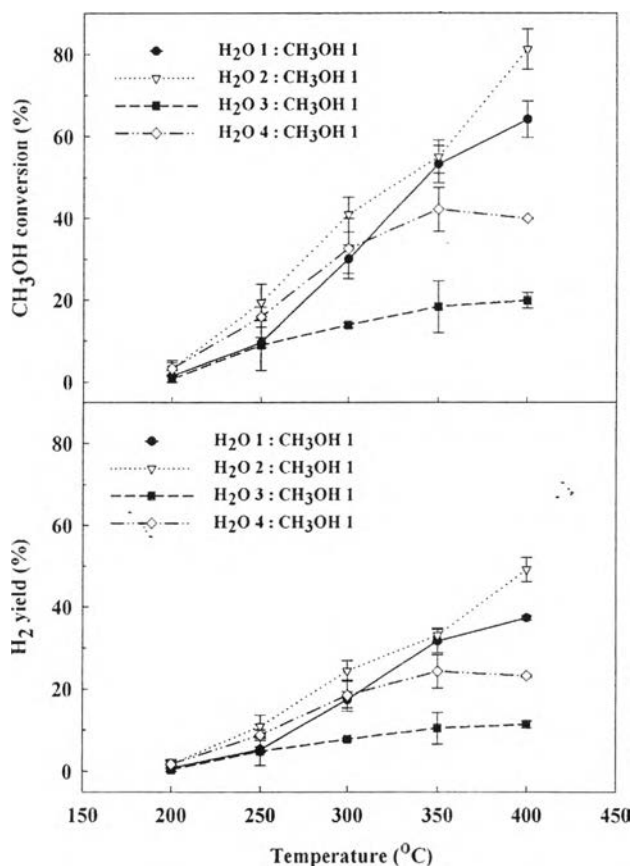


Figure 2.5 Effect of S/C (steam/carbon) molar ratio on methanol conversion and hydrogen yield over 1 wt% Au/CeO₂ catalyst calcined at 400 °C (Pojanavaraphan *et al.*, 2012).

In 2006, Pinzari *et al.* indicated that the temperature also affected on the gas effluent composition in the SRM, as shown in Figure 2.6. The SRM activity was less pronounced below 300 °C, whereas above this temperature was catalytically active, as evidenced by the simultaneous increase of H₂ and CO₂ and the decrease of CH₃OH and H₂O compared to those at inlet concentrations. Furthermore, the presence of by-products—CO, CH₄, and DME—was also detected at high temperature. To demonstrate the side reactions existing at high temperature,

DCM reaction was simplified as the first step of SRM to produce CO in this case, and the DEH reaction could produce DME, resulting in an incomplete methanol conversion.

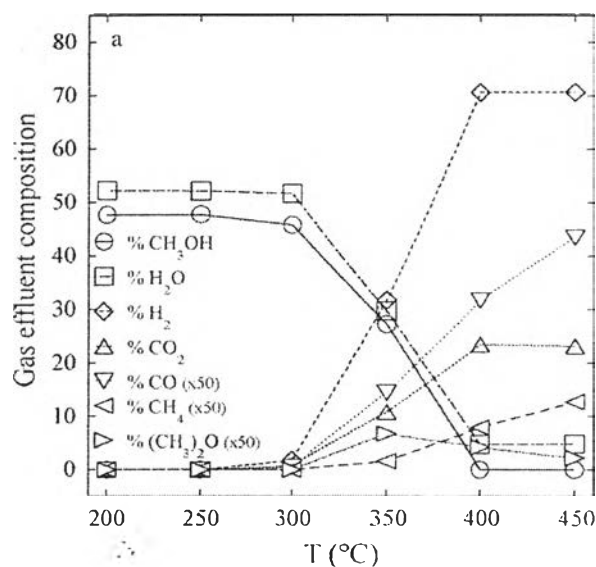
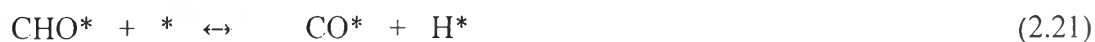


Figure 2.6 Effect of temperature on the gas effluent composition in the SRM reaction over $Zn_{10}Ti_{90}$ (Pinzari *et al.*, 2006).

2.4.1.2 Mechanism and Kinetics of Methanol Steam Reforming

The kinetic studies and reaction mechanisms of all oxygenated alcohols basically follow a similar mechanism in which they preferably adsorb on the catalyst surface, and subsequent cleavage of O–H, C–H, C–O, and C–C bonds produces adsorbed species, such as H, C, O, or CO which react to form H_2 and CO (Dauenhauer *et al.*, 2006). For example, Mhadeshwar and coworker (2005) proposed the following mechanism for the DCM that occurred during the SRM reaction over the catalyst surface. They suggested that the DCM started with the C–H bond cleavage to form a hydroxymethyl group which then converted to formaldehyde by O–H bond cleavage.





where * is the adsorbed site

Santacesaria and Carra (1983) proposed the reaction sequence of DCM followed by WGS reaction, so the CO produced firstly in the reaction sequence definitely had equal or greater concentration than that from the WGS equilibrium. Besides, Jiang *et al.* (1993a,b) proposed the elementary surface reaction mechanisms and derived the Langmuir–Hinshelwood (LH) expression. They suggested that CO was formed via decomposition of methyl formate (Eqs. (2.20)–(2.22)).



In order to interpret the rate expression, Peppley *et al.* (1999a,b) developed the rate from LH model by considering SRM, DCM, and WGS reactions with dual site mechanism, and they found the different route of CO formation in all reaction mechanisms. In contrast, a semi-empirical model of the kinetics of the SRM over CuO/ZnO/Al₂O₃ catalyst has been developed by Amphlett *et al.*, 1994 using the reaction schemes of irreversible reaction of SRM and DCM reactions. It was found that the WGS reaction could be neglected without substantial loss in accuracy. The rate equations for both reactions can be written as follows:

$$r_{\text{CH}_3\text{OH}} = -k_1 C_{\text{CH}_3\text{OH}} - k_2 \quad (2.27)$$

$$r_{\text{H}_2\text{O}} = -k_1 C_{\text{CH}_3\text{OH}} \quad (2.28)$$

$$r_{\text{CO}_2} = k_1 C_{\text{CH}_3\text{OH}} \quad (2.29)$$

$$r_{\text{CO}} = k_2 \quad (2.30)$$

$$r_{\text{H}_2} = 3k_1 C_{\text{CH}_3\text{OH}} + 2k_2 \quad (2.31)$$

As mentioned above, the reaction rate of methanol and water consumption depended only on the concentration of methanol but not on water concentration. Furthermore, the reaction rate of CO formation is a zero-order rate, which means that the formation of CO was not affected by the concentration of methanol or water.

Typically, the differences in reaction rate and reaction mechanism linking with SRM activity are well known to be dependent on the characteristic properties of the selected catalyst. For instance, Henderson *et al.* (2002) inferred that over oxide surfaces were the active sites of water dissociation. During hydrogen production in this study, ceria is highly reduced and more oxygen anion vacancies are created on the ceria surface. Trimm *et al.* (1994) reported that CeO_2 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. To support these statements, Men *et al.* (2004) provided the SRM reaction mechanism occurring on the Cu/CeO_2 catalyst, as shown in Figure 2.7, which contained four distinct steps: (i) the adsorption of methanol and water at the Cu/CeO_2 interface, (ii) the surface reaction and the desorption of gaseous products, (iii) the migration of surface oxygen from CeO_2 to the reduced Cu (oxygen reverse spillover), (iv) the regeneration of partially oxidized copper and oxygen vacancies. Consequently, the tracing of the exact SRM mechanism is being still the attractive issue for many researchers.

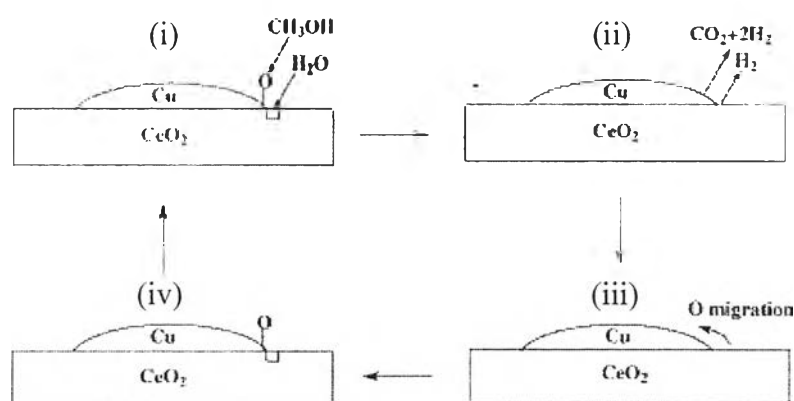
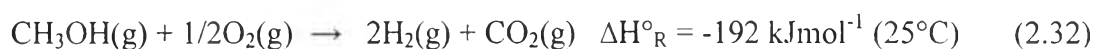


Figure 2.7 Proposed reaction mechanism for SRM at the Cu/CeO_2 interface (Men *et al.*, 2004).

2.4.2 Partial Oxidation of Methanol (POM)

Partial oxidation reaction is a reaction that partially oxidizes fuels to CO and H₂ rather than fully oxidizes to CO₂ and H₂O, as shown in Eq. (2.32). This reaction produces only 2 moles of hydrogen per mole of methanol (Pinzari *et al.*, 2006). Although the POM reaction produces less favorable H₂/CO₂ ratios, there are several advantages over steam reforming. For instance, there is no steam required and the reaction rate is higher than steam reforming. However, the main drawback of this reaction is highly exothermic, so it is difficult to control the temperature of the system (Pinzari *et al.*, 2006). In addition, too much releasing heat could lead to an easy explosion and the hot spot in the bed of packed catalyst. To avoid the risk of these unexpected phenomena, the oxygen-carbon (O/C) ratio is another important factor to control the efficiency of the POM reaction. For example, based on the previous studies, the O/C ratios greater than 1 could decrease the carbon or coke formation, whereas very high H₂ and CO yields could be obtained at this ratio (Roin, 2002). Nonetheless, the effect of O/C ratio on the product distributions for alcohol fuel has not yet been accomplished due to the complex mechanism over the catalyst surface using in the POM reaction.



According to the previous literature reviews, Cu–Zn catalysts have been found to be very active for the POM at reaction temperature of 215 °C, where the rates of methanol and oxygen conversion increased strongly with increasing temperature to selectively produce H₂ and CO₂ (Alejo *et al.*, 1997). The rate of CO formation was very low throughout the temperature range explored (200–225 °C) and H₂O formation decreased for temperature above 215 °C. The results showed that the maximum methanol conversion was obtained after increasing the Cu contents to Cu₄₀Zn₆₀ catalyst, probably due to its highest copper metal surface area, which was catalytically active for the POM. In contrast, increasing further Cu loadings could suppress the catalytic activity. In addition, the non-reduced catalysts displayed very low activity, where H₂ was in minute amount. As another measurement of catalytic activity of the Cu–Zn catalyst, the turn over frequency (TOF) values as a function of

reaction temperature was also determined under the use of $\text{Cu}_{40}\text{Zr}_{60}$ catalyst, as shown in Figure 2.8. When correlating the catalyst composition with the TOF value (not shown here), it was found that the TOF was higher for the low-copper catalysts and thereafter decreased slightly, and kept constantly at Cu-loadings above 50 %atom. The variation of TOF suggested that the enhancement in reactivity was a consequence of a change in the nature of the active sites.

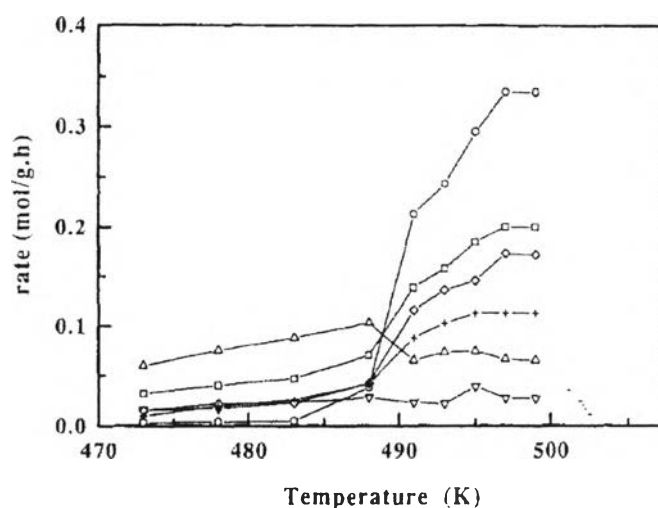


Figure 2.8 Partial oxidation of methanol over the catalyst $\text{Cu}_{40}\text{Zn}_{60}$: (□), CH_3OH conversion; (+), O_2 conversion; (○), H_2 ; (◇), CO_2 ; (Δ), H_2O ; (▽), CO (Alejo *et al.*, 1997).

Alejo *et al.* (1997) have tested the POM activity over the Cu/ZnO catalysts with various compositions, and they found the different catalytic activities, which was the consequence of the variation of Cu^0 metal surface area over the ZnO phase. According to the catalysts with Cu concentrations in the range of 40–60 wt%, the copper metal surface area seemed to be the main factor for determining the reaction rate. Recently, the combination of the noble metal and the copper as the bimetallic catalyst became being the attractive way to significantly enhance the POM activity. For instance, Ou *et al.* (2008) studied the effect of bimetallic Au–Cu/ TiO_2 (1 wt% Au–1 wt% Cu) and found that the bimetallic showed superior activity than the pure Au and Cu catalysts, including the selectivity and stability at low temperature of

100 °C, as shown in Figure 2.9. This was because the Cu metal could form the strong interaction with the Au metal and also stabilized the size of Au nanoparticles for prevailing the Au sintering. Similarly, the same role of the Au–Cu bimetallic catalyst in the POM was also observed in the Au–Cu/TiO₂–Fe₂O₃ (Chang *et al.*, 2009). However, the development of the bimetallic catalyst is still designed for the selective catalyst in the low-temperature H₂ production route.

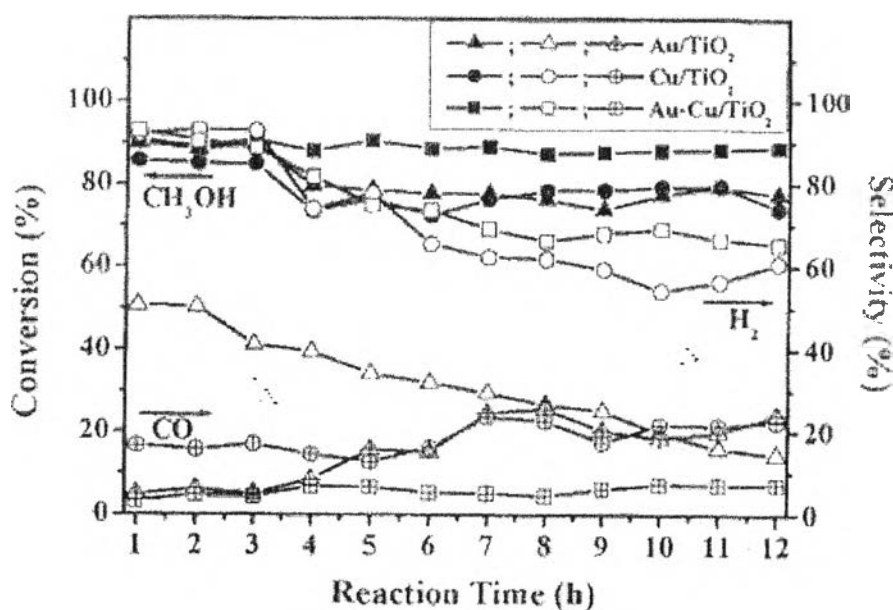
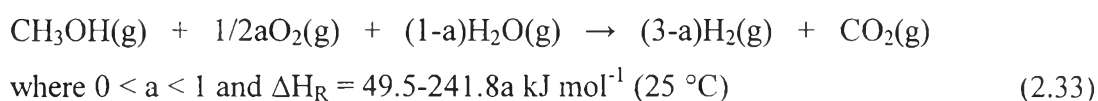


Figure 2.9 Catalytic performance of Au/TiO₂, Cu/TiO₂, Au–Cu/TiO₂ catalysts for CH₃OH conversion, H₂ selectivity and CO selectivity for POM (uncalcined, dried at 373 K; pH, 7; O₂/CH₃OH ratio, 0.3; reaction temperature, 523 K) (Ou *et al.*, 2008).

2.4.3 Oxidative Steam Reforming of Methanol (OSRM or Autothermal)

Autothermal reforming—can be called as combined reforming (CRM)—is commonly referred to a combination of steam reforming (SRM) and partial oxidation (POM) by feeding air and steam altogether into the reactor to achieve the heat utilization. The reaction of the OSRM is expressed in general Eq. (2.33):

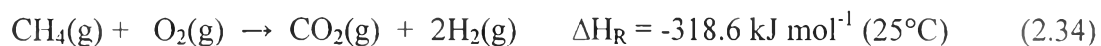


where a is the stoichiometric coefficient for steam reforming and partial oxidation.

When the methanol is reacted with a mixture of O_2 and steam in a “thermo reactor” over a catalyst surface, the heat produced from the POM (exothermic reaction) can transfer to supply the SRM (endothermic reaction), resulting in thermal balance or adiabatic reaction (Perez *et al.*, 2007). Compared with SRM, OSRM reaction has the advantages of a smaller reactor volume and a simpler reactor design (Turco *et al.*, 2007). In addition, this reaction allows the reaction to proceed at much higher rates in the reactor (Perez *et al.*, 2007). The main reasons why is fed oxygen in this reaction are to require less energy—require lower temperature than SRM process—and reduce the amounts of CH_4 and coke produced, while providing the higher H_2 yield and a lower CO yield under optimal operating conditions (Hong *et al.*, 2008).

Agrell *et al.* (2003) studied the SRM, POM, and OSRM reactions and found that in the OSRM reaction low CO levels with the following selectivity toward H_2 : SRM>OSRM>POM. They observed that the addition of O_2 to the SRM reaction appears to be an effective way to decrease the CO content in the product.

Pinzari *et al.* (2006) investigated the comparison between the SRM and CRM performances, as shown in Figure 2.10a and b, respectively. The presence of O_2 in CRM process did not seem to modify the methanol conversion, but it was helpful to decrease CH_4 and CO formation, allowing a higher CO_2 selectivity, by Eq. (2.34) for CH_4 and CO oxidation, respectively. However, there was no significant difference in term of temperature effect for both SRM and CRM.



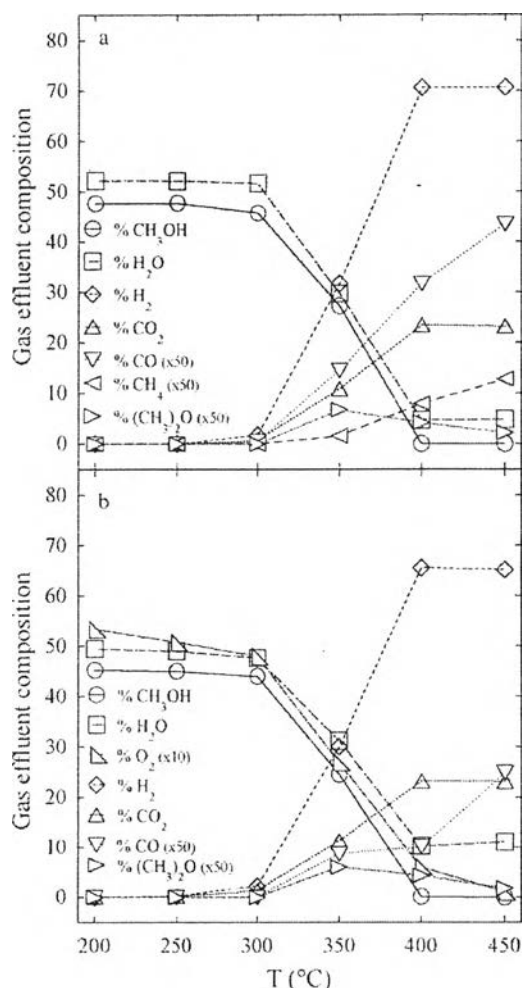


Figure 2.10 Effect of temperature on the gas effluent composition in the SRM (a) and CRM (b) reactions over $Zn_{10}Ti_{90}$ (Pinzari *et al.*, 2006).

Similar to our previous work (Pojanavaraphan *et al.*, 2012), we also compared the selectivities of gas products for SRM and OSRM reactions, as shown in Figure 2.11, it was found that the SRM gave much higher H_2 selectivity than OSRM at all reaction temperatures. Interestingly, the selectivity to H_2 substantially decreased, whereas the CO_2 selectivity increased considerably with increasing O_2 content in the reaction. These results inferred that the existence of POM reaction was taking place at a significant extent. Both CO and CO_2 were produced in noticeable amounts under POM reaction since the CO_2 selectivity was increased to the maximum value when the highest O_2/CH_3OH was used, while the CO could not be produced via methanol decomposition, or possibly' diminished by the CO oxidation.

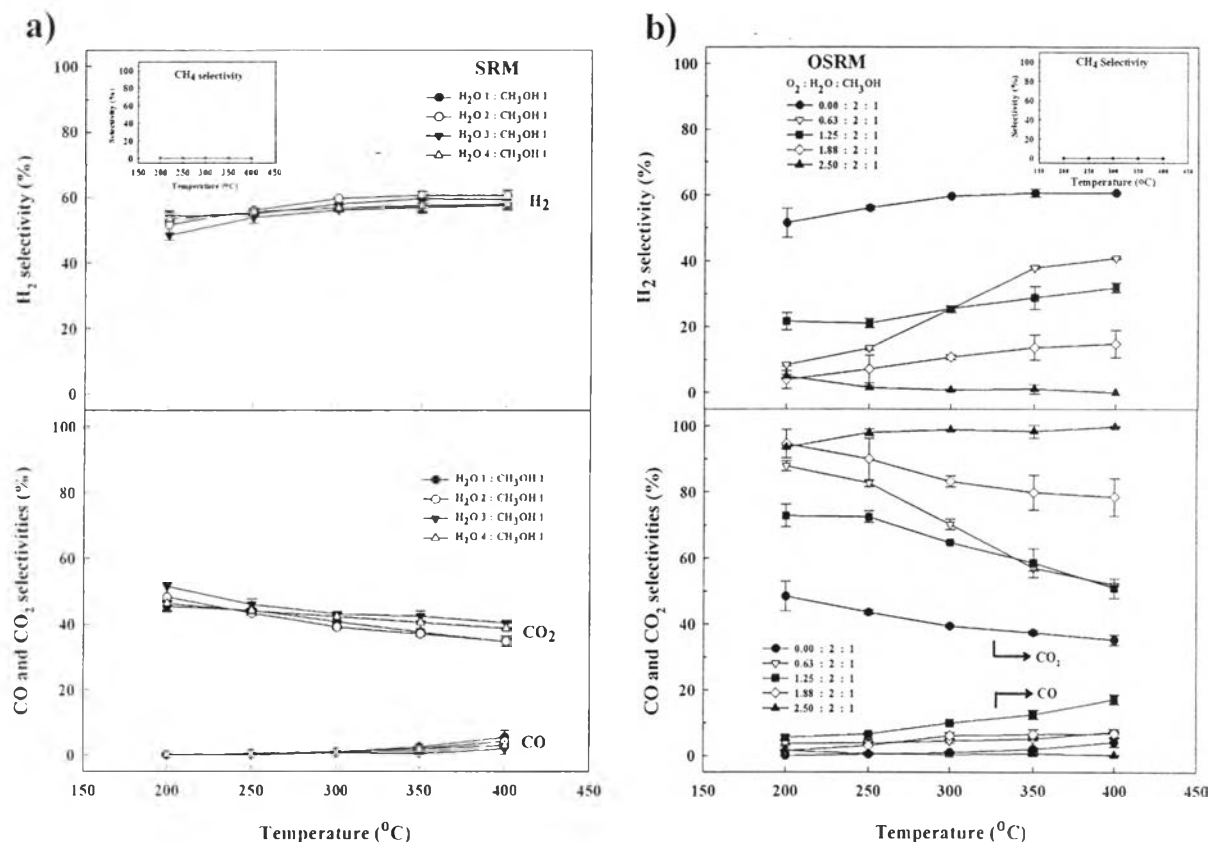


Figure 2.11 Comparison between the product gas selectivity of (a) SRM and (b) OSRM reactions over 1 wt% Au/CeO₂ catalyst calcined at 400 °C (Pojanavaraphan *et al.*, 2012).

Despite the obvious advantages of the ability to conduct a reaction with minimal need for heat transfer, autothermal operation is difficult to achieve due to heat losses from the system, which are typically compensated for by running at higher oxygen-to-carbon (O/C) ratios (Haynes *et al.*, 2011). On the other hand, too much O₂ feeding into the reaction causes the shifting from OSRM to POM, which has less favorable H₂ yield. Besides, the selection of the suitable feed compositions is very difficult to control the stable adiabatic reaction due to the fact that the competition between the SRM and POM can occur instead, resulting in the fluctuation in OSRM activity (Pojanavaraphan *et al.*, 2012). In term of practical process, the OSRM strongly requires a separation plant to remove N₂ from air to reduce process gas volumes. Indeed, the oxygen separation is very capital intensive

(almost 40% of total cost) and generally precludes the large-scale applications. Like any system that uses water, appropriate insulation is needed for applications in colder climates, and added space would be required for a reservoir in an already confined area (assuming for transportation use). Attempts to mitigate storage problems have looked into recycling the fuel cell exhaust to provide the necessary water requirements to maintain reforming capabilities under OSRM conditions (Shekhawat *et al.*, 2007). As mentioned previously, the progress on the fuel processor linked to the OSRM unit is still in the development and unclear what solution will be used in a commercial unit at this time.

2.5 Catalysts Development for Steam Reforming of Methanol and Preferential CO oxidation

The potential of SRM for hydrogen production in PEMFC applications makes researchers try to develop the catalysts for satisfactory performance. The Cu-based catalysts are the conventional catalyst for methanol reforming; however, they still have the drastic disadvantages of fast deactivation and pyrophoric characteristics at higher temperature than 270 °C. Hence, the non-copper catalysts or the co-addition of another active metal have been investigated for the hope that the better performance might be found. Before going to the non-copper catalysts, the introduction of Cu-based catalysts is necessary for understanding the basic knowledge of its properties.

2.5.1 Copper-based Catalysts

In general, the activity of Cu-based catalysts greatly depends on the status of copper, such as copper oxidation state (Hernández *et al.*, 2007), copper dispersion, metal surface area, and particle size (Shen *et al.*, 2002). However, the pyrophoric substance—rapid deactivation of Cu-based catalyst due to sintering of the metal at temperature near and above 300 °C—is a barrier to the application in the reforming process (Twigg *et al.*, 2003) due to its very low melting point (~400 °C); therefore, its sintering potential is much greater than other metals. Again, the thermal

stability of the Cu catalyst is also an issue for Cu particle size, which can be avoided by adding some precious metals (Zr, Al, Ce, Zr, etc.) together.

Especially for the Cu/Zn/Al systems, this combination catalyst (Jiang *et al.*, 1993) has been widely used as the commercial catalyst for SRM, OSRM, and low-temperature WGS reactions according to its catalytically active. The promoting of Al₂O₃ plays the major roles in increasing the active surface area and improving the thermal stability of the catalyst (Turco *et al.*, 2007). Additionally, the Zn metal could limit the sintering and improving the dispersion of Cu for both Cu/Al₂O₃ (Figueiredo *et al.*, 1998) and Cu/ZnO (Turco *et al.*, 2007; Shen *et al.*, 1997; Amphlett *et al.*, 2001) catalysts. In order to achieve the best chemical properties in the described catalyst, combining the Cu metal with appropriate amounts of Zn and Al metals is strongly considered during the catalyst preparation (Chang *et al.*, 2010).

Interestingly, adding Zr metal in the Cu/ZrO₂ catalyst presented the advantage in great CO reduction with high methanol conversion during the methanol reforming, compared to the commercial catalyst (Ritzkopf *et al.*, 2006). Jeong *et al.*, (2006) found that ZrO₂ added into the Cu/Zn-based catalyst also enhanced copper dispersion on the catalyst surface. Among the catalysts tested, Cu/ZnO/ZrO₂/Al₂O₃ exhibited the highest methanol conversion and the lowest CO concentration in the outlet gas. The selection of Zr in the catalyst might be the attractive choice in this case.

Similar to the zirconium, the promoting of cerium (Ce) metal was also efficient for CO reduction as well. Using cerium the SRM could be carried out at lower temperature with high methanol conversion, results in suppression of DCM and RWGS eventually end-up with the low CO and H₂-rich product stream. Patel *et al.* (2006) reported that cerium promoted Cu–Zn–Ce–Al oxide catalysts improved the activity and H₂ selectivity greatly and also kept the CO formation at very low content. Moreover, cerium also stabilizes the copper–alumina catalysts effectively that was confirmed by a long run-time deactivation studies of Cu–Zn–Ce–Al oxide catalysts, compared to those containing only zinc promoter. Liu *et al.* (2002) found that a 3.9 wt% Cu/CeO₂ catalyst prepared by co-precipitation technique exhibited a conversion of 53.9 % for the SRM at 240 °C, which was higher than the conversions of 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. Men *et al.* (2004) studied the Cu/CeO₂ and proposed 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 was the active site for SRM and the oxygen reverse spillover from ceria to copper is involved in the catalysis cycle.

2.5.2 Non Copper-based Catalysts

Metals from group 8, 9 and 10, especially Pd, are highly active in POM (Cubeiro *et al.*, 1998). The Pd-based catalysts show a high selectivity at low temperature. Iwasa *et al.* (1995) observed the large improvement in catalytic activity of Pd/ZnO by reducing the catalysts at higher temperatures, where the metallic Pd was greatly modified as a result of the formation of Pd–Zn 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. Moreover, Yunhua *et al.* (2006) demonstrated that the strong interaction between metallic Pd and ZnO during H₂ pretreatment to form PdZn alloy could maximize the methanol conversion and CO₂ selectivity in the SRM. Although Pd has higher melting point than copper and is expected to be more resistant to sintering, the stability of PdZn alloy is still an issue of concerning.

The main drawbacks of this precious metal are that the Pd is an active catalyst for DCM, which leads to large amount of CO formation (Liu *et al.*, 2006), and Pd metal is too expensive. However, the different trend of Pd/ZnO in the SRM was observed by Chin and coworkers (2002), who found the highly active Pd/ZnO catalyst with very low CO selectivity. Under the conditions examined, the decomposition activity was minimal.

Focussing on the kinetic observation, Dagle and coworkers (2008) studied PdZnAl catalysts for the WGS, SRM, and RWGS reactions and found that for SRM, the CO selectivities were observed to be lower than the calculated equilibrium values over a range of temperatures for all H₂O/C ratios, while the reaction rate constants were approximately of the same for both WGS and SRM. These posulated that according to an irrelevant reaction of WGS in the SRM mechanism, Pd/ZnO/Al₂O₃ was not beneficial because it acted as the active WGS

catalysts. However, RWGS rate constants were about 20 times lower than that of SRM, suggesting that RWGS reaction could be one of the sources of small amount of CO during the SRM. According to all above statements, the tracing of another active low-temperature catalyst might be more beneficial and challenging for the SRM reaction in terms of both higher H₂ selectivity and lower CO selectivity.

2.5.3 Gold-based Catalysts

According to the disadvantages of the Cu-based catalysts described previously, many researchers started focusing on gold-based catalysts, defined as more suitable catalyst for automotive application in fuel cells. Although gold (Au) is well known as poorly active catalyst for high-temperature reaction, this catalyst has been recently popular due to its potential applicabilities to commercial applications and environmental importance (Cameron *et al.*, 2003). Corti *et al.* (2005) supported that the potential to apply catalysis by gold in practical uses could be likely involved within four broad application areas;

- pollution and emission control technologies,
- chemical processing of a range of bulk and speciality chemicals,
- the emerging 'hydrogen economy' for clean hydrogen production and fuel cell systems,
- sensors to detect poisonous or flammable gases or substances in solution.

One of the potential advantages is that the use of Au catalysts is offered to be lower cost and greater price stability, compared to other precious metal catalysts. In fact, gold is substantially cheaper (on a weight for weight basis) and considerably more plentiful than platinum. The reactions which Au has already been demonstrated to be a strong catalyst included;

- oxidation of 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, e.g. hydrogenation of CO and CO₂.

The physical properties of the Au metal was summarised into Table 2.5. From this information, Au has very high melting point, so the sintering of Au nanoparticles can be neglected during the reaction, and the thermal stability is expected to be better than the Cu catalyst.

Table 2.5 Physical properties of Au (<http://en.wikipedia.org/wiki/Gold>)

Property	Value
Atomic number	79
Atomic weight	196.967 g·mol ⁻¹
Density	19.3 g·cm ⁻³
Liquid density at m.p.	17.31 g·cm ⁻³
Melting point	1064.18 °C
Boiling point	2856 °C
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

In order to better understand the characteristic performances of both Au and Cu catalysts in the methanol reforming, Manzoli *et al.* (2004) have evaluated the performance in each catalyst through H₂/CO and CO₂/CO ratios in the OSRM, as recorded in Table 2.6. The H₂/CO ratios followed the order: Cu/ZnO > Cu/TiO₂ > Au/ZnO > Au/TiO₂. The bad performance of gold catalysts was found in low H₂/CO ratio, suggesting that gold is far less efficient than copper in term of H₂ production at high reaction temperature. However, the high CO₂/CO ratios were obtained for gold catalysts, indicating that the occurrence of the CO preferential oxidation reaction was more favorable to produce more CO₂ contents. This could be inferred that gold is very efficient in CO oxidation at low temperature. As mentioned previously, the working on the H₂ production from methanol reforming over Au-based catalyst is

still studied in a few numbers due to the unclear mechanism on the catalyst surface. The studying of chemical properties of the Au catalyst is essential for designing the selective activity for SRM.

Table 2.6 H₂/CO and CO₂/CO ratios estimated on the different Au and Cu catalysts after a long contact time of interaction with a methanol-water-oxygen mixture (1:1:0.2) at 200 °C (Manzoli *et al.*, 2004)

Catalyst	H ₂ /CO ratio	CO ₂ /CO ratio
Cu/ZnO	16.27	0.93
Cu/TiO ₂	15.66	0.91
Au/ZnO	11.25	1.15
Au/TiO ₂	8.00	1.34

Normally, the activity of Au catalysts is known to be dependent on the Au dispersion, Au natural site, Au particle size, and interaction between Au and support (or by itself) (Pojanavaraphan *et al.*, 2012). For instance, the strong Au–Au interaction of the Au/CeO₂ catalyst prepared by deposition-precipitation was responsible for the OSRM activation (Pojanavaraphan *et al.*, 2012). Yi *et al.* (2010) also found that the Au/CeO₂ catalyst exhibited the long life-time with full methanol conversion at 300 °C over the SRM reaction, while no Au sintering was observed. Grisel *et al.* (2002) indicated that Au nanoparticles (≤ 5 nm) on metal oxides—such as Mg(OH)₂, Al₂O₃, TiO₂, and SiO₂—was responsible for the superior activity for CO oxidation at low temperatures. Especially, the Au/Mg(OH)₂ containing icosahedral Au₁₃ cluster has extremely high CO oxidation activity (Cunningham *et al.*, 1998). Interestingly, El-Moemen *et al.* (2009) demonstrated that the deactivation of Au catalyst was related to the build-up of stable monodentate carbonate species rather than arising from an irreversible sintering of the Au nanoparticles. These surface carbonates either directly blocked the active sites, or the access of reaction intermediates to the active sites. For the Au catalyst's preparation route, Haruta *et al.* (2001) found that depositing Au nanoparticles on metal oxides by means of co-

precipitation and deposition-precipitation could exhibit surprisingly high catalytic activity for CO oxidation at low temperature of 200 °C. The adjusted pH in the Au precursor was also important for designing the nanosize of Au particle during the preparing step (Haruta *et al.*, 1997), as mentioned in Figure 2.12.

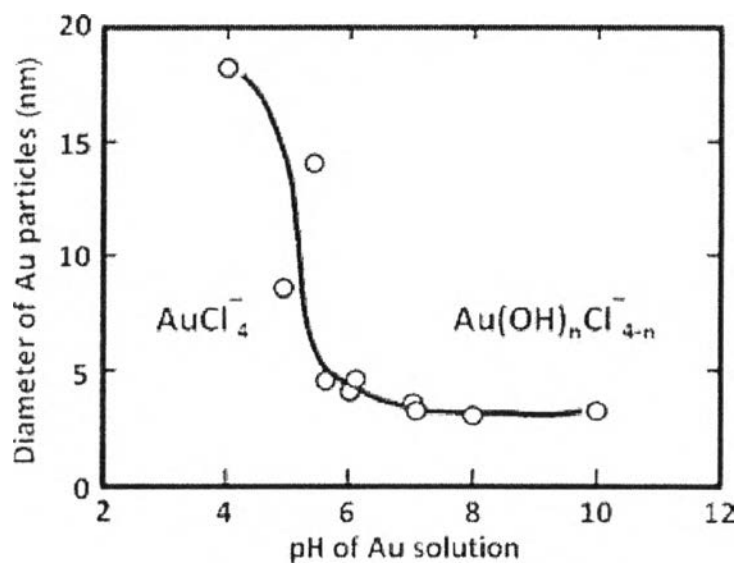


Figure 2.12 Mean diameter of Au particles as a function of pH of the HAuCl_4 solution employed in preparing Au/TiO_2 catalysts via the deposition-precipitation method (Haruta *et al.*, 1997).

Being an inspiring result, Goodman *et al.* (1998) proposed the model of Au/TiO_2 correlated between the turn over frequency (TOF) for CO oxidation and the Au particle size (Figure 2.13). The maximum TOF was achieved at Au diameter of 3.5 nm (3 atoms thick), where Au partially lost its metallic nature in this case. They suggested that (i) this transition might lead to the high catalytic activity, and (ii) the catalytic activity of Au/TiO_2 catalyst strongly depended on the Au cluster size with a maximum occurring at about 2–3 nm.

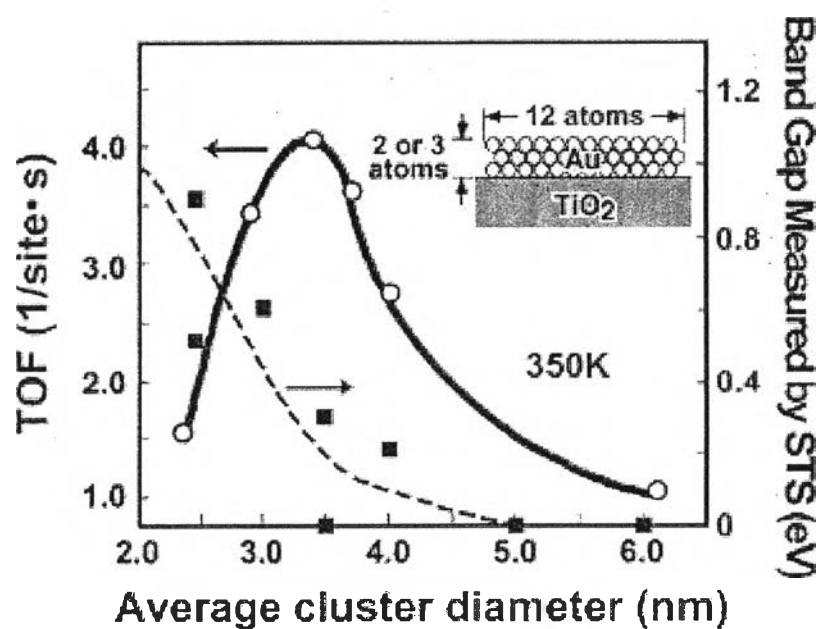


Figure 2.13 Turn over frequencies and band-gap measure by STM as a function of the diameter of Au islands deposited on TiO₂ (Goodman *et al.*, 1998).

2.6 Support Selection for Gold Catalysts

The most significant factor for the active Au catalyst is focused on the support selection, which also related with the catalytic performance. Among the metal oxides, ceria (CeO₂) is used as a support because the functions of CeO₂ and its composition have attracted numerous investigations because it has high oxygen storage capacity (OSC) or oxygen vacancy, which allows itself to store and release active oxygen to provide good performance in CO oxidation and SRM reaction (Srisiriwat *et al.*, 2009). In the other words, the cations Ce⁴⁺ is quite easily reduced into the form of nonstoichiometric oxides between CeO₂ and Ce₂O₃, and the surface lattice oxide ions are readily mobilized, so that cation vacancies are common. It was shown that ceria plays the role of an active support capable of producing oxygen. The advantages of the use of CeO₂ as the support over active Au metal was found to keep high and stable Au dispersion during the catalytic operation (Andreeva *et al.*, 2002).

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 CeO_2 influence on the energetic properties by lowering the activation energy for oxygen migration (Vidmar *et al.*, 1997). In further studies, the chemical properties of ceria were successively developed by the incorporation of triple cations, M^{3+} ($\text{M} = \text{Fe}, \text{La}, \text{etc}$), into the ceria lattice (Kongzhai *et al.*, 2008). This incorporation can enhance the formation of vacancies in the anion sublattice during the charge balancing, where the redox properties in ceria can be improved. The addition of another interesting support, Fe_2O_3 , with CeO_2 has been receiving much attention due to the creation of an active solid solution phase ($\text{Ce}_x\text{Fe}_{1-x}\text{O}_2$), which could be beneficial for many applications (Kongzhai *et al.*, 2008). Generally, the Fe_2O_3 or hematite is well known as the active catalyst for the WGS reaction for mainly H_2 production and CO reduction. According to the good perspective of Fe_2O_3 support in CO reduction, Andreeva *et al.* (1996) reported that $\text{Au}/\alpha\text{-Fe}_2\text{O}_3$ exhibited high catalytic activity in low-temperature WGS reaction, whose the mechanism of WGS reaction on $\text{Au}/\alpha\text{-Fe}_2\text{O}_3$ catalyst was simplified in Figure 2.14.

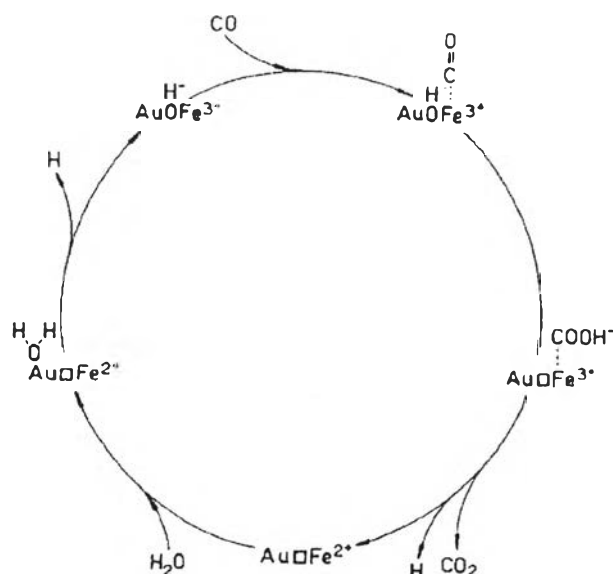


Figure 2.14 Probable scheme of the WGS reaction on the $\text{Au}/\alpha\text{-Fe}_2\text{O}_3$ catalysts (Andreeva *et al.*, 1996).

With different vision, Makkee *et al.* (2005) also proposed another schematic model of CO oxidation on the prepared Au/Fe₂O₃ (Figure 2.15), which were totally explained with steps by steps as follows:

- (1) adsorption of CO onto hydrated Au particle,
- (2) formation of hydroxycarbonyl, spillover to Au–support interface (i), and oxidation to bicarbonate by lattice oxygen (ii),
- (3) decomposition of the bicarbonate to produce CO₂ and H₂O,
- (4) further CO adsorption on Au particle and O₂ adsorption in oxygen vacancy of the Fe₂O₃,
- (5) H₂O attack of carbonate at interface for further bicarbonate formation (6).
- (7) decomposition of bicarbonate yields CO₂, and recycles OH to continue the catalytic cycle (8),
- (9) reaction of bicarbonate with OH to form H₂O and stable carbonate at interface.

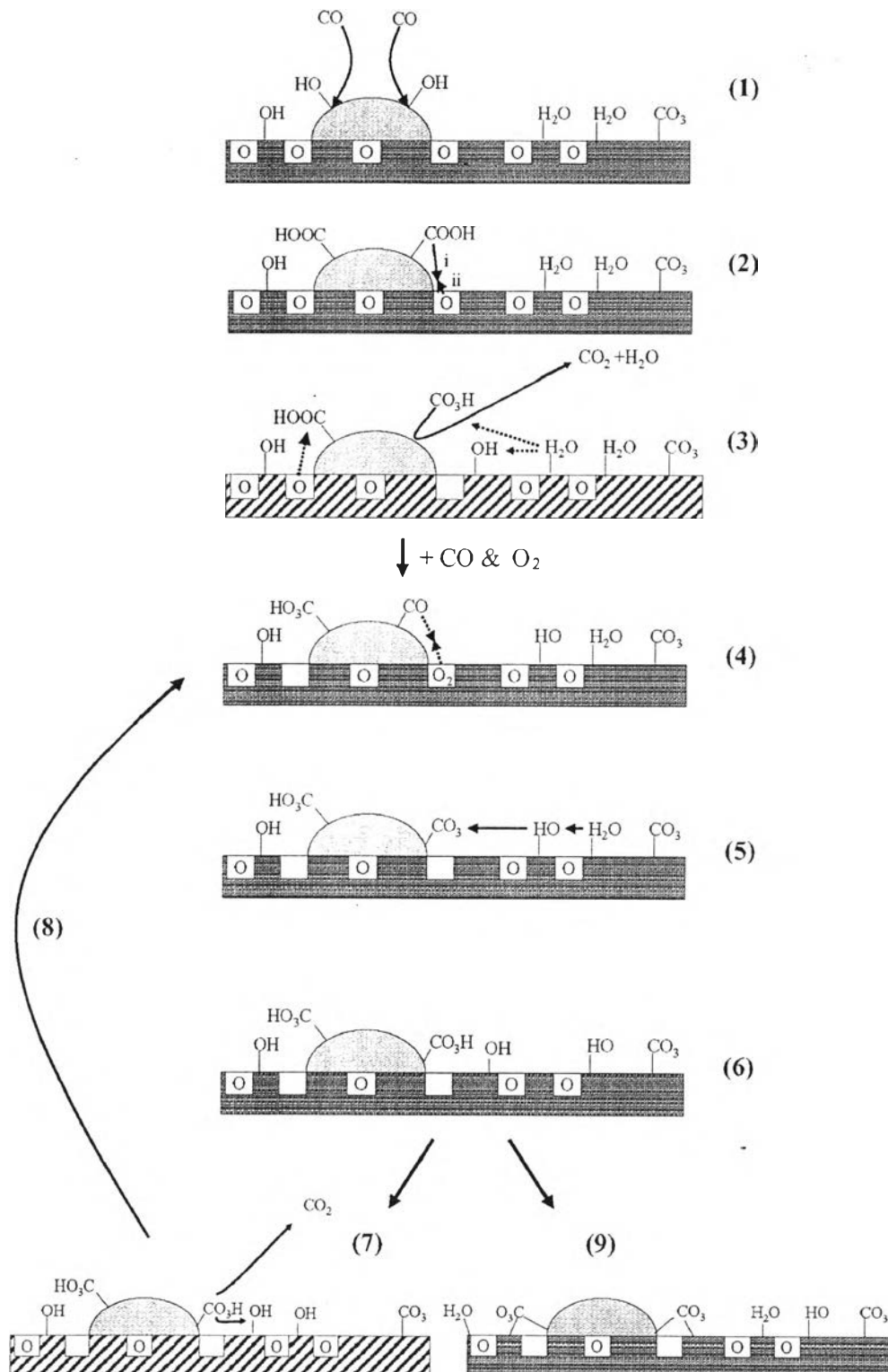


Figure 2.15 Schematic model of oxidation of CO on as prepared (dried) Au/Fe₂O₃ (Makkee *et al.*, 2005).

To date, the combination of the $\text{CeO}_2\text{-Fe}_2\text{O}_3$ and $\text{CeO}_2\text{-ZrO}_2$ as the mixed oxide supports for Au deposition showed high activity for many reactions, according to the strong Ce-Fe and Ce-Zr interactions in the solid solution (Tabakova *et al.*, 2011). In addition, the solid solution formation of the mixed oxide support played the role in the increment of oxygen vacancies, resulting in the significant improvement of the catalytic activity. Similar to our research group, Shuenka *et al.* (2009) have tested a series of $\text{Au/CeO}_2\text{-Fe}_2\text{O}_3$ prepared by deposition-coprecipitation technique on SRM. The results showed the trends of methanol conversion in the whole range of reaction temperature (200–450 °C) as ordered: $\text{Au/Ce}_8\text{Fe}_1 > \text{Au/CeO}_2 > \text{Au/Fe}_2\text{O}_3 > \text{Au/Ce}_1\text{Fe}_8 > \text{Au/Ce}_1\text{Fe}_1$, while there was no significant difference in H_2 selectivity (~75 %) for all samples. The results revealed that the Ce/Fe ratio played the role in limiting the solubility of incorporated Fe^{3+} species inside Ce^{4+} lattice, where excess Fe^{3+} could favored in segregation out of the solid solution instead. Based on all previous studies, it would be beneficial to deal with the Au-based catalysts, which contain high oxygen vacancies support, especially for CeO_2 system, for achieving the high activity either H_2 production route or CO reduction route at low operating temperature.

All of these statements are the motivation to introduce Au over ceria-based support on the MFP performance (SRM + PROX). The expected results will cover high H_2 selectivity and yield, complete CH_3OH conversion, and ultra low CO concentration. The parameters considered of SRM unit involve support preparation route, Au content, calcination temperature, gas pretreatment, support composition, bimetallic catalyst, steam-to-methanol molar ratio, stability test, and regeneration test. The effective parameters of PROX unit involve the comparison between single- and double-stage reactors, amount of O_2 feeding (O_2/CO molar ratio and O_2 split ratio), and amount of use catalyst (weight split ratio).