CHAPTER II
THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Fuel Cell

A fuel cell is an electrochemical energy conversion device that converts hydrogen and oxygen into electricity, heat, and water. The source fuel of hydrogen could be hydrocarbons or alcohols that react with an oxidant. The basic principle of the fuel cell is illustrated in Figure 2.1, which the core of each fuel cell consists of an electrolyte and two electrodes. At the negative anode, a fuel such as hydrogen is being oxidized, while at the positive cathode, oxygen is reduced. Ions are transported through the electrolyte from one side to the other. Fuel cells have many advantages over conventional power sources such as reducing dependence on fossils fuels, long life time, high efficiency, non-pollutant, minimal maintenance cost, etc. The chemical reactions involved in the anode and cathode and its overall reactions are given as below.

$$\text{Anode reaction} : H_2 \rightarrow 2H^+ + 4e^- \tag{2.1}$$

$$\text{Cathode reaction} : (1/2)O_2 + 2H^+ + 2e^- \rightarrow H_2O \tag{2.2}$$

$$\text{Overall reaction} : H_2 + (1/2)O_2 \rightarrow H_2O \tag{2.3}$$

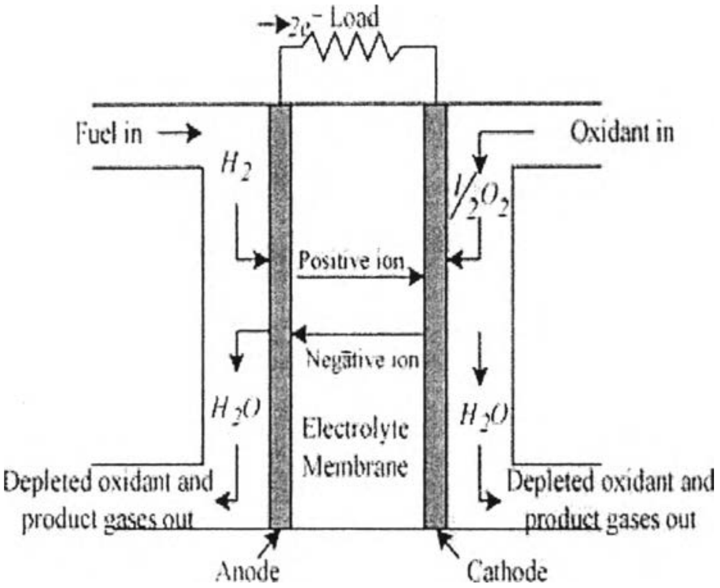

Figure 2.1 Fuel cell operation diagram (Kirubakaran *et al.*, 2009).

2.1.1 Classification of Fuel Cells

There are several types of fuel cell (Table 2.1) which they can classify by the electrolyte material and operating temperature, including proton exchange membrane fuel cells (PEMFCs), alkaline fuel cells (AFCs), phosphoric acid fuel cells (PAFCs), molten carbonate fuel cells (MCFCs), and solid oxide fuel cells (SOFCs). The categories of fuel cell indicate the cell materials, operating temperature, electrode reactions and applications. PEMFCs, AFCs, and PAFCs use hydrogen as a fuel and operate at low temperature, where SOFCs and MCFCs operate at high temperatures. From the different in fuel cell, proton exchange membrane fuel cells (PEMFCs) are a promising candidate to be the future power source.

Table 2.1 Major types of fuel cells currently under development (Giddey *et al.*, 2012)

Fuel Cell	**Fuel/Anod. Reaction**	**Electrolyte**	**Oxidant/Cath. Reaction**	**T (^oC)**
PAMFC	H_2 $H_2 = 2H^+ + 2e^-$	H^+	Air as oxidant $1/2O_2 + 2H^+ + 2e^- = H_2O$	60–120
AFC	H_2 $H_2 + 2OH^- = 2H_2O + 2e^-$	OH^-	Air as oxidant $1/2O_2 + H_2O + 2e^- = 2OH^-$	<100
PAFC	H_2 $H_2 = 2H^+ + 2e^-$	H^+	Air as oxidant $1/2O_2 + 2H^+ + 2e^- = H_2O$	120–220
MCFC	CH_x,CO,H_2 $H_2 + CO_3^{2-} = H_2O + CO_2 + 2e^-$	CO_3^{2-}	Air as oxidant $1/2O_2 + CO_2 + 2e^- = CO_3^{2-}$	600–800
SOFC	CH_x,CO,H_2 $H_2 + O^{2-} = H_2O + 2e^-$	O^{2-}	Air as oxidant	800–1000

2.1.2 Proton Exchange Membrane Fuel Cell

The proton exchange membrane fuel cells (PEMFCs), also called the solid polymer fuel cells (SPFCs). PEMFCs are made from polymer electrolyte membranes as proton conductor and Platinum (Pt)-based materials as a catalyst. The fuel as hydrogen is activated by the catalyst to form proton ion (H^+) and eject electron (e^-)

at the anode. The proton passes through the membrane whereas the electrons are forced to flow to the external circuit and generate the electricity. Then the electron flows back to the cathode and interact with oxygen and proton ion to form water. The structure of PEMFC is shown in Figure 2.2. These fuel cells are a prime candidate for many applications because they have many advantages such as high power density, low corrosion, and long life, as shown in Table 2.2. Moreover, they operate at low temperature which allows fast start-up and shut-down. Therefore, PEMFCs are particularly suitable for use in vehicles and in portable applications.

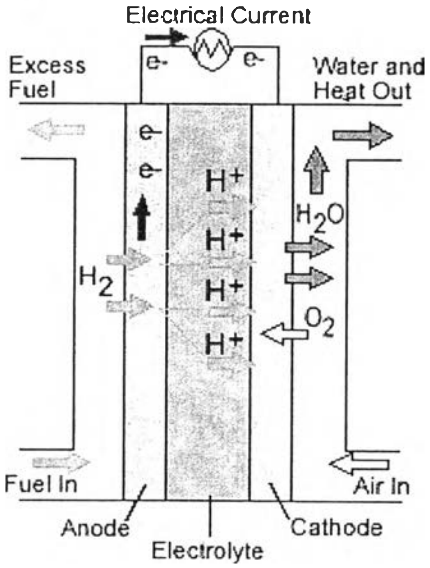

Figure 2.2 Fuel cell's diagram (http://www.fuelcellmarkets.com/fuel_cell_markets/proton_exchange_membrane_fuel_cells_pemfc/4,1,1,2502.html).

Table 2.2 PEMFCs technologies (http://tractors.wikia.com/wiki/Fuel_cell)

Common Electrolyte	**Operating temperature**	**Typical Stack Size**	**Efficiency**	**Application**	**Advantages**	**Disadvantages**
Perfluoro sulfonic acid	50–100 °C 122–212 °F Typically 80 °C	<1 kW–100 kW	60% transportation 35% stationary	• Backup power • Portable power • Distributed generation • Transportation • Specialty vehicles	• Solid electrolyte reduces corrosion & electrolyte management problems • Low temperature • Quick start-up	• Expensive catalysts • Sensitive to fuel impurities • Low temperature waste heat

2.2 Hydrogen Fuel

Hydrogen is widely produced and considered to be the future energy due to its high potential in reducing emission of pollutants, greenhouse gases, and various energy supplies. A variety of feedstock can be used to produce hydrogen such as natural gas, coal, as well as renewable energy sources such as biomass and water with input from renewable energy sources, as shown in Figure 2.3. It can be produced from varieties of process technologies such as

- Steam reforming (steam methane reforming - SMR)
- Partial oxidation (POX)
- Autothermal reforming (ATR)

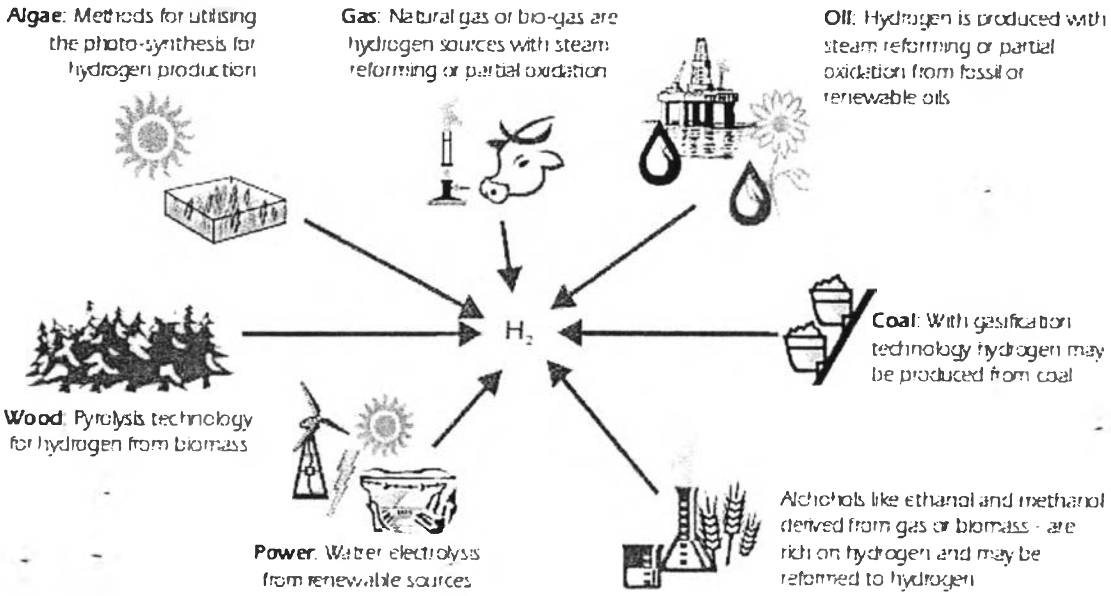

Figure 2.3 Some feedstock and process alternatives (Riis *et al.*, 2006).

2.2.1 Production of Hydrogen

2.2.1.1 Steam Methane Reforming

Steam methane reforming (SRM) is widely used process for hydrogen production and the flow process is shown in Figure 2.4. SRM is an endothermic reaction and requires external heat input. The process typically consists of two steps which the first step, methane is reacted with steam in the presence of a catalyst to produce hydrogen and carbon dioxide, as shown in Equation (2.4). The process occurs at temperature range of 500–900 °C and pressure of 30 atm. In the second step, the product gas of CO passes through the water-gas shift reaction (WGS) to produce hydrogen and carbon dioxide, as shown in Equation (2.5). This step is exothermic reaction and flavors at lower temperature. WGS reaction often has two stages. A high temperature reactor operates at about 350–475 °C, and then follows by a lower temperature about 200–250 °C.

SRM reaction : $CH_4 + H_2O \leftrightarrow CO + 3H_2$ $\Delta H^o_{298} = + 206$ kJ/mol (2.4)

WGS reaction : $CO + H_2O \leftrightarrow CO_2 + H_2$ $\Delta H^o_{298} = - 102$ kJ/mol (2.5)

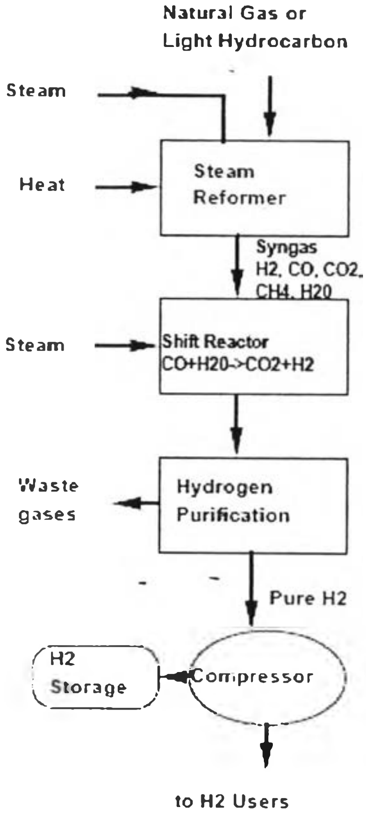

Figure 2.4 Steam reforming process (Ogden, 2001).

2.2.1.2 Partial Oxidation (POX)

Partial oxidation (POX) is used to produce hydrogen from variety of feed such as coal, methane, and heavy hydrocarbon. Typical material flow of partial oxidation is shown in Figure 2.5. The general reaction is shown in Equation (2.6) which hydrogen is produced through the partial combustion of methane with oxygen gas to carbon monoxide and hydrogen, as shown in Equation (2.7) and the process is an exo-thermic reaction and it is more compact than SRM as there is no need for any external heating of the reactor.

General POX reaction : $C_nH_m + \frac{1}{2} nO_2 \rightarrow nCO + (m/2)H_2$ (2.6)

POX of methane reaction : $CH_4 + (\frac{1}{2}) O_2 \rightarrow CO + 2H_2$

$\Delta H^\circ_{298} = -36$ MJ/kmol (2.7)

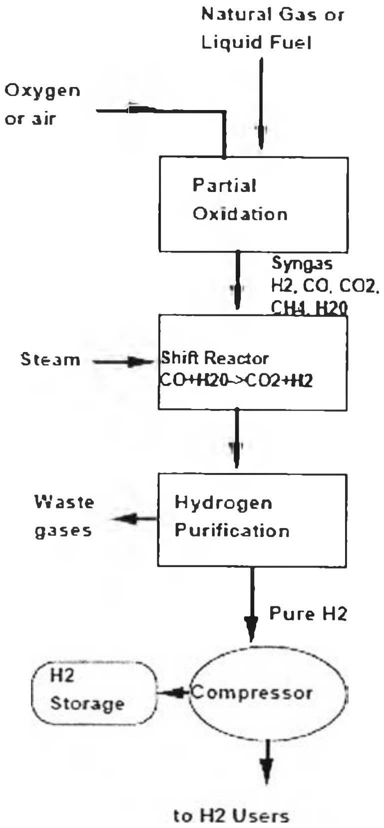

Figure 2.5 Partial oxidation process (Ogden, 2001).

2.2.1.3 *Autothermal Reforming (ATR)*

Autothermal reformer (ATR) is a combination of steam reforming and partial oxidation systems. A hydrocarbon feed (methane or a liquid fuel) is reacted with both steam and air to produce hydrogen. Methane is the main fuel for hydrogen production and the reactions are shown in Equations (2.8) and (2.9) with exothermic and endothermic, respectively. The total reaction is exothermic and it releases the heat that means the reactor does not need any external heat. The outlet temperature from the reactor is in the range of 950–1100 °C, and the gas pressure can be as high as 100 bar. So, autothermal reforming is simpler and more compact than steam reforming as well as a lower capital cost. Then the CO gases are converted to H_2 through the WGS reaction and hydrogen purification stages are needed.

SRM reaction : $CH_4 + H_2O \leftrightarrow CO + 3H_2 \quad \Delta H^o_{298} = + 206,16$ kJ/mol CH_4 (2.8)

POX reaction : $CH_4 + ½\, O_2 \rightarrow CO + 2H_2 \quad \Delta H^o_{298} = - 36$ MJ/kmol CH_4 (2.9)

The above processes for hydrogen production have many benefits however, each process still has the challenges and they were summarized in Table 2.3.

Table 2.3 Comparison of technologies for H_2 production from natural gas (Riis *et al.*, 2006)

Technology	**SMR**	**ATR or POX**
Benefits	• High efficiency • Emissions • Costs for large units	• Smaller size • Costs for small units • Simple system • Lower efficiency
Challenges	• Complex system • Sensitive to natural gas qualities	• H_2 purification • Emissions/flaring

2.2.2 Production of Hydrogen from Methanol

Methanol is a liquid fuel that is easily be stored and transported than hydrogen. Because of its property in high hydrogen to carbon ratio, low boiling point (64.7 °C) and no C–C bonds; therefore, it is a suitable fuel for hydrogen production. Methanol can be produced from natural gas, coal, other fossil fuels as well as renewable resources. Moreover, there are various reactions that can be used to produce hydrogen from methanol such as decomposition, partial oxidation, steam reforming and oxidative steam reforming. Table 2.4 (Qi *et al.*, 2007) shows the complete reforming of various fuels that requires different amounts of O_2 and energy. Among all of them, methanol is the most attractive fuel for reforming because it requires mild reforming conditions and has potential for attainment of highest possible efficiency.

Table 2.4 Fuel types and their maximum possible reforming efficiencies (Qi *et al.*, 2007)

Fuel	**$C_nH_mO_z$**	**Calculated thermo-neutral O_2/fuel ratios (x_0) and maximum theoretical efficiencies for various fuels**						
		n	m	z	**ΔH_f (kcal/gmol)**	$m/2n$	x_0	**Efficiency (%)**
Methanol	CH_3OH	1	4	1	- 57.1	2	0.230	96.3
Methane	CH4	1	4	0	- 17.9	2	0.443	93.9
Acetic acid	$C_2H_4O_2$	2	4	2	- 116.4	1	0.475	94.1
Ethane	C_2H_6	2	6	0	- 20.2	1.5	0.771	92.4
Ethylene	C_2H_4	2	6	2	- 108.6	1.5	0.418	95.2
Ethanol	C_2H_6O	2	6	1	- 66.2	1.5	0.608	93.7
Pentene	C_5H_{10}	5	10	0	- 5.0	1	1.595	90.5

Fuel	$C_nH_mO_z$	Calculated thermo-neutral O_2/fuel ratios (x_0) and maximum theoretical efficiencies for various fuels						
		n	m	z	ΔH_f (kcal/gmol)	$m/2n$	x_0	Efficiency (%)
Pentane	C_5H_{12}	5	12	0	- 35.0	1.2	1.814	91.5
Cyclo-hexane	C_6H_{12}	6	12	0	- 37.3	1	2.143	90.7
Benzene	C_6H_6	6	6	0	11.7	0.5	1.784	88.2
Toluene	C_7H_8	7	8	0	2.9	0.57	2.161	88.6
Iso-octane	C_8H_{18}	8	18	0	- 62.0	1.13	2.947	91.2
Gasoline	$C_{7.3}H_{14.8}O_{0.1}$	7.3	14.8	0.1	- 53.0	1.01	2.613	90.8

2.2.2.1 Methanol Decomposition (MD)

Methanol decomposition is the basic method to generate hydrogen from the reverse of methanol synthesis reaction. It can produce hydrogen and carbon monoxide, as shown in Equation (2.10). However, this reaction produces high content of CO; therefore, it is more pollution and not appropriate for fuel cell applications.

MD reaction : $CH_3OH \leftrightarrow CO + 2\ H_2$ $\Delta H^o_{298} = 92.0$ kJ/mol (2.10)

2.2.2.2 Partial Oxidation of Methanol (POM)

Partial oxidation of methanol is an exothermic reaction that methanol reacts with oxygen to produce hydrogen and carbon dioxide according to Equation (2.11).

POM reaction : $CH_3OH + (1/2)O_2 \rightarrow CO_2 + 2H_2$ $\Delta H^o_{298} = -\ 192.0$ kJ/mol (2.11)

2.2.2.3 Methanol Steam Reforming (MSR)

Methanol steam reforming is an endothermic reaction that the methanol reacts with water to produce hydrogen and carbon dioxide according to Equation (2.12). MSR can produce high yield of hydrogen.

MSR reaction : $CH_3OH + H_2O \rightarrow CO_2 + 3H_2 \quad \Delta H^{o}_{298} = 49.7$ kJ/mol (2.12)

2.2.2.4 Oxidative Steam Reforming of Methanol (OSRM)

A combination of steam reforming and partial oxidation of methanol referred to the oxidative steam reforming of methanol (OSRM). The OSRM reaction is a mixture of methanol, water and air as follows in Equation (2.13).

OSRM reaction : $CH_3OH + 0.5H_2O + 0.25O_2 \longrightarrow CO_2 + 2.5H_2$

$\Delta H^{o}_{298} = -71.4$kJ/mol (2.13)

The advantages of the OSRM reaction are (Velu and Suzuki, 2003) :

1) The reaction can be operated at lower temperature than that of the SRM reaction.

2) Since the heat necessary for the endothermic SRM reaction is supplied in situ by the exothermic POM reaction, an external heat supply can be avoided.

3) Easy start-up of the fuel processor.

4) The mild exothermicity of the reaction avoids hotspot operation, which usually accompanies the POM reaction.

5) The reaction produces H_2 with very low outlet CO levels compared to that obtained in the SRM reaction.

6) Under optimized operating conditions the reaction produces close to 3 mol of H_2 from 1 mol of methanol.

7) Owing to the above reasons, the overall cost of the fuel processor unit can be minimized.

2.3 CO Removal

The hydrogen-rich stream from hydrogen production generally contains 40–60% H_2, 1–3% CO, 20% CO_2, and N_2 as the remainder where CO is the specie that affect on the efficiency of fuel cell. Figure 2.6 shows the effect of CO in poisoning the Pt anode catalyst. Small amount concentration of CO (20 ppm) will cause at least a 50% loss in efficiency in the medium-current density range (Gray and Frost, 1998). CO will adsorb and block on the active sites. In order to obtain the high performance of fuel cell, separation and purification of H_2 are necessary. There are various techniques to improve the reformate gas such as water-gas shift (WGS), membrane, selective CO oxidation, etc.

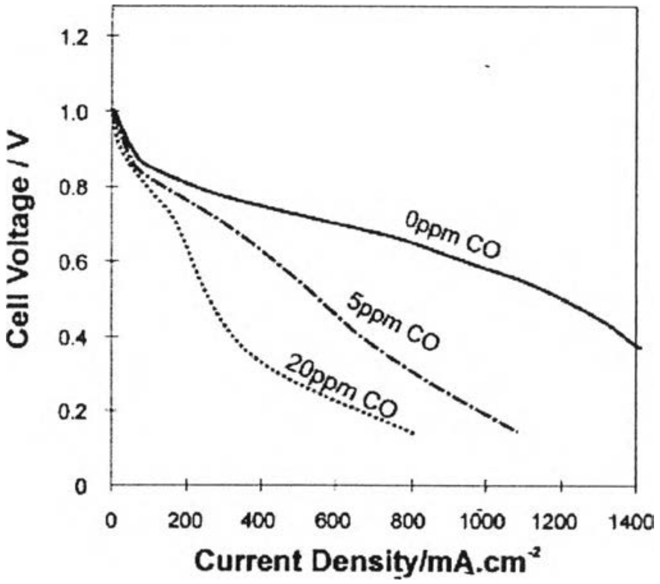

Figure 2.6 Anode poisoning by CO in reformate. (Gray and Frost, 1998).

2.3.1 Water-Gas Shift (WGS)

The water-gas shift is the reaction for removing CO and converting to CO_2 and additional H_2, as shown in Equation (2.14). WGS is moderately exothermic reaction which it flavors low temperature for high CO removal.

WGS reaction : $H_2O + CO \leftrightarrow H_2 + CO_2$ $\Delta H^{o}_{298} = -41.1$ kJ/mol (2.14)

The equilibrium conversion of CO depends on the reaction temperature; therefore, at lower temperature may not active enough to achieve the chemical equilibrium. From thermodynamic, at high temperatures the conversion is equilibrium limited and it is also limited by kinetic at low temperatures. The reduction of CO to acceptable concentration relates to high and low temperature where the high temperature (254–450 °C) can reduce to 3–4% of CO. Then the low temperature reaction (200–300 °C) can reduce the CO content to 0.5–1% (Trimm, 2005). However, it can operate only single temperature WGS reactor. At low-temperature WGS activity, Pt–group metals (PM), Au, or Cu are suitably added in small amounts that vary from 1 to 10 weight percent (wt %) (Fu *et al.*, 2003). For Fe–Cr catalysts, it has been developed for high temperature WGS (Natesakhawat *et al.*, 2006). Addition of CuO, CoO, and ZnO (5 wt.%) to Fe–Cr catalysts, it was found that Cu–promoted could be improved the activity of Fe–Cr catalysts and it exhibited the high activity at 380 °C (Andreev *et al.*, 1986).

2.3.2 Preferential CO Oxidation (PROX)

The most effective technique for CO clean-up is preferential CO oxidation (PROX) or selective CO oxidation. PROX can achieve almost 100% CO conversion with minimal H_2 oxidation and it operates at low temperature (100–150 °C). This reaction can reduce amount of CO to below 10 ppm before entering to the PEMFC (Park *et al.*, 2009) and the flow diagram of PROX is shown in Figure 2.7. The following reactions (2.15–2.16) can occur in the PROX system.

CO oxidation reaction : $CO(g) + (1/2)O_2(g) \rightarrow CO_2(g)$

$$\Delta H^{o}_{298} = -282.98 \text{ kJ/mol} \qquad (2.15)$$

H_2 oxidation reaction : $H_2(g) + (1/2)O_2(g) \rightarrow H_2O(g)$

$$\Delta H^{o}_{298} = -241.82 \text{ kJ/mol} \qquad (2.16)$$

Both reactions are highly exothermic and flavor to operate at low temperature. There are two competitive reactions in PROX reactor. The desired reaction is CO oxidation, as shown in Equation (2.15), whereas the H_2 oxidation should be avoided, as shown in Equation (2.16). Comparison the two reactions, the heat of reaction for CO oxidation is higher than that of H_2 oxidation, which could be made that CO oxidation is favored than H_2 oxidation. Figure 2.7 shows the purification process by PROX.

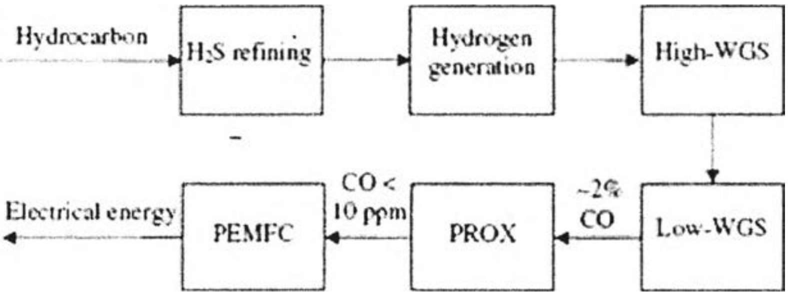

Figure 2.7 Flow diagram of hydrogen purification by CO-PROX (Mishra and Prasad, 2011).

2.3.3 Membrane

Membrane is the one method that uses for separation and purification hydrogen by a physical barrier according to a schematic of the semipermeable membrane separation process, as shown in Figure 2.8. The driving force is often pressure or concentration gradient across the membrane. There are various types of membranes which can be classified into polymeric, metallic, and inorganic membranes. Among of them, the Pd metal has the ability as the material for hydrogen separation (Ockwig and Nenoff, 2007). For high efficiency of membranes, they should have high separation, selectivity, permeability, stability, as well as durability.

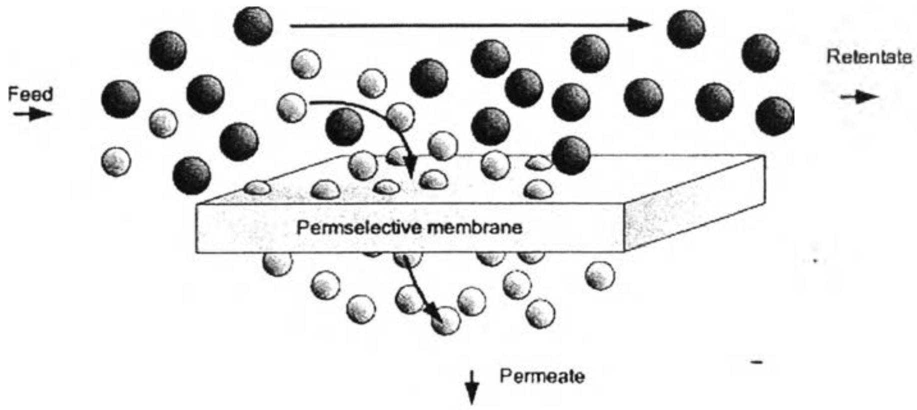

Figure 2.8 Simplified concept schematic of membrane separation (Lu *et al.*, 2007).

2.3.4 CO Methanation

Another method of CO removal from hydrogen gas mixture is CO methanation, as illustrated in Equation (2.17). CO methanation is highly exothermic reaction and it does not require the additional gas as oxygen (air). However, the disadvantage of this removal is that it consumes three moles of hydrogen in one mole to convert every one mole of CO.

$$CO(g) + 3H_2(g) \rightarrow CH_4(g) + H_2O(g) \qquad \Delta H^o_{298} = -205.813 \text{ kJ/mol} \qquad (2.17)$$

CO methanation is used over different supported metal catalysts for CO removal in hydrogen-rich gas stream. For example, Ni/ZrO_2 and Ru/TiO_2 are the most effective catalysts by decreasing a concentration of CO from 0.5% to 20 ppm though the CO methanation (Takenaka *et al.*, 2004).

2.4 Catalysis by Gold

Gold has long been considered as the active of metal catalyst for many chemical reactions and Haruta was the first researcher to show that gold was the marvelous catalyst at ambient temperature (Haruta *et al.*, 1987). Gold catalyst has unique property (Chen and Goodman, 2006). If the diameter of gold is less than 5 nm, it had been found to be active for many reactions as low temperature CO oxidation (Haruta *et al.*, 1987), propylene epoxidation (Chou and McFarland, 2004), water-gas shift reaction (Fu *et al.*, 2003), NO reduction/dissociation (Ueda and Haruta, 1999), hydrogenation (Bond *et al.*, 1973), SO_2 dissociation (Rodriguez *et al.*, 2002) and selective oxidation (Bianchi *et al.*, 2000). Moreover, many researches revealed the application of gold in various areas such as chemical processing, pollution control, sensors, and fuel cell technology.

2.4.1 Physical and Chemical Properties of Gold

To achieve the gold catalyst, it is supposed to know the physical and chemical properties of gold. Gold has a number of interesting of physical properties, as shown in Table 2.5. It is malleable, ductile, as well as heavy metal. It has considerable better electrical conductivity as compared with platinum. Besides, it has ability to resist the corrosion than other metals (Cameron *et al.*, 2003).

Table 2.5 Physical properties of gold
(http://chemistry.about.com/od/elementfacts/a/gold.htm)

Property	Gold (Au)
Atomic Number	79
Atomic Weight	196.9665
Electron Configuration	$[Xe]6s^1 4f^{14} 5d^{10}$
Density (g/cc)	19.3
Melting Point (°K)	1337.58
Boiling Point (°K)	3080
Appearance	soft, malleable, yellow metal
Atomic Radius (pm)	146

Property	Gold (Au)
Specific Heat (@20° C J/g mol)	0.129
Fusion Heat (kJ/mol)	12.68
Evaporation Heat (kJ/mol)	~340
First Ionizing Energy (kJ/mol)	889.3
Oxidation States	3, 1 (The oxidation states -1, +2 and +5 exist but are rare.)
Lattice Structure	Face-Centered Cubic (FCC)
Lattice Constant (Å)	4.080

The chemistry and physics of gold is dominated by relativistic effect. This relativistic effect consists of three components, as s-orbital and, to a smaller extent, p-orbital contraction, spins orbit coupling, and f-orbital expansion. The unique yellow color of gold derived from the relativistic effect. Relativistic effects leaded to increased Van der Waals interaction and increased physisorption energies on gold surfaces (Schwerdtfeger, 2002). Gold catalyst was very reactive, especially in the gas phase, and Au (I) and Au (III) are the most stable for gold. In study of gold systems were best for some reactions has been demonstrated both in the synthesis of vinyl chloride from acetylene and in the low temperature oxidation of CO.

2.5 Activity of Supported Gold Catalyst

There are many factors can be used to increase the activity of gold catalysts in preferential CO oxidation reaction such Au particle size, oxidation state, nature of the support, length of the perimeter interface between gold particles and the support, and preparation method.

2.5.1 Size of Gold Particle

It is generally agreed that the catalytic activity of gold catalysts depends on the particles size of gold and it has been found that gold particles of less than 5 nm diameter is active for low temperature CO oxidation (Haruta *et al.*, 1989). They suggested that the particles size distributed to the activity by limiting the availability of sites for oxygen adsorption. Due to the sites were located at the interfacial perimeter around the metal particles. For example, Au/TiO_2 catalysts were prepared with the different methods for PROX of CO in H_2 stream (Sangeetha *et al.*, 2009). It was found that the catalyst prepared by photo-deposition method exhibited higher CO conversion and CO selectivity than those prepared by the deposition-precipitation method. The differences in activity could be attributed to the difference in chemical state of gold particles and the particle size of gold. The catalyst prepared by photo-deposition had a smaller particle size (1.5 nm). It had higher CO conversion at low temperature (<50 °C). However, the CO conversion and CO selectivity is low between 50 and 100 °C.

2.5.2 Nature of the Active Site and Reaction Mechanism

The nature of the active site and reaction mechanism for CO oxidation are also the points of interesting in many researches. The active catalysts generally have 2–5 nm Au crystallites and have a variety of sizes to give a high performance (Oh *et al.*, 2002). Figure 2.9 shows a model of active site for CO oxidation, which suggests an ensemble of metallic Au atoms and Au cations with hydroxyl ligands (Costello *et al.*, 2002). The OH–group proposes to associate with Au cation and Au^+ component seems to have more preferable than Au^{3+} component.

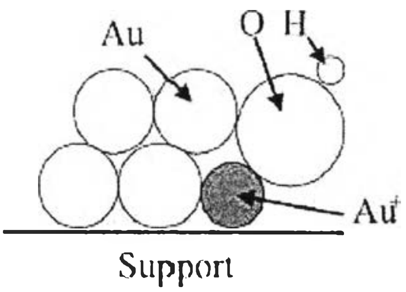

Figure 2.9 Schematic drawing of an active site for CO oxidation (Costello *et al.*, 2002).

The active site also involves to the perimeter of the gold particles or the gold support interface (Grisel *et al.*, 2002). For Au/ γ–Al_2O_3 for room temperature CO oxidation, a reaction mechanism model of the active site is shown in Figure 2.10. The react ion occurs by insertion of an adsorbed CO into the Au^+–OH bond to form a hydroxycarbonyl. The possible reaction can be divided to pathways for the hydroxycarbonyl. The first pathway is that hydroxycarbonyl is oxidized to a bicarbonate, which is then decarboxylated to Au^+–OH^- and CO_2. Another one is decarboxylation of the hydroxycarbonyl to CO_2 and Au–H, and the latter is oxidized to Au^+–OH^-. However, the reaction mechanism would be different depending on the type of support (Haruta, 2004).

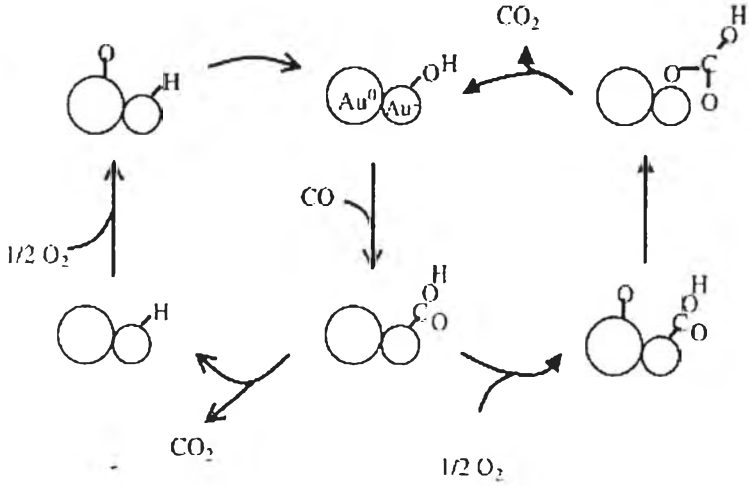

Figure 2.10 Proposed mechanism of CO oxidation on supported Au catalyst (Costello *et al.*, 2002).

The possible mechanism reaction for the CO oxidation in the presence of H_2 is shown in Figure 2.11 and it could be accounted for the 3 steps: (1) the absence of a support effect on the H_2 oxidation rate, (2) the absence of a support effect on the CO oxidation rate in the PROX reaction, (3) a support-dependent hydrogen effect on the CO oxidation rates (Rossignol *et al.*, 2005). It is an Eley-Rideal-type mechanism and the dissociation of O_2 does not happen on gold particles because it could be involved in the oxidation of H_2 that is dissociation of H_2 on the gold particle and then react with O_2 molecule from the gas phase. The PROX reaction will proceed on the gold particles, which it react between an adsorbed CO molecule and H–O–O species to form CO_2.

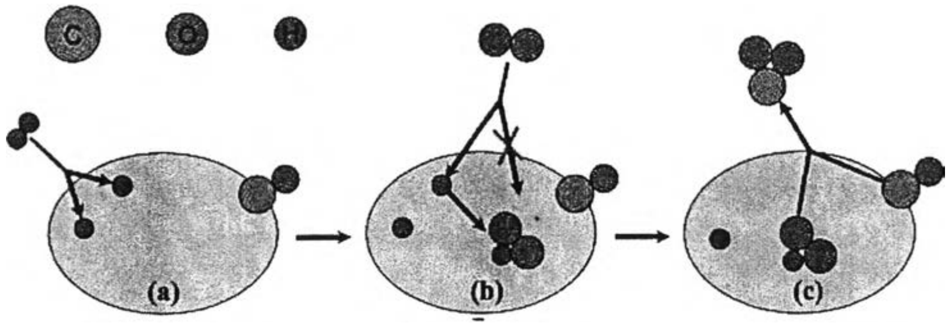

Figure 2.11 Possible mechanism involved in the oxidation of CO in the presence of H_2, including (a) adsorption of CO and H_2 and dissociation of H_2 on a gold particle, (b) reaction of gas phase O_2 with adsorbed H atom and (c) reaction of the resulting oxidizing species with adsorbed CO to give CO_2 (Rossignol *et al.*, 2005).

2.5.3 Effect of Support

The support material plays an important role for the activity of a gold catalyst. It has been reported that gold on reducible oxide has high activities for CO oxidation (Overbury *et al.*, 2004) which could be partially reduced, such as TiO_2, Fe_2O_3, and Co_3O_4. Haruta and co-workers studied the novel gold catalysts for low temperature of CO oxidation and H_2 oxidation (Haruta *et al.*, 1989). They were prepared via co-precipitation from an aqueous solution of $HAuCl_4$, and the nitrates of various transition metals. From all of them, $Au/\alpha\text{–}Fe_2O_3$, Au/Co_3O_4, and Au/NiO were highly active for CO oxidation because the combination of gold and transition metal oxides enhanced the catalytic activities. When compared with unsupported Au powder and supported Au catalyst (Au/TiO_2) for CO oxidation, it was found that the Au/TiO_2 has more higher rate constant of CO oxidation than Au powder (Iizuka *et al.*, 1999). The supported gold catalysts on different metal oxides (TiO_2, ZnO, ZrO_2, and SiO_2) were studied and found that Au/TiO_2 exhibited the highest activity of CO oxidation than other supports due to the Au particles formed on TiO_2 were smaller than those formed on any other supports, and were in the range commonly associated with gold catalytic activity (Chou *et al.*, 2004). It suggested that the effect of support may influence on the activity through the mechanisms, stabilization of particles, formation of active oxygen reactant intermediate and stabilization of Au particles (Overbury *et al.*, 2004). There are several roles of support in activating nanosized of gold particles; it had been proposed that the defects on the support might affect on the adsorption energy and the electronic structure adlayer (Chen and Goodman, 2006). In case of Au/Fe_2O_3 was more active than Au/TiO_2, probably that FeO_x is more easily reducible support and disordered structure to facilitate the formation of anion vacancies near gold particle (Wu *et al.*, 2004). The results showed that the catalyst had high activity and long life time for CO oxidation at ambient temperature, including resistant to moisture and high CO_2 concentration. The model catalysts, Au/Al_2O_3, Au/ZrO_2, and Au/TiO_2, were investigated for CO oxidation both in absence and presence of H_2 (Rossignol *et al.*, 2005). They were produced by laser vaporization of a metallic gold rod followed by deposition of the formed clusters onto the support powders. The results found that they had the similar activity for all three systems (Au/Al_2O_3 << Au/ZrO_2 < Au/TiO_2).

Gold-based catalyst is also effective for CO oxidation in the presence of H_2 which is based on Haruta's demonstration (Haruta *et al.*, 1987) and various reducible metal oxide supports are the key role that can supply oxygen to facilitate the reaction. Nanosized Au supported on CeO_2 and that supported on MnO_2 have been reported to be good catalysts in preferential oxidation of CO in a H_2 stream (PROX), owing to their high activity and selectivity to CO oxidation, and their resistance toward H_2O and CO_2 (Chang *et al.*, 2006). Au catalysts on different types of support (TiO_2, Co_3O_4–CeO_2 mixed oxide, CeO_2, Co_3O_4, Al_2O_3) prepared by deposition-precipitation method were compared for CO oxidation and preferential oxidation of CO in H_2 stream (Liotta *et al.*, 2010). Figure 2.12 shows the degree of CO conversion of various Au supported catalysts in the PROX reaction. It revealed that Au/Co_3O_4–CeO_2 and Au/CeO_2 showed the same high CO oxidation activity in the presence of H_2 and it could be ordered the activity to Au/Co_3O_4–CeO_2 > Au/CeO_2 > Au/TiO_2 > Au/Co_3O_4 > Au/Al_2O_3. This was because Co_3O_4–CeO_2 and CeO_2 reducible oxides stabilized Au^{3+}/Au^{+} ionic species and produced active gold catalysts for the reaction. In addition, the presence of oxygen vacancies made them high activity and good selectivity.

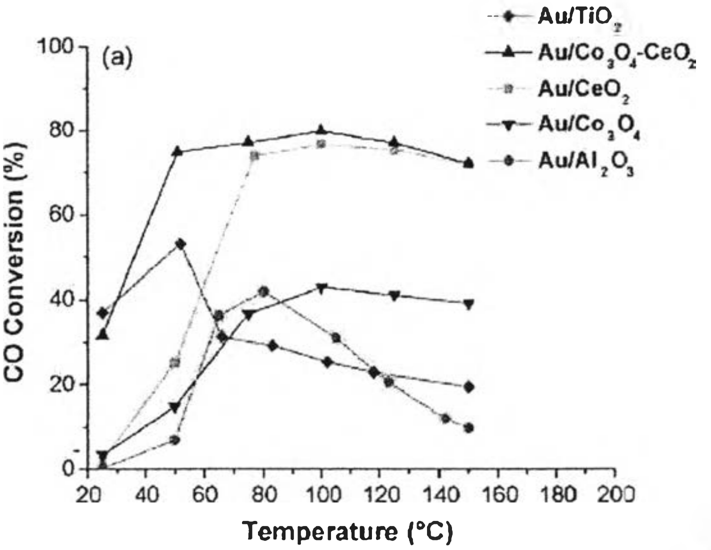

Figure 2.12 Effect of support type on CO conversion over Au supported catalysts. Reaction mixture: 70% H_2 + 1% CO + 1% O_2, He as balance (Liotta *et al.*, 2010).

CeO_2 is one of the most attractive oxides with unique catalytic properties for PROX due to its distinct defect chemistry and the ability to exchange lattice oxygen with the gas phase. These properties include the promotion of the precious metal dispersion, the enhancement of the catalytic activity at the interfacial metal-support sites and the promotion of CO removal through oxidation employing lattice oxygen (Trovarelli, 1996). Nanosized gold supported on CeO_2 has been reported to be a good catalyst in PROX in H_2 stream (Yi *et al.*, 2010). Luguna *et al.* (2010) evaluated the structural effects caused by doping element on the CeO_2 network which a series of Au catalysts supported on CeO_2 with 10% mol of Zr, Zn, and Fe for PROX (Laguna *et al.*, 2010). The catalysts were prepared by a pseudo sol-gel method throughout the thermal decomposition of the corresponding metallic propionates. Doping with Zr and Fe caused the solid solution that enhanced oxygen-storage properties but it occurred the surface segregation in case of Zn. The catalytic activity was highly promoted by Au in all cases, being the doped gold catalysts more active than Au/CeO_2 at low temperature (Figure 2.13) and Au/CeFe10 catalyst showed the highest reducibility percentage. However, doping with Zr enhanced the formation of surface oxygen vacancies more than Zn and Fe. It also increased the dispersion of gold nanoparticles for Au/CeZr10 catalyst. Therefore, CeO_2-

modified mixed oxides improved the activity of catalyst by increasing interaction metallic particle at surface and promoting metallic dispersion.

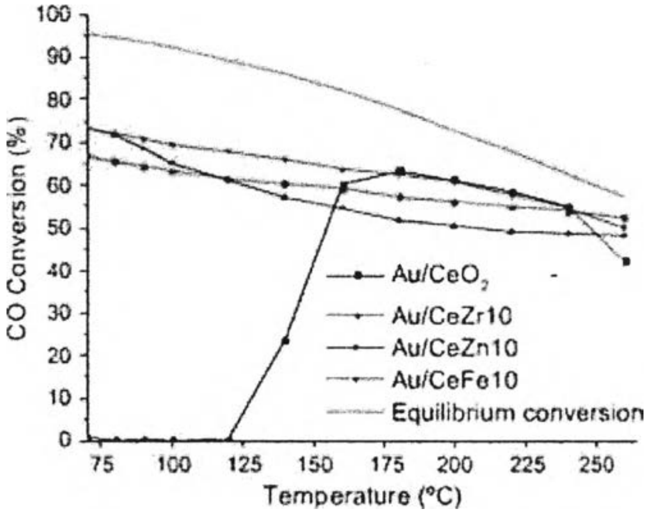

Figure 2.13 CO conversion during the PROX reaction over the studied gold catalysts (Laguna *et al.*, 2010).

2.5.4 Preparation Methods

It is an essential to select a suitable method for preparing the catalysts and there are variety methods such as impregnation, co-precipitation, photo-deposition, urea-nitrate combustion method, and etc. Table 2.6 shows a comparative study of recent literature in various preparation methods for PROX. It was found that the activity of Au catalyst depends very strongly on the preparation methods. Among the preparation methods, co-precipitation is the most useful and simplest method of preparation. In study of Au/CeO$_2$ for PROX, it was revealed that co-precipitation methods exhibited the highest activities with 98% CO conversion when compared to impregnation and sol-gel methods (Luengnaruemitchai *et al.*, 2004). For Au over CeO$_2$–CoO$_3$ catalysts prepared via deposition-precipitation, it also had 91% CO conversion and 51% selectivity at 80 °C (Wang *et al.*, 2008). A comparative study was investigated in photo-deposition and deposition-precipitation methods in a series of Au/TiO$_2$ catalysts for CO oxidation in the presence of H$_2$. It was found that a high gold dispersion and narrow size distribution was obtained for both photo-deposition and deposition-precipitation methods. The photo-deposition method showed higher CO conversion and CO selectivity than those prepared by the deposition-precipitation method (Sangeetha *et al.*, 2009).

Table 2.6 Recent literature review at a glance on PROX of CO in H_2 rich gases for gold based catalysts (Mishra and Prasad, 2011)

Catalyst	Preparation method	Operating parameter	Remarks
1% Au/CeO_2	a. Impregnation b.Co-precipitation c. Sol-gel	1% CO, 0.5–2%O_2 2%CO_2, 2–6% H_2O, 40% H_2–He, 110 °C, 30,000 ml /g h.	98% conversion, stable, co-precipitation Au/CeO_2 exhibiting the highest activities. No significant effect of H_2O & CO_2 on CO selectivity.
Pt–Au bimetallic catalyst	a. Impregnation on sol-gel b. Single step sol-gel	0.5–1%CO, 1% O_2, 40% H_2, 0–10% H_2O, and 0–25% CO_2, 50–90 °C	90% conversion, Catalyst prepared by single step sol-gel method exhibited an excellent catalytic activity for PROX of CO.

Catalyst	Preparation method	Operating parameter	Remarks
Nano-gold catalysts	Photo-deposition (PD)	1.33%CO, 1.33%O_2, 65.33%H_2–He, 50 °C, 30,000 ml/g h	99% conversion, not stable, PD method facilitates to prepare gold particles as small as 1.5 nm. Very active and selective in PROX.
Au/CeO_2–Co_3O_4	Deposition-precipitation	1%CO,1% O_2, 50% H_2, 80 °C, 30,000 ml/g h	91% conversion shows higher activity than Au/Co_3O_4, Au/CeO_2 & CeO_2–Co_3O_4 composite oxide.
Au/doped Ceria	Deposition-precipitation	1% CO, 1.25% O_2, 50% H_2, 15% CO_2, 10% H_2O–He, 50 °C	96.6 % conversion, improved tolerance towards the presence of CO_2 and H_2O in the PROX.

Catalyst	Preparation method	Operating parameter	Remarks
Au/ZnO nano-catalysts	Ultrasonication Double impregnation. Washing dry	5% CO, 10% O_2–He, 200 °C	100% conversion, best results obtained with ZnO prepared by chemical vapour-deposition with Au loaded by ultrasonication
Cu–Au/Al_2O_3 catalysts	Deposition-precipitation	1% CO,0.5–1.5% O_2, 30% H_2,0–30% CO_2, 0–10% H_2O –He, 50 °C	97% conversion, H_2O positively effects CO conversion & selectivity, CO_2 diminishes the same
Au/ZnO Au/ZnOFe$_2$O$_3$	Photo-deposition under UV-light	1% CO, 1% O_2, 40 % H_2, 0–10% CO_2, 10 % H_2O–He, 50 °C	100% conversion, catalysts exhibited excellent activity, even in presence of CO_2 & H_2O