



CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Fuel cells

2.1.1 The Basics of Fuel Cell

Fuel cells are electrochemical devices converting chemical energy of H_2 fuel and O_2 from the air to water and generating electricity, and heat without combustion. Fuel cells offer a clean and highly efficient way to produce electricity, and heat. However, fuel cell is electrochemical reaction thus high temperature is not required to achieve high efficiency, and fuel cells are free from Carnot's law of efficiencies.

2.1.2 Type of Fuel Cells

There are several different fuel cell types. Fuel cells are usually named according to their electrolyte and categorized according to their operation temperature. For low-temperature fuel cells operate at temperatures below $200^\circ C$ such as Polymer Electrolyte Membrane Fuel Cell (PEMFC), Direct Methanol Fuel Cell (DMFC), Phosphoric Acid Fuel Cell (PAFC), and Alkaline Fuel Cell (AFC). Moreover, high-temperature fuel cells operate at temperatures between $600^\circ C$ and $1000^\circ C$ such as Solid Oxide Fuel Cell (SOFC), and Molten Carbonate Fuel Cell (MCFC).

Figure 2.1 depicts that fuels can be fed into the anode of the high-temperature fuel cells (SOFC and MCFC) directly. Nevertheless, the separated reformer compartments can manage the temperature of the stack, which are thermally integrated within the stack to produce a mixture of fuel and syngas (H_2 and CO). PAFC and PEMFC are the low-temperature fuel cells whose external reformers are required to maintain the operating temperature that the fuel is consumed in. Moreover, dilution of the H_2 fuel reduces performance of the cells, resulting in significant efficiency losses compared with operation on pure H_2 . It should be noted that the AFC stack cannot be operated on reformat fuels because of the presence of CO_2 in these gases.

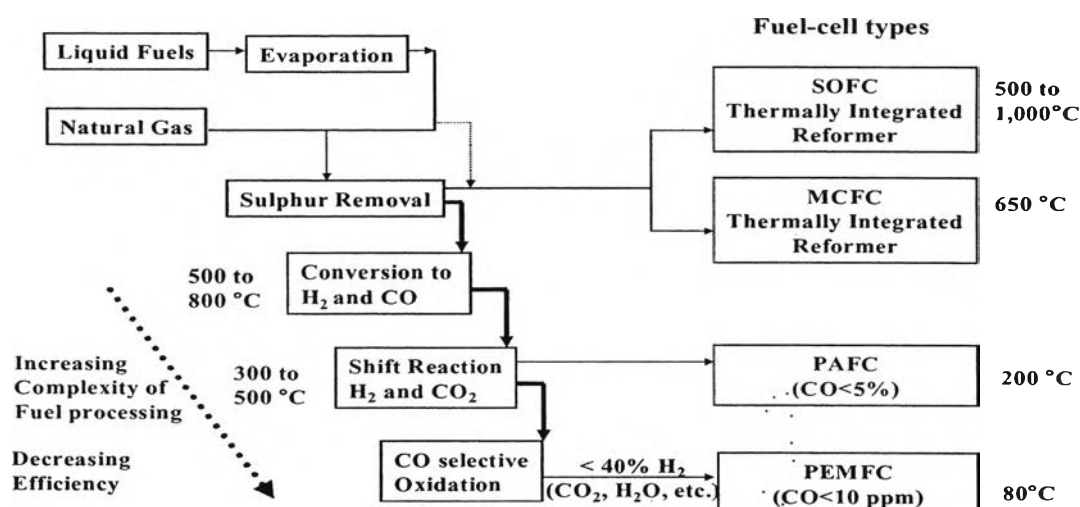


Figure 2.1 Fuel-cell types and fuel processing. (Materials for fuel-cell technologies Brian C. H. Steele and Angelika Heinzl, *Nature* 414, 345–352).

The oxidation reaction takes place at the anode (+) and involves the liberation of electrons (for example, $\text{O}^{2-} + \text{H}_2 \rightarrow \text{H}_2\text{O} + 2\text{e}^-$ or $\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$). These electrons travel around the external circuit producing electrical energy by means of the external load, and arrive at the cathode (-) to participate in the reduction reaction (for example, $1/2\text{O}_2 + 2\text{e}^- \rightarrow \text{O}^{2-}$ or $1/2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}$). It should be noted that as well as producing electrical energy and the reaction products (for example, H_2O and CO_2), the fuel-cell reactions also produce heat. The reaction products are formed at the anode of SOFC, MCFC and AFC types, and at the cathode for PAFC and PEMFC types. This difference has implications for the design of the entire fuel-cell system, including pumps and heat exchangers. To maintain the composition of the electrolyte component in the MCFC system, CO_2 has to be recirculated from the anode exhaust to the cathode input. Additionally, the composition of the polymeric-membrane electrolyte has to be carefully controlled during operation by an appropriate 'water management' technology. The comparison of five fuel cells can be concluded Table 2.1.

Table 2.1 Comparison of five fuel cell technologies (Sharon Thomas and Marcia Zalbowitz at Los Alamos National Laboratory in Los Alamos, New Mexico)

Fuel Cell	Electrolyte	Operating Temperature (°C)	Electrochemical Reactions
Polymer Electrolyte/ Membrane (PEM)	Solid organic polymer poly-perfluorosulfonic acid	60–100	Anode: $\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$ Cathode: $1/2 \text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}$ ----- Cell: $\text{H}_2 + 1/2 \text{O}_2 \rightarrow \text{H}_2\text{O}$
Alkaline (AFC)	Aqueous solution of potassium hydroxide soaked in a matrix	90–100	Anode: $\text{H}_2 + 2(\text{OH})^- \rightarrow 2\text{H}_2\text{O} + 2\text{e}^-$ Cathode: $1/2 \text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow 2(\text{OH})^-$ ----- Cell: $\text{H}_2 + 1/2 \text{O}_2 \rightarrow \text{H}_2\text{O}$
Phosphoric Acid (PAFC)	Liquid phosphoric acid soaked in a matrix	175–200	Anode: $\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$ Cathode: $1/2 \text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}$ ----- Cell: $\text{H}_2 + 1/2 \text{O}_2 \rightarrow \text{H}_2\text{O}$
Molten Carbonate (MCFC)	Liquid solution of lithium, sodium and/ or potassium carbonates, soaked in a matrix	600–1000	Anode: $\text{H}_2 + \text{CO}_3^{2-} \rightarrow \text{H}_2\text{O} + \text{CO}_2 + 2\text{e}^-$ Cathode: $1/2 \text{O}_2 + \text{CO}_2 + 2\text{e}^- \rightarrow \text{CO}_3^{2-}$ ----- Cell: $\text{H}_2 + 1/2 \text{O}_2 + \text{CO}_2 \rightarrow \text{H}_2\text{O} + \text{CO}_2$ (CO_2 is consumed at cathode and produced at anode)
Solid Oxide (SOFC)	Solid zirconium oxide to which a small amount of yttria is added	600–1000	Anode: $\text{H}_2 + \text{O}^{2-} \rightarrow \text{H}_2\text{O} + 2\text{e}^-$ Cathode: $1/2 \text{O}_2 + 2\text{e}^- \rightarrow \text{O}^{2-}$ ----- Cell: $\text{H}_2 + 1/2 \text{O}_2 \rightarrow \text{H}_2\text{O}$

2.1.3 Polymer Electrolyte Membrane Fuel Cell (PEMFC)

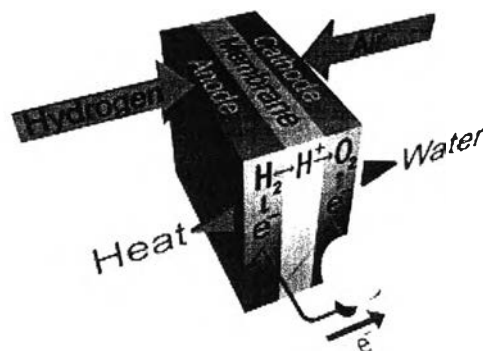
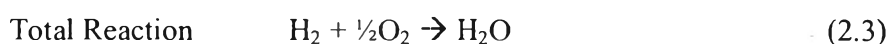
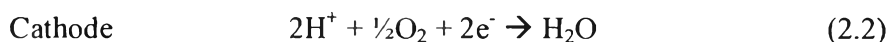
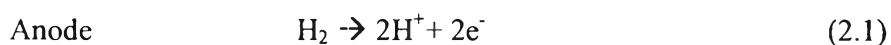


Figure 2.2 Diagram of fuel cell.

(http://www.che.sc.edu/centers/PEMFC/about_fuelcell_1.html)

In Polymer Electrolyte Membrane Fuel Cell (PEMFC) is shown in Figure 2.2. H_2 fuel is oxidized on the anode which hydrogen is split into protons and electrons on the anode and then protons are transported through the electrolyte to the cathode, and electrons move through an external circuit. For O_2 reduced on the cathode which protons, electrons and oxygen combined to produce water and heat. Equations 2.1, 2.2, and 2.3 illustrate the fuel cell operation.



From above equation a four electron reduction process occurs in a multi-step sequence. Pt is a catalyst, capable of generating high rates of O_2 reduction at low temperature, typically 80°C .

2.1.4 Processing Hydrocarbon Fuels into Hydrogen

Since hydrogen is difficult to store in a vehicle, the processors of fuel need to convert the hydrocarbon fuel (methanol or gasoline) to a H₂ rich gas so as to use in the fuel cell. The steam reforming is a conventional technology used to convert methanol to H₂ rich gas, this technology involves in the reaction of steam (water) and pre-vaporized methanol at 200°C. The produced gasses are H₂, carbon dioxide (CO₂), carbon monoxide (CO), and excess steam (water) which passes through a shift reactor to convert CO to CO₂ as well as additional H₂ by feeding water and using catalysts. After that the third reactor called Preferential Oxidation (PROX) reactor which injecting the air, oxygen will react with remaining CO over the catalysts to convert to CO₂. The final gasses will contain rich H₂, CO₂, nitrogen (N₂), and traces of CO.

2.2 Production of Hydrogen

One of the most perspective ways of drastic automotive pollution reduction is the transformation from internal combustion engines to electric ones powered by hydrogen fuel cells. However, there are many advantages and disadvantages for H₂ fuel.

The advantages of H₂ fuel are major source of clean, inexhaustible, efficient, and economical energies. While the disadvantages of H₂ fuel are hydrogen storage, transportation and filling connected with its extremely low density, and heavy explosion ability.

Steam reforming of natural gas is widely used in industry today which its offer an efficient, economical, and widely used process for hydrogen production, and provides near- and mid-term energy security and environmental benefits such as steam methane reforming (SMR), methanol steam reforming (MSR), and ethanol steam reforming (ESR).

2.2.1 Steam Methane Reforming (SMR)

Steam reforming of natural gas sometimes referred to as steam methane reforming (SMR) is the most common method to produce bulk hydrogen as

well as the hydrogen used in the industrial synthesis of ammonia. It is also the least expensive method. However, SMR process in large industrial plants for use in numerous applications, which it is a cleaner source than petroleum and according to its high content in hydrogen, the total CO₂ emitted in any process for the production of chemicals is lower than when carbon is used as a source—naphtha, heavy oil, methanol, and coal.

In addition, the methane molecule composing of a single C-atom surrounded by four H-atoms (CH₄), the sp³ hybridization of the atomic orbitals of carbon means that the C-H bonds are very strong. The converting CH₄ to the any other products are less thermodynamically stable than the CH₄ reactant and leading to the conversion to undesired products denoted as carbon oxide. Consequently, undesired products are necessary to remove by convert CO to CO₂ and H₂, water gas shift (WGS).

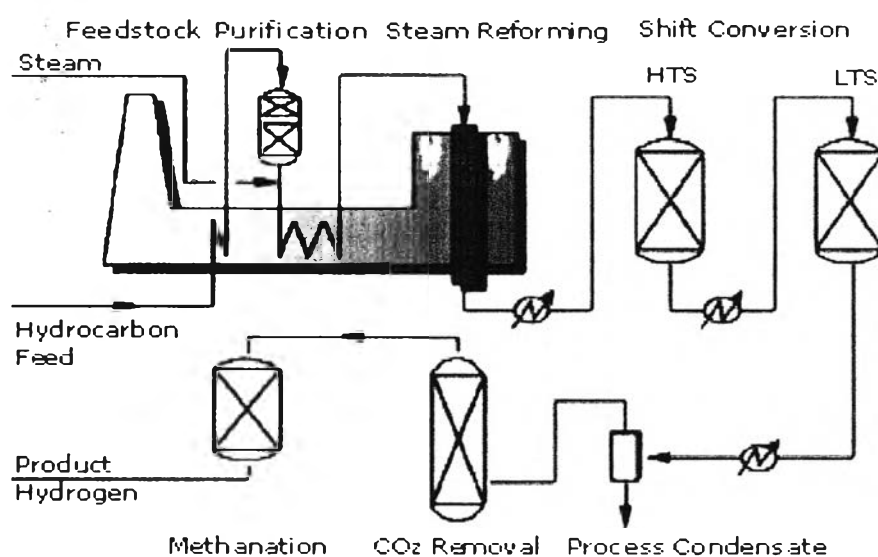


Figure 2.3 Steam methane reforming process.

(<http://www.getenergysmart.org/Files/HydrogenEducation/6HydrogenProductionSteamMethaneReforming.pdf>)

The steam methane reforming (SMR) process consists of the following two steps, as shown in Figure 2.3.

1 Reformation of Natural Gas

The first step of the SMR process involves methane reacting with steam (H_2O) at $750\text{--}800^\circ\text{C}$ over a nickel catalyst to produce a synthesis gas (syngas), a mixture primarily made up of H_2 and CO (Equation 2.4)



2 Shift Reaction

In the second step, known as a water gas shift (WGS) reaction, CO produced from the first reaction is reacted with steam over a catalyst to form H_2 and CO_2 . This process occurs in two stages, consisting of a high temperature shift (HTS) at 350°C and a low temperature shift (LTS) at $190\text{--}210^\circ\text{C}$.

There are two types of WGS catalysts which are commercially used. One is a HTS catalyst, which consists of oxides of iron and chromium and is used to reduce the carbon monoxide. The second one is a LTS catalyst that is copper on a mixed support composed of zinc oxide and aluminum oxide normally used to reduce the CO concentration.

Hydrogen produced from the SMR process includes some impurities such as CO_2 , CO , and hydrogen sulfide (H_2S). The SMR may be composed of a further purification depending on use such as feedstock purification removing sulfur (S) and chloride (Cl) and product purification removing CO .

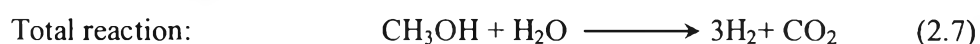
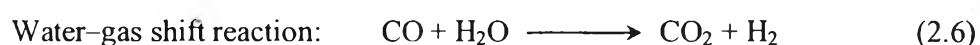
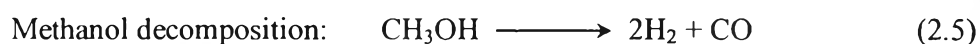
2.2.2 Methanol Steam Reforming (MSR)

Methanol fuel has some advantages over other liquid fuels such as gasoline, and diesel fuel. Liquid methanol can be produced by fermentation process. It is easily adaptable to the current infrastructure, transported and stored, and high hydrogen density. However, methanol as a fuel has some important disadvantages connected with its high toxicity, low availability on ordinary basis and coal-natural gas based production technology, which will lead to additional CO_2 emissions.

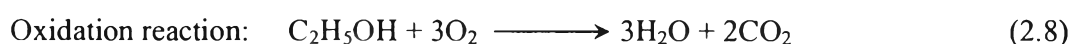
Currently, methanol steam reforming (MSR) process is the most favorable process of hydrogen production compared to the decomposition and partial oxidation of methanol, resulting from the ability to produce gas with CO_2 high con-

centration and CO₂ high selectivity. In addition, MSR process requires endothermic reaction with temperature lower than 100°C which provided from the catalytic burner device. Nevertheless, MSR requires temperature level about 200°C under sufficient catalyst for high conversion from the methanol to hydrogen.

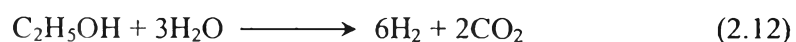
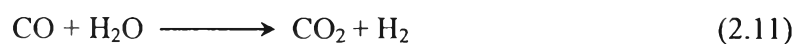
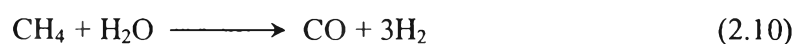
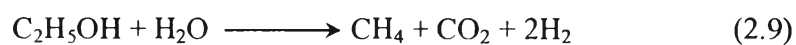
According to the catalytic reforming of methanol with steam, the well-known reactions involved in this process consist of methanol decomposition and WGS reactions.



Type of alcohol as a liquid fuel is ethanol. The advantages of ethanol are non-toxic liquid easily accessible in our daily life, high energy density, and ease off handling and the fact that it can be employed for producing hydrogen in order to use in fuel cells. There are two step reactions. The first step is the oxidation of fraction of the ethanol (Equation 2.8) which is fed into the catalytic reactor to generate the heat required for the steam reforming reaction as a second step (Equations 2.9—2.12):



Steam reforming reaction:



The side products of these reactions are CO, acetone, and methane etc. The catalyst for these reactions should have high oxidation activity coupled with ability of hydrocarbons activation. A further was step is required to remove the excess of CO.

2.3 CO Removal Methods

The purification step of the reformatè necessary to reduce the CO content in H₂-rich stream may involve both high and low temperature water gas shifts (WGS), followed by preferential CO oxidation reaction (PROX of CO).

2.3.1 Water Gas Shift (WGS) Reaction

The purpose of the WGS reaction is to increase H₂ yield by converting CO from the reformatè gas to CO₂ coupled with water, as shown in Equation 2.13.



The WGS reactor is an important auxiliary unit of the fuel processor. The water gas shift reaction is a reversible chemical reaction, in which CO and H₂ are favored at low temperature. The WGS reaction is a moderately exothermic chemical reaction ($\Delta H_{298}^\circ = -41 \text{ kJ mol}^{-1}$) and hence its equilibrium constant decreases with the temperature, and high conversions are favored by low temperatures (Figure 2.4). Due to the thermodynamic limitation of WGS reaction at high temperatures and at low temperatures it is kinetically limited, normally performed in two steps. In industry, WGS reaction is carried out at two temperature regimes, high temperature (400–500°C) and low temperature (200–300°C) shift reactions. It is well known that the metals like Pt and Pd are not work well in the WGS reaction because they are not easily oxidized by water. In general, the catalyst used in the WGS reaction is commercially available. The WGS reactors convert about 20% CO to 1% CO using the typical catalysts, which are Fe/Cr-based catalyst in the HT-water gas shift reaction and CuO/ZnO/Al₂O₃ catalyst in the LT-WGS.

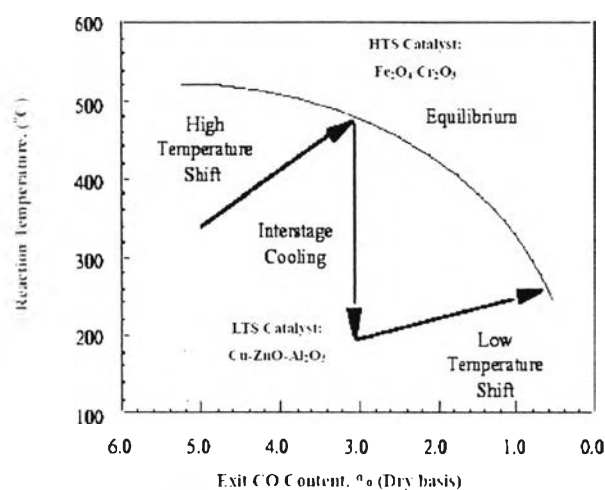


Figure 2.4 Schematic graph of water gas shift reaction (Twigg *et al.*, 1989).

The conventional Fe/Cr-based catalysts have the advantages of low cost, long life and resistant to sulfur, but they are not active below 350°C (Trimm, 2005). Afterward, the H₂-rich stream has to induce into the LT-WGS reactor further. Binary CuO–ZnO and ternary CuO–ZnO–Al₂O₃ and CuO–ZnO–Cr₂O₃ mixed oxide catalysts have been widely employed commercially in the LT-WGS reaction. However, after the LT-WGS reactor, the CO concentration in the H₂-rich stream which remains about 0.5–1%, is still too high for the PEMFC, thus PROX of CO reaction required to reduce CO is still needed for further study.

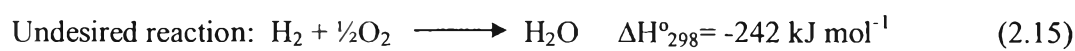
2.3.2 Preferential Oxidation or Selective Oxidation of CO

The steam reforming of alcohols and hydrocarbon typically produce hydrogen-rich gas containing some impurities such as carbon monoxide (CO)—a toxic gas—more than 100 ppm. The CO causes a physical deterioration of Pt-catalyzed anode in PEMFC at low temperature. Consequently, the numerous technique available for CO removal—e.g. pressure swing adsorption, catalytic methanation, Pd membrane separation, and preferential CO oxidation reaction (PROX of CO). However, PROX of CO seems to be the one of optimal methods to solve CO problem as a result of simple and economical technique under operating at low temperature range of 80 to 120°C. Many advantages of PROX have been reported, not only keeping the low operating cost, but also decreasing the CO content to the acceptance

level (<10 ppm) without the excess hydrogen consumption that occurs during catalytic methanation before the H₂-rich fuel can be fed into PEMFCs.

In addition, the catalyst for the PROX of CO must be effective in removing CO from a reformat gas. The most important requirements for the PROX catalysts are as follows (Zhao *et al.*, 2007):

- High CO oxidation rate at low temperatures
- High CO conversion (>99%) at a wide operating temperature range (80-200°C)
- High CO selectivity or the catalyst must not oxidize a significant quantity of H₂
- Good resistance to deactivation in the presence of H₂O and CO₂ in the reformat stream



Many researchers mainly focused on the improvement of the high performance catalyst for this process. The suitable catalyst should be active and very selective for CO oxidation at a relatively low temperature, while minimizing the hydrogen oxidation to water. Many different metals—Au, Pt, Ru, and Rh—based catalysts have been investigated for the PROX reaction. Pt-based catalysts are effectively catalyze CO to CO₂ at high temperatures (Avgouropoulos *et al.*, 2005), while Au-based catalysts present a great potential for achieving a high conversion at low temperatures, when the Au particle size is smaller than 5 nm. (Kahlich *et al.*, 1999; Rosignol *et al.*, 2005; Avgouropoulos *et al.*, 2006).

2.4 Physical and Chemical Properties of Gold

In the physical properties, Pt is a versatile catalytic metal and is widely used in commercial applications both for chemical processing and pollution control, notably in automobile exhaust catalytic systems whereas Au exhibits all the properties

expected of a metal in terms of luster, hardness, ductility, malleability, and high thermal and electrical conductance. Moreover, Au is surpassing among the metallic elements due to its resistance to oxidation and corrosion.

To understand why Au differs from any other metals, for these reasons, its properties is necessary to be known as Table 2.2:

Table 2.2 Physical properties of gold compared to platinum (Catalysis by Gold, Geoffrey C. Bond, Catherine Louis, and David T. Thompson)

Property	Pt	Au
Atomic number	78	79
Atomic mass	195.08	196.9665
Electronic configuration	$[\text{Xe}]4f^{14}5d^96s^1$	$[\text{Xe}]4f^{14}5d^{10}6s^1$
Structure	fcc	Fcc
Lattice constant (nm)	0.392	0.408
Metallic Radius (nm)	0.1385	0.1442
Density (g cm^{-3})	21.41	19.32
Melting temp. ($^{\circ}\text{C}$)	1769	1064
Boiling Temp. ($^{\circ}\text{C}$)	4170	2808
Sublimation enthalpy (kJ mol^{-1})	469 ± 25	343 ± 11
First Ionization energy (kJ mol^{-1})	866	890

For the chemical properties of Pt, Au, and others metal of the adjacent elements are dominated by the relativistic stabilization of $6s$ level. The $6s^2$ 'inert pair effect' is well known to inorganic chemists. Additionally, electrons in the $5d$ level become more easily mobilized for chemical reaction. Thus the electronic configuration of Pt is $5d^96s^1$ while that of palladium (Pd) is $4d^{10}$, and this explains that the Pt^{4+} is so much more easily available than Pd^{4+} . In case of gold is $5d^{10}6s^1$, its chemistry is determined by the easy activation of $5d$ electrons and its desire to obtain a further electron to complete the $6s^2$ level and not to lose the one it has. This latter effect awards it a much greater electron affinity and higher first ionization energy than

those of copper (Cu) or silver (Ag) and accounts for the ready formation of Au^+ state. The former effect obviously explains the predominance of Au^{3+} has the $5d^8$ configuration (even the Au^{5+} state ($5d^6$) is accessible as in AuF_5). Its electronic structure determines its nobility, and its inability in the massive form to interact with oxygen or sulfur compounds is in line with the stability of its oxide Au_2O_3 , decomposes at about 170°C and probably has a positive heat of formation. The electronic state of gold atoms in the massive state is not, however, exactly that of the free atom, since a weak white line on the leading edge of the X-ray absorption edge signifies a small number holes in the d -band caused by d - s hybridization. The electron affinity of Pt is almost as large as that of Au.

2.5 Activity of Supported Gold Catalyst

The supported gold-based nanoparticles seem to be one of the best promising candidates for PROX of CO because using gold in this reaction is certain its catalytic activity at low temperature as compared with the other metals from platinum group. However, the best activity and selectivity is shown in a narrow range of Au particles (5—10nm). For oxidation of CO at low temperature, catalysts comprising small (<5 nm) gold particles supported preferably on reducible oxide such as TiO_2 , $\alpha\text{-Fe}_2\text{O}_3$ except for least active oxide (CdO , Cr_2O_3 , SiO_2) whose diameter of gold is larger than 20 nm. However, the activity of a supported gold catalyst for the CO oxidation is dependent on three characteristics. There are gold (Au) particle size, chemical nature of support, and its physical structure, which are controlled by the chosen preparation of method.

2.5.1 Catalyst Preparation

The preparation techniques are the important factor affecting stability and activity of the resulting catalysts; however, deposition-precipitation (DP) and co-precipitation (CP) are better methods than impregnation (IMP) for CO oxidation due to its characteristic properties e.g. more active. Furthermore, DP technique had the advantage over CP, in that all active Au remained on the support surface and none of the active Au was buried within it (Haruta, 1993). Small gold particle sup-

ported on various reducible oxides such as α -Fe₂O₃, Ce₂O₃, and TiO₂ were first obtained by DP. This method performed by adding sodium carbonate (Na₂CO₃) to aqueous solution of HAuCl₄, the pH of suspension is usually adjust 7 or 8 by adding precipitate agent—Na₂CO₃ or NaOH— after that it is heated at 80°C under stirring for 1hr. finally, and is washed with water usually at 50°C to remove excess ions, CO₃²⁻ and Cl⁻, the precipitate is dried at 100°C overnight, and often calcined in air at higher temperature. However, products after calcined at a variety of temperatures which appear that gold precursors (chloro or hydroxy species) will decompose to metal at fairly moderate temperatures because often no further treatment is necessary to achieve catalytic activity. Furthermore, gold species in a positive oxidation state will be active (Au³⁺ active species for oxidation of CO).

Hoflund *et al.* (1995) investigated the Au/MnO_x catalytic performance characteristics for low-temperature CO oxidation. They found that Au/MnO_x prepared by co-precipitation, even with no pretreatment these catalysts are superior to the best, pretreated platinumized tin oxide (Pt/SnO_x) catalysts under the conditions tested. Besides, deactivation test showed that the activity of Au/MnO_x slightly decreased due to carbon dioxide retention on the surface. The optimum gold content was 10 % of the manganese content, and a lithium promotor results in improved catalytic behavior over K- or Na-promoted Au/MnO_x.

Grunwaldt *et al.* (1999) studied the catalytic activity of Au/TiO₂ and Au/ZrO₂ catalysts for low-temperature CO oxidation which supported gold catalysts were prepared by immobilizing gold colloids of about 2 nm size on TiO₂ and ZrO₂ in aqueous solution. The gold particles nearly retained their size after immobilization on both supports. In addition, gold particles on TiO₂ showed CO conversion directly after preparation and drying. Significant activity of gold on ZrO₂ was only observed after calcination in air. They proposed that CO adsorption was reversible on all catalysts and weaker on the most active catalysts. The number of low-coordinated gold sites was much higher on TiO₂, whereas on ZrO₂ more positively polarized gold atoms were found. This behavior was traced to the shape of the gold particles, which affects the number of low-coordinated gold atoms and is dependent on support and treatment.

Schumacher *et al.* (2003) suggested that highly active Au/TiO₂ catalysts for low-temperature CO oxidation can be prepared by a modified deposition–precipitation procedure. The maximal activity of these catalysts was obtained after applying a newly developed reductive conditioning method that results in Au/TiO₂ catalysts with small metallic Au particles (<2 nm). For the deactivation of the catalysts during reaction, both of H₂-free and H₂-rich reaction atmospheres was caused by the accumulation and deposition of by-products on the catalyst's surface, but not by sintering of the gold particles.

2.5.2 Catalyst Support

The catalytic behavior of noble metal/reducible oxide comparison of catalytic performance for low-temperature CO oxidation was studied (Gardner *et al.*, 1991). Interestingly, Au/MnO_x is most active sustaining nearly 100% CO conversion for 10,000 min at 75°C. It also retains high activity at 50 and 30°C with negligible decay in activity. Furthermore, other catalysts including Au/CeO_x and Au/Fe₂O₃ also perform well. The Cu/MnO_x exhibits a high initial activity, but it decays rapidly. After the decay period the activity remains very stable, making Cu/MnO_x is a potential candidate for long-term applications.

Rossignol *et al.* (2005) studied the activity of Au/Al₂O₃, Au/ZrO₂ and Au/TiO₂ over the PROX in the presence of H₂. The catalysts were produced by laser vaporization of a metallic gold rod followed by deposition of the formed clusters onto the support powder. This technique allowed to obtain a narrow size distribution of highly dispersed gold particle on the support and, more importantly, it showed similar Au sizes on any support. The reactivity order found for CO oxidation (Au/Al₂O₃, <<Au/ZrO₂ < Au/TiO₂) was changed. In fact, in the presence of H₂, the reaction rates for the CO oxidation become rather similar to all three systems.

PROX of CO in H₂-rich stream over Au/CeO₂-Co₃O₄ catalysts was investigated (Wang *et al.*, 2008). They found that Au/CeO-Co₃O₄ exhibited much higher catalytic activity in CO PROX of CO than Au/Co₃O₄ and Au/CeO₂. The Au/CeO₂-Co₃O₄ showed 100% CO conversion with 75% selectivity even at ambient temperature. Moreover, both reduction and oxidation pretreatments can improve the catalytic activity and selectivity of Au/CeO₂-Co₃O₄ in PROX of CO. Typically, over

oxidation pretreatment Au/CeO₂-Co₃O₄ (Ce/Co = 0.2) showed 91% CO conversion and 51% selectivity at 80°C as long as 260 h.

2.5.3 H₂O and CO₂ Influence on Catalytic Activity

The effects of H₂O and CO₂ on PROX of CO in H₂-rich gases over Au/ α -Fe₂O₃ at 80°C were investigated (Schubert *et al.*, 2004). They found that addition of CO₂ reduced the CO oxidation rate and selectivity, which based on the concentration of CO₂ over the gold particles or at gold-metal oxide interface. Furthermore, the deactivation was accelerated due to the increasing of carbonate formation on the catalyst surface. In contrast, moisture results in an opposite effect. It enhanced the selectivity by suppressing the competitive H₂ oxidation reaction and the CO oxidation rate was slightly accelerated. The deactivation is significantly diminished, which is ascribed to the transformation of surface carbonates into thermal less stable bicarbonate species. However, the effect of water addition depends strongly on the reaction temperature. Finally, the negative influence of CO₂ on the PROX performance over Au/ α -Fe₂O₃ compared to CO₂ free gas mixture. Simultaneously, a comparative study of the catalytic activity and stability of Au/MnO_x and Au/FeO_x catalysts for the CO oxidation in the presence of hydrogen was also studied with the simulated reformed gas in the temperature range of 50–190°C (Luengnaruemitchai *et al.*, 2005). They reported the effects of CO₂ and H₂O in the feed gas on the catalytic activity of both catalysts as well as their stability were also investigated. The Au/MnO_x gave 93% conversion and 58% selectivity at 130°C while Au/FeO_x gave 98% conversion and 53% selectivity at 50°C. Interestingly, both catalysts could resist up to 10% H₂O while their activities were suppressed in the presence of 20% of CO₂. The deactivation was not observed during stability test for both catalysts. Recently, in situ FT-IR measurements for Au/TiO₂ and Au/Al₂O₃ under flow condition of the CO oxidation over supported gold nanoparticles at atmospheric pressure were studied (Daté *et al.*, 2007). They found that the Au particles remain neutral (Au⁰) in the presence of oxygen, while negatively charged particles (Au^{δ-}) are formed in the absence of oxygen, as a result of the charge transfer from the oxygen vacancies. Moisture did not significantly affect the adsorption states of CO over Au/TiO₂ and

Au/Al₂O₃. Enhancement of the CO₂ production by moisture was observed over Au/Al₂O₃, which is accompanied by the decomposition of carbonate by moisture.