



CHAPTER II LITERATURE REVIEW

2.1 Fuel Cells

Fuel cells are electronic devices that generate electricity via the chemical reaction. It composes of an electrolyte layer in contact with an anode (negative) and a cathode (positive) on either side. The reactions that produce electricity occur at the electrodes. It acts as the electron carrier from one electrode to another.

Hydrogen and Oxygen are required for the operating of fuel cells. Advantages of the fuel cell technology are:

- It generates a little amount of pollution
- The product from the fuel cells reaction is harmless (water)
- Fuel cells are attractive alternative to oil dependency
- It can reduce the greenhouse gas problems

There are many types of fuel cells. They are characterized by the different type of electrolyte, operating temperature, and reaction take places in the fuel cells, as shown in Table 2.1. Each of them has advantages and disadvantages, and potential applications relate to each other.

Table 2.1 Types of fuel cells (http://en.wikipedia.org/wiki/Fuel_cell)

Fuel Cell Name	Electrolyte	Operating Temperature(°C)
Metal Hydride	Aqueous alkaline solution	> 20
Electro-galvanic	Aqueous alkaline solution	< 40
Direct Formic Acid	Polymer membrane	< 40
Microbial	Polymer membrane or Humic acid	< 40
Reversible	Polymer membrane	< 50
Direct Methanol	Polymer membrane	90–120
Reformed Methanol	Polymer membrane	250–300

Fuel Cell Name	Electrolyte	Operating Temperature(°C)
Formic Acid	Polymer membrane	90–120
Proton Exchange Membrane	Polymer membrane	50–120
Phosphoric Acid	Molten phosphoric acid	150–200
Molten Carbonate	Molten alkaline carbonate	600–650
Direct Carbon	Several different	700–850
Planar Solid Oxide	O ²⁻ conducting ceramic oxide	700–1000

However, only a few types of fuel cells can be used as practical in the moment since some of them need more improvement and development about the efficiency, cost, and hydrogen source. Nowadays the most popular fuel cell is PEM Fuel Cells. Because it has many advantages such as: operate at low temperatures, mass production, affordable cost, compactness, good durability, less warm up time, low weight and volume, and very high power density. Then, it is the first candidate for the transportation and some stationary applications. Therefore, PEM fuel cells are primarily suited for use in passenger vehicles, such as car and bus.

The PEM fuel cells use a solid polymer membrane as its electrolyte. Typically, the anode and cathode catalysts consist of one or more precious metals, particularly Pt supported on anode. The PEM fuel cells mechanism is explained (Equations 1–3) and shown in Figure 2.1. Firstly, H₂ stream is fed to the anode side where the chemical reaction strips them of their electrons. Then, H₂ atom is ionized and carried a positive charge. After that, membrane at the center separates the proton to the cathode side while leaving the electron behind. Next, the catalyst at the cathode side let hydrogen nuclei and oxygen from the air recombine to get water as a product. The negative charges electrons provide the current through wire to do work in the same time.

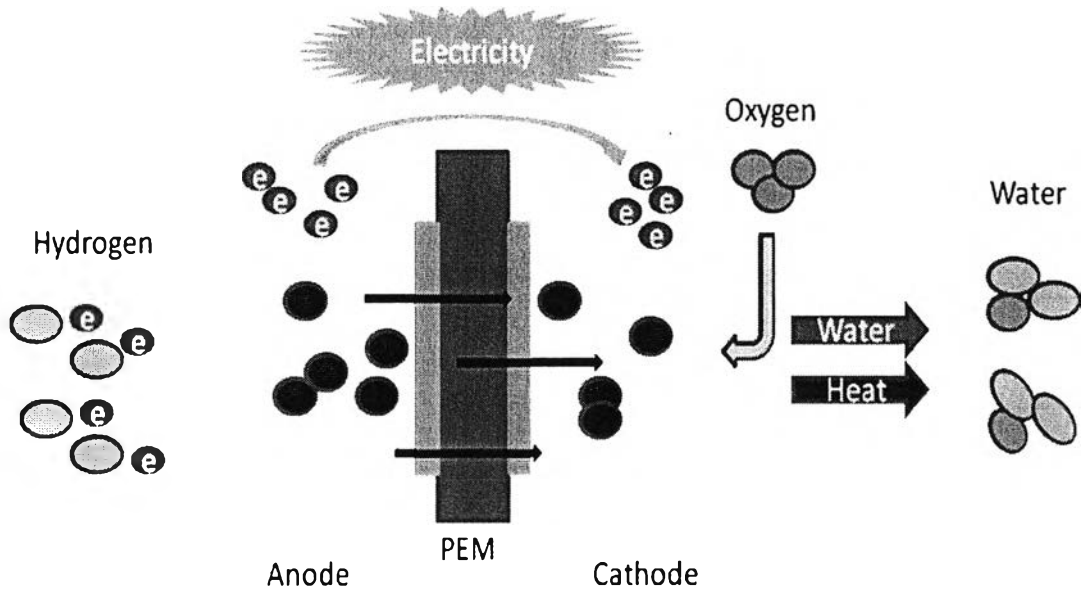
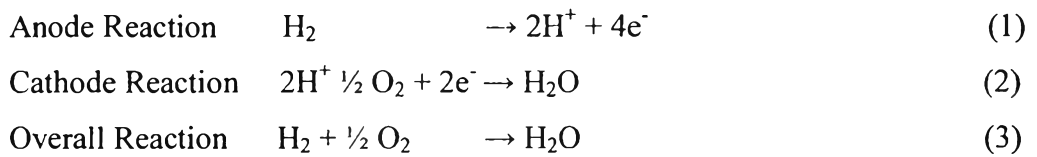


Figure 2.1 Diagram of PEM fuel cells.



A significant barrier for using this type of fuel cells is H_2 storage problem, since the H_2 in tank is in compressed gas form in pressurized tank and low energy density of H_2 , which is so difficult to fill into the tank. Another problem is lack of H_2 resource. Therefore, we can apply the high mass of H_2 from the reforming unit in refinery plant to fill in the vehicles.

2.2 Hydrogen Production Process

Hydrogen is a basic chemical element with atomic number equal to 1. At standard temperature and pressure, H_2 is a colorless, odorless, nonmetallic, tasteless, and highly flammable diatomic gas with molecular formula H_2 .

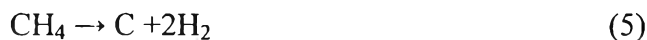
There are many applications of H_2 , for example, large quantity of H_2 are generated and consumed by the petroleum and petrochemical industries. The large application is from the processing where upgrade gasoline quality, the production of

ammonia, hydrodealkylation, hydrodesulfurization, and hydrocracking. Furthermore, H₂ has wide applications in physics and engineering. It can be used as a shielding gas in welding methods such as hydrogen atomic welding. H₂ can also be used as a rotor coolant in the electrical plant. In more recent applications, H₂ can be used as fuel in fuel cells for transportation vehicles such as hybrid cars and buses.

In addition, H₂ can be produced by many ways such as in laboratory and industry. The most economical and important way is the production of H₂ from hydrocarbons, especially natural gas. For commercial H₂, it usually comes from the reforming of natural gas at 700–1000°C where H₂O vapor reacts with CH₄ to yield CO and H₂ (Equation 4). Steam reforming is widely used in industry to produce H₂ and syngas (CO and H₂).



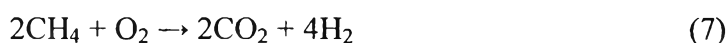
However, the amount of product is affected by coke or carbon formation due to the operating conditions at high pressures (Equation 5).



After that, the CO needs to be removed from the stream by the water gas shift (WGS) reaction. This reaction is very important for commercial sources of CO₂.



Other important sources of H₂ production are the partial oxidation of hydrocarbons. This reaction is more difficult to control due to the exothermic nature of the reaction and coking problem.



Autothermal is a combination method between steam reforming and partial oxidation reactions by feeding both water and oxygen into the reaction. This method

has more efficient for the heat integration between the exothermic of partial oxidation and endothermic of reforming unit, which can generate H_2 more than operate only partial oxidation reaction.

The development of fuel processors is needed to convert hydrocarbon into H_2 , a schematic of the overall fuel processing/fuel cells system is shown in Figure 2.2. The PEM fuel cells is accomplished by the series of reactor including reforming, desulfurization, water gas shift (WGS), and CO removal by the PROX of CO. The reforming of natural gas is an efficient, economic, and widely used process for H_2 production. The efficiency of steam reforming is about 65 to 75%. Natural gas also is very easy to handle, so it is a widely available source in the USA and Canada.

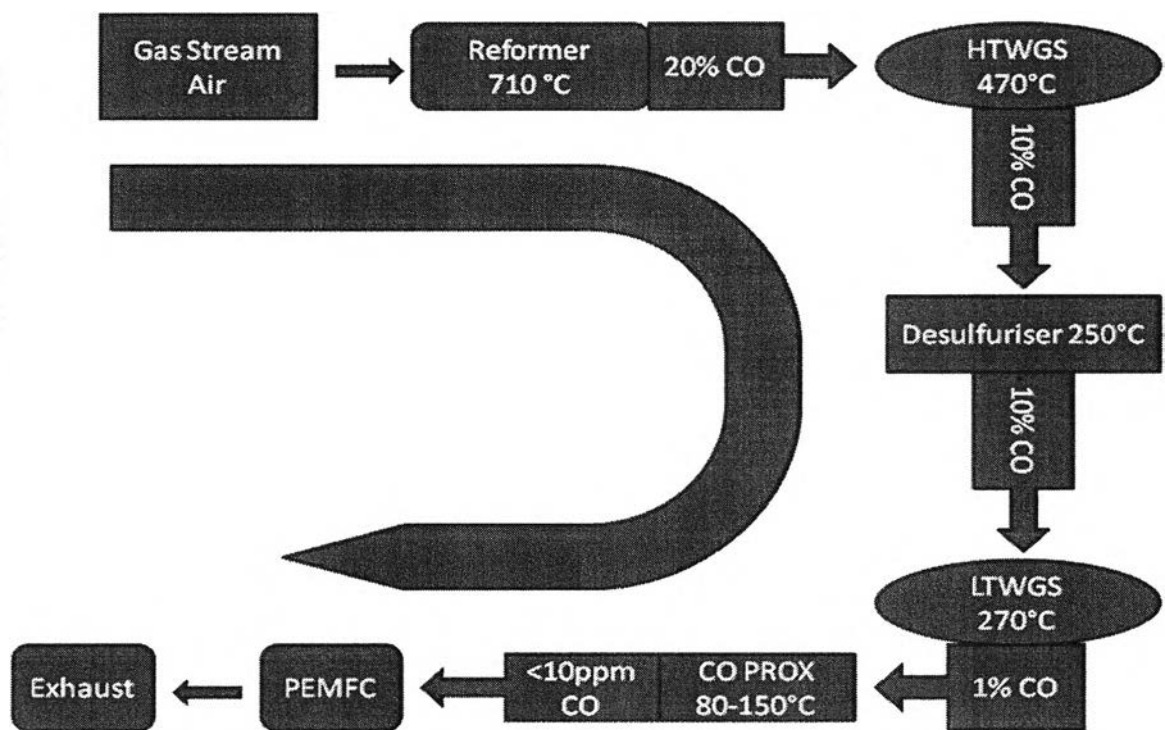


Figure 2.2 Schematic of a gasoline process for H_2 production (Rosso *et al.*, 2004).

2.3 CO Removal Methods

Carbon monoxide has a chemical formula CO and it is a colorless, odorless and tasteless gas. It composes of carbon atom link with one oxygen atom. It is a product from the combustion of carbon containing compound. CO is a toxic gas and

chemical; therefore, it can harmful to human body and cathode catalyst of PEM fuel cells. As mentioned previously, H₂ produced from the reforming process contains about 20% CO. The cathode of PEM fuel cells may be poisoned by the over limitation of CO concentration. Therefore, CO must be removed as much as possible by using any process, as shown below:

2.3.1 Water Gas Shift

WGS is a chemical reaction between H₂O and CO to produce CO₂ and H₂.



This reaction has two important parts, which are high temperature shift (HTS) and low temperature shift (LTS). The operation temperature of HTS and LTS are 350–470°C and 160–270°C, respectively. The catalyst used in HTS and LTS stages will less active at temperatures below 300°C and above 270°C.

2.3.2 Pressure Swing Adsorption

Pressure swing adsorption (PSA) is a technique used to separate gas mixture by using the differences in physical properties of each gas with adsorbent material. Normally, this separation is operated at ambient temperature. For special adsorption, zeolites are used as a molecular sieve in adsorption at high pressure and for desorption of adsorbent the pressure is switched to low pressure.

CO removal is a primary application of PSA. The advantages of PSA are high purity hydrogen (99.9%–99.999% mole), high hydrogen recovery (90%), and low investment and operation cost. Moreover, PSA can separate other gas mixture in other industries, for instances, the oxygen production in medical industry.

2.3.3 Membrane Filtration

Membrane is a device used to separate the component of gas or liquid mixture on the basic of their relative permeation rate through membrane material. There are various methods to enable substances to penetrate a membrane such as the application of high pressure. There are two primary membranes, which are organic and inorganic membranes.

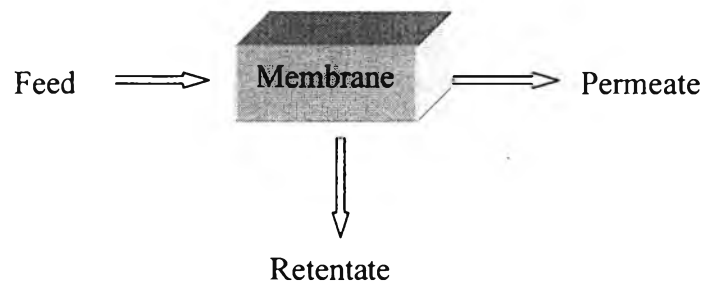


Figure 2.3 A simple membrane module.

2.3.4 Methanation

The methanation reactor converts any CO back to CH₄ using a small amount of H₂ to affect the reaction.



This reaction is conducted in a fixed-bed catalytic reactor at temperature about 370–427°C. The reaction is exothermic reaction, and if the feed concentration of CO is more than 3%, it is necessary to recycle some of the cooled exit gas to dissipate the heat of reaction. The preceding description is somewhat idealized, because the actual reactions are more complicated. The actual process conditions of temperature, pressure, and steam/carbon ratios are compromise for several factors (Andersson *et al.*, 2008).

2.3.5 Preferential or Selective Oxidation of CO

In comparison with other approaches, the PROX has been suggested to be the simplest and most cost effective method for removing CO in the presence of H₂ for the fuel cells application. Efficient catalysts for PROX reaction need to fulfill these three parameters (Avgouropoulos *et al.*, 2006).

- High oxidation rate
- High selectivity with respect to the undesired H₂ oxidation reaction
- Stability with reaction time

The elimination of CO from the hydrogen stream is a key point to develop the hydrogen application.

The WGS reaction can significantly reduce CO concentration to 1–0.5% in the hydrogen stream. As shown in Figure 2.2, the PROX of CO stage is between LTS unit and PEM fuel cells in order to reduce the CO concentration to reach the PEM fuel cells limitation. The operating temperature of PROX is between 80 and 150°C. This reaction requires a catalyst that is active for CO oxidation (Equation 9). On the other hand, the catalyst must not oxidize hydrogen via H₂ oxidation (Equation 10).



However, PROX still has two side reactions, which are the water gas shift and the reverse water gas shift (RWGS) reactions (Equation 11).



The aim of PROX is to oxidize only CO but not oxidize hydrogen. Then, the oxidation can be controlled by controlling the temperature. Lomello-Tafim *et al.* (2004) tested the PROX of CO in H₂ stream over highly loaded Au/ZrO₂ catalyst. They found that CO conversion is largely enhanced at low temperatures (T < 125°C) when H₂ is present in the gas mixture, the conversion of H₂ is decreased at the same temperature range. At 70°C, CO and H₂ conversion are 68 and 20%, respectively. However, at 120°C, CO and H₂ conversion are about 50 and 40%, respectively. In addition, the side reactions have not much effect on the fuel cells efficiency or durability because the WGS reaction can reduce lots of concentration of CO from the stream. For RWGS reaction, it can produce methane, which would not harmful to the PEM fuel cells.

The effect of H₂O present in the reformat stream on the catalytic performance in CO oxidation was studied by Daté and Haruta (2001). The effect of moisture in the reactant gas on CO oxidation over Au/TiO₂ catalyst had been quantitatively investigated over a wide range of concentrations from 0.1–6,000 ppm. Moisture enhanced the reaction more than 10 times up to 200 ppm H₂O, while further

increasing the moisture content it suppressed the reaction. The apparent activation energy is, however, independent of the amount of moisture. The amount of moisture adsorbed on the catalyst influence the activity rather than the moisture content in the gas phase.

Several types of catalysts have been tested in the literature for the PROX in order to get the best CO conversion and selectivity. The examples of the catalysts are Au (Tsubota *et al.*, 1998), Pd (Ferrauto *et al.*, 2003), Pt (Minemura *et al.*, 2005), and bimetallic Au-Pt (Luengnaruemitchai *et al.*, 2008). It has been shown that the supported Au catalysts are significantly more active than the Pt-based catalysts. Apart from the metal, the support plays an important role on the conversion and selectivity in this reaction; therefore, a large number of supports have been investigated.

2.4 Properties of Gold

The atomic configuration of gold ($Z = 79$) is $[\text{Xe}]4f^{14}5d^{10}6s^1$. It is in group 11 of periodic classification of elements. In the past, gold is less important in chemical engineering area because it is an inert element and its cost is very expensive.

Table 2.2 Properties of gold

Properties	Au
Atomic number	79
Atomic mass	196.97
Electronic configuration	$[\text{Xe}]4f^{14}5d^{10}6s^1$
Metallic radius (nm)	0.1442
Structure	fcc
Melting temperature (°C)	1063
Boiling temperature (°C)	2807

Concerning our area of specific interest, Au catalysts are rarely used in the catalysis applications; however, Haruta *et al.* (1993) showed that Au disperse on

oxide surface extremely active on the CO oxidation. They also prove that Au with nano-sized can active even at ambient temperature.

In 2006, Avgouropoulos *et al.* compared the catalytic performance of Au/CeO₂ and CuO/CeO₂ for the PROX reaction in the presence of excess H₂. They prepared the catalysts by a DP method. The result showed that the Au/CeO₂ is significantly more active at temperature lower than 120°C, while CuO/CeO₂ gave higher selectivity at a higher operating temperature.

Moreover, Au catalysts can be used in many reactions such as NO_x reduction, CO and CO₂ hydrogenation, CO oxidation, WGS reaction, and total oxidation of hydrocarbon. Therefore, gold catalyst became interesting for many researchers. A nice overview of the Au testing in many applications is shown in Figure 2.4.

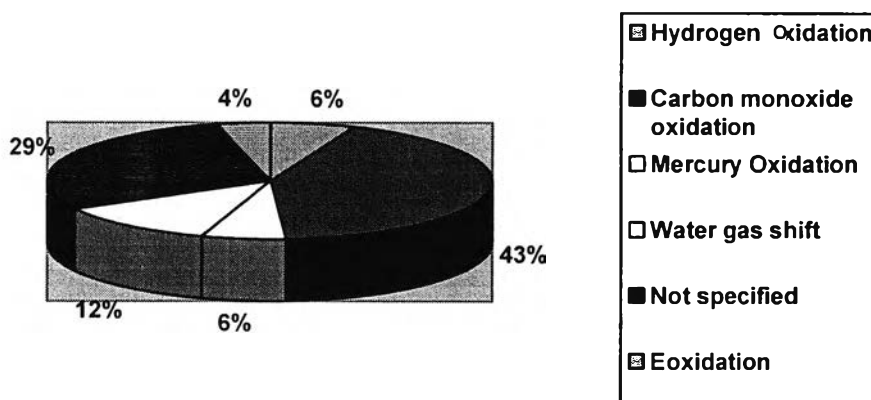


Figure 2.4 Application of Au catalysts ('CatGold' World Gold Council, 2003).

Figure 2.4 represents the percentage in each research area in Au catalyst. In the moment, Au has already been used in the commercial application (e.g. BP Chemical uses a Au-Pd alloy for the so call 'Leap Process' within its vinyl acetate monomer plant).

2.5 Au as Catalysts

The catalytic activities of supported Au catalysts depend on many factors, which are particle size of gold, catalyst support, structure of catalysts, and catalyst preparation method.

2.5.1 Particle Size

It is generally accepted that the particle size of small gold (2–5 nm) stabilized with metal oxide exhibits a high catalytic performance. The critical diameter of Au particle is approximately 2 nm. When the particle size of gold smaller than 2 nm, it may not behave like bulk gold; however, it behaves similar to Pt or Pd (Bond, 2006).

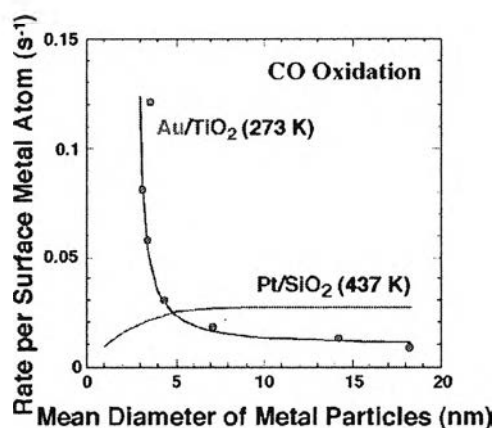


Figure 2.5 Effect of particle size on the CO oxidation rate (Haruta *et al.*, 2004).

The catalyst pretreatment can control the particle size and catalytic activity of Au catalyst. The optimum pretreatment temperature depends on the type of support, due to the difference in strength interaction between gold (precursor) and the support. A low calcination temperature (100–400°C) is required to convert the gold precursor into the catalytically active species (Zanell *et al.*, 2005).

2.5.2 Catalyst Support

The catalytic properties are strongly affected by the type of support. It can affect to the CO oxidation conversion and selectivity. Most of researchers suggest that metal oxide support is more suitable for the CO oxidation compared to other types of support. Au/ α -Fe₂O₃, Au/TiO₂, Au/CoO_x, Au/NiO_x, AuMg(OH)₂, Au/CeO₂, Au/SnO₂, Au/MnO_x, and Au/ γ -Al₂O₃ were used and tested for PROX reaction. Among the catalyst studied, it was found that Au/ α -Fe₂O₃ exhibits a significantly enhanced activity for CO oxidation (Schubert *et al.*, 2001). They studied the activity, selectivity, and long-term stability of different metal oxide support gold catalysts for CO oxidation. The reaction temperature was carried out at 80°C. There are two types of metal oxide support catalysts in CO oxidation reaction which are the neutrally (Au/ γ -Al₂O₃) and reducible transition metal oxide, such as (Fe₂O₃, CeO₂, and TiO₂). The result showed that latter has more active than the former. The selectivity strongly depends on the type of support. The best catalysts tested in the simulated methanol reformat using a PROX reaction is Au/ α -Fe₂O₃ due to its high activity in combination with a high selectivity. From the result, it was found that after 1,000 min time-on-stream, Au/ α -Fe₂O₃ was the most active catalyst.

Furthermore, Rossignal *et al.* (2005) studied the catalytic performance of Au/Al₂O₃, Au/ZrO₂, and Au/TiO₂ for PROX reaction in the presence of H₂. They studied the influence of the support on the catalytic activity. The operating temperature for their experiment was in the range of 25–420°C. From the results, they concluded that the Au/TiO₂ catalyst was more active for CO oxidation reaction than other catalysts. However, Au/TiO₂ was less active for H₂ oxidation than Au/Al₂O₃ and Au/ZrO₂ catalysts.

2.5.3 Structure of Catalyst

Many researchers found that Au particles are not uniform in size and most of gold particles are not hemisphere. All kind of crystallite morphologies are thinkable, in which the correlation between surface area, perimeter length, and particle diameter are completely different. The contact of Au with support is very important because the interface between Au and support act as an active site for reaction. The contact will differ in each preparation method. It has been reported that the deposition-precipitation method (DP) yields hemispherical with the TiO₂ support

and impregnation method gives spherical particle on the support (Bocuzzi *et al.*, 2001), as shown in Figure 2.6.

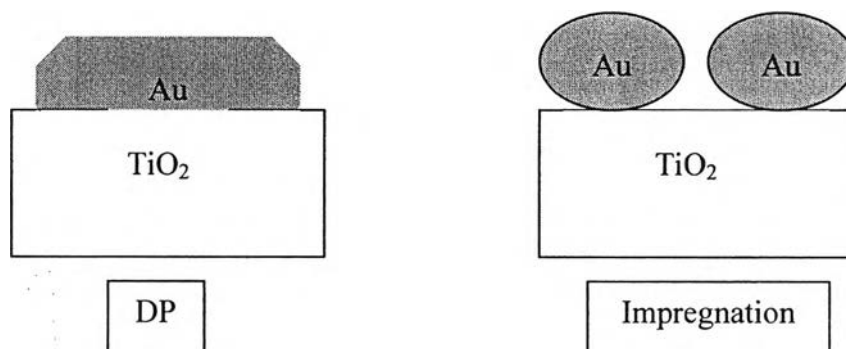


Figure 2.6 Interaction of Au with support prepared by DP and impregnation methods (Bocuzzi *et al.*, 2001).

2.5.4 Catalyst Preparation Method

The effect of catalyst preparation on the catalytic activity has been investigated. There are many ways to introduce Au on the support (e.g. co-precipitation and deposition-precipitation) and pH is one of the main factors, which has more influence on the particle size, the particle shape, and the amount of residue chloride which is poison to the Au catalyst. Moreover, the calcination temperature has also affect on the particle size of Au.

The adsorption of CO on Au/TiO₂ has been investigated by Iizuka *et al.*, (1997). The 3.3 wt% Au/TiO₂ with 3.5 nm mean particle diameter of Au was prepared by DP. The adsorption of CO on Au/TiO₂ was 90% reversible and satisfied the Langmuir isotherm. The result indicated that a reaction between oxygen adsorbed on the surface of small Au particles with CO is one of the most major reaction pathways in forming CO₂.

Therefore, Galletti *et al.* (2007) tested the catalytic performance of Au/TiO₂ catalysts prepared by DP for PROX in a H₂-rich gas. It was found that PROX can lead to a reduction of the CO content in the H₂-rich gas derived from hydrocarbon reforming down to at least 10 ppm. The Au based catalysts, especially supported on TiO₂, were prepared and tested in PROX at 40–180°C. The catalysts

prepared by DP method were studied by varying pH (with NaOH) and some other parameters during the preparation procedure. The result showed that the catalyst prepared by DP method with low pH and calcined at 300°C was found to be the most suitable one for PROX at low operating temperatures.

Moreau and Bond (2006) studied the influence of some physicochemical parameters on the activity and stability for the oxidation of CO. The Au/TiO₂ (P-25) prepared by DP method was studied in the PROX reaction using a plug flow reactor. They reported that pH can control the gold particle size. The XRD result showed that pH is decreased with increasing the particle sizes of Au. At pH 6 and 9, the Au particle size equal to 4–20 and 1.5–4 nm, respectively. The maximum CO conversion required the particle size of Au around 3 nm. Based on those results, it can be concluded that the optimum pH for the catalyst preparation is 9.

The effect of Cl⁻ on support Au catalysts in PROX reaction was studied by Oh *et al.* (2002). The Au catalyst is generally prepared from Cl⁻ containing Au precursors and their properties are highly sensitive to preparation procedures. The effect of Cl⁻ on the catalytic performance of highly active Au/Al₂O₃ catalyst in the PROX of CO was found to affect the activities in two different ways. It facilitates the agglomeration of Au particles during heat treatment, and it inhibits the catalytic activity by poisoning the active site.

The effect of calcination temperature was studied by Dimitratos *et al.* (2006). The XPS result informed that there are Au⁰ (active site for oxidation) and Au³⁺ in the calcined sample but there is no active site appear with uncalcined sample. They concluded that the calcination is the transformation of Au³⁺ to Au⁰, whereas the reduction process is the converting of Au⁰ to Au³⁺.

The effect the calcination temperature on the CO oxidation was studied over the Au/TiO₂ catalysts prepared by a DP method. (Bocuzzi *et al.*, 2001). Three samples calcined at 200, 300, and 600°C have mean diameter of Au particles of 2.4, 2.5, and 10.6 nm, respectively. The first two catalysts exhibited 100% CO conversion at the temperature below -33°C, whereas the latter catalyst exhibited 100% CO oxidation at temperature above 27°C.

2.6 TiO₂ as Metal Oxide Support

Many types of metal oxide supports have been shown to exhibit the outstanding activity at very low temperature for the PROX reaction. There are many Au supported on metal oxide support catalysts have been tested with the simulated methanol reformat, for example, Au/ α -Fe₂O₃, Au/TiO₂, Au/CoO_x, Au/NiO_x, AuMg(OH)₂, Au/CeO₂, Au/SnO₂, Au/MnO_x, and Au/ γ -Al₂O₃. Schubert *et al.* (2001) tested the activity of their catalysts, which are Au/ α -Fe₂O₃, Au/TiO₂, Au/CoO_x, Au/CeO₂, Au/SnO₂. It was found that the selectivity of each catalyst is in the range of 45–80% [Au/ α -Fe₂O₃ (60–65%), Au/MgO and Mg(OH)₂ (65–70%), Au/Co₃O₄ (75–80%), Au/CeO₂ (75–80%) and Au/TiO₂ (45–50%)].

There are significant numbers of experiments about the Au supported on TiO₂ catalysts. In 2002, Daté *et al.* studied the catalytic performance of Au/TiO₂ catalyst under ambient condition. The best performance was obtained with the catalyst calcined at 200°C and left at room temperature for a few days.

Chang *et al.* (2005) studied the mechanisms of CO oxidation over Au/TiO₂ using FTIR spectroscopy and product analysis. They studied the CO oxidation over Au/TiO₂, which was performed at -27–90°C. The result showed that the CO oxidation reaction can occur at all tested temperature range. There is no completion for CO and O₂ adsorption in the temperature range studied suggesting that CO and O₂ adsorption occurred at different types of sites. In addition, the desorption of product (CO₂) was investigated by mass spectroscopy.

The commercial TiO₂ support was compared with the TiO₂ sample synthesized by sol-gel method. Both supports were used as a support for Au catalysts in PROX reaction. The XRD results showed that commercial TiO₂ is in anatase form but TiO₂ prepared by sol-gel method is in rutile form. Moreover, from HRTEM, samples gave the pore size almost equal to the size of Au; therefore, Au was deposited on the surface of support only. For the commercial support, the particle size was varied from 10 to 100 nm. The amount of Au was found on the surface lower than a sol-gel method. Most of Au particles were embedded on the support in the form of hemispherical shape and the average size was about 10 nm.

In summary, TiO_2 exhibits high activity as other catalysts but it provides very low selectivity. Therefore, the development of the PROX system by increasing the number of reactor and pretreatment of the prepared catalyst could improve the selectivity of the catalyst.

2.7 Multi-Stage Reactor

Nowadays there are attempt to consider with the reactor design. The performance of single-stage and double-stage reactor of PROX reaction was investigated. The motivation behind operating the PROX reactor system in a cascaded multi-stage mode is base on the hypothesis that the number of catalytic sites that participate in CO oxidation could be increased compared to those participate in H_2 oxidation. For example, if we consider single-stage PROX reactor system where all oxygen is introduced at the inlet, the downstream section of the reactor with low CO concentration may provide free active sites for H_2 oxidation, thereby utilizing a large portion of the unused oxygen. However, if we split the same amount of oxygen between stage arranged in series in some ideal ratio, we could reduce the possibility of occurrence of this phenomena since each stage operates under limited oxygen content. Moreover, the design of reactor has much effect with the selectivity and conversion of PROX reaction.

There are many parameters that can be varied when operating the multi-stage reactor mode for instance:

- Number of stages
- Amount of catalyst loaded in each reactor.
- Amount of oxygen is fed into each reactor.
- Temperature in each stage
- Cost consideration

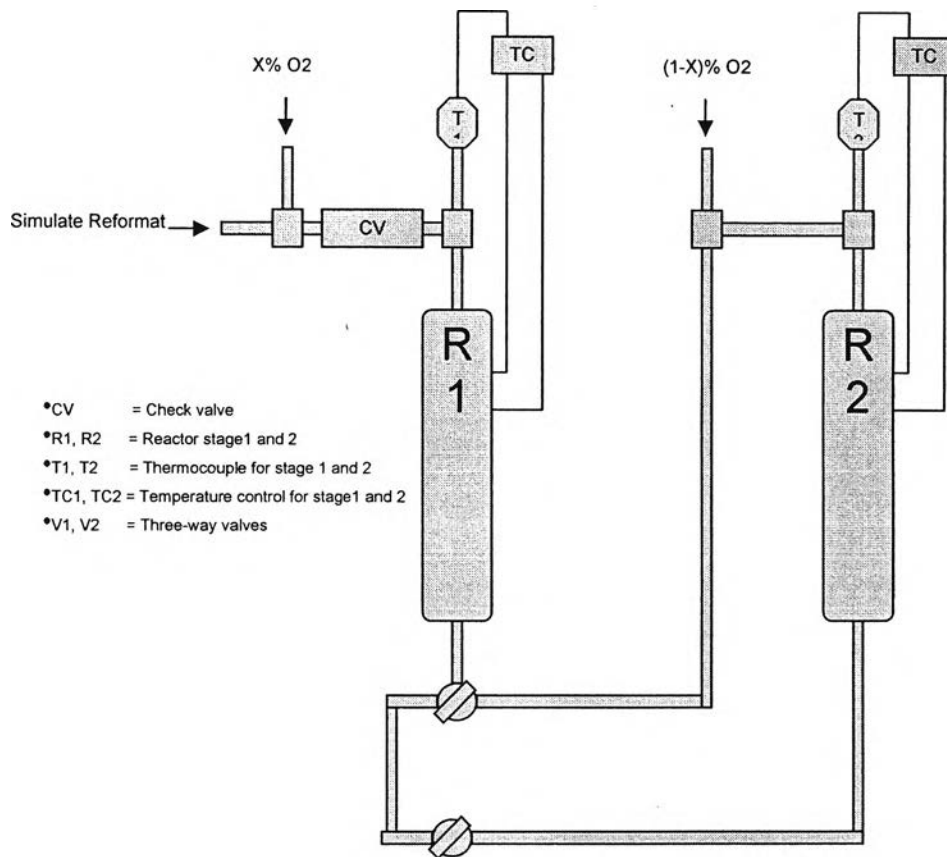


Figure 2.7 Schematic of double-stage packed-bed reactor for PROX (Srinivas and Gulari, 2006).

The conversion and selectivity of PROX reaction for two stages reactor are defined as follows:

$$\%CO \text{ conversion} = \frac{[CO]_{in} - [CO]_{out}}{[CO]_{in}} \times 100$$

$$\%O_2 \text{ conversion} = \frac{[O_2]_{in} - [O_2]_{out}}{[O_2]_{in}} \times 100$$

$$\%PROX \text{ selectivity} = \frac{1/2 \times ([CO]_{in} - [CO]_{out})}{[O_2]_{in} - [O_2]_{out}} \times 100$$

In 2006, the multi-stage reactor for PROX was studied with a few researchers. Srinivas and Gulari (2006) investigated the performance of PROX operated in double-stage packed bed reactors. Pt/ γ -Al₂O₃ was used as a catalyst in the experiment and it was found that at 180°C is the optimum performance of single-stage mode. At this temperature, CO conversion and PROX selectivity were 98.61 and 49.3, respectively. The optimum performances of double-stage mode for different O₂ split ratios are shown in Table 2.3

Table 2.3 Overall optimum process performance of double-stage mode for different O₂ split ratios (Srinivas and Gulari, 2006)

O ₂ split ratio	80:20	70:30	60:40	50:50	40:60
Stage1					
Temperature (°C)	220	230	230	230	230
CO conversion (%)	82.23	73.27	63.11	49.70	39.64
PROX selectivity (%)	51.39	52.34	52.59	49.70	49.55
Stage2					
Temperature (°C)	180	170	170	190	190
CO conversion (%)	97.96	99.50	99.68	98.93	99.07
Stage2					
PROX selectivity (%)	43.53	44.32	45.96	49.75	49.84
Overall					
CO conversion (%)	99.64	99.87	99.88	99.45	99.45
PROX selectivity (%)	49.82	49.93	49.94	49.73	49.72

From Table 2.3, they concluded that the optimum oxygen fed between double-stage reactors was 60:40. The multi-stage reactor was also studied by Ahluwalia *et al.* (2005). They studied the performance of PROX reactor with noble-metal catalyst, Pt-based catalyst, which is active at room temperature. The optimization algorithm is used to determine the operating conditions that can reduce CO concentration to 10 ppm. They found that single-stage reactor can completely reduce CO concentration

with maximum inlet CO concentration approximately 1.05%, whereas the maximum inlet CO concentration in a double-stage reactor is about 3.1%. Moreover, the amount of H₂ is reduced by addition of second and third stages.

In addition, Luengnaruemitchai *et al.* (2008) used AuPt/Zeolite catalysts to study the effect of multi-stage reactor on the activity of the catalyst. They varied the temperature and oxygen split ratio between each reactor to find the optimum reaction conditions, which are 130°C and 170°C for first and second reactor, respectively, and oxygen split ratio at 50:50.

2.8 Catalytic Deactivation

The TiO₂ supported gold catalyst has an instinct advantage over other CO oxidation catalysts but it tends to deactivate with storage condition. From 2.5.1, the Au particle size is an important parameter to prepare an active catalyst for this reaction. The possibility of changes the structure and activity occurring during storage is a constant worry and threat to the particle application of supported gold catalysts. Many researchers reported that the storage condition can affect to the performance of the catalyst. The gold metal particles sizes are very sensitive to the light and ambient air. In 2005, Zanella and Loius. observed that Au/TiO₂ catalyst stored in ambient air and light, the particle size grow from 2 to 5 nm within a few weeks. They separated the sample into two groups. The catalyst was kept in a desiccator only showed small gold particle with an average size of 2.3 nm and narrow size distribution, whereas the sample stored in air exhibited much larger particle of 20–200 nm. From the experiment, they recommended that the way to avoid sintering of gold particle after the preparation is to store the sample in a desiccator under vacuum and in the dark conditions. The dark can prevent the gold particle sintering. Moreau and Bond (2006) studied the condition for storing the catalyst (in the dark and in daylight) and it was found that the catalyst which stored in the dark provided better activity than the catalyst that exposed to the light catalyst. In 2007, Lee *et al.* studied the storage effect on the catalytic activity of Au/TiO₂. They proposed that the fresh catalyst has the same activity as the sample that was wrapped with black tape for 5 months. In contrast, the sample that exposed to light exhibited lower activities than fresh catalyst.

The XPS and UV-vis results indicated that following exposure to light during storage, the gold on the support was slowly reduced to gold metal.