สำนักงานวิทยทรัพยากร จุฬาลงกรณ์มหาวิทยาลัย

CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEWS

2.1 Fuel Cell

A fuel cell is an electrochemical device that produces electricity silently and without combustion. A fuel cell consists of two electrodes, an anode and a cathode, with an electrolyte sandwiched in between. Figure 2.1 shows a diagram of a typical fuel cell. O_2 passes over one electrode and H_2 over the other, generating electricity, water, and heat. Unlike other electrochemical devices such as batteries, a fuel cell only requires a continuous flow of H_2 and does not run down or require recharging. It will produce energy in the form of electricity and heat as long as fuel is supplied.

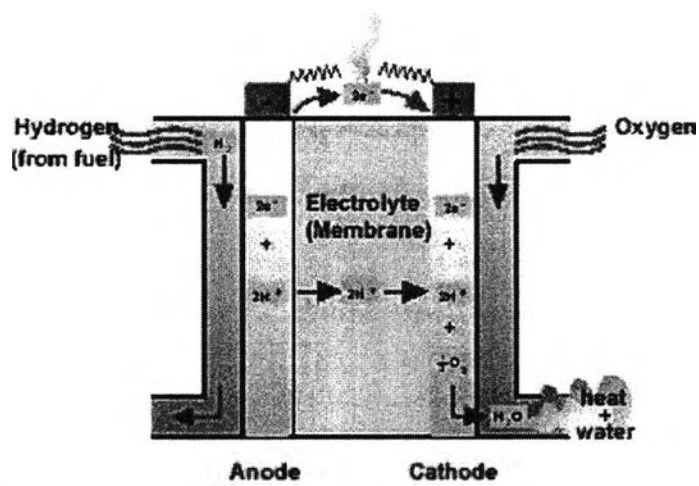

Figure 2.1 A fuel cell membrane electrode assembly operation.
[Ref. http://www.atp.nist.gov/eao/ir-7161/chapt2.htm]

Fuel cells thus make usable energy in the form of electricity and heat by combining H_2 and O_2 from the air in an electrochemical reaction. For stationary applications, H_2 is typically made on-site from natural gas by means of a reformer. Fuel cells are highly energy efficient, extracting two to three times more useful energy from fuels than other generation methods. Since a fuel cell has no moving parts in its core system, its reliability can be high. Because fuel cells do not involve combustion,

the device produces no air pollutants when operating with pure H_2 as a fuel, and greatly reduces air pollutants when operating with reformed H_2.

Table 2.1 lists the different types of fuel cells. The primary difference between each is the type of materials used in the fuel cell stack to generate the chemical reaction needed to make electricity. A few of the most promising types are included Proton Exchange Membrane (PEM), Phosphoric Acid Fuel Cell (PAFC), Molten Carbonate Fuel Cell (MCFC), and Solid Oxide Fuel Cell (SOFC).

Table 2.1 Fuel cell comparisons

Type	Electrolyte	Operating temperature (°C)	Commercial applications	Limitation
PEM	Solid polymer, proton-conducting electrolyte	50 to 90	Transportation, stationary, portable power	High manufacturing costs, needs pure H_2, heavy auxiliary equipment
PAFC	Phosphoric acid	190 to 210	Stationary	Low efficiency, expansive catalyst, limited service life
MCFC	Potassium carbonate	630 to 650	Stationary	Electrolyte instability, limited service life
SOFC	Yurium - stabilized Zirconia	800 to 1000	Transportation, stationary, portable power	High operating temperature, high manufacturing costs

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2.2 Hydrogen Production

H_2 can be produced from a variety of feedstocks, including fossil resources such as natural gas and coal, as well as renewable resources such as biomass and water with input from renewable energy sources (e.g. sunlight, wind, wave or hydropower). A variety of process technologies can be used, including chemical, biological, electrolytic, photolytic and thermo-chemical. Each technology is in a different stage of development, and each offers unique opportunities, benefits and challenges. Local availability of feedstock, the maturity of the technology, market applications and demand, policy issues, and costs will all influence the choice and timing of the various options for H_2 production. An overview of the various feedstocks and process technologies is presented in Figure 2.2.

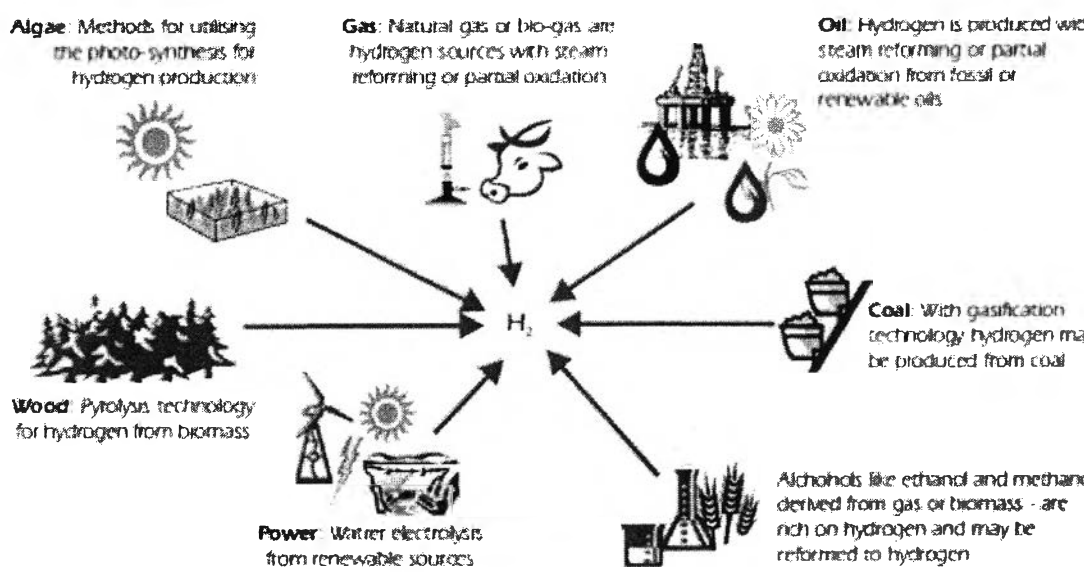

Figure 2.2 Some feedstock and process alternatives.
[Ref. http://www.iea.org/Textbase/papers/2006/hydrogen.pdf]

Several technologies are already available in the marketplace for the industrial production of H_2. The first commercial technology, dating from the late 1920s, was the electrolysis of water to produce pure H_2. In the 1960s, the industrial production of H_2 shifted slowly towards a fossil-based feedstock, which is the main source for H_2 production today.

H_2 can currently be produced from natural gas by means of three different chemical processes including steam reforming (SMR), partial oxidation (POX), and autothermal reforming (ATR).

2.2.1 Steam Reforming

Steam reforming involves the endothermic conversion of CH_4 and H_2O vapor into H_2 and CO in Equation (1). The heat is often supplied from the combustion of some of the methane feed-gas. The process typically occurs at temperatures of 700 to 850 °C and pressures of 3 to 25 bar. The product gas contains approximately 12 % CO, which can be further converted to CO_2 and H_2 through the water-gas shift reaction in Equation (2).

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad \Delta H_{rxn,298K} = 206\ kJ/mol \qquad (1)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \Delta H_{rxn,298K} = -41\ kJ/mol \qquad (2)$$

2.2.2 Partial Oxidation

Partial oxidation of natural gas is the process whereby H_2 is produced through the partial combustion of methane with O_2 gas to yield CO and H_2 in Equation (3). In this process, heat is produced in an exothermic reaction, and hence a more compact design is possible as there is no need for any external heating of the reactor. The CO produced is further converted to H_2 as described in Equation (2).

$$CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2 \qquad \Delta H_{rxn,298K} = -36\ kJ/mol \qquad (3)$$

2.2.3 Autothermal Reforming

Autothermal reforming is a combination of both steam reforming in Equation (1) and partial oxidation in Equation (3). The total reaction is exothermic, and so it releases heat. The outlet temperature from the reactor is in the range of 950 to 1,100 °C, and the gas pressure can be as high as 100 bar. Again, the CO produced is converted to H_2 through the water-gas shift reaction in Equation (2). The need to purify the output gases adds significantly to plant costs and reduces the total efficiency.

2.2.4 Carbon Dioxide Reforming

Carbon dioxide reforming of methane or dry reforming to produce synthesis gas has recently gained high attention. This reaction has important advantages over steam reforming process such as; (a) both CH_4 and CO_2 are the greenhouse gases, (b) it can produce low H_2/CO ratio, which is suitable for using as the feedstock in Fischer-Tropsch process to synthesize liquid fuel, and (c) it can be used as chemical energy transmission systems and energy storage in the form of CO and H_2. The carbon dioxide reforming between CH_4 and CO_2 is shown in Equation (4). With an approximate 10-15% CO_2 fed, approximate 10-15% is being generated.

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \qquad \Delta H_{rxn,298K} = 261\ kJ/mol \qquad (4)$$

2.3 Gas Clean-up

After H_2 is extracted from the hydrocarbon fuel in the reforming stage, conditioning H_2 rich stream is necessary before it can be used in the PEM fuel cell electrode for power generation. A problem is the competitive adsorption of H_2 and CO on the Pt sites. CO preferentially adsorbs on the Pt electrocatalyst, thus blocking the access of H_2 to the surface and resulting in the degradation of the fuel cell performance. Lowering the CO concentration by decreasing the temperature of the reforming reactor would inevitably lead to a loss in efficiency, due to lower methane conversion and lower H_2 yield. Therefore, several chemical processes are required for CO clean-up immediately following the reforming stage. The goal is to reduce the concentration of CO below the tolerance limit of the electrode (typically <10 ppm on a dry basis), while minimizing any losses in efficiency.

2.3.1 Water Gas Shift Reaction

Water Gas Shift (WGS) reaction is independent of pressure and is slightly exothermic therefore exhibits lower equilibrium conversion with increasing temperature. Consequently, lowering the reaction temperature favors higher conversion but requires more catalyst and results in a larger reactor. These two opposing trends often lead to a practical limit to how much CO can be removed from the flow

stream. The lower temperature limit of operation often depends on the kinetic limitations of the process. Therefore, the reaction is normally carried out in two stages.

Therefore, the gas at the outlet of two-stage WGS reactor typically contains 45-75 vol.% H_2, 15-25 vol.% CO_2, a few vol.% H_2O, traces of unconverted fuel and ~0.5 vol.% CO. Thus, WGS reaction can provide a high degree of CO conversion but cannot achieve the low level of CO to prevent significant degradation of the PEM fuel cell stack performance.

Four technologies for CO removal were assessed for their competitive roles and advantages in fuel processor/PEM technology. Two technologies are based on physical separation. These are pressure swing adsorption (PSA), and palladium membrane separation, in which a 10-20 micron thick defect-free palladium membrane is used to separate H_2. The other two methods are based on catalytic reactions to reduce the CO level down to below 50 ppm, including the methanation and the preferential oxidation of CO.

Most designs use preferential CO oxidation (PROX) where low levels of CO are oxidized in the presence of high H_2 concentrations in order to reduce its concentration below the tolerance limit. This process, however, must be highly selective in order to minimize loss of H_2, and involves a catalyst that helps to discriminate the reactivity of O_2 in favor of CO over that of H_2.

2.3.2 Preferential Oxidation of CO in Excess of H_2

The exit concentration of CO from the WGS reactor is about 0.1-1.0 % depending on operating conditions. It is essential to remove CO from the stream because it poisons the Pt anode of the PEM fuel cell. Whereas some manufacturers have a specification of 50 ppm of CO, others have an objective to reduce the CO to <10 ppm. The most effective mechanism for CO removal for fuel cell quality H_2 is selective oxidation of CO. The process to achieve this is called preferential oxidation of CO in H_2 excess (PROX) and includes two parallel reactions:

$$CO + \frac{1}{2}O_2 \rightarrow CO_2 \qquad \Delta H_{rxn,298K} = -283\ kJ/mol \qquad (5)$$

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O \qquad \Delta H_{rxn,298K} = -242\ kJ/mol \qquad (6)$$

Both reactions are highly exothermic; therefore, it is crucial to remove heat from the reactor and to keep the temperature at near isothermal conditions. The adiabatic temperature rise for a typical reformate stream exiting a low temperature shift reactor with 5,000 ppm CO and with 2,500 ppm added O_2 is -228 °C (assuming 100% selectivity to CO oxidation). Therefore, depending on the operating window of the specific catalyst formulation, the catalyst temperature has to be controlled. This can be accomplished by varying the inlet temperature to the PROX reactor to account for the temperature rise along the length of the reactor or use of a staged reactor with inter-stage cooling.

In order to achieve the sub 10 ppm CO levels needed for PEM fuel cell applications, CO conversions of 90% or more are needed in the PROX unit. Because of the high ratio of H_2 to CO (>>100:1) in the reformate gas, the catalyst needs to be highly selective. Stoichiometric amounts of O_2 are desirable to keep the selectivity toward CO conversion high. Any O_2 remaining after conversion of CO will react with H_2, thus decreasing the effectiveness of the reactor.

The inlet temperature of the PROX reactor should ideally be less than or equal to the low temperature WGS reactor exit temperature generally found just upstream of the PROX reactor. This would allow easy transition, without heat exchangers or control schemes, into the PROX reactor. However, the selectivity for CO oxidation is reduced compared to H_2 oxidation at higher temperatures. In practice, no catalyst gives 100 % selective for CO, and so some H_2 is inevitably lost. O_2 from the air is a readily available oxidant. However, the additional nitrogen introduced with the air increases the dilution of H_2 rich gas, and contributes further towards a loss of efficiency at the fuel cell anode. For these reasons, selective oxidation of CO is only viable when CO concentrations are already low.

2.4 Platinum and Gold

Noble metals, which ones are highly active for the oxidation of pure CO for the preferential oxidation of CO (PROX). Oh and Sinkevitch (1993) studied the activity and selectivity of several catalytic systems based on noble metals. The best results were obtained with alumina supported Pt, Ru and Rh catalysts.

Pt catalysts are by far the most extensively studied catalysts. Pt is currently a component in the catalyst for the control of automobile exhaust emissions, where its main role in the oxidation of CO and hydrocarbons. As a result of this practical importance and due to the apparent simplicity of this reaction for studies at a fundamental level, the oxidation of CO over Pt has received considerable attention.

Despite occasional references in the older literature to the ability of Au to catalyze certain reactions, the metal has until recently had the reputation of being one of the least catalytically useful. Even as early as 1925, it was known that Au surfaces were capable of catalyzing the oxidation of CO to CO_2. Gold catalysts were also tested for this reaction. In fact, while pure gold is a poor catalyst for most reactions, mainly due to weak interactions with most adsorbates, several authors have shown that highly dispersed gold supported on metal oxides was active at low temperatures (even below 0 °C) in the CO oxidation reaction.

Au has the atomic number as 79, the atomic configuration as [Xe] $4f^{14}5d^{10}6s^{1}$, and therefore lies in Group 11(IB) of the periodic classification of elements. It is a congener of copper and silver, which often being referred to as the "coinage metals", and lies between Pt in group 10 and mercury in group 12. Concerning our area of specific interest, Pt is a versatile catalytic metal and is widely used in commercial applications for both chemical processing and pollution control, notably in automobile exhaust catalytic systems. While Au exhibits all the properties expected of a metal in term of luster, hardness, ductility, malleability, high thermal and electrical conductance, high resistance to oxidation and corrosion. A comparison between physical properties of Au and Pt is shown in Table 2.2.

Table 2.2 Physical Properties of Au and Pt

Property	Pt	Au
Atomic number	78	79
Atomic mass	195.08	196.97
Electronic configuration	$[Xe]4f^{14}5d^{9}6s^{1}$	$[Xe]4f^{14}5d^{10}6s^{1}$
Structure	fcc	fcc
Metallic radius(nm)	0.1385	0.1442
Melting temperature (K)	2042	1337
Boiling temperature (K)	4443	3081

2.5 Zeolite

Zeolites are microporous crystalline aluminosilicates, made up of TO_4 where T represents Si or Al with O atoms connecting neighboring atoms. If there are only Si atoms in T positions, the structure of this kind is silica (SiO_2) which is an un-charged structure. Once the Al is incorporated into the Si framework, the +3 charge of Al made the framework negatively charged, and the extraframework cations are required in order to keep the overall framework neutral.

$$M^{m+}_{n/m} \quad [Si_{1-n}Al_nO_2] \quad nH_2O$$

(extraframework cation) (framework) (sorbed phase)

The Si/Al ratio can vary from 1 to infinity, the completely siliceous form being polhymorphs of SiO_2. The lower limit of Si/Al is 1 because any two AlO^{-4} tetrahedra is not favored to sit next to each other due to electrostatic repulsion between them. In this work, we focus on the mordenite zeolite, which is used in variety of applications, for examples, C5/C6 paraffin isomerization, aromatics alkylation and transalkylation, xylene isomerization, catalytic NOx reduction, exhaust gas purification, etc. In addition, high metal dispersions may be favored in the zeolite pore. The mordenite zeolite (MOR) is a zeolite with 12-membered (6.7 × 7.0 Å) channels. They are in parallel to each other along the z direction and interconnected by 4.8 Å

deep 8-membered pockets. The composition of hydrated mordenite zeolite is usually close to [Na^{+}_{8} (Al_8Si_{40} O_{96}). $24H_2O$].

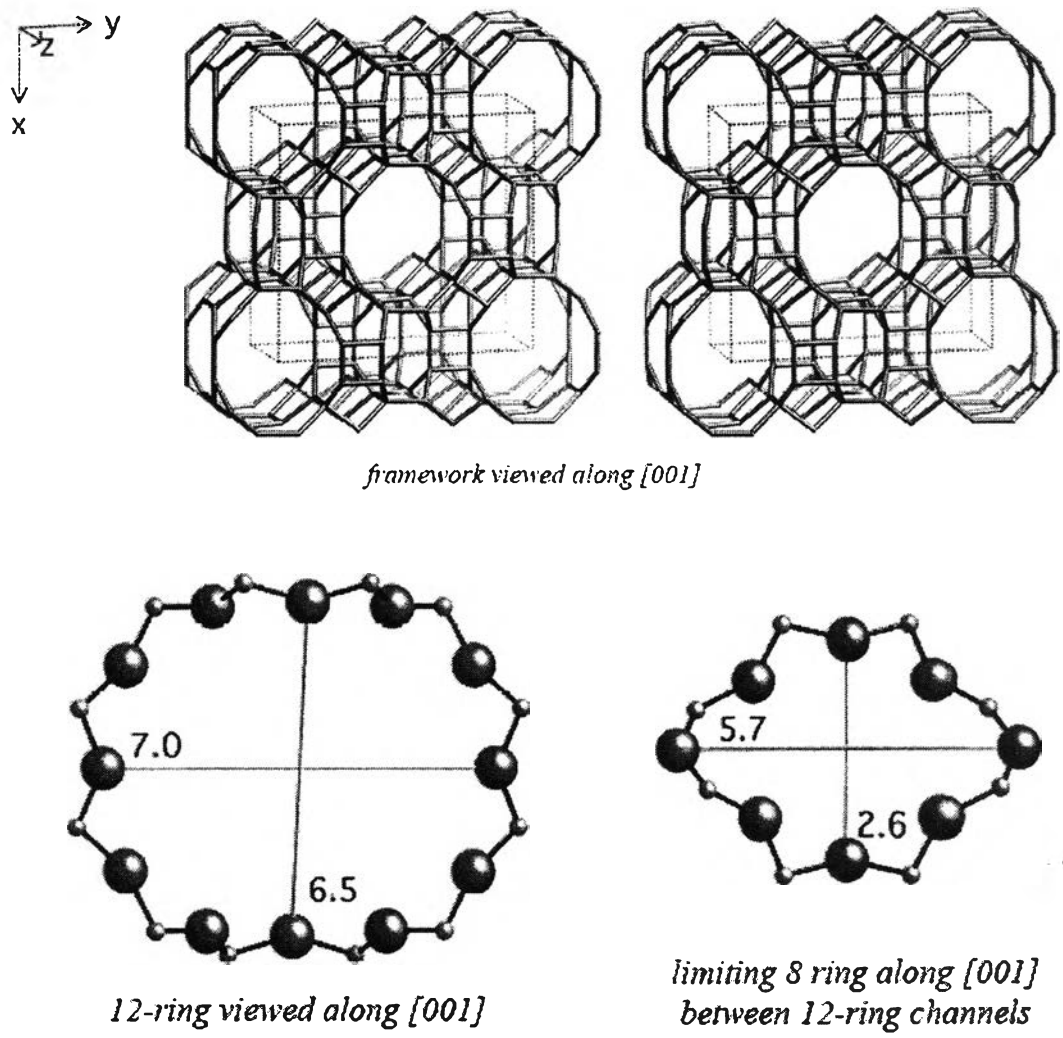

Figure 2.3 Lattice structure of mordenite zelolite showing parallel chanels of ~ 7.0 Å in z axis and the interconnecting pockets of 4.8 Å in y axis.
[Ref. http://zeolites.ethz.ch/IZA-SC/Atlas_pdf/MOR.pdf]

2.6 Literature Reviews

Watanabe *et al.* (1995) proposed the Pt supported in the cage of A-type zeolite catalysts for the removal of 1% CO from H_2-rich gas by the preferential oxida-

tion of CO, which is extremely superior to conventional Pt/Al_2O_3 catalyst. In 1997, Igarashi *et al.* have studied Pt supported on zeolite catalysts with different sizes of the molecular cages for the selective oxidation of CO. They found that the selectivity is affected by the supports materials and decreased in the following order: A-type zeolite > mordenite > X type zeolite > Al_2O_3. Pt supported on mordenite showed the highest CO conversion among the catalyst examined and had almost similar selectivity to that of A-type zeolite. Besides, they attempted to develop further active and selective catalysts for the preferential oxidation of CO by various metals (Pt, Ru, Pd, Co and Pt-Ru) supported on mordenite in 2000. Pt-Ru/mordenite exhibited fairly high selectivity at 150 °C. In addition, Rosso *et al.* (2004) have studied a variety of catalytic materials consisting of noble metal supported on A-type zeolite, which Pt, Pd and Ru-based catalysts prepared by impregnation. 1% Pt/3A catalyst showed the complete CO conversion in a wide temperature range (180-260 °C), showing the highest selectivity for the CO oxidation.

Kotobuki *et al.* (2005) investigated the preferential oxidation activity of Pt/mordenite, Fe/mordenite and Pt-Fe/mordenite. They found that Pt/mordenite and Fe/mordenite did not show any activity at 50 °C, but Pt-Fe/mordenite exhibited remarkable PROX activity up to extremely high space velocity at the same temperature.

The interest in studying Au catalysts has increased substantially since Haruta *et al.* (1989) discovered that these catalysts are predictable active for low temperature CO oxidation. The activity of Au catalyst depended on the nature of the support, preparation method, the Au concentration and the Au particle size. The key point in the production of an active gold catalyst is the well-dispersed particles within the nanometer size range. To achieve this, several preparation methods have been proposed in the literature, mainly based on the precipitation, at basic pH, of a gold precursor deposited on an inorganic oxide; the various preparation techniques have been discussed by Bond and Thompson in a review paper (1999).

In 2001, Haruta proposed that a specific emphasis is put on the effect of the size of Au particle on the catalytic performance. Au could be highly dispersed on a variety of metal oxides by means of co-precipitation and deposition-precipitation techniques; it exhibited high catalytic activity for CO oxidation at room temperature

even below 0 °C. Nevertheless, the catalytic activity of CO oxidation arise from the reaction of CO adsorbed on the step, edge, and corner sites of metallic Au particle with O_2 molecules adsorbed at the perimeter sites on the support surfaces.

The discovery of these catalyst motivated further work with Au with the goal of investigating the catalytic behavior of supported Au nanoparticles for many reactions especially CO oxidation and PROX.

Luengnaruemitchai *et al.* (2004) found that the activity of Au/CeO_2 catalyst for selective CO oxidation depends very strongly upon the preparation method, and co-precipitation prepared Au/CeO_2 catalyst showed the highest activities.

The several of material supported catalysts for CO oxidation used Au as metal active site. Wolf and Schuth (2002) investigated that highly active Au catalysts based on TiO_2, ZrO_2, Al_2O_3 and Co_3O_4 were prepared by deposition-precipitation. By contrast, SiO_2 was an unsuitable support material for the deposition-precipitation method. The catalytic activity of Au/metal oxide catalysts depended strongly on the pH during precipitation and the temperature of calcination. The optimum pH value is slightly dependent on the support and lies between pH 8 and 9. When the temperature of calcination increased, the catalytic activity in the CO oxidation decreased. According to the results from XRD and TEM, the increased catalytic activity with increasing pH value and decreasing calcination temperature could be attributed to a decrease in Au particle size.

Kung *et al.* (2003) summarized that recent progress in resolving different laboratories. It has been found that residual chloride in the sample is a very effective poison of the active site because the adsorbed chloride is to cause agglomeration of Au particles and low catalytic activity. Although, the amount of chloride adsorbed decreased when deposition-precipitation method by using chloroauric acid at a pH ranging 7 to 8. Besides, they found that the particle size of Au could be made smaller by addition of Mg citrate in the preparation solution. Catalysts prepared without citrate contained larger Au particles, were less active catalytically, and were less selective for CO oxidation. Thus a very small fraction of Au was associated with the active site. This implied that the activity per active site is very high.

The dispersion of Au^+ species inside the zeolites accounted for the enhancement of the catalytic performance of the Au^+/NaY catalysts, i.e., improving the CO adsorption (Mohamed *et al.*, 2000).

Wan *et al.* (2005) showed that nano-gold was prepared in different types of zeolite (Y, β and mordenite) for the CO oxidation in pH-adjusted chloroauric acid solution. The Au loading in zeolite depended strongly on the aluminum loading in zeolite, and on the shape and the pore structure of zeolite. The TPR study indicated that the reduction of Au species in different types of zeolite by H_2 depended on the structure of zeolite. Y-type zeolite required higher temperatures for the reduction, but β or mordenite zeolite required the lower temperatures. These results implied that larger Au species were formed in the larger pores of Y-type zeolite; in contrast, smaller Au species were formed in the smaller pores of β or mordenite zeolite. During the reaction, 32.7 ml/min of synthetic air and 0.33 ml/min of CO, the catalytic activity and the stability of Au in Y-type zeolite (12.4 wt. % Al) were much better than those of Au in β or mordenite zeolite, because the straight channels in β or mordenite zeolite facilitated the sintering of Au. In contrast, the cage-like pores in Y type zeolite can prevent the sintering of Au during CO oxidation. However, this study did not focus the selectivity of catalyst in reformed gases.

In the preceding work, Srinivas and Gulari (2006) have investigated the performance of a preferential CO oxidation reactor operating in two modes – single and two-stage on a Pt/γ-Al_2O_3 catalyst in a packed-bed microreactor system consisting of two cascaded stages. The two-stage mode of operation performed significantly better than the single-stage mode by offering a minimum CO outlet composition of 11 ppm. This was observed at an oxygen split ratio of 60:40, with the first stage operating at 230 °C and the second stage at 170 °C. The two-stage system is more suited to handling fluctuations and transients that are common occurrences in real system.

Attemps to promote the catalytic activity of Pt by addition of Au appear at first to have had contradictory results. Wang *et al.* (2006) studied the effect of Pt on Au (1.5) /ZnO catalyst for PROX. Further studies showed that dropping the Pt improved the stability of catalyst.

Monyanon *et al.* (2006) have investigated the catalytic activity of a series of $PtAu/CeO_2$ prepared by the single-step sol-gel method, using urea as the hydrolysis agent for PROX. The bimetallic catalysts ($PtAu/CeO_2$) are more active than mono-metallic catalysts (Pt/CeO_2, Au/CeO_2). The catalysts gave the smallest ceria crystallite size and strong interaction between active metals and support. Additionally, the blockage of catalytic active sites by adsorbed H_2O and CO_2 in the feed stream decreased the activity of the $PtAu/CeO_2$ catalysts.