

CHAPTER II

LITERATURE SURVEY

The energy infrastructure of the world is about to change fundamentally. Increasing environmental problems, the finiteness of fossil fuel reserves, as well as issues of security and finance connected to the import of fossil fuels combined forces a rethinking about the way we handle our energy requirements.

Fuel cells offer the most potential for improved energy efficiency and environmental compatibility in comparison to combustion engines. There are several types of fuel cells and the polymer electrolyte fuel cell (PEFC) or proton exchange membrane (PEM) has been attracting very much attention particularly for use in transportation. The fuels that are currently used with this type of fuel cell are H₂ and methanol. Normally, pure H₂ provides the ideal fuel for the fuel cell anode since it simplifies system integration, and maximizes system efficiency. There are, however, several serious difficulties regarding to the use of H₂ in vehicles. In addition to potential safety concerns there is a need for an acceptable refueling infrastructure. The development of such an infrastructure should meet the requirements of commercial viability. Technology for converting alcohols or hydrocarbons into a H₂ rich supply is based upon steam reforming, partial oxidation, or a combination of both, autothermal reforming. The steam reforming of fuels is becoming an attractive possibility for the fuel cell applications due to the chemical storage of H₂ at increased energy densities. However, the H₂ produced from reformed gas contains a small amount of CO which can restrict the performance of the anodes severely as illustrated in Figure 2.1. Even a few parts per million CO produces a substantial degradation in fuel cell performance, particularly at high current densities.

Many studies have shown the negative effect of CO on the performance of PEFC fuel cell (Götz and Wendt, 1998 and Rohland and Plzak, 1999). The use of Pt-Ru alloys as anode catalyst has shown that CO is oxidized at more negative potentials as compared to pure Pt and that a significant improvement of the fuel cell performance (Metikos-Hukovic and Omanovic, 1998). Palladium-based membrane purification, methanation and selective CO oxidation are the methods of reducing CO content in the feed to the range of 10 ppm or lower with minimum loss of H₂. In

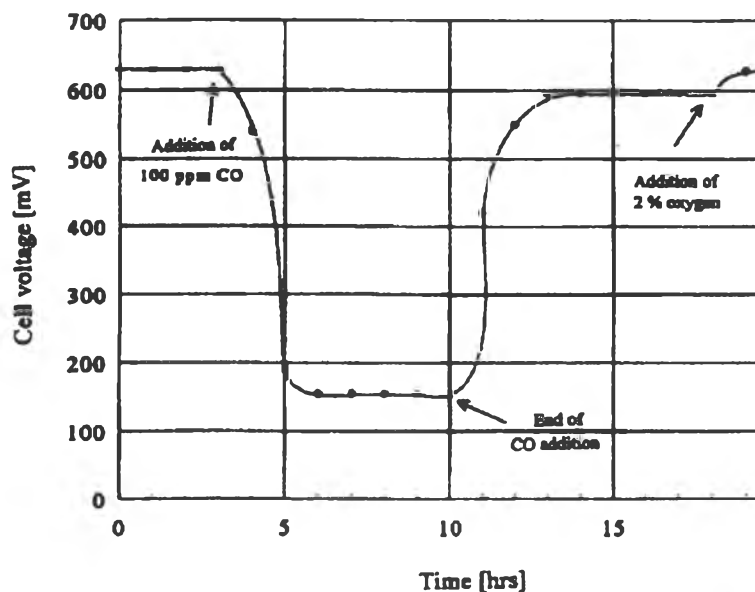


Figure 2.1 Influence of CO on a PEM fuel cell operated on a H_2 at a current density of 100 mA m^{-2} at 70°C (Götz and Wendt, 1998).

order to satisfy the fuel gas requirements of the fuel cell with respect to a low CO content in the reformat, selective CO oxidation is the most effective method. This method has been described by Gottesfeld and Pafford (1988) consisting in the feed of oxygen into the fuel gas stream. This has been achieved by selectively oxidizing CO to CO_2 . The same current/voltage characteristic as in pure H_2 has been observed for 100 ppm CO in H_2 when 4.5% O_2 was injected. To achieve this goal, the reformat gas passes through a small reactor containing a supported metal catalyst. The injection of a small amount of O_2 into a reactor causes a significant reduction of the CO amount. However, along with the CO, varying amounts of H_2 the desired product is also oxidized leading to a loss in efficiency.

For this reason, this work is focused on the development of catalysts for selective CO oxidation with minimal loss of hydrogen. Cleaning up the reformed gas prior to injection into fuel cells by oxidizing CO to CO_2 is the simplest method. Ideally, the catalyst must selectively oxidize about 1% (10,000 ppm) CO to 10 ppm without oxidizing any of the 40-70% H_2 present. Therefore, the main goal of the proposed study is to develop, test and characterize the alternative catalysts, which are

better than the currently used hydrogen purification catalyst, Pt/Al₂O₃ in terms of activity and durability for the use in fuel cells.

2.1 Fuel Cell

In principle, a fuel cell operates like a battery. Unlike a battery, a fuel cell does not run down or requires recharging. It will produce energy in the form of electricity and heat as long as fuel is supplied. As shown in Figure 2.2, a fuel cell consists of a fuel electrode (anode) and an oxidant electrode (cathode) sandwiched around an electrolyte. A fuel, normally H₂, reacts at the anode and O₂ reacts at the cathode.

The nature of the electrolyte determines the identity of the dominant migrating ion, as the following (Rohland and Plzak, 1999):

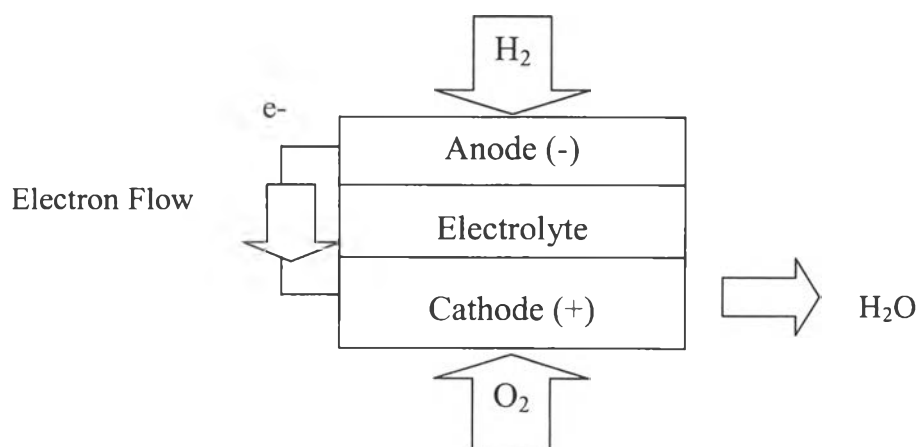
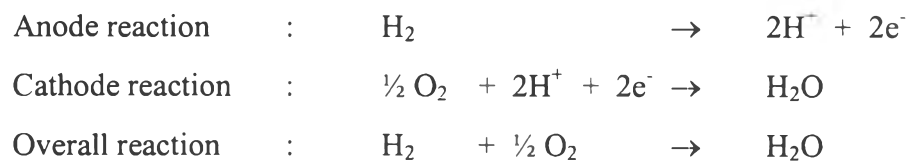


Figure 2.2 The simple diagram of the fuel cells.

The fuel is oxidized or reacts anodically over an electrocatalyst. Freeing electrons that then do work as they pass through an external circuit before reducing O_2 at the cathode. Both processes involve fuel being oxidized by O_2 but the mechanism of electrochemical oxidation is totally different from that of combustive oxidation.

There are six main fuel cell systems in various stages of development. These fuel cell systems are given in Table 2.1. Of various fuel cell systems considered, polymer electrolyte fuel cell (PEFC) technology, as used in electric vehicles, operating at a relatively low temperature between 80 and 130°C (Gottesfeld and Pafford, 1988) seems to be the most suitable for terrestrial transportation applications. The PEFC uses a polymer membrane as its electrolyte. This membrane is an electronic insulator, but an excellent conductor of hydrogen ions (Kordesch and Simader, 1996). There are many advantages of PEFC which are high efficiency, solid non-corrosive electrolyte, low temperature, rapid start-up, high power density, insensitive to differential pressure and insensitive to CO_2 .

2.2 Energy Conversion Efficiency

The theoretical maximum efficiency of a heat engine is given by Appleby and Foulkes (1989).

$$E_{\max} = \frac{T_1 - T_2}{T_1}$$

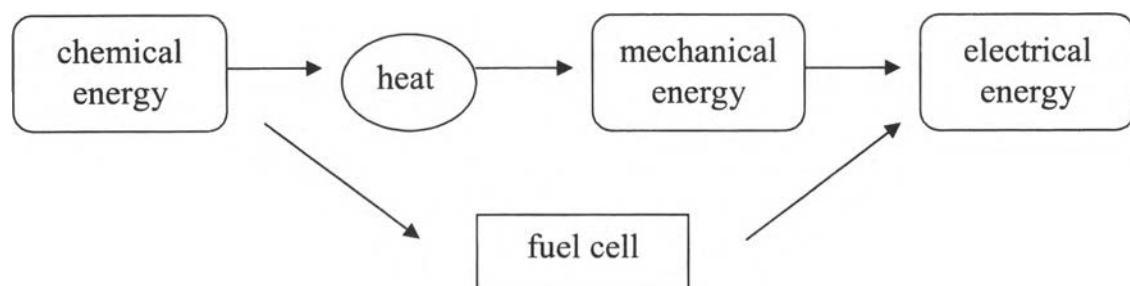
where T_1 is the absolute temperature of the hot inlet gases

T_2 is the absolute temperature of the hot outlet gases.

Since $T_2 < T_1$, the maximum efficiency is always less than unity. This so-called Carnot Efficiency is intrinsic to any energy converter that operates between a source and sink temperature. The energy conversion efficiency of a real system will be even lower than the Carnot Efficiency because of energy losses incurred during the various steps of the conversion process:

Table 2.1 Fuel cell types.

Fuel cell type	Electrolyte	Operating temperature (°C)
1. Alkaline (AFC)	Potassium hydroxide	50-90
2. Proton exchange membrane or Polymer electrolyte (PEMFC) or (PEFC)	Solid proton conducting polymer	50-125
3. Phosphoric acid (PAFC)	Orthophosphoric acid	190-210
4. Molten carbonate (MCFC)	Lithium/potassium carbonate mixture	630-650
5. Solid oxide (SOFC)	Stabilized zirconia	900-1000
6. Direct methanol (DMFC)	Sulphuric acid or solid polymer	50-120

**Figure 2.3** Direct energy conversion with fuel cells in comparison to conventional indirect technology.

Since the change in thermal energy between the reactants and products of a combustion reaction is given by the change in enthalpy (ΔH). The efficiency of an energy conversion device usually based on how much energy produced relative to the enthalpy change for the process. However, in an electrochemical converter, all the free energy change (ΔG) is available as electrical energy; thus the intrinsic maximum energy conversion efficiency or the ideal efficiency is given by

$$E_{\max} = \frac{\text{ideal work}}{\text{energy supplied}} = \frac{\Delta G}{\Delta H} = 1 - \frac{T\Delta S}{\Delta H}$$

Like Carnot machines, fuel cells can never approach ideal efficiencies. The heat released to the surroundings by a real fuel cell is always greater than reversible heat. Therefore, the ultimate electrical conversion efficiency in the cell is given by

$$E_{\text{overall}} = E_{\max} \times E_V \times E_F$$

where E_{\max} is intrinsic maximum efficiency

E_V is voltage efficiency

E_F is Faradaic efficiency which is also known as current efficiency.

Generally, the fuel cell system has the highest free energy efficiency of 60-80%. The total efficiency often includes the thermal and electrical energy.

2.3 Gas Clean-up Systems

In order to minimize the total expenditure of energy and total emissions for the fuel cell cycle from the primary source carrier to the vehicle, H_2 must first of all be produced from natural gas or other fuels (Höhlein *et al.*, 1996). The configuration with fuel storage, fuel processing with a heat/water management, H_2 purification, PEFC and electric drive results in a drive system for vehicles which will provide considerable emission advantages as compared with conventional vehicles is shown

in Figure 2.3. In this work, we will focus on the hydrogen purification or gas conditioning unit.

Under normal running conditions the product H_2 stream contains 5-25 % CO_2 , a few % H_2O and 0.5-1% CO . The trace amounts of CO in the stream cause a devastating deterioration of the energy efficiency of the fuel cell as shown in Figure 2.1. Thus in order to obtain optimum performance the total concentration of CO should be reduced to below 10 ppm before it enters the fuel cells.

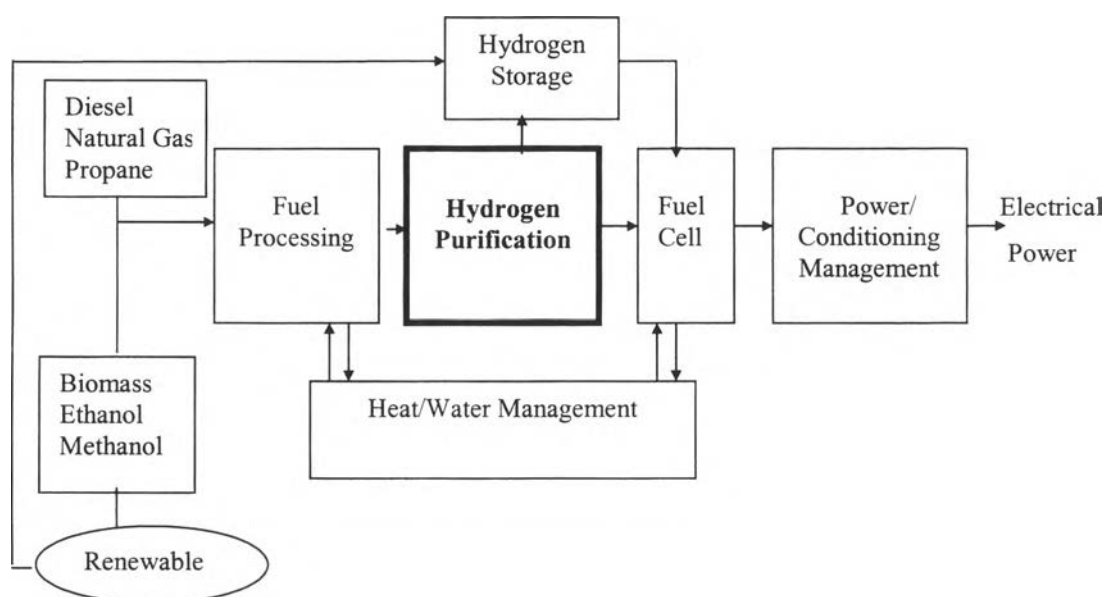


Figure 2.4 Fuel cell systems.

The selective CO oxidation or preferential catalytic oxidation of CO (PROX) in a H_2 atmosphere was proposed and tested by several groups. The first patent on preferential catalytic oxidation of CO was awarded to Engelhard (1963). Oh and Sinkevitch (1993) studied the activity of alumina supported Ru , Rh , and Pt catalysts. Ru and Rh were very selective compared to Pt in oxidizing CO in the presence of H_2 diluted with N_2 at $130^\circ C$. However, the gas composition of 900 ppm CO , 800 ppm O_2 and 0.85 % H_2 in N_2 background was very different from the reformed gas that is generated by reforming a liquid hydrocarbon or methanol.

The concept of using a zeolite support on Pt catalyst was applied for this reaction by Watanabe *et al.* (1995) and Igarashi *et al.* (1997). Kinetic studies of selective CO oxidation on Pt/Al₂O₃ and Au/Fe₂O₃ catalysts in simulated reformed gas (75% H₂, the rest is N₂) over a wide range of CO concentration (0.02-1.5%) were reported by Kahlich *et al.* (1997) and Kahlich *et al.* (1999). In addition to the noble metal catalysts other catalysts have also been investigated such as CoO catalyst (Teng *et al.*, 1999). Korotkikh and Farrauto (2000) investigated that Pt/Al₂O₃ catalyst promoted by a base metal oxide showed high selectivity and activity.

Recently, the metal oxide supports such as Al₂O₃ (Bethke and Kung, 2000), MnO_x (Torres Sanchez *et al.*, 1997), Fe₂O₃ (Guczi *et al.*, 2002), MgO-Al₂O₃ (Grisel *et al.*, 2002) were found to promote the activity of Au on selective CO oxidation and the catalytic combustion of volatile organic compounds (Sciré *et al.*, 2003). In the literature, it was found that the activity of the supported Au catalyst depends sensitively on the support material (Haruta *et al.*, 1993, and Yuan *et al.*, 1996, Scubert *et al.*, 2001). It was suggested that the high activity observed on supported Au catalyst with easily reducible oxide supports results from cooperative effects of the support material, its propensity for facile adsorption and storage of oxygen.

However, it should be noted that the above studies were carried out with unrealistic simulated reformed gas composition which no CO₂ and H₂O in the feed. There is also still a need for lowering the operating temperature to the PEFC condition. Therefore, in this work the investigation of selective CO oxidation with the composition of simulated reformed gas by adding water vapor and CO₂ in the gas stream and alternative catalysts are focused.

2.4 Cerium Oxide

Among the different metal oxides used as the support of Au and Pt for CO oxidation, cerium oxide or ceria (CeO₂) is one of the interesting metal oxides. CeO₂ is the oxide of the rare-earth metal cerium (Ce), which may exist in several compositions, due to the capacity of Ce to switch between the two oxidation state of Ce³⁺ and Ce⁴⁺. CeO₂ possesses the face centered cubic fluorite structure, which consists of a cubic close packed array of Ce⁴⁺ cations with all tetrahedral holes

occupied by O₂. In reductive atmospheres, Ce⁴⁺ ions on a stoichiometric surface are readily reduced to Ce³⁺. This enables the reversible addition and removal of O₂, thus allowing CeO₂ to act as O₂ storage material in oxidation reactions. CeO₂ is of interest for its potential applications in automobile exhausts.

CeO₂ has been a major component of the automotive three way catalysts (TWC) since the beginning of the 1980s. A number of functions have been ascribed to CeO₂, including promoting water gas shift activity (Barbier and Duprez, 1994 and Diwell *et al.*, 1991), maintaining the dispersion of the catalytic metals and stabilizing the surface area of the support (Ozawa and Kimura, 1990). Extensive research work, in particular during the past 10 years, has shown that CeO₂ affects a number of catalytic reactions. It has several important features: due to a facile redox reaction it exhibits O₂ storage capacity, it improves the CO oxidation (Breyse *et al.*, 1972 and Breyse *et al.*, 1973) and hydrocarbon oxidation, and it is an active center for the NO_x decomposition even in the absence of a noble metal. Summers and Ausen (1979) claimed that CeO₂ donated O₂ to Pt in their study of the oxidation of CO on Pt/CeO₂ catalyst. The facts gathered indicate that oxygen adsorbed on interfacial Pt/Ce sites and ceria lattice oxygen provides oxygen for CO oxidation. CeO₂ has been found to lower CO oxidation activation energy, enhances reaction activity and tends to suppress the usual CO inhibition effect (Shalabi *et al.*, 1996). In addition, the percentage loading of Ce has been shown to affect CO oxidation on Pt (Tiernan and Finlayson, 1998) and it promotes the activity of Pt in both lean and rich reactant gases for CO oxidation (Holmgren *et al.*, 1999).

The O₂ storage is simply described as a cyclic reduction and oxidation of the O₂-storing component CeO₂:



and



The importance of having a large contact area between Pt and CeO₂ was shown by Nunan *et al.* (1992), who correlated the synergistic reduction of Pt and

CeO₂ with the degree of Pt/CeO₂ interaction and proposed the benefits of Ce include improved noble metal dispersion. The influence of CeO₂ addition to a platinum group metal-PM (Pt, Pd or Rh)/Al₂O₃ catalyst on the mechanism for the CO oxidation has been investigated by several authors. Moreover, they found that the CeO₂ crystal structure is very important for the activity of CO oxidation. The cooperative effects of CeO₂-Pd on the kinetic of CO oxidation over Pd/CeO₂-ZrO₂ were also investigated (Bekyarova *et al.*, 1998).

Consequently, we chose CeO₂ as the support for studying selective catalytic oxidation of CO in the presence of H₂ based on the above properties of CeO₂.

2.5 Platinum, Palladium and Gold

Platinum group metals (PGM) e.g. Pd, Pt, and Rh have been used as oxidation catalyst in catalytic converters to treat automobile exhaust emissions (Barshad and Gulari, 1985 and McCarthy *et al.*, 1975).

The high catalytic activity of Pt and other group VIII metals is mainly due to their partially unfilled d-electron bands, which have band energy levels that are suitable for breaking bonds of adsorbed molecules (Masel, 1996). PGM are very good oxidation catalysts and this property is used to affect the total oxidation of pollutants-hydrocarbon (HC) and CO to CO₂, and H₂O in industrial fume abatement and automotive anti-pollution applications. Pt catalyst is a versatile catalytic metal and widely used for the oxidation of H₂, lower aliphatic alcohols and some other fuels in fuel cells, other electrochemical applications and pollution control, notably in automobile exhaust catalytic systems. Pd metal is known to have a better resistance to thermal sintering, and lower price (Not any more it costs the same as Pt) than Pt and Rh, and good selectivity for the oxidation of hydrocarbon and CO (Bunluesin *et al.*, 1998 and Noh *et al.*, 1999) and water-gas shift reaction (Shido and Iwasawa, 1993 and Whittington *et al.*, 1995).

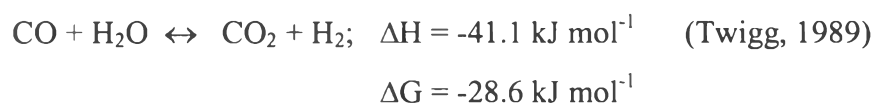
Gold has the atomic configuration [Xe] 4f¹⁴ 5d¹⁰ 6s¹, and it lies between Pt in group X and mercury in group XII. It is instructive to compare and contrast the properties of these metals. Au is unique among the metallic elements because of its resistance to oxidation and corrosion. Au exhibits all the properties expected of a

metal in terms of luster, hardness, ductility, high thermal and electrical conductance (Bond and Thompson, 1999). The supported Au catalysts have been found to be very active for CO oxidation reaction (Haruta, 1993, Haruta *et al.*, 1989 and Lin *et al.*, 1993).

For a catalyst to be applicable for fuel cell applications, the effects of water and CO₂ on the catalytic activity need to be known. Based on our inspection of the literature we find, Pt/CeO₂ could be one of the best candidates for selective CO oxidation. Contact between the metal and ceria could lead either to electronic or geometric perturbations in the surface of the metal particles, or atom transfer between ceria and the metal may be responsible for the need oxidation activity. From preliminary results, we found that Pd/CeO₂ and Au/CeO₂ catalysts also work well for selective CO oxidation. Therefore, majority of this thesis is focused on the performance of Pt/CeO₂ and Au/CeO₂ in selective oxidation of CO in the presence of large amounts of H₂ over the temperature range of 50 to 190°C. The results of Pd/CeO₂ catalyst are shown in Appendix.

2.6 Water-gas Shift Reaction

Water gas shift (WGS) is the preferred reaction for CO removal. Conversion of CO by the water gas shift increases the H₂ yield as well as getting rid of CO from ~10% to ~0.5-1%.



There are two types of WGS catalysts which are commercially used. One is a high temperature shift catalyst, which consists of oxides of iron and chromium and is used at 400-500°C to reduce the carbon monoxide to around 2-5%. The second one is a low temperature shift catalyst composed of copper, zinc oxide and alumina and is normally used between 200 and 400°C to reduce the CO concentration to ~1%. The thermodynamics of the WGS reaction are well known in that at high

temperatures the conversion is equilibrium limited and at low temperatures it is kinetically limited. Commercially a combination of the two catalysts is used with in between cooling.

Demand for H₂, a product of the shift reaction, will undoubtedly become even greater in the future, since new uses for H₂ are expected to appear. Recently, a new interest in the development of superior WGS catalysts used in fuel processors for PEFC fuel cells has been widely discussed. One of the major technical hurdles to fuel cell commercialization is the need to perform reliably under highly variable power loads, and deliver a gas stream containing very low levels of CO. CO is a poison to all electrocatalysts employed in PEFC fuel cells, and its presence results in rapid degradation of performance.

The WGS reactor is a critical component of the fuel processor in fuel cell system. Its function is to reduce the CO content to intermediate levels, which can then be further reduced in a subsequent step such as preferential oxidation step. Due to its industrial importance, the WGS has been studied extensively. Commercial catalysts used for WGS reactions are unsuitable for transportation due to their insufficient reactivity (high weight and volume). Moreover, the commercial low temperature catalyst (copper/zinc oxide/alumina) can not be exposed to air which is a distinct disadvantage for automotive use. Therefore, the need for low-temperature WGS catalysts is critical to the commercial success of automotive PEFC fuel cell systems.

Extensive research, in particular during the past 10 years, has shown that the conventional iron and chromium-based shift catalysts possess many problems. Recently, Au based catalysts have gotten very much attention because of their catalytic activity in low temperature CO oxidation, and catalytic combustion of hydrocarbons. Furthermore, Au catalyst shows potentially high activity for WGS reaction when supported on Fe₂O₃ (Andreeva *et al.*, 1996, Andreeva *et al.*, 1996 and Andreeva *et al.*, 1998). The Au/Fe₂O₃ catalyst was well documented to be a good catalyst for low temperature WGS reaction due to a specific interaction between Au and ferric oxide support.

It is generally known that precious metals like Pt, Rh, and Pd are not good shift catalysts because they are not easily oxidized by water. On the other hand, the

oxidation of Ce_2O_3 by water to give H_2 is thermodynamically favorable. In our studies on selective CO oxidation in the presence of H_2 at a reaction temperature of 110°C , we found that the catalyst material being developed is based on CeO_2 and uniformly incorporated Pt and Au. Pt/ CeO_2 sol-gel and Au/ CeO_2 co-precipitation catalysts exhibited both high activity and selectivity for the same reaction. The primary goal of this phase of our research is to determine the potential of these ceria based catalysts for low temperature WGS.

In this dissertation we report the results of our characterization and activity studies of the low temperature WGS reaction on Pt/ CeO_2 , Pt/ $\text{CeO}_2\cdot\text{Al}_2\text{O}_3$, Au/ CeO_2 , Au/ $\text{CeO}_2\cdot\text{Al}_2\text{O}_3$ catalysts and their comparison to Au/ Fe_2O_3 catalyst.