

CHAPTER II

BACKGROUND AND LITERATURE REVIEW

2.1 Fuel Cell

A fuel cell is an electrochemical energy conversion device. It was first to be used in Gemini space program in the 1960s as auxiliary power source and it also provided drinking water for the astronauts. It generates electricity from an electrochemical reaction in which oxygen (air) and a fuel (*e.g.* hydrogen) combine to form water. There are several different types of fuel cells, each using a different chemistry. Fuel cells are usually classified by the type of electrolyte they used. Some types of fuel cells work well for use in stationary power generation plants. Other may be useful for small portable applications or for powering cars.

Table 2.1 Type of fuel cell [Cameron, 1991]

	Alkaline fuel cells (AFC)	Proton exchange membrane fuel cells (PEMFC)	Phosphoric acid fuel cells (PAFC)	Molten carbonate fuel cells (MCFC)	Solid oxide fuel cells (SOFC)	Direct methanol fuel cells (DMFC)
Electrolyte	Potassium hydroxide	Polymer membrane	Immobilised phosphoric acid	Immobilised molten carbonate	Mixed oxide ceramics	Polymer membrane
Operating Temperature	60-90 °C	80-130°C	180-210°C	650°C	500-1,000°C	60-130°C
Efficiency %	50-60	40-60	36-38	45-60	50-65	40
Power output kW	20	< 250	> 10,000	> 1,000	< 250	< 10
Applications	Spacecraft, submarine	Cars, buses, residential, local area	Local power stations	Power stations	Small power stations	Portable, micro, battery replacements

The proton exchange membrane fuel cell (PEM fuel cell), also called polymer electrolyte membrane, and is one of the most promising technologies. This is the type of fuel that will end up powering cars, buses and may be even in house. The PEM fuel cell consists of two electrolyte (anode and cathode), as shown in Figure 2.1.

In an operation, the fuel and oxidant will be charged to the anode and cathode, respectively. Those steps are:

- At the anode, hydrogen molecules give up electrons, forming hydrogen ions. The process is possibly done by the platinum catalyst.
- The proton exchange membrane then allows protons to flow through, but not electrons. As a result, the hydrogen ions flow directly through the proton exchange membrane to the cathode, while the electrons flow through the external circuit.
- As they travel to the cathode through the external circuit, the electrons produce electrical current. This current can perform useful work by powering any electrical device (such as an electric motor or a light bulb).
- At the cathode, the electrons and hydrogen ions combine with oxygen to form water.

And the whole reactions are as follow:

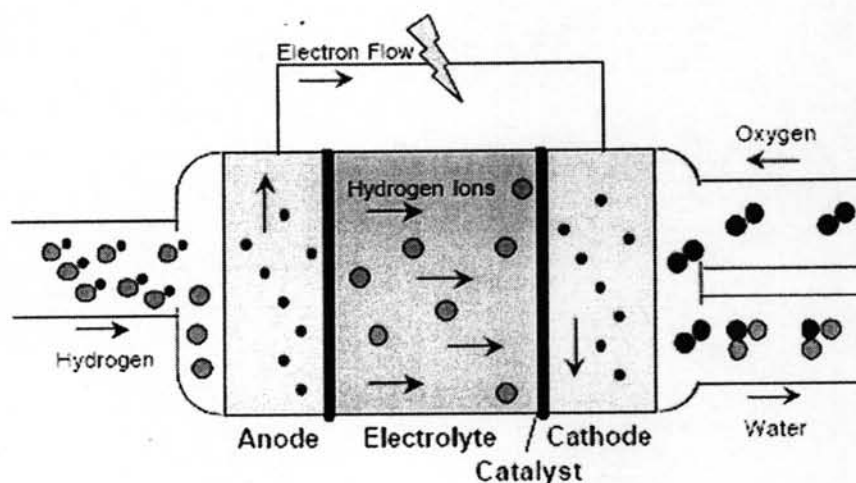
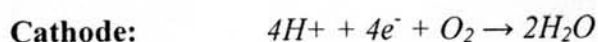


Figure 2.1 Drawing diagram of proton exchange membrane fuel cell

[www.fuelcelltoday.com].

This reaction is clean and non-pollution. The only byproducts are water and heat. In a single fuel cell, it produces only about 0.7 volts. To get this voltage up to a reasonable level, many separate fuel cells must be combined to form a fuel-cell-stack.

PEM fuel cells operate at a fairly low temperature (about 80 °C), which means they warm up quickly and do not require expensive containment structures. PEM fuel cell has many unique characteristics that make it appropriate for a portable application and an automobile, such as quick start up, transient response, long life stack, and low operating temperatures. However, there are some disadvantages as well; for example, water-management problem, expensive electrode catalyst and polymer membrane, and poor CO tolerance, PEM fuel cell requires pure H₂ to be an ideal fuel, especially CO-free H₂ since only a trace amount of CO can significantly decrease the performance of the PEM fuel cell.

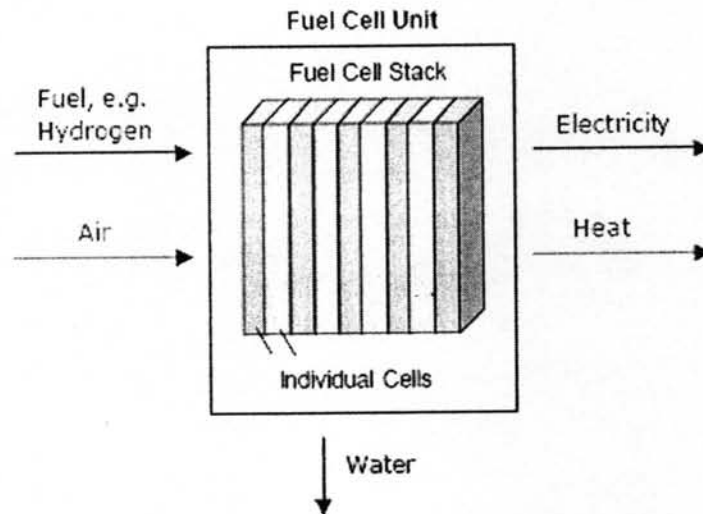


Figure 2.2 Drawing of proton exchange membrane fuel cell stack
[www.fuelcelltoday.com].

2.2 Hydrogen

Hydrogen is the simplest element and most plentiful gas in the universe. Hydrogen is colorless, odorless and tasteless. Each hydrogen molecule has two atoms of hydrogen, which accounts for the H_2 . Hydrogen is the lightest element, with a density of 0.08988 grams per liter and standard pressure, yet it has the highest energy content per unit weight of all the fuels (52,000 Btu/lb.), or three times the energy of a pound of gasoline.

Hydrogen is never found alone on earth. It is always combined with other elements such as oxygen and carbon. Hydrogen can be extracted from virtually any hydrogen compound and is the ultimate clean energy carrier. It is safe to manufacture. And hydrogen's chemical energy can be harnessed in pollution-free ways.

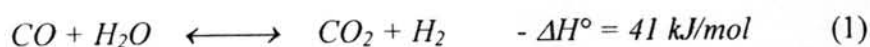
In PEM fuel cell, hydrogen has some limitations that make it impractical for use in most applicants. For instance, there is no hydrogen pipeline system for human residence and it is difficult to storage H_2 in the tank at gas station.

Hydrogen is difficult to store and distribute. So it would be much more convenient if fuel cells could use fuels that are more readily available. This problem is addressed by a device called a reformer. A reformer turns hydrocarbon or alcohol fuel into hydrogen, which is then fed to the fuel cell. Unfortunately, reformer is not perfect. They generate a gas which contains 8-12% CO besides hydrogen and CO_2 . This CO must be converted with the help of steam to CO_2 and hydrogen via the water-gas shift (WGS) reaction before a final clean-up step can reduce the CO content to < 10-50 ppm for the fuel cell. Such low CO levels are needed at the fuel cell anode to efficiently carry out the electrochemical oxidation of hydrogen.

A fuel cell system which includes a "fuel reformer" can utilize the hydrogen from any hydrocarbon fuel – from natural gas to methanol, and even gasoline. Since the fuel cell relies on chemistry and not combustion, emission from this type of a system would still be much smaller than emission from the cleanest fuel combustion processes.

2.3 Water-Gas Shift Reaction

Water-Gas Shift Reaction (WGSR) is the process whereby water, in the form of steam, and carbon monoxide gas, CO, are catalytically shifted to carbon dioxide (CO₂) and hydrogen (H₂). This reaction was developed industrially in conjunction with ammonia synthesis for a century, since it provides a way of increasing yield of hydrogen from synthesis gas and simultaneously decreasing the CO content. CO is a poison for ammonia-synthesis catalysts and for most metallic hydrogenation catalysts, and must be reduced to a very low level.



Since the shift reaction (Equation 1) is mildly exothermic to the right, the maximum conversion at equilibrium is attained at the lowest temperatures. Pressure has no significant effect on the equilibrium because there is no volume contraction. The equilibrium conversion as a function of temperature is shown in Figure 2.3.

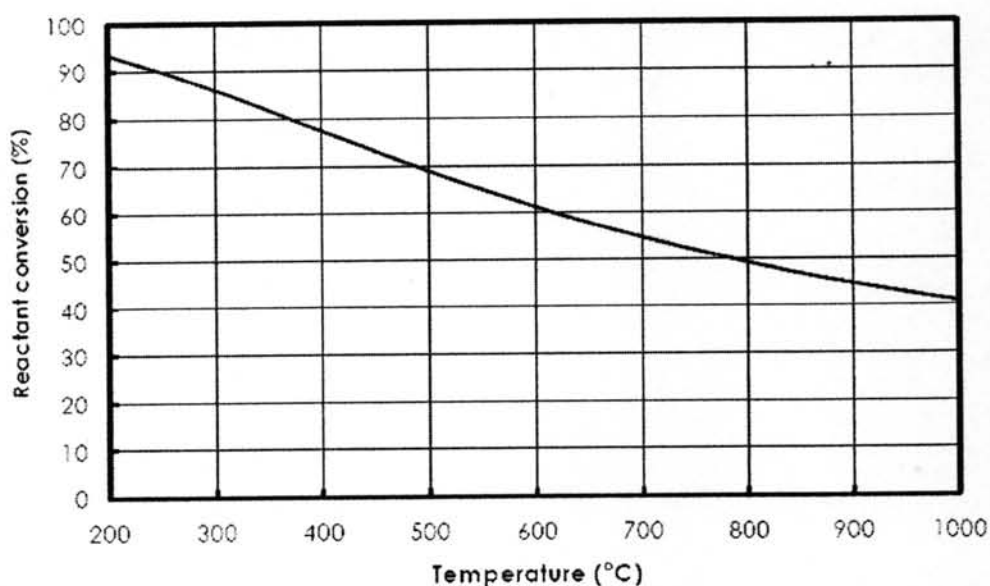


Figure 2.3 Equilibrium conversions for the water-gas shift reaction

$$[CO]_o = [H_2O]_o, [CO_2]_o = [H_2]_o = 0.$$

The WGSR is governed both by thermodynamics (equilibrium CO contents are lower at low temperatures) and by Arrhenius-like reaction kinetics (catalysis rates increase at higher temperatures). Therefore, two WGS reactors are typically employed in a fuel processing system: one at high temperatures for initial CO conversion, and a second at low temperatures to exploit lower equilibrium CO contents. The WGSR is also exothermic, so that heat management is a critical component of any fuel processing strategy employing WGS reactors. This dual-stage WGS reaction strategy is shown schematically in Figure 2.4.

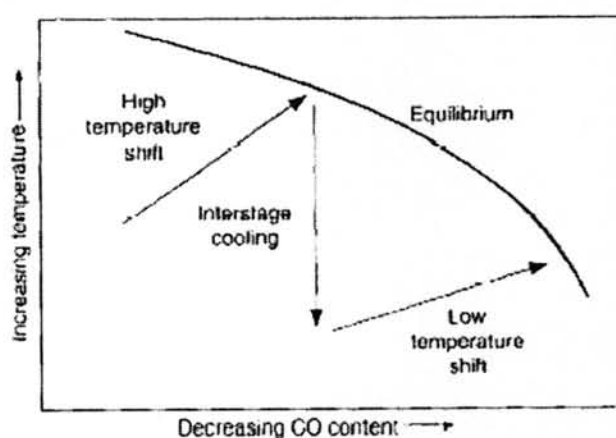


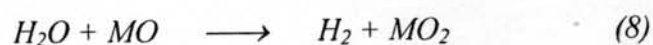
Figure 2.4 Schematic showing operation of dual-stage WGSR scheme [Swartz *et al.*, 2001].

Despite the fact that the WGSR has been recognized for over a century, there is still some discussion about the reaction mechanism. Shido and Iwasawa (1991, 1993) have used fourier transfer infra red spectroscopy (FTIR) and temperature programmed desorption (TPD) to suggest that the reaction proceeds via the formation of an adsorbed formate group which decomposed to hydrogen and CO₂. They concluded that bidentate formate species, produced by reaction of CO with the terminal hydroxyl groups of ceria, are the reaction intermediates. The rate-determining step is the decomposition of the bidentate formate to hydrogen and unidentate carbonate (Equation 2-6).

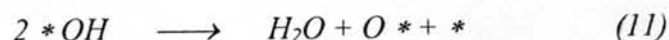
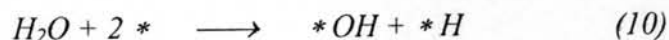




Several other groups have suggested that a redox mechanism is predominant (Bunluesin *et al.*, 1998 and Li *et al.*, 2000).



Recent density functional theory (DFT) calculations (Marrikakis, 2005) have suggested that the process involves interaction of two *OH groups.



Arguments for and against the different mechanisms on high and low temperature catalysts are presented by Rhodes *et al.* (1995). At the higher temperatures, where the iron-based catalyst is active, the redox mechanism predominates, as confirmed by the fact that formate coverage decreases over the range of 250-400 °C, while catalytic activity increases (Diagne *et al.*, 1990). Whether or not the formate mechanism actually contributes to the overall process under these conditions is a mute point.

Nevertheless, some questions concerning the adsorption and activation of CO and water still remain. Up to now, there are no FTIR studies useful to clarify WGS mechanism on Au/CeO₂ catalysts. In 1999, Bocuzzi *et al.*, studied low-temperature WGS on Au/α-Fe₂O₃ and Au/TiO₂ catalysts. There was evidence that hydrogen dissociates on gold sites and spillover on the oxides at room temperature.

Furthermore, Tabakova *et al.* (2003) also studied LTWGS on Au/CeO₂ catalysts with FTIR. They found that the reduction of Au/CeO₂ in hydrogen already at 100° C procedures the exposure at the surface of negatively charged gold sites and of oxygen vacancies on ceria surface. An electron transfer from the support to the very small gold clusters occurs. The Au/CeO₂ interface plays a decisive role in the surface structure of the catalyst by modifying the gold and ceria oxidation state. After reduction, the CO adsorption capacity on the gold particles is increased. They also concluded that the WGSR proceeds at the boundary between small metallic gold particles and ceria, where CO adsorption on gold and H₂O dissociation on ceria defects take place. The production of bands typical formate species confirms their role as intermediates in the WGSR.

2.3.1 High-Temperature Water-Gas Shift Catalyst

The original catalyst was first used by BASF starting in 1915, and its composition has not been changed much since. The catalyst is basically Fe₃O₄, the stable iron phase under reaction conditions, plus some chromia that act as a textural promoter to minimize sintering. A typical composition contains about 55 wt % Fe and 6 wt % Cr. The catalyst is supplied with a low sulfur content (for example, < 0.07 percent) when the high-temperature converter is to be followed by a low-temperature reactor in which the catalyst used is highly sensitive to low concentrations of sulfur compounds. The catalyst is unsupported, usually prepared by a precipitation process, and is available in the form of tablets or rings.

As prepared, the iron is in the form of Fe₂O₃, which is reduced to Fe₃O₄ (magnetite) before use, usually in situ. The chromium forms an iron-chromium spinel [Fe(II)Fe(III)_{2-x}Cr_xO₄]. This exothermic reduction reaction must be carefully controlled, as by the use of a high concentration of steam diluent, to prevent damage to the catalyst. The catalyst is resistant to sulfur compounds, but this is of little concern if the synthesis gas is prepared by steam reforming since an essentially sulfur-free feed is required for this reaction.

The gas composition fed to the water-gas shift reactor may vary considerably, depending on the feedstock and process used to generate the synthesis gas. Typically, after removal of CO₂ by scrubbing, a large excess of steam is added to the

synthesis gas. The mixture is then passed through an adiabatic converter containing the catalyst. Sufficient steam must be added to prevent formation of an ironcarbide phase that could cause synthesis of hydrocarbons by the Fischer-Tropsch synthesis reaction. Rostrup-Nielsen and Nielsen (1985) gave a plot of conditions under which an oxide phase may be expected to convert to a carbide phase. Conditions under which a carbided iron catalyst for Fischer-Tropsch synthesis is converted in part to an oxide are given by Satterfield *et al.* (1986). Reduction of the Fe_3O_4 to metallic iron could catalyze the formation of carbon from CO, and this must also be considered.

An inlet temperature of about 350 °C or more must be attained for an adequate reaction rate to be achieved, but the maximum temperature is limited to about 530-550 °C. The reaction is moderately exothermic and the increase in temperature through the reactor may vary considerably depending on the feed gas composition. The pressure is determined by the requirements in other portions of the process, but may be as high as 3 MPa or more. Higher pressure increases the reaction rate, so a smaller vessel can be used. The superficial contact time is of the order of 3 to 9 s (calculated for wet gas at standard temperature and pressure) but may be 1 s or less in high-pressure operation. Normal catalyst life is several years, but is decreased somewhat at higher pressures.

2.3.2 Low-Temperature Water-Gas Shift Catalyst

Considerable CO remains in equilibrium (*e.g.*, about 3 mol %, dry basis) at the exit temperature with use of the aforementioned catalyst. In earlier processes the CO was removed together with CO_2 by scrubbing with copper liquor (*e.g.*, an aqueous solution of copper ammonium formate). A substantial improvement came about by the development of a low-temperature shift catalyst, first introduced commercially in 1962. With its use the exit gas from the first converter is cooled, usually by quenching with water, which supplies additional steam, and passed into a second converter. Here additional reaction is achieved over a catalyst containing copper, zinc oxide, and alumina which is similar to the catalyst used in methanol synthesis. Copper metal and zinc oxide are the stable forms under reaction conditions, and the

catalyst is active at temperatures as low as 200 °C, approximately the lowest that can be used without condensation of steam at typical elevated pressures. Currently Cu/ZnO/Al₂O₃ is used as a standard LTS catalyst.

Copper metal is the active species, and one role of the zinc oxide may be to protect the copper from poisoning by adsorbing traces of sulfur compounds and reacting with them. The zinc oxide may also act as a support for the copper. This catalyst is more sensitive to deactivation by thermal sintering than the high-temperature shift catalyst, since copper has a relatively low melting point. A maximum operating temperature of about 250 °C is typical. The temperature rise through the reactor is about 15 °C, and the superficial contact time (calculated for wet gas at standard temperature and pressure) is about one second.

Representative ICI catalysts have compositions, before reduction, of CuO, 32 to 33 wt%; ZnO 34 to 53 wt%; Al₂O₃ 15 to 33 wt%. Under poison-free conditions Al₂O₃-based catalysts apparently have higher activities and greater resistance to deactivation with time-on-stream than Cr₂O₃-based catalysts, although some commercial catalysts contain chromia instead of alumina. However, detailed manufacturing methods are important in addition to composition. If poisons are under control, catalyst life is typically 1 to 2 years. On a commercial Cu-ZnO-Al₂O₃ catalyst operated at 1.3 MPa, the reaction becomes diffusion-limited above about 200 °C.

The activity and stability to aging may be markedly affected by the method of precipitation of the catalyst, as is also true of the similar catalyst used for methanol synthesis. For maximum activity and stability, the copper crystallites must be as small as possible and separated from one another by the zinc oxide and alumina promoters. These must be even more finely divided than the copper crystallites for maximum effectiveness. In a commercial catalyst the copper crystallites may typically be about 4 nm initially and about 8 nm after 6 months of operation. The reduction of the copper oxide to metallic copper is highly exothermic and must be carried out carefully, at a temperature not exceeding 220 to 230 °C, to avoid sintering. The used catalyst is pyrophoric and is therefore discharged under an inert gas such as nitrogen and then typically doused with water.

The catalyst is poisoned by sulfur and chlorine compounds at concentrations in the range of 1 ppm. However, sulfur compounds react preferentially with the zinc oxide to form zinc sulfide, leaving the copper active. Chlorine causes deactivation of the catalyst by accelerating the sintering of copper, caused by the formation of volatile copper and zinc chlorides. Use of the low-temperature shift catalyst makes it possible to lower the carbon monoxide content in the exit gas to about 0.2 to 0.4 mol%. This is then further reduced to the parts-per-million range by catalytic methanation, a much more satisfactory process than copper liquor scrubbing.

In some applications, carrying out the shift reaction on a gas stream containing concentrations of sulfur compounds that would rapidly poison the aforementioned catalysts may be desirable. In the event a CoMo catalyst, *e.g.*, 4.5 wt% CoO, 15.0 wt% MoO₃, in the sulfided state may be used, on a support stable to water vapor at reaction temperature. In this type of application, various organosulfur compounds may be converted simultaneously to H₂S. This may then be removed together with CO₂ in a subsequent scrubbing operation.

These CoMo catalysts are promoted with an alkali, potassium being both effective and inexpensive, and used in the sulfided form. As such they are reported to be comparable in activity to the Cu-ZnO/Al₂O₃ catalysts at, *e.g.*, 260° C. These CoMo catalysts have been used industrially since the early 1970s and are marketed by several catalyst manufacturers, but little information has been published about their performance. They appear to be effective and stable at temperatures in the range of about 450 °C to about 200 °C. (The lower temperature is limited by the dew point.) These catalysts have a life of the order of 2 years. The CoMo catalysts are several times more active in the sulfided form than in the nonsulfided form, so a minimum ratio of H₂S-H₂O is needed in the gas for maximum activity. In the sulfided form, the CoMo catalyst is reportedly somewhat more active at high temperatures than the conventional iron-chromia catalyst in the fresh form. A study of the water-gas-shift kinetics over a sulfided CoMo/Al₂O₃ catalyst was performed over a pressure range of 0.5 to 2.7 MPa, 250 to 300 °C and at gas hourly space velocities (GHSV) of from 4800 to 24,000 hr⁻¹ (Satterfield, 1991).

2.4 Catalyst Development

Commercially available catalysts used for this reaction are mixed oxides (Cu/ZnO) partially reduced and activated in situ. Unfortunately, they are sensitive to start-up/shut-down cycles and may be pyrophoric (de-activate on exposure to air), which is acceptable for industrial use but imposes limitations for smaller applications (Ladebeck *et al.*, 2003). The activity of existing WGS catalysts is generally low, and a large fraction of reactor volume is occupied by the WGS part of the fuel processor for H₂ production. It is advantageous to carry out the WGSR at low temperature to move the reaction equilibrium in favour of hydrogen production. The catalyst has to be sufficiently achieving equilibrium conversion at temperature below 270C to achieve CO concentrations below 0.5% CO.

2.4.1 Active Metal

Gold-based catalysts have received great attention since Haruta *et al.* (1989 and 1993) discovered that gold exhibits surprisingly high catalytic activity for CO oxidation at temperature as low as -73° C when it is deposited as nanoparticles on metal oxides. The increased interest and rapidly growing number of investigations on supported nano-gold catalysts is due to their potential applicability to many reactions of both environmental and industrial relevance.

The gold catalysts, Au/ α -Fe₂O₃ and Au/ZrO₂, prepared with co-precipitation method were first applied to WGSR and Au/ α -Fe₂O₃ was found to be higher activity than commercial CuO/ZnO/Al₂O₃ catalyst at low temperature while Au/Al₂O₃ prepared in the same way had virtually no activity at all (Andreeva *et al.*, 1996), suggesting that it was cooperation between the gold and the Fe₂O₃ support that was responsible for the high activity. One year later, the LT-WGS activity of Au/TiO₂, prepared by deposition-precipitation (DP), was also found to be comparable to the commercial Cu/ZnO/Al₂O₃ catalyst (Sakurai *et al.*, 1997). Therefore, the DP method was modified with Au/ α -Fe₂O₃ catalyst and was achieved higher LT-WGS activity than that from co-precipitation method (Andreeva *et al.*, 1998) with the same average size of gold particle (~2 nm). However, Au/TiO₂ catalyst was found to be almost completely inactive at any temperature on LT-WGS reaction con-

dition composed of H_2 , CO , CO_2 , and H_2O (Bocuzzi et al., 1999). The more insight into the surface intermediates on zeolite-encapsulated gold catalysts was first studied with Au on NaY, Na-Modernite, and Na-ZSM-5 (Mohamed *et al.*, 2000). It was proven that dual Au^+ and Au^0 are the active sites for the WGS, especially when it encapsulated inside NaY zeolite rather than in Na-mordernite and Na-ZSM-5 catalysts.

Ceria-based catalysts have been studied as an alternative to the commercially $CuO/ZnO/Al_2O_3$ LT-WGS catalyst. For gold on ceria support catalyst, Fu and co-workers (2001) studied high gold loading (5-8%) on ceria for LT-WGS with two preparation methods, DP and co-precipitation (CP). The addition of gold significantly increased the reducibility of the ceria surface oxygen which was controlled by the crystallite size of ceria. The Au/CeO_2 catalytic activity correlated well with its reducibility. However, Andreeva et al. (2002) concluded that the 3% and 5% Au/CeO_2 has comparable LT-WGS activity and stability. The stability of gold-ceria after three months remains stable, suggesting from TPR result that the reduction/oxidation process take place readily in the presence of gold and 3% Au/CeO_2 has the optimal ratio between surface gold active centers and free ceria surface being capable to produce oxygen.

Haruta *et al.*, (2002) also found that supported Au catalysts are applicable to the H_2 production through low-temperature WGS reaction and selective CO oxidation in H_2 -rich streams, to the selective partial H_2 of butadiene, acetylene and unsaturated aldehyde, and to the liquid-phase selective oxidation of glycols.

Tabakova and co-workers (2003) used FTIR to investigate Au/CeO_2 catalyst on LT-WGS reaction. They concluded that the WGS proceeded at the boundary between small metallic gold particles and ceria, where CO adsorption on gold and H_2O dissociation on ceria defects take place. The production of bands typical of formate species confirmed their role as intermediates in the WGS.

While platinum based catalyst are found to be less selective than Au and Cu based catalysts, Mavrikakis *et al.* (2004) used periodic density functional theory (DFT) calculation and micro-kinetic modeling to compare selectivity for the preferential oxidation (ProX) with respect to H_2 based on studies of elementary reaction steps on the (111) facet of Au, Cu and Pt. The results showed that at low-

temperatures both Au and Cu should be more selective PROX catalysts than Pt. At higher temperatures, Pt and Cu lose a small fraction of their selectivity, whereas Au shows a substantial selectivity loss, mainly because of the weak CO binding.

The deactivation and regenerability of Au/CeO₂ catalyst was studied in the simulated reformat mixture (10%CO, 22%H₂O, 6%CO₂, and 43%H₂ in N₂). Although the initial activity of Au/CeO₂ was higher than commercial catalyst, but it is subjected to deactivation due to the oxygen-deficiency and causing the formation of carbonate and/or formats on the catalyst surface. However, the deactivation could be fully regenerated by calcination in air (Kim and Thompson, 2005). The effect of simulated reformat LT-WGS reactant in mild condition (1.3%CO, 5.7%H₂, and 3.1%H₂O in helium) was also investigated with Au/CeO₂ and Pt/CeO₂ and found that Au/CeO₂ achieved more activity at lower temperature. Pt/CeO₂ produced methane at high temperature resulted in a decreased of H₂ yield at above 250 °C.

Tabakova *et al.* (2006) studied a comparative of IB group (i.e. Au, Ag, Cu) over ceria catalysts with two different preparation techniques (DP and modified version of deposition-precipitation, MDP) on LTWGS reaction. They found that Ag/CeO₂ catalysts are almost completely inactive because metallic adsorbs very weakly CO and Au/CeO₂ catalysts showed the best catalytic activity.

Last year, gold using mesoporous zirconia support was first studied on LT-WGS reaction by Idakiev *et al.* (2006). They discussed that the mesoporous with high specific surface area and narrow pore size distribution could enhance the WGS activity and facilitate the formation of well dispersed and the stable gold particles. The result was concluded that the WGS activity was improved also the stability. The deactivation of the catalyst is due to their ability to adsorb CO and accumulate it as carbonates. By the way, the deactivation can be fully restored by calcined in air.

2.4.2 Metal Oxide Support

The addition of gold to some oxidic systems leads to an increase in their catalytic activity which is probably due to synergism between the gold and the metal oxide species. The peculiar structure and properties of the gold/metal oxide interface are the result of this specific interaction. The nature of the support exerts a decisive influence on the catalytic activity of gold-containing catalysts. Therefore,

many study of the influence of gold based on metal oxides have been investigated. Au/ α -Fe₂O₃ and Au/TiO₂ catalysts in the LTWGS reaction were studied by Andreeva *et al.* (1996 and 1998) with a high catalytic activity results. Depending on the preparation technique, the Au/TiO₂ samples drastically change their catalytic activity. Four years later, a series of Au/ZnO, Au/ZrO₂, Au/Fe₂O₃-ZnO and Au/Fe₂O₃-ZrO₃ catalysts was studied and it was concluded that well-crystallized supports led to higher catalytic activity (Andreeva *et al.* 2000).

In 2001, Fu *et al.* found that the nanostructure Au/CeO₂ has better activity and more stable than Au/TiO₂ catalyst. They referred to Bunluesin's work which reported that ceria is a better choice than alumina as a support for the noble metals in the catalytic converter because it drastically improves their low-temperature activity for CO oxidation (Bunluesin *et al.*, 1995) and the water-gas shift reaction (Bunluesin *et al.*, 1998). Fu *et al.* reported that the addition of gold significantly increased the reducibility of the ceria surface oxygen. The amount of surface oxygen available for reduction has been controlled by the crystallite size of ceria.

Ceria is well known as one of the major supports widely used in the three-way catalytic activity.

2.4.3 Mechanism of Gold-Ceria Catalyst for Water-Gas Shift

Consideration of the mechanism of this reaction on gold catalysts is made difficult by the variety of interpretations placed upon the experimental results. There are essentially three conflicting proposals:

- (1) Reaction on or close to Au⁰ particles, with adjacent oxide ions, formed from water molecules, acting as oxidant.
- (2) Reaction involving Au ^{δ +} cations and redox processes on the support.
- (3) Reaction mediated by formate ions on the support.

The problem is highlighted by two spectroscopic studies of the reaction on Au/CeO₂. One of them focus on the role of Au⁰ particles, while recognizing the existence of Au^{x+} and of carbonate, bicarbonate and formate species that show IR absorption between 1200 and 1800 cm⁻¹, but these are regarded as spectators and not reaction intermediates. Fig. 2.5 shows a full reaction scheme has been developed on

this basis by Andreeva and co-workers. After initial creation of anion defects by reaction of oxide ions close to Au^0 particles with CO, reaction proceeds by their re-oxidation by water with the liberation of H_2 ; further oxidation utilizes oxygen ions originating in the water molecule. In this mechanism, no role is assigned to formate ions or lattice oxygen other than that coming from the water; it accords with mechanism (1) above. A mechanism awarding a major role to Au^0 particles, perhaps in association with $\text{Au}^{\delta+}$ species, is clearly indicated by the XAFS/XANES results obtained with $\text{Au}/\text{CeO}_2\text{-ZrO}_2$ mentioned above.

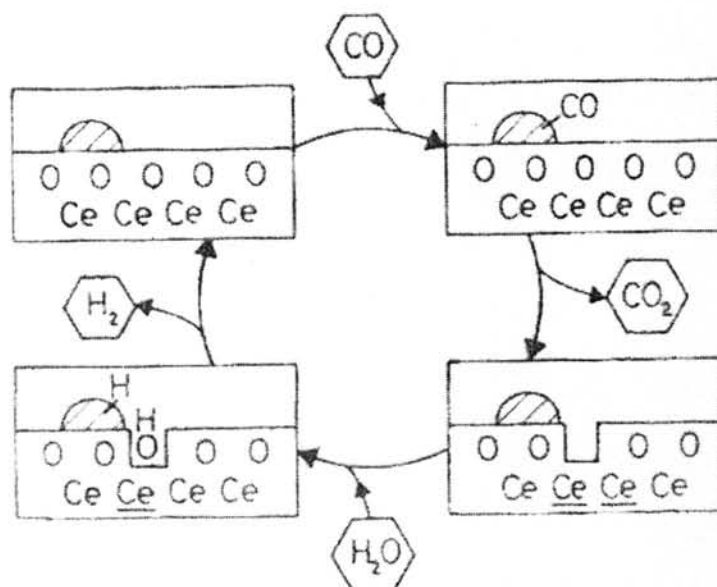


Figure 2.5 Mechanism (1) for WGS on Au/CeO_2 , $\text{O}=\text{O}^{2-}$, $\text{Ce}=\text{Ce}^{4+}$, $\underline{\text{Ce}}=\text{Ce}^{3+}$.

The other study notes the formation of geminal hydroxyl groups on the cerium ions and proposes their reaction with CO to give formate ion, which then decomposes into products. The exact way in which this happens was not however made clear, and the role of the gold was not emphasized. This mechanism, corresponding to (3) above, is supported by the results of transient experiments showing that H_2 and CO were formed simultaneously, and not sequentially as would be required by the ceria redox mechanism (2). The service provided by the gold may then be to make $\text{Au}^{\delta+}$ species (or possible $\text{Au}^{\delta+}$ species as in mechanism (2) above), on which CO adsorbs before reacting with a Ce^{3+} -OH to give the formate ion. The hy-

droxyl group may have been created either by H₂ spillover or by reaction of water with a surface anion vacancy made by loss of a lattice oxide ion.

Clearly a definitive mechanism cannot be established on the basis of the available evidence. It would be incorrect to conclude that one mechanism was right and the other wrong, and in particular it is risky to rely solely on spectroscopic measurements, which by their very nature show only snapshots of parts of the process, however informative they may be. The lack of any detailed kinetic analysis or reaction model is keenly felt, as is the absence of isotopic tracing. The only kinetic expression published so far has been obtained using an Au/CeO₂-ZrO₂ catalyst: it shows

$$r = P_{CO}^{0.75} P_{H_2O}^{0.57} P_{CO_2}^{-0.27} P_{H_2}^{-0.99}$$

This does not immediately suggest a mechanism or the location of the active centers, but the strong inhibition by H₂ might indicate its slow reversible release from a water molecule or from hydroxyl groups that it has formed (Fig. 2.5). This cycle can of course work in either direction.

The reducibility of the ceria support when gold is present also occurs at lower temperature than in its absence, but only the surface layer is reduced. Redox process thought to occur with Au/CeO₂ even at room temperature; water appears to re-oxidize anion vacancies close to the metal, and the failure of XANES measurements to show any change in the Ce³⁺/Ce⁴⁺ ratio on exposure of a reduced catalyst to water vapour even at 450 °C may be due to the limited number of sites participating in redox reactions. Re-oxidation of reduced ceria surfaces by water in the absence of metal has long been known.

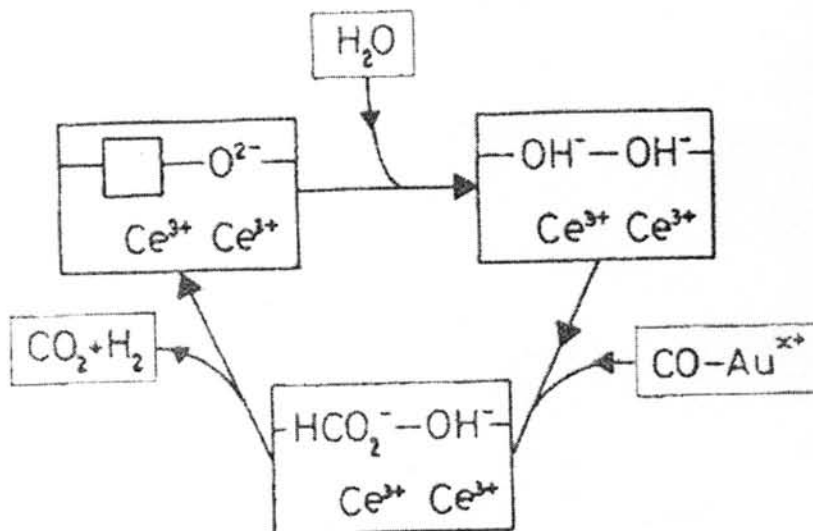


Figure 2.6 A mechanism involving formate species proceeding only on the support.

One could also envisage a mechanism proceeding entirely on the ceria support, make use of anion defects created by CO migrating from Au^0 particles or perhaps even from Au^{x+} ions or clusters (Fig. 2.6). This also provides a role for germinal hydroxyl groups and formate ions. Any more specific formulation of mechanism also needs to incorporate the detailed structure of the ceria surface, which contains two types of oxygen. It has also been suggested that gold particles nucleate preferentially on pre-existing defects. Recent DFT calculations led to a mechanism that is certainly plausible and that incorporates features of the other proposals. It was concluded that gold atoms can be oxidized by ceria, and that only $\text{Au}^{\delta+}$ could absorb CO strongly enough for subsequent catalysis, which proceeded through a formate species. The active site were neither single atoms nor large particles, but 'ultra-small gold clusters' of four gold atoms that were positively charged and anchored on an anion defect. Importance was attached to the empty nonbonding f states of ceria that act as an electron buffer in reactions, rather as the delocalized Fermi-level states in metals do (Bond *et al.*, 2006).

2.4.4 Preparation Method

Gold has a much lower melting point (1063 °C) than Pt group element (Pd; 1550 °C and Pt; 1769 °C). Moreover, the melting point of gold in a highly dispersed state is expected to be as low as 327 °C due to the quantum size effect. Haruta and co-workers (2002) showed that the incipient wetness impregnation is unsuitable to produce highly dispersed gold catalysts. They developed four techniques that allow depositing gold nanoparticles on certain metal oxides: co-precipitation (DP), co-sputtering (CP), deposition-precipitation (DP) and gas-phase grafting. DP has advantage over CP in that it yields a narrower particle size distribution and has Au localized only on the surface of the support. A detailed review of this preparation method can be found elsewhere (Kozlov *et al.*, 1999).

The influence of synthesis procedure has been also mentioned in LTWGS reaction. Tabakova *et al.* (2004) investigated the activity of Au/CeO₂ catalysts prepared by two different methods (DP and Modified DP). They found that the preparation technique strongly influenced the catalytic activity due to the large differences in gold particles size and to the availability of active gold sites in close contact with ceria defects on the surface. They concluded that the DP method is better than MDP method.

For Cu/CeO₂, the copper particles size is almost unaffected by the preparation method. In this case more important factor for a high activity is the availability of active copper species in close contact with ceria defects on the surface. For Au/CeO₂, the application of different preparation techniques for Au/CeO₂ catalyst leads to different gold particles size. This property plays a decisive role for the activity of this catalytic system (Tabakova *et al.* 2006).

2.4.5 Reaction Condition

Most of the studies of the WGS have investigated on supported gold catalysts, such as Au/ZrO₂, Au/TiO₂, and recently Au/CeO₂ (Denkwitz *et al.* 2007). However, most studies were performed in idealized reaction gas mixtures, mainly in dilute water-gas (CO, H₂O, and N₂). The reaction in realistic or simulated reformat have been investigated only in a limited number of studies (Fu *et al.* 2005,

Sakurai *et al.* 2005, Kim and Thompson 2005, and Denkwitz *et al.* 2007) as shown below in the Table 2.2.

Table 2.2 The conclusion of experiment details of WGSR using realistic or simulated reformat as a reactant

Literature surveys	Catalyst details	Composition and condition	Time	% Conversion
Fu <i>et al.</i> , 2005	4.7 Au/CeO ₂ (10% La doped), DP, 650°C	11%CO, 26%H ₂ O, 26%H ₂ , 7% CO ₂ with helium	1000 min / at 300 °C / 6,000 h ⁻¹	70%
Sakurai <i>et al.</i> , 2005	2.8 Au/CeO ₂ , DP, 400°C, 4 hrs	1.3%CO, 3.1%H ₂ O, 5.7% H ₂ with helium	at 250 °C / 51,500 h ⁻¹	90%
Denkwitz <i>et al.</i> , 2006	4.5 Au/CeO ₂ , DP, 400°C, 2 hrs	1%CO and 99% H ₂ + 2%H ₂ O	at 180 °C	77%