

## CHAPTER II

### THEORETICAL BACKGROUND AND LITERATURE REVIEW

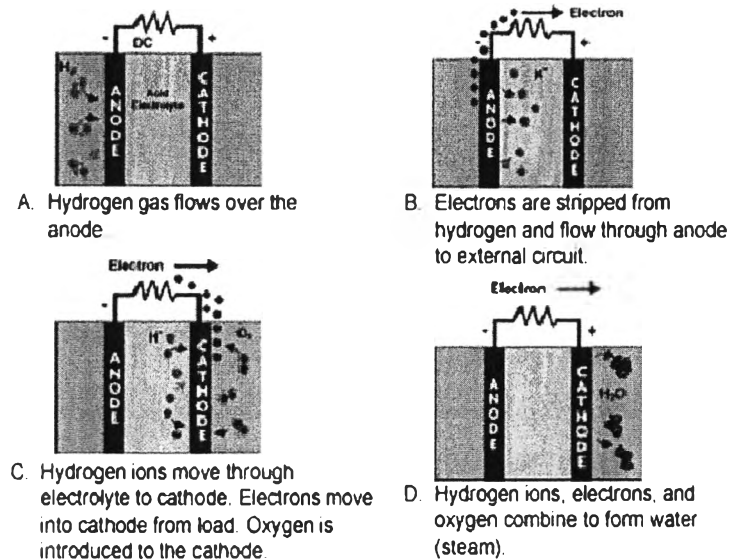
#### 2.1 Fuel Cells

##### 2.1.1 Basic Principles of Fuel Cells

A fuel cell is a device that produces electricity through a chemical reaction between a source fuel and an oxidant. The source fuel could be almost anything that can be oxidized, including hydrogen, methane, propane, methanol, diesel fuel or gasoline. The only byproducts are water and a small amount of nitrous oxide if air is used as the oxidizer. Currently, the focus of many of the major development attempting to develop fuel cells for terrestrial applications, including transportation, stationary or portable power uses. Fuel cells have many characteristics that make them favorable as energy conversion devices. Two of the most attractive features for terrestrial application are the combination of relatively high efficiency and low emissions. Some other characteristics that fuel cells offer are: no moving parts in the energy converter; quiet; modular installations to match load; good reliability; and remote and unattended operation.

##### 2.1.2 How a Fuel Cell Works

The basic structure of a fuel cell consists of an electrolyte layer in contact with a porous anode and cathode on either side. A schematic representation of a fuel cell with the reactant/product gases and the ion conduction flow directions through the cell is shown in Figure 2.1. In a typical fuel cell, gaseous fuel containing, e.g.,  $H_2$ , is fed continuously to the anode compartment and an oxidant (i.e., oxygen or air) is fed continuously to the cathode compartment. The electrochemical reactions take place at the electrodes to produce an electric current. The electrons released will flow through an outer circuit so that the electrical power produced can be utilized.



**Figure 2.1** Basic working concepts of a Fuel Cell. (<http://www.dg.history.vt.edu/ch5/fuelcells.html>)

### 2.1.3 Fuel Cell Types and Potential Applications

There are five basic types of fuel cell under consideration for distributed generation applications which characteristics and applications are shown in table 2.1 and table 2.2. Two of these fuel cell types, polymer electrolyte membrane (PEM) and phosphoric acid fuel cell (PAFC) have acidic electrolytes and rely on the transport of  $H^+$  ions. Two others, alkaline fuel cell (AFC) and carbonate fuel cell (MCFC) have basic electrolytes that rely on the transport of  $OH^-$  and  $CO_3^{=}$  ions, respectively. The fifth type, solid oxide fuel cell (SOFC), is based on a solid-state ceramic electrolyte in which oxygen ions ( $O^-$ ) are the conductive transport ion. Each fuel cell type has been designed to operate at optimum temperatures, which are a balance between the ionic conductivity and component stability. These temperatures differ significantly among the five basic types, ranging from near-ambient to as high as 982 °C. The proton conducting fuel cell type generates water at the cathode and the anion conducting fuel cell type generates water at the anode.

**Table 2.1** Characteristics of major fuel Cell types

	<b>PEMFC</b>	<b>AFC</b>	<b>PAFC</b>	<b>MCFC</b>	<b>SOFC</b>
<b>Type of Electrolyte</b>	H <sup>+</sup> ions (with anions bound in polymer membrane)	OH <sup>-</sup> ions (typically aqueous KOH solution)	H <sup>+</sup> ions (H <sub>3</sub> PO <sub>4</sub> solutions)	CO <sub>3</sub> <sup>=</sup> ions (typically, molten LiKACO <sub>3</sub> eutectics)	O <sup>=</sup> ions (Stabilized ceramic matrix with free oxide ions)
<b>Typical construction</b>	Plastic, metal or carbon	Plastic, metal	Carbon, porous ceramics	High temp metal, porous ceramic	Ceramic, high temp metals
<b>Internal reforming</b>	No	No	No	Yes, Good temp match	Yes, good temp match
<b>Oxidation</b>	Air to O <sub>2</sub>	Purified Air to O <sub>2</sub>	Air to Enriched Air	Air	Air
<b>Operational Temperature</b>	65–85 °C	90–260 °C	190–210 °C	650–700 °C	750–1000 °C
<b>DG System Level Efficiency, %HHV</b>	25 to 35 %	32 to 40 %	35 to 45 %	40 to 50 %	45 to 55 %
<b>Primary Contaminate Sensitivities</b>	CO, Sulfur, and NH <sub>3</sub>	CO, CO <sub>2</sub> , and Sulfur	CO < 1%, Sulfur	Sulfur	Sulfur

Source; EEA

**Table 2.2** The different fuel cells that have been realized and are currently in use and development

	AFC (Alkaline)	PEMFC (Polymer electrolyte membrane)	DMFC (Direct methanol)	PAFC (Phosphoric acid)	MCFC (Molten Carbonate)	SOFC (Solid oxide)
Operating temp. (°C)	<100	60–120	60–120	160–220	600–800	800–1000 low temp. (500–600) possible
Anode reaction	$\text{H}_2 + 2\text{OH}^- \rightarrow 2\text{H}_2\text{O} + 2\text{e}^-$	$\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$	$\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 6\text{H}^+ + 6\text{e}^-$	$\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$	$\text{H}_2 + \text{CO}_3^{2-} \rightarrow \text{H}_2\text{O} + \text{CO}_2 + 2\text{e}^-$	$\text{H}_2 + \text{O}^{2-} \rightarrow \text{H}_2\text{O} + 2\text{e}^-$
Cathode reaction	$1/2\text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{OH}^-$	$1/2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}$	$3/2\text{O}_2 + 6\text{H}^+ + 6\text{e}^- \rightarrow 3\text{H}_2\text{O}$	$1/2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}$	$1/2\text{O}_2 + \text{CO}_2 + 2\text{e}^- \rightarrow \text{CO}_3^{2-}$	$1/2\text{O}_2 + 2\text{e}^- \rightarrow \text{O}^{2-}$
Applications	Transportation, Space, Military, Energy storage systems			Combined heat and power for decentralised stationary power systems	Combined heat and power for stationary decentralised systems and for transportation (trains, boats,...)	
Realised power	Small plants 5– 15 kW modular	Small plants 5–250 kW modular	Small plants 5 kW	Small–medium sized plants 50–11 kW	Small power plants 100 kW–2MW	Small power plants 100–250 kW
Charge carrier in the electrolyte	$\text{OH}^-$	$\text{H}^+$	$\text{H}^+$	$\text{H}^+$	$\text{CO}_3^{2-}$	$\text{O}^{2-}$

#### 2.1.4 Prospects of Proton Exchange Membrane Fuel Cell

The need for an efficient, non-polluting power source for vehicles in urban environments has resulted in increased attention to the option of fuel cell powered vehicles. Of various fuel cell systems considered, the PEM fuel cell technology seems to be the most suitable one for the terrestrial transportation applications. This is due to its low temperature of operation (hence, faster cold start), excellent CO tolerance and a combination of high power density and high energy conversion efficiency. Moreover, there is no free corrosive liquid in PEM fuel cells. They are able to withstand large pressure differentials. The material corrosion problems are minimal and they have demonstrated longevity. Compared to internal combustion engines, fuel cell has a more efficient conversion process. The internal combustion engine is less efficient due to the conversion of chemical into thermal and then thermal to mechanical energy. If cars were powered by electricity generated from fuel cell, there would be no combustion involved. For a fuel cell powered electric vehicle, the fuel is stored in the vehicle's fuel tank and air is obtained from the atmosphere. As long as the vehicle's fuel tank contains fuel, the fuel cell will produce energy in the form of electricity and heat. The introduction of fuel cells into the transportation sector will increase fuel efficiency and become an important strategy/technology to mitigate climate change. As fuel cell vehicles begin to operate on fuels from natural gas or gasoline, greenhouse gas emission will be reduced by 50%. In the future, the combination of high efficiency fuel cells and fuels from renewable energy sources such as ethanol would nearly eliminate greenhouse gas emissions. PEM fuel cells, under consideration by vehicle manufacturers around the world as an alternative to the internal combustion engine, are the focus of this research.

## **2.2 Proton Exchange Membrane Fuel Cell**

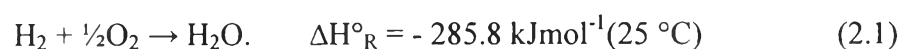
This type of fuel cell was initially developed in the 1960s for the first NASA manned spacecraft. The PEMFC uses a solid polymer electrolyte and operates at low temperatures, about that of boiling water. Over the past ten years, the PEMFC has received significant media coverage due to the large investment the auto

industry has made in the technology. Due to their modularity and apparent ease of manufacturing, much has been made of the reformer/PEMFC system for residential DG applications. As a result of the inherent size flexibility of fuel cells, the technology may be used in applications with a broad range of power needs. This is a unique feature of fuel cells and their potential application ranges from systems of a few watts to megawatts. generates water at the cathode and the anion conducting fuel cell type generates water at the anode.

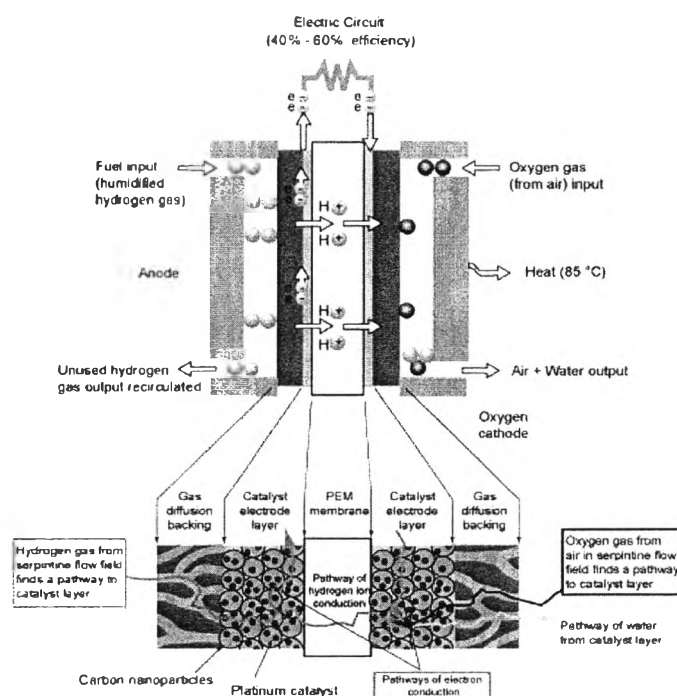
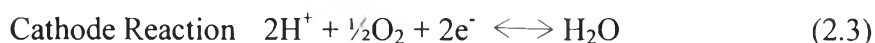
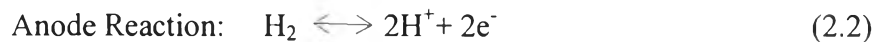
Fuel cells are basically a refuelable battery. Recent breakthroughs in PEM fuel cells have turned the technology into a potential consumer product with applications as replacements for rechargeable batteries, to remote power for houses, to power for automobiles. Neutron imaging of PEM fuel cells allows one to analyze the mass flow of water through the GDL and out of the fuel cell through the flow channels. Water balance in a fuel cell is critical to the operation of the cell. Without proper humidification of the membranes the proton conduction will not work. Water that is formed at the cathode must leave the cathode quickly to allow oxygen to reach the cathode catalyst layer. This is where neutrons can play a role in analyzing the effectiveness of the gas diffusion layer and water channels in removing water from the fuel cell.

### 2.2.1 PEM Fuel Cell Basics

- Fuel cells are operationally equivalent to a battery.
- The reactants or fuel in a fuel cell can be replaced unlike a standard disposable or rechargeable battery.
  - For automotive applications hydrogen is the fuel choice.
- Low temperature (~85 °C) Polymer Electrolyte Membrane (PEM) type cells are the standard devices.
  - Electrochemical energy comes from the reaction:



• Theoretically, the maximum voltage that this reaction can generate is 1.2 V. However, in practice the cell usually generates about 0.7 V to 0.9 V and about  $1 \text{ W.cm}^{-2}$  of power.



**Figure 2.2** Schematic representation of the PEM fuel cell (<http://www.fuelcell/NIST/NIF-PEM/FuelCells.mht>)

### 2.2.2 Problems to Overcome

There are still some significant problems to overcome before fuel cells become widely used. Poisoning of the fuel cell by Carbon Monoxide (CO) drastically reduces the life of low temperature fuel cells. This gas is present in the hydrogen supply to the cell when the hydrogen is created by reforming fossil fuels or coal gasification, and is difficult to filter out. High temperature fuel cells do not suffer from CO poisoning; however the high temperatures increase the effect of sources of corrosion. A lifetime of 40,000 hours is expected in stationary power applications and 5,000 in automotive applications before fuel cells can compete with conventional systems.

## 2.3 Gas Clean-up

Reforming hydrocarbons into hydrogen always produces small amounts of CO in the gas stream. This CO is not a problem for high-temperature fuel cells that can use CO as a fuel for the anode reaction. CO must be eliminated before being fed into a low-temperature fuel cell. The gas clean up can be done in several ways. The first step is a water-gas shift conversion of CO into CO<sub>2</sub> hereby producing more hydrogen. The CO content is reduced to the equilibrium value at a specific temperature (in the range of 1% CO; it decreases with decreasing temperature). The next step of CO removal has to be very efficient since it needs to lower the CO content to values in the ppm range so that fuel can be fed into the fuel cell. The three most common techniques are selective oxidation, methanation, and the use of a selective membrane. An increase of CO tolerance of PEMFCs can be achieved by applying an electrical pulse to the cell which induces an over potential to the anode. The high potential at the anode clears the surface of CO through oxidation to CO<sub>2</sub>. The cleaning of the surface is fast and is repeated on a regular basis. As the re-adsorption of CO is slow the applied pulses can clean the surface faster than the CO re-poisons it. The pulse duration is short and therefore the decrease of operating time can be tolerated.

### 2.3.1 Water-Gas Shift Reaction

The water-gas shift reaction involves the conversion of CO into CO<sub>2</sub> using steam as an oxidant (Eq.2.4). A normal reformer unit usually employs both a high temperature shift reactor and a low-temperature shift bed. The high-temperature shift reactor uses Fe<sub>3</sub>O<sub>4</sub> catalysts and temperatures above 350 °C to produce CO<sub>2</sub> from CO and steam. The low temperature reactors operate at around 200 °C and employ CuO/ZnO catalysts. After the low temperature shift reactor the fuel stream still contains a certain amount of CO (0.5–1%) which is still too high for low temperature fuel cells. Therefore, a second cleaning step has to be carried out.





### 2.3.2 Selective Oxidation of CO

Selective oxidation of CO occurs over some catalysts which oxidize mainly CO and not hydrogen. Catalysts used for this purpose are usually alumina (Al<sub>2</sub>O<sub>3</sub>) supported structures. Ru and Rh supported on alumina are amongst the most active catalysts. Near to complete CO conversion can be achieved at temperatures as low as 100 °C. Cu particles dispersed on alumina are cheaper, easier to make and combined with ZnO, they also have a high catalytic activity for CO oxidation. The activity depends on the particle size of Cu with smaller particles being more active. Selective oxidation prevents the loss of hydrogen as opposed to the methanation process which is described in the next section (Oh *et al.*, 1993).

### 2.3.3 Methanation

A different approach to CO removal is taken by the methanation process. In this process CO is reacted with hydrogen to form methane and water. The amount of hydrogen needed to carry out this reaction is, however, three times the amount of CO removed. The reaction for this process is:



CO<sub>2</sub> present in the gas stream can react with the produced water in a reverse water-gas shift reaction (Eq. 2.6) thereby producing the unwanted CO. Methanation can work for removal of CO but severe restrictions are necessary to make this process viable in a gas clean up system.



### 2.3.4 Membranes

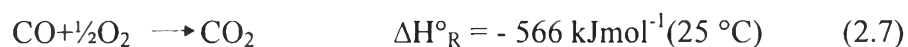
Pd alloy membranes can be very effective in the removal of CO from the fuel stream. The gas is fed through the membrane through which hydrogen permeates selectively. This technique requires a rather large pressure difference and a relatively high temperature which reduces the efficiency of the system (the efficiency depends on the possibility of heat supply by the fuel cell system). The use

of membranes was already mentioned before in the reforming section whereby the methanol steam reforming and the reforming of hydrocarbons can be directly combined with a membrane to produce clean hydrogen.

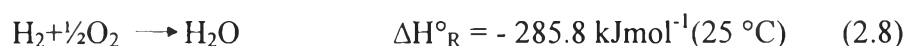
A combined system with different catalytic stages can prove to be the best answer to the problem of gas clean-up. The second cleaning step should take the CO level down to around 5–100 ppm which can then be fed to the fuel cell without significant losses.

#### 2.4 Preferential Oxidation or Selective Oxidation of CO

The development of practical fuel cell power for automotive transportation and for stationary applications will require the development of fuel processors that convert liquid fuels into H<sub>2</sub> and CO<sub>2</sub>. These fuel processors will contain compact catalytic reactors that carry out a number of reactions between the fuel, oxygen, and steam: partial oxidation, steam reforming, water-gas shift, and selective oxidation of CO in the final hydrogen stream. Fuel processors must be compact, mechanically durable, quick-starting, responsive to transient demands, and inexpensive. The gas stream that is fed to the fuel cell must have a very low (< 10 ppm) concentration of CO to avoid poisoning the fuel cell electrode (Rohland *et al.*, 1999). The final selective oxidation step requires a catalyst that is active for the oxidation of CO (Eq.2.7) in order to reduce the concentration of CO from about 1% to less than 10 ppm in the presence of high concentrations of steam, using a minimum volume of catalyst.



However, the catalyst must not oxidize a significant quantity of hydrogen (Eq.2.8)



Since H<sub>2</sub> is the fuel used at the anode of the fuel cell, nor should it have a strong preference to the water gas shift reaction (Eq.2.8). Hydrogen that is consumed by H<sub>2</sub>

oxidation during the selective oxidation step must be replaced by increasing the size of the fuel processor and increasing the rate of feed to the fuel processor. Therefore, the catalyst not only must be highly active for the oxidation of CO, it also must be highly selective for oxidation over H<sub>2</sub> oxidation. The process described above is known as “preferential oxidation” in the fuel cell community, and is often referred to using the acronym “PROX”.

## 2.5 Catalysis by Gold

Gold has traditionally been regarded as an inactive catalytic metal because its chemisorption ability is too small compared with, for example, the platinum group metals (PGM). The history to use Au as a catalyst dates back to the beginning of the 20<sup>th</sup> century when Au gauzes were reported as catalysts for H<sub>2</sub> oxidation in 1906. The earliest reference where Au has been reported as catalyst for CO oxidation comes from Bond and Thompson in 2000 (Bond *et al.*, 2000). A significant contribution towards gold catalysis is made by Hutchings who suggested that the very high standard electrode potential of Au (+1.4 V) would make AuCl<sub>3</sub> a very effective catalyst for hydrochlorination of ethyne (Hutchings *et al.*, 1996). However, it was Haruta whose work in 1987 brought the most important breakthrough in the history of Au catalysis. He showed that Au-based catalysts with Au nanoparticles of a size in the range of 2 to 5 nm are very active for CO oxidation even at sub-ambient temperature. Since then, catalysis by gold has attracted a lot of attention and CO oxidation is probably the most studied reaction (Haruta *et al.*, 1989 and Fajin *et al.*, 2008). However, the advent of nanoparticles gold on high surface area oxide supports has demonstrated a high catalytic activity in many chemical reactions including water-gas shift reaction (WGS), reduction of NO with propene, CO or H<sub>2</sub>; reactions with halogenated compounds; water or H<sub>2</sub>O<sub>2</sub> production from H<sub>2</sub> and O<sub>2</sub>; removal of CO from hydrogen streams; hydrochlorination of ethyne; selective oxidation, e.g. epoxidation of olefins; selective hydrogenation and hydrogenation of CO and CO<sub>2</sub> (Camero *et al.*, 2003).

### 2.5.1 Physical and Chemical Properties of Gold

To understand the chemisorptive and catalytic properties of metallic gold requires some knowledge about gold. First, it is necessary to review the physical properties of gold (Table 2.3) as a way of finding out what these bonds are like. Gold is unique among the metallic elements because of its resistance to oxidation and corrosion: it has a long history of usage in coinage and in jewelry, and we may, therefore, expect to find that the reasons for its chemical nobility will also shed light on the nature of the bonds linking the individual gold atoms in the solid. Gold exhibits all the properties expected of a metal in terms of luster, hardness, ductility, malleability, and high thermal and electrical conductance. The parameters which reflect the strength of interatomic bonding, such as melting temperature and vaporization energy, suggest that this is strong in gold and very precise measurements of metallic radius show the gold atom is slightly small. Gold is unique in a number of respects: it is the most electronegative metal, comparable to selenium, and only slightly more electropositive than sulfur and iodine (Bond *et al.*, 2000). Its electron affinity is actually greater than that of oxygen, and the corollary of this is the very high value of the  $\text{Au}^+/\text{Au}^0$  couple (11.691 V). Gold readily forms alloys with other metals and intermetallic compounds of definite composition with copper, aluminum, tin, and titanium. Its color is more reminiscent of that of copper than silver, and in the Periodic Table, it lies next to the only metal that is liquid at normal temperatures (Rapson *et al.*, 1984).

**Table 2.3** Physical properties of gold (<http://www.ienntech.com/periodic/elements/au.htm>)

Phase	Solid
Atomic number	79
Atomic mass	196.9655 g.mol <sup>-1</sup>
Electronegativity coordinating to Pauling	2.4
Density	19.3 g.cm <sup>-3</sup> at 20 °C
Melting point	1062 °C
Boiling point	2000 °C
Vanderwaals radius	0.144 nm
Ionic radius	0.137 nm (+1)
Isotopes	7
Electronic shell	[ Xe ] 4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>1</sup>
Energy of first ionisation	888 kJ.mol <sup>-1</sup>
Energy of second ionisation	1974.6 kJ.mol <sup>-1</sup>
Standard potential	+1,68 V ( Au <sup>+</sup> / Au )
Discovered	c.a. 3000 BC

For the chemical properties of Pt, Au, and other metal of the adjacent elements are dominated by the relativistic stabilization of 6s level. The 6s<sup>2</sup> ‘inert pair effect’ is well known to inorganic chemists. Additionally, electrons in the 5d level become more easily mobilized for chemical reaction. Thus the electronic configuration of Pt is 5d<sup>9</sup>6s<sup>1</sup> while that of palladium (Pd) is 4d<sup>10</sup>, and this explains that the Pt<sup>4+</sup> is so much more easily available than Pd<sup>4+</sup>. In case of gold is 5d<sup>10</sup>6s<sup>1</sup>, its chemistry is determined by the easy activation of 5d electrons and its desire to obtain a further electron to complete the 6s<sup>2</sup> level and not to lose the one it has. This latter effect awards it a much greater electron affinity and higher first ionization energy than those of copper (Cu) or silver (Ag) and accounts for the ready formation of Au<sup>1-</sup> state. The former effect obviously explains the predominance of Au<sup>3+</sup> has the 5d<sup>8</sup> configuration (even the Au<sup>5+</sup> state (5d<sup>6</sup>) is accessible as in AuF<sub>5</sub>). Its electronic structure determines its nobility, and its inability in the massive form to interact with

oxygen or sulfur compounds is in line with the stability of its oxide  $\text{Au}_2\text{O}_3$ , decomposes at about 170 °C and probably has a positive heat of formation. The electronic state of gold atoms in the massive state is not, however, exactly that of the free atom, since a weak white line on the leading edge of the X-ray absorption edge signifies a small number holes in the *d*-band caused by *d-s* hybridization. The electron affinity of Pt is almost as large as that of Au.

### 2.5.2 Potential Applications

Gold catalysis is a rapidly developing topic of both academic and industrial research and significant advances have been made (Bond *et al.*, 1999). Natural requirements for application of gold catalysis at a practical level are reliable methods of preparation and long-term mechanical and catalytic stability of the gold catalysts. Performance criteria, including activity and durability and commercially viable methods of catalyst preparation are important as well. Based on the current research efforts being devoted to gold, there is reason for optimism that many new practical applications for gold-based catalysts could emerge over the next decade. Innovative recent research has suggested that along with many other applications gold-based catalysts are potentially capable of being effectively employed in fuel cells and hydrogen fuel processing, owing to their promising technical performance, relatively low stable price and greater availability of gold compared with the PGM. The employment of gold catalysts could therefore produce a welcome reduction in the capital cost of fuel cell installations. The areas in which gold has already been demonstrated to be a strong catalyst can be divided into three categories, as shown in Table 2.4 (Corti *et al.*, 2005 and Bond *et al.*, 2000).

**Table 2.4** Applications of gold-based catalysts

<b>Pollutional emission control</b>	<b>Chemical processing</b>	<b>Water gas shift reaction</b>
Low temperature air purification	Production of vinyl chloride	Selective oxidation of CO in the presence of Hydrogen (PROX)
Catalytic wet air oxidation	Production of propene oxide	Gold as an electrocatalyst
Mercury oxidation in coal-fire power stations	Direct production of hydrogen peroxide (H <sub>2</sub> O <sub>2</sub> )	
Automotive emission control	Production of nylon precursors	
Reduction of NO with Propene, CO or H <sub>2</sub>	Hydrotreating distillations Selective hydrogenation Food processing Hydrochlorination of ethyne	

## 2.6 Activity of Supported Gold Catalyst

Many metal-based catalysts have been found to be active for selective CO oxidation, including Pt, Ru, Rh, and Au. The selective oxidation of CO in the presence of hydrogen was first studied using a Pt/Al<sub>2</sub>O<sub>3</sub> catalyst in 1963. Igarashi *et al.* (1997) investigated the effect of the support on the selectivity of Pt catalysts for CO oxidation and found that Pt supported on mordenite showed the highest selectivity, as well as high conversion of CO during oxidation at low oxygen concentration. In the same year, Kahlich *et al.* (1997) studied the suitable catalyst for competitive oxidation of CO in the presence of H<sub>2</sub>, and the most commonly used partial oxidation catalysts (alumina-supported Pt, Pt/Fe, Ru, and Rh) are unsuitable

since the required temperature in the range of 150 to 200 °C to be effective, and even then significant conversion of H<sub>2</sub> is observed, while highly dispersed Au nanoparticles supported on selected metal oxides. Avgouropouloi *et al.*, 2002 and Schubert *et al.*, 2004 found that the different Au/MeO<sub>x</sub> catalysts exhibit higher activity in the CO oxidation than conventional Pt group or Cu-based catalysts, since they are able to remove CO from reformed fuels with an extraordinarily high reaction rate and good selectivity at much lower temperatures, but again H<sub>2</sub> was oxidized together with CO at temperature >70 °C (Torres Sanchez *et al.*, 1997).

Explanations for the high activity of gold nanoparticles in various reactions can broadly be divided into the following four categories:

- (I) effect of particle size,
- (II) nature of the active sites in gold catalysis,
- (III) the role of support/additive, and
- (IV) the influence of preparation method including the pretreatment conditions.

#### 2.6.1 Particle Size Effects

Effect of particle size, it was recognized in the early work on the oxidation of CO using gold that activity increased as the particle size decreased. The more recent work on a range of oxide-supported catalysts has confirmed this. The optimum size for gold particles on both oxide and molecular sieve supports is less than 5 nm, and their size can be made within this range by careful control of the conditions used in preparation. Reduction of the particle size is accompanied by a number of beneficial effects: for instance, (i) surface area is increased; (ii) concentration of low coordinated step, edge and kink sites is increased; (iii) the length of the periphery per unit mass of the particle increases due to contraction of a large number of atoms with support; (iv) because the overlap of the electron orbitals decreases as the average number of bonds between atoms decrease, the surface atoms become more reactive and start to behave more as individual atoms (Haruta and Date, 2001). Torres Sanchez *et al.* (1997) demonstrated that high activities are obtained from Au/MnO<sub>x</sub> catalyst with atomic ratio of Au/Mn = 1/50 exhibits a higher catalytic activity for CO oxidation. It may be explained by the fact that the



turnover frequency (TOF) base on the number of surface gold atom exponentially increases with a decrease in particle diameter. Later, Grisel *et al.* (2002) investigated the effect of Au particle size and the oxidic additive by using several alumina-supported gold catalysts. The pure  $\text{MO}_x$  catalysts are not very active in low-temperature CO oxidation. No significant CO conversion was found below 150 °C, a temperature at which full conversion is reached over a  $\text{Au}/\text{Al}_2\text{O}_3$  catalyst with 4 nm Au particles. The CO oxidation activity of the alumina-supported metal oxides decreases in the order:  $\text{CoO}_x > \text{FeO}_x > \text{NiO}_x > \text{CrO}_x \gg \text{MgO}$  and  $\text{ZnO}$ . Addition of  $\text{MO}_x$  to  $\text{Au}/\text{Al}_2\text{O}_3$  greatly influences the CO conversion in the low temperature region. The addition of  $\text{MO}_x$  has a large beneficial effect on the activity at low temperatures. The  $\text{Au}/\text{MnO}_x/\text{Al}_2\text{O}_3$  catalyst with an average particle size of 4.2–1.4 nm compared to  $\text{Au}/\text{Al}_2\text{O}_3$  with an average particle size of 3.6–1.4 nm. In fact, the CO conversion over  $\text{Au}/\text{MnO}_x/\text{Al}_2\text{O}_3$  is higher at ambient temperature than that over the  $\text{Au}/\text{Al}_2\text{O}_3$  catalyst at 150 °C. Most probably, the role of  $\text{MO}_x$  is twofold. Firstly, the oxide may stabilize small gold particles throughout preparation and activity measurements (structural promoter effect). Secondly, the oxide may actively take part in one of the steps involved in the catalytic cycle (i.e. it acts as a co-catalyst). Another task of the support as suggested on theoretical grounds is to influence the electronic structure of Au at the interface where charge transfer between the support (particularly negatively charged defects F centres) and gold particles has been proposed. A number of other studies in literature highlight the role of the particle size in various reactions (Haruta *et al.*, 2002, Bond *et al.*, 1999, and Haruta, 2004). It has been proposed that the high activity of small gold particles may result from a quantum size effect with respect to the thickness of the gold, based on the commencement of metal-to-non-metal transition (Valden *et al.*, 1998). As mentioned above, low coordinated atoms on the small particles are also expected to play a importance role in the activity of supported Au catalysts. Note that the shape of a particle affects the relative amount of such low coordinated sites (Grunwaldt *et al.*, 1999). Since the shape of a gold particle depends on the gold-support interaction, the support is expected to have a large effect on the number of edge and corner atoms on the particle. It should be realized that the activity related to gold-based catalyst cannot be solely explained on the basis of particle size effects because metal oxides

supports (e.g.  $\text{TiO}_2$ ,  $\text{Fe}_2\text{O}_3$ ) may supply active oxygen (Haruta *et al.*, 1989). For Au catalysts supported on these reducible oxides, it was proposed that the size of the gold particle is not very important (Schubert *et al.*, 2001).

### 2.6.2 Nature of Active Sites in Gold Catalysis

The nature of the active site especially in the extensively studied CO oxidation reaction remains a controversial issue in Au catalysis and until now no general consensus exists. As mentioned above, gold particle size is important but not sufficient to account for all the secrets of the high activity of Au-based catalysts. As discussed to some extent already above, various factors have been suggested in the literature to be important for this high catalytic performance including:

(i) Periphery or Au-support interface,

(ii) Step sites on the surface and strain defects (Lin *et al.*, 1993, Boccuzzi *et al.*, 2001, and Grisel *et al.*, 2002). Haruta *et al.* (2001) using a mechanical mixture of Au colloids of about 5 nm with  $\text{TiO}_2$  powder, clearly showed that higher calcinations temperature gives higher catalytic activity, although Au particles grew to larger particles (Tsubota *et al.* 1989) while larger number of step, edges, corners in smaller Au particles increases the catalytic activity for CO oxidation, smooth surface of metallic Au do not adsorb CO at room temperature, indicating that CO is adsorbed only on steps, edges, and corner sites. Thus, smaller metallic Au particles are preferable (Boccuzzi *et al.*, 2001). Contact with the support contributes to an addition increase in the catalytic activity at least by one order of magnitude. An atomic-level model for activation at the periphery by the redox cycle between  $\text{Au}^{3+}$  (more likely  $\text{Au}^+$ ) and  $\text{Au}^0$  is proposed by Bond and Thompson (Bond *et al.*, 2000).

(iii) Small gold clusters that have nonmetallic electronic properties due to a quantum size effects, (Mavrikakis *et al.*, 2000)

(iv) Higher oxidation states e.g.  $\text{Au}^{3+}$ . Trivalent gold has been considered responsible for high activity in reactions such as CO oxidation, hydrochlorination of ethyne, the water gas shift reaction and Au has been suggested as an active site (Sanchez *et al.* 1999, Wallace *et al.* 2002, and Abbet *et al.* 2001) when gold is deposited on supports containing defects (F-centres). According to

another model  $\text{Au}^{1+}$  (and not Au) would be able to satisfy the requirement that Au cations must be stable in reducing environments and also in the neighborhood of metallic gold for an ensemble of metallic gold atoms; Au cations with hydroxyl ligands and Au-OH has been proposed as the cationic component (Bond *et al.*, 2000).

(v) Another important factor for the enhanced activity of gold catalysts proposed by a number of authors is the presence of water (particularly for PROX reaction) in the feed. Superior CO oxidation activity of Au particles has been observed on irreducible supports such as  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ , (Date *et al.* 2004 and Hvolbaek *et al.* 2007) provided water was present. Numerous studies have focused on the effect of  $\text{H}_2\text{O}$  addition, which is present under PROX conditions. In particular, it showed that water promotes CO oxidation on  $\text{Au/TiO}_2$ ,  $\text{Au/Al}_2\text{O}_3$  and  $\text{Au/SiO}_2$ , and they proposed a mechanism in which  $\text{H}_2\text{O}$  allows  $\text{O}_2$  activation and decomposition of carbonate by-products. In this way, water helps to regenerate the catalyst, for example  $\text{Au/Al}_2\text{O}_3$ . However, an optimum amount of moisture increases the reaction rate and an excess water may depress the rate attributed to blocking of active sites (Date *et al.*, 2001).

### 2.6.3 Effect of Support

Understanding the role of the support towards the activity of Au-based catalysts is very important. Kahlich *et al.* (1999) studied in  $\text{Au/Fe}_2\text{O}_3$  catalysts calcined at 400 °C but found that significant  $\text{H}_2$  oxidation occurred at 80 °C. In 2003, Qiao *et al.* (2003) showed that non-calcined  $\text{Au/Fe}_2\text{O}_3$  catalysts, dried only at 120 °C, were very selective for CO oxidation in the presence of  $\text{H}_2$  at 25 °C, but the selectivity was lost at higher temperatures. London *et al.* (2005) studied  $\text{Au/Fe}_2\text{O}_3$  catalysts prepared by co-precipitation for CO oxidation in the absence of  $\text{H}_2$ . They subsequently investigated the addition of  $\text{H}_2$  to the reactant gases (2:1  $\text{H}_2$ :CO molar ratio) in the absence of excess  $\text{CO}_2$ , and this led to a decrease in CO conversion. Drying the 5 wt%  $\text{Au/Fe}_2\text{O}_3$  at 120 °C gave a catalyst that was active for  $\text{H}_2$  oxidation at 27 °C. Catalysts calcined at 550 °C, whether for 3 h or 8 h, retain considerable CO oxidation activity but show no oxidation of  $\text{H}_2$  even at 73 °C.

Calcination of the material at lower temperature, e.g. 400 °C, gave a catalyst with activity for H<sub>2</sub> oxidation at 73 °C. Interestingly, calcination at 400 °C followed by calcination at 550 °C did not reproduce the performance of a catalyst calcined only at 550 °C. This demonstrates the extreme sensitivity of this catalyst system to the calcination conditions. Calcining at 600 °C completely destroys the catalyst activity. Comparison with Au/Fe<sub>2</sub>O<sub>3</sub> and Au/MnO<sub>x</sub> catalysts, both catalysts were prepared by co-precipitation with different calcination temperatures (300 °C for Au/MnO<sub>x</sub> and 400 °C for Au/Fe<sub>2</sub>O<sub>3</sub>). Crystallite size of Au/MnO<sub>x</sub> and Au/Fe<sub>2</sub>O<sub>3</sub> were uniform about 10 nm and 3 nm, respectively. For activity measurement of CO oxidation in H<sub>2</sub> rich stream, it was found that Au/MnO<sub>x</sub> gave 93% conversion and 58% selectivity at 130 °C while Au/Fe<sub>2</sub>O<sub>3</sub> gave 98% conversion and 53% selectivity at 50 °C. Based on their activity, Au/Fe<sub>2</sub>O<sub>3</sub> exhibits much higher activity and selectivity at low temperatures than that of Au/MnO<sub>x</sub> mainly result from the very different metallic particle sizes of two catalyst. Both catalysts could resist to H<sub>2</sub>O concentration up to level 10% and CO<sub>2</sub> caused the detrimental effect over both catalysts, which the effect over Au/MnO<sub>x</sub> was stronger in the comparison with Au/Fe<sub>2</sub>O<sub>3</sub> (Luengnaruemitchai *et al.*, 2005). Next research work, Verakit *et al.* (2006) developed the new catalyst, Au/Fe<sub>2</sub>O<sub>3</sub>-MnO<sub>x</sub> prepared by deposition-precipitation, which provided 100% CO conversion and 56% PROX selectivity at 60 °C. The result showed that the remarkably higher reducibility exhibited higher catalytic activity. It could be concluded that one of the important factors is type of support since the different support result in different catalytic activity. It has further been shown theoretically that defects on supports like TiO<sub>2</sub> play a key role in the adhesion of the gold particles on the support, hence influencing particle shape and size. In case of reducible oxides such as TiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, the defects help to anchor Au firmly, and the support might be the source of active oxygen for an oxidation reaction (Schubert *et al.*, 2001). From a practical point of view, the choice of the support is determined by the type of reaction to be catalyzed. For example: CO oxidation is catalyzed successfully at ambient temperature by Au supported on about any oxidic support material, except on irreducible oxides like SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>. It has been reported that Au/TiO<sub>2</sub> is the most active catalyst for this reaction (Cameron *et al.*, 2003, Hvolbaek

*et al.*, 2007, and Quinet *et al.*, 2009). A number of studies showed 100% conversion of CO to CO<sub>2</sub> at low temperature when the CO oxidation catalyst is composed of dispersed Au nanoparticles supported on TiO<sub>2</sub> (Bocuzzi *et al.*, 2001, Date *et al.*, 2004, and Schumacher *et al.*, 2004). Moreover, an active role of TiO<sub>2</sub> adsorption and O-supply for CO oxidation, adsorption of CO, hydrogen and water, O<sub>2</sub> activation by water, and O<sub>2</sub> reaction with H<sub>2</sub>, has been proposed (Matthiesen *et al.*, 2009). In addition, for partial oxidation of hydrocarbons, especially if H<sub>2</sub> and O<sub>2</sub> are present in the feed, only TiO<sub>2</sub> and Ti-silicate supported Au catalysts perform efficiently. Possible supports for gold based catalysts for WGS include oxides of Ti, Ce, and Fe. From a comparative study of the WGS reaction using Au/Fe<sub>2</sub>O<sub>3</sub>, Au/Co<sub>3</sub>O<sub>4</sub>, and Au/TiO<sub>2</sub>, it was established that Au/TiO<sub>2</sub> is the most active catalyst, confirming the superiority of TiO<sub>2</sub> over  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> as a support. Okumura *et al.* (1998) used CVD method to prepared Au/TiO<sub>2</sub>, Au/Al<sub>2</sub>O<sub>3</sub>, and Au/SiO<sub>2</sub> catalysts. The average gold particle diameters were 3.8, 6.5, and 3.5 nm, respectively and the turnover frequencies were 0.02, 0.02, and 0.01 s<sup>-1</sup>, respectively. Small differences suggest that similar activities were obtained over a range of gold particle size and different supports. It has been proposed that the metal oxide support serves as the oxygen supplier, and the active support materials such as TiO<sub>2</sub> (Schumacher *et al.*, 2004) and Fe<sub>2</sub>O<sub>3</sub>, which can supply oxygen to the Au particles (Schubert *et al.*, 2001), have been reported to be very active for CO oxidation. In addition, supports such as Al<sub>2</sub>O<sub>3</sub>, Au/Al<sub>2</sub>O<sub>3</sub>, and SiO<sub>2</sub>, which cannot supply oxygen to the Au particles, were found to need more in activation for high activity. Although such an effect may contribute to the activity of gold catalysts, the fact that Au supported on the inert MgAl<sub>2</sub>O<sub>4</sub>, SiO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub> support has high catalytic activity as well (Mavrikakis *et al.*, 2000) indicates that even if the support effect is important, it is not the only reason behind the high activity of gold catalysts. Grunwaldt *et al.* (1999) reported a strong support effect on the activity of the catalysts. They prepared Au/TiO<sub>2</sub> catalysts by the adsorption of gold colloid onto the support. Au/TiO<sub>2</sub> achieved 21% and 100% conversions at 32 °C and 80 °C, respectively, whereas the Au/ZrO<sub>2</sub> catalyst was inactive at both temperatures. This data indicated the effect of different supports in stabilizing the gold particles. Sangeetha *et al.* (2009) investigated the catalytic properties of Au/CeO<sub>2</sub>-TiO<sub>2</sub> prepared by deposition-precipitation method

and it indicated that gold particle dispersed highly on the supports and formed particle size less than 3 nm. Au/CeO<sub>2</sub>-TiO<sub>2</sub> (1:9) catalyst showed CO conversion of 94% and CO selectivity of 91% at 25 °C. When the temperature increased, the CO conversion reached 100% at 50 °C and then decreased. With an increase in the Ce/Ti ratio from 1:9 to 3:7, there was a decrease in CO conversion at room temperature. Since the gold particle size was similar, it could be suggested that the intensity of oxygen supplied from support weakened. The Au/TiO<sub>2</sub> oxidized CO easier than Au/CeO<sub>2</sub> when the temperature was below 70 °C. The addition 4.8 mol% of CuO as a promoter demonstrated >95% CO conversion when the temperature was higher than 65 °C and the CO selectivity also improved substantially. Thus, the additive CuO along with the promoter and amorphous oxide ceria and titania not only enhances the electronic interaction, but also stabilizes the nanosize gold particles and thereby enhancing the catalytic activity for PROX reaction to greater extent.

#### 2.6.4 Preparation Methods

Eight methods for gold catalysts preparation are summarized in Table 2.5, which include deposition of nanoparticles of gold on a variety of support materials. Three factors: the size of the Au particles, strong contact between Au particles and the support, and selection of the right support are of crucial importance. Therefore, the catalytic performances of gold catalysts markedly depend on the preparation methods and conditions. Impregnation methods are not favorable mainly because Au has a lower affinity for metal oxides than Pd and Pt and it is, thus relatively difficult to deposit Au as nanoparticles on metal oxide supports in this way. In addition, during calcination of HAuCl<sub>4</sub> crystallites on the support, chloride ions markedly enhance the coagulation of gold particles (Haruta *et al.*, 2004). For example, Gardner *et al.* (1991) prepared supported gold catalyst on various base-metal oxides including MnO<sub>x</sub>, Fe<sub>2</sub>O<sub>3</sub>, and CeO<sub>2</sub>, which all samples were synthesized via co-precipitation from aqueous HAuCl<sub>4</sub> and the nitrate of the corresponding support metal. The composition of the materials is approximately 5 atom% Au/MnO<sub>x</sub>, 20 atom% Au/CeO<sub>2</sub>, and 5 atom% Au/Fe<sub>2</sub>O<sub>3</sub> on a Au/metal basis. In each case the appropriate precursor solutions were added dropwise to a stirred solution of

sodium carbonate at room temperature. After being washed and dried the precipitates were calcined in air at 400 °C for 4 h. The Au/CeO<sub>2</sub> exhibits very high activity at 75 °C, oxidizing greater than 80% of the available CO oxidation and then the data indicated that Au/MnO<sub>x</sub> was the most active catalyst examined in this study. At 75 °C, Au/MnO<sub>x</sub>, sustains nearly 100% CO<sub>2</sub> yield over a 10,000-minute period, and excellent activity is also observed at 50 and 30 °C. It was interesting in two Au/Fe<sub>2</sub>O<sub>3</sub> samples that were prepared in the different temperature of the wash water utilized (25 and 80 °C). The result provides an interesting comparison between Au/Fe<sub>2</sub>O<sub>3</sub>#1 and Au/Fe<sub>2</sub>O<sub>3</sub>#2. The activity of Au/Fe<sub>2</sub>O<sub>3</sub>#1 is clearly superior although some decay in performance is evident. Surface Cl is generally believed to inhibit low-temperature CO oxidation. Therefore, the difference in activity of the two samples may be attributable to poisoning by surface chlorine (originating from the gold precursor HAuCl<sub>4</sub>) which is not as effectively removed by washing with cold water compared to hot water. Nevertheless, it is interesting to note that the activity of Au/Fe<sub>2</sub>O<sub>3</sub>#2 steadily increases with time (negative or inverse decay). This behavior may be a consequence of some surface process which removes the surface Cl as the reaction proceeds. Hence, it is very important to choose a suitable preparation technique, depending on the kind of support material used such as basic or acidic metal oxides or carbonaceous material.

Among the other techniques mentioned in Table 2.5, co-precipitation is a useful and the simplest method of preparation. However, the deposition-precipitation (DP) method is the easiest to handle and is used for producing commercial Au catalysts (Haruta *et al.*, 2004).

The aim of the present work is to investigate the catalytic properties of Au/Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> in PROX reaction. It is interesting to study the effect of adding Fe<sub>2</sub>O<sub>3</sub> on the catalytic properties of Au/TiO<sub>2</sub> catalyst. Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> supports was prepared by incipient-wetness impregnation while Au/Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> catalysts were prepared by deposition-precipitation, they were characterized by several techniques to correlate catalytic properties to catalytic performance., and their tolerance to the presence of CO<sub>2</sub> and H<sub>2</sub>O has been tested. The effect of O<sub>2</sub> pretreatment on catalyst activity and selectivity was also tested.

**Table 2.5** Summary of preparation techniques for Au catalyst

<b>Approach</b>	<b>Preparation technique</b>	<b>Support material</b>
Preparation of mixed precursors of Au and the metal component of supports	co-precipitation (hydroxides or carbonates) CP	Be(OH) <sub>2</sub> , TiO <sub>2</sub> , Mn <sub>2</sub> O <sub>3</sub> , Fe <sub>2</sub> O <sub>3</sub> , Co <sub>3</sub> O <sub>4</sub> , NiO, ZnO, In <sub>2</sub> O <sub>3</sub> , SnO <sub>2</sub>
	amorphous alloy (metals) AA	ZrO <sub>2</sub>
	co-sputtering (oxides) in the presence of O <sub>2</sub> CS	Co <sub>3</sub> O <sub>4</sub>
Strong interaction of Au precursors with support materials	deposition-precipitation (HAuCl <sub>4</sub> in aqueous solution) DP	Mg(OH) <sub>2</sub> , Al <sub>2</sub> O <sub>3</sub> , TiO <sub>2</sub> , Fe <sub>2</sub> O <sub>3</sub> , Co <sub>3</sub> O <sub>4</sub> , NiO, ZnO, ZrO <sub>2</sub> , CeO <sub>2</sub> , Ti- SiO <sub>2</sub>
	liquid phase grafting (organogold complex in organic solvent) LG	TiO <sub>2</sub> , MnO <sub>x</sub> , Fe <sub>2</sub> O <sub>3</sub>
	gas phase grafting (organogold complex) GG	all kinds, including SiO <sub>2</sub> , Al <sub>2</sub> O <sub>3</sub> -SiO <sub>2</sub> , and activated carbon
Mixing colloidal Au with support materials	colloidal mixing CM	TiO <sub>2</sub> , activated carbon
Model catalyst using single crystal supports	vacuum deposition VD (at low temperature)	Defects sites on MgO, SiO <sub>2</sub> , TiO <sub>2</sub>