



CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Fuel Cells

2.1.1 Basics of Fuel Cell

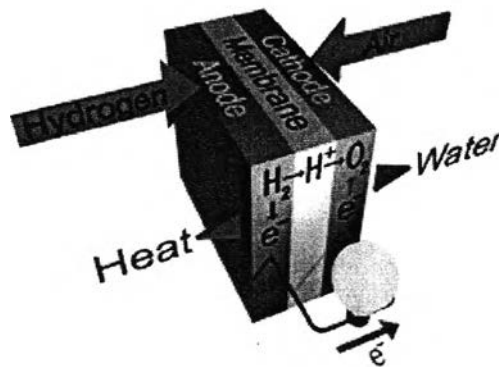


Figure 2.1 Diagram of fuel cell.(http://www.che.sc.edu/centers/PEMFC/about_fuelcell_1.html)

A fuel cell converts fuel to power which more efficient than an internal combustion engine. A fuel cell uses fuel and oxygen in the air in order to produce electricity, water, and heat. A fuel cell emits only water in case the hydrogen as fuel. The anode side of fuel cell, a platinum catalyst, the hydrogen flows into its side while the hydrogen is separated into electrons and protons. The electrons (hydrogen ions) pass through the membrane. As the cathode side, the electrons and oxygen combine with hydrogen ions to produce water, the electrons flow from the anode side to cathode side (external circuit) because they cannot pass through the membrane by this behavior consumes the power which generated by the cell. About 0.7 volts is the voltage of one single cell enough for a light bulb but less for a car so the cells in series is carried out to operate the voltage according to the number of cells stacked.

2.1.2 Type of Fuel Cells

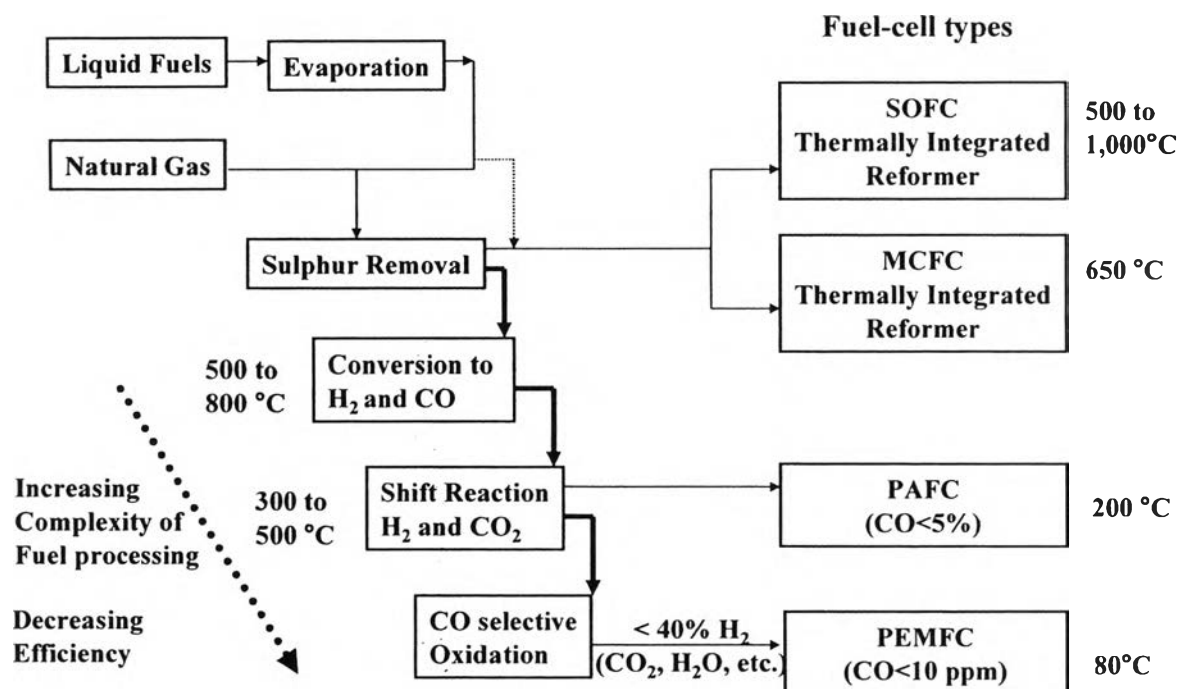


Figure 2.2 Fuel-cell types and fuel processing. (Steele, B.C.H. and Heinzel, A., Nature, 414, 345–352)

From above picture, fuels can be fed into the anode of the high-temperature fuel cells (SOFC (Solid Oxide Fuel Cell) and MCFC (Molten Carbonate Fuel Cell)) directly. Nevertheless, the separated reformer compartments can manage the temperature of the stack, which are thermally integrated within the stack to produce a mixture of fuel and syngas (H₂ and CO). PAFC (Phosphoric Acid Fuel Cell) and PEMFC (Polymer Electrolyte Membrane Fuel Cell) are the low-temperature fuel cells whose the external reformers are required to maintain the operating temperature that the fuel is consumed in. Moreover, dilution of the H₂ fuel reduces performance of the cells, resulting in significant efficiency losses compared with operation on pure H₂. It should be noted that the AFC (Alkaline Fuel Cell) stack cannot be operated on reformat fuels because of the presence of CO₂ in these gases.

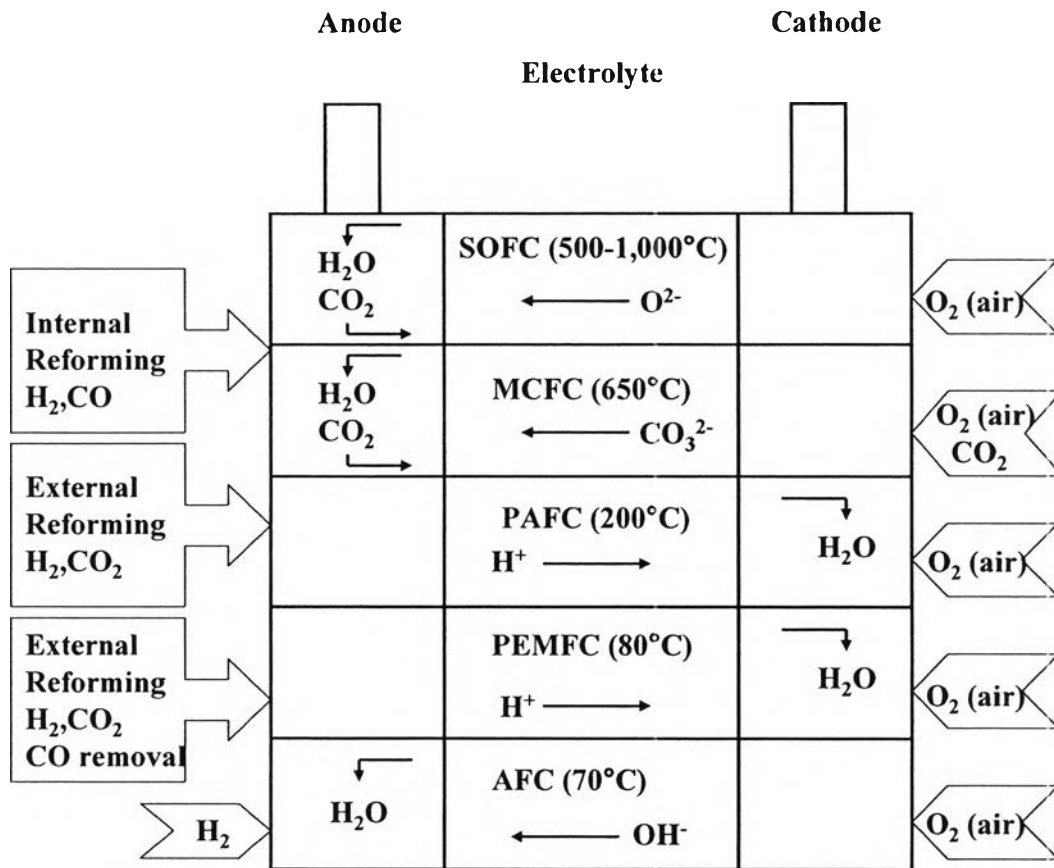


Figure 2.3 Summary of fuel-cell types. (Steele, B.C.H. and Heinzl, A., Nature, 414, 345–352)

The oxidation reaction takes place at the anode (+) and involves the liberation of electrons (for example, $O^{2-} + H_2 \rightarrow H_2O + 2e^-$ or $H_2 \rightarrow 2H^+ + 2e^-$). These electrons travel round the external circuit producing electrical energy by means of the external load, and arrive at the cathode (-) to participate in the reduction reaction (for example, $1/2O_2 + 2e^- \rightarrow O^{2-}$ or $1/2O_2 + 2H^+ + 2e^- \rightarrow H_2O$). It should be noted that as well as producing electrical energy and the reaction products (for example, H₂O and CO₂), the fuel-cell reactions also produce heat. The reaction products are formed at the anode for SOFC, MCFC and AFC types, and at the cathode for PAFC and PEMFC types. This difference has implications for the design of the entire fuel-cell system, including pumps and heat exchangers. To maintain the composition of the electrolyte component in the MCFC system, CO₂ has to be

recirculated from the anode exhaust to the cathode input. Additionally, the composition of the polymeric-membrane electrolyte has to be carefully controlled during operation by an appropriate 'water management' technology. The comparison of five fuel cells can be concluded in Table 2.1.

Table 2.1 Comparison of five fuel cell technologies (Thomas, S. and Zalowitz, M., Los Alamos National Laboratory in Los Alamos, New Mexico)

Fuel Cell	Electrolyte	Operating Temperature (°C)	Electrochemical Reactions
Polymer Electrolyte/Membrane Fuel Cell (PEMFC)	Solid organic polymer poly-perfluorosulfonic acid	60 - 100	Anode: $\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$ Cathode: $\frac{1}{2} \text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}$ ----- Cell: $\text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O}$
Alkaline Fuel Cell (AFC)	Aqueous solution of potassium hydroxide soaked in a matrix	90 - 100	Anode: $\text{H}_2 + 2(\text{OH})^- \rightarrow 2\text{H}_2\text{O} + 2\text{e}^-$ Cathode: $\frac{1}{2} \text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow 2(\text{OH})^-$ ----- Cell: $\text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O}$
Phosphoric Acid Fuel Cell (PAFC)	Liquid phosphoric acid soaked in a matrix	175 - 200	Anode: $\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$ Cathode: $\frac{1}{2} \text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}$ ----- Cell: $\text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O}$

Molten Carbonate Fuel Cell (MCFC)	Liquid solution Of lithium, sodium and/ or potassium carbonates, soaked in a matrix	600 - 1000	Anode: $\text{H}_2 + \text{CO}_3^{2-} \rightarrow \text{H}_2\text{O} + \text{CO}_2 + 2\text{e}^-$ Cathode: $\frac{1}{2} \text{O}_2 + \text{CO}_2 + 2\text{e}^- \rightarrow \text{CO}_3^{2-}$ ----- Cell: $\text{H}_2 + \frac{1}{2} \text{O}_2 + \text{CO}_2 \rightarrow \text{H}_2\text{O} + \text{CO}_2$ (CO ₂ is consumed at cathode and produced at anode)
Solid Oxide Fuel Cell (SOFC)	Solid zirconium oxide to which a small amount of yttria is added	600 - 1000	Anode: $\text{H}_2 + \text{O}^{2-} \rightarrow \text{H}_2\text{O} + 2\text{e}^-$ Cathode: $\frac{1}{2} \text{O}_2 + 2\text{e}^- \rightarrow \text{O}^{2-}$ ----- Cell: $\text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O}$

2.1.3 Polymer Electrolyte Membrane Fuel Cell

As known that the fuel cells have five types, the Polymer Electrolyte Membrane (PEM) Fuel Cell or called Proton Exchange Membrane Fuel Cell is an attractive type for using in vehicles. The structure of Polymer Electrolyte Membranes shown as follows;

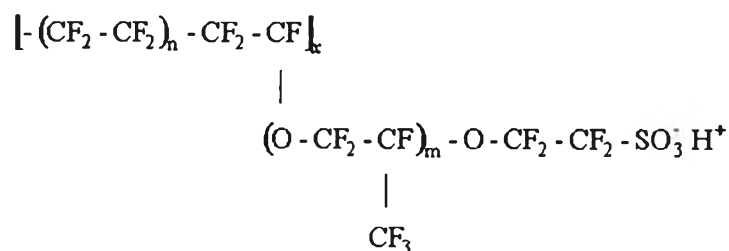


Figure 2.4 Chemical structure of membrane material; Nafion™ by DuPont. (<http://www.annso.freesurf.fr/PEMFC20.gif>)

This membrane consists of three regions:

- (1) The Teflon-like, fluorocarbon backbone, hundreds of repeating

- CF₂ – CF – CF₂ – units in length,
- (2) The side chains, –O– CF₂ – CF – O– CF₂ – CF₂ –, which connect the molecular backbone to the third region,
- (3) The ion clusters consisting of sulfonic acid ions, SO³⁻ H⁺.

The following two reactions of electrochemistry of fuel cells are involved:



From the above equation a four electron reduction process occurs in a multi-step sequence. Pt is a catalyst, capable of generating high rates of O₂ reduction at low temperature, typically 80°C.

2.2 Production of Hydrogen

Hydrogen is a major source of clean, inexhaustible, efficient, and economical energies, which its production is currently produced by the steam reforming of methane. Methane is a cleaner source than petroleum and according to its high content in hydrogen, the total CO₂ emitted in any process for the production of chemicals is lower than when other petroleum fuel is used as a source. The process employed for the production of hydrogen is Steam Methane Reforming (SMR) owing to its economical and largest process. Furthermore, the recent approaches involved in methane decomposition, partial oxidation, and the CO₂ (dry) reforming of methane, and the reforming of low-molecular weight alcohols such as methanol and ethanol.

2.2.1 Steam Methane Reforming (SMR)

The methane molecule composing of a single C-atom surrounded by four H-atoms (CH₄), the sp³ hybridization of the atomic orbitals of carbon means that the C-H bonds are very strong. The converting CH₄ to the any other products are less thermodynamically stable than the CH₄ reactant and leading to the conversion to un-

desired products denoted as carbon oxide. Consequently, undesired products are necessary to remove by convert CO to CO₂ and H₂, Water-Gas Shift (WGS). Steam methane reforming, converting natural gas and other hydrocarbons into syngas, takes place over a nickel catalyst according to the reaction:



The SMR process consists of as follows:

1. *Reformation of Natural Gas*—the first step involves methane reacting with steam at 750–800°C—produce a syngas including a mixture primarily made up of H₂ and CO.

2. *Shift Reaction*—the second step as known as a water gas shift (WGS) reaction—consists of a high temperature shift (HTS) at 350°C and a low temperature shift (LTS) at 190–210°C. CO is produced from the first reaction and then reacted with steam over a catalyst so as to form H₂ and CO.

Further purification process is needed, depending on as the impurity of feedstock such as sulfur (S), chloride (Cl), and removing CO₂.

2.2.2 Methane Decomposition

Methane decomposition process needs a metal catalyst that able to break the C-H bonds of methane molecule and maintain a high and sustained activity for long time. Conventional catalysts for methane decomposition are Fe, Ni, Co or their alloys especially Ni-Al and Ni-Cu-Al catalysts. These are very active at low temperatures (500–600°C), but show low activity at temperatures higher than 700°C because they cannot decompose methane at that higher temperature well caused by a rapid deactivation after contact with methane. Methane decomposition is a moderately endothermic process, which the energy required for one mol of hydrogen product is 45.1 kJ at 800°C. So as to success, it is necessary that the metal catalyst should remain isolated from the carbon deposit by reforming nanometer-sized carbon structure such as tubes, whiskers, and fibres. Methane decomposition process absents a high temperature shift (HTS) and low temperature shift (LTS) water gas shift and CO removal.

2.2.3 Partial Oxidation and CO₂ Reforming (Dry Reforming) of Methane

The partial oxidation of methane (POM) is an interesting process, resulting from solving the difficulties of SMR:

1. It is a highly endothermic process and a huge amount of energy is required—a 20% surplus of methane for burning is essential to supply the reaction heat.
2. It is necessary to overheat water up to the reaction temperature (>1073°C) to maintain the H₂O/CH₄ ratio around three times the stoichiometric value in order to avoid carbon deposition, the additional energy must be supplied.
3. The H₂/CO ratio of the produced syngas is three or higher because certain important process using this syngas (methanol synthesis, Fischer-Tropsch process, etc.) required a ratio of three, it is necessary to employ modified SMR reactors (Autothermal Reforming ATR, Combined Reforming CMR), or to modify the syngas composition by reverse Water Gas Shift (WGS).



The main advantage of this process is that the partial oxidation is an exothermic reaction which leads to a significant reduction of the costs. On the other hand, the main disadvantage is the separating of oxygen from air lead to higher cost. Seeing that the use of air as oxidant to still controversial since it guides to an increase in energy consumption and flow to the units, and the dilution of the syngas with N₂. The use of oxygen-permeable ceramic membranes has been considered as a good alternative for the separation of oxygen from air.

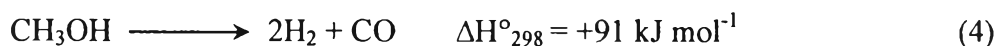
The CO₂ reforming of methane occurs:



CO₂ is a very efficient energy carrier and its recycling increase the efficiency of the plant. The major obstacle associated with the CO₂ reforming reaction is the deactivation of the catalysts due to carbon deposition. POM and CO₂ reforming have a parallel interest because the active catalysts, the reaction mechanisms, and the deactivation processes have several features in common. Pt/ZrO₂ catalysts are very stable for the CO₂ reforming of methane. Recently, the use of promoters such as cerium oxide can improve the activity and stability of Pt/ZrO₂ catalysts under severe deactivating reaction conditions. The CO₂ reforming of methane has been explained by a two-step mechanism that involves the occurrence of CH₄ decomposition on metal particle and of CO₂ dissociation on oxygen vacancies of the support at the same time. Increasing the reducibility of the support, there is an increase in the number of oxygen vacancies formed near the metal particle, improving the ability of the support to dissociate CO₂ and the subsequent cleaning capacity. Therefore, a higher degree of reduction results in a catalyst with higher activity and stability during the CO₂ reforming of methane. The addition of cerium oxide to zirconia increases the reducibility and oxygentransfer ability of the support, improving the activity and stability of the catalyst.

2.2.4 Methanol Decomposition

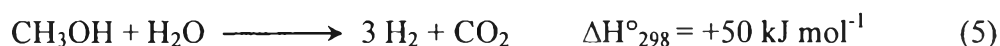
The decomposition of pure methanol is the most basic way to generate H₂ from methanol, which has a couple of advantages over other potential fuels. Unlike gasoline or diesel fuel, liquid methanol can be readily produced from biomass, it is easily adaptable to the current infrastructure, it is easily transported and stored, and finally it has a high hydrogen density.



This reaction is endothermic, heat must be provided to maintain the reaction, and can be performed over metals from Group 10, among which Ni and Pd have been most widely studied. Palladium seems to be the most effective for methanol decomposition and in the case of Pd supported on CeO₂, observed that the decomposition reaction of methanol is sensitive to the metal structure of the catalyst.

2.2.5 Methanol Steam Reforming

The steam reforming of methanol (SRM) is known as a reverse reaction of methanol synthesis.

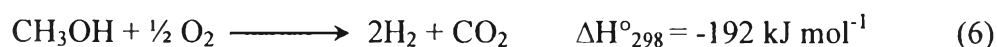


It is the most favorable process of hydrogen production compared to the decomposition and partial oxidation of methanol, resulting from the ability to produce gas with high concentration and high selectivity for carbon dioxide. SRM is an endothermic reaction, which the energy needed for the reaction can be provided from the catalytic burner device. With the superiority of its high methanol conversion, high hydrogen concentration, and mild reaction condition, many research groups take into consideration. SRM process for fuel cell drive system consists of a methanol reformer, catalytic burner—provides heat for the reformer and converts all burnable gases in the flue gas into water and carbon dioxide, gas cleaning unit—reduces CO concentration of the hydrogen-rich product, and PEMFC.

The catalysts used in this reaction are commonly copper-based catalysts, meaning the main active component is copper. Metal oxide supports play a role in enlarging the surface area of the active component and a lesser sintering of metal particles leading to the stability in reaction..

2.2.6 Partial Oxidation of Methanol

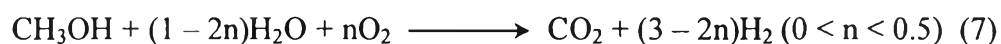
Partial oxidation is a fast and exothermic reaction:



With respect to the exothermic reaction, the advantage of this reaction is that an additional energy supply for the reaction is unnecessary. However, its behavior should be taken into consideration when designing the reactor. Increasing the temperature rapidly causes the sintering of metal particles to deactivate the catalyst. The hydrogen concentration up to 67% in a product stream can be achieved when methanol is partially oxidized with pure oxygen in the feed. Due to the high content

of nitrogen in the air, this causes dilution of the product gas with nitrogen. As a result, the maximum theoretical hydrogen content in such a system is lowered to 41%. The decrease of the hydrogen content in the product stream influences strongly the performance of the electricity production in fuel cell.

2.2.7 Autothermal Reforming of Methanol



Autothermal reforming (ATR) is interesting for use in generating hydrogen to power portable and automobile fuel cells. ATR combines endothermic steam reforming and exothermic partial oxidation to produce a near zero reaction enthalpy. Varying the ratio of feed methanol/oxygen will achieve the desired start-up times. In vehicle applications, the catalyst need to have good activity at low temperatures to start off the reaction and should be stable at high temperatures to maintain the activity.

2.2.8 Ethanol Oxidation

The advantage of ethanol is its high energy density and ease of handling and the fact that it can be employed for producing hydrogen in order to use in fuel cells. The first step in the process is the oxidation of fraction of the ethanol which is fed into the catalytic reactor to generate the heat required for the steam reforming reaction:



These processes must be combined because most catalysts used for steam reforming are also active for the combustion reaction. A further water gas shift reaction step is required to remove the excess of CO.

2.3 Hydrogen Purification

The most-appropriate choice hydrogen purification technology depends on performance criteria (hydrogen recovery and feed and product conditions) and operational requirements (flexibility, reliability, feed pretreatment, and by-product recovery), as summarized in Tables 2.2 and 2.3.

Table 2.2 Process considerations for hydrogen purification technology (Membrane Filtration Handbook Practical Tips and Hints by Jørgen Wagner, B. Sc. Chem. Eng)

Factors	PSA	Membrane	Cryogenic
Minimum feed H ₂ , %	50	15	15
Feed pressure, psig	150–1,000	200–2,000	200–1,200
H ₂ purity, %	99.9+	98 max.	97 max.
H ₂ recovery, %	up to 90	up to 97	up to 98
CO + CO ₂ removal	Yes	No	No
H ₂ product pressure	Approximately feed	Much less than feed	Approximately feed

Table 2.3 Operational considerations for hydrogen purification technology (Membrane Filtration Handbook Practical Tips and Hints by Jørgen Wagner, B. Sc. Chem. Eng)

Factors	PSA	Membrane	Cryogenic
Feed pretreatment	No	Yes	Yes
Flexibility	Very high	High	Average
Reliability	High	High	Average
Factors	PSA	Membrane	Cryogenic
By-product recovery	No	Possible	Yes
Ease of expansion	Average	High	Low

2.3.1 Pressure Swing Adsorption (PSA)

The PSA adsorb the impurities from a hydrogen-rich gas onto a fixed bed of adsorbents at high pressure. Consequently, the impurities are adsorbed into an

offgas stream in order to produce extremely pure hydrogen. After adsorption, the bed, still at high pressure, is taken off-line and the regeneration cycle starts. This comprises a series of pressure reductions in a controlled sequence in order to recover the pure hydrogen remaining in the vessel after the adsorption cycle. The recovery of this hydrogen is achieved by repressurising those vessels at lower pressure to bring them back on-line, ready for adsorption. As the pressure in the vessels is reduced, the impurities previously adsorbed on the bed are progressively desorbed into the offgas system. This typically comprises a large offgas drum which, together with a control system designed to minimize pressure fluctuations, provides a buffer for the downstream systems.

2.3.2 Membrane Filtration

The membrane systems are depended on the difference in permeation rate between hydrogen and impurities across a gas-permeable polymer membrane. The permeation consists of two sequential mechanisms—the gas phase component need to dissolve firstly into the membrane after that diffuse through it to the permeate side. Because the solubility bases on the chemical composition of the membrane and diffusion on the structure of the membrane, hence different components, different solubility and permeation rates. Gases can have high permeation rates due to high solubility, high diffusivity, or both. The driving force for both solution and diffusion is the partial pressure difference across the membrane between the feed and permeate sides. Gases with higher permeability, such as hydrogen, enrich on the permeate side of the membrane, and gases with lower permeability enrich on the non-permeate side of the membrane because of the depletion of components with high permeability. The first fraction of the gas to permeate through the membrane consists primarily of the components with the highest permeability. As a larger fraction of the feed gas is allowed to permeate, the relative amount of the components with lower permeability increases in the permeate stream. In hydrogen separations, higher purity hydrogen is associated with lower recovery, and lower purity hydrogen is associated with higher recovery. The effect of hydrogen purity on recovery is much more dramatic with membrane systems than with PSA or cryogenics units. A fairly small change in hydrogen purity can change the recovery significantly.

2.3.3 Cryogenic Process

Hydrogen has a high relative volatility compared with hydrocarbons. By cooling the feed stream against the warming product and tail gas streams in brazed aluminum multi-pass heat exchangers, the process will condense the required amount of feed impurities. The refrigeration can be obtained by external refrigeration packages or by turbo expansion of the hydrogen product. The partial condensation process is normally applied to hydrogen-hydrocarbon separations which the feed must be pretreated, feeding at high pressure and cooling against a stream leaving the cryogenic unit to the temperature at the majority of the C_{2+} hydrocarbons condense, so as to remove water and other components that could freeze in the system. The two-phase stream is sent to a separator where the hydrogen-methane vapor stream is taken overhead and further cooled to a temperature low enough to give the desired hydrogen purity. While, the cooled stream is fed to another separator and the hydrogen product is taken overhead. The hydrogen is heated against the hydrogen methane, from the first separator and the feed, by using heat exchanger before leaving the cryogenic unit. The liquid methane from the second separator is expanded to a suitable pressure so that it will vaporize against the hydrogen-methane stream from the first separator. If necessary, the additional cooling is provided by expanding part of the C_{2+} hydrocarbons product. Consequently, the cryogenic unit will split the feed in to the three products—a high purity hydrogen stream, a methane rich stream at fuel gas pressure, and a C_{2+} hydrocarbon product—or may be two phase.

2.4 Photodeposition

According to literature reviews, photodeposition is an excellent procedure to make active gold catalysts, because of the extent of gold deposits on supports, heat treatment is unnecessary, and narrow gold particle size distribution. Moreover, Chan and Barteau, M.A. (2005) reported that this technique distinguishes individual Au nanoparticles with diameters less than 1 nm, which is not possible with other techniques, and they claimed that nano-support particles are beneficial for raising highly uniform metal nanoparticles in the 1-2 nm size range. However, the support selection

is important to be concerned because not almost supports are suitable for using this technique.

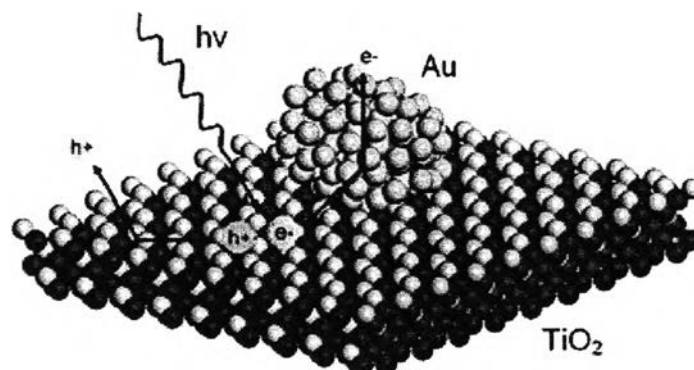


Figure 2.5 Photodeposition of gold nanoparticles on titanium dioxide has been performed under modified conditions to produce smaller particles and enhanced catalytic activity. (Photochem. Photobiol. Sci., 2007, 6, 829–832)

2.5 Selective Oxidation of Supported Gold

In general, the adsorption characteristics and catalytic properties of Au depend crucially on particle size, controlled by the preparation method and the support. The catalytic activity of gold in CO oxidation has been found that it is greatly improved when used in form of nanoparticles in the range 3–5 nm and deposited on certain oxidic supports. However, not only the size of the supported gold particles, but also the interaction between these Au particles and the support influence on the catalytic performance. Additionally, the preparation technique is an important factor affecting stability and activity of the resulting catalysts. Generally, the active Au catalysts are obtained by deposition-precipitation or co-precipitation methods, as compared to incipient wetness method. Moreover, thanks to the high mobility of the gold nanoparticles, high surface area supports are needed to stabilize the nanoparticles in a dispersed state. The catalytic activity in oxidation reactions is enhanced when the gold is deposited onto oxide supports having the ability to undergo redox cycles such as CeO₂, V₂O₅ or TiO₂.

2.6 Physical and Chemical Properties of Gold

To understand why the gold metal was selected in this work and why it differs from any other metals, its properties are necessary to be known as shown in Table 2.4.

Table 2.4 Physical properties of gold compared to those of platinum (Catalysis by Gold, Geoffrey C.Bond, Catherine Louis, and David T. Thompson)

Property	Pt	Au
Atomic number	78	79
Atomic mass	195.08	196.9665
Electronic configuration	[Xe]4f ¹⁴ 5d ⁹ 6s ¹	[Xe]4f ¹⁴ 5d ¹⁰ 6s ¹
Property	Pt	Au
Structure	fcc	fcc
Lattice constant (nm)	0.392	0.408
Metallic Radius (nm)	0.1385	0.1442
Density (g cm ⁻³)	21.41	19.32
Melting temp. (K)	2042	1337
Boiling Temp. (K)	4443	3081
Sublimation enthalpy (kJ mol ⁻¹)	469 ± 25	343 ± 11
First Ionization energy (kJ mol ⁻¹)	866	890

The chemical properties of Pt, Au, and others metal of the adjacent elements are dominated by the relativistic stabilization of 6s level. The 6s² ‘inert pair effect’ is well known to inorganic chemists. Additionally, electrons in the 5d level become more easily mobilized for chemical reaction. The electronic configuration of gold is 5d¹⁰6s¹, its chemistry is determined by the easy activation of 5d electrons and its desire to acquire a further electron to complete the 6s² level and not to lose the one it has. The latter effect awards it a much greater electron affinity and higher first ionization potential than those of Cu or Ag, and accounts for the ready formation of Au⁻¹

state, which has the $5d^8$ configuration (even the Au^{+5} state ($5d^6$) is accessible as in AuF_5^{29}). 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 Au_2O_3 , decomposes at about 433K 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.

The surface of massive Au shows some modest catalytic properties, and it is important to realize this, with highly dispersed forms the activity per unit mass of metal will be dependent *inter alia* upon the fraction of atoms at the surface, and this will clearly increase as the mean particle size is made smaller.

The Au physical properties, Au crystallizes in the face-centred cubic (fcc) habit, its lattice constant being fractionally smaller than silver in compounds and complexes. As a result of the relativistic contraction of $6s$ level while in some respects the properties of gold reflect its greater atomic mass compared to copper and silver (density), the greater strength of the Au-Au bond being a consequence of its shorter than expected length.

2.7 Structure and Property of Zinc Oxide (ZnO)

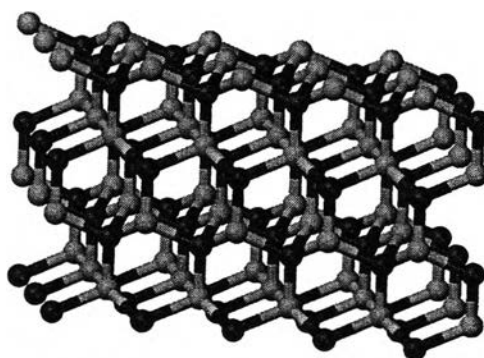


Figure 2.6 Structure of zinc oxide. (<http://en.wikipedia.org/wiki/Image:Zincite-3D-balls.png>)

Zinc oxide is an amphoteric oxide as indicated by its reactivity toward both acids and bases:

- In acid: $\text{ZnO} + 2 \text{HCl} \rightarrow \text{ZnCl}_2 + \text{H}_2\text{O}$
- In base: $\text{ZnO} + 2 \text{NaOH} + \text{H}_2\text{O} \rightarrow \text{Na}_2[\text{Zn}(\text{OH})_4]$

Most ZnO has character, even in the absence of intentional doping. Native defects such as oxygen vacancies or zinc are often assumed to be the origin of this, but the subject remains controversial. An alternative explanation has been proposed, based on theoretical calculations, that unintentional substitutional hydrogen impurities are responsible.

2.8 Low-Temperature CO Oxidation

Hoflund *et al.* (1995) studied the catalytic performance of Au/MnO for low-temperature CO oxidation. They found that Au/MnO catalysts, even with no pretreatment, are superior to the best, as compared to the pretreated platinized tin oxide (Pt/SnO) catalysts under the conditions tested. Besides, the very small decay observed for Au/MnO catalysts is mostly due to carbon dioxide retention. The optimum gold content has been determined to be 10% of the manganese content, and a lithium promotor results in improved catalytic behavior over K- or Na-promoted Au/MnO. In 1996, Haruta *et al.* investigated the low-temperature catalytic combustion of methanol and its decomposed derivatives over supported gold catalysts ($\alpha\text{-Fe}_2\text{O}_3$, TiO_2 , etc.). The supported gold catalysts are less active in H_2 oxidation, but exhibit much higher activities in CO oxidation. Especially, gold supported on manganese oxide is effective in the selective CO removal from hydrogen. Besides these studies, in 1999, Grunwaldt *et al.* compared the Au/ TiO_2 and Au/ ZrO_2 catalysts for low-temperature CO oxidation, which gold catalysts were prepared by immobilizing gold colloids of about 2 nm size on TiO_2 and ZrO_2 in aqueous solution. It was observed that the gold particles nearly retained their size after immobilization on both supports. At the calcination temperature of 400°C, the catalysts were slight sintering. CO adsorption was reversible on all catalysts and weaker on the most active catalysts. The number of low-coordinated gold sites was much higher on TiO_2 , whereas

on ZrO_2 more positively polarized gold atoms were found. This behavior was traced to the shape of the gold particles, which affects the number of low-coordinated gold atoms and is dependent on support and treatment. In 2002, Grisel *et al.* showed the oxidation of CO over $Au/MO_x/Al_2O_3$ in a hydrogen-rich environment, which $Au/MgO/Al_2O_3$ is able to oxidize CO selectively in hydrogen-rich gases (~70 vol.%) at the temperatures relevant to hydrogen fuel cell applications (70–100°C). The presence of MgO enables the preparation of small, stable Au particles on Al_2O_3 with high surface area and, in this way, improves both low-temperature CO oxidation and H_2 oxidation compared to Au/Al_2O_3 . Addition of MO_x and FeO_x to $Au/MgO/Al_2O_3$ further enhances low-temperature CO oxidation with improved CO_2 selectivity. The increase in CO oxidation activity is attributed to the implementation of new routes for supplying active oxygen, e.g., via lattice oxygen. The better CO_2 selectivity also probably results from suppression of H_2 oxidation at low temperatures. Since then Schumacher *et al.* (2003) demonstrated the preparation and conditioning procedure to get the high active Au/TiO_2 catalysts for low-temperature CO oxidation. Using a modified deposition–precipitation procedure and a new reductive conditioning method, Au/TiO_2 catalysts with small metallic Au particles (<2 nm) and a very high activity for low-temperature CO oxidation were prepared. The particles are stable during reaction; a decreasing activity is caused by the accumulation of by-products on the catalyst. In 2004, Panzera *et al.* showed the activity of ceria-supported Au catalysts for fuel cell applications. The influence of catalyst heat treatment, reaction temperature, gas composition, and space velocity on the CO conversion and CO_2 selectivity has been evaluated. Air calcination at 500°C resulted in the establishment of adequate interfacial metal oxide properties, which are essential to promote the selective CO oxidation. CO conversion close to 100% was obtained at 120°C, whereas CO_2 selectivities not higher than 40% were obtained in the entire temperature range investigated (80–120°C). The presence of CO_2 in the inlet stream negatively affected both CO conversion and CO_2 selectivity. Both calcined and uncalcined Au/CeO_2 catalysts resulted to be very stable, as demonstrated by 120 hours endurance tests. And then Rossignol *et al.* (2005) explored the selective oxidation of CO over the model gold-based catalysts in the presence of H_2 . The model catalysts (Au/Al_2O_3 , Au/ZrO_2 , and Au/TiO_2) were produced by laser vaporization of a metallic gold rod

followed by deposition of the formed clusters onto the support powders. This technique allows to obtain a narrow size distribution of highly dispersed gold particles on the support and, most importantly, similar sizes over whatever the support. A boost in the conversion of CO was observed in the presence of H₂ at low temperature; the extent of this boost is dependent on the support identity was changed. While Av-gouropoulos *et al.* (2006) compared the Au/CeO₂ and Au/CuO for preferential CO oxidation reaction. The catalytic properties are strongly affected by the synthesis procedure, i.e. deposition–precipitation (DP) and modified deposition–precipitation (MDP), mainly in the case of gold. The DP method leads to the preparation of more active PROX catalysts than the MDP one. Highly dispersed and more easily reducible gold or copper oxide species are formed on the catalyst surface and enhance the catalytic activity. Au/ceria catalysts are significantly more active, while CuO/ceria ones are remarkably more selective. The presence of CO₂ and H₂O causes a significant decrease in the catalytic activity, especially in the case of the gold catalyst. However, this deactivation is fully reversible. Both catalysts exhibit a perfectly constant behavior with the time on stream.

2.9 Effect of Pretreatment Conditions on CO Oxidation

The effect of pretreatment conditions on CO oxidation over supported Au catalysts was reported by Park and Lee (1999). Gold catalysts supported on Fe₂O₃, TiO₂, and Al₂O₃ showed decreasing activity with increasing calcination temperatures, while the activity of Al₂O₃-supported catalyst showed activity substantially lower than that of the other two catalysts. With increasing the calcination temperature, the phase transition of gold from Au(OH)₃ through Au₂O₃ to metallic gold was observed. The oxidized gold species were more active than metallic gold. Furthermore, facile formation of the interface between gold and support appears to be critical for high CO oxidation activity of supported gold catalysts. Horv'ath *et al.* (2000) studied the effect of treatment on structure and catalytic activity of Au/Fe₂O₃ catalyst prepared by co-precipitation. By comparing the structure of the samples after various treatments and their activity in the CO oxidation, the results showed the stability of the gold particle size during the treatments. However, after oxidation, a slight shift in

the Au 4f binding energy towards lower values points to the formation of an electron-rich state of the metallic gold particles compared to that revealed in the as-prepared sample. In the reduced sample, the presence of a crystalline maghemite-c phase indicates a change in the support morphology. In the CO oxidation, the oxidized sample shows the highest activity and it might be the result of the cooperative effect of goethite (FeO) and the electron-rich metallic gold nanoparticles. A function of H₂ pretreatment made the adsorption and reaction of CO, O₂, and CO+O₂ on the catalyst surface from 27 to 197°C. Moreover, the reaction routes involved in the oxidation of CO over polycrystalline gold were different from those over the Au/Fe₂O₃ catalyst. Thus, while the simultaneous adsorption of the reactant molecules was responsible for this reaction on Au metal, the redox mechanism involving the removal and subsequent replenishment of lattice oxygen played a role in both the Au/Fe₂O₃ and Fe₂O₃ catalysts, where the presence of gold promoted these steps (Gupta and Tripathi, 1999). At the same time, Tripathi *et al.* studied the microcalorimetry, adsorption, and reaction of CO, O₂, and CO+O₂ over Au/Fe₂O₃, Fe₂O₃, and polycrystalline gold catalysts. The results demonstrated that the oxidation of CO on both Fe₂O₃ and Au/Fe₂O₃ occur by means of similar redox mechanisms involving the removal and replenishment of lattice oxygen, where the presence of gold promotes these processes. The carbonate-like species, formed on both Fe₂O₃ and Au/Fe₂O₃ during the adsorption of CO or CO+O₂, are stable below 102°C and are regarded to be more by-products that do not play a major role in the CO oxidation process, particularly at low reaction temperatures (<127°C). The larger gold particles inhibited the formation of CO_{ad} species during exposure of Au/Fe₂O₃ to CO+O₂; this was accompanied by a decrease in the adsorption of both CO and O₂ and a decrease in the formation of CO₂. The promotional effect of gold is attributed to the presence of small (nanosize) Au crystallites that facilitate the chemisorption of CO molecules because of their inherent defective structural sites. Tabakova *et al.* (2000) studied the influence of the microscopic properties of the support on the catalytic activity of Au/ZnO, Au/ZrO₂, Au/Fe₂O₃, Au/Fe₂O₃-ZnO, and Au/Fe₂O₃-ZrO₂ catalysts for the WGS reaction. The gold catalysts on well crystallized supports, Au/Fe₂O₃ and Au/ZrO₂, displayed higher catalytic activity in the water gas shift (WGS) reaction in comparison with the sam-

ples on amorphous and not well crystallized supports—Au/ZnO, Au/ZrO₂, Au/Fe₂O₃–ZnO, and Au/Fe₂O₃–ZrO₂.

2.10 Effect of Nanoparticles of Gold on CO Oxidation

Making the nanoparticles of gold is an attractive method to achieve the best properties of catalysts reported by Mavrikakis (2000). Self-consistent density functional calculations for the adsorption of O and CO on flat and stepped Au(111) surfaces are used to investigate effects, which may increase the reactivity of Au. They found that the adsorption energy does not depend on the number of Au layers if there are more than two layers. Steps are found to bind considerably stronger than the (111) terraces and an expansive strain has the same effect. On this basis they suggested that the unusually large catalytic activity of highly-dispersed Au particles may in part be due to high step densities on the small particles and/or strain effects due to the mismatch at the Au–support interface. Haruta and Daté (2001) reported the advances in the catalysis of Au nanoparticles. Gold catalysts have recently been attracting rapidly growing interests due to their potential applicabilities to many reactions of both industrial and environmental importance. For low-temperature CO oxidation mechanistic arguments are summarized, focusing on Au/TiO₂ together with the effect of preparation conditions and pretreatments. The quantum size effect is also discussed in the adsorption and reaction of CO over Au clusters smaller than 2 nm in diameter. In addition, recent developments are introduced in the epoxidation of propylene, water-gas-shift reaction, hydrogenation of unsaturated hydrocarbons, and liquid-phase selective oxidation.

2.11 Effect of Moisture on CO Oxidation

Daté and Haruta (2001) investigated the effect of moisture on CO oxidation over Au/TiO₂ catalyst. From this study indicated that moisture enhances the reaction by more than 10 times up to 200 ppm H₂O, while further increasing the moisture content suppresses the CO oxidation reaction. However, the apparent activation en-

ergy is independent of the amount of moisture, which adsorbed on the surface influences the activity rather than the moisture content in the gas phase.

2.12 Effect of Chloride on CO Oxidation

Oh *et al.* (2002) studied the effect of chloride on supported Au catalysts. Supported Au catalysts are generally prepared from chloride containing Au precursors and their properties are highly sensitive to preparation procedures. To better understand and control the variables important in the preparation of these catalysts, the effect of chloride on the catalytic performances of highly active Au/Al₂O₃ catalysts in the selective catalytic oxidation of CO (SCO) was probed. The complex manner in which Cl⁻ affected Au catalysis was deconvoluted in a series of complementary experiments where chloride was quantitatively removed and added. The residual chloride was found to affect the activities in two different ways. It facilitates the agglomeration of Au particles during heat treatment, and it inhibits the catalytic activity by poisoning the active site. Interestingly, chloride poisoning is not only observed at the steady state, it is in fact more pronounced in the transient toward steady state. In order to better assess the poisoning effect of Cl⁻, phosphate was introduced to the support surface as a postsynthesis treatment before the addition of Cl⁻ in some experiments. The results showed that activity suppression was observable at a Cl⁻/Au molar ratio as low as 0.0006. Thus a very small fraction of Au is associated with the active site. This implies that the activity per active site is extremely high.

2.13 Effect of Calcination Temperature on the CO Oxidation

Boccuzzi *et al.* (2001) revealed the effect of calcination temperature on the CO oxidation using a catalytic, TEM, and FTIR study of Au/TiO₂ nanosized samples. Three Au/TiO₂ catalysts, with the same Au loading and with different particle sizes, were prepared by the deposition-precipitation method followed by calcination at three different temperatures, 200, 300, and 600°C. The mean diameters of Au particles were 2.4, 2.5, and 10.6 nm, respectively. On all the samples, the CO adsorption and CO-O₂ interactions were different. The higher catalytic activity on CO oxidation

found for the samples calcined at 200 and 300°C is related to the higher concentration of step sites over the Au surfaces and to a higher concentration of step sites at the borderline with the support. At -183°C, CO and molecular oxygen are competitively adsorbed on step sites. By CO preadsorption on hydrated catalysts, the reaction with O₂ gives CO₂ already at -183°C, while by oxygen preadsorption the reaction is completely inhibited, unless moisture is present in the gas phase. An effect of CO coadsorption has been evidenced on water dissociation on gold sites or at the interface with the support, producing atomic hydrogen. The hydrogen reacts with the oxygen, producing a reactive species, quickly dissociated in nascent oxygen and OH groups. Moreover, the reaction with ¹⁸O₂ at -183°C in the presence of moisture produces only C¹⁶O¹⁸O, giving evidence that there is no direct participation of oxygens of the support and of the water in the reaction. At room temperature, other reaction channels become operative, involving oxygen species activated on the support, as shown by the extensive exchange reactions occurring with the support oxygen.

2.14 Activity, Selectivity, and Long-Term Stability of Catalysts for CO Oxidation

In 2001, Schubert *et al.* investigated the activity, selectivity, and long-term stability of different metal oxide supported gold catalysts for the preferential CO oxidation in H₂-rich gas. A comparative study of the catalytic performance and long-term stability of various metal oxide supported gold catalysts during preferential CO oxidation at 80°C in a H₂-containing atmosphere (PROX) reveals significant support effects. Compared to Au/ α -Al₂O₃, where the support is believed to behave neutral in the reaction process, catalysts supported on reducible transition metal oxides, such as Fe₂O₃, CeO₂ or TiO₂, exhibit a CO oxidation activity of up to one magnitude higher at comparable gold particle sizes. The selectivity is equally found to strongly depend on the employed metal oxide, amounting, *e.g.*, up to 75% for Au/Co₃O₄ and down to 35% over Au/SnO₂. The deactivation, which is observed for all samples with progressing time on stream, except for Au/ α -Al₂O₃, is related to the build-up of surface carbonate species. The long-term stability of the investigated catalysts in simulated methanol reformat depends crucially on the ability to form such byproducts, with

magnesia and Co_3O_4 supported catalysts being most negatively affected. Overall, Au/CeO_2 and, in particular, $\text{Au}/\alpha\text{-Fe}_2\text{O}_3$ represent the best compromise under the applied reaction conditions, especially due to the superior activity and the easily reversible deactivation of the latter catalyst.

2.15 Effect of Preparation Method of Photodeposition on CO Oxidation

Preferential oxidation of CO in hydrogen stream over nano-gold catalysts prepared by photodeposition method was explored by Chang *et al.* (2008), which a series of gold catalysts supported on TiO_2 were prepared by photodeposition method. The power of UV light, irradiation time, and initial gold concentration are the effects of preparation parameters on the characteristics of the catalysts. The result in the lower power source lamp can deposit small gold particles on the support, which in turn was responsible for the enhanced catalytic activity. These catalysts were very active and selective in the PROX reaction. However, the small gold particles were not stable as long as the reaction temperature was 450 °C. Before this exploration, the study of photocatalytic properties of TiO_2 modified with gold nanoparticles in the degradation of oxalic acid in aqueous solution interested Iliev *et al.* (2006). The immobilized TiO_2 is modified with nanosized gold particles by the photoreduction method to obtain different noble metal loading (0.05–0.4 wt.%). The degradation of oxalic acid has been studied in aqueous solution photocatalyzed by band-gap-irradiated TiO_2 , modified with nanosized gold particles. The presence of low amounts of gold on the TiO_2 surface leads to an increase of its photocatalytic activity. The adsorption properties of the catalysts, as well as the noble metal content on the surface of the support, influence the efficiency of the photocatalytic.

From above benefits of photodeposition method, it is interesting to prepare in the others supports; Fe_2O_3 , CeO_2 , ZnO , etc., in order to improve the activity and selectivity. As far as Fe_2O_3 is concerned because of its activity, which is investigated that it provides a high activity as well as TiO_2 . However, from a theoretical point of view, Fe_2O_3 can transform to Fe_3O_4 leading to the decrease of adsorption and oxidation of CO. Additionally, the routes of the reaction in the oxidation of CO over polycrystalline gold are different from the desired form of Fe_2O_3 . Consequently, while

the adsorption of the reactant molecules is responsible for this reaction on Au metal, at the same time the redox mechanism involved in the removal and subsequent replenishment of lattice oxygen plays a role in both the Au/Fe₂O₃ and Fe₂O₃ catalysts, where the presence of gold promoted. Besides, the studied of the selectivity for CO oxidation using Pd metal, found that the support of ZnO is better than Al₂O₃ and CeO₂. As a result, it is necessary to study the effects of factors when employs Fe₂O₃ and ZnO as a composited support to achieve the high activity and selectivity.