

Au-BASED CATALYST DESIGN FOR SELECTIVE CO OXIDATION IN
HYDROGEN-RICH STREAMS

by

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to my family and professors

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ABSTRACT

Au-BASED CATALYST DESIGN FOR SELECTIVE CO OXIDATION IN HYDROGEN-RICH STREAMS

The objective of this study was to investigate the selective CO oxidation over Au/ γ -Al₂O₃ catalyst modified with various metal oxide promoters (such as Mg, Mn, Fe, Ni, Ce, and Co) in hydrogen-rich environment. All catalysts contained 1 wt.% Au, 1.25 wt.% promoter over Al₂O₃ as a support. The catalysts were prepared by the impregnation of the metal oxides to γ -Al₂O₃ support followed by the homogeneous deposition precipitation of the gold over composite MO_x/ γ -Al₂O₃ support and tested in a microflow reaction system both in the absence and the presence of H₂O and CO₂. The temperature programmed oxidation (TPO) technique was performed in order to investigate the activity of catalyst in the temperature range of 80-150 °C. The Au loading of the catalysts were verified by Atomic Absorption Spectrometry using an ATI Unicam 929. In order to understand the surface structure and distribution of nanosized gold particles, catalysts were characterized by using high resolution transmission electron microscopy (HRTEM).

Compare to Au/ γ -Al₂O₃ catalyst, the metal oxide promoted (especially MnO_x and MgO) Au/MO_x/ γ -Al₂O₃ exhibited higher catalytic activity towards CO oxidation at the gradient temperatures. The effect of CO₂ in the reaction stream was negative as expected but it was balanced even improved by the addition of H₂O for Au/MgO/ γ -Al₂O₃ catalyst, which elucidated the best performance under realistic reaction conditions (in presence of H₂O and CO₂).

The catalysts containing 1.25 weight per cent and 2.5 weight per cent Mg exhibited comparable CO conversions while the conversion decreased drastically by the further increase of Mg content to 5 per cent.

At the temperatures above 130 °C, the H₂O loading of 0 vol.%, 5 vol.%, 10 vol.% demonstrated no sign of enhancement in CO conversion over Au/MgO/ γ -Al₂O₃ while the

addition of H₂O increased the conversion significantly at lower temperatures and this increase become more apparent at the higher H₂O per cent.

The CO conversion decreased as the CO₂ content of the feed increased (mostly appeared in the temperatures of 120-150 °C). This effect was significant when the conversion in the absence and presence of 5 vol.% CO₂ were compared, while there was no remarkable difference between 5 vol.% to 25 vol.% CO₂ content at operational temperature of fuel cell.

ÖZET

HİDROJENCE ZENGİN GAZ KARIŞIMLARINDA SEÇİMLİ CO OKSİDASYONU İÇİN Au-BAZLI KATALİZÖR TASARIMI

Bu çalışmanın amacı farklı metal oksit geliştiricileri (Mg, Mn, Fe, Ni, Ce, Co gibi) ile değiştirilmiş Au/ γ -Al₂O₃ katalizörünün seçimli CO oksidasyonunun hidrojen zengin ortamlarda araştırılmasıdır. Tüm Au bazlı katalizörler ağırlıkça % 1 Au, ve ağırlıkça % 1.25 geliştirici ile destek maddesi olarak Al₂O₃ içermektedir. Katalizörler metal oksitlerin γ -Al₂O₃ destek maddesine emdirilmesini takiben MO_x/ γ -Al₂O₃ kompozit destek metali üzerine altının homojen tortu çöktürmesi ile hazırlanmış ve mikroakış reaksiyon sisteminde H₂O ve CO₂ varlığında ve yokluğunda test edilmiştir. 80-150 °C sıcaklığı aralığında katalizörün aktivitesini incelemek için sıcaklık programlı oksidasyon tekniği uygulanmıştır. ATI Unicam 929 atomik absorpsiyon spektrometresi ile katalizörün Au yüklemeleri doğrulanmıştır. Yüzey yapısı ve nano boyuttaki altın partiküllerinin dağılımının anlaşılması için katalizörler yüksek çözünürlüklü geçirmeli elektron mikroskobu kullanımı ile karakterize edilmiştir.

Au/ γ -Al₂O₃ katalizörüne karşın metal oksit destekli Au/MO_x/ γ -Al₂O₃ değişen sıcaklıklarda CO oksidasyonuna karşı yüksek katalitik aktivite göstermiştir. Bunun daha ilerisinde gerçek koşullar (H₂O ve CO₂ varlığında) altında katalitik aktivitede en iyi performansı gösteren Au/MgO/ γ -Al₂O₃ katalizörü için H₂O'nun eklenmesinin CO₂'nin negatif etkisini dengelemiş hatta daha da iyileştirmiştir.

Ağırlıkça yüzde 1.25 ve 2.5 Mg içeren katalizörler benzer CO dönüşümleri göstermesine rağmen Mg içeriğinin yüzde 5'e kadar artışı dönüşümü sert bir biçimde azaltmıştır.

130 °C üzerindeki sıcaklıklarda, hacimce yüzde 0, hacimce yüzde 5, hacimce yüzde 10, H₂O yüklemelerinin Au/MgO/ γ -Al₂O₃ üzerindeki CO dönüşümünde geliştirici bir belirti göstermemesine rağmen düşük sıcaklıklarda H₂O eklenmesi dönüşümü belirgin olarak artırmış ve bu artış yüksek H₂O yüzdelerinde daha da belirginleşmiştir.

Beslemedeki CO₂ içeriğinin artması (çoğunlukla 120 ile 150 °C sıcaklıkları arasında) CO dönüşümü azalmıştır. Dönüşüm hacimce yüzde 5 CO₂ varlığında ve yokluğunda karşılaştırıldığı zaman bu etki daha da belirginleşirken yakıt hücresinin çalışma sıcaklığında hacimce yüzde 5 ile 25 CO₂ içeriğinde CO dönüşümünde dikkate değer bir değişim gerçekleşmemiştir.

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LIST OF SYMBOLS/ABBREVIATIONS

ΔH°	Enthalpy of the reaction at the standart conditions
AFC	Alkaline Fuel Cell
ATR	Autothermal Reforming
MCFC	Molten Carbonate Fuel Cell
NMRO	Noble Metal Reducible Oxide
PEMFC	Proton Exchange Membrane Fuel Cell
PEM	Polymer Electrolyte Membrane
PROX	Preferential Oxidation
SEM	Scaning Electron Microscopy
SPFC	Solid Polymer Fuel Cell
SOFC	Solid Oxide Fuel Cell
TEM	Transmission Electron Microscopy
TPR	Temperature Programmed Reduction
TPO	Temperature Programmed Oxidation
XRD	X-Ray Diffraction

1. INTRODUCTION

One of the major challenges for mankind in the future is predicted as the development of the cleaner, more reliable and more efficient methods of generating energy. Currently, the main sources of energy such as coal, petroleum (and petroleum by products) and natural gas provide about 66% of the world's electrical power and 95% of the world's total energy demand which include heating, transportation, power generation and other uses (Fossil 2007). The growth of industrial economies, the consumption rates of natural resources including the fossil fuels and increasing environmental concerns have recently highlighted the necessity of exploring more efficient and environmentally benign energy sources and technologies.

One of the most promising solutions for small-scale stationary applications in the short run and mobile applications in the long run, meeting the increasingly stringent legislation standards set for air pollution control, is the hydrogen powered fuel cells, which are about twice as efficient as the internal combustion engine and produce little or no primary pollutants. (Önsan, 2007)

The main challenge that encountered in the development of hydrogen-based fuel cell power system is the storage of highly flammable hydrogen with a large specific volume. Due to insufficient infrastructure and safety concerns, the storage of hydrogen on-board does not seem to be feasible today. To overcome this difficulty, it is proposed that the hydrogen can be produced on-site from a conventional fuel such as natural gas, gasoline or other hydrocarbons using a fuel processor (Önsan, 2007).

At present, the production of hydrogen is primarily achieved via catalytic steam reforming, partial oxidation and autothermal reforming of natural gas or steam reforming of methanol (Amphlett *et. al.*, 1994). However, in all of these processes, CO is formed as a by-product and must be subsequently removed because of its poisoning effect on the Pt-based anode catalyst used in the PEM fuel cell. During poisoning of the anode, CO molecules preferentially adsorb onto the platinum catalyst surface blocking active sites from hydrogen. In order to avoid significant poisoning effect of CO on the anode catalyst,

the CO level in the hydrogen stream has to be reduced to below 10 ppm (Poirier and Sapundzhiev, 1997; Otsuka *et. al.*, 2002).

The negative effects of CO on electrocatalysis can be alleviated in a number of ways such as pressure and temperature swing adsorption (PSA/TSA), methanation, palladium-based membrane separation and water-gas shift coupled preferential CO oxidation (PROX). Of these methods, the water-gas shift coupled preferential CO oxidation has exhibited superiority in means of less energy intensity and lower cost comparing to adsorption, and less hydrogen consumption rates comparing to methanation (Korotkikh and Farrauto, 2000). However in preferential CO oxidation, inevitable side reaction of hydrogen combustion occurs, and hence the selection of PROX catalyst is an essential consideration to minimize this side reaction (Kim and Lim, 2002).

The catalysts currently used include Pt, Ru, Rh, which need temperatures of at least 150-200 °C to operate efficiently, but experience a significant loss of selectivity at higher temperatures because the thermal desorption of CO enables H₂ oxidation and gradually decrease in the activity due to inhibition of oxygen adsorption by adsorbed CO (Kahlich *et. al.*, 1999).

Ever since Haruta *et al.*, discovered superior catalytic activity of supported gold nanoparticles over CO oxidation in low temperatures, the platinum group metals supremacy has started to decay due to the relatively lower stable prices and greater availability of gold (Haruta *et. al.*, 1989; Cameron *et. al.*, 2003). The supported gold catalysts can also oxidize CO more selectively at the fuel cell operating temperature, making them an attractive candidate for PROX applications (Sanchez *et. al.*, 1997). Additionally, Au based catalysts exhibit superior activity at much lower temperatures (< 100 °C) as compared to Pt (< 200 °C), and the catalytic activity enhancement in the presence of moisture and less sensitivity to the presence of CO₂ further make Au an attractive candidate for selective CO oxidation reaction.

A wide range of oxide supported gold catalysts have been investigated for preferential oxidation of CO. In comparative studies, it has been shown that the support

material employed can have a significant effect on the activity of Au/MO_x catalysts for the selective CO oxidation reaction (Schubert *et. al.*, 2001a). The differences in the activities of various catalysts are ascribed to the varying ability of the supports to supply oxygen to facilitate the CO oxidation reaction in presence of hydrogen, and to the size differences in the gold clusters depending on the method of preparation. It is commonly believed that the gold is more active in the form of small clusters (Haruta, 1997).

The coprecipitation, deposition-precipitation and vapor-deposition are the most commonly used methods to prepare gold catalysts. The catalysts synthesized by deposition-precipitation method is superior to those prepared by coprecipitation in obtaining narrower particle size distributions (average Au particle size < 5 nm), and ensuring that the majority of the active components remain on the surface of the support. The wet-impregnation procedure, on the other hand, is known to result in poor CO oxidation (Haruta *et. al.*, 1993). The conventional wet-impregnation method's drawback is attributed to the quantum size effect caused by the lower melting point of gold in a higher dispersed state (Choudhary and Goodman, 2002).

In this thesis, a study on the effects of various promoters on the activity of Au/Al₂O₃ catalysts for the selective CO oxidation is presented. The catalysts were synthesized by employing homogeneous deposition-precipitation method. The reaction tests were carried out in a microflow reaction system equipped with automated gas flow system, and a temperature controlled reactor. Temperature programmed reaction technique was performed in order to investigate the activity of the catalysts in the temperatures between 50-150 °C. The product stream was analyzed by HPR-20 mass spectrometer.

At first, the effects of calcination and reduction environments over Au/Al₂O₃ were studied. Then the promotional effects of ceria, cobalt, nickel, magnesium, manganese, and iron were investigated. Au/MgO/Al₂O₃ catalyst was chosen to study the effects of promoter weight percent, and the CO₂ and H₂O content of the feed since this catalyst showed an excellent catalytic ability for CO oxidation in the presence of both CO₂ and H₂O at the fuel cell operating temperatures.

The Au loading of the catalysts were verified by Atomic Absorption Spectrometry using an ATI Unicam 929. In order to understand the surface structure and distribution of nanosized gold particles, catalysts were characterized by using high resolution transmission electron microscopy (HRTEM) and environmental scanning electron microscopy (ESEM).

This thesis is comprised of five chapters. Chapter 2 contains a literature survey on fuel cells, the hydrogen production methods from various sources and the selective CO elimination using water-gas shift coupled preferential CO oxidation. The essentials of catalyst selection for CO oxidation in H₂ rich streams, factors affecting catalytic activity of gold based catalyst and a brief survey of catalyst preparation methods regarding the metal oxide-supported gold catalyst are also described in Chapter 2. Chapter 3 presents the catalyst preparation procedures with further information of characterization of the catalysts, the reaction system used and, the conditions for catalytic activity measurements. Chapter 4 is comprised of the results and discussion of factors that effecting catalytic activity. Conclusions from this study and suggestions for future work are posted in Chapter 5.

2. LITERATURE REVIEW

The desire to explore an innovative high efficiency energy power source system and complying the low-emission standards by reducing CO and NO_x emissions is becoming more popular due the volatility of the world-wide petroleum market and concerns over global warming. In response to these critical needs, the fuel cells, as one of the clean energy technologies of the future, and the related issues such as hydrogen production and cleaning up from CO have been studied extensively in the recent years.

2.1. Fuel Cells

2.1.1. Fuel Cell History and Backgrounds

Lawyer and scientist William Grove, performed the first demonstration of hydrogen-oxygen fuel cell with very dilute sulfuric acid in 1839, defined the fuel cell as an energy conversion device that uses chemical energy of reactants to obtain electrical energy, giving much higher conversion efficiencies than any conventional thermo-mechanical system without polluting the environment.

A fuel cell consists of an anode and cathode, to which a reductant and oxidant are supplied. The porous electrodes are separated by an ion-conducting electrolyte. Every hydrogen molecule splits into two H⁺ ions and two electrons by a catalytic reaction whereas two negative charged oxygen ions are formed from oxygen molecule by the catalyst at the cathode. The electrons go through an external circuit to serve an electric load while the ions move through the electrolyte medium toward the oppositely charged electrode. At this electrode (cathode), oxygen reacts with electrons taken from the anode and hydrogen ions form the electrolyte to create water (Song, 2002).

Addition of several cells together to form a fuel cell stack is achieved in order to conditioning the output power for the load, and also linking it to the user interface (Ralph and Hards, 1998).

2.1.2. Types of Fuel Cells

To date there are five major types of fuel cells under development, depending on both composition and operating temperature of the electrolyte. The alkaline fuel cells (AFCs), the proton exchange membrane fuel cells (PEMs) and the phosphoric acid fuel cells (PAFCs) operate at low temperatures (<250 °C), whereas the molten carbonate fuel cells (MCFCs) and solid oxide polymer fuel cells (SOFCs) operate at high temperatures (>650 °C) (Choudhary and Goodman, 2002).

MCFC's and SOFC's are characterized by their direct reaction capability and therefore do not require a noble metal catalyst. For these fuel cells, the variety of fuels is much more diverse as the fuel cells are innocuous to CO and CO₂ contaminations. However, the high temperatures required for these cells impose difficulties in their maintenance and operation making them unsuitable for quick start-up applications. Both PEMFC's and AFC's, on the other hand, have low platinum catalyst loadings, fast start-up, and minimal corrosion. However, the liquid electrolyte in AFC's exhibited handling problems. PEMFC's avoid this problem due to occupying solid polymer electrolyte. Both of this fuel cells are sensitive to CO and CO₂ and therefore fuel conditioning is required if fossil fuels are used (Prater, 1994).

Of those mentioned, PEMFC's possess a series of advantageous features that make them leading candidate for mobile power applications or for small stationary power units due to its lower operation temperatures, low platinum catalyst loadings, sustained operation at high current density, low weight, compactness, potential for low cost and volumes, fast start-ups, long life potentials, minimum corrosion properties and suitability to discontinuous operations (Ghenciu, 2002).

2.1.3. The PEM Fuel Cell

PEM fuel cell is first developed by General Electric for applications in the NASA space program in 1960s. The electrolyte used in the PEM fuel cell is a solid polymer membrane and on each side of the membrane a porous catalytic (usually platinum on carbon) electrode is bonded. The ion-exchange membrane commonly used is a fluorinated

sulfonic acid polymer, which consist of a fluorocarbon polymer backbone to which sulfonic acid groups is attached (Song, 2002).

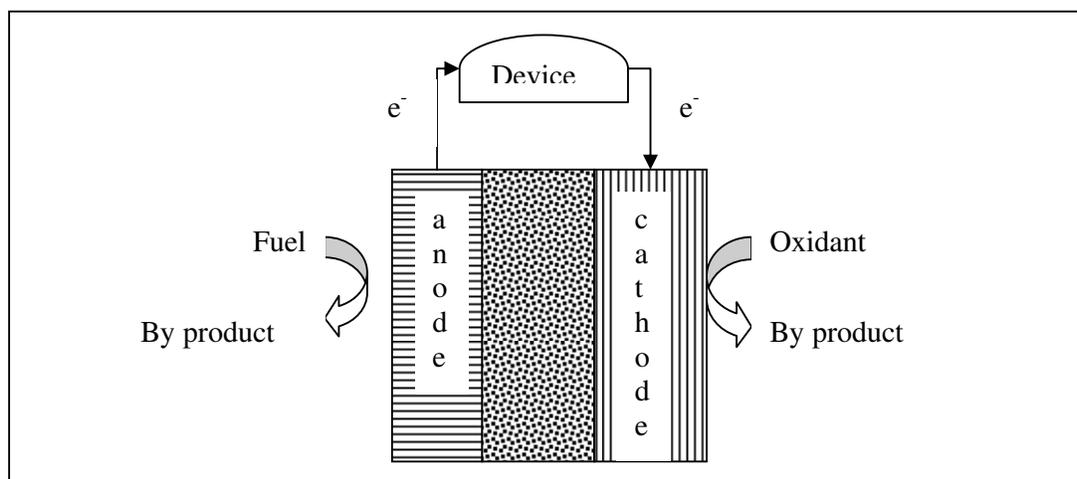


Figure 2.1. Schematic diagram of PEM fuel cell

The negative ions are rigidly secured in the structure on the membrane, while the positive ions contained in the membrane are mobile and thus free to carry positive charge through the membrane (Figure 2.1). The mobility of these protons is mitigated by hydration of the solid polymer. Overall, fuel is oxidized electrochemically and each cell produces approximately 0.6-0.7 eV electricity (Trimm and Önsan, 2001).

The reactions at the anode and the cathode, respectively, are:

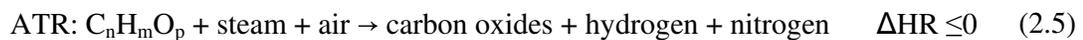
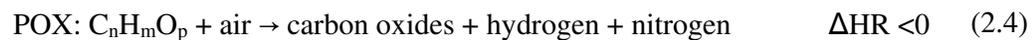
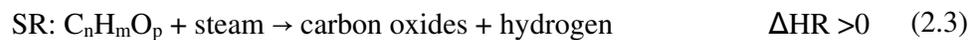


The use of PEM fuel cells requires the production of pure H_2 with no more than 10 ppm CO (Song, 2002). CO-free H_2 generation on site of the fuel cell-powered application using existing fuel like natural gas and gasoline is emerging as the technology of choice because it utilizes existing infrastructure and avoids on site H_2 storage. It is now agreed that such a H_2 production system will involve a combination of three different reactions

steps in series: hydrocarbon fuel oxidation state, water-gas-shift (WGS) and preferential oxidation (PROX) (Song, 2002; Choudhary and Goodman, 2002).

2.2. Conventional Hydrogen Production Methods for Fuel Cells

The hydrogen as a key reactant and an energy carrier agent can be produced from various fuels sources including existing fossil fuels, which offer the required transition time to renewable resources. The natural gas, LPG, gasoline, diesel, ethanol, and methanol are pronounced as the promising hydrogen sources, and the hydrogen can be derived from these carriers by means of steam reforming (Reaction 2.3), direct partial oxidation (Reaction 2.4), and autothermal reforming as given in Reaction 2.5. (Önsan, 2007).



In either steam reforming or partial oxidation, the heat management (thermal integration of the fuel processor) becomes a key to achieve high efficiencies (Joensen and Rostrup-Nielsen, 2002). The autothermal reforming (also known as indirect partial oxidation) combines the thermal effects of partial oxidation and steam reforming; the partial oxidation supplies heat for the subsequent endothermic steam reforming and water gas shift reaction which eventually decreases the operation temperature. This process is carried out in the presence of a catalyst, which controls the reaction pathways and thereby determines the relative extents of the oxidation and steam reforming reactions (Ahmed and Krumpelt, 2001). The net result is a slightly exothermic process.

In general autothermal reforming has a better capacity for start-up than steam reforming, because the unit can be quickly brought up to desired operating temperature by running in combustion mode for a short time (Zalc and Löffler, 2002). Therefore, indirect partial oxidation is accepted to be the most promising route to produce hydrogen from hydrocarbon fuels for mobile applications (Ahmed and Krumpelt, 2001).

A critical factor affecting the development of fuel cell is the degree of purity of the hydrogen fuel. In any case, the hydrogen-rich gas mixture by partial oxidation or steam reforming of hydrocarbon fuels generally comprises of significant amounts of CO up to concentrations of 8 vol% on the dry basis, depending on the hydrocarbon fuel used, unfortunately this traces of CO present in the reformed gas mixture can lead to a poisoning effect on the platinum based anode electrode of the fuel cell by blocking the anode electrode catalyst surface (Ruettinger *et. al.*, 2003). To overcome this problem, the reformer is coupled with a water-gas-shift reactor to oxidize the CO.

2.3. Water-Gas-Shift Reaction

The water-gas shift reaction (Reaction 2.6) is a critical stage in fuel processors not only for preliminary carbon monoxide clean up but also for additional hydrogen generation prior to the further elimination of carbon monoxide (Ghenciu, 2002). The reaction is reversible and the forward rate is strongly inhibited by the reaction products.



where $\Delta H = -41.2 \text{ kJ.mol}^{-1}$ and $\Delta G = -28.6 \text{ kJ.mol}^{-1}$ (Wen *et. al.*, 2007; and Li *et. al.*, 2000). WGS units are placed downstream of the reformer to lower the CO content and improve the H₂ yield (Ghenciu, 2002; Idakiev *et. al.*, 2004).

The WGS reaction is moderately exothermic and equilibrium limited. Hence the equilibrium conversion of CO is dependent largely on the reaction temperature, and the lower temperature is more favorable for higher CO removal. On the other hand, from the view point of kinetics, the reactant gases are not active enough to reach the chemical equilibrium at low temperature; the favorable kinetics can be achieved at higher temperatures. Therefore, there should be an optimum temperature for WGS reaction. Thermodynamics mandates that the optimum temperature is between 200 and 280°C to achieve desired conversion levels. In addition, CO₂ in the reformed gases suppresses WGS reaction according to Le Chatelier's principle (Shishido *et. al.*, 2006; Tanaka *et. al.*, 2003).

Consecutive high-temperature (300-450 °C) and low-temperature (200-300 °C) WGS converters are used to reduce the CO content first to 3%-4% and then to 0.5%-1%, respectively (Trimm, 2005). If the reformer effluent contains less than 5% CO, a single low-temperature WGS reactor is preferred for reducing the CO content to < 2% in the WGS exit (Avci *et. al.*, 2001). These two stage catalytic processes in series produce a hydrogen-rich stream containing 40-75% H₂, 15-25% CO₂, 15-30% H₂O, 0 -25% N₂, and 0.5-1% CO (Sedmak *et. al.*, 2004). Thus the reduction of CO to less than 1% is achieved; further CO clean-up system is a necessity for preventing the poisoning affects of CO on anode Pt catalyst. Consequently, the deep removal of CO from the H₂ stream after hydrocarbon fuel reforming and water-gas-shift reactions is an essential requirement for the PEMFC which is viewed as the most promising technology for small-scale stationary applications in the short run and mobile applications in the long run.

2.4. Preferential CO Oxidation in H₂-Rich Streams

Reduction of traces of CO to the acceptable levels before entering the fuel cell is achieved in a number of ways such as pressure and temperature swing adsorption (PSA/TSA), methanation, palladium-based membrane separation and preferential CO oxidation (PROX). Although separation through a membrane is feasible, the flux is usually too slow that makes the membrane separation technique inadequate for the application in final CO removal. The removal of CO by methanation has the advantage of less hydrogen lost compare to the selective oxidation but the on board use of Ni based catalyst, which is the most promised choice for this process, is considered to a potential health hazard. Hence the methanation is probably best applied in the context of service station conversion processes.

Among them, the selective oxidation has been accepted as the most efficient way to achieve this goal (Trimm, 2005). To achieve low CO concentration, the PROX reactor is placed between the low-temperature shift reactor (200 °C) and the fuel cell (80 °C) (Cheekatamarla *et. al.*, 2005). In this system, the possible four reactions can occur.



The methanation reaction (Reaction 2.9) should be avoided (unless the CO concentration is quite low) since it consumes relatively large amounts of hydrogen compared with the preferential CO oxidation (PROX) (Ko et. al., 2006). The oxidation is rapid and responds quickly to changes in the operation conditions, but the selectivity is a serious issue in the PROX unit, because the oxidation of hydrogen leads to a diminished process efficiency and increased water management problems (Zalc and Löffler, 2002).

There are three obvious possibilities to be considered for an efficient PROX unit. One may be finding a catalyst that adsorbs CO but not H₂, so favoring selective CO oxidation. Another possibility is to select a temperature at which CO is oxidized but H₂ is not. Finally, as the third choice, a catalyst may be found where both CO and H₂ are oxidized, but the kinetic parameters lead to preferential oxidation of CO at the cost of only small amounts of H₂ loss. In all cases, it is very important to control oxygen-carbon monoxide ratio and temperature of the reaction (Trimm and Önsan, 2001). Hence, successful PROX catalyst should achieve full CO conversion and suppress H₂ oxidation within a temperature range where the lower limit does not permit the condensation of the steam in the reformat and the upper limit does not promote RWGS and methanation (Önsan, 2007).

In the light of these possibilities, the most important requirements for a catalyst to be employed for selective CO oxidation can be listed as:

- High CO oxidation activity,
- High selectivity with respect to the undesired H₂ oxidation. The ideal case is to be inactive for oxidation of H₂,

- Activity between the temperature region defined by the temperature level of the low-temperature shift reactor unit (~ 200 °C) and that of the H₂-PEM fuel cell (~ 80 °C),
- Tolerance towards the presence of CO₂ and H₂O in the feed.

2.5. Low Temperature Selective CO Oxidation Catalysts

To date, most of the proposed catalysts for carbon monoxide oxidation are alumina supported platinum group metals, zeolite supported platinum catalysts or gold-based and copper-based catalysts. Although the precious group metals (Pt, Rh, Ru, Au) have an advantage of good activity for CO oxidation, their drawbacks are highlighted as high cost regarding limited availability, decrease of selectivity at high temperatures, and requirements of two-stage reactors to reduce CO levels below 10 ppm (Park *et. al.*, 2004).

The interest has been shown through the use of noble metals (Pt, Pd, Rh, Au, Ag) and metal oxides (SnO₂, MnO_x, Fe₂O₃, CoO_x, TiO₂, ZrO₂) together as a catalyst to eliminate CO selectively. The noble metal reducible oxide (NMRO) catalysts, each having two active sites, seem to provide a synergistic interaction in the two component materials. Indeed neither the noble metal nor the reducible oxide alone can catalyze carbon monoxide oxidation at temperatures < 100 °C. One or more of three types of synergetic interaction between the two catalysts components are said to be responsible for the high efficiency observed at low temperatures (Trimm and Önsan, 2001):

- Each of two components may have independent functions in the mechanism of catalytic carbon monoxide oxidation.
- The properties of one component may be modified by the presence of the other. Two components may associate at the atomic level in such a way as to form unique active sites.

Although the mechanism of CO oxidation over these materials is not known in detail, their low-temperature activity is generally attributed to the fact that the noble metal chemisorbs CO while the reducible oxide provides sites for dissociative O₂ adsorption (Kang *et. al.*, 1993).

2.5.1. Platinum-Group Metal Catalysts in Hydrogen Rich Environment

Catalysts proposed for selective CO oxidation in H₂-rich gases are usually alumina supported Pt, Ru, and Rh with the operating temperatures of 120-160 °C. The temperature dependence of the CO oxidation activity and selectivity in H₂-rich gases were investigated. For example, Oh and Sinkevitch reported the selectivities of 40%, 80%, and 80% for Pt/ γ -Al₂O₃, Ru/ γ -Al₂O₃, Rh/ γ -Al₂O₃, respectively, while approximately full conversion of 1% CO was achieved. Under the conditions of reformat gases, Brown et al., observed 25% selectivities over both Ru/ γ -Al₂O₃ and Rh/ γ -Al₂O₃ catalysts, while selectivities of Pt/zeolite-A and Pt/ γ -Al₂O₃ are obtained in the range of 40%-50% for almost complete CO conversion (Trimm and Önsan, 2001).

Selective oxidation of 1% CO on Pt/ γ -Al₂O₃ catalyst promoted by base metal oxide in a hydrogen- rich environment was also studied by Korotkikh and Farrauto (2000) and the high selectivity and activity was observed in relatively low temperatures.

The study conducted by Mergler *et al.* (1996) showed that the Pt-CeO_x/Al₂O₃ catalyst initially converted more CO to CO₂ than does Pt/Al₂O₃ alone does. Although over 60% CO conversion was obtained, the activity of the catalyst dropped and the catalyst became even worse than Pt/Al₂O₃. The only exception was observed when oxidation cycle was proceeded with reduction. In that case, the activity of the catalyst remained better than Pt/Al₂O₃ over the whole temperature range, probably due to partial reduction of the ceria during the reaction.

The CO oxidation reaction on Pt-CeO₂/Al₂O₃ may consist of the formation of CO₂ via reduction of the interfacial ceria by CO absorbed on Pt, and noncompetitive Langmuir-Hinshelwood mechanism is assumed on the metal/oxide interface. CeO₂ has also been proposed as a direct source of oxygen, and in this way oxidation reactions proceed at the metal-support interface (Serre *et al.*, 1993).

The addition of Co, Ni, Mn, as promoter over Pt/ γ -Al₂O₃ further enhances the selective CO oxidation activity. These entire catalysts exhibit 90% CO conversion at below

175 °C. Pt-Co/ γ -Al₂O₃ show almost complete CO conversion in the temperatures of 25-175 °C. Although the Ni promoted Pt/ γ -Al₂O₃ exhibits lower conversions than Co promoted Pt/ γ -Al₂O₃ catalyst at room temperature, Ni catalyst is more efficient than Co catalyst within the temperatures of 200-300 °C (Suh *et. al.*, 2005).

Törnroona *et al.* (1997) studied the promoting effect of cobalt oxide on Pt. According to their study, CO starts to be desorbed from cobalt sites at about 100 °C and creates vacancy for oxygen absorption and subsequent reaction between CO and O₂. When the oxygen atoms are present and close to the interface between Pt and Co, the reaction may spillover to Pt by the reaction of oxygen with CO adsorbed on Pt site, which suggests that the reaction starts on Co and spills over to Pt, where more rapid light off takes place.

Ince *et al.* (2005) conducted a study of using 1.25 wt% Ce as a second promoter on 1.4 wt% Pt-1.25 wt% Co/Al₂O₃ catalyst. In that work, the full CO conversion was achieved at 90 °C, while nearly 45% selectivities towards CO oxidation was obtained. The effect of O₂ to CO ratio over CO oxidation was also investigated. 1.4 wt% Pt-1.25 wt% Co/Al₂O₃ catalyst works reasonably well even at 0.5% O₂ with 100% CO conversion at 90 °C.

According to the experimental study of Uğuz (2007), experiments using gas streams containing 1.0 per cent CO, 1.0 per cent O₂, 60 per cent H₂ and 25 per cent CO₂ in the absence of H₂O resulted in decreased CO conversion due to the addition of CO₂. However, the experiments using gas streams containing 1.0 per cent CO, 1.0 per cent O₂, 60 per cent H₂, 25 per cent CO₂ and 10 per cent H₂O resulted in increased CO conversions with the addition of H₂O, and under these conditions it was observed that the catalyst with Pt-Co-Mg loadings on γ -alumina support led to 100% CO conversion at 383 K, and it was found to be a good candidate for CO oxidation in hydrogen rich streams in the presence of H₂O and CO₂ for use in fuel cell applications.

Schubert *et al.* (2001b) inspected carbon-supported Pt-Sn catalyst for low temperature CO oxidation. The increasing temperature decreased the selectivity steadily. However, in the temperature range of 0-20 °C, the selectivity was reached to 85% while it decreased to 45% at 120 °C. This selectivity is comparable with the selectivity exhibited by

conventional Pt/Al₂O₃ catalyst at higher temperatures (200 °C). The significant decrease in CO coverage with temperature on this system was attributed to the decrease of the selectivity towards CO oxidation.

Igarashi *et al.* (1997) investigated Pt supported on alumina, A-type, mordenite and x-type zeolites. Pt/A-zeolite catalyst showed higher CO oxidation selectivity as compared to Pt/Al₂O₃ at similar conversion levels. Subsequent studies involving a series of catalysts (Pt/A, Pt/mordenite, Pt/X, Pt/Al₂O₃) showed that the Pt/mordenite catalyst required the least amount of excess oxygen for the complete conversion of CO (1 per cent) in presence of excess of hydrogen. The selectivity for CO oxidation versus H₂ oxidation follows the order of zeolite A > mordenite > zeolite X > alumina. The use of a two-stage reactor further increased the effectiveness of the Pt/mordenite catalyst. Hence the catalyst performance was not significantly influenced by the presence of water in the feed stream.

2.5.2. Copper Based Catalysts in Hydrogen Rich Environment

Selective oxidation can also be achieved using nanoparticulate metals of the same group. Cu based catalysts appeared to be promising in selective CO oxidation, either as supported CuCl or as Cu-CeO₂ solid catalyst. Trimm (2005) examined the kinetics of CO oxidation on this catalyst and suggested that the lattice oxygen could be involved, even at low temperatures. The 99% CO conversions with 65% selectivities were obtained at quite high temperatures of 165 °C.

CuO-CeO₂ oxide catalyst was also proposed as a candidate for the selective oxidation of CO in the presence of excess hydrogen. Mixed oxide of CuO-CeO₂ can be used in the temperature range of 100-200 °C with a selectivity of 95–90% for complete 1% CO conversion; they are slightly more active and significantly more selective than Pt-based catalysts at a lower reaction temperature; they are less active but much more selective than Au-based catalysts (Avgouropoulos *et al.*, 2002).

CeO₂ enhances CO oxidation for the CuO-CeO₂ catalyst through a synergistic effect. Cerium oxide is well known to have a high oxygen exchange capacity

(Travarelli *et al.*, 1997), which is related to the capacity of cerium to change oxidation states reversibly between Ce^{4+} and Ce^{3+} by receiving or giving up oxygen. CO oxidation is thought to proceed at the metal–support interfacial perimeter. The reduction of CeO_2 has been demonstrated to proceed via a surface reaction that involves the reductant CO (Cordatos *et al.*, 1996). Hence, the oxygen from the support oxidizes CO adsorbed on the metal particle at the interface (Zafirir and Gorte, 1993), and the oxygen vacancies are then replenished by O_2 .

Park *et al.* (2004) have found that the addition of 0.2% Co over CuO– CeO_2 was beneficial for CO oxidation. The operational temperature to achieve 99% CO conversion was found to be wide (150–220 °C), although narrowed to 210–220 °C in the presence of CO_2 and water. The selectivity at 205 °C was found to be 80% in the latter case. The enhancement in the activity was attributed to the formation of two new kinds of Cu species that improved the active sites.

The mixed oxide catalyst Cu/ Al_2O_3 –ZnO also exhibited excellent activity for removal of a small amount of CO in reformat from methanol. The catalytic activity was strongly related to Cu particle size, which is related to the spinel-type Cu–Al–Zn oxides. The catalysts calcined at 500–700°C achieved 90% CO conversion at the reaction temperature of 150°C in the presence of 2% O_2

Doping zirconium into CeO_2 increased the mobility of lattice oxygen and enhanced the CO oxidation activity of the 7%CuO/ $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2\text{Al}_2\text{O}_3$ catalyst in the H_2 -rich feed. The promotion of CO oxidation became weaker as the amount of Zr^{4+} increased above 10%. The 7%CuO/ $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2\text{Al}_2\text{O}_3$ (20%) catalyst was more active than 7%CuO/ $\text{CeO}_2\text{Al}_2\text{O}_3$ (20%), but slightly less active than the 7%CuO/ $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$ without incorporated Al_2O_3 . A small amount of Zr^{4+} dopant and an appropriate amount of incorporated Al_2O_3 yielded a good candidate such as 7%CuO/ $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2\text{Al}_2\text{O}_3$ (20%) for a PROX unit in a PEMFC. Its activity was comparable with, and its selectivity was much larger than, that of 5% Pt/ Al_2O_3 catalyst (Chen *et al.*, 2007).

2.5.3. Gold Based Catalysts in Hydrogen Rich Environment

Amongst those precious metals, the gold based catalysts have received wide attention ever since Haruta found that supported gold catalyst are highly active for the oxidation of CO at low temperatures when deposited as nanoparticles on metal oxides (Haruta *et al.*, 1993) Its higher activity makes the gold another, even better, candidate for CO oxidation in addition to the platinum and copper catalysts at low temperatures.

Gold resides in Group 11 of the periodic table, along with copper and silver. Platinum and mercury are in Group 10 and 12 in the same row. The position of the gold in the periodic table implies a potential for catalytic activity. Some of its physical properties make it very similar to platinum. Gold possesses some unique characteristics. For example, it is the most electronegative metal and only slightly more electropositive than sulfur and iodine. These results in another unique feature of its chemistry; it does not react with other electronegative elements such as sulfur or oxygen and only soluble in a few acids (Bonds and Thompson 1999).

However gold's low activity was generally explained by the absence of partially filled d orbitals, which makes metallic gold unable to chemisorb small molecules, Bond and Sermon (1973) presented the first hint that Au might not always be poorly active when dispersed as small nanoparticles, for hydrogenation over Au/SiO₂ prepared by calcination at a temperature as low as 383~401 K. After Bond and Sermon discovery, Paravano *et al.* (1978) exhibited the oxygen and hydrogen transfer reactions activity over Au/MgO and Au/Al₂O₃ catalysts.

The new era has been opened for gold catalyst after Haruta *et al.* (1987) illustrated that the metal oxide supported nano-size gold particles are in fact the most active catalyst for low temperature (-70 °C) CO oxidation.

Interestingly, although unsupported Au catalysts have higher H₂ oxidation activity than CO, the trend is reversed for highly dispersed supported Au catalysts (Haruta *et al.*, 1993). For the supported Au catalysts, the samples with smaller particle sizes had a much

greater activity for CO oxidation over H₂ oxidation at low temperatures (pertinent to the operating temperature of PEM cells: 80 °C).

The supported gold catalysts found to be active for low temperature oxidation of CO include Au/TiO₂, Au/Fe₂O₃, Au/Co₃O₄, Au/ZrO₂, Au/Al₂O₃, and Au/CeO₂. The support plays a vital role in determining the activity of gold catalysts. The role of metal oxide is suggested to be stabilization of gold nanoparticles on which the reaction takes place (Haruta, 1997). Some other investigators have proposed that the reaction occurs on the gold/support interface where the metal oxide acts as an oxygen donor (Bollinger and Vannice, 1996; Schubert *et al.*, 2001).

2.5.3.1. Au/Fe₂O₃ Catalyst. Kahlich *et al.* (1999) screened Au/ α -Fe₂O₃ catalyst for preferential oxidation of CO in H₂-rich environment, using simulated reformat (75 kPa H₂, 0.025–1.5 kPa CO, balance N₂) at atmospheric pressure with P_{O₂}/P_{CO} ratios between 0.25 and 10. A strong initial deactivation of 30% was observed in the first 2 h time-on-stream, which slowed down during the next 8 h and finally reached to a steady state; a similar deactivation behavior was also reported for Au/TiO₂ catalysts (Trimm and Onsan, 2001);(Haruta *et al.*, 1993).

Avgouropoulos *et al.* (2002) have also investigated Au/ α -Fe₂O₃ in a comparative study of three different catalysts (Pt/ γ -Al₂O₃, Au/ α -Fe₂O₃, CuO-CeO₂). Among those catalysts, Au/ α -Fe₂O₃ catalyst exhibited superiority to the other two for selective CO oxidation at relatively low temperatures (< 80-120 °C, depending on the contact time and the feed composition), whether CO₂ or both CO₂ and H₂O were presented in the reactant feed. However, Au/ α -Fe₂O₃ was the most sensitive towards the deactivation caused by the presence of CO₂ and H₂O in the feed, losing a considerable portion of its activity during the first 80 h under reaction conditions.

For Au/ α -Fe₂O₃, a large amount of oxygen can be adsorbed on the support, which most likely represents the oxygen supply during reaction. The existence of the O₂ reservoir on the support reduces the dependence of the turnover frequency on the gold particle diameter, since O₂ dissociation is no longer rate-limiting. As consequence, the TOF is not

governed by the particle size effects as were suggested for the inert support materials. This, however, makes the performance probably sensitive toward the microcrystalline structure of the metal-support interface so that the activity of such system depends crucially upon the pretreatment method (Schubert *et al.*, 2000).

Hutchings *et al.* (2006) have reported that among the existence of both metallic and cationic form of gold species in Au/Fe₂O₃, the presence of a significant fraction of cationic gold is essential for CO oxidation.

2.5.3.2. Au/CeO₂ Catalyst. The reducibility of the support is an important factor in obtaining good activity for the catalyst. Ceria is one of the relatively easily reducible metal oxides. Ceria is currently used as a key component in three-way automotive exhaust catalyst system. Metal-ceria systems are found to be several orders of magnitude more active than other oxide supported catalysts for various redox reactions due to the high oxygen storage capacity and the reducibility of the ceria (Stephanopoulos, 2001). In addition to its oxygen storage capability, CeO₂ also prevents alumina from sintering at high temperature and improves the dispersion and thermal stability of noble metals (Park and Ledford, 1998).

Many studies have been conducted over ceria-supported gold catalyst for the water-gas shift (WGS) reaction due to its high activity and stability for the reaction. Liu and Stephanopoulos (1995) were the first to carry the investigation to CO oxidation at room temperature over Au/CeO₂, containing 5 wt% Au. Epling *et al.* (1996) have shown Au/CeO₂ containing 10% Au as an active catalyst for low temperature oxidation of CO. Bera and Hegde (2002) have reported a new preparation method (combustion method) for enhancing the CO oxidation activity over 1% Au/CeO₂. However, the catalyst is shown to be active for the reaction at high temperature of 250-300 °C.

Luengnaruemitchai *et al.* (2004) have observed the effects of preparation method (sol-gel, impregnation, co-precipitation), O₂ ratio, water vapor, and CO₂ concentration in the feed stream on the selective CO oxidation over Au/CeO₂ catalyst in the temperature range of 50-190 °C. The Au/CeO₂ co-precipitation catalyst had the best performance

among the three methods of catalyst preparation. The temperature at which the activity of the Au/CeO₂ co-precipitation catalyst was maximum (nearly 60% CO conversion with 90% CO selectivity) was 110 °C. At higher temperature, there was a continuous decrease in selectivity, indicating higher activation energy for the H₂ oxidation than for the CO oxidation. The CO conversion increased with increasing O₂ concentration while the CO selectivity decreased. With 0.5%, 1% and 2% O₂ concentrations, the maxima in CO conversion were 70%, 92% and 98% at 110 °C, respectively. The selectivities at the point of maximum conversion for 0.5%, 1%, and 2% O₂ concentration were 64%, 62% and 48%, respectively. The effect of water vapor at low temperatures (<110 °C) suppressed the CO conversion. Detrimental effect of water at low temperatures is attributed to the strong adsorption of water on the active sites. However, at high temperatures water seemed to be slightly favorable for the catalyst activity since it provided hydroxyl group, which was necessary for reaction to take place. The increasing CO₂ concentration from 2% to 20% reduced the activity of the Au/CeO₂ catalyst, the maximum conversion dropped from 92% to 85%. The selectivity of the catalyst was not significantly impacted by the presence of CO₂ in the feed.

Recently, Venezia *et al.* (2005) have described the relationship between the structure and the CO oxidation activity of Au/CeO₂ catalysts prepared by various methods and have reported that Au/CeO₂ catalysts prepared by deposition-precipitation was the most active for the low temperature oxidation of CO.

In Li *et al.* (2006)'s study, the promoter effect of Mn on Au/CeO₂ catalyst in preferential oxidation of CO in H₂ rich stream was observed. The selectivity increased with increase in Mn content. The 1% Au/Mn_{0.5}Ce_{0.5}O₂ catalyst, calcined at 180 °C, showed 93.3% CO conversion at 80 °C, which decreased slightly to 88.1% as reaction temperature increases to 100 °C. Selectivity of all catalysts, containing Ce, toward CO oxidation decreased significantly when the reaction temperature increased from 25 to 50 °C and continued to decline slightly with change of temperature from 50 to 100 °C. The 1% Au/Mn_{0.5}Ce_{0.5}O₂ catalyst, calcined at 120 °C, exhibited the highest CO conversion of 97.8% and highest selectivity (49.3%) at 80 °C. The high activity of Au/MnO₂-CeO₂ catalyst had been attributed to the synergistic effects of CeO₂-MnO₂ composite oxides

with minor Ce^{3+} species and the coexistence of metallic and nonmetallic gold species within nano-gold particle (<5 nm).

2.5.3.3. Au/TiO₂ Catalyst. Au/TiO₂ is pronounced as the most intensively studied catalyst for CO oxidation while neither Au nor TiO₂ is active for CO oxidation but the combination of their properties generates surprisingly high catalytic activity. On Au/TiO₂ catalysts, the reaction was observed even at temperature as low as 90 K (Bocuzzi and Chiorino, 2000).

The improved catalytic activities for the CO oxidation can be ascribed to the interaction between gold and TiO₂, because the perimeters of Au-TiO₂ interfaces are assumed to act as the important active site (Grunwaldt and Baiker, 1999) which in turn depends on the preparation methods. In comparison with the preparation methods, the catalyst prepared by deposition precipitation (DP) method was superior to the catalysts prepared by incipient wetness. The reason of DP method superiority was attributed to yielding hemispherical gold particles, which strongly attached to TiO₂ by epitaxial contact with their flat planes, Au (111) to anatase TiO₂ (112) and rutile TiO₂ (110), yielding the longest Au/TiO₂ perimeter interface apart from fine dispersion with small gold particles (Haruta, 2004).

A pronounced effect of the H₂ as the co-reactant on the CO adsorption/reaction characteristics was also analyzed under conditions relevant for the polymer electrolyte fuel cells (PEFCs). The results showed that (i) H₂ affected the CO oxidation, most probably by competing hydrogen adsorption on the Au nanoparticles and reaction with oxygen, which resulted in a significantly higher CO reaction order, that (ii) formate and carbonate species formed during the reaction represented (reaction inhibiting) side products, but did not take part in the reaction as reaction intermediate, at least not under present reaction conditions, and that (iii) the formation of formate and carbonate species was inhibited during reaction in a H₂-rich atmosphere (Schumacher *et al.*, 2004).

The catalytic activity of 2 wt% Au/TiO₂ catalysts was evaluated by implementing two different deposition-precipitation methods, varying pH (with NaOH) and some other parameters during the preparation procedure in the study of Galletti *et al.* (2007) within a

100 ml/min reaction feed of the following composition: 37% H₂, 5% H₂O, 18% CO₂, 0.5–1% CO, 1–2% O₂ and helium as balance. The catalysts prepared by deposition-precipitation method, using lower pH values and calcined at 300 °C were found to be the most suitable ones for the CO-PROX at low temperatures with a reducing CO value to 10 ppm within a temperature range of at least 60–80 °C with operating at $\lambda=4$, which is defined as the concentration of O₂ in the feed divided by the concentration of O₂ needed to oxidize completely all the CO in the feed. Complete CO conversion was still reached for more than 30 h of operation showing a certain stability level for the catalyst.

Chang *et al.* (2007) investigated the catalytic activity of nanosized gold catalysts, prepared by deposition-precipitation method, supported on MnO₂-TiO₂ for preferential oxidation of carbon monoxide in H₂ stream under the reactant gas composition of 1.33% CO, 1.33% O₂, 65.33% H₂, and He for balance. The addition of MnO₂ on Au/TiO₂ catalyst improved the selectivity of CO oxidation without sacrificing CO conversion in hydrogen stream between 50 and 100 °C. The improvement in the selectivity could be attributed to the interactions of gold metal with MnO₂-TiO₂ support and the optimum combination of metallic and electron-deficient gold on the catalyst surface. Au/MnO₂-TiO₂ catalyst with Mn/Ti ratio of 2/98 demonstrated an excellent performance on CO conversion as well as the selectivity at 80 °C. However, a decrease in CO conversion at higher temperatures was observed. This suggested that hydrogen was easier to react with oxygen at higher temperature under the existence of metallic gold.

2.5.3.4. Au/MnO_x Catalyst. Chang and McCarthy (1996) reported that MnO_x has high oxygen storage along with faster oxygen absorption and oxide reduction rates, which could be used to reduce the amount of CO in exhaust of natural gas powered vehicle. MnO_x has good O₂ uptake (oxidation) and O₂ release (reduction) rates at temperatures below 600 °C.

Based on the previous studies over gold based catalyst, Haruta and co-workers selected Au/MnO_x catalysts for investigating the PROX reaction. The Au loading was found to play a crucial role; the catalyst with Mn/Au = 50 not only exhibited higher CO oxidation activity than the sample with Mn/Au = 19, but also a greater relative oxidation activity for CO with respect to H₂. Subsequent studies focused on the former sample,

which showed greater than 95% CO conversion (1% CO, 1% O₂, balance H₂) between 50-80 °C and 85% CO conversion at 120 °C, thereby indicating a larger contribution from the H₂ oxidation at higher reaction temperatures (Sanchez *et al.*, 1997).

Luengnaruemitchai *et al.* (2005) investigated the effect of CO₂ and H₂O over Au/MnO_x catalyst with the reformat gas composition of 1% CO, 2% CO₂, 1% O₂, 2.6% H₂O, and 40% H₂ balanced in He. The Au/Mn catalyst with atomic ratio of 1/30 showed an increase in CO oxidation activity till the operating temperature of 130 °C while CO conversion decrement was observed with the temperatures above 130 °C. This catalyst gave the highest conversion and selectivity of 93% and 58%, respectively at the relatively low temperature of 130 °C. Au/MnO_x catalyst could resist up to 10% H₂O in the reactant feed while CO oxidation activity was suppressed in the presence of 20% CO₂, whereas 48 h stability was observed.

The reversible transformation between MnCO₃ and manganese oxides occurred during the reaction, which might act as a more effective support for Au for selective CO oxidation was reported in the literature. Lee *et al.* (2001) also confirmed that the strong interaction between gold particles and MnO_x support, which is induced by treatment at 400 °C, was responsible for the improved catalytic activity for low temperature CO oxidation.

2.5.3.5. Au/CoO_x Catalyst. Due to its high CO oxidation activity in CO-O₂ mixtures even at the ambient temperatures, the cobalt oxide is used in this reaction widely. It was shown that Co₃O₄/Al₂O₃ with pre-oxidized cobalt oxide had high CO oxidation activity even without a noble metal. The main reason for this is that the CO is unable to block the cobalt oxide surface from O₂ absorption as it does on platinum. However, the activity of cobalt oxide decreases significantly in the presence of water and hydrocarbons (Thormählen *et al.*, 1999).

Jansson *et al.* (2001) proposed the following mechanism for CO oxidation reaction on Co₃O₄/Al₂O₃ without the presence of hydrogen.

- CO is absorbed on the cobalt oxide surface,
- The absorbed CO reacts with activated oxygen already present on the cobalt oxide surface. The produced CO₂ is then desorbed from surface, also carbonate species might be formed as an intermediate,
- The reduced cobalt is deoxidized by gas phase oxygen or it is further reduced by CO, thus deactivating the site,
- CO₂ can be absorbed on the surface and from surface carbonate species.

The study by Haruta *et al.* (1989) illustrated the complete conversion of CO at 30 °C in the presence of 76% relative humidity on Au/NiO and Au/Co₃O₄ coprecipitated catalysts with 50% selectivities at 73 °C and 66 °C, respectively.

The promoter effect of CeO₂ on Au/Co₃O₄ catalyst over preferential oxidation of CO in H₂-rich stream was investigated by Wang *et al.* (2008). Ce promoted catalyst exhibited much higher catalytic activity in CO-PROX than Au/Co₃O₄ and Au/CeO₂. Over Au/Co₃O₄, 100% CO conversion with about 50% selectivity towards CO₂ was obtained at 120–140 °C. Especially, Au/CeO₂–Co₃O₄ showed good activity and selectivity even at ambient temperature, where CO was completely converted to CO₂ with 75% selectivity.

Mergler *et al.* (1996) and Hatura *et al.* (1993) suggested similar mechanisms for Pt or Au containing catalyst. According to them, CO is absorbed on Pt or Au site, while oxygen is supplied by CoO_x. The reaction between CO_{ads} and O_{ads} takes place either in the interface between Pt or Au with CoO_x. The oxygen-spillover to the Pt or Au sites is also possible. The mutual interaction between cobalt oxide and ceria may enhance the catalyst reducibility and oxygen in CeO₂–Co₃O₄ composite oxide, which are important for CO oxidation and can then improve the CO PROX activity.

2.5.3.6. Au/Al₂O₃ Catalyst. Al₂O₃ is the most common kind of oxide used as support in industrial catalytic process. The active alumina is much more widely used in catalytic applications than the silica and the carbon since it is not only an excellent support, but it is also very active as a catalyst in its own right for several applications (Ertl and Weitkamp, 1999).

The γ -alumina and η -alumina, which are also called active aluminums, are the most important transition oxides for catalytic applications. γ -alumina is especially used for applications where the high surface area and the high thermal and mechanical stability are required. In particular, γ -Al₂O₃ surface has been demonstrated to be abundant in cation vacancies; about one ninth of metal atom in the alumina lattice is vacant. The unique surface structure of γ -Al₂O₃ may favor stabilizing Au clusters. Moreover, γ -alumina's capacity to store and release physically adsorbed water is highly pronounced (Han *et al.*, 2007).

Al₂O₃ and MgO supported catalysts exhibited a lower, but still considerable activity, as evidenced by their TOFs. These materials have a low ability to adsorb or storage oxygen at low temperatures. For inert supports like Al₂O₃, the activity seems to depend very critically on the diameter of the gold particles, and only the extremely small particles (< 2nm) yield highly active samples. The increasing TOF with smaller particle size was explained by an enhanced dissociative adsorption of oxygen on small gold particles, due to a higher density of reactive defect sites or gradual change in the electronic structure at decreasing size (Cunningham *et. al.*, 1998; Bondzie *et. al.*, 1999). Therefore, at temperatures below 100 °C, Au/ γ -Al₂O₃ catalyst is announced as the most active catalyst in the presence of H₂. The great improvements in activity can be obtained and the temperature range of CO conversion can be enlarged.

A comparison study on the effects of various promoter (Cr, Mn, Fe, Co, Ni, Cu, and Zn) on CO oxidation over Au/ γ -Al₂O₃ at the low temperatures was performed with the reactant flow of 30 ml/min, comprised of 2 vol% CO and 2 vol% O₂ in He as balance (Grisel and Nieuwenhuys,2001a). The addition of MnO_x enhanced the catalyst performance enormously. Next to MnO_x, the addition of NiO_x and ZnO_x, was also enhanced the catalytic activity while this enhancement was in lesser extent in the case of FeO_x and CoO_x. The catalytic activity can be summarized in the following order: MnO_x>NiO_x>ZnO_x>FeO_x>CoO_x>CrO_x>CuO_x. It was also found that the catalytic activity depends on both the gold particle size and the nature of the support.

Griesel and Nieuwenhuys (2001b) subsequently showed that addition of MgO and MnO_x to Au/Al₂O₃ catalysts further improved the CO oxidation activity as well as the selectivity for CO₂ formation in the presence of H₂. The selectivity for the PROX reaction was found to be greater than 90% for temperatures below 100 °C on both catalysts. While the positive effect of MgO was attributed to the stabilization of the nano-Au particles, that of MnO_x was related to its ability to supply active O₂ resulting in higher oxidation activity. Interestingly, the H₂O effects on CO oxidation for two catalysts were radically different; while it had a positive influence on the catalysts containing MgO, it proved to be detrimental for the Au/MnO_x/Al₂O₃ catalyst. The different effect of H₂O for the two catalysts was ascribed to the different CO oxidation mechanisms.

According to Grisel *et al.*'s (2002) study, the second promoter effect was screened over Au/MgO/Al₂O₃ catalysts, which is eligible to oxidize CO selectively in H₂-rich gases at the temperatures relevant to hydrogen fuel cell applications. Addition of MnO_x and FeO_x to Au/MgO/Al₂O₃ further enhances low-temperature CO oxidation with improved CO₂ selectivity. Whereas MnO_x addition improved CO oxidation activity over the entire temperature range of 25-300 °C for all λ of 1, 2 and 4, the effect of FeO_x is most pronounced at low temperatures.

The work conducted by Centeno *et al.* (2006) revealed a sharply catalytic performance in the CO oxidation reaction by elucidating the Ce addition as a promoter over Au/Al₂O₃ catalyst. This effect is due to: (i) the higher dispersion of gold on CeO₂/Al₂O₃ as compared to Al₂O₃ and (ii) a strong promoting effect of ceria in the oxidation of the Au⁰ sites for CO adsorption. This was a further evidence for the fact that the isolated Au⁺ sites were more active in CO oxidation than metallic gold particles.

2.6. Nano-Sized Gold Based Catalyst Preparation Methods

The catalyst preparation method has strong effects on the activity of the catalyst. The chemical and physical properties of a catalyst are determined by the history of the preparation procedure. The catalyst preparation may be considered as combination of several different unit operations each of which has important effect on the properties of the

catalyst produced. Common preparation methods for supported catalysts are multi-step processes consisting of following steps (Kılaz, 1999).

- Distributing a precursor compound over the support surface either by impregnation, ion exchange, precipitation, reaction of organometallic surface cluster compound with functional groups or vapor phase deposition of a precursor compound,
- Drying and calcination of the catalyst,
- Transformation of the precursor compound into the active metallic phase by reduction.

Many preparation methods were employed to obtain high activity and selectivity. Both support properties and active metal type are important in the selection of the preparation method. The most of the catalysts for selective CO oxidation reaction were prepared by co-precipitation, deposition-precipitation or impregnation.

Gold has a much lower melting point (1063 °C) than other Pt group elements (Pd: 1550 °C; Pt: 1769 °C). Moreover the melting point of gold in a highly dispersed state is expected to be as low as 323 °C due to the quantum size effect. Another reason is that chloride ion markedly enhances the coagulation of Au particles during calcination of H₂AuCl₄ crystallites dispersed on the support surfaces. It is therefore difficult to synthesize highly dispersed gold catalysts by the conventional wet-impregnation method. However, some researchers have indicated that a modified wet impregnation method can also be employed for preparing active Au catalysts (Tsai *et. al.*, 2007). Besides modified impregnation method, other synthesis techniques such as deposition-precipitation (DP), co-precipitation (CP) and vapor deposition (VD) can be successfully employed to obtain highly dispersed nano-gold catalysts (Choudhary and Goodman, 2002).

2.6.1. Coprecipitation Method

Among the three techniques, the coprecipitation is the most useful and the simplest way of preparation. An aqueous solution of H₂AuCl₄·4H₂O and water soluble metal salts, most preferably nitrates, is poured into an aqueous alkaline solution under agitation in a

few minutes. After aging for 1 hour, the precipitates is washed with water until the pH of the supernatant reaches a steady value of 7 and then filtered in order to prevent Au nanoparticles from coagulation. The procedure stated above makes the co-precipitation method different from impregnation method in that the catalyst precursor is almost free from Na and Cl ions (Haruta, 2004).

The careful control of the concentration of the metal salts solution in the range of 0.1- 0.4 M/l, with the pH in the range of 7-10, and the temperature in the range of 47-87 °C of the aqueous H₂AuCl₄ solution, enables the selective deposition of Au(OH)₃ only on the surface of the support metal oxides without precipitating in the liquid phase. The applicability of coprecipitation is limited to metal hydroxides or carbonates that can be coprecipitated with Au(OH)₃. Actually, Au can be supported in the form of well-dispersed nanoparticles on α -Fe₂O₃, Co₃O₄, NiO, and ZnO while not on TiO₂, CrO₃, MnO_x, and CdO. In the case of TiO₂, the addition of Mg citrate during or after coprecipitation is necessary to obtain good dispersion of Au nanoparticles, while on the case of MnO₂ precipitation in aqueous LiCO₃ solution leads to better catalytic activity for selective CO oxidation in H₂ stream (Haruta, 2004).

2.6.2. Deposition Precipitation Method

The deposition precipitation method is the easiest to handle and is used for producing commercial Au catalysts. DP has the advantage over CP in that all of the active components remain on the surface of the support and none active gold component is buried within it (Wang *et al.*, 2003). However, some of the gold precursor could be lost during the deposition-precipitation method because the loading is limited upon the properties of support materials while losses are negligible for the coprecipitation method.

The pH of the H₂AuCl₄ solution is adjusted at a fixed point in the range of 6 to 10, and is selected primarily based on the isoelectric point (IEP) of the metal oxide support. The isoelectric point is the pH at which there is no net charge on the surface. The isoelectric point varies for different oxides but the surface charge tendency follows this general form.

As the neutralizer, NaOH or KOH is preferable to Na₂CO₃ or K₂CO₃ regarding hydroxides can adjust the pH of HAuCl₄ solution with smaller amount than carbonates and accordingly bring weaker ionic strength of the solution. With the careful control of the concentration around 10⁻³ M/l, pH, and the temperature in the range of 47-87 °C of the aqueous HAuCl₄ solution, the homogeneous dispersion of Au(OH)₃ on the metal oxide supports is achieved if the specific surface areas are larger than 10 m² g⁻¹ (Haruta, 2004). However the only drawback of DP is the non-applicability to metal oxides, which have the IEPs of below 5, and to activated carbon.

Using urea (CO(NH₂)₂) makes the deposition possible where urea acts as a delay base since there is no reaction when it is dissolved in a suspension of the support in the aqueous metal salt solution at room temperature; hydrolysis only occur when the solution is heated above 60 °C. Deposition precipitation with urea (DPU) is applicable to the same supports as for DP at a fixed pH. DPU also leads to small gold particles, but with a longer precipitation time (at least 4h instead of 1h). However, the DPU has the advantage that all the gold in solution is deposited onto the support; therefore there is no loss of gold in solution, and the loading can be easily controlled.

With this method, the ease of preparation a set of samples with the same gold loading but different particle sizes is obtained by systematically varying the time allowed (Bond *et al.*, 2006).

According to Zanella *et al.* (2002), the aging of the solution for 16 hours leads to a high loading of about 8 wt% of small Au nanoparticles over TiO₂ when homogeneous precipitation using urea as a neutralizer is applied.

2.6.3. Chemical Vapour Deposition Method

In chemical vapor deposition (CVD), a volatile organogold compound reacts with the surface of a support, on which it decomposes to zero-valent particles of gold, or if the support is a flat surface, to a coherent film.

Dimethylgold acetylacetonate is the only compound that has proved suitable for this purpose. Adsorption of its vapour at 33 °C on dried oxides, including silica, mesoporous MCM-41, and carbon supports, gave after calcination small gold particles, but with a broader size distribution than is given by DP. However the preparation must be conducted in the absence of moisture and air. Therefore the catalysts made in CVD must necessarily remain laboratory curiosities, as the method is quite unsuited to manufacture on a large scale (Bond *et. al.*, 2006).

2.6.4. Chemical Direct Anionic Exchange Method

Direct anionic exchange (DAE) is a method that employs the electrostatic forces that exist between the support and the noble metal in solution to create the final material. Unlike deposition-precipitation, where the pH is varied to precipitate the metal in the form of a metal hydroxide on to the support, DAE utilizes charge interactions to bind the metal (gold or platinum) to the opposite charged support.

Inorganic oxides tend to polarize and acquire a surface charge when suspended in an aqueous solution. The degree of the surface charge depends on the isoelectric point of the oxide and the pH of the solution.



Therefore at a pH below the isoelectric point of the support, the support acquires a positive charge and can be used for anionic adsorption (Equation 2.11). Likewise at a pH above the isoelectric point, the support is negatively charged and can be used for cationic adsorption.

3. EXPERIMENTAL WORK

3.1. Materials

3.1.1. Chemicals

The chemicals used in the catalysts are listed in Table 3.1.

Table 3.1. Chemicals used in catalyst preparation

Chemicals	Formula	Grade	Source	Molecular Weight (g mole ⁻¹)
Gold(III) chloride trihydrate	HAuCl ₄ .3H ₂ O	Extra Pure	Aldrich	393.83
Cobalt nitrate hexahydrate	Co(NO ₃) ₂ .6H ₂ O	Extra Pure	Merck	291.04
Mangan(II) nitrate Tetrahydrate	Mn(NO ₃) ₂ .4H ₂ O	Extra Pure	Merck	251.01
Magnesium nitrate Hexahydrate	Mg(NO ₃) ₂ .6H ₂ O	Extra Pure	Merck	256.41
Nickel(II) nitrate hexahydrate	Ni(NO ₃) ₂ .6H ₂ O	Extra Pure	Merck	290.81
Cerium(III) nitrate hexahydrate	Ce(NO ₃) ₂ .6H ₂ O	Extra Pure	Merck	434.23
Iron(III) nitrate nonahydrate	Fe(NO ₃) ₂ .9H ₂ O	Extra Pure	Merck	341.6
Aluminium oxide	Al ₂ O ₃	Extra Pure	ZeochmEU	101.96

3.1.2. Gases and Liquids

The liquids and gases used in this study were listed with their applications and specifications in the Table 3.2 and Table 3.3. All of the gases used in this study were supplied by BOS and HABAŞ Companies, Istanbul, Turkey.

Table 3.2. Applications and specifications of the gases used

Gas	Application	Specification
Carbon monoxide	Reactant, MS calibration	99.0% HABAŞ
Oxygen	Reactant, MS calibration	99.99% BOS
Carbon dioxide	Reactant, MS calibration	99.99% BOS
Hydrogen	Reactant, Reducing agent, MS calibration	99.99% BOS
Helium	Reactant (Inert), MS calibration	99.99% BOS

Table 3.3. Applications and specifications of the liquids used

Liquid	Application	Specification
Water	Reactant, cleaning	Distilled

3.2. The Experimental Set-Up

The experimental systems used in this work can be classified mainly into four groups:

- **Catalyst Preparation System:** The loading of promoters (Mg, Mn, Fe, Ni, Co, Ce) on γ -Al₂O₃ support before the addition of Au was employed by incipient wetness impregnation method, whereas Au was deposited on the composite MO_x/ γ -Al₂O₃ supports by homogeneous deposition precipitation (HDP) method afterwards.
- **Microreactor System:** The catalytic activity of the catalysts for selective CO oxidation reaction was tested in a microreactor system. The system includes mass flow controllers for inlet gases, a liquid pump for water feed, temperature-controlled heated connecting lines and a fixed bed flow reactor in a vertical furnace coupled with a programmable temperature controller.
- **Analysis System:** The quantitative determination of the composition of the feed and product streams is conducted by using mass spectrometer.
- **Catalyst Characterization System:** This group of systems involves ESEM (EDAX), AAS and HRTEM analyses.

The structural analyses of the catalyst samples were carried out at the Boğaziçi University Advanced Technologies R&D Center with Environmental Scanning Electron Microscopy-Backscattered Composition Imaging (ESEM-BCI) and Energy Dispersive X-ray Analysis (EDAX) using a Philips XL30 ESEM-FEG system which has a maximum resolution of 2 nm. The ESEM specimen was dispersed on a copper grid coated with a carbon.

For elemental analysis of the catalysts, Unicam 929 Atomic Absorption Spectrometer was employed regarding to the confirmation of Au metal loading.

The determination of metal particle size and distribution over support was employed by the implementation of HRTEM analyses. Prior to HRTEM analyses, approximately 1 mg of used Au/MgO/ γ -Al₂O₃ catalyst was suspended in 5 ml ethanol and subjected to ultrasonic treatment in a sonicator for 30 min and the resulting suspension put drop-wise

on a standard copper grid coated with a porous carbon film and dried at ambient temperature.

3.2.1. Catalyst Preparation System

For the loading of metal oxides as a promoter over $\gamma\text{-Al}_2\text{O}_3$ support, pore volume impregnation method was implemented. The system used for catalyst preparation is comprised of a Retsch UR1 ultrasonic mixer which provides uniform mixing and contact of the solution with the support, a vacuum pump, a Masterflex computerized-drive peristaltic pump which is used for addition of the solution that will be impregnated, a vacuum flask, a beaker and silicone tubing (Figure 3.1).

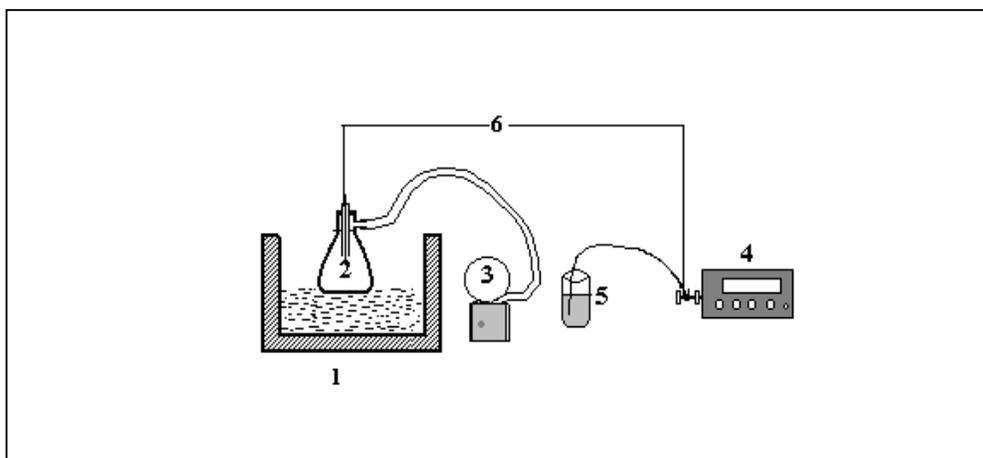


Figure 3.1. The impregnation system: 1. Ultrasonic mixer 2. Vacuum flask
3. Vacuum pump 4. Peristaltic pump 5. Beaker 6. Silicone tubing

The deposition of Au over metal oxide promoted $\text{MO}_x/\gamma\text{-Al}_2\text{O}_3$ support was achieved by the implementation of HDP method. The system used in HDP process consists of a stirrer to achieve homogenous mixing, a heater circulation bath for controlling the temperature of the HDP process, a pH meter for determination of the solution's alkalinity to achieve precise precipitation of the Au over the surface of the support not within it (Figure 3.2).

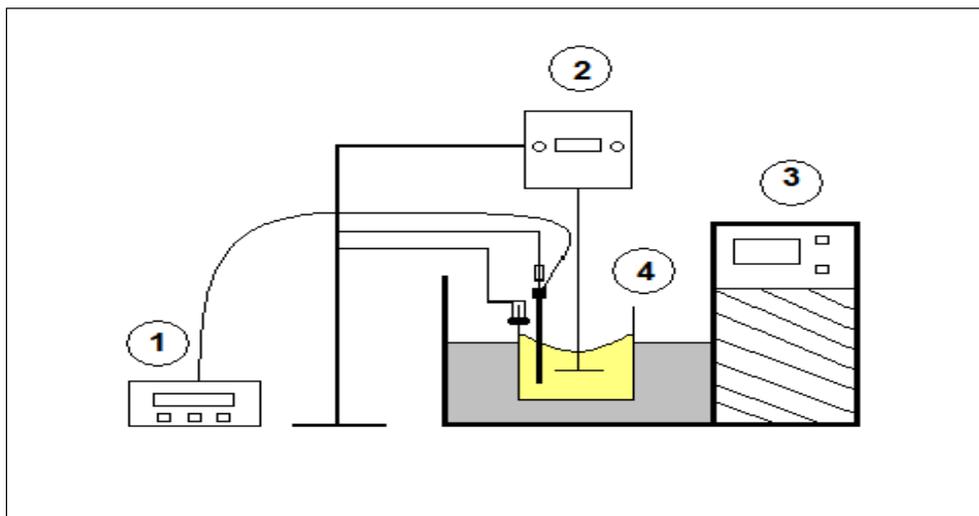


Figure 3.2. The HDP system: 1. pH meter 2. Stirrer 3. Heater circulation bath
4. Beaker

3.2.2. Microflow Reactor System

The research grades of CO, CO₂, He, H₂, O₂ gases from pressurized cylinders were carried by 1/4", 1/8", and 1/16" OD stainless steel and copper tubing with brass and stainless steel fittings. The flow rates of the gases with the optimum pressure of 30 psi were controlled by Brooks 5850E mass flow controllers coupled with 4-Channel Brooks 0154 control panel.

In order to provide homogeneous mixing, the reactant gases were passed through the primary mixing region before the water feed was introduced. In order to achieve evaporation of water, the gas mixture was heated before reaching the water mixing point using 2 m-long Seres heating tape controlled by a 16-gauge wire K-type sheathed thermocouple placed along the heated lines and connected to a Dixel XT110C on/off digital temperature controller. The distilled water was introduced into the heated gas stream via an Agilent 1200 Isocratic HPLC pump.

After humidification of the gas stream, the gas mixture was sent to the reaction segment include a down-flow 4 mm ID× 58.5 cm stainless steel fixed-bed reactor placed in

2.4 cm ID× 50 cm furnace controlled to $0.5\pm$ K with an Eurotherm 2408 programmable temperature controller (Figure 3.3). The K-type sheathed thermocouple was placed at the midst of the catalyst outside the microreactor. The fitting of reactors, which are outside the furnace, are isolated by ceramic wool to prevent heat loss and maintain stable reaction conditions.

The water introduced into the feed and produced during the reaction was separated from the product gases using a cold trap consist of an ice box and coiled tubing, which was used to increase contact time of gases in the trap.

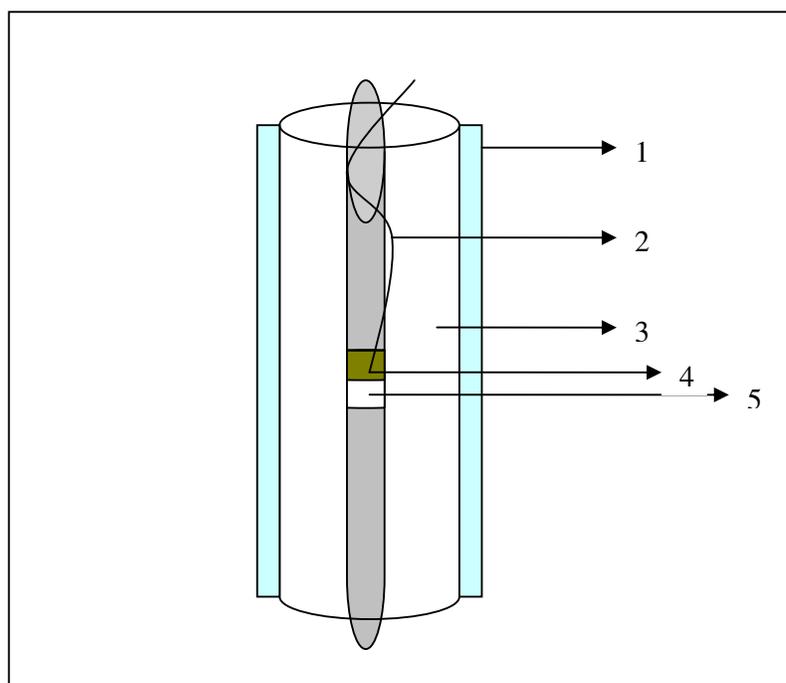


Figure 3.3. Reactor and furnace system: 1.Ceramic wool insulation 2.Thermocouple
3.Furnace 4.Catalyst 5.Catalyst bed

3.2.3. Product Analysis System

After the removal of the H_2O in the reaction stream, the product stream was analyzed using a Hiden Hal 210 mass spectrometer connected to a personal computer and employing MASoft software. The entire microflow reaction system is presented in Figure 3.4

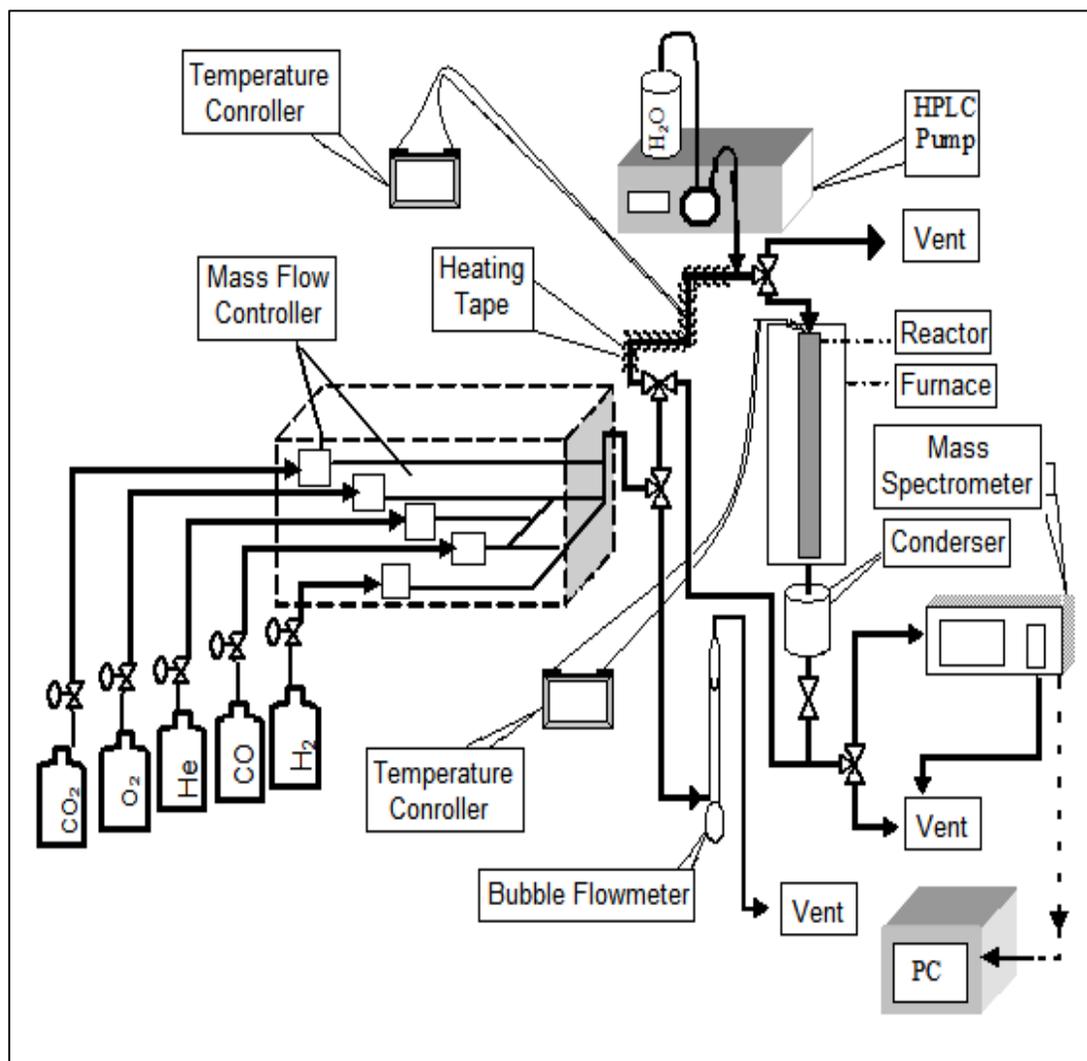


Figure 3.4. The microreactor flow and product analysis system

3.3. Catalyst Preparation

The loading of metal oxide as a promoter to the γ -Al₂O₃ support was achieved by the implementation of incipient to wetness impregnation method. The MO_x/ γ -Al₂O₃ composite support's promoter (Ce, Co, Ni, Mn, Mg, Fe) per cent was selected as 1.25 wt % of the total catalyst weight. The experimental setup shown in Figure 3.1 was utilized in order to load the metal oxides over γ -Al₂O₃ support, whereas the experimental setup shown in Figure 3.2 was used to obtain the nanosized gold particles over MO_x/ γ -Al₂O₃ composite by

applying the homogeneous deposition precipitation method using urea as a precipitating agent.

The procedure had six parts:

- Evacuating the support
- Contacting the support with the precursor solution
- Drying of the slurry obtained
- Calcination of the metal oxide promoted support
- Loading of Au over the composite material by HDP method
- Filtration and drying of the catalyst

The alumina support was crushed and sieved into 45-60 mesh size (344-255 μm). A measured amount of support was placed in a vacuum flask and kept under the vacuum for 30 min to remove the trapped air in the pores. This was accompanied by mixing the catalyst in a Retsch UR 1 ultrasonic mixer.

Before impregnation of the metal oxide solution over $\gamma\text{-Al}_2\text{O}_3$ support, the metal salt was dissolved in 1.21 ml of water per gram of alumina support, which is the amount of water to wet the one gram alumina. A Master flex computerized-drive peristaltic pump was employed to feed the precursor solution of the metal oxide to the vacuum flask at a rate of 0.5 ml/min via silicon tubing. After the addition of metal oxide precursor solution, the slurry was mixed under vacuum for 90 min by the ultrasonic mixer in order to obtain a uniform distribution of the active component. The proceeding step was to dry the slurry in an electrical oven at 80 $^\circ\text{C}$ at least for 16 hours regarding to obtain water free composite support.

In order to convert the salt or hydroxide form of the active components into oxides by reacting with air at high temperature for enhancing the surface and mechanical properties of the catalysts, the calcinations step was employed just before the loading of Au. Metal oxide composite support ($\text{MO}_x/\gamma\text{-Al}_2\text{O}_3$) was calcined in a flow of air at 400 $^\circ\text{C}$ with a heating rate of 5 $^\circ\text{C}/\text{min}$ and kept at this temperature for 120 min.

The addition of 1 wt% Au over $\text{MO}_x/\gamma\text{-Al}_2\text{O}_3$ was achieved by HDP method using urea as precipitating agent, similar to the procedure of Grisel and Nieuwenhuys (2001). Just as the name implies, the gold was precipitated from aqueous solution, at pH 7-8 electrostatic forces that exist between the support and the gold allow for the deposition of the gold.

An aqueous solution of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (Aldrich, 99.9%) was used as Au precursor. 25 ml of an 8.12×10^{-4} M $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (Aldrich, 99.9%) solution was added to the $\text{MO}_x/\gamma\text{-Al}_2\text{O}_3$ support suspending in 80 ml demineralized water. 100 ml solution of an 0.84 M excess urea was added in order to gradually increase pH. The suspension was vigorously stirred and heated to 70 °C in order to gradually decompose the urea. This temperature was maintained until the pH of the solution reached to 7-8 (aged for 4 hours). This procedure was carried out with a minimal exposure to light in order to avoid possible photochemical reactions of the Au precursors. The suspension was then cooled down, suction filtered, washed with de-ionized water and dried overnight at 100 °C.

The $\text{Au}/\gamma\text{-Al}_2\text{O}_3$ catalyst was calcined in a flow O_2 at 300 °C with an increment of 5 °C/min and kept at this temperature for additional 120 min to test the calcinations effect on the performance.

3.4. Catalytic Activity Measurements

All catalysts were reduced before the reaction, and kept under He flow until the reaction test was performed. All Au-based catalysts have the same reduction procedure as given below (Table 3.5).

After reduction at 300 °C, all the catalysts were cooled to the reaction temperature (150 °C) in the flow of 50 ml/min He. After reaching the reaction temperature, helium was trapped within the reactor until the reaction gases were sent to the reactor. In the presence of H_2O and CO_2 in the feed, however, the mixture of reaction gases was vented for 60 min in order to obtain homogeneous reaction stream. The activity tests took place in the microreactor flow system shown in Figure 3.3.

Table 3.4. Reduction program for Au-MO_x/ γ -Al₂O₃ catalyst
(M= Mg, Fe, Mn, Ce, Co, Ni or none)

Segments	Starting and End Temperatures	Segment Gas
First Segment	Heating from 25 °C to 300 °C with a heating rate of 10 °C/min	H ₂ with flow rate of 50 ml/min
Second Segment (Reduction)	Keeping constant at 300 °C for 30 min	H ₂ with flow rate of 50 ml/min
Third Segment	Cooling down to reaction temperature	He with flow rate of 50 ml/min

The temperature programmed reaction (TPR) was applied to investigate the activity of catalyst in the temperature range of 50-150 °C in the absence of H₂O and CO₂, whereas the temperatures range of 80-150 °C was selected in the presence of H₂O and CO₂ to avoid the condensation of water. All experiments were performed at the atmospheric pressure. The data were taken continuously with Hiden Hal 201 mass spectrometer.

Two sets of reaction mixtures were used for catalytic activity test;

- The first set was comprised of 60 ml/min H₂, 38 ml/min He, 1 ml/min CO, and 1 ml/min O₂ in the absence of CO₂ and H₂O.
- The second set consisted of 60 ml/min H₂, 3 ml/min He, 1 ml/min CO, and 1 ml/min O₂, 25 ml/min CO₂, 10 ml/min H₂O.

In addition to the reaction conditions above, the effects of H₂O and CO₂ per cents in the reaction stream on CO conversion and selectivity over Au/MgO/ γ -Al₂O₃ were also studied by changing their flowrates balancing with helium.

The summary of the reaction conditions are given in Table 3.10, the results are presented and discussed in Chapter 4.

Table 3.5. Reaction conditions for catalytic activity test

Parameter	Value
γ -Al ₂ O ₃ Support Particle Size	45-60 mesh size (344-255 μ m)
Catalyst Amount	0,25 g
Reaction Temperature	(For absence of H ₂ O and CO ₂) 50-150 °C (For presence of H ₂ O and CO ₂) 80-150 °C
Reactant Total flow rate	100 ml/min
W/F Ratio	2.5 mg.min/ml

4. RESULTS AND DISCUSSION

4.1. Catalyst Characterization

The Au loading as well as particle size and particle was determined to understand the unique characteristics of Au/MO_x/Al₂O₃ catalysts. For that purpose, Atomic Absorption Spectrometry (AAS), Environmental Scanning Electron Microscopy (ESEM), Energy Dispersive X-Ray Analysis (EDAX), High Resolution Transmission Electron Microscopy (HRTEM) measurements were performed.

4.1.1. Atomic Absorption Spectrometry Analysis

The amount of metal loaded on Au/MO_x/Al₂O₃ catalysts was measured using a Unicam 929 Atomic Absorption Spectrometer, and the results of Au loadings are given in Table 4.1.

Table 4.1. AAS results of Au loading in Au/MO_x/Al₂O₃ catalysts

Catalyst	Intended Au loading (wt %)	Measured Au loading (wt%)
Au/ γ -Al ₂ O ₃	% 1	% 0.354
Au/MgO _x / γ -Al ₂ O ₃	% 1	% 0.360
Au/MnO _x / γ -Al ₂ O ₃	% 1	% 0.557
Au/FeO _x / γ -Al ₂ O ₃	% 1	% 0.675
Au/CeO _x / γ -Al ₂ O ₃	% 1	% 0.761
Au/CoO _x / γ -Al ₂ O ₃	% 1	% 0.643
Au/NiO _x / γ -Al ₂ O ₃	% 1	% 0.449

The difference in the targeted and actual loading may be attributed to the pH of the homogeneous deposition precipitation method being employed. It has been shown that, at the lower pH, Au loading was higher. However the residual chloride is also high at the low pH values making the catalyst less active. This is partially related to the degree of

hydrolysis of Au-Cl bond of the Au complex at different pHs. Although the higher pH generates much more active catalysts, the Au loading is generally less than 1% (Yang *et. al.*, 2005).

4.1.2. ESEM Analysis on Au/MgO/ γ -Al₂O₃

The microstructure, morphology and composition of samples were studied by environmental scanning electron microscopy (ESEM) and energy dispersive X-ray analysis (EDAX).

After the reaction-sample (in the presence of H₂O and CO₂) of Au/MgO/ γ -Al₂O₃ catalyst was analyzed for this purpose. A sample of ESEM micrographs of Au/MgO/ γ -Al₂O₃ are presented in Figure 4.1, and a representative metal oxide contents are tabulated in Table 4.2.

Table 4.2. The result of elements weight per cent in EDAX analyses

Element	Weight per cent (EDAX)
Mg	% 3.30
Al	% 50.51
O	% 42.66
Au	% 3.54

The EDAX data were obtained by focusing on the regions containing highly contrast spots of the Au/MgO/ γ -Al₂O₃ catalyst, shown in Table 4.2, indicating the presence of small intensity broad Au peaks coupling with similar intensity of Mg and higher intensity Al and O peaks. The elemental contents of all the parts of the analyzed particle appeared to be relatively uniform. The results obtained by EDAX confirmed that the Cl⁻ removal achieved by implementation of successful catalyst washing procedure.

ESEM picture of the 1 wt.% Au/MgO/ γ -Al₂O₃ catalyst shows composite particles consisting essentially agglomerations of smaller particles. Although the randomly shaped bright and dark particles were detected, the metal identities couldn't be determined with the magnification of 5000x showing that higher magnification is required to identify the Au particles.

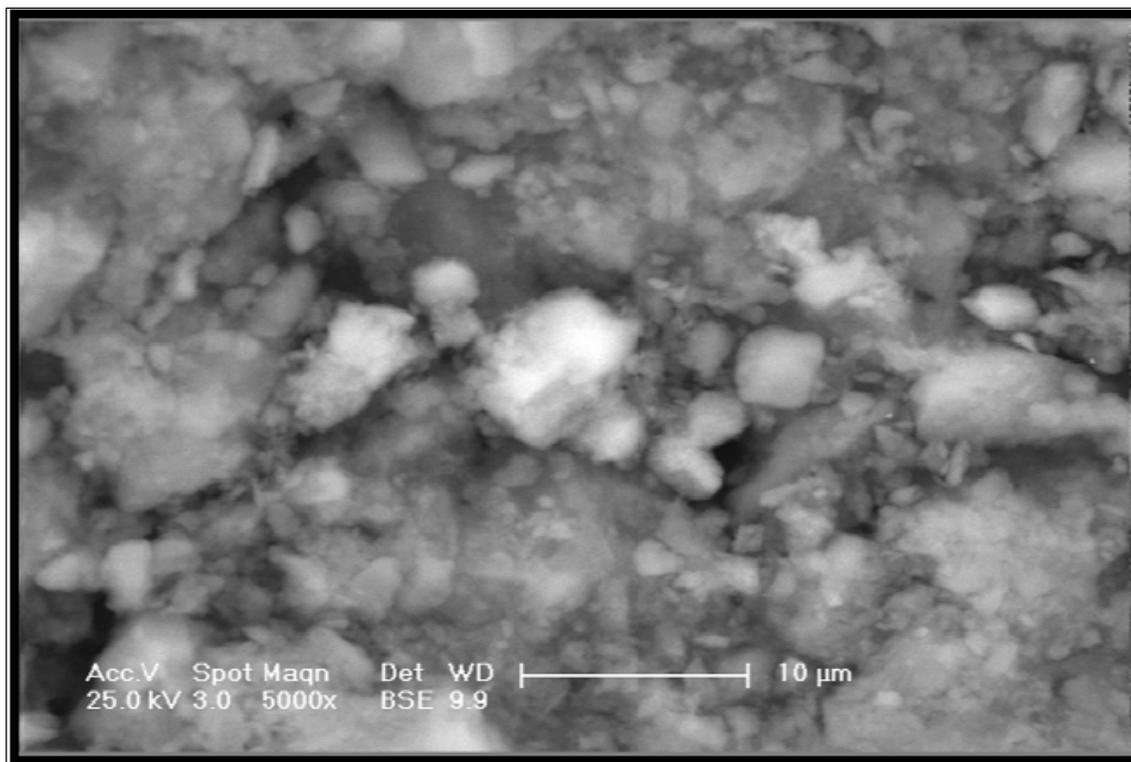


Figure 4.1. ESEM micrograph of 1 wt.% Au/1.25 wt.% MgO/ γ -Al₂O₃ (5000x)

4.1.3. HRTEM Analysis on Au/MgO/ γ -Al₂O₃

Since an atomic level understanding of the structure and electronic properties is required to gain an accurate, fundamental view of catalytic properties (activity, selectivity and durability), the transmission electron microscopy (TEM) analysis over after-reaction sample (in the presence of H₂O and CO₂) of Au/MgO/ γ -Al₂O₃ catalyst was performed. A typical HRTEM image of the gold particles of Au/MgO/ γ -Al₂O₃ catalyst is shown in Figure 4.2.

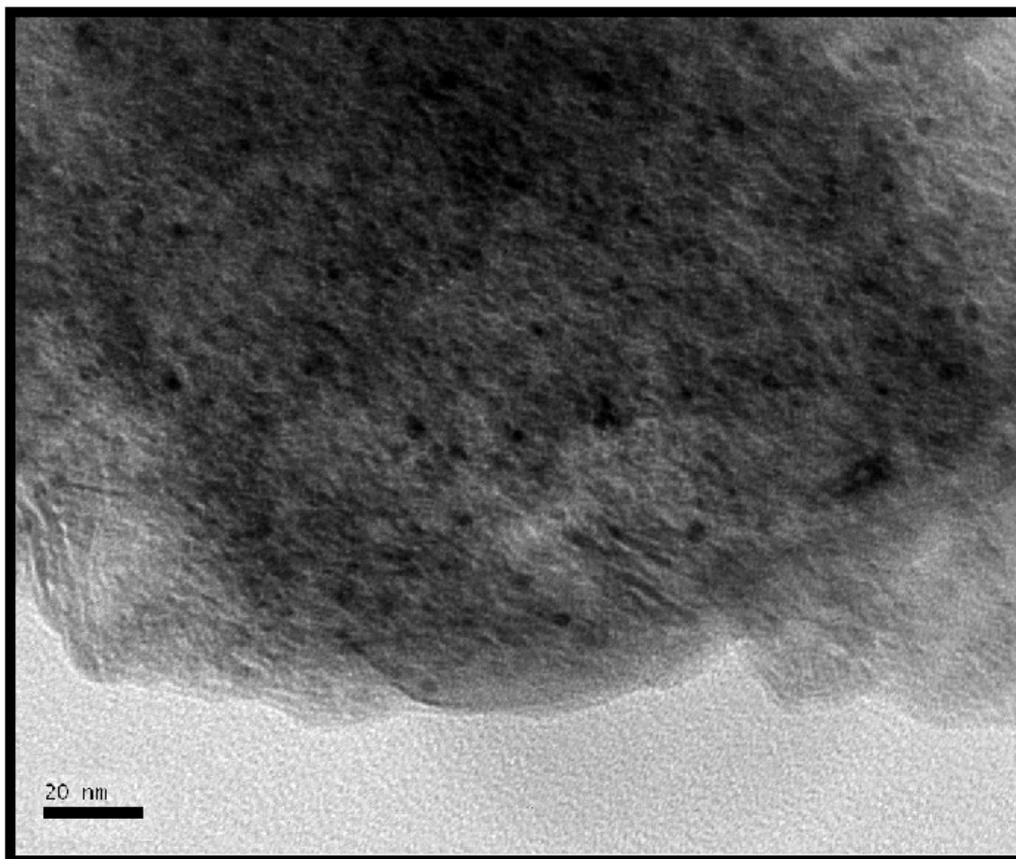


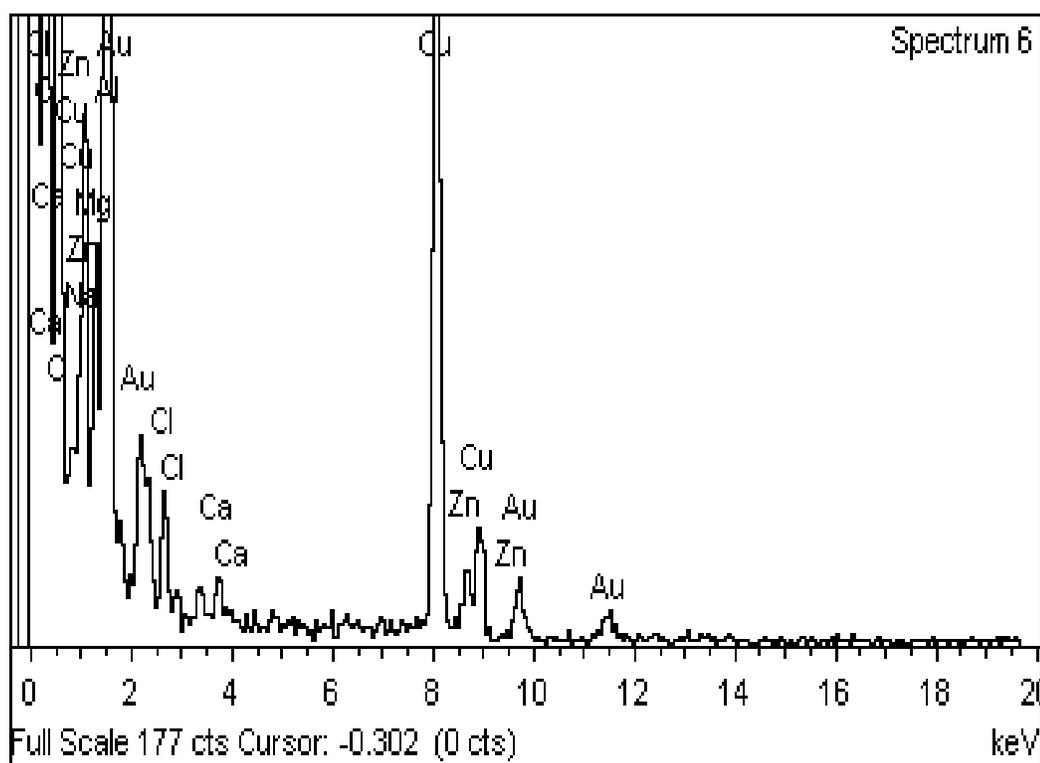
Figure 4.2. HRTEM micrograph of 1 wt.% Au/1.25 wt.% MgO/ γ -Al₂O₃

The gold particles (the dark spherical spots) are fairly homogeneously distributed over the alumina support (grey regions). They were small (less than 5 nm) and generally well separated from one another. However, in some points Au particles appear to be more aggregated as denoted by the presence of well defined and intense dark zones. The gold particles shown in this picture were representative of the majority of the particles present. The results unambiguously show that this catalyst contains 2-5 nm size gold particles.

The results of the representative EDAX analysis of the sample presented in Figure 4.2 are tabulated in Table 4.2, and the related spectrum is presented in Figure 4.3. The EDAX analysis of the used sample was also confirmed that the dark spherical points on the micrograph were denoted as the Au. Some impurities (Ca, Cl, Zn) were also detected in the large spectrum peak of Au and Mg (Figure 4.3).

Table 4.3. The result of elements weight per cent in EDAX analyses

Element	Weight per cent (EDS)
O	% 45.40
Al	% 45.09
Mg	% 1.71
Au	% 3.03
Impurities	% 4.78

Figure 4.3. EDAX results of used sample of 1 wt.% Au/1.25 wt.% MgO/ γ -Al₂O₃

4.2. Preferential Carbon Monoxide Oxidation

In this section of the thesis, the results of a comparative study of catalytic performance of Au/MO_x/Al₂O₃ catalysts (M= Mn, Mg, Fe, Ni, Co, Ce) for selective CO oxidation are presented. The effects of various parameters (such as calcination and reduction conditions, promoter type, promoter weight per cent, CO₂ and H₂O per cent in the reaction feed) on CO conversion and selectivity were studied. The conversion (X_{CO}), and the selectivity towards CO oxidation (S_{CO}) are defined as follows:

$$\text{CO conversion (\%)} = \frac{[\text{CO}]_{\text{in}} - [\text{CO}]_{\text{out}}}{[\text{CO}]_{\text{in}}} \times 100 \quad (4.1)$$

$$\text{O}_2 \text{ conversion (\%)} = \frac{[\text{O}_2]_{\text{in}} - [\text{O}_2]_{\text{out}}}{[\text{O}_2]_{\text{in}}} \times 100 \quad (4.2)$$

$$\text{Selectivity Towards CO (\%)} = \frac{0.5 \times ([\text{CO}]_{\text{in}} - [\text{CO}]_{\text{out}})}{[\text{O}_2]_{\text{in}} - [\text{O}_2]_{\text{out}}} \times 100 \quad (4.3)$$

The amount of liquid water used in the experiments was calculated as:

$$V_{\text{Steam}(H_2O)} = \frac{V_{\text{Liquid}(H_2O)} \times \rho_{H_2O} \times R \times T}{MW_{H_2O} \times P} \quad (4.4)$$

Where $\rho=1000 \text{ g.L}^{-1}$; $P=1 \text{ atm}$; $R=0.082 \text{ L.atm.mol}^{-1}.\text{K}^{-1}$; $T=298 \text{ K}$ and $W_{H_2O}=18 \text{ g.mol}^{-1}$.

The composition of the reactor outlet stream was continuously measured and the data taken in every 5 °C gradient were used for the conversions and selectivity calculations. The results for all the reaction conditions are given in the following sections.

The experimental error was determined by individually testing the same catalyst twice with the same reaction conditions. The Au/ γ -Al₂O₃ catalyst (reduced in 4 vol.% H₂ in balance He) was tested in this manner and the results tabulated in Table 4.4.

Table 4.4. The experimental error determination of Au/ γ -Al₂O₃

Temperature (°C)	First test of Au/ γ -Al ₂ O ₃	Second test of Au/ γ -Al ₂ O ₃	Error (%)
150	27.45	27.89	1.57
145	32.32	32.59	0.83
140	34.58	34.84	0.75
135	37.49	37.61	0.32
130	41.64	41.09	1.32
125	44.66	44.65	0.02
120	47.48	47.50	0.04
115	50.67	50.43	0.47
110	54.16	54.82	1.20
105	58.06	58.01	0.08
100	61.48	61.05	0.70
95	64.93	65.13	0.30
90	68.03	68.35	0.47
85	72.52	71.81	0.98
80	76.32	76.61	0.38
75	80.15	80.47	0.39
70	83.96	83.68	0.33
65	87.73	87.67	0.07
60	90.96	90.98	0.02
55	92.81	93.78	1.03
50	91.24	92.72	1.59

4.2.1 Selective CO Oxidation in the Absence of CO₂ & H₂O

4.2.1.1. Effects of Calcination and Reduction Conditions on the Catalytic Activity. The first study was conducted in order to determine the effect of calcination and reduction conditions over CO conversion. For that purpose 1wt.% Au/ γ -Al₂O₃ catalyst was selected as the target of interest. The reactions were carried out in the temperature range of 150-50 °C using a feed stream composition of 1% CO, 1% O₂, 60% H₂, and He in balance (in the absence of CO₂ and water).

Prior to the reaction, the both calcined and uncalcined catalyst were reduced in hydrogen environment to illustrate the calcination effect on the CO conversion since the previous activity measurements and FTIR studies indicated that reduced Au-based catalysts were superior to oxidized ones in low-temperature CO oxidation. The results are presented in Table 4.5 and summarized in Figure 4.4.

It is clear from the comparison of the results obtained over the calcined and uncalcined catalysts that the calcination treatment of Au/ γ -Al₂O₃ catalyst suppressed CO oxidation. Since the small Au particles (1-6 nm) are beneficial for low temperature CO oxidation, the observed decrease in activity is probably due to sintering effect.

The study conducted by Grisel and Niewenhuys (2001) is consistent with our results by illustrating the detrimental effect of calcination treatment. In their study, the effect of calcination and reduction over CO oxidation was compared in terms of the lowest temperature for 99% CO conversion ($T_{99\%}$), which was found as 151 °C for the reduced catalyst whereas 213 °C temperature was monitored for calcined one.

In addition, Gluhoi *et al.* (2006) also reported that the catalytic behavior of Au/ γ -Al₂O₃ catalyst mainly depended on the treatment procedure being employed prior to reaction. In order to illustrate the calcination effect on catalytic activity of Au/ γ -Al₂O₃ towards CO oxidation, various temperatures (150, 200, 300 or 500 °C) in calcination treatment were employed. The calcination at 200 °C without any additional treatment results in the highest activity among the calcined Au/ γ -Al₂O₃ catalyst. Less active catalysts

were obtained following calcinations at 500 °C (due to the some sintering), or at 150 °C (most likely due to incomplete reduction of Au³⁺ to Au⁰).

After implementation of only H₂ treatment over Au/ γ -Al₂O₃ catalyst at different temperatures (150, 200, 300, 500 °C), it was concluded that the most active treatment prior to reaction was the implementation of H₂ reduction at 200 °C.

Table 4.5. CO conversion of 1wt.%Au/ γ -Al₂O₃ at different treatments prior to reaction

Temperature (°C)	CO Conversion (%)		
	With calcination, reduced in pure H ₂	Without calcination, reduced in 4 vol.% H ₂ in He balance	Without calcination, reduced in pure H ₂
150	24.25	27.89	33.82
140	33.97	34.84	39.60
130	39.21	41.09	46.07
120	43.46	47.50	51.66
110	49.28	54.82	58.69
100	53.76	61.05	64.83
90	59.56	68.35	72.44
80	65.08	76.61	79.78
70	69.95	83.68	86.92
60	72.67	90.98	93.60
50	65.05	92.72	97.90

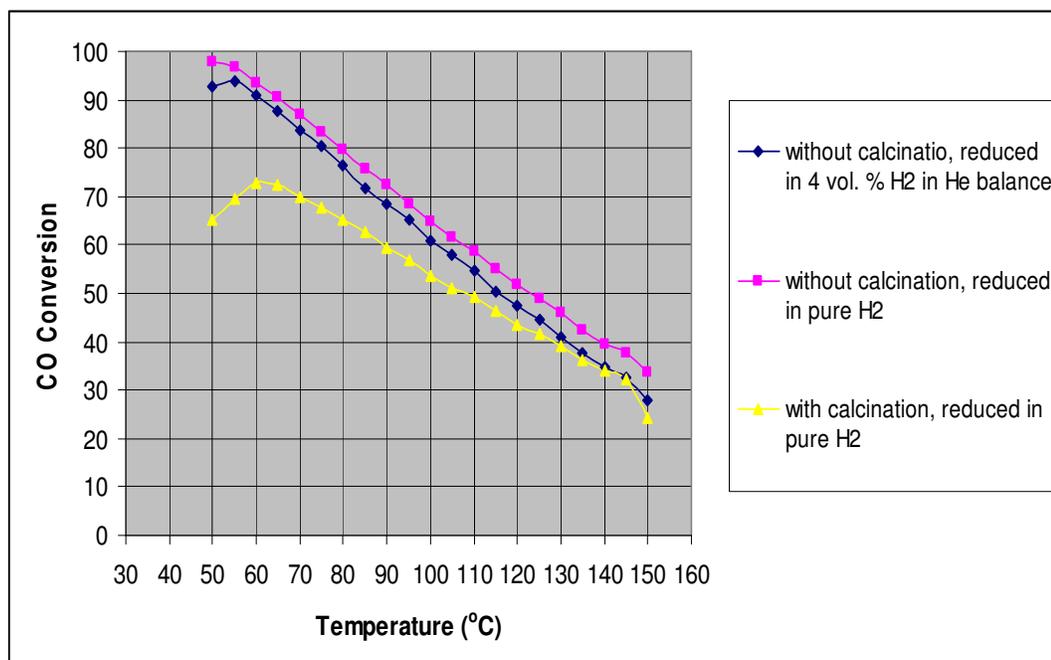


Figure 4.4. The effect of calcination and reduction of 1 wt. %Au/ γ -Al₂O₃ catalyst on CO oxidation

After determination of calcination's detrimental effect, the reduction conditions were also studied by changing the reduction environment. In order to elucidate the reduction effect, 2 different reduction conditions were employed. As illustrated in Figure 4.4, the effect of reduction in pure H₂ was concluded to be superior over reduction in 4 vol.% H₂ in He balance in all temperatures observed. Hence only the reduction in pure H₂ was employed as pretreatment for the rest of the experiments.

4.2.1.2. Effect of Promoters (Fe, Ni, Co, Ce, Mg, Mn) on Catalytic Activity In order to determine the effect of promoter type on the catalytic activity, 6 metal oxide promoters were tested. The promoter amount was kept constant at 1.25wt% of the total catalyst weight in all experiments. The reactions were carried out in the temperature between 50-150 °C using a feed stream composition of 1% CO, 1% O₂, 60% H₂, and He in balance.

The pure MO_x/ γ -Al₂O₃ catalysts are not very active in low-temperature CO oxidation. No significant CO conversion was found in the literature below 150 °C. The CO conversion activity of the alumina-supported metal oxides decreases in the order of:

$\text{CoO}_x > \text{FeO}_x > \text{MnO}_x > \text{NiO}_x > \text{CrO}_x \gg \text{MgO}$ and ZnO . The addition of MO_x to $\text{Au}/\gamma\text{-Al}_2\text{O}_3$ greatly influences the CO conversion in the low temperature region. Since none of the selected MO_x alone was found to be active at low temperatures (Grisel *et. al.*, 2002).

Generally, the CO conversion over supported Au catalysts (Grisel *et. al.*, 2001; Grisel *et. al.*, 2002) was reported to decrease when H_2 is introduced into the reaction mixture, even though some exceptions exist, like $\text{Au}/\text{MgO}/\text{Al}_2\text{O}_3$.

On the other hand, the beneficial effects of H_2 (mostly related to the prevention of deactivation and regeneration) on the CO oxidation over gold catalyst was also reported. For instance, Costello and co-workers have demonstrated that while the activity of $\text{Au}/\text{Al}_2\text{O}_3$ catalyst declined rapidly with the time on stream in CO oxidation, the presence of hydrogen during selective CO oxidation successfully prevented deactivation. They also showed that a deactivated $\text{Au}/\text{Al}_2\text{O}_3$ catalyst (after reaction in CO oxidation) could be regenerated by exposure to H_2 (or water vapor) at room temperature.

These results suggest that the active sites probably contain hydroxyl groups, which can be removed by CO oxidation. These hydroxyl groups would participate in the reaction, possibly by reaction with CO, forming an active intermediate in the CO_2 production pathway. Deactivation during CO oxidation would then be due to the depletion of the hydroxylated active sites when the reaction intermediate transforms into a stable surface species. These surface species, possibly surface carbonates, can be removed by reaction with hydrogen to regenerate the hydroxyl groups (Costello *et. al.*, 2002; Cameron *et al.*, 2003).

Thus it seems obvious that, in the presence of H_2 , two phenomena should occur simultaneously. One of these, which have a negative effect on CO oxidation, would be a competition of adsorption between H_2 and CO. The other one, which has a beneficial effect on CO oxidation, would be the appearance of additional reactive intermediates produced in the presence of H_2 (Rossignol *et. al.*, 2005).

However the hydrogen is the primary component in the feed stream for the fuel cell application and it should be in the feed stream regardless of its positive and negative effects. Hence the effects of the promoters (and the other parameters) were studied only in the presence of a realistic amount of hydrogen in the feed.

The first study was the examination of Au/FeO_x/γ-Al₂O₃ catalyst regarding catalytic activity in gradient temperatures. CO conversions at different temperatures are presented in Table 4.6 and Figure 4.5. The addition of FeO_x on Au/γ-Al₂O₃ as a promoter exhibited detrimental effect over CO conversion in all temperatures studied. The maximum conversion was reached at 50 °C (the lowest temperature tested) for both Au/FeO_x/γ-Al₂O₃ and Au/γ-Al₂O₃ catalysts. About 97% CO conversion was obtained for Au/γ-Al₂O₃ catalyst at 50 °C compare to the 84% in Au/FeO_x/γ-Al₂O₃.

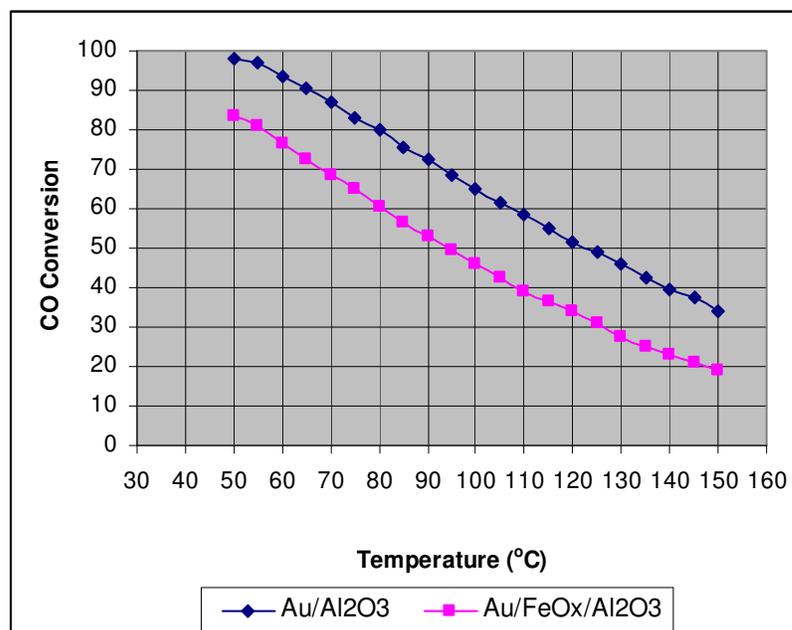
The possible explanation of the activity decrease by the addition of FeO_x is attributed to the H₂ rich environment, in where the Au/FeO_x/γ-Al₂O₃ catalytic activity towards H₂ oxidation exceeds the one of CO oxidation.

However, according to the study of Grisel *et. al.*, (2002), FeO_x addition as a second promoter over Au/MgO/Al₂O₃ catalyst improved the CO conversion activity in H₂ rich gas (70 vol%) at low temperatures.

The presence of MO_x typically reduced the hysteresis effect, especially for FeO_x. The same positive catalytic activity improvement was also observed by the implementation of the FeO_x as a first promoter on Au/γ-Al₂O₃ catalyst in Wang *et. al.*, (2002) study, in where the reaction feed balance in the absence of H₂ was selected as CO: 0.5%, O₂: 21.1, N₂.

Table 4.6. CO conversion and selectivity results for 1 wt.%Au/1.25 wt %FeO_x/γ-Al₂O₃

Temperature (°C)	CO Conversion (%)	O ₂ Conversion (%)	Selectivity (%)
150	19.03	99.68	9.55
140	22.82	99.92	11.42
130	27.42	100.00	13.71
120	33.90	99.43	17.05
110	39.25	99.90	19.64
100	46.15	99.62	23.16
90	53.08	100.00	26.54
80	60.52	99.77	30.33
70	68.27	99.88	34.18
60	76.57	99.84	38.35
50	83.66	98.36	42.53

Figure 4.5. CO conversion comparison for 1 wt.%Au/1.25 wt.%FeO_x/γ-Al₂O₃ and 1 wt.%Au/γ-Al₂O₃

Secondly, the effect of Ni promoter over CO conversion was investigated in gradient reaction temperatures. There are limited researches in the literature regarding the used of Ni as a promoter in selective CO oxidation reaction. Table 4.7 illustrates the performance of Ni promoted Au/ γ -Al₂O₃ catalyst on preferential CO oxidation reaction in the temperature range of 50-150 °C.

Table 4.7. CO conversion and selectivity results for 1 wt.%Au/1.25 wt.%NiO_x/ γ -Al₂O₃

Temperature (°C)	CO Conversion (%)	O ₂ Conversion (%)	Selectivity (%)
150	19.59	99.85	9.81
140	22.08	100	11.04
130	26.76	99.85	13.40
120	34.28	99.70	17.19
110	40.32	99.99	20.16
100	47.65	100	23.83
90	56.15	99.46	28.23
80	64.33	99.44	32.35
70	72.79	99.77	36.48
60	82.84	99.52	41.62
50	80.33	84.48	47.54

Likewise Au/FeO_x/ γ -Al₂O₃ catalyst, the decrease in reaction temperature has exhibited positive effect on CO conversion for Au/NiO_x/ γ -Al₂O₃. Although nearly 84% CO conversion was obtained at 55 °C, the Ni promoter effect over CO conversion was still detrimental since the conversion in the absence of any promoter was higher (Figure 4.5).

Moreover the activity (both in terms of CO and O₂) declined sharply from 55 °C to 50 °C as a different behavior from unpromoted and Fe-promoted Au/Al₂O₃. This suggests that Ni might have blocked the active sides that needed for the CO oxidation and further

accelerates the activity lost below 55 °C compare to the results obtained for unpromoted one.

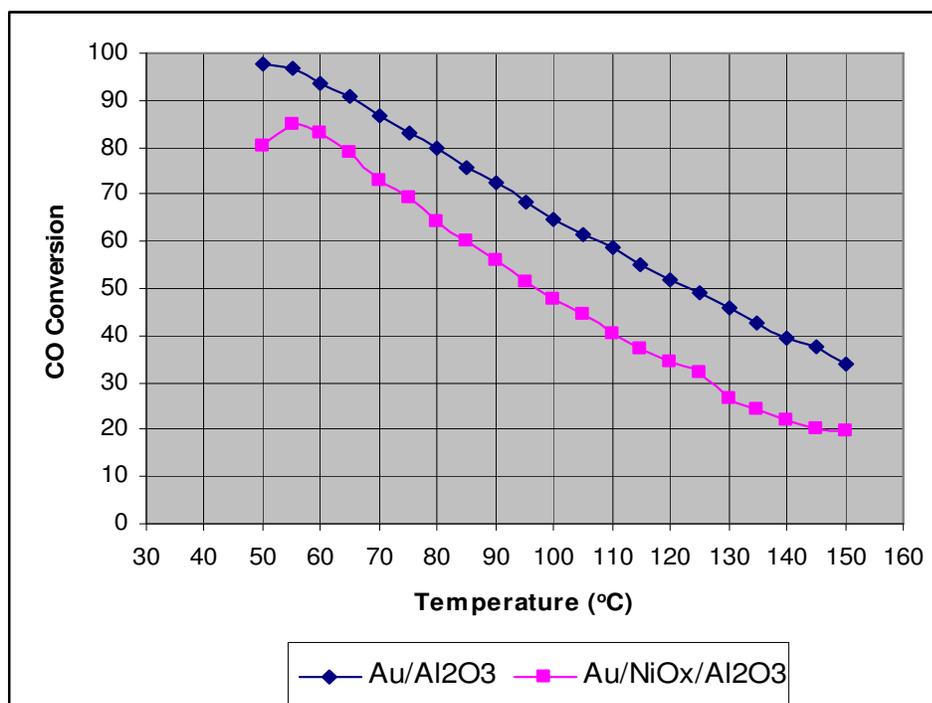


Figure 4.6. CO conversion comparison for 1 wt.%Au/1.25 wt.%NiO_x/γ-Al₂O₃ and 1 wt.%Au/γ-Al₂O₃

The addition of alkali metal ions to noble metal can affect the CO and O₂ adsorption properties significantly. The effect of alkaline metal is strongly related to the basicity strength of alkali metal ions (Minemura *et. al.*, 2006).

As shown in Figure 4.7, the addition of Ce to the alumina supported gold catalyst exhibited negative effect on the catalytic activity in the CO oxidation reaction in hydrogen-rich stream with the maximum CO conversion of 87% at 50 °C. Despite the activity lost in CO conversion, Au/CeO_x/γ-Al₂O₃ didn't show any sign of slowdown in catalytic activity below 55 °C, as Ni promoted (even unpromoted Au/γ-Al₂O₃) exhibited.

This property may be attributed to the fact that Ce promoter might be improved the thermal stability of noble metals. All results of this experiment show that addition of ceria stabilizes a more oxidized state.

Table 4.8. CO conversion and selectivity results for 1 wt.%Au/1.25 wt.%CeO_x/γ-Al₂O₃

Temperature (°C)	CO Conversion (%)	O ₂ Conversion (%)	Selectivity (%)
150	24.75	100	12.38
140	30.13	99.58	15.13
130	34.22	99.79	17.15
120	40.47	99.92	20.25
110	46.60	99.89	23.33
100	53.08	100	26.54
90	59.44	99.93	29.74
80	66.75	100	33.38
70	73.14	99.87	36.62
60	80.18	100	40.09
50	86.58	99.77	43.39

Due to a facile redox reaction cycle, ceria exhibits oxygen storage capacity and improves the CO and hydrocarbon oxidation.

According to Ko *et. al.*, (2006), addition of ceria enhances the catalytic activity significantly at low temperatures compare to Au/γ-Al₂O₃ in the reaction feed of just 10 vol.% H₂ with the maximum CO conversion of 90%. In their study, reduced Au/CeO_x/γ-Al₂O₃ catalyst exhibited Au⁰-CO band intensely, compare to Au/γ-Al₂O₃ in FTIR spectra (indicating a deeper auto-reduction of gold). Evidently, the stabilization of cationic gold is due to the presence of Ce. The possible explanation of the catalytic activity improvement in Ko et al.'s study may be the addition of 10 wt.% Ce loading in contrast to our 1.25 wt.%, which is not sufficient to enhance the catalytic activity of Au/γ-Al₂O₃.

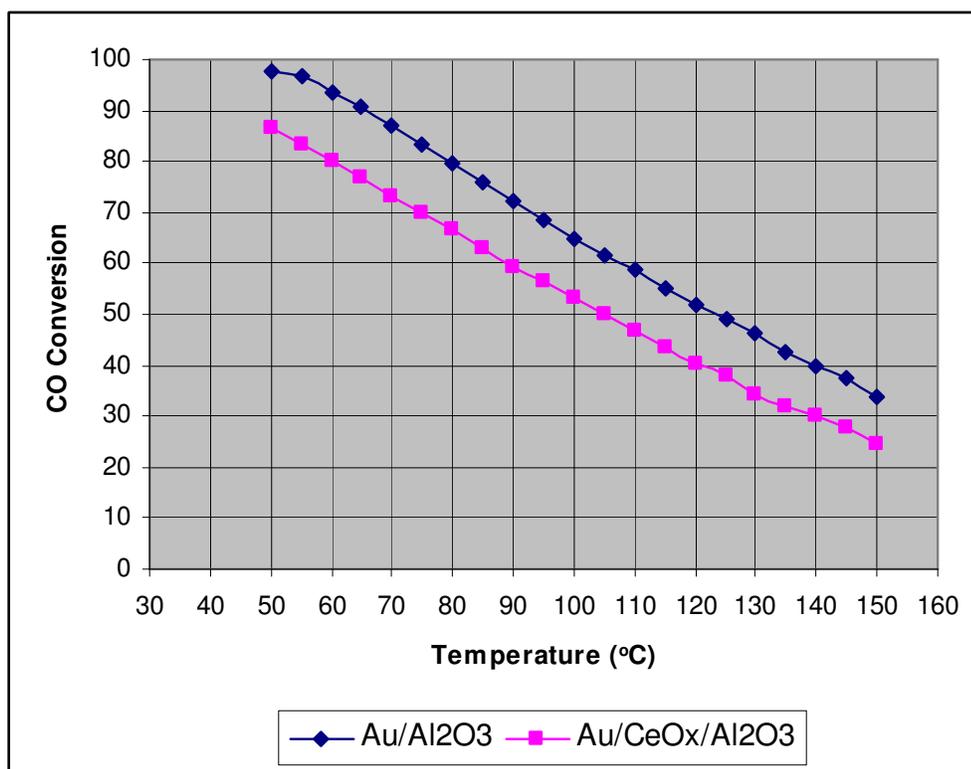


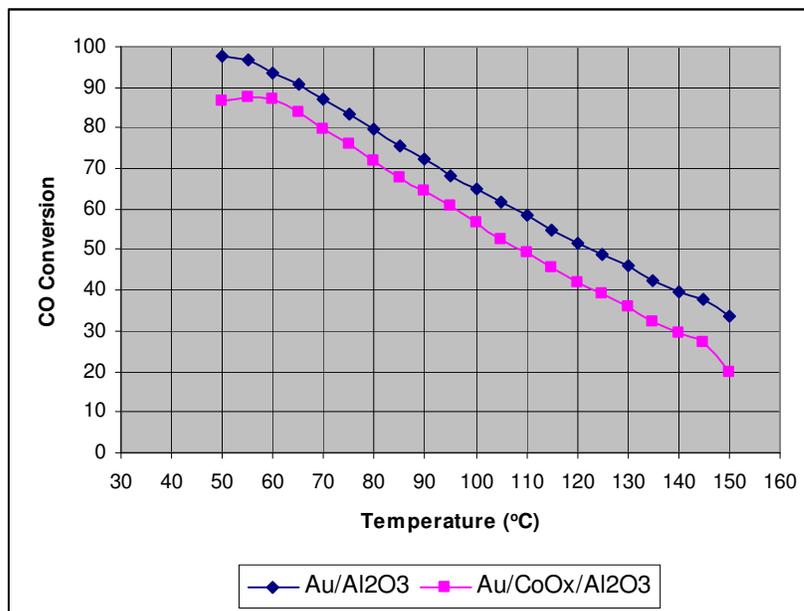
Figure 4.7. CO conversion comparison for 1 wt.%Au/1.25 wt %CeO_x/γ-Al₂O₃ and 1 wt.%Au/γ-Al₂O₃

The addition of Co as a promoter to Au/γ-Al₂O₃ showed detrimental effect on catalytic activity of CO oxidation. As it is illustrated in Table 4.9 and Figure 4.8, the maximum conversion of nearly 88% was obtained at 55 °C in the hydrogen-rich reaction environment for Au/CoO_x/γ-Al₂O₃.

Like Ce, Fe, Ni containing catalysts, the temperature decline has positive effect on CO oxidation for Au/CoO_x/γ-Al₂O₃ catalyst. However, the CO conversion stated to decline below 55 °C as it was observed over the Ni promoted catalyst. On the other hand, the study of Wang *et. al.*, (2003), which used the absence of H₂ feed as the reaction environment, contradicted with our results. In their study, the addition of Co over Au/γ-Al₂O₃ as a promoter exhibited the second most active catalyst (illustrating the 100% CO conversion at 290 °C) among the MO_x promoted ones with the reaction feed of 0.5% CO, 21.1% O₂, and 78.4% N₂.

Table 4.9. CO conversion and selectivity results for 1 wt.%Au/1.25wt.%CoO_x/γ-Al₂O₃

Temperature (°C)	CO Conversion (%)	O ₂ Conversion (%)	Selectivity (%)
150	19.65	99.12	9.91
140	29.34	99.85	14.69
130	36.11	99.36	18.17
120	42.14	100	21.07
110	49.14	100	24.57
100	56.66	100	28.33
90	64.33	99.90	32.20
80	71.83	100	35.92
70	79.57	100	39.79
60	87.06	97.90	44.46
50	86.76	91.21	47.56

Figure 4.8. CO conversion comparison for 1 wt.%Au/1.25 wt.%CoO_x/γ-Al₂O₃ and 1 wt.%Au/γ-Al₂O₃

Unlike to Ni, Ce, Co, Fe promoted Au/ γ -Al₂O₃ catalysts, the addition of MgO as a promoter to Au/ γ -Al₂O₃ demonstrated no significant change in the CO oxidation activity and selectivity towards CO, compare to the unpromoted Au/ γ -Al₂O₃, in almost all temperature tested (Table 4.10 Figure 4.9).

However these results are slightly different with the results of Grisel and Nieuwenhuys (2001). In their study, the beneficial effect of MgO was observed and its influence on the CO conversion was ascribed to the stabilization of small Au particles, which were intrinsically more active in CO than H₂ oxidation. In addition, also MgO prevented small Au particles on γ -Al₂O₃ from sintering to a certain extent up to 300 °C.

Table 4.10. CO conversion and selectivity results for 1 wt.%Au/1.25 wt.%MgO/ γ -Al₂O₃

Temperature (°C)	CO Conversion (%)	O ₂ Conversion (%)	Selectivity (%)
150	29.72	99.98	14.86
140	33.77	99.67	16.94
130	43.02	99.88	21.54
120	50.47	99.81	25.28
110	57.20	100	28.60
100	65.25	99.84	32.68
90	72.47	100	36.24
80	80.75	100	40.38
70	87.36	99.76	43.79
60	93.71	100	46.86
50	97.81	100	48.91

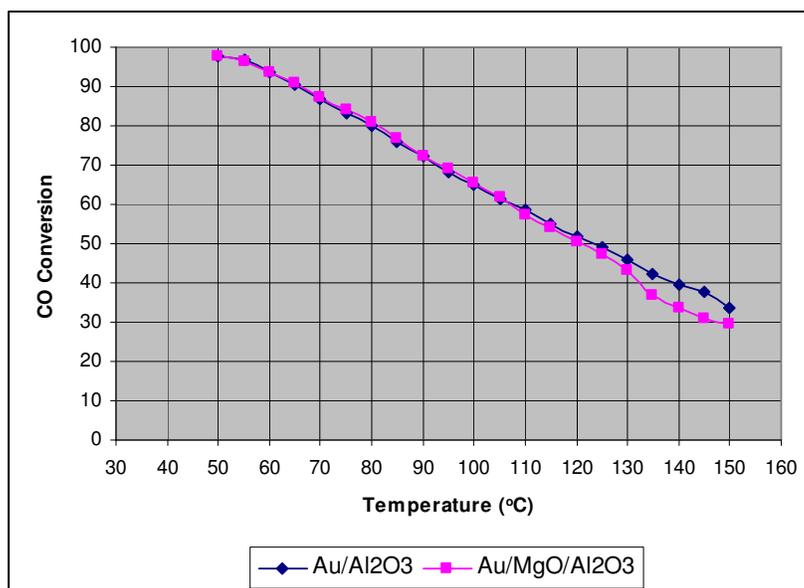


Figure 4.9. CO conversion comparison for 1 wt.%Au/1.25 wt.%MgO/ γ -Al₂O₃ and 1 wt.%Au/ γ -Al₂O₃

Figure 4.9 shows the conversion of CO over Au/MgO/ γ -Al₂O₃ catalyst when H₂ is present in the reactant flow. At low temperatures, relatively high CO conversions were obtained (nearly 98% at 50 °C). In addition, the hydrogen oxidation on this multi-component catalyst suppressed, leading to an overall increase of the selectivity towards CO in the temperature range relevant for the fuel cell applications (70 °C). However, at higher temperatures the CO conversion decreased, whereas the H₂ conversion increased.

The addition of Mn promoter demonstrated some slight superiority over the unpromoted one. Our results demonstrated maximum CO conversion of nearly 99% for Au/MnO_x/ γ -Al₂O₃ catalyst at 50 °C (Table 4.11 and Figure 4.10). At temperatures above 50 °C the surface coverage of CO becomes so low that it no longer poisons H₂ oxidation. This transition stage is marked by a decrease in E_a for H₂ oxidation and initiates an accelerated O consumption by H₂ at the expense of CO₂ formation, and so lowering S_{CO}.

The enhancement in CO oxidation activity by the addition of Mn is larger than expected from the presence of small Au particles alone. According to the results obtained by Grisel *et. al.*, (2002), the Au/MnO_x/ γ -Al₂O₃ catalyst with an average particle size of

4.2 nm had a $T_{95\%}$ that was 100 degrees lower than that found for Au/ γ -Al₂O₃ with an average particle size of 3.6 nm.

Table 4.11. CO conversion and selectivity results for 1 wt.%Au/1.25 wt.%MnO_x/ γ -Al₂O₃

Temperature (°C)	CO Conversion (%)	O ₂ Conversion (%)	Selectivity (%)
150	30.90	99.92	15.46
140	40.30	99.93	20.16
130	45.78	99.70	22.96
120	53.31	99.64	26.75
110	59.69	99.33	30.05
100	67.35	99.01	34.01
90	75.22	99.60	37.76
80	82.11	99.82	41.13
70	88.73	99.99	44.37
60	94.85	99.35	47.74
50	98.65	99.95	49.35

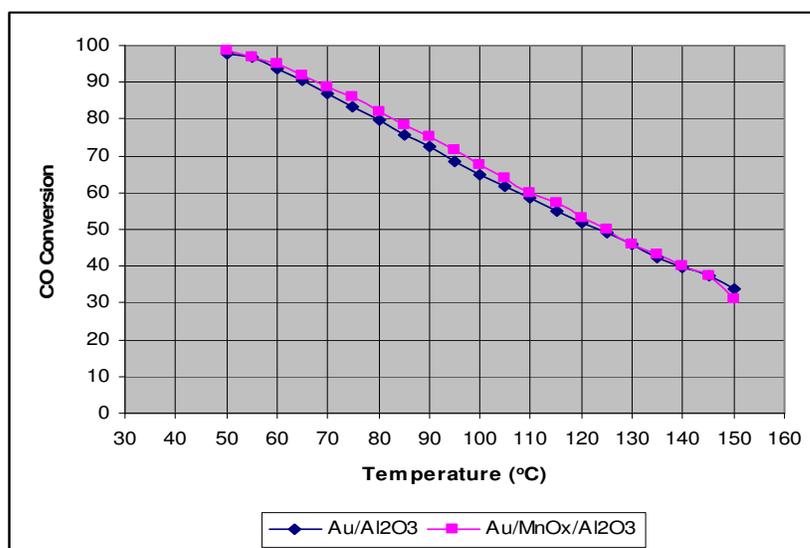


Figure 4.10. CO conversion comparison for 1 wt.%Au/1.25 wt.%MnO_x/ γ -Al₂O₃ and 1 wt.%Au/ γ -Al₂O₃

Based on the highest CO conversion obtained in the temperatures between 50-150 °C, it can be concluded that the order of the catalysts in CO oxidation activity is Au/MnO_x/γ-Al₂O₃ > Au/MgO_x/γ-Al₂O₃ = Au/γ-Al₂O₃ > Au/CoO_x/γ-Al₂O₃, Au/CeO_x/γ-Al₂O₃ > Au/FeO_x/γ-Al₂O₃ > Au/NiO_x/γ-Al₂O₃ (Figure 4.11.).

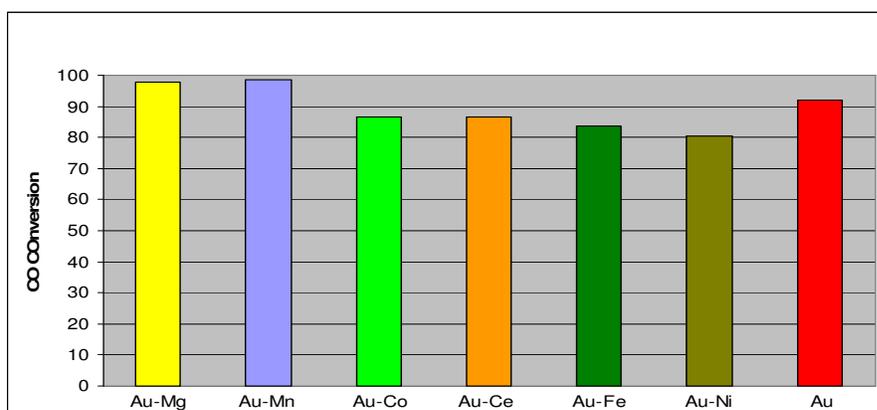


Figure 4.11. CO conversion comparison for 1 wt.%Au/1.25 wt.%MO_x/γ-Al₂O₃ (M = Mg,Mn, Fe, Co, Ce, Ni) and 1 wt.%Au/γ-Al₂O₃

4.2.2. Selective CO Oxidation in the Presence of CO₂ and H₂O

The composition of the reformate gas after the water gas shift reactor is approximately 40–60%H₂, 10–25%CO₂, 10–20% H₂O and 20–25% N₂, 0.5–2% CO. Hence the CO oxidation activity of a catalyst that will be used in fuel cell applications should be also investigated in the presence of H₂O and CO₂. In general, the addition of moisture to the reaction stream is resulted in an enhancement of CO oxidation by reducing the carbonate-like species on Au/Al₂O₃ catalyst during reaction (Zou *et. al.*, 2007). Other possible explanation of activity enhancement with the addition of H₂O to the reaction was ascribed to the removal of CO by water-gas shift reaction. On the other hand, the addition of CO₂ to the reaction environment can cause reverse water-gas shift reaction, which further increase CO concentration by consuming H₂.

In this part of the thesis, the effect of promoters over CO oxidation reaction are investigated within the temperatures of 80-150 °C, using reformate gas stream composition of 1% CO, 1% O₂, 60% H₂, 25% CO₂, 10%H₂O and He in balance.

The CO conversion results for Au/MO_x/γ-Al₂O₃ (M=Mn, Mg, Fe, Ni, Ce, Co) catalysts in the presence of water and CO₂ are given in Figure 4.12 while the performance of the catalysts in the absence of water and CO₂ were summarized for comparison in Figure 4.13. It is clear that the addition of promoters, except Ni, over Au/γ-Al₂O₃ catalyst enhanced the CO conversion in presence of water and CO₂ environment, compare to unpromoted one.

The activity order for CO oxidation is Au/MgO_x/γ-Al₂O₃> Au/MnO_x/γ-Al₂O₃> Au/CeO_x/γ-Al₂O₃> Au/CoO_x/γ-Al₂O₃> Au/FeO_x/γ-Al₂O₃> Au/γ-Al₂O₃> Au/NiO_x/γ-Al₂O₃. It was also observed that the addition of CO₂ and H₂O inversely affected CO conversion for the Ni, Mn, Co, Ce, and Fe promoted catalyst while the effect was positive for Mg.

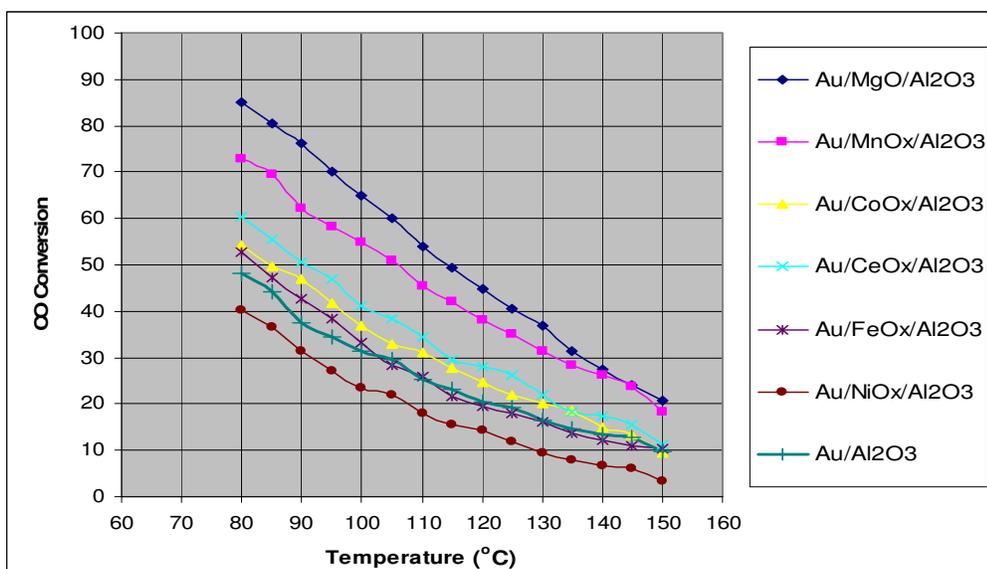


Figure 4.12. CO conversion comparison for 1 wt.%Au/1.25 wt.%MO_x/γ-Al₂O₃ catalysts in the presence of H₂O and CO₂

According to the study by Grisel and Nieuwenhuys (2001), the presence of H₂O in the reaction stream suppressed the CO conversion of Au/MnO_x/γ-Al₂O₃ catalyst. The decline in CO oxidation activity of Au/MnO_x/γ-Al₂O₃ catalyst was attributed to the poisoning of oxygen vacancies in MnO_x by H₂O addition. Another possible explanation

might be attributed H₂O blockage of CO adsorption sites over the Au catalyst (Table 4.12 and Figure 4.14).

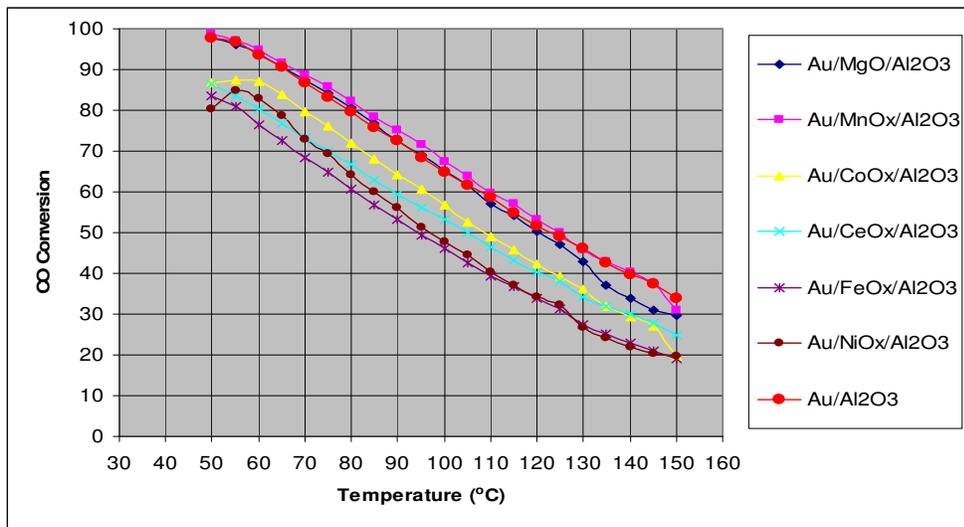


Figure 4.13. CO conversion comparison for 1 wt.%Au/1.25 wt.%MO_x/γ-Al₂O₃ catalysts in the absence of H₂O and CO₂

Table 4.12. CO conversion and selectivity results for 1 wt.% Au/1.25 wt.% MnO_x/γ-Al₂O₃ in H₂O and CO₂ environment

Temperature (°C)	CO Conversion (%)	O ₂ Conversion (%)	Selectivity (%)
150	18.39	98.30	9.35
140	26.20	98.74	13.27
130	31.30	98.56	15.88
120	38.02	98.58	19.28
110	45.28	98.09	23.08
100	54.83	99.47	27.56
90	62.17	98.72	31.49
80	72.79	98.79	36.84

Only the addition of Mg over Au/γ-Al₂O₃ catalyst slightly increased the CO conversion in the presence of H₂O and CO₂. The enhancement in catalytic performance of

Au/MgO/ γ -Al₂O₃ catalyst was ascribed to the positive effect of water at low temperatures, which is more dominant than the negative effect of CO₂ (Table 4.13 and Figure 4.15). The positive effect of H₂O was revealed by two explanations, first the activation of OH⁻ groups towards CO oxidation, second as the supporting influence of H₂O over oxygen activation.

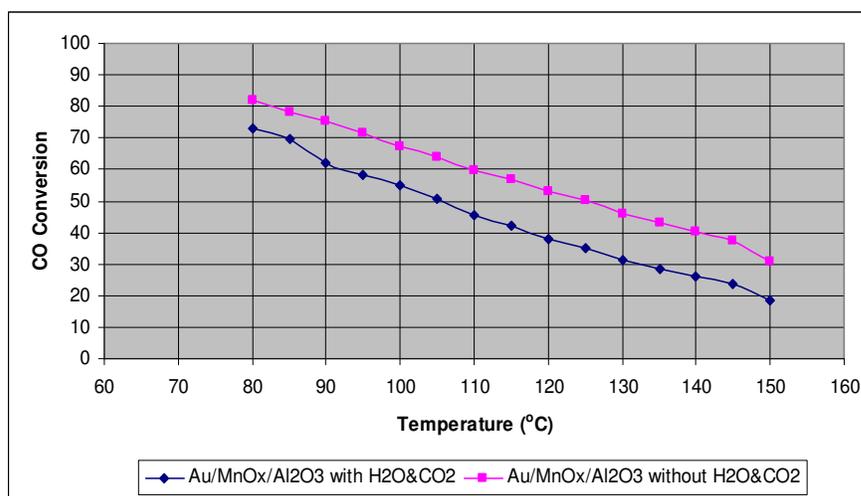


Figure 4.14. CO conversion comparison for 1 wt.% Au/1.25 wt.% MnO_x/ γ -Al₂O₃ catalyst in the absence of CO₂ and H₂O versus in the presence of CO₂ and H₂O

Table 4.13. CO conversion and selectivity results for 1 wt.% Au/1.25 wt.% MgO/ γ -Al₂O₃ in H₂O and CO₂ environment

Temperature (°C)	CO Conversion (%)	O ₂ Conversion (%)	Selectivity (%)
150	20.58	98.63	10.43
140	27.41	99.35	13.79
130	36.76	98.70	18.62
120	44.80	99.47	22.52
110	54.10	98.90	27.35
100	64.97	99.03	32.80
90	76.19	98.97	38.49
80	85.19	98.71	43.15

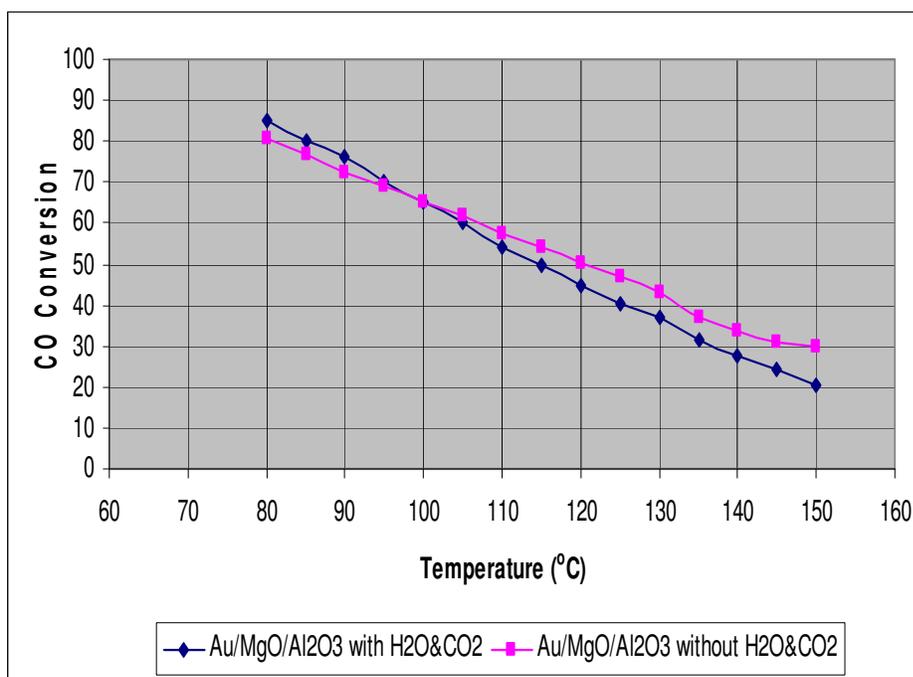


Figure 4.15. CO conversion comparison for 1 wt.% Au/1.25 wt.% MgO/ γ -Al₂O₃ catalyst in the absence of CO₂&H₂O versus in the presence of CO₂ and H₂O

The study conducted by Bethke and Kung (2000) also contributed to our results by illustrating the essentials of Mg citrate addition during preparation of Au/ γ -Al₂O₃, which yielded catalysts with smaller Au particles. They ascribed this to the ability of citrate ligands to break up Au(OH)₃ clusters in the solution. However, traces of MgO present after oxidation may also stabilize small Au particles and further the oxide may actively take part in one of the steps involved in the catalytic cycle.

By taking the account of the highest CO conversion (nearly 86% at 80 °C), obtained over Au/MgO/ γ -Al₂O₃ in the presence of H₂O and CO₂ environment, this catalyst was selected as the target of interest for further investigations. The further evaluations of Au/MgO/ γ -Al₂O₃ catalyst over CO conversion are the effects of promoter content, H₂O and CO₂ per cent in the feed, and durability of the catalyst.

4.2.3. Mg Loading Effect of Au/MgO/ γ -Al₂O₃

To study the effect of Mg content on the catalyst activity, three Au/MgO/ γ -Al₂O₃ catalysts with Mg loadings of 1.25 wt.%, 2.5 wt.%, 5 wt.% were prepared. Prior to the reaction tests, all the catalysts were treated the same way as stated above. The catalytic activity were measured in the reaction stream of 1% CO, 1% O₂, 60% H₂, 25% CO₂, 10% H₂O and He as balance, within the temperatures of 80-150 °C. The conversion results for three catalysts were tabulated in Table 4.13, 4.14 and 4.15, and summarized in Figure 4.16.

Table 4.14. CO conversion and selectivity results for 1 wt.%Au/2.5 wt.% MgO/ γ -Al₂O₃ in H₂O and CO₂ environment

Temperature (°C)	CO Conversion (%)	O ₂ Conversion (%)	Selectivity (%)
150	35.52	98.57	18.02
140	39.22	98.32	19.95
130	46.71	99.27	23.53
120	51.72	98.66	26.21
110	60.57	99.30	30.50
100	67.58	98.70	34.24
90	75.94	98.81	38.43
80	83.72	98.92	42.32

The 1 wt.%Au/5wt.%MgO/ γ -Al₂O₃ catalysts showed significantly lower activity especially at low temperatures, indicating that this catalyst could not be suitable for the intended use. Although 2.5wt.% Mg containing catalyst was superior to the catalyst with 1.25% Mg at high temperatures, this superiority was diminished below 90 °C, and 1.25% Mg containing catalyst started to perform slightly better. The maximum CO conversions over 1.25 wt.% and 2.5 wt.% Mg loaded Au/MgO/ γ -Al₂O₃ catalyst were 85.17% and 83.72% at 80 °C, respectively. Hence 1.25 wt.% Mg containing catalyst was chosen for the remaining part of the thesis.

Table 4.15. CO conversion and selectivity results for 1 wt.%Au/5 wt.% MgO/ γ -Al₂O₃ in H₂O and CO₂ environment

Temperature (°C)	CO Conversion (%)	O ₂ Conversion (%)	Selectivity (%)
150	25.24	99.21	12.72
140	28.53	99.03	14.40
130	34.01	98.55	17.26
120	38.55	99.03	19.46
110	45.59	98.98	23.03
100	46.70	92.74	25.18
90	33.59	70.00	23.99
80	21.54	39.20	27.47

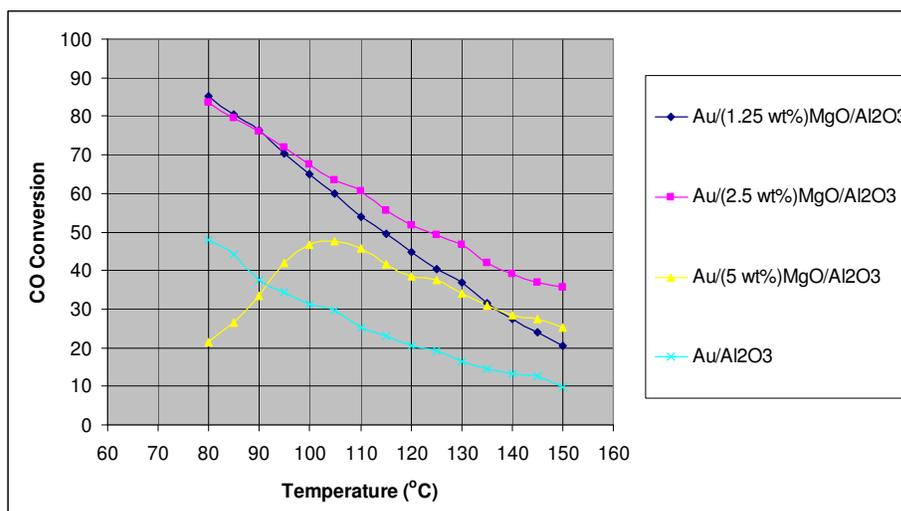


Figure 4.16. The effect of MgO content over CO oxidation performance of Au/MgO/ γ -Al₂O₃

4.2.4. Effect of H₂O

In order to elucidate the effect of H₂O content on the CO oxidation activity of Au/MgO/ γ -Al₂O₃ catalyst, three reaction environments with different H₂O percent in the feed were studied (Table 4.16, Table 4.17, Table 4.18 and Figure 4.17). It was found that

the decline in reaction temperature resulted on the increase of CO conversion and selectivity for all catalysts tested in different H₂O contents. It was also observed that the increase in H₂O concentration positively affected CO conversion at low temperatures while the differences were diminished at relatively high temperatures (above 130 °C).

Table 4.16. CO conversion and selectivity results for 1 wt.%Au/1.25 wt.% MgO/ γ -Al₂O₃ in 0% H₂O and 25% CO₂ environment

Temperature (°C)	CO Conversion (%)	O ₂ Conversion (%)	Selectivity (%)
150	20.38	99.43	10.25
140	28.57	99.01	14.43
130	36.08	99.36	18.16
120	40.51	98.93	20.47
110	47.46	98.79	24.02
100	54.44	99.50	27.36
90	61.13	98.75	30.95
80	68.12	99.13	34.36

Table 4.17. CO conversion and selectivity results for 1 wt.%Au/1.25 wt.% MgO/ γ -Al₂O₃ in 5% H₂O and 25% CO₂ environment

Temperature (°C)	CO Conversion (%)	O ₂ Conversion (%)	Selectivity (%)
150	21.24	99.00	10.73
140	27.18	98.47	13.80
130	32.98	99.45	16.58
120	38.34	98.57	19.45
110	47.02	99.10	23.72
100	55.22	99.69	27.70
90	64.49	98.17	32.85
80	74.90	98.35	38.08

Table 4.18. CO conversion and selectivity results for 1 wt.% Au/1.25 wt.% MgO/ γ -Al₂O₃ in 10% H₂O and 25% CO₂ environment

Temperature (°C)	CO Conversion (%)	O ₂ Conversion (%)	Selectivity (%)
150	20.58	98.63	10.43
140	27.41	99.35	13.79
130	36.76	98.70	18.62
120	44.80	99.47	22.52
110	54.10	98.90	27.35
100	64.97	99.03	32.80
90	76.19	98.97	38.49
80	85.19	98.71	43.15

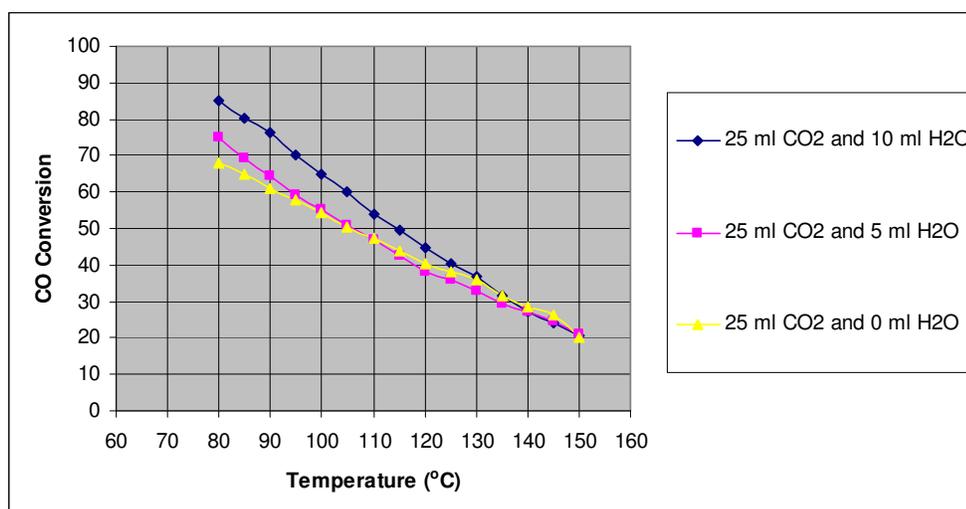


Figure 4.17. The effect of H₂O content over CO oxidation performance of Au/MgO/ γ -Al₂O₃

The enhancement in catalytic activity towards CO oxidation in the presence of H₂O in the reaction environment might be attributed to the fact that H₂O causes reconstruction of the (smallest) Au particles and may so engender an altered re-activity. The participation

of the H₂O-derived species, i.e. –OH, in the reaction mechanisms act as a promoter and cause an enhancement in CO conversion (Grisel and Nieuwenhuys; 2001).

According to the study of (Kung *et. al.*, 2003), the complex effect of water may be attributed to its multiple roles in the reaction. One of the possible improvements of H₂O addition was ascribed to the removal of chloride poison by hydrolyzing the Au-Cl bond. Another possibility is the decomposition of deactivating species on the catalyst surface. The active interface sites may be covered with inert carbonate species, being accumulated during the reaction. The moisture is expected to decompose the carbonate species, which was recently confirmed by Costello *et. al.*, (2003) in their isotope effect experiments.

4.2.5..Effect of CO₂

Although the addition of H₂O on the reaction environment improved CO conversion of Au/MgO/ γ -Al₂O₃ catalyst, the presence of CO₂ content of the reaction feed slightly diminished the positive effect of H₂O. The conversion results for three catalysts were tabulated in Table 4.13, 4.19, 4.20, 4.21, and summarized in Figure 4.18.

Table 4.19. CO conversion and selectivity results for 1 wt.% Au/1.25 wt.% MgO/ γ -Al₂O₃ in 10% H₂O and 0% CO₂ environment

Temperature (°C)	CO Conversion (%)	O ₂ Conversion (%)	Selectivity (%)
150	37.35	99.62	18.75
140	43.42	100	21.69
130	52.45	99.64	26.35
120	62.18	100	31.08
110	72.32	100	36.01
100	82.08	99.92	41.07
90	90.32	100	45.04
80	96.43	100	48.20

Table 4.20. CO conversion and selectivity results for 1 wt.% Au/1.25 wt.% MgO/ γ -Al₂O₃ in 10% H₂O and 5% CO₂ environment

Temperature (°C)	CO Conversion (%)	O ₂ Conversion (%)	Selectivity (%)
150	24.99	100	12.50
140	32.74	99.86	16.39
130	40.35	99.90	20.20
120	48.61	99.82	24.35
110	57.06	100	28.53
100	66.98	99.80	33.56
90	75.82	99.50	38.10
80	86.30	99.70	43.28

Table 4.21. CO conversion and selectivity results for 1 wt.% Au/1.25 wt.% MgO/ γ -Al₂O₃ in 10% H₂O and 10% CO₂ environment

Temperature (°C)	CO Conversion (%)	O ₂ Conversion (%)	Selectivity (%)
150	28.53	99.38	14.35
140	31.01	100	15.51
130	39.62	100	19.81
120	47.44	99.42	23.86
110	57.00	99.63	28.61
100	66.14	99.95	33.09
90	75.91	99.21	38.26
80	85.11	99.62	42.72

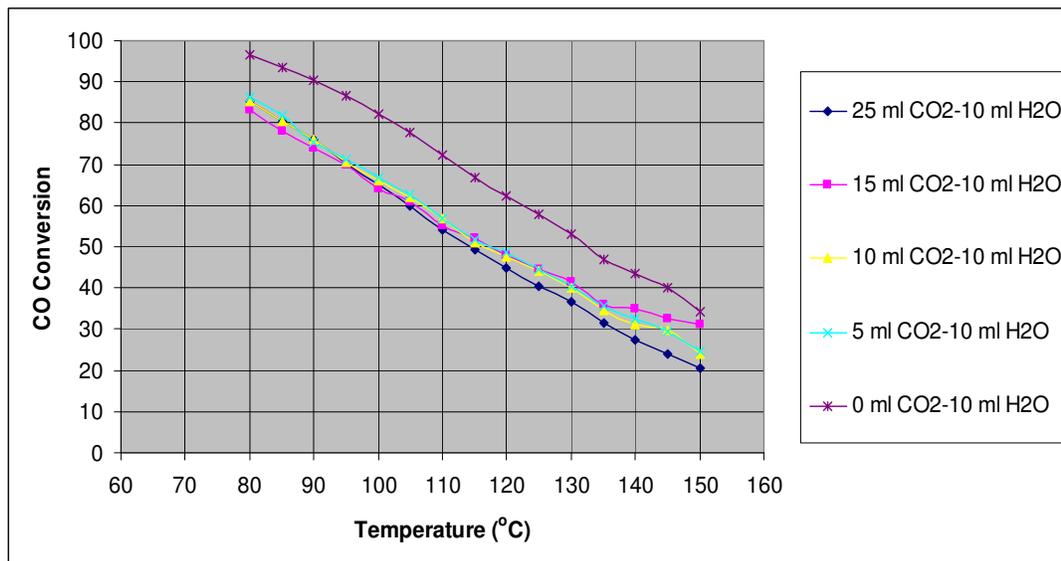


Figure 4.18. The effect of CO₂ content over CO oxidation performance of Au/MgO/γ-Al₂O₃

Although the phenomena of decrease in activity with the addition of CO₂ in the reaction environment was observed, the increase in CO₂ content from 5 vol.% to 25 vol.% did not cause any detrimental effect over CO oxidation activity for Au/MgO/γ-Al₂O₃ catalyst at the operational temperature of fuel cell (Figure 4.18). The selectivity of the catalyst was not significantly impacted by the presence of CO₂ in the feed.

4.2.6. Durability test of Au/MgO/γ-Al₂O₃ in H₂O and CO₂ environment

The catalytic activity of Au/MgO/γ-Al₂O₃ was measured at constant temperature for 21 h in order to test the catalyst's stability with time. The reactant gas was 1% CO, 1% O₂, 60% H₂, 25% CO₂, 10% H₂O and He in balance. The operating temperature was selected at 90 °C, which is quite appropriate for the fuel cell application. Au/MgO/γ-Al₂O₃ catalyst did not show any sign of deactivation in the entire test period. On the contrary, a gradual increase in CO conversion was observed as a good sign for the potential use of the catalyst (Table 4.22 and Figure 4.19).

Table 4.22. CO conversion and selectivity results at time on stream for 1 wt.% Au/1.25 wt.% MgO/ γ -Al₂O₃ in 10% H₂O and 15% CO₂ environment

Time (hour)	CO Conversion (%)	O ₂ Conversion (%)	Selectivity (%)
1 h	63.57	98.97	32.12
2 h	64.75	99.00	32.70
3 h	61.72	99.06	31.15
4 h	66.94	99.05	33.79
5 h	65.23	99.04	32.93
6 h	65.54	98.99	33.10
7 h	68.03	99.07	34.33
8 h	69.54	98.41	35.33
9 h	67.16	98.26	34.17
10 h	69.23	98.10	35.29
11 h	69.85	98.08	35.61
12 h	69.19	97.95	35.32
13 h	72.60	97.91	37.07
14 h	70.49	97.64	36.10
15 h	70.81	97.76	36.22
16 h	70.68	97.97	36.07
17 h	72.87	97.98	37.19
18 h	73.05	97.74	37.37
19 h	72.59	97.55	37.21
20 h	72.38	97.47	37.13
21 h	71.83	97.58	36.81

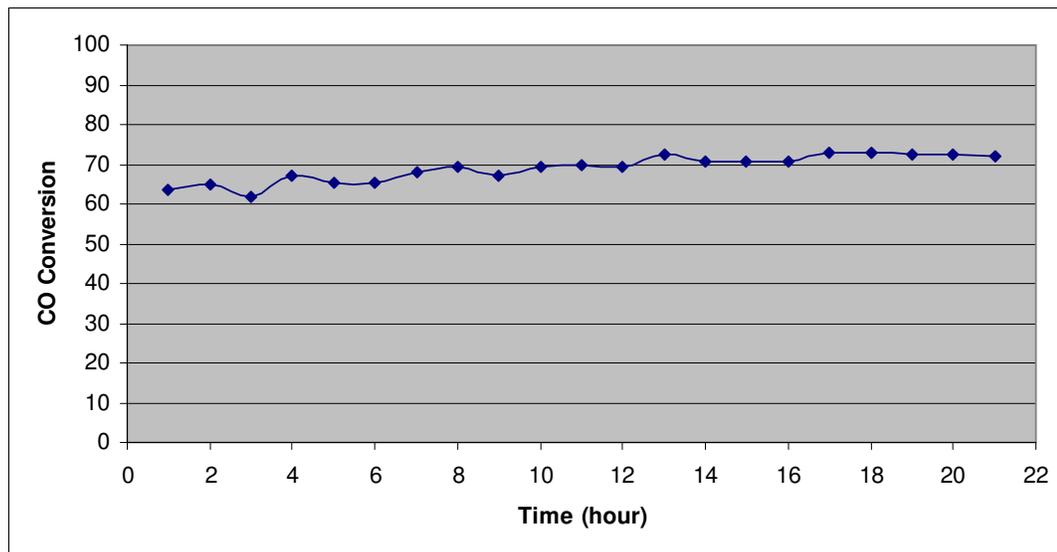


Figure 4.19. Durability test for Au/MgO/ γ -Al₂O₃ catalyst in the presence of H₂O and CO₂

5. CONCLUSIONS AND RECOMMENDATIONS

Conclusions

The purpose of this study was to investigate the promoter effect on Au/ γ -Al₂O₃ catalyst for the selective CO oxidation reaction. The desired result was to create a catalyst that is capable of 100% CO conversion with reasonable selectivity with a reaction temperature range between 80 and 150 °C. The conclusions drawn were summarized below.

The conclusions of the experiments using gas streams containing 1% CO, 1% O₂, 60% H₂ and balance He (in the absence of CO₂ and H₂O);

- Prior to reduction, the effect of calcination at 300 °C on CO oxidation activity was found to be negative over Au/ γ -Al₂O₃ catalyst. The reduction treatment in 100% H₂ environment demonstrated superiority over 4 vol.% H₂ in He balanced one.
- The reaction temperature has considerable negative effects on CO conversion for Au/ γ -Al₂O₃ in the hydrogen-rich reaction environment in contrast to the positive effect of temperature observed by Grisel and Nieuwenhuys, 2001 in the absence of H₂. The decrease in reaction temperature from 150 °C to 50 °C also demonstrated a significant increase in CO oxidation activity over promoted Au/MO_x/ γ -Al₂O₃ catalyst (M = Mg, Mn, Fe, Ni, Co, Ce) in the hydrogen-rich reaction stream.
- The addition of 1.25wt.% Mn to 1wt.%Au/ γ -Al₂O₃ catalyst improved the CO conversion in the reaction temperatures between 50-150 °C, compare to the unpromoted one, while the effects of Ni, Fe, Co and Ce addition was proven to be detrimental. The effect of Mg addition, on the other hand, was negligible.
- The maximum CO conversion of 97.81% and 98.65% were obtained at 50 °C for 1 wt.%Au/1.25 wt.%MgO/ γ -Al₂O₃ and 1 wt.%Au/1.25 wt.%MnO_x/ γ -Al₂O₃ catalysts, respectively. Based on the highest CO conversion obtained in the temperatures between 50-150 °C it was concluded that the order of the catalysts in

CO oxidation activity was $\text{Au/MnO}_x/\gamma\text{-Al}_2\text{O}_3 > \text{Au/MgO}_x/\gamma\text{-Al}_2\text{O}_3 = \text{Au}/\gamma\text{-Al}_2\text{O}_3 > \text{Au/CoO}_x/\gamma\text{-Al}_2\text{O}_3, \text{Au/CeO}_x/\gamma\text{-Al}_2\text{O}_3 > \text{Au/FeO}_x/\gamma\text{-Al}_2\text{O}_3 > \text{Au/NiO}_x/\gamma\text{-Al}_2\text{O}_3$.

The conclusions of the experiments using gas streams containing 1% CO, 1% O₂, 60% H₂, 25% CO₂, 10 vol.% H₂O and balance He (in the presence of CO₂ and H₂O);

- Alike in the absence of H₂O and CO₂ reaction environment, the decrease in the reaction temperature from 150 °C to 80 °C increased the CO conversion in the presence of CO₂ and H₂O.
- All promoted catalysts, excluding one promoted by Ni, exhibited a better catalytic activity toward CO oxidation than the unpromoted Au/γ-Al₂O₃ catalyst within the reaction temperatures of 80 °C-150 °C, indicating that the addition of promoters is beneficial in the real reaction environment.
- The addition of Mg over Au/γ-Al₂O₃ catalyst slightly increased CO conversion in the presence of H₂O and CO₂, compare to its performance in the absence of H₂O and CO₂, indicating that it could be a good candidate for the practical applications. However, the conversion was still below the desired 100% (it was close 86% at 80 °C) requiring some more improvement.
- The Au/MgO_x/γ-Al₂O₃ demonstrated 21 h of stability at 90 °C as a good sign of the potential use of the catalyst.

The conclusions of the experiments using different Mg weight content in the Au/MgO/Al₂O₃ catalyst;

- Catalysts containing 1.25 weight per cent and 2.5 weight per cent Mg exhibited comparable CO conversions while the 1 wt.%Au/5wt.%MgO/γ-Al₂O₃ catalyst showed significant lower activity nearly in all temperatures observed. At fuel-cell operating temperatures (80-90 °C), the increase in Mg content from 1.25 wt% to 2.5 wt% did not show any significant improvement over the CO oxidation activity.

The conclusions of the experiments using different H₂O content in the reaction environment over Au/MgO/Al₂O₃ catalyst;

- The temperatures above 130 °C, 5 vol.% and 10 vol.% H₂O loading demonstrated no sign of enhancement in CO conversion. However at low temperatures as the H₂O loading was increased from 0 vol.% to 10 vol.%, significant improvement in CO oxidation activity over Au/MgO/ γ -Al₂O₃ catalyst was observed.

The conclusions of the experiments using different CO₂ content in the reaction environment over Au/MgO/Al₂O₃ catalyst;

- CO conversion tended to decrease as CO₂ content of the reaction environment increased (mostly appeared in the temperatures of 120-150 °C). This effect became significant in the comparison of the performance of the catalyst at 0 and 5 vol.% CO₂ while there was no remarkable difference between 5 vol.% to 25 vol.% CO₂ content at operational temperature of the fuel cell.

5.2 Recommendations

According to the results of the present study, the following points are thought to be beneficial for the future studies on catalytic low temperature CO oxidation in hydrogen rich streams:

- The importance of different types of γ - Al_2O_3 support such as nanofibers should be investigated in order to achieve higher CO oxidation activities.
- Catalysts preparation procedures possess vital effects over catalytic activity by influencing not only gold particle size but also the distribution over the support. By taking the account of the importance of these properties, new preparation methods such as direct anionic exchange (DAE), reverse microemulsion technique (RME), modified impregnation method should be employed.
- Drying conditions of both the $\text{MO}_x/\gamma\text{-Al}_2\text{O}_3$ composite support and $\text{Au}/\text{MO}_x/\gamma\text{-Al}_2\text{O}_3$ catalyst should be investigated in order to define the effect of H_2O besides the addition of H_2O to the reaction environment
- The effect of calcination environment should be expressed by temperature program oxidation tests and oxidation state of gold should be found by employing XPS analyzes.
- The temperature programmed reduction test should be employed for all promoted $\text{Au}/\text{MO}_x/\gamma\text{-Al}_2\text{O}_3$ catalyst not only in H_2 environment but also in the presence of H_2O and CO in order to find the best reduction temperature.
- Kinetic experiments may be conducted for finding an empirical kinetic expression for preferential CO oxidation reaction over the $\text{Au}/\text{MgO}/\text{Al}_2\text{O}_3$ catalyst.
- The stability of the catalysis should be tested for industrial use. The optimum catalyst obtained, should be tested in industrial scales using reactors at real sizes.

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