

SELECTIVE CO OXIDATION OVER MONOLITHIC Au/Al₂O₃
PROMOTED BY METAL OXIDES

by

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to my family

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ABSTRACT

SELECTIVE CO OXIDATION OVER MONOLITHIC Au/Al₂O₃ PROMOTED BY METAL OXIDES

The objective of this study was to investigate the preparation methods of cordierite monolithic Au/MgO/Al₂O₃ catalysts for selective carbon monoxide oxidation in a hydrogen rich environment. In this comparative study, the walls of the monolithic structures were firstly coated with alumina by colloidal coating method in order to enlarge the surface area of the catalyst. The loading of the metal oxide promoter (MgO) to the monolithic structure was applied by impregnation method. Gold was loaded to the MgO/Al₂O₃/cordierite monolith catalysts using five different methods namely, wet impregnation, co-precipitation, dry impregnation, deposition-precipitation and homogeneous deposition precipitation. Deposition precipitation technique was applied both at 70°C and room temperature, and homogeneous deposition precipitation method was applied by using two different precipitating agents which are acetamide and urea. The catalysts were then reduced in H₂ with a flow rate of 50 cm³ min⁻¹ for 2 hours and tested for selective carbon monoxide oxidation in a hydrogen rich stream. The comparison of the gold loading methods was studied at 110°C and the MgO and Au content of the catalysts were selected as 1.25 wt% and 1 wt% respectively. Catalysts with 0.5 wt% and 0.16 wt% Au content were also studied in order to determine the Au loading effect. The effects of Au and MgO loading, W/F ratio and O₂ content were investigated in the temperature range of 50-150°C under a total flow of 100.6 ml/min. Finally, the effect of temperature ascent and descent was investigated. The highest CO conversion (77.30%) was achieved via homogeneous deposition precipitation method using urea as the precipitating agent at 90°C with the catalyst compositions of 1 wt% Au/1.25 wt% MgO/Al₂O₃ and with the feed compositions of 0.99% CO, 1.59% O₂, 59.64% H₂ and balance He.

ÖZET

METAL OKSİTLER İLE DESTEKLENMİŞ MONOLİTİK Au/Al₂O₃ İLE SEÇİMLİ CO OKSİDASYONU

Bu çalışmanın amacı, hidrojen zengin ortamlarda seçimli karbon monoksit oksidasyonu için kordierit monolitik Au/Al₂O₃ katalizörlerin hazırlama metotlarının incelenmesidir. Bu karşılaştırmalı çalışmada, monolitik yapının duvarları ilk olarak, katalizörün yüzey alanını genişletmek amacıyla koloidal kaplama metodu uygulanarak alumina ile kaplanmıştır. Metal oksit destekleyicinin (MgO) monolitik yapıya yüklenmesi emdirme yöntemi ile sağlanmıştır. Altın, MgO/Al₂O₃/kordierit monolitik katalizörlerine ıslak emdirme, kuru emdirme, birlikte çöktürme, tortu çöktürmesi ve homojen tortu çöktürmesi olmak üzere beş farklı metot ile yüklenmiştir. Tortu çöktürmesi yöntemi hem 70°C’de hem de oda sıcaklığında, homojen tortu çöktürmesi yöntemi ise asetamid ve üre olmak üzere iki farklı çöktürme aracı kullanılarak uygulanmıştır. Daha sonra, katalizörler 2 saat boyunca 50 cm³/min akış hızındaki H₂ altında indirgenmiş ve hidrojen zengin ortamda seçimli karbon monoksit oksidasyonu için test edilmiştir. Altın yükleme metotları 110°C’de çalışılmıştır ve MgO ile Au içerikleri sırasıyla %1.25(ağ) ve %1(ağ) olarak seçilmiştir. Au yükleme etkisinin incelenmesi için %0.5(ağ) ve %0.16(ağ) Au içerikli katalizörler ile de çalışılmıştır. Au ve MgO yüklenmesi, W/F oranı ve O₂ içeriğinin etkileri 50-150°C sıcaklık aralığında ve toplam 100.6 cm³min⁻¹ akış altında incelenmiştir. Son olarak, sıcaklıkta iniş ve çıkış etkisi incelenmiştir. En yüksek CO dönüşümü (77.30%), çöktürme aracı olarak üre kullanılarak homojen tortu çöktürme yöntemi ile 90°C’de, %1(ağ) Au/ %1.25(ağ) MgO/Al₂O₃ içeriğindeki katalizör kullanarak %0.99 CO, %1.59 O₂, %59.64 H₂ ve dengeleyici miktarda He içeren akım altında elde edilmiştir.

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LIST OF SYMBOLS/ABBREVIATIONS

| | |
|--------|--------------------------------------|
| W/F | Residence Time |
| AFCs | Alkaline Fuel Cells |
| ATR | Autothermal Reforming |
| CLPG | Chemical Liquid Phase Grafting |
| CP | Co-precipitation |
| CVD | Chemical Vapor Deposition |
| DP | Deposition Precipitation |
| GC | Gas Chromatograph |
| HDP | Homogeneous Deposition Precipitation |
| HTS | High Temperature Shift |
| ICP | Inductively Coupled Plasma |
| ID | Internal Diameter |
| IM | Impregnation |
| IPOX | Indirect Partial Oxidation |
| IW | Incipient Wetness |
| LTS | Low Temperature Shift |
| MCFCs | Molten Carbonate Fuel Cells |
| OD | Outer Diameter |
| PAFCs | Phosphoric Acid Fuel Cells |
| PEMFCs | Proton Exchange Membrane Fuel Cells |
| PGM | Pt Group Metal |
| POX | Partial Oxidation |
| ppm | Parts per million |
| PROX | Preferential Oxidation |
| SOFCs | Solid Oxide Fuel Cells |
| SR | Steam Reforming |
| TCD | Thermal Conductivity Dedector |
| TPR | Temperature Programmed Oxidation |
| WGS | Water-Gas-Shift |

1. INTRODUCTION

In our modern world, there is a growing demand for energy. According to Energy Information Administration, over the next 25 years, world demand for liquid fuels and other petroleum is expected to increase more rapidly in the transportation sector, especially for the non-OECD countries. The dependence of liquid fuels for transportation sector is the major cause of air pollution and global warming (International Energy Outlook, 2008; Ying, 2006).

In an ongoing effort to both meet the increasing energy demand of the world and to preserve the global environment, industrialized countries should lead the development of renewable energy technologies (Sadiq Al-Baghdadi and Shahad Al-Janabi, 2005; European Commission, 2003).

One of the novel approaches designed to meet this demand is the fuel cell technology (Onsan, 2007). Fuel cells have gained enormous attention from both the research institutions and companies as a renewable alternative to fossil fuels offering the reduction of greenhouse gas emissions and air pollution with the only outputs of electricity, pure water and waste heat (Carrette *et al.*, 2000; Scrivano *et al.*, 2009).

Among the all types of fuel cells, the proton exchange membrane fuel cells fuelled with hydrogen are considered to be the most promising and attractive candidate for a wide variety of power applications (Gokaliler *et al.*, 2008; Wee, 2007). However, for the full commercialization, it is essential to achieve the continuous availability of hydrogen as a fuel, whose storage, transportation and availability are the major problems encountered (Wee, 2007; Avci *et al.*, 2002).

The hydrogen production can be achieved by steam reforming (SR), partial oxidation (POX) or auto-thermal reforming (ATR). All of these processes produce carbon monoxide which causes deactivation of the electrodes used in fuel cells. PEM fuel cells can only tolerate trace amounts of carbon monoxide; however reduction of carbon monoxide concentration to an acceptable level of 10-50 ppm can not be achieved only via water-gas-

shift reaction. In order to reduce the CO concentration, preferably, less than 10 ppm, selective carbon monoxide oxidation is the most promising alternative (Trimm, 2005; Park *et al.*, 2009).

High CO oxidation activities and low hydrogen oxidation activities are the major requirements of PROX catalysts (Chouldhary and Goodman, 2002). Researchers have reported a large number of catalysts meeting these requirements such as, metal oxide catalysts, supported Ru, Rh, Ir catalysts or supported Pt catalysts (Ko *et al.*, 2006). Ever since Haruta *et al.* (1987) reported gold catalysts to be highly active for CO oxidation at temperatures as low as -70°C , supported gold catalysts has gained a wide attention among the other precious metals (Hutchings, 2007). Although, science of gold catalysis is still quite new and undeveloped compared with the PGMs (Platinum group metals), it has already been concluded by many researchers that supported gold catalysts have the highest activity for selective carbon monoxide oxidation (Cameron *et al.*, 2003).

On the other hand, development of monolithic catalysts has been one of the major achievements of recent years in heterogeneous catalysis science. Monoliths are generally used as the supports for the catalytically active components or as the catalyst themselves (Tomašić and Jović, 2006). Monoliths can be made up from either metals or ceramics such as cordierite (Pérez-Cadenas *et al.*, 2005). Monolithic catalysts have numerous advantages over conventional particulate catalysts such as; high specific surface, low pressure drop, good interphase mass transfer, mostly insignificant resistance to mass transfer by intraphase diffusion through a catalytic layer, good thermal and mechanical properties, easy scale up and efficient catalyst usage (Tomašić and Jović, 2006; Gulijk *et al.*, 2005).

The activity of the gold catalysts is quite sensitive to the preparation technique (Yang *et al.*, 2005). Co-precipitation, deposition-precipitation and homogeneous deposition precipitation are the most common techniques for gold based catalyst preparation. However, the application of gold over the monolithic structures is quite new and undiscovered.

The aim of the present study was to investigate the preparation methods of monolithic Au/MgO/Al₂O₃ catalysts for selective carbon monoxide oxidation in a

hydrogen rich environment. For that purpose, the cordierite monolithic structures were firstly wash-coated with alumina by using its colloidal dispersion. Next, the loading of MgO promoter on the alumina supported monoliths was employed by impregnation method. The most critical point of this thesis was the loading of gold as nanoparticles on the MgO/Al₂O₃/cordierite monolith catalysts. At that point, five different methods were applied namely, wet impregnation, co-precipitation, dry impregnation, deposition-precipitation and homogeneous deposition precipitation for Au loading. Each method was modified for monolithic structure usage. The other investigations were carried out with the most promising method. All of the monolithic catalysts were finally tested for selective carbon monoxide oxidation in a micro-reactor flow system in the temperature range of 50-150°C.

This thesis is comprised of five chapters. Section 2 involves a literature survey including a brief introduction to fuel cells, hydrogen production via reforming processes, followed by water gas shift reaction and preferential carbon monoxide oxidation. Next, detailed information is given for PROX catalysts and monolithic catalysts, including preparation methods. Section 3 involves all of the experimental systems and catalyst preparation procedures. The results obtained in the experiments are presented and analyzed in Section 4. Finally, the conclusions and recommendations for future work are discussed in Section 5.

2. LITERATURE SURVEY

2.1. Background to Energy Resources

The population of the world is rising continuously in the developing countries and the population growth between 2000 and 2030 is expected to be mainly concentrated on urban areas of the world. Therefore, the demand for commercial energy resources is expected to increase at a greater rate in the upcoming years. The dependence on the oil for transportation in the growing urban areas is the major reason of air pollution and global warming which threatens the world (Omer, 2008; Ying, 2006).

In an ongoing effort to both meet the increasing energy demand of the world and to preserve the global environment, emerging trends suggest to shift the present oil-dependent transportation system to natural gas in the short-run and the main objective in the long-run is to shift to readily available, high efficiency and pollution-free fuels (Ying, 2006; Sadiq Al-Baghdadi and Shahad Al-Janabi, 2005). One of the novel approaches designed to meet this demand is the fuel cell technology (Onsan, 2007).

2.2. Fuel Cells

2.2.1. Fuel Cell Concept

The fuel cell concept is more than 150 years old and the first successful application was achieved in 1932 by Francis Bacon (Gencoglu and Ural, 2008). After a long period of pre-commercial development, a growing interest has been observed for the fuel cell technologies and today hundreds of companies around the world are working towards making fuel cell technology pay off (Scrivano *et al.*, 2009; Thomas and Zalbowitz, 2007). Fuel cells are efficient, clean, quiet, modular and environmentally safe (Cook, 2001). Therefore, they are widely considered to be one of the most attractive energy conversion technologies of the future, promising a pollution-free and high efficiency power generation, especially for powering transportation vehicles (Ozdemir *et al.*, 2004; EG&G Technical Services, 2004).

A fuel cell is defined as an electrochemical device of power generation that converts the chemical energy contained in fuels directly into the electricity (Chang *et al.*, 2009). A typical fuel cell consists of an ionically conductive but electrically non-conductive electrolyte in contact with two porous electrodes that are anode and cathode on either side. Fuel- generally hydrogen- is supplied to the anode and the oxidant- often the oxygen from the air- is supplied to the cathode, thereby causing electrochemical reactions (Ramani, 2006).

Basically, hydrogen molecules split into electrons and protons over the negatively charged electrode. The protons produced are transferred, through the electrolyte, toward the oppositely charged electrode where they combine with oxygen to produce water as the primarily by-product, while the electrons are forced to go around the electrolyte to the cathode, thereby creating an electric current (Ramani, 2006).

A fuel cell is not bounded by the thermodynamic limitations of heat engines such as the Carnot efficiency, as the electrolyte also serves as a barrier between the fuel and the oxidant. Therefore, no actual combustion occurs and practically fuel cells can yield 100% efficiency (Ramani, 2006; EG&G Technical Services, 2004).

As a single fuel cell is not adequate to produce the necessary electric output, cells are connected in arrays in order to produce a cell stack. A fuel cell stack consists of desired number of repeating fuel cell units, each consisting of an anode, cathode, electrolyte and a bipolar separator plate (Figure 2.1) (Carrette *et al.*, 2000; Energy Center of Wisconsin, 2000). These stacks must be replaced during 5-10 year periods in stationary applications and must be available at low costs and be compatible with earlier generations (Department of Energy, 2003).

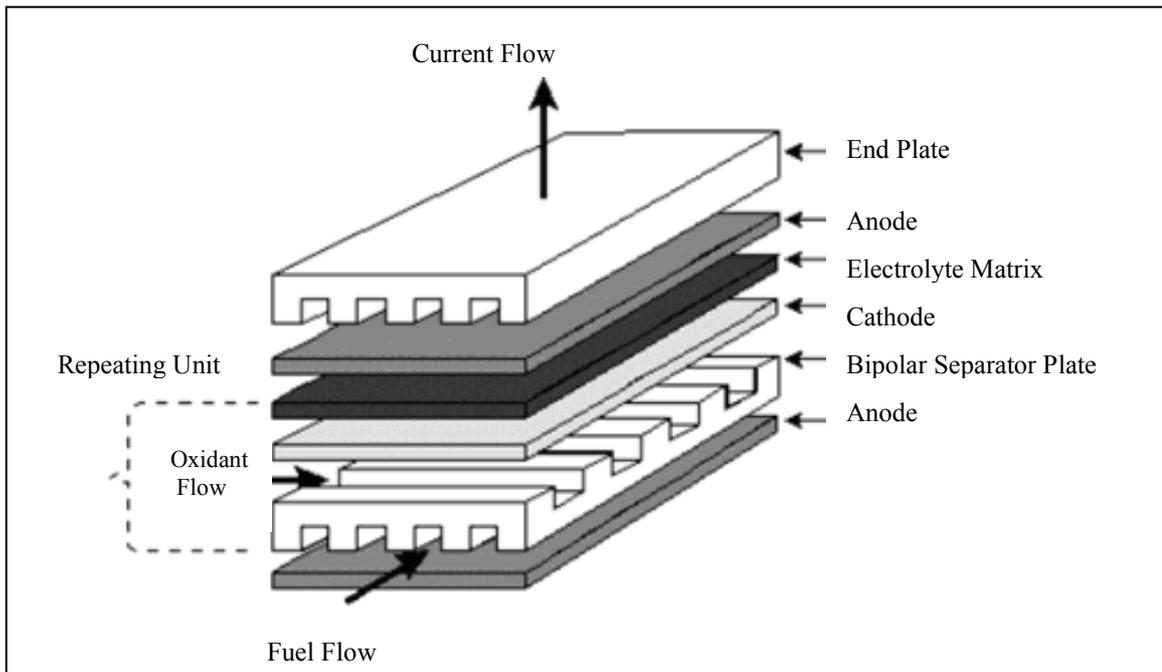


Figure 2.1. Components of a fuel cell stack (Energy Center of Wisconsin, 2000)

2.2.2. Types of Fuel Cells

The material used for the electrolyte and the design of the supporting structure determine the type and performance of the fuel cells. Main types of fuel cells that are in different stages of development are:

- Proton Exchange Membrane Fuel Cells (PEMFCs)
- Alkaline Fuel Cells (AFCs)
- Phosphoric Acid Fuel Cells (PAFCs)
- Molten Carbonate Fuel Cells (MCFCs)
- Solid Oxide Fuel Cells (SOFCs)

The operation temperatures for these fuel cells are $\sim 70\text{-}90^\circ\text{C}$ for PEMFCs, $\sim 65\text{-}220^\circ\text{C}$ for AFCs, $\sim 180\text{-}220^\circ\text{C}$ for PAFCs, $\sim 650\text{-}700^\circ\text{C}$ for MCFCs and $\sim 800\text{-}1000^\circ\text{C}$ for SOFCs (Song, 2002; EG&G Services, 2000).

High-temperature fuel cells, which are solid oxide fuel cells (SOFCs) and molten carbonate fuel cells (MCFCs) have been mainly used for large scale stationary power

generation and these fuel cells can use both CO and H₂ as the fuel. MCFCs generally use LiK or LiNa carbonate as an electrolyte (Hoogers, 2003; Song 2002). The main features of MCFCs are the requirement of CO₂ at the cathode for efficient operation and the corrosive feature of the electrolyte used, which affects the fuel cell life (Holland *et al.*). The solid nonporous metal oxide electrolyte in the SOFCs minimize hardware corrosion and allow for flexible design shapes but at the same time, denotes a relatively low conductivity which lowers the performance of the fuel cell. For both fuel cells, the high temperature operation allows achieving high reaction rates without the need for expensive catalysts but also, limits the materials selection and results a difficult fabrication process (Holland *et al.*; Carrette *et al.*, 2000).

Low-temperature fuel cells are alkaline fuel cells (AFCs), phosphoric acid fuel cells (PAFCs) and the proton exchange membrane fuel cells (PEMFCs). The AFCs were the first practical working fuel cell which further developed for the Apollo space program (Bidault *et al.*, 2009). AFCs have the main advantage of achieving high overall electric efficiencies; however the major disadvantages of AFCs are that they are very sensitive to CO₂ and CO poisoning, and the CO₂ adsorption of the strongly alkaline electrolytes such as NaOH or KOH reduces electrolyte conductivity (Hoogers, 2003; Holland *et al.*). The PAFCs are less sensitive to CO than other types of low-temperature fuel cells, however the corrosive nature of the H₃PO₄ electrolyte requires usage of expensive materials in the stack and cathode-side oxygen reduction is slower than that of for the AFCs (Hoogers, 2003; EG&G Technical Services, 2004).

Among the all types of fuel cells, the proton exchange membrane fuel cells (PEMFCs), also known as polymer electrolyte membrane fuel cells, fuelled with hydrogen are considered to be the most promising and attractive candidate for a wide variety of power applications ranging from portable/micropower and vehicle applications to large-scale stationary power systems for buildings and distributed generation (Gokaliler *et al.*, 2008; Wee, 2007). As the name of the cell implies, the heart of the PEM fuel cell is the solid polymer membrane which allows protons to be transferred from one side of the electrolyte to another (Ying, 2006). A schematic diagram of a PEM fuel cell summarizing the working principle is seen in Figure 2.2.

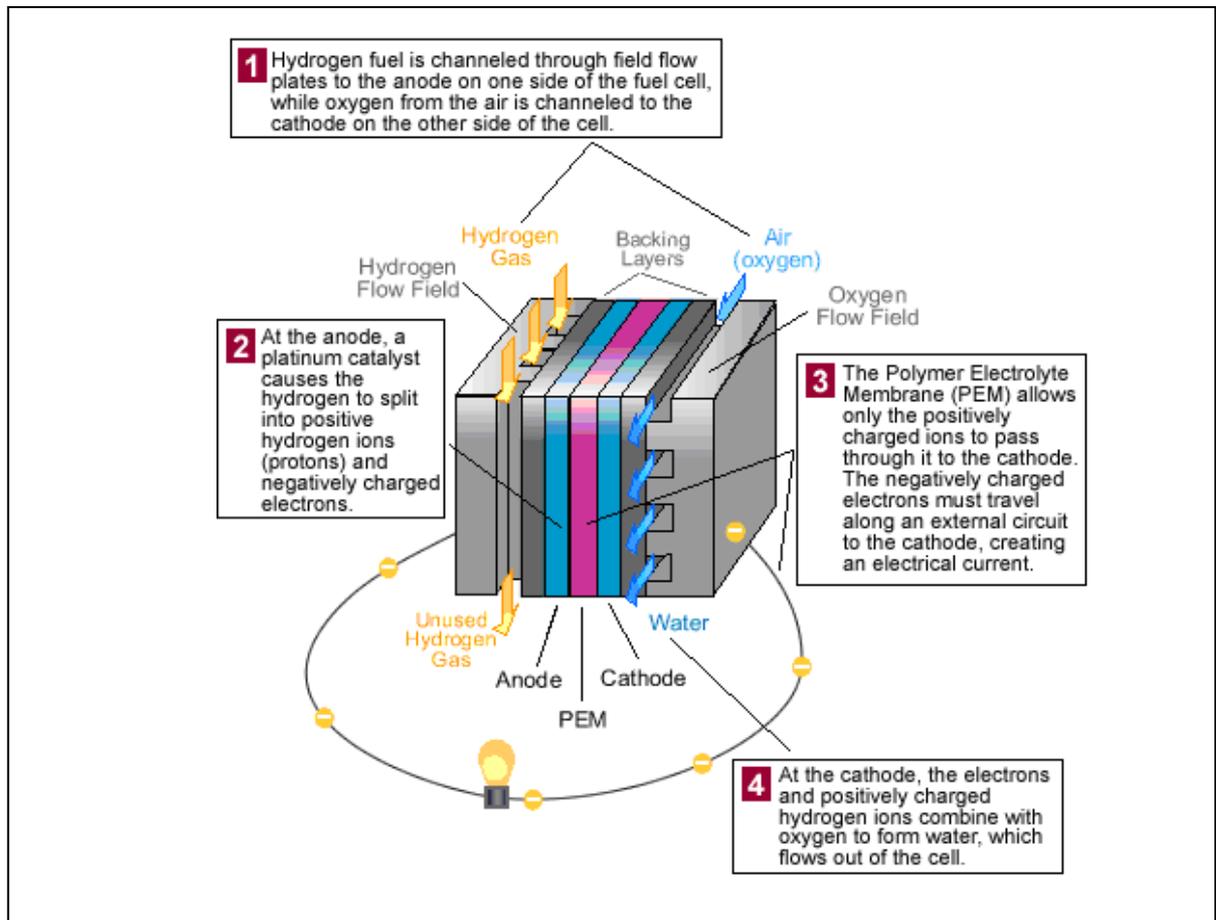
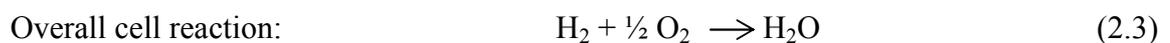
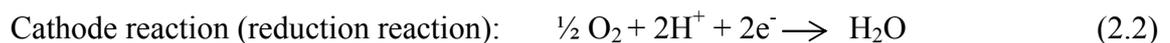


Figure 2.2. Schematic diagram of a PEM fuel cell (Ying, 2006)

The reactions occurring at the electrodes of a PEM fuel cell are as follows and the only by-products are water and waste heat (Sadiq Al-Baghdadi and Shahad Al-Janabi, 2005; Ersoz *et al.*, 2003):



PEM fuel cells have many advantages such as low operating temperature, quick start-ups, sustained operation at a high current density, low weight, compactness, the potential for low cost and volume, long stack life, suitability for discontinuous operation and

eliminated environmental damage due to electrolyte leakage (Tirnovan *et al.*, 2008; Baschuk and Li, 2009; Wee, 2007). These cells can also tolerate CO₂ but are quite sensitive to CO which reduces the efficiency (Ying, 2006).

2.2.3. Fuels for Fuel Cells

Despite the promising achievements of PEM fuel cells, it is still long way before they can successfully and economically replace conventional turbines and internal combustion engines. For full commercialization of the low-temperature fuel cells including PEM fuel cell, it is essential to achieve the continuous availability of hydrogen as a fuel, whose storage, transportation and availability are the major problems encountered (Wee, 2007; Avci *et al.*, 2002).

Alternative fuels to hydrogen are also being studied such as ethanol, methanol, propane and even cleaner gasoline. But, these fuels are not available everywhere. More obviously, one location may prefer ethanol, other may prefer gasoline and most of these fuels require different engine technologies for efficient operation, while hydrogen can be produced from all of these feedstocks, as well as many others. Therefore, this advantage makes hydrogen a universal fuel (Schilke, 2001; Holladay, 2009).

Hydrogen is an ideal source of chemical energy for fuel cell applications however, it is not itself an energy source and it is not readily available in the free form in the nature. (Avci *et al.*, 2004; Department of Energy, 2003). Therefore, the pure hydrogen with only trace amounts of residual sulphur and carbon monoxide must be generated economically by chemical reactions before fuel cells can be commercially accepted as a cleaner and more efficient alternative to traditional energy systems (Farrauto, 2003).

2.3. Hydrogen Production and CO Removal Methods for Fuel Cells

The long-term strategy for the hydrogen production for the fuel cell utilization is to produce hydrogen from renewable sources and technologies such as converting water by electrolysis using wind or solar power, producing hydrogen from biomass photo-

catalytically by sunlight. In the near and medium-term future, however, the hydrogen is more likely to be produced from the fossil fuels (Department of Energy, 2003).

There are two options for supplying hydrogen on-board. The first option is a hydrogen storage unit and the second is a fuel processor. The problems associated with the storage of hydrogen have led the on-board catalytic conversion of existing fuels to hydrogen via fuel processors receive much more attention. The fuel processor-fuel cell system efficiency is well above the efficiency of a conventional internal combustion engine (Avci *et al.*, 2004).

In a fuel processor, three catalytic reactions run in series (Caglayan *et al.*, 2005):

- (i) Reforming of hydrocarbons to hydrogen
- (ii) Water-gas shift reaction for decreasing carbon monoxide concentration, while increasing hydrogen concentration
- (iii) Preferential carbon monoxide oxidation, which reduces carbon monoxide in the reformer product to levels less than 4 ppm

2.3.1. Reforming of Hydrocarbons to Hydrogen

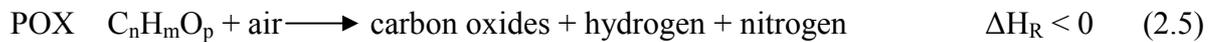
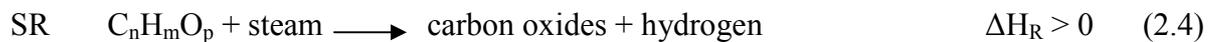
Steam reforming (SR), partial oxidation (POX) and auto-thermal reforming (ATR) are the major reforming technologies for hydrogen production.

Steam reforming gives the highest quantity of hydrogen in the product stream with a H_2/CO ratio of $\sim 3:1$. SR has also advantages over other reforming processes with a lower operating temperature ($>180^\circ C$ for methanol, di-methyl ether, and other oxygenated hydrocarbons that are readily activated, and $>500^\circ C$ for most other conventional hydrocarbons). It only uses steam and does not require oxygen (Holladay, 2009; Onsan 2007). However, the requirements of considerable heat input and high catalyst loadings make it unlikely to be used for hydrogen generation. Also, it has the highest emissions of the three reforming processes. The combination of steam reforming with water-gas-shift is called as indirect partial oxidation (IPOX) and can supply sufficient heat into the system for carrying out the endothermic steam reforming (Avci *et al.*, 2004; Holladay *et al.*, 2009).

Partial oxidation process converts hydrocarbons into hydrogen by partially combusting the hydrocarbon with oxygen. POX is favored at high temperatures (>800-1000°C). POX has the advantages over SR that it does not require a catalyst for operation, has minimal methane slip, and is more sulphur tolerant than the other processes. However, the hydrogen in the product stream is with the H₂/CO ratio of ~1:1 to 2:1.

Autothermal reforming uses steam in addition to POX. Significant advantages of ATR over POX and SR includes being conducted at lower pressure than POX reforming, having a low methane slip, and it can be stopped and started very rapidly while producing larger amount of hydrogen than POX. However, both ATR and POX require a complex oxygen separation unit in order to feed pure hydrogen into the reactor or require dilution of the product gas with nitrogen (Holladay *et al.*, 2009; Onsan 2007).

The hydrocarbon reforming reactions are as follows (Onsan, 2007):



2.3.2. Water-Gas-Shift (WGS) Reaction

Production from hydrocarbons through steam reforming, partial oxidation and autothermal reforming are the most common ways for obtaining hydrogen. However, the produced gas stream through these processes includes about 10-15% carbon monoxide, which has a poisoning effect for PEM fuel cells (Yan *et al.*, 2009; Gunawardana *et al.*, 2009).

In order to reduce the poisoning problem, CO can be converted to CO₂ through water-gas-shift reaction by using the 10-12% water contained in the reformat gasses (Hua *et al.*, 2005). The water-gas-shift reaction additionally produces more H₂, while reducing the CO (Pradhan *et al.*, 2009):



Water-gas-shift reaction usually contains two stages with a cooling apparatus between them. In the first stage, a high temperature shift (HTS) is carried out in 350-400°C zone and the CO level is reduced to 2-3 vol%. In the second stage, this time a low temperature shift (LTS) is carried out in 180-200°C zone and the CO level is reduced to approximately 0.3 vol% (Pradhan *et al.*, 2009; Lim *et al.*, 2009).

WGS reaction is exothermic and thermodynamic equilibrium controlled. So, it is favorable at low temperatures according to Le Chatelier's principle. However, the catalysts are not active enough to attain equilibrium at low temperatures. Commercially, Fe₂O₃-Cr₂O₃ oxide based catalysts are usually used as HTS catalysts and a mixed oxide of CuO-ZnO-Al₂O₃ catalysts are usually used as LTS catalysts. Although catalysts have been commercially applied to chemical plants successfully, the complicated activation steps of commercial WGS catalysts are not suitable for fuel cell utilization. Instead of these high temperature and low temperature stages, a mid temperature shift catalyst can also be used to bring down the CO content to ≤1 vol% (Pradhan *et al.*, 2009; Lim *et al.*, 2009).

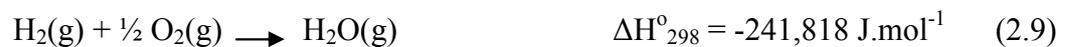
2.3.3. Preferential CO Oxidation (PROX) in H₂ Rich Streams

Reduction of carbon monoxide concentration in the gas stream below 100 ppm can not be achieved only via water-gas-shift reaction. As the commercial water-gas-shift catalysts show low catalytic activities at low temperatures, the final carbon monoxide concentration in the hydrogen stream is approximately 1 vol% after WGS reaction (Park *et al.*, 2009). However, low temperature fuel cells are extremely sensitive towards impurities especially to CO, which reduces the overall fuel cell performance. The PAFCs can tolerate up to 2% CO, while PEM fuel cells can tolerate only trace amounts (Chang *et al.*, 2008; Choudhary and Goodman, 2002).

Reduction of carbon monoxide to the trace amounts can be achieved by various processes such as separation of hydrogen by diffusion through a membrane, methanation and preferential oxidation. Among these processes, the preferential oxidation of carbon monoxide is the simplest and the most cost-effective; therefore the most promising system

for the removal of final traces of CO. Preferential oxidation of carbon monoxide has lots of advantages: the oxidation is rapid and responds quickly to changes in operating conditions (Trimm, 2005; Avgouropoulos *et al.*, 2008).

The following reactions are carried out in a PROX system (Park *et al.*, 2009):



In reaction (2.8), the CO/O₂ ratio is between 0.5 and 1. The rate of reaction (2.9) is high over non-selective catalysts. This situation results almost complete consumption of oxygen and therefore, decreased CO conversion and selectivity (Huanling *et al.*, 2007; Tompos *et al.*, 2008). Reaction (2.10) is called methanation and should be avoided, because methanation reaction consumes larger amount of hydrogen than PROX and it is necessary to eliminate CO with a minimum hydrogen loss (Ko *et al.*, 2006; Tompos *et al.*, 2008).



The significant parameters affecting the process are then, selection of the best catalysts and operating conditions that minimize the oxidation of hydrogen (Trimm, 2005; Tompos *et al.*, 2008).

2.4. PROX Catalysts

The requirements of an ideal PROX catalyst should include (Avgouropoulos *et al.*, 2008; Faubion, 2007):

- High overall activity
- High selectivity with respect to the undesired H₂ oxidation side reaction
- Tolerance to high levels of CO₂ and H₂O present in the reformat gas

- Operation temperature between the outlet temperature of the low temperature WGS and the inlet of the PEM fuel cell

Researchers have reported a number of catalysts meeting these requirements. These catalysts can be classified as metal oxide catalysts, supported Ru, Rh, Ir catalysts, supported Pt catalysts and supported gold catalysts (Ko *et al.*, 2006).

2.4.1. Metal Oxide Catalysts

The usage of catalysts containing a pair of transition metal and its oxide has been claimed to be active in preferential oxidation of carbon monoxide. These catalysts include copper/copper oxide, silver/silver oxide and the higher and lower oxides of cerium (Park *et al.*, 2009).

Teng *et al.* (1999) examined 3d transition metal oxides for the catalysis of the carbon monoxide oxidation in a hydrogen rich environment. At high temperatures, most of the metal oxides were reduced to lower oxides or metallic phases due to the highly reductive condition used, which resulted high selectivity to the H₂ oxidation and CH₄ formation. Among 3d transition metal oxides, CoO was reported to show the best performance for this reaction.

Among the mixed metal oxides, CuO-CeO₂ has been reported to be quite active for PROX by several groups. Gurbani *et al.* (2009) studied CuO-CeO₂ catalyst prepared by wet impregnation and deposition-precipitation methods. Catalysts prepared by wet impregnation resulted with a high surface area and small particle size, as well as a great activity and selectivity, while catalysts prepared by deposition precipitation resulted with a lower activity for PROX suggesting the lower intimate contact between CuO and ceria. According to Gamarra and Martínez-Arias (2009), the ability of CuO-CeO₂ catalysts for PROX is mainly due to the synergistic redox properties produced upon formation of CuO-CeO₂ interfacial sites.

2.4.2. Supported Ru, Rh and Ir Catalysts

Among Ru, Rh and Ir catalysts, the supported Ru catalysts have been reported to be more active for the PROX (Park *et al.*, 2009). Echigo *et al.* (2003) studied the performance of the Ru catalyst in a single stage carbon monoxide preferential oxidation removal reactor for residential polymer electron membrane fuel cell cogeneration systems and reported that the outlet CO concentration was reduced below 1 ppm even with a oxygen to carbon monoxide ratio of 1.5.

Huang *et al.* (2007) performed an experimental investigation for the cleanup of CO over Pt/Al₂O₃ and Ru/Al₂O₃ catalysts and examined the effects of transition metals Co and Fe addition to Ru/Al₂O₃ catalyst. They reported that Ru/Al₂O₃ catalysts produce a higher methane yield than the Pt/Al₂O₃ catalysts and the methane yield is related to the level of noble metal addition and the temperature. They concluded that, CO conversion over Ru/Al₂O₃ catalyst increased with the increased Ru at the temperatures below 80°C. Moreover, the CO conversion rate was significantly improved by the addition of transition metals Fe and Co. However, the addition of Fe to the Ru/Al₂O₃ reduces the methane yield more compared with the addition of Co.

2.4.3. Supported Pt Catalysts

Pt based catalysts are studied by several groups and known to be highly active for PROX especially in the presence of a promoter such as Co, Ce, Fe, Sn oxides (Kim *et al.*, 2008; Uguz and Yildirim, 2009).

Jain *et al.* (2009) reported a study of modified alumina supported Pt based catalysts with various metal oxides promoters for selective oxidation of CO in the presence of excess hydrogen. Among the elements tested, the activities of the promoters followed the trend Co \approx Fe>Mn>Sn \approx Cu \approx Ni>Cr. A better activity and selectivity was observed at low promoter loadings of 0.15-0.25 wt%.

Akin *et al.* (2001) studied the effects on preparation parameters on physical properties and activity over Pt-SnO₂/γ-Al₂O₃. The catalyst with the Pt:Sn ratio of 1:6 resulted the highest CO conversion between 323-423°C.

Kim *et al.* (2008) studied Pt-Co/Al₂O₃ catalysts with different Co/Pt ratios for PROX. The Pt/Al₂O₃ catalysts were prepared by impregnation method and the Co promoter was added by incipient to wetness method. The activity of the catalyst towards PROX increased with the addition of the Co promoter as well as with the Co/Pt ratio.

Ince *et al.* (2005) studied the selective low temperature CO oxidation in hydrogen-rich streams over Pt-Co-Ce/Al₂O₃ catalysts. 100% conversion was achieved with the ratios of 1.4 wt% Pt-1.25 wt% Co-1.25 wt% Ce/Al₂O₃ at 90°C with a feed of 1% CO, 1% O₂, 60% H₂ and balance He. In more realistic conditions, with the addition of 25% CO₂ and 10% H₂O, 100% conversion was achieved at 110°C for 300 min time-on-stream.

Gunay and Yildirim (2008) modeled the design of Pt-Co-Ce/Al₂O₃ catalyst for the low temperature CO oxidation in hydrogen streams using artificial neural networks in order to analyze the effects of Pt wt%, Co wt%, Ce wt%, calcinations temperature and time. The Pt-Co-Ce/Al₂O₃ catalysts were prepared by incipient to wetness impregnation method. CO conversion increased with the increasing Pt wt%, Co wt% and Ce wt%. However, the most significant parameter was concluded to be Pt wt% rather than the effects of Co and Ce.

2.4.4. Supported Gold Catalysts

The discovery of gold based catalysts has gained wide attention among the other precious metals since Haruta *et al.* (1987) reported gold catalysts to be highly active for CO oxidation at temperatures as low as -70°C. Since then, the high reactivity of nanosized gold particles has become the basis of new discoveries (Hutchings, 2007).

The gold catalysis is rapidly developing. However, gold catalysis is still quite new and undeveloped compared with the Pt group metals (PGMs). Gold based catalysts have the potential advantages over Pt group metals with their lower cost, relatively greater price

stability and greater availability in addition to their promising technical performance. On the other hand, the expected increase in the demand of gold due to its novel commercial uses as a catalyst should be taken into consideration. This increased demand will result in strains on gold supply and therefore increase in the prices of gold (Cameron *et al.*, 2003; Corti *et al.*, 2005).

The studies on the gold based catalysts have been widely reported in the literature; however there is still no clear picture of the origin of the catalytic activity. This is most probably due to the unusual sensitivity of small gold particles to the environment resulting difficulties in reproducing the synthesis of gold catalysts and problems associated with the catalytic tests. Therefore, the results reported in literature concerning gold catalysis are often contradictory (Li *et al.*, 2006).

The nature of the support plays a vital role in determining the activity of gold catalysts (Pillai and Deevi, 2006). Some of the most studied supported gold catalysts are Au/CeO₂, Au/MnO_x, Au/Fe₂O₃, Au/TiO₂, Au/ZnO and Au/Al₂O₃.

2.4.4.1. Au/CeO₂ Catalysts. The reducibility of the support affects the activity of the gold catalysts. Being an easily reducible metal oxide, ceria is currently used as a support for gold catalysts. Many studies conducted for Au/CeO₂ catalysts for low-temperature CO oxidation (Pillai and Deevi, 2006).

Pillai and Deevi (2006) investigated ceria supported gold catalysts prepared by deposition-precipitation method. Catalysts with a gold content of 1 wt% were highly active for room temperature CO oxidation.

Romero-Sarria *et al.* (2008) prepared stainless steel monolithic catalysts coated with 1% Au/CeO₂ catalysts and investigated their activity in CO oxidation both in dry and wet conditions. Although the activity in wet and dry conditions was similar at the temperatures lower than 80°C, the activity in wet conditions was higher at high temperatures.

Manzoli *et al.* (2008) modified ceria by the addition of various cations such as Sm³⁺, La³⁺ and Zn²⁺. The catalysts were prepared by co-precipitation technique and their

activities for the PROX reaction were investigated. The addition of Sm^{3+} , La^{3+} and Zn^{2+} to the Au/CeO₂ catalysts positively affected their activity towards CO oxidation. Addition of these cations also enhanced the tolerance of the Au/CeO₂ catalysts towards CO₂ and H₂O.

2.4.4.2. Au/MnO_x Catalysts. Having a superior ability to activate and supply oxygen, MnO_x combined with gold nanoparticles have also been studied for low temperature CO oxidation. Au/MnO_x catalysts are generally prepared by co-precipitation method. However, the final material obtained by this method contains alkaline metals, which is undesired, and a high amount of gold loading is required for high activity (Wang *et al.*, 2008).

Au/TiO₂ has been reported to be very active for CO oxidation as well as for hydrogen oxidation which results low selectivity of CO oxidation. On the other hand, Au/MnO₂ has been reported to have high selectivity of but low activity for CO oxidation (Chang *et al.*, 2007). From that point Chang *et al.* (2007) investigated Au/MnO₂-TiO₂ catalyst for preferential oxidation of CO in a H₂-rich environment. The catalysts were prepared by deposition-precipitation method. They concluded that Au/MnO₂-TiO₂ catalysts were more active than Au/TiO₂ attributed to the effects of gold particle size and gold-support interactions.

Wang *et al.* (2008) studied single phase manganese(III) oxide ($\alpha\text{-Mn}_2\text{O}_3$) which have previously reported to have better redox properties and structural stability leading to be more effective than other MnO_x materials. The Au/ $\alpha\text{-Mn}_2\text{O}_3$ catalyst prepared by deposition-precipitation method resulted with a high activity and stability toward low-temperature CO oxidation both in the presence and absence of H₂ under mild conditions.

2.4.4.3. Au/Fe₂O₃ Catalysts. Au/Fe₂O₃ catalysts are among the most commonly studied catalysts for preferential CO oxidation. Khoudiakov *et al.* (2005) compared Au/Fe₂O₃ catalysts prepared by deposition-precipitation with urea and co-precipitation methods. They reported in their study that, with the same amount of gold precursor, the catalysts prepared by deposition-precipitation resulted with a higher activity compared with the co-precipitation method due to the complete precipitation of gold from the preparation solution.

Scirè *et al.* (2008) studied Au/Fe₂O₃ catalysts prepared by deposition-precipitation or co-precipitation for selective oxidation of CO, and investigated the effect of pretreatment conditions, and they found that the catalytic activity was strongly affected by catalyst pretreatment procedure. The conversion was found to decrease with the increasing calcinations temperature over both catalysts prepared by deposition-precipitation and co-precipitation.

2.4.4.4. Au/TiO₂ Catalysts. The dispersion and average size of the gold particles are strongly dependent on the nature of the support. Centeno *et al.* (2003) investigated the deposition of gold on TiO₂, TiO_xN_y and TiN by deposition-precipitation technique with the same experimental conditions. Among the catalyst studied, the best performance was obtained over the TiO₂ supported catalyst with a homogeneous distribution of gold particle smaller than 4 nm.

Chang *et al.* (2008) studied the effects of preparation variables of Au/TiO₂ catalyst in photodeposition method for the preferential oxidation of CO at various temperatures with O₂/CO ratio of 1. The catalysts were obtained with a particle size of 1.5 nm with a low-power UV source at an optimum irradiation time. The gold loading, as well as the size of gold nanoparticles deposited on TiO₂, increased with the increasing irradiation time at the high power (400 W) of light source.

Zanella *et al.* (2005) studied Au/TiO₂ catalyst prepared by two different methods which are cation adsorption (CA) with [Au(en)₂]³⁺ and deposition-precipitation with urea and NaOH. In the case of cation adsorption method, small gold particles were obtained, however the catalyst loading was low. Also, in the case of deposition precipitation with NaOH method, a limited amount of gold was deposited on TiO₂ support. However, in the case of deposition precipitation with urea method, all the gold that present in the preparation solution was deposited on the TiO₂ surface.

Li *et al.* (2006) also investigated Au/TiO₂ catalysts prepared by deposition-precipitation with NaOH and impregnation methods. In the case of deposition-precipitation method, the catalysts were obtained with a good reproducibility due to the exact control of the pH and the drying conditions. On the other hand, wet impregnation method followed

by ammonia steam treatment surprisingly resulted in 2-4 nm gold particles highly dispersed on the TiO₂ surface. Therefore, they reported that, impregnation method could also be used for the preparation of Au/TiO₂ catalysts.

2.4.4.5. Au/ZnO Catalysts. As the Au/TiO₂ and Au/Fe₂O₃ catalysts are not stable in the presence of H₂O and CO₂, Au/ZnO catalysts were also studied for the low temperature selective CO oxidation.

Wang *et al.* (2003) investigated the catalytic performance of Au/ZnO catalysts for carbon monoxide oxidation at ambient temperature. The catalysts were prepared by coprecipitation method using Na₂CO₃ as precipitating agent. The catalysts showed high catalytic activity and stability for CO oxidation.

Souza *et al.* (2008) also investigated Au/ZnO catalysts prepared by precipitation-deposition method. The gold content was found to be dependent on competition among ions and exposure to light.

2.4.4.6. Au/Al₂O₃ Catalysts. The gold particles, if they are present as nanoparticles, supported on γ -Al₂O₃ have been investigated to be efficient catalysts for the selective oxidation of CO at low temperatures (Georgaka *et al.*, 2008; Mozer *et al.*, 2009).

Bethke and Kung (2000) reported the results of a study for Mg promoted Au/Al₂O₃ catalysts for preferential oxidation of carbon monoxide. The Au-Mg/Al₂O₃ catalysts were synthesized by deposition-precipitation method. The Mg was added with the Mg:Au ratio of 1.55. The catalysts were active in preferential oxidation of carbon monoxide in H₂-rich stream. The selectivity and activity of the catalysts were found to be dependent on the preparation procedure particularly, on whether Mg citrate was added to the preparation solution or not.

Pansare *et al.* (2005) studied Au/ γ -Al₂O₃ catalysts with varying Cl⁻ impurity concentrations and average particle sizes, and they compared these catalysts with a Pt/ γ -Al₂O₃ catalyst using reaction kinetics and steady-state isotropic transient kinetic analysis. The Au based catalysts were prepared by deposition-precipitation (DP) method, while Pt

based catalysts were prepared by incipient to wetness impregnation method. Both catalysts showed high catalytic activities. However, Au/Mg/Al₂O₃ catalysts yielded the smallest Au particles and the least Cl⁻ content. Therefore, they reported in their study that Mg helps to reduce the particle size of gold and the residual Cl⁻ content.

Gold supported on non-reducible alumina was reported to be very poor for CO oxidation in the absence of hydrogen by many researchers. However, in a hydrogen-rich stream, the activity of the Au/Al₂O₃ has significantly increased. Focusing on that point, Quinet *et al.* (2008) investigated Au/ γ -Al₂O₃ catalysts for a better understanding of the hydrogen effect on preferential CO oxidation. Au/ γ -Al₂O₃ catalysts were prepared by direct anionic exchange method. 1.42*10⁻⁴ M HAuCl₄ solution was added to the support and stirred for 1 hour at 70°C. Next, the slurry was filtered and washed with warm deionized water. In order to minimize the residual chloride, the catalyst was suspended in an ammonia solution for 1 hour. Then, the slurry was again filtered and washed with deionized water. Finally, the catalyst was dried at 120°C overnight, followed by calcinations in air at 300°C for 4 hours with a ramp of 0.5°C/min. They reported that the positive effect of hydrogen is not only due to the water promotion but also, the hydrogen is directly involved in the reaction mechanism.

Moroz *et al.* (2008) reported the catalytic properties of Au/Al₂O₃ catalysts prepared via various processes, which are deposition-precipitation (DP), incipient wetness, chemical liquid-phase grafting (CLPG) and chemical vapor deposition (CVD). The catalysts were tested for the preferential CO oxidation. The catalysts prepared by DP method produced the smallest gold particles with the narrowest size distribution. The catalysts prepared by impregnation followed by reduction with H₂ also resulted as a promising method with rather uniform size distribution. However, the catalysts prepared by CVD were characterized with an “egg shell” type distribution of the supported component unlike the catalysts prepared by DP or incipient wetness methods. On the other hand, CLPG catalysts were obtained only in the form of large metal crystallites. Small gold nanoparticles without residual chloride were found to be highly active for preferential CO oxidation.

Mozer *et al.* (2009) investigated Cu promoted Au/Al₂O₃ catalysts for preferential oxidation of carbon monoxide. The catalysts were prepared by deposition-precipitation

method at room temperature. An aqueous solution of HAuCl_4 at pH 8 was added to the $\gamma\text{-Al}_2\text{O}_3$ and deionized water under vigorous stirring. The solution was kept at pH 8 via an aqueous solution of NaOH. CuCl_2 solution was added to the suspension and stirred for 2 hours. Next, the suspension was vacuum filtered, washed twice with deionized water and dried at 120°C for 16 hours. Calcination was avoided due to sinterization of gold particles during thermal treatment. Through this method small gold particles were obtained. Addition of the Cu promoter increased CO selectivity, decreasing the H_2 consumption.

2.5. Effect of Mg Promoter for Au/ Al_2O_3 Catalysts

The presence of an alkali metal generally increases the activity and selectivity of the precious metal catalyst. This enhancement is explained by the interaction between CO and the precious metal. Moreover, the electron density of the precious metal is increased due to the electron transfer from the alkali metal to the precious metal (Cho *et al.*, 2006). Hence, many researchers investigated the effect of alkali promoter on the catalyst activity and selectivity.

Grisel and Nieuwenhuys (2001a) studied the catalytic activity of Au/ Al_2O_3 and Au/ $\text{MO}_x/\text{Al}_2\text{O}_3$ (M= Cr, Mn, Fe, Co, Ni, Cu and Zn) for CO oxidation. Addition of the promoter to the Au/ Al_2O_3 highly increased the activity. In another study, Grisel and Nieuwenhuys (2001b) studied the selective oxidation of CO on Au/ Al_2O_3 and Au/ $\text{MO}_x/\text{Al}_2\text{O}_3$ (M= Mg, Mn) catalysts. Addition of MgO and MnO_x increased the CO oxidation activity and selectivity towards CO_2 . For both Au/MgO/ Al_2O_3 and Au/ $\text{MnO}_x/\text{Al}_2\text{O}_3$ selectivity towards CO_2 observed above 0.90 in the presence of hydrogen. The positive effect of the Mg promoter was explained with the stabilization of small gold particles that are more active in CO oxidation.

Szabó *et al.* (2008) tested Au/ Al_2O_3 catalysts modified with Mg promoter in CO oxidation. Results obtained from activity tests showed that Mg promoted Au/ Al_2O_3 catalysts were highly active.

Tezcanli (2008) studied the effects of various promoters (Ce, Co, Ni, Mg, Mn and Fe) on the activity and structure of the Au/ Al_2O_3 catalysts for preferential oxidation of CO.

The metal oxide promoter was loaded to the alumina support by using incipient to wetness impregnation method and the deposition of the gold nanoparticles was achieved by homogeneous deposition precipitation method using urea as the precipitating agent. The catalysts containing 1.25 wt% Mg and 2.5 wt% Mg resulted in comparable CO conversions. However, when the Mg wt% was increased to 5, activity decreased significantly nearly in all temperatures. The maximum CO conversion was achieved at 50°C with 1 wt% Au and 1.25 wt % MgO.

2.6. Effect of Preparation Variables for Au/MgO/Al₂O₃ Catalysts

Although several studies on gold based catalysts have been published, there is still no clear picture of the origin of the catalytic activity of gold catalysts. Moreover, the results obtained from the literature concerning gold catalysis are often contradictory due to the unusual sensitivity of small gold particles to the environment which leads reproducibility problems (Li *et al.*, 2006). Therefore, it is crucial to prepare gold based catalysts through a careful procedure in order to obtain nano-sized gold particles well dispersed on the support (Carabineiro and Thompson, 2007).

The nature of the Au active site has not been resolved for CO oxidation reaction. But, researchers mostly agreed that there is a significant correlation between the activity and the particle size of gold (Yang *et al.*, 2005). The selectivity also depends on the gold particle size. The critical diameter of gold particles seems to be 2 nm because the gold nanoparticles that are smaller than 2 nm behave rather different than bulk gold, and this critical diameter approximately corresponds to a 3 or 4 atoms thickness on the support (Bethke and Kung, 2000; Nieuwenhuys *et al.*, 2004). This dependence was explained by Haruta and Daté (2001) that the active catalysts contain metallic gold which give CO absorption band at 2112 cm⁻¹ are not responsible for steady-state high catalytic activity, and the smooth surfaces of the metallic gold do not adsorb CO at room temperature. Therefore CO is adsorbed only on steps, edges and corner sites making the nano-sized gold particles more active.

The activity of gold catalysts also strongly depends on the nature of the support. In fact, among the various supported gold catalysts studied, Au/Al₂O₃ shows one of the

largest variations in activity (Yang *et al.*, 2005). Addition of various MO_x promoters to the Au/Al₂O₃ results with an enhancement in activity and it has been proved that Au/MgO/Al₂O₃ catalysts are highly active in low-temperature CO oxidation (Szabó *et al.*, 2008; Nieuwenhuys *et al.*, 2004).

In addition to the particle size of the gold, and the nature of the support and promoter, the residual chloride has also significant impact on the activity of gold catalysts because the chloride is a very potent inhibitor of the carbon monoxide oxidation activity. Furthermore, the chloride ions and the gold easily combine to form bridges, favoring the growth of the particles upon heating. The residual chloride causes the agglomeration of gold, thus affects the reducibility of Au cation and the particle size, and suppresses catalytic activity. The amount of residual chloride is generally minimized by adsorption of gold at a high pH and by washing the catalyst with deionized water for several times before drying (Yang *et al.*, 2005; Ivanova *et al.*, 2006).

Depending on the preparation technique, the pH of the synthesis solution is also important for activity. In most techniques pH is adjusted to 7-10. At a lower pH, Au loading is higher; however the residual chloride is also higher and therefore, activity gets lower. On the other hand, at a higher pH, it is possible to obtain much more active catalysts although the Au loading is lower. For an efficient catalyst, the aim is to obtain the catalyst with a higher gold loading and a proportionally higher activity. Hence a careful control of the pH during the preparation procedure is critical (Yang *et al.*, 2005; Moreau *et al.*, 2007).

The gold nanoparticles have a much lower melting point (about 673 K) compared with the bulk gold that is 1346 K. The calcination at high temperatures should be avoided to prevent sinterization of gold particles (Nieuwenhuys *et al.*, 2004; Mozer *et al.*, 2009). According to the study of Tezcanlı (2008) the calcination of the Au/Al₂O₃ catalysts at 300°C prior to reduction treatment has a negative effect over the CO oxidation activity.

The optimum reduction temperature depends on the nature of the support, because the interactions between gold and the support are different (Nieuwenhuys *et al.*, 2004). According to the study of Tezcanlı (2008) reduction treatment in 100% H₂ environment also has superiority over the treatment in 4 vol% H₂ in He balance.

The contact of the gold nanoparticles with the support is quite important in the catalytic activity. Therefore, it has also been reported by several researchers that the activity of the gold catalysts is quite sensitive to the preparation technique (Nieuwenhuys *et al.*, 2004; Yang *et al.*, 2005). All of these procedures should be carried with minimum exposure to light in order to minimize possible light-sensitive reactions of the Au precursor (Mozer *et al.*, 2009).

2.7. Preparation Methods for Nano-sized Au Catalysts

In 1985, Schwank (1985) commented that “in spite of its low intrinsic activity, the gold can influence the activity and selectivity of Group VIII metals”. In fact, gold was an attractive candidate for catalysis in many applications. Actually, the turning point of catalysis by gold was the following two inventions (Hutchings and Haruta, 2005):

- The prediction that gold would be the best catalyst for hydrochlorination of acetylene and,
- The discovery that supported nano-sized gold particles are highly active for carbon monoxide oxidation at low temperature

When Haruta discovered that composite oxides of gold with 3d transition metals of Group VIII were much more active for carbon monoxide oxidation even at -76°C , it had been a turning point for both him and catalysis community (Hutchings and Haruta, 2005). After that, there has been a growing interest on catalysis by gold.

In order to obtain an active gold catalyst as nanoparticles well dispersed on the support, the preparation procedure is crucial (Carabineiro and Thompson, 2007). Highly dispersed gold catalysts can be produced via co-precipitation, deposition-precipitation, homogeneous deposition precipitation, impregnation, vapor phase methods and grafting.

2.7.1. Co-Precipitation Method

Co-precipitation (CP) method is one of the first to be used to prepare gold catalysts (Carabineiro and Thompson, 2007). In this method, an aqueous solution of HAuCl_4 and a

metal nitrate is poured into an aqueous solution of Na_2CO_3 in order to obtain a hydroxide or carbonate precipitate (Haruta, 1997). The two hydroxides are precipitated simultaneously and aged for 1 hour. Afterwards, the precipitates are washed with water, filtered, dried overnight and calcined in order to obtain powder catalysts.

The main point to obtain gold nanoparticles homogeneously dispersed on the support is that the metal salt concentration has to be around $0.1\text{-}0.4 \text{ ML}^{-1}$. In addition to this, the careful control of the pH in the range of 7-10 and temperature between $47\text{-}87^\circ\text{C}$ are the important factors to be cared during the preparation process (Carabineiro and Thompson, 2007).

2.7.2. Deposition Precipitation Method

Deposition precipitation method is one of the easiest methods to handle for gold based catalyst preparation. In this method, the pH of an aqueous solution of HAuCl_4 is adjusted to a fixed point in the range of 6-10. Then, a metal oxide support in any form, powder, honeycomb, thin film, etc. is immersed in the solution under vigorous stirring. In order to keep the solution at that pH range and minimize the presence of residual chloride an aqueous solution of NaOH is used. After stirring for 2 hours, the catalyst is filtered, washed with deionized water and dried at 120°C for 16 hours (Haruta 1997; Mozer *et al.* 2009).

In this method the dispersion and size of the gold catalysts strongly depends on the pH. At pH values higher than 6, the main species in the gold solution is transferred from AuCl_4^- to $[\text{Au}(\text{OH})_n\text{Cl}_{4-n}]^-$ ($n=1\text{-}3$) and the Au catalysts are obtained smaller than 4 nm (Haruta, 1997). At pH values lower than 6, on the other hand, the hydrolysis of Au decreases. It has been reported that, pH 7-8 are preferable depending on the support and the value of n is close to 3 at this pH range (Carabineiro and Thompson, 2007).

2.7.3. Homogeneous Deposition Precipitation Method

Homogeneous deposition precipitation method leads to the smallest average gold size, hence the highest activity among all preparation methods. In this method, an aqueous

solution of hydrogen tetrachloroaurate(III) (HAuCl₄) and excess urea are added to the support. The initial pH is approximately 4. The suspension is vigorously stirred and heated to 70°C in order to decompose urea (Georgaka *et al.*, 2008):



The formation of CO₂ shifts the reaction completely to the right. Also, with the formation of OH⁻, the pH of the solution increases gradually and since the pH is controlled through a chemical reaction, which takes place throughout the whole solution, a much more homogeneous solution is obtained compared with other methods (Georgaka *et al.*, 2008).

The temperature is maintained at 70°C until the pH of the solution slowly and gradually increases to 7-8. Then, the suspension is filtered, washed with demineralized water several times in order to remove residual Cl⁻ and dried overnight (Georgaka *et al.*, 2008; Grisel and Nieuwenhuys, 2001a).

2.7.4. Impregnation Method

Impregnation is the classical method to prepare supported noble metal catalysts. This method involves impregnation of a support with a large volume of a metal salt solution. An alternative variation of this method is incipient wetness method (IW) in which the pores of the support are filled with the solution (Carabineiro and Thompson, 2007).

Generally, conventional impregnation method has not been considered as an effective method to prepare gold catalysts, because it is difficult to obtain Au particles smaller than 10 nm by this method and this leads to low catalytic activity for low-temperature CO oxidation. However, some researchers have reported modified impregnation methods that can be applied for gold catalysts and these catalysts can be as active as the ones prepared by co-precipitation method (Li *et al.*, 2006; Lee and Gavriilidis, 2002).

2.7.5. Vapor Phase Methods and Grafting

These two methods are similar to each other. In the vapor-phase method, which is also called as chemical vapor deposition (CVD) method, the vapor of an organic gold compound, typically dimethyl-gold(III)-acetyl acetonate, is transported onto an evacuated metal oxide support. Then, the adsorbed organic gold compound is pyrolyzed in air to decompose it into small gold particles (Haruta, 1997).

In the grafting method, a gold complex in solution reacts with the surface of a support and the compounds $[\text{Au}(\text{PPh}_3)]\text{NO}_3$ and $[\text{Au}_9(\text{PPh}_3)_8](\text{NO}_3)_3$ are grafted onto a surface for a number of wet hydroxides. However, the size of gold particles obtained by these methods are relatively large and are not effective (Carabineiro and Thompson, 2007).

2.7.6. Chemical Direct Anionic Exchange Method

This method involves the exchange of protons and other cations of the support with the cations of the active metal. This process is generally effective with zeolites to produce Au/zeolite systems. Some researchers also reported the direct anionic exchange method of the gold species with the hydroxyl groups of an alumina support (Carabineiro and Thompson, 2007). For the complete removal of residual Cl^- , the catalyst is washed with a concentrated solution of ammonia after drying. However, the gold oxide and the ammonia can produce fulminating gold which is explosive, so can be dangerous (Carabineiro and Thompson, 2007).

2.8. Monolithic Catalysts

According to some authors, the development of monolithic catalysts has been one of the major achievements in heterogeneous catalysis of the recent years. Monoliths are mostly used as the support of the catalytically active components or as the catalyst if the catalytic component is an integral part of the monolith structure (Pérez-Cadenas *et al.*, 2005; Tomašić and Jović, 2006).

2.8.1. Characteristics of Monoliths

The term “monolith” is a combination of mono, means “single”, and lithos, means “stone”, in Greek language. A monolithic catalyst support is defined as a thin-walled honeycomb structure made from ceramics like cordierite ($2\text{MgO}\cdot 2\text{Al}_2\text{O}_3\cdot 5\text{SiO}_2$) or metals such as stainless steel or metal alloys. Although the metallic monoliths have better mechanical durability, at high temperatures they have limited thermal stability due to melting, corrosion, etc. which is not the case with the ceramic monoliths. Moreover, the amount of catalyst on the walls in a given volume of the metallic monolith is less than that of the ceramic monolith. Therefore, for the chemical controlled reactions, the ceramic monoliths are preferable compared with the metallic ones. Thickness of the channel walls as well as the shapes of the channels (oval, square, etc.) and the porosity of the ceramic monolith depend on the specific requirements of the process (Giroux *et al.*, 2005; Tomašić and Jović, 2006; Pérez-Cadenas *et al.*, 2005). The monolithic structure used in thesis is presented in Figure 2.3.



Figure 2.3. The monolithic structure used in this study

The first successful application of monolithic catalysts was in the automobile exhaust treatment. After that, many applications become available in the areas like three-way catalysts; diesel catalysts for the abatement of liquid particulate and gaseous carbon monoxide and hydrocarbons; ozone abatement in aircraft; natural gas engines; ozone destruction on automobile radiators; CO and hydrocarbon oxidation in small engines; selective reduction of NO_x; destruction of volatile organic compounds from chemical plants, domestic sources and restaurants; catalytic combustion, hydrogen generation for the

fuel cell; steam reforming of hydrocarbons; water gas shift catalysts and preferential carbon monoxide oxidation (Avila *et al.*, 2005).

Monolithic catalysts have numerous advantages which make them superior related to conventional particulate catalysts (Tomašić and Jović, 2006; Gulijk *et al.*, 2005):

- High specific surface area
- Low pressure drop
- Good interphase mass transfer
- Mostly insignificant resistance to mass transfer by intraphase diffusion through a catalytic layer (which is usually very thin)
- Good thermal and mechanical properties
- Easy scale up
- Efficient catalyst usage

Monoliths also have some disadvantages such as laminar flow through the channels yielding a high residence time distribution which is undesired for high conversion levels, lack of interconnectivity between channels, and poor radial heat conductivity (Campanati *et al.*, 2003).

2.8.2. Preparation of Monolithic Catalysts

The bare cordierite monoliths are not suitable for the catalyst applications due to their low surface area (typically $0.7 \text{ m}^2/\text{g}$) (Nijhuis *et al.* 2001). Therefore, the monolithic catalysts are most commonly prepared by depositing a layer of catalytically active, high surface area component or appropriate support such as $\gamma\text{-Al}_2\text{O}_3$ containing one or more catalytically active components to the walls or inside the walls of mostly inert monolith. If the monolith structure is available in the required support material, then the catalytically active phase can be directly deposited on the monolith. However, if the monolith is not available in the required support material, this support material should first be coated on the monolithic substrate through a process known as wash-coating (Figure 2.4) (Tomašić and Jović, 2006; Campanati *et al.*, 2003).

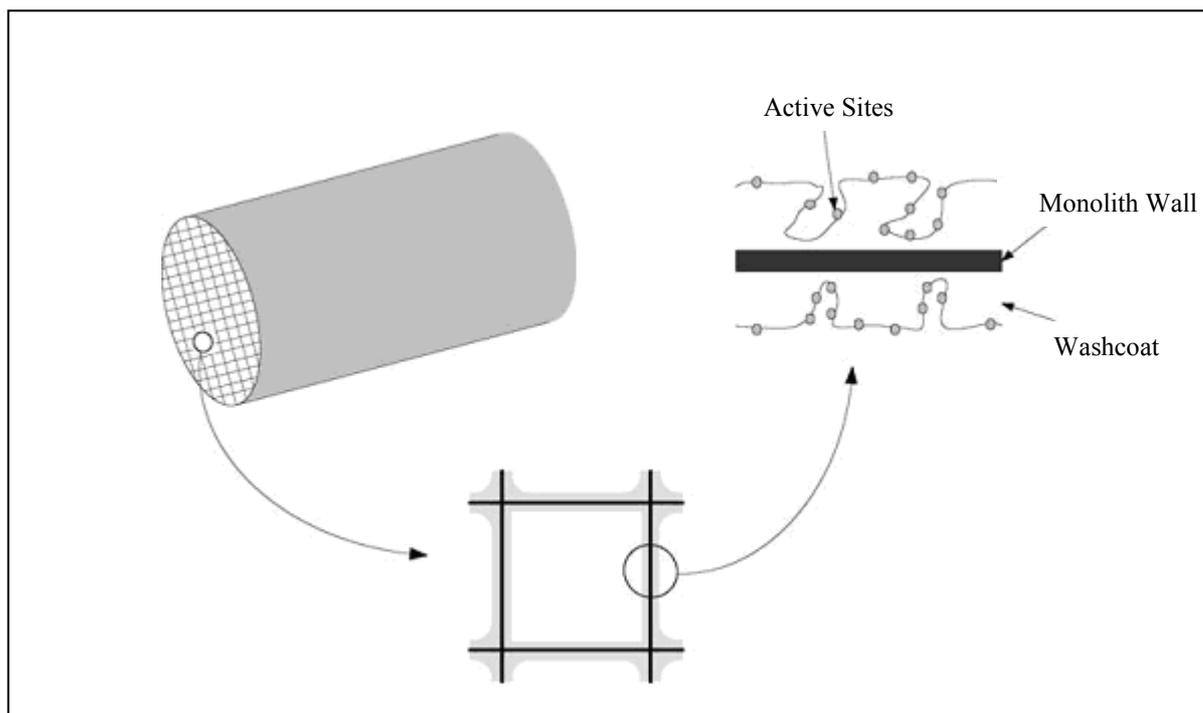


Figure 2.4. Schematic diagram of a monolith structure (Tomašić and Jović, 2006)

A support layer can be coated onto the ceramic monolith by applying either colloidal coating, sol-gel method or slurry coating and other techniques (Tomašić and Jović, 2006). The easiest way to put a wash-coat layer on a monolith support is colloidal coating method. For silica and alumina colloidal solutions of the wash-coat material are readily available. Other solutions are also available on demand.

The active phase loading, dispersion and distribution are very important for monolithic catalysts. These active elements can be involved into the monolithic structure during the wash-coating step or by using any well-known method from literature such as impregnation, precipitation, co-precipitation, deposition precipitation, ion exchange, etc. Among these methods impregnation is the easiest way to deposit the active phase onto the monolith (Vergunst *et al.*, 2001; Tomašić and Jović, 2006).

Villegas *et al.* (2007) studied the complete preparation procedure for Ni/ γ -Al₂O₃ coated cordierite monoliths and examined the effect of drying procedure on Ni distribution for wet impregnation method. The drying method applied either oven; microwave or room

temperature drying has a strong effect on Ni distribution. Microwave or room temperature drying resulted with a more homogeneous distribution.

Doker (2008) investigated the preparation methods for cordierite monolithic Pt-Co-Ce-Al₂O₃ catalysts. In this comparative study wash-coating of alumina support onto the monolith structure was applied with various techniques that are colloidal coating, slurry coating and aluminum nitrate coating. The general methodology of wash-coating was done through first wetting or filling the channels with the coating solution and then clearing the channels by forcing the air through them, followed by drying and calcination at 700°C. The bare, colloidal, slurry and aluminum nitrate coated monoliths were analyzed by total surface area measurements, ESEM and polarization optical microscope. Through the other wash-coating methods, the colloidal coating was obtained as the most promising one. The deposition of the active phase to the alumina supported monoliths was achieved by co-impregnation technique followed by microwave drying and calcination at 550°C. 15 minutes was selected as a suitable impregnation period. 100% CO conversion was obtained with alumina wash-coated and 1.4 wt% Pt-1.25 wt% Co- 1.25 wt% Ce impregnated monolithic catalysts for the preferential carbon monoxide oxidation.

The discovery of the superior catalytic activity of supported gold catalysts for the oxidation of carbon monoxide has stimulated extensive research on them (Moreau *et al.*, 2007). However, application of gold on a monolith structure is quite new and the preparation techniques are yet unclear in the literature.

Moreau *et al.* (2007) developed a preparation method for coating of Au/TiO₂ on a cordierite monolith. TiO₂ was wash-coated by applying a colloidal dispersion of TiO₂ combined with Degussa P-25 TiO₂ that has been washed, dried and crushed. Then, the deposition of the active phase was achieved by immersing TiO₂ coated monoliths in a solution of HAuCl₄ raised to pH 9 by NaOH. The solution was agitated by a magnetic stirrer in order to have the solution passed through the channels of the monolith, and was dried at 373 K. Au/TiO₂/Cordierite monoliths prepared through these procedures yield a high activity for the carbon monoxide oxidation.

Lee and Gavriilidis (2002) prepared gold catalysts supported on γ -Al₂O₃ powder by dry impregnation with HAuCl₄ solutions at different pH values and they extended their study to the wash-coated monoliths. The monoliths were cut to 6-7 mm in diameter and 50 mm in length. In the preparation of Au/ γ -Al₂O₃ monolithic catalysts, first the monolith was coated with alumina. Addition of gold to the monolith was applied by dry impregnation. The alumina coated monolith was immersed in 100 ml water mixed with 20 ml 2.5×10^{-3} M HAuCl₄ aged at pH 9 for 4 hours and stirred for 1 hour followed by washing with 500 ml hot water, drying at 120°C overnight and calcinations at 300°C for 4 hours. Similar high CO oxidation activity was observed over both the particulate and monolithic catalysts.

3. EXPERIMENTAL PROCEDURE

3.1. Materials

3.1.1. Chemicals

The chemicals used for catalyst preparation and their properties are listed in Table 3.1.

Table 3.1. Chemicals used in catalyst preparation

| Chemicals | Formula | Grade | Source | Molecular Weight (g/mole) |
|-------------------------------------|---|------------|-------------|---------------------------|
| Aluminum Oxide Colloidal Dispersion | Al_2O_3 | Research | Alpha Aesar | 101.96 |
| Magnesium nitrate Hexahydrate | $\text{Mg}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ | Extra Pure | Merck | 256.41 |
| Gold(III) chloride trihydrate | $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ | Extra Pure | Aldrich | 393.83 |
| Urea | $\text{CO}(\text{NH}_2)_2$ | Extra Pure | Merck | 60.06 |
| Sodium Hydroxide | NaOH | Pure | Merck | 40.00 |
| Sodium Carbonate | Na_2CO_3 | Lab. Grade | Aksın Kimya | 106.00 |
| Acetamide | $\text{C}_2\text{H}_5\text{NO}$ | Extra Pure | Merck | 59.07 |

3.1.2. Gases and Liquids

The gases and liquids used in this study are listed with their applications and specifications in Table 3.2 and Table 3.3 respectively. All of the gases used in this study, except carbon monoxide, were obtained from BOS Company, Istanbul, Turkey. CO was supplied by HABAS Company, Istanbul Turkey.

Table 3.2. Applications and specifications of the gases used

| Gas/Standard | Application | Specification |
|----------------------------|--------------------------|---|
| Carbon monoxide | Reactant, GC calibration | 99.0% HABAS |
| O ₂ /He mixture | Reactant | 70.3 vol. % O ₂ in He BOS |
| Hydrogen | Reactant, reducing agent | 99.99% BOS |
| Helium | Reactant (Inert) | 99.99% BOS |
| Helium | GC Carrier | 99.99% BOS |

Table 3.3. Applications and specifications of the liquids used

| Liquid | Application | Specification |
|--------|--------------------|---------------|
| Water | Reactant, cleaning | Distilled |

3.2. The Experimental Systems

The experimental systems used in this work can be described in three groups:

- **Catalyst Preparation System:** This system was used for the coating of monoliths with alumina, loading of the promoter (Mg) by impregnation method and deposition of Au by various methods (Wet impregnation, dry impregnation, co-precipitation, deposition-precipitation and homogeneous deposition precipitation).
- **Micro-reactor Flow System:** The catalytic activity of the catalysts was tested in a micro-reactor flow system for selective CO oxidation. The system consists of mass flow controllers for inlet gases and fixed bed flow reactor in a vertical furnace coupled with a programmable temperature controller.

- **Product Analysis System:** The concentrations of the reaction products and feed gases were determined by product analysis system that consists of a gas sampling section, a gas chromatograph and a data processor.

3.3. Catalyst Preparation

The cordierite monolithic support was firstly wash-coated with alumina by applying colloidal coating method, which gives the highest surface area amongst the other possible wash-coating methods according to the study of Doker (2008). After that, alumina colloidal coated monoliths were impregnated with Mg precursor solution. The Mg promoter per cent was selected as 1.25 wt% of the coated alumina weight according to the study of Tezcanli (2008). Finally, the deposition of Au was achieved by various methods that are wet impregnation, dry impregnation, co-precipitation, deposition-precipitation and homogeneous deposition precipitation.

3.3.1. Pretreatment of Monolithic Supports

Firstly, the commercial cordierite monolithic support, Corning Celcor thin-wall substrate, (kindly provided by Professor D. Uner of METU) was cut in cylinders of 11 mm diameter and 20 mm length. The diameter of the monolith cylinders was arranged to fill the inner diameter of the 1/2" stainless steel micro-reactor. The monolith cylinders were then washed with acetone in order to open the pores of and remove the impurities caused by handling during the cutting procedure, and dried in microwave oven.

3.3.2. Wash-coating with Alumina

The cordierite monolithic support was wash-coated with alumina by colloidal coating method as shown in Figure 3.1. After the pretreatment process, bare cordierite monolith cylinders were weighed and then dipped vertically into the colloidal alumina solution for two minutes. The excess solution was evacuated from the channels of the cylinders by a flow of compressed air. The monolith cylinders were dried in a microwave oven operated at 180 W for 40 min. The procedure was repeated until a 13-15 wt% increase was observed. Finally, the coated monolith was calcined in air at 973 K for two hours, with a temperature ramp of 2.5°C/min.

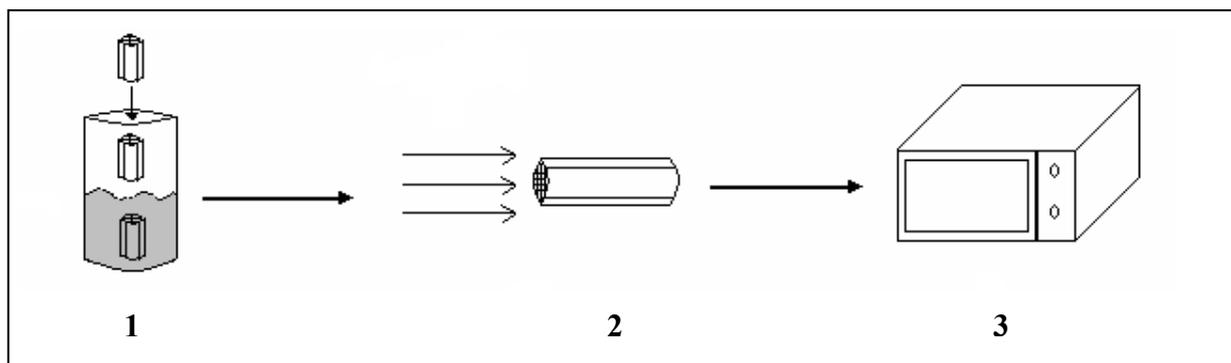


Figure 3.1. The alumina wash-coating system: 1. Dipping Procedure 2. Compressed Air Flow 3. Microwave Oven (Doker, 2008)

3.3.3. Loading of Mg Precursor

The loading of Mg promoter to the alumina coated monolithic support was achieved by the implementation of wet impregnation method. The Mg promoter weight per cent was selected as 1.25 wt% as it was used for the particulate catalyst.

An alumina coated monolith cylinder was put vertically in an open ended glass tube. The glass tube was placed into a vacuum flask and fixed by a plastic cork. The Mg precursor ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) solution was poured into the flask which was kept under vacuum via a vacuum pump. Masterflex computerized-drive peristaltic pump was used to circulate the Mg precursor solution at a rate of $5 \text{ cm}^3 \text{ min}^{-1}$ via silicone tubing. One end of silicone tubing was dipped into the precursor solution and the other end was placed into the open ended glass tube and fixed by a plastic cork. The vacuum pump and peristaltic pump were operated simultaneously and when the first droplet of the Mg precursor solution dripped over the alumina coated monolith, the impregnation time was started. The Mg precursor solution was circulated from the flask and dipped over the channels of the monolith for 15 minutes. The monolith was dried in a microwave oven for 40 minutes at 180 W and then calcined overnight at 823 K.

The impregnation system used for the loading of Mg promoter is presented in Figure 3.2. This system was also used for Au loading by wet impregnation method.

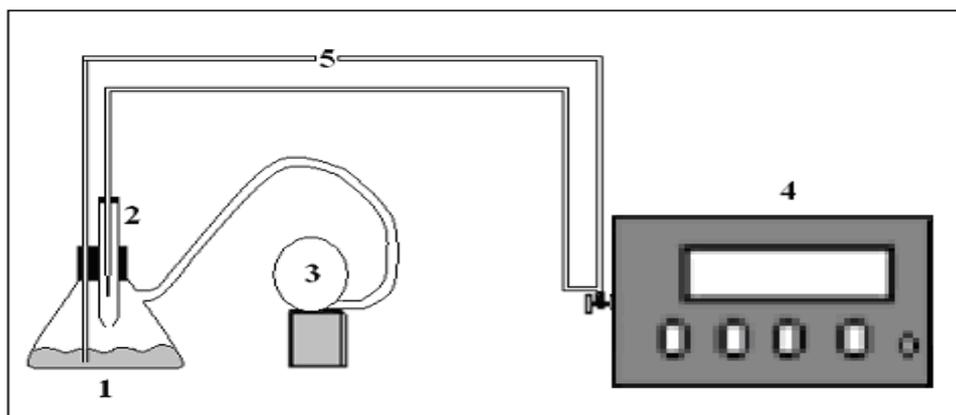


Figure 3.2. The impregnation system: 1. Vacuum Flask 2. Glass tube
3. Vacuum pump 4. Peristaltic pump 5. Silicone tubing (Doker, 2008)

3.3.4. Deposition of Au

Deposition of gold over Mg promoted Al_2O_3 wash-coated cordierite monolith support was achieved via various methods that are wet impregnation, dry impregnation, co-precipitation, deposition-precipitation and homogeneous deposition precipitation. Au weight per cent was selected as 1 wt% of the coated alumina weight for all experiments except the ones performed to see the effects of Au loading. $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (Aldrich, 99.9%) was used as Au precursor. All of the preparation techniques were carried with minimum exposure to light in order to minimize possible light-sensitive reactions of the Au precursor.

Au loading by wet impregnation method was applied by using the impregnation system described for promoter loading in section 3.3.3. In the procedure, 1 wt% $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (Aldrich, 99.9%) was dissolved in 25 ml water and circulated over $\text{Mg}/\text{Al}_2\text{O}_3/\text{cordierite}$ monoliths for 1 hour each. The catalysts were then washed with water and dried at 120°C for 16 hours.

Dry impregnation method was applied similar to the procedure of Lee and Gavriilidis (2002). Three $\text{Mg}/\text{Al}_2\text{O}_3/\text{monolith}$ cylinders were immersed in 100 ml water mixed with 20 ml $2.5 \cdot 10^{-3}$ M $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (Aldrich, 99.9%) aged at pH 9 for 4 hours. 0.5 M NaOH solution was used to adjust the pH of the solution. The solution was then stirred for 1 hour.

Afterwards, the monoliths were washed with 500 ml of hot water (95°C) and dried in air at 120°C for 16 hours.

Co-precipitation method was applied similar to the procedure described by Haruta (1997) and Carabineiro and Thompson (2007). In this method, 1 wt% $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (Aldrich, 99.9%) dissolved in 25 ml water and 10 ml solution of 0.2 M $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were poured into 150 ml solution of 1 M Na_2CO_3 . Three $\text{Mg}/\text{Al}_2\text{O}_3$ /cordierite monolith cylinders were immersed in the solution and aged at 70°C for 1 hour. Then, the monoliths were washed with hot water (95°C) several times and dried at 120°C for 16 hours.

Deposition-precipitation method was applied both at 70°C and room temperature. NaOH is used as precipitating agent. This method was processed similar to the procedure of Mozer *et al.* (2009). Firstly, 1 wt% $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (Aldrich, 99.9%) was dissolved in 25 ml water and pH of the solution was adjusted to 8 by using 0.5 M NaOH solution. Three monoliths were immersed in 200 ml deionized water and mixed with $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ solution at pH 8. The solution was kept at the constant pH of 8 under vigorous stirring for 2 hours. Finally, the monoliths were washed with deionized water and dried at 100°C for 16 hours.

In the case of homogeneous deposition precipitation method, the procedure reported by Grisel and Nieuwenhuys (2001) was followed. Three monolith cylinders were immersed in 100 ml deionized water. When the temperature was fixed at 70°C, 1 wt% $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (Aldrich, 99.9%) dissolved in 25 ml water was added under vigorous stirring. The pH of the solution was gradually increased to 7-8 by the decomposition of 100 ml solution of a 0.84 M excess urea. The solution was aged at 70°C for 4 hours. Then, the monoliths were washed with hot (95°C) water and dried at 120°C for 16 hours. It was reported the use of acetamide or hydrolyzable derivatives instead of urea was also possible (Patent DE740634, GB1220105). So, the same procedure was repeated by using acetamide as the precipitating agent with the same conditions.

The experimental system for deposition of Au over $\text{Mg}/\text{Al}_2\text{O}_3$ by the implementation of HDP method is presented in Figure 3.3. The system consists of a stirrer to achieve homogeneous mixing, a heater circulation bath to fix the temperature of the process and a

pH meter to determine the alkalinity of the solution. The methods CP and DP were also implemented by using this system, but without using the heater circulation bath.

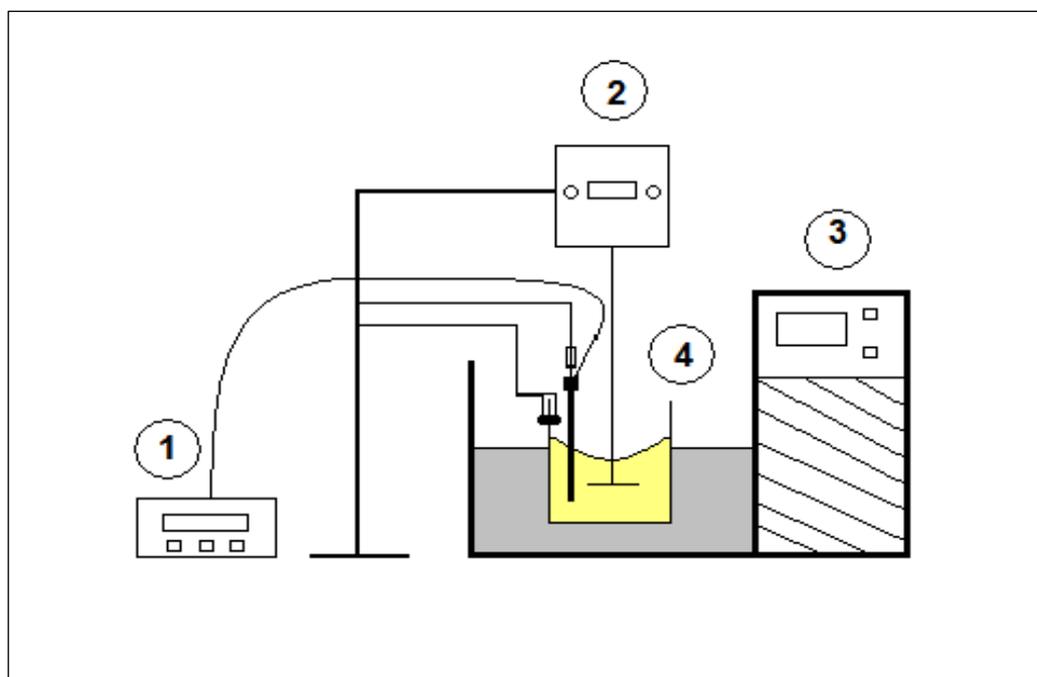


Figure 3.3. The HDP system: 1. pH meter, 2. Stirrer, 3. Heater circulation bath
4. Beaker (Tezcanli, 2008)

3.4. Reductive Pretreatment

All catalysts were reduced before the reaction and kept under He flow until the reaction test was performed. The outline of the reduction program for Au/Mg/Al₂O₃ catalysts is given in Table 3.4.

Table 3.4. Reduction program

| Segments | Starting and End Temperatures | Segment Gas |
|-------------------------------|--|---|
| First Segment | Heating from 25°C to 300°C with a heating rate 10°Cmin ⁻¹ | H ₂ with flow rate of 50 cm ³ min ⁻¹ |
| Second Segment (Reduction) | Keeping constant at 300°C for 30 min | H ₂ with flow rate of 50 cm ³ min ⁻¹ |
| Third Segment | Overnight cooling down to 25°C | He with flow rate of 25 cm ³ min ⁻¹ |

3.5. Micro-reactor Flow System

In the micro-reactor flow system, research grades of pure CO, H₂, He gases and O₂/He mixture were carried by 1/2", 1/4" and 1/8" OD stainless steel or brass tubing and fittings. Four Brooks 5850E mass flow controllers were used to control the flow rates of the inlet gases. After being mixed, the reaction gases were sent into the reaction section, which consists of an 11.5 mm ID and 55 cm long stainless steel fixed-bed down-flow micro-reactor located in a 2.4 cm ID x 40 cm furnace controlled to ±0.1 K by a Shimaden FP-21 programmable temperature controller (Figure 3.4).

Three monoliths were put into the reactor tube to form the catalyst bed in the constant temperature region of the furnace. A 1/16" K- type stainless steel sheathed thermocouple was positioned in the center point of the catalyst bed and curled outside the micro-reactor to monitor the temperature of the furnace. The spaces between inlet and outlet of the reactor-furnace were isolated by ceramic wool in order to prevent heat loss and maintain stable temperature profile.

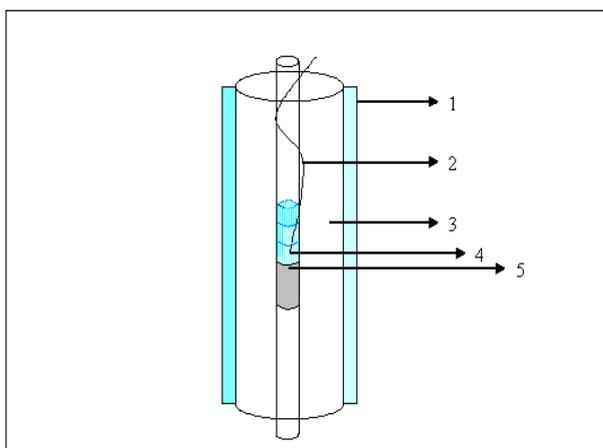


Figure 3.4. Reactor and furnace system: 1.Ceramic wool insulation 2.Thermocouple
3. Furnace 4.Monoliths 5.Catalyst bed (Doker, 2008)

The reactant gases entering the reactor or the product gases leaving the reactor were then sent either to the gas chromatograph sampling unit which has a calibrated one cm^3 sample loop for analysis or to the soap bubble meter through two on-off valves. The soap bubble meter is used for measuring the flow rate of the effluent at the ambient temperature.

3.6. Product Analysis System

A cold trap was used at the exit of the micro-reactor to condensate the water which was produced during the reaction. The cold trap included two ice boxes and coiled tubing in order to increase the contact time of flow through a cold environment.

The reactant and product streams were analyzed by an ATI UNICAM 610 Series, temperature-controlled and programmable gas chromatograph equipped with a thermal conductivity detector (TCD), ATI UNICAM 4815 Computing Integrator and CTR I concentric column. Reactant and product gas analysis conditions are given in Table 3.5.

Table 3.5. Reactant and product gas analysis conditions

| | |
|---------------------------|---------------------------|
| Column Type | CTR I (Concentric Column) |
| Outer Column Packing | Activated Molecular Sieve |
| Inner Column Packing | Porous Polymer Mixture |
| Column Oven Temperature | 303 K |
| Carrier Gas | Helium |
| Carrier Gas Flow Rate | 35 ml/min |
| Detector Type | Thermal Conductivity |
| Detector Current | 120 mA |
| Filament Temperature | 513 K (Low sensitivity) |
| Detector Oven Temperature | 373 K |
| Injector Oven Temperature | 323 K |

The entire system used in the experiments is shown in Figure 3.5.

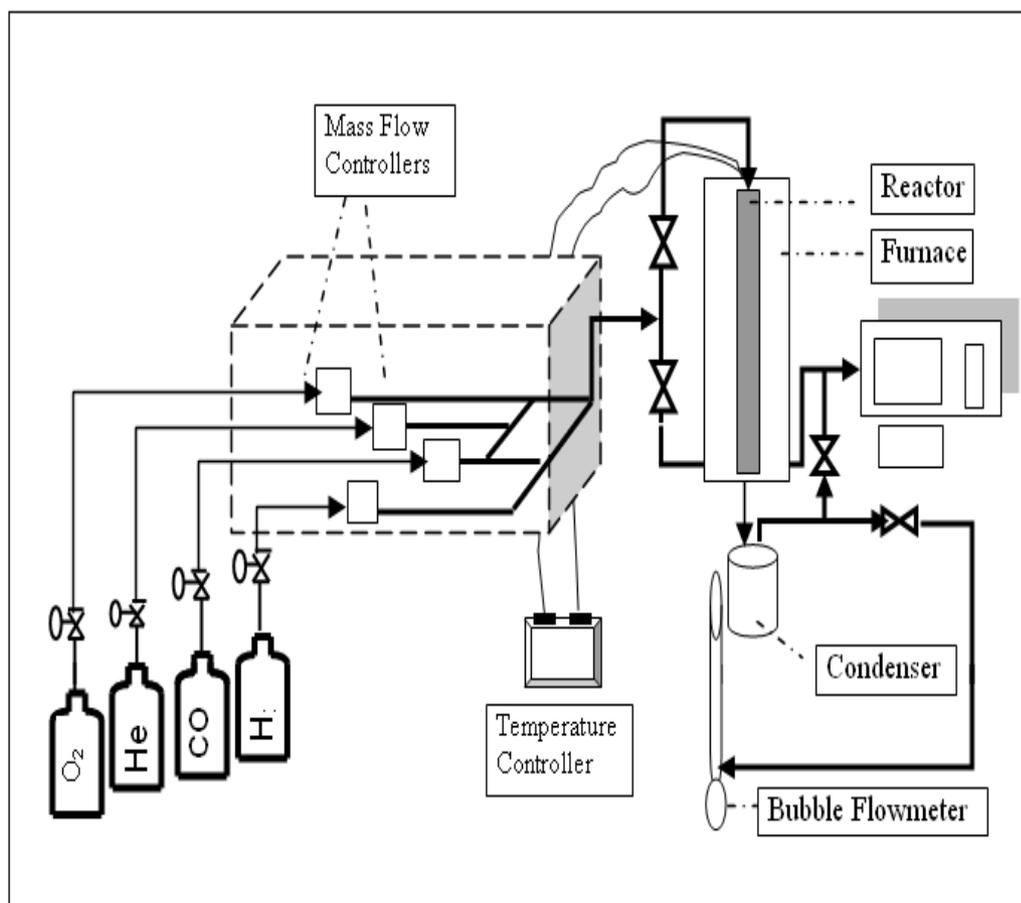


Figure 3.5. The micro-reactor flow and product analysis system (Doker, 2008)

3.7. Catalytic Activity Measurements

The activity tests were carried out in a micro-reactor flow system. After reduction at 300°C, the catalysts were cooled overnight. The temperature is then raised to the reaction temperature under a stream of 50 cm³min⁻¹ He with a ramp of 10°C/min. The temperature programmed reaction (TPR) was applied to test the catalytic activities of all the catalysts under a total flow of 100 cm³min⁻¹ in the temperature range of 50-150°C. The reaction was started at 150°C and reduced to 50°C with 20°C intervals. The samples for each temperature setting were taken after 30 minutes and 60 minutes. All the experiments were performed at atmospheric pressure. The reaction mixture used for catalytic activity tests is comprised of 60 ml/min H₂, 38 ml/min He, 1 ml/min CO and 1.6 ml/min O₂. In order to investigate the effect of O₂ composition over the CO activity, an experiment was also carried under 1 ml/min O₂.

The reaction conditions in the catalytic activity tests are given in Table 3.6.

Table 3.6. Reaction conditions for catalytic activity tests

| Parameter | Value |
|-----------------------------------|---|
| Catalyst Amount (For 3 monoliths) | 250 mg |
| Catalyst Amount (For 2 monoliths) | 166.67 mg |
| Catalyst Amount (For 1 monolith) | 83.34 mg |
| Reaction Temperatures | 50-150°C |
| Reactant Total Flow | 100.6 cm ³ min ⁻¹ |
| W/F Ratio (For 3 monoliths) | 2.49 mg.min.cm ⁻³ |
| W/F Ratio (For 2 monoliths) | 1.66 mg.min.cm ⁻³ |
| W/F Ratio (For 1 monolith) | 0.83 mg.min.cm ⁻³ |

The catalyst amount depends on the loaded alumina during the wash-coating. The intended alumina coating over the bare monolithic structure was 13-15 wt%. The first dipping for 2 minutes generally led to an increase of 9-12 wt%. So, a second dipping was employed in order to increase the alumina loading to the intended level which generally yielded a 15-20 wt% increase. In order to define the W/F ratio, the catalyst

amount for three monoliths was assumed to be approximately 250 mg corresponding the amount of alumina loading of 13-15% over three bare monoliths after the second dipping so that the results could be compared with the particulate catalysts which is usually loaded to the reactor as 250 mg in our laboratory.

3.8. Catalyst Characterization

The amount of Au and Mg loaded on the monolithic catalysts were measured on an ICP (Inductively Coupled Plasma) by TUBITAK.

4. RESULTS AND DISCUSSION

4.1. Catalyst Characterization

ICP analysis was performed by TUBITAK to determine the Au and Mg loadings. The results which are given in Table 4.1 represent the Au and Mg loadings for monolithic Au/MgO/Al₂O₃ catalysts and the result given in Table 4.2 represents the Mg loading over alumina coated monoliths before any treatment for Au loading.

Table 4.1. ICP results of Au and Mg loading for monolithic Au/MgO/Al₂O₃ catalysts

| Method | Intended Au loading (wt%) | Measured Au loading (wt%) | Intended Mg loading (wt%) | Measured Mg loading (wt%) |
|--|---------------------------|---------------------------|---------------------------|---------------------------|
| Wet Impregnation | 1% | 0.998 | 1.25% | - |
| Co-precipitation | 1% | 0.569 | 1.25% | 1.24% |
| Dry Impregnation | 1% | 0.620 | 1.25% | 1.24% |
| Deposition-precipitation at 70°C | 1% | 0.114 | 1.25% | 1.24% |
| Deposition-precipitation at 25°C | 1% | 0.380 | 1.25% | 1.22% |
| Homogeneous Deposition Precipitation with Acetamide | 1% | 0.423 | 1.25% | 1.14% |
| Homogeneous Deposition Precipitation with Urea (1 wt.% Au) | 1% | 0.547 | 1.25% | 1.19% |
| Homogeneous Deposition Precipitation with Urea (0.5 wt.% Au) | 0.5% | 0.195 | 1.25% | 1.19% |
| Homogeneous Deposition Precipitation with Urea (0.16 wt.% Au) | 0.16% | - | 1.25% | 1.22% |
| Homogeneous Deposition Precipitation with Urea (absence of Mg) | 1% | 0.562 | - | - |

Table 4.2. ICP results of Mg loading for monolithic MgO/Al₂O₃ catalysts

| Method | Intended Mg loading (wt%) | Measured Mg loading (wt%) |
|--------------|---------------------------|---------------------------|
| Impregnation | 1.25% | 1.20% |

The difference in the targeted and actual loading of Au may be attributed to the method employed and the pH of the preparation solution. It has been proved that, at a lower pH, the Au loading is higher. However, the residual chloride is also higher which lowers the activity. At a higher pH, although the Au loading is lower, generally less than 1%, it is possible to obtain much more active catalysts (Yang *et al.*, 2005). The analysis results show that the highest Au loading was observed for the impregnation method, which has resulted the lowest CO conversion and as the pH of the preparation solution increases to 7-9 depending on the method, the Au loading decreases. The targeted and actual loadings of Mg percent, on the other hand, are quite close with each other. This is an expected result considering that the loss in the material is minor in the impregnation method as in the case of Au loading.

The surface area of the alumina coated monolith was measured on a Micrometrics Flowsorb II-2300 by nitrogen adsorption from N₂-He mixtures using the multipoint technique and the BET equation by Doker (2008) and determined to be 14.35 m²/g.

4.2. Selective Carbon Monoxide Oxidation

This thesis presents the evaluation of the most promising cordierite monolithic Au/Al₂O₃ catalyst preparation method. The catalysts were tested for selective carbon monoxide oxidation in a micro-reactor flow system. After determining the most promising preparation method, the effect of Au and MgO loadings, W/F ratio, O₂ composition in the feed stream, temperature descent and ascent on CO conversion were studied. The results obtained for all reaction conditions are presented and discussed in the following sections. The conversion of CO was defined and calculated as follows:

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

4.2.1. Effect of Preparation Method

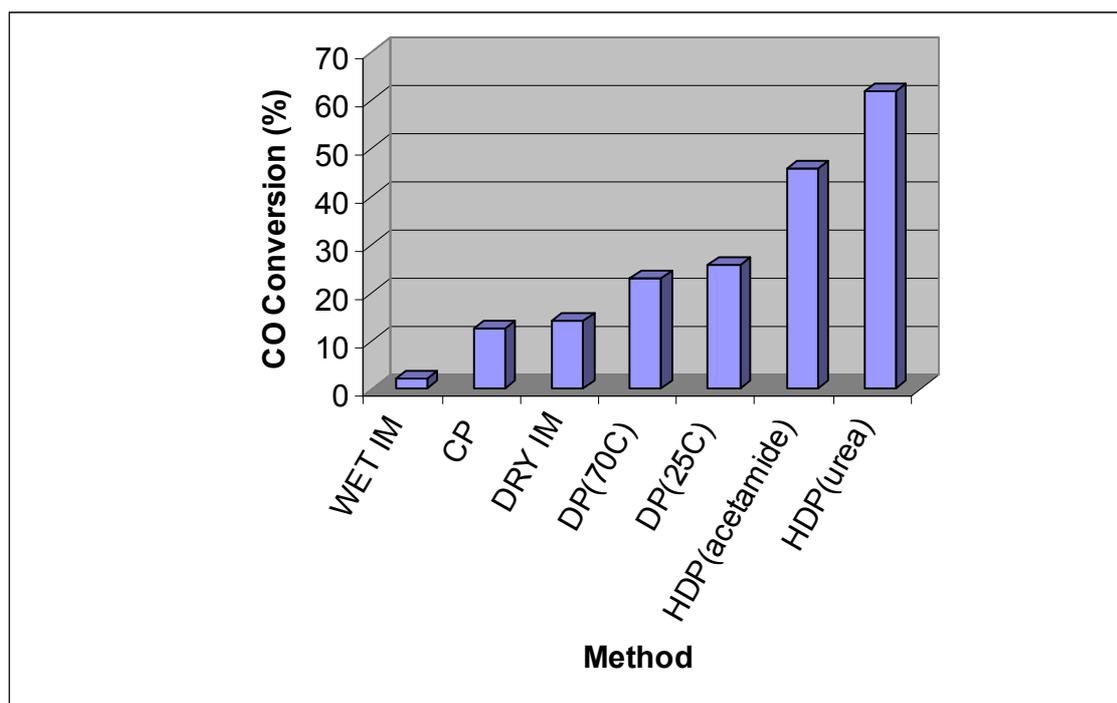
The first studies for the thesis were conducted in order to determine the most promising monolithic Au/Al₂O₃ catalyst preparation method. According to the study of Doker (2008), the most effective way to wash-coat the alumina over the cordierite monolithic structure was determined to be the colloidal coating method. According to the same study, the addition of the promoters to the alumina wash-coated monoliths was successfully achieved by wet impregnation method.

In the present study, the cordierite monolithic structures were firstly wash-coated with alumina by using its colloidal dispersion and next, the addition of Mg promoter was achieved by wet impregnation method. The addition of Au to the MgO/Al₂O₃ monolithic catalysts was conducted by various methods which are, wet impregnation, co-precipitation, dry impregnation, deposition-precipitation and homogeneous deposition precipitation. The compositions of the catalysts were selected as 1 wt% Au and 1.25 wt% Mg according to the study of Tezcanli (2008).

The catalysts prepared by each method were reduced in H₂ with a flow rate of 50 cm³min⁻¹ for 2 hours and tested for selective carbon monoxide oxidation at 110°C. The total inlet gas flow was 100.6 cm³min⁻¹ with compositions 0.99% CO, 1.59% O₂, 59.64% H₂ and balance He. The reaction data was taken in 30 min intervals and all of the results given in this section of the thesis include the data obtained after 1 hour of reaction. The CO conversions obtained by each method are presented in Table 4.3 and plotted in Figure 4.1.

Table 4.3. CO conversion over monolithic Au/MgO/Al₂O₃ catalysts at 110°C

| Method | CO conversions (%) |
|--|--------------------|
| Wet Impregnation | 2.20 |
| Co-precipitation | 12.38 |
| Dry Impregnation | 14.1 |
| Deposition-precipitation at 70°C | 23.13 |
| Deposition-precipitation at 25°C | 25.71 |
| Homogeneous Deposition Precipitation with Acetamide | 45.7 |
| Homogeneous Deposition Precipitation with Urea | 61.82 |

Figure 4.1. Effect of preparation method over monolithic Au/MgO/Al₂O₃ catalysts at 110°C

It is clear from the comparison of the different Au loading methods that, the CO activity increases with the usage of methods respectively, wet impregnation, co-precipitation, dry impregnation, deposition-precipitation and homogeneous deposition precipitation for Au loading.

The lowest activity was observed with the conventional impregnation method. In the literature, the low catalytic activity of gold based catalysts prepared by conventional impregnation method was reported and linked to the difficulty of obtaining the catalysts in nano-size and also the high amount of residual chloride ions (Lee and Gavriilidis, 2002). However, with a modified impregnation method such as dry impregnation that was studied in this thesis yielded a higher CO conversion that was similar that of obtained by co-precipitation method.

Although co-precipitation method is another simple method to prepare gold based catalysts, the low catalytic activity obtained by the application of this method is related to the fact that some of the gold is buried within the support and the particles are obtained with large size distributions by Carabineiro and Thompson (2007).

Deposition-precipitation method was considered to be a suitable method for gold based catalyst preparation by Mozer *et al.* (2009). In this thesis, deposition precipitation method was applied both at 70°C and room temperature. As a result, it is concluded that the preparation temperature does not have a significant effect on the activity of the catalysts prepared by this method.

For the homogeneous deposition precipitation method, both acetamide and urea were used as a precipitating agent. HDP with urea resulted with a higher activity compared by using acetamide as the precipitating agent.

The most promising method for monolithic Au/MgO/Al₂O₃ catalysts is obviously homogeneous deposition precipitation method by using urea as the precipitating agent. For particulate Au/Al₂O₃ catalysts, a study by Georgaka *et al.* (2008) agrees this result by reporting that homogeneous deposition precipitation method leads to the smallest average gold size among the all gold based catalyst preparation methods, so leads the highest activity. According to Georgaka *et al.* (2008) the homogeneity of the preparation solution is linked to the gradual increase of the pH due to decomposition of urea. Also, Grisel and Nieuwenhuys (2001a) used homogeneous deposition precipitation method using urea as precipitating agent in their study of oxidation of CO and CH₄ over particulate

Au/MO_x/Al₂O₃ catalysts in order to obtain similar Au loading and dispersion of nano-sized gold particles.

In the study of Tezcanli (2008), it was found that 1 wt% Au/1.25 wt% MgO/Al₂O₃ particulate catalysts prepared by homogeneous deposition precipitation method using urea as the precipitating agent exhibits 57.2% CO conversion at 110°C in a gas flow of 100 cm³ min⁻¹ containing 1% CO, 1% O₂, 60% H₂ and balance He. In the present study, the CO conversion for monolithic Au/MgO/Al₂O₃ catalysts by using the same method, but modified for monolithic structures resulted a higher conversion at the same temperature.

4.2.2. Effect of Au Loading

The effect of Au loading was investigated over monolithic Au/MgO/Al₂O₃ catalysts prepared by homogeneous deposition precipitation method by using urea as the precipitating agent for selective carbon monoxide oxidation in the temperature range of 50 to 150°C. The CO conversions were evaluated for 1 wt% Au, 0.50 wt% Au and 0.16 wt% Au loadings (Table 4.4). The comparison of the effect of each Au loading on CO oxidation can be seen from Figure 4.2 more obviously.

Table 4.4. CO conversion over monolithic Au/MgO/Al₂O₃ catalysts with different Au loadings

| Temperature (°C) | CO conversions (%) | | |
|------------------|--------------------|----------|----------|
| | 1% Au | 0.50% Au | 0.16% Au |
| 150°C | 42.93 | 34.48 | 19.62 |
| 130°C | 49.79 | 38.36 | 24.45 |
| 110°C | 65.69 | 42.70 | 30.19 |
| 90°C | 77.30 | 35.42 | 21.32 |
| 70°C | 66.33 | 28.75 | 22.87 |
| 50°C | 46.42 | 14.78 | 9.69 |

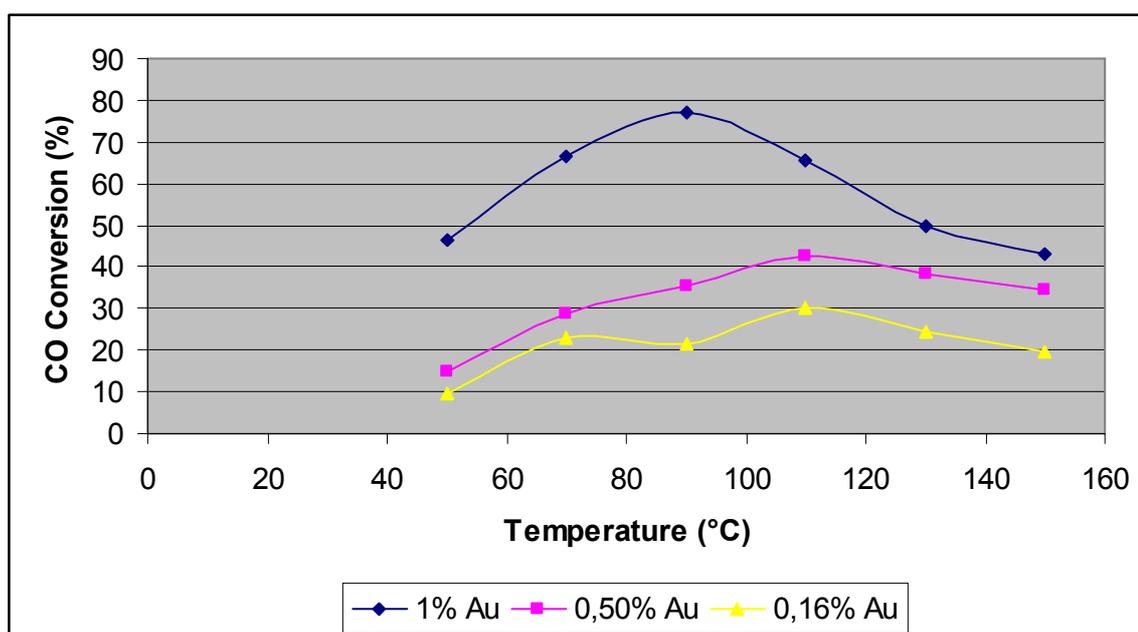


Figure 4.2. Effect of Au loading over monolithic Au/MgO/Al₂O₃ catalysts

As the Au content of the catalyst increases, CO conversion also increases. The catalyst containing 1% Au resulted with the highest CO activities at all temperatures in the 50-150°C range. At high temperatures, the CO conversion is relatively lower. But, as the temperature decreases, the conversion increases and becomes maximum at 90°C with a conversion of 77.30%. When the temperature is continued to decrease up to 50°C, the CO conversion also decreases. For the catalyst containing 0.50% Au, the general view is similar that of for the catalyst containing 1% Au. However, this time the maximum CO conversion was obtained at a higher temperature (110°C) and decreases after that temperature. For the case of the catalyst containing 0.16% Au, the temperature which the maximum CO conversion obtained was 110°C just like for the case of the catalyst containing 0.50% Au. At 90°C and 70°C a similar conversion was obtained and after decreasing the temperature to 50°C, the conversion decreased.

When comparing the results which were obtained for monolithic catalysts with the composition of 1wt% Au/1.25 wt% MgO/Al₂O₃ catalysts with the results of a previous study by Tezcanli (2008) which investigated particulate catalysts with the composition of 1 wt% Au/1.25 wt% MgO/Al₂O₃, it can be concluded that the type of the catalyst whether it is a monolithic structure or particulate, affects the conversion. In the study of Tezcanli (2008), it was reported that, CO conversion increases with the decrease in the temperature.

The maximum CO conversion for particulate Au/MgO/Al₂O₃ catalysts as high as 97.81% was obtained at 50°C and at higher temperatures, the conversion was decreased.

The temperature at which the maximum conversion is obtained may change depending on the Au content as well as the catalyst type whether monolithic or particulate; however, the existence of such a maximum is a common observation in selective CO oxidation. Although the CO oxidation rate increases with increasing temperature, the H₂, which is in larger amounts, is also adsorbed and oxidized at high temperatures blocking the active center available for CO. This is also important for the effect of W/F ratio and it will be explained further in Section 4.2.4.

4.2.3. Effect of MgO Loading

In the literature it has been reported that the presence of an alkali metal increases the activity and selectivity of the precious metal catalyst. This enhancement is explained by the interaction between CO and the precious metal. More obviously, these alkali metals increase the interaction between CO and the precious metal, therefore the CO content on the catalysts increases (Cho *et al.*, 2006).

Tezcanli (2008) studied the effects of various promoters (Ce, Co, Ni, Mg, Mn and Fe) on the activity and structure of the Au/Al₂O₃ catalysts for preferential oxidation of carbon monoxide. Catalysts containing 1.25 wt% Mg and 2.5 wt% Mg resulted in comparable CO conversions. However, when the Mg wt% was increased to 5, activity decreased significantly nearly in all temperatures. The maximum CO conversion was achieved at 50°C with 1 wt% Au and 1.25 wt% MgO.

In the study of Grisel and Nieuwenhuys (2001a), the catalytic activity of Au/Al₂O₃ and Au/MO_x/Al₂O₃ (M= Cr, Mn, Fe, Co, Ni, Cu and Zn) for CO oxidation were investigated and it is reported that addition of the promoter to the Au/Al₂O₃ highly increased the activity. In an another study by Grisel and Nieuwenhuys (2001b), they concluded that the addition of MgO promoter to the Au/Al₂O₃ particulate catalysts significantly increases the CO oxidation rates due to reduced average gold particle size.

Also, Szabó *et al.* (2008) concluded that the CO oxidation activity of Au/Al₂O₃ catalysts was modified with the addition of Mg promoter.

In this part of the thesis, in order to understand the effect of the promoter the experiments were processed both in the presence and absence of the MgO promoter. The results were summarized in Table 4.5 and figured out in Figure 4.3.

Table 4.5. CO conversion over monolithic Au/MgO/Al₂O₃ catalysts in the presence and absence of MgO

| Temperature (°C) | CO conversions (%) | |
|------------------|--------------------|--------|
| | 1.25% MgO | 0% MgO |
| 150°C | 42.93 | 38.21 |
| 130°C | 49.79 | 37.25 |
| 110°C | 65.69 | 54.00 |
| 90°C | 77.30 | 64.42 |
| 70°C | 66.33 | 70.00 |
| 50°C | 46.42 | 48.18 |

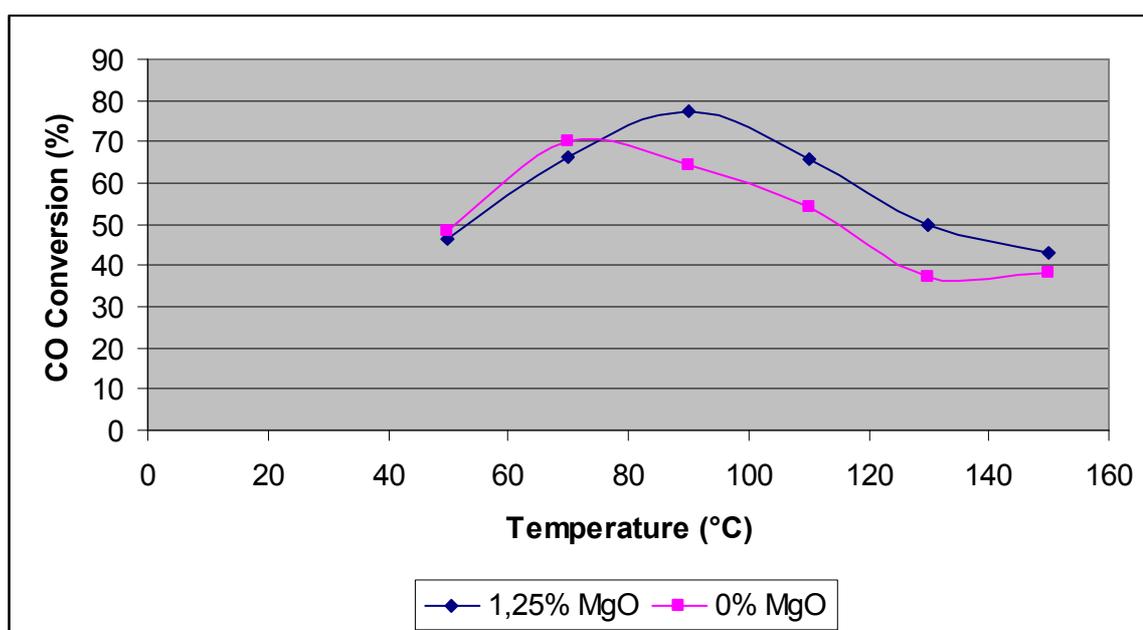


Figure 4.3. Effect of MgO loading over monolithic Au/MgO/Al₂O₃ catalysts

In the absence of the promoter, at high temperatures that are 150°C and 130°C, the CO conversion was nearly same. After decreasing the temperature, the conversion increased and the maximum CO conversion was 70% and observed at 70°C. After that point, with the decrease in temperature to 50°C, the conversion decreased. However, in the presence of promoter, the maximum conversion was 77.30% and obtained at 90°C. The enhancement in the activity towards CO oxidation with the addition of promoter, agrees the results reported by Tezcanli (2008), Grisel and Nieuwenhuys (2001) and Szabó *et al.* (2008).

4.2.4. Effect of W/F Ratio

The amount of the catalyst has a significant effect on the conversion. In this thesis, the effect of W/F ratio on the conversion was investigated by three individual experiments for the selective CO oxidation reaction with the usage of respectively 3, 2 and 1 monolith. The results are detailed in Table 4.6 and the corresponding graph is attached in Figure 4.4.

Table 4.6. CO conversion over monolithic Au/MgO/Al₂O₃ catalysts with different W/F ratios

| Temperature (°C) | CO conversions (%) | | |
|------------------|--------------------|------------|------------|
| | 3 monolith | 2 monolith | 1 monolith |
| 150°C | 42.93 | 43.74 | 48.83 |
| 130°C | 49.79 | 50.98 | 67.80 |
| 110°C | 65.69 | 72.13 | 52.10 |
| 90°C | 77.30 | 52.90 | 29.85 |
| 70°C | 66.33 | 32.53 | 13.07 |
| 50°C | 46.42 | 22.76 | 30.56 |

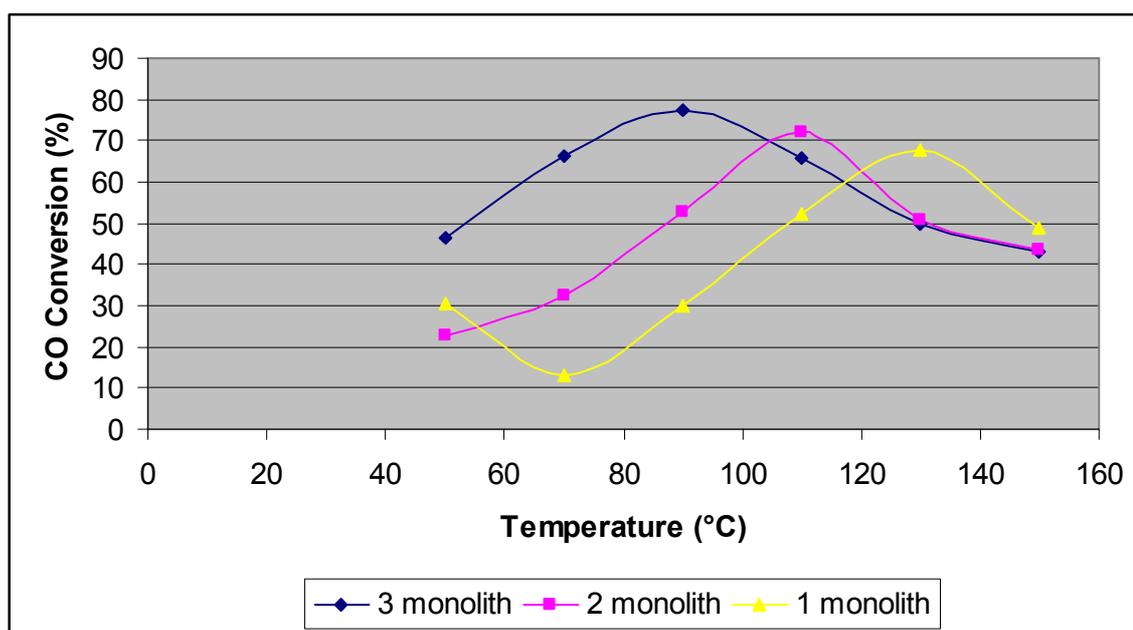


Figure 4.4. Effect of W/F ratio over monolithic Au/MgO/Al₂O₃ catalysts

In this study, the maximum CO conversion was obtained with the usage of 3 monoliths in the micro-reactor. It was 77.30% and obtained at 90°C. The conversion decreased with the decreasing monolith amount. The maximum CO conversion for the experiment with the usage of 2 monoliths yielded a lower maximum CO conversion of 72.13% and was obtained at a higher temperature that was 110°C. For the case of the experiment with 1 monolith, the maximum conversion was obtained at a higher temperature than for the 2 monolith and 3 monolith systems which was 130°C. For each case, the CO conversion decreased with the decrease in temperature after the temperature which gave the maximum conversion. However, for the case of 1 monolith used experiment, after 70°C an unexplainable increase occurred in the conversion for 50°C.

The decrease in the CO conversion with decreasing temperature at low W/F ratios can be explained with the relative selectivity towards CO and H₂. The studies in the absence of H₂ indicates that, under the temperature range used in this study, the CO conversion increases with increasing temperature similar to the trend observed in this work at low W/F ratios (Gavril *et al.*, 2006). In addition to this, it is also known that the H₂ oxidation increases with increasing temperature and it becomes significant at high temperatures (Quinet *et al.*, 2008).

At high W/F ratios, with the usage of three monoliths for example, the H₂ conversion increases with increasing temperature more than the increase of CO oxidation, and the high concentration of H₂ in the feed consumes O₂ which causes to the decreases in CO conversion. This is also evident from the fact that O₂ concentration is always 100% in almost all the temperatures studied with three monolithic catalysts. On the other hand, at low W/F ratios, with the usage of two monoliths or a single monolith for example, the number of active sites is just sufficient to oxidize CO, which is more favorable, and an increasing CO conversion with temperature was observed as the case in the absence of H₂. This is also evident from the fact that with the usage of two monoliths or a single monolith, O₂ conversion decreases.

Throughout the all experiments in this study three monoliths were used in the micro-reactor flow system which gives the highest conversion rates. For that purpose, the cordierite structure was cut in cylinders of 11 mm diameter and 20 mm length. The diameter of the monoliths was arranged to fill the inner diameter of the 1/2" stainless steel micro-reactor. Three of these monoliths were used in each experiment. It was also possible to use a single monolithic catalyst with 11 mm in diameter and 60 mm length, however using the same amount of catalyst in three pieces results an easier and more effective coating and active phase loadings. On the other hand, the W/F ratio for three monolithic catalysts (2.5 mg.min.cm³) was equal to the W/F ratio of the particulate catalysts used by Tezcanli (2008). Doker (2008) also studied Pt-Co-Ce/Al₂O₃ monolithic catalysts with this same W/F ratio.

4.2.5. Effect of O₂ Composition

In the selective CO oxidation, oxygen reacts with CO and converts it to CO₂ and also it reacts with H₂ in order to produce H₂O as the byproduct. With efficient catalysts and conditions, oxidation of hydrogen can be minimized, so CO conversion is increased. The amount of O₂ has a significant effect on CO conversion. In order to investigate this effect, two different O₂ compositions in the feed stream was studied with the usage of three monolithic catalysts in the compositions of 1 wt% Au/1.25 wt% MgO/Al₂O₃ in the temperature range of 50-150°C while the CO concentration was kept constant. The effect of O₂ composition was investigated under 1.6 ml/min and 1 ml/min O₂ flow respectively.

The data which were obtained from each experiment were presented in Table 4.7 and Figure 4.5.

Table 4.7. CO conversion over monolithic Au/MgO/Al₂O₃ catalysts with different O₂ compositions

| Temperature (°C) | CO conversions (%) | |
|------------------|--------------------|----------|
| | 1.6 ml/min | 1 ml/min |
| 150°C | 42.93 | 25.00 |
| 130°C | 49.79 | 30.08 |
| 110°C | 65.69 | 49.80 |
| 90°C | 77.30 | 60.35 |
| 70°C | 66.33 | 56.00 |
| 50°C | 46.42 | 58.64 |

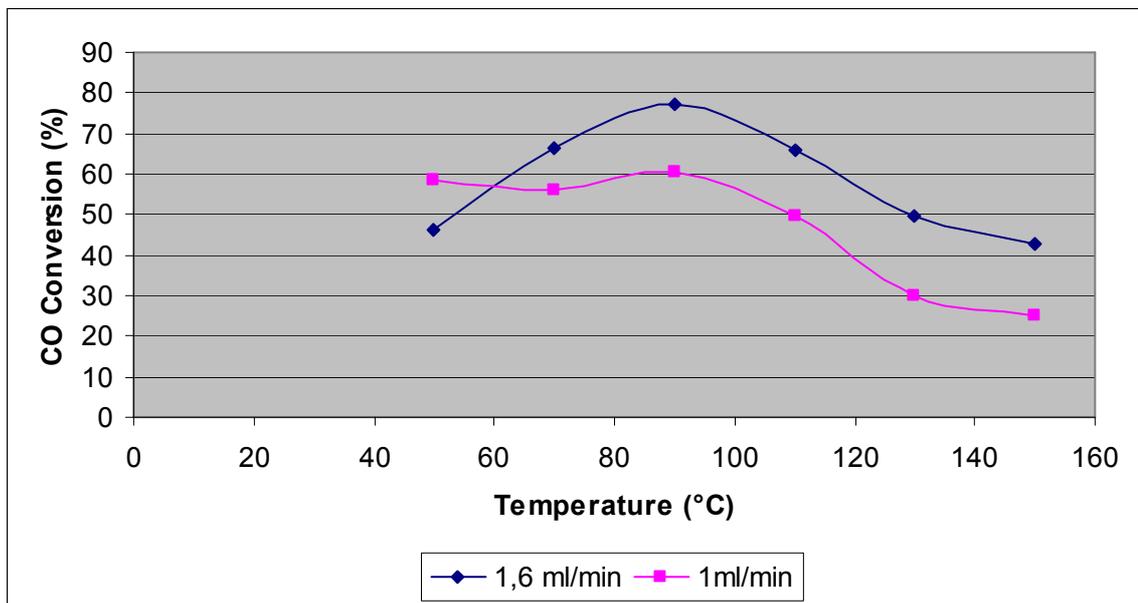


Figure 4.5. Effect of O₂ composition over monolithic Au/MgO/Al₂O₃ catalysts

It can be interpreted from Figure 4.5 that CO conversion is decreased significantly when the O₂ concentration is decreased from 1.6 ml/min to 1 ml/min. Georgaka *et al.* (2008) also reported that higher oxygen than the stoichiometrical amount was necessary in order to obtain a high CO conversion rate in the temperature range that PEM fuel cells work. So, this study agrees the enhancement in activity with the usage of excess oxygen.

For the both experiments, the maximum CO conversion was observed at 90°C and decreases after that with the decreasing temperature. However, between 70°C and 50°C the conversion stays nearly constant for the case of O₂ flow of 1 ml/min. At this temperature range, unexpectedly the CO conversion becomes higher than the conversion obtained with 1.6 ml/min.

Mozer *et al.* (2009) also studied the effect of O₂ concentration on selective CO oxidation over particulate Au/Al₂O₃ catalysts. For that purpose, they investigated the CO conversion and selectivity varying with the usage of 0.5%, 1% and 1.5% O₂ in the feed stream. They concluded that, the CO conversion increases with the increasing O₂ concentration; however they also reported that, with the usage of 1.5% O₂ there was a small decrease in the selectivity. They also reported in their study that, their result agrees the study by Manasilp and Gulari (2002). So, although a significantly higher CO conversion was observed with the usage of nearly 1.6% O₂ in this thesis, and as well as in the studies of Mozer *et al.* (2009), due to the small decrease in selectivity reported by both Mozer *et al.* (2009) and Manasilp and Gulari (2002), the usage of 1% O₂ is more preferable for selective CO oxidation.

4.2.6. Temperature Descent and Ascent Effect

The reactions were carried with decreasing the temperature from 150°C to 50°C. Decreasing the temperature from 150°C to 50°C or increasing from 50°C to 150°C gives similar conversions. So that, each method can be used for monolithic Au/MgO/Al₂O₃ catalysts. The results of each method are presented in Table 4.8 and figured out in Figure 4.6.

Table 4.8. CO conversion over monolithic Au/MgO/Al₂O₃ catalysts with increase and decrease in temperature

| Temperature (°C) | CO conversions (%) |
|------------------|--------------------|
| 130°C | 43.33 |
| 90°C | 80.40 |
| 50°C | 68.60 |
| 90°C | 84.30 |
| 130°C | 43.13 |

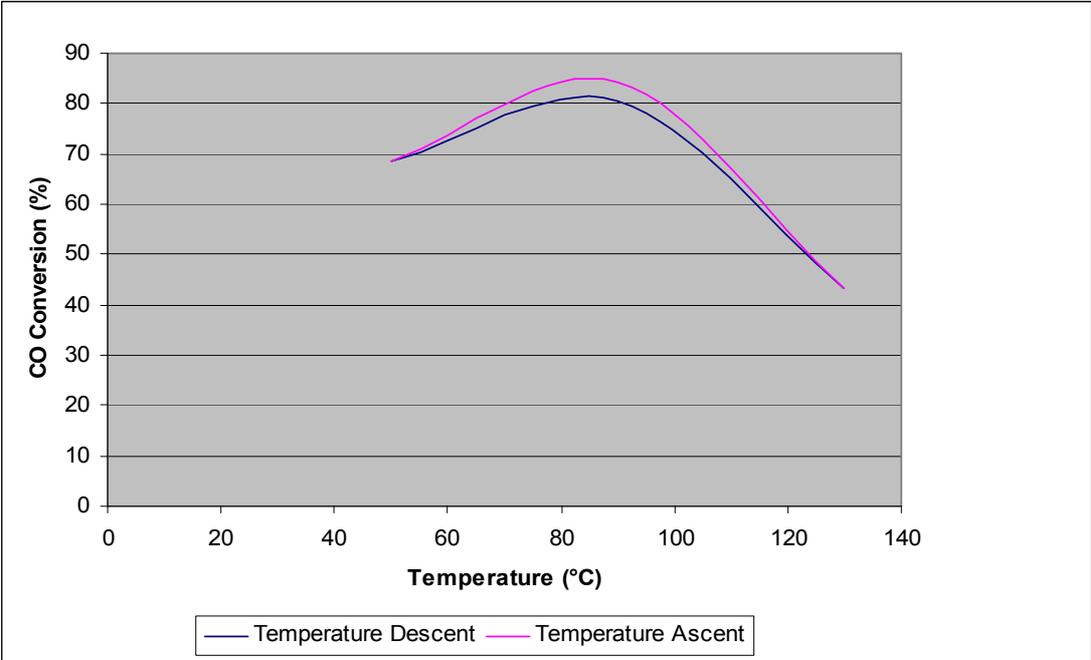


Figure 4.6. Effect of temperature ascent and descent

5. CONCLUSIONS AND RECOMMENDATIONS

5.1. Conclusions

The purpose of this study was to investigate the preparation methods of monolithic Au/MgO/Al₂O₃ catalysts for selective carbon monoxide oxidation in a hydrogen rich environment. In this comparative study, the cordierite monolithic structures were firstly wash-coated with alumina by using colloidal coating method. The loading of MgO promoter on the alumina supported monoliths was employed by impregnation method. The most critical point of this thesis was the loading of gold as nanoparticles on the MgO/Al₂O₃/cordierite monolith catalysts. For that purpose, five different methods were applied namely, wet impregnation, co-precipitation, dry impregnation, deposition-precipitation and homogeneous deposition precipitation. Deposition-precipitation technique was applied both at 70°C and room temperature. Also, for the homogeneous deposition precipitation method, acetamide and urea was used as the precipitating agent. ICP analysis was conducted by TUBITAK in order to determine the actual loadings of Au and Mg. The desired result in this thesis was to design the most promising method to deposit gold as nano-particles over the monolithic structure and obtain a high CO conversion in the temperature range between 50°C and 150°C.

The following conclusions can be drawn from this study:

- The highest CO conversion (77.30%) was achieved via homogeneous deposition precipitation method using urea as the precipitating agent at 90°C with the catalyst compositions of 1 wt% Au/1.25 wt% MgO/Al₂O₃ and with the feed compositions of 0.99% CO, 1.59% O₂, 59.64% H₂ and balance He.
- The CO conversion increases with the application of gold deposition techniques respectively, wet impregnation, co-precipitation, deposition-precipitation and homogeneous deposition precipitation.
- Impregnation method applied for the deposition of gold over monolithic catalysts yields the lowest CO conversion. However, with the modified impregnation methods, such as dry impregnation, it is possible to obtain a higher conversion.

- The preparation temperature of deposition-precipitation method whether at 70°C or at room temperature does not have significant effect on the CO conversion.
- Homogeneous deposition precipitation method yields the highest CO conversion in the temperature range of 50-150°C regardless of the precipitating agent. However, homogeneous deposition precipitation method using urea instead of acetamide results a significantly higher CO conversion at all temperatures.
- As the Au loading of the catalyst increases, the CO conversion also increases. The catalyst containing 1 wt% Au resulted with the highest CO conversion compared with the catalysts containing 0.5 wt% Au and 0.16 wt% Au at all temperatures in the 50-150°C range.
- The addition of 1.25 wt% MgO to the 1 wt% Au/Al₂O₃ monolithic catalyst enhanced the CO conversion at all temperatures in the range of 50°C to 150°C.
- In the absence of the promoter, the maximum CO conversion was 70% and observed at 70°C. However, in the presence of promoter, the maximum conversion was 77.30% and obtained at 90°C.
- The W/F ratio has a significant effect on the catalyst activity. The usage of three monoliths with the total W/F ratio of 2.5 mg.min.cm³ yielded the highest CO conversion.
- The CO:O₂ ratio is one of the parameters affecting the CO conversion towards CO₂. Two different O₂ compositions in the feed stream was studied with the usage of three monolithic catalysts in the compositions of 1 wt% Au/1.25 wt% MgO/Al₂O₃ in the temperature range of 50-150°C while the CO concentration was kept constant. Between 150°C and 70°C, as the O₂ content of the feed stream was increased from 1% to 1.6%, the CO conversion increased significantly. However, with further decrease in temperature up to 50°C, the CO conversion stayed nearly constant for the case that 1% O₂ was used and for that period, the CO conversion became higher than that of for the case of 1.6% O₂ was used.
- The reactions were carried with decreasing the temperature from 150°C to 50°C. Decreasing the temperature from 150°C to 50°C or increasing from 50°C to 150°C gives similar conversions. So that, each method can be used for monolithic Au/MgO/Al₂O₃ catalysts.

5.2. Recommendations

According to the results of the present study, the following points are thought to be worthwhile for future studies regarding selective carbon monoxide oxidation in a hydrogen rich environment:

- There are limited studies regarding the applications of gold onto the monolithic structures. More studies can be employed in this field.
- The nature of the support plays a vital role in determining the activity of monolithic gold catalysts. Wash-coating of various other supports such as CeO_2 , MnO_x , Fe_2O_3 , TiO_2 or ZnO can be applied onto the monolithic structures for supported Au catalysts.
- Au loading over metallic monoliths can be investigated.
- Other wash-coating methods such as, slurry or aluminum nitrate coating methods can be applied for monolithic catalysts.
- Kinetic experiments of monolithic catalysts can be conducted.
- Specially designed reactors for monolithic catalysts can be created allowing measurement of temperature inside the channels of monolithic structures.
- Addition of other promoters such as Mn, Fe, Ni, Co, Ce or addition of both Mg and Mn promoters can be investigated.
- New Au loading systems can be designed to be used in the homogeneous deposition precipitation method in order to reduce the destruction caused by the stirrer.
- The effect of the presence of CO_2 and H_2O can be investigated.
- Colloidal gold solution with nano-particle sizes can be investigated for Au loading effectiveness.
- The durability tests over Au based monolithic catalysts can be investigated.
- The stability of the Au based monolithic catalysts can be tested for industrial use with the optimum one.

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