A PARAMETRIC STUDY OF SELECTIVE CO OXIDATION USING PARTICULATE AND MONOLITHIC Pt-Co-CeO_2 CATALYSTS

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to my family

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ABSTRACT

A PARAMETRIC STUDY OF SELECTIVE CO OXIDATION USING PARTICULATE AND MONOLITHIC Pt-Co-CeO_2 CATALYSTS

The objective of this thesis was to conduct a parametric study of selective CO oxidation using particulate and monolithic Pt-Co-CeO_2 catalyst supported on alumina. In this comparative study, the monolithic catalysts were prepared by applying a layer of alumina support on to the walls of a cordierite monolithic carrier by colloidal coating method, termed as wash-coating, and then impregnating active components. Colloidal alumina coated and 1.4%Pt-1.25%Co-1.25%Ce impregnated monolithic catalysts were tested for the preferential CO oxidation reaction in a micro-reactor flow system under a total flow of 100 cm^3 min^{-1} using reaction temperatures in the 110-170°C range and typical feed compositions. The effect of calcination temperature, reaction temperature, Co content and residence time on catalyst activity and selectivity was investigated. The most suitable calcination temperature was found to be 700°C for monolithic catalysts which exhibited the highest catalytic activity towards CO oxidation approaching 100 per cent CO conversion at a temperature of 170°C in a feed containing 1.0 mol per cent CO, 1.0 mol per cent O_2 and 60.0 mol per cent H_2 with balance helium. The Pt and Co loadings on monolithic catalyts were determined by Inductively Coupled Plasma (ICP) analysis. In the light of ICP results indicating lower active component loadings on the cordierite structure, particulate 1.18%Pt-0.06%Co-1.25%Ce/γ-Al_2O_3 was prepared to match the monolithic catalyst composition and was tested for preferential CO oxidation in a micro-reactor flow system under a total flow of 100 cm^3 min^{-1} using reaction temperatures in the 90-150°C range. 99.4% conversion was obtained over the particulate catalyst at 130°C in a feed containing 1.0 mol per cent CO, 1.0 mol per cent O_2 and 60.0 mol per cent H_2 with balance helium.

ÖZET

SEÇİMLİ KARBON MONOKSİT OKSİDASYONU İÇİN PARTİKÜL VE MONOLİTİK KAZATİZÖRLERİN KARŞILAŞTIRILMASI

Bu parametrik çalışmada, monolit ve parçacıklı yapılar üzerine yüklenmiş Al_2O_3 destekli Pt-Co-CeO_2 katalizörlerinin seçimli karbon monoksit oksidasyonu etkinlikleri karşılaştırıldı. Monolit katalizörler, seramik monolit taşıyıcının iç duvarlarına aluminyum oksit çözeltisinin koloidal kaplama yöntemi kullanılarak yüklenmesinin ardından Pt-Co-Ce içeren metal tuzu çözeltilerinin birlikte emdirilmesi ile hazırlandı. Monolit katalizörlerin seçimli karbon monoksit oksidasyonu etkinlikleri 100 cm^3/dakika toplam gaz akışı içerisinde ve 110-170°C sıcaklık aralığında belirlendi. Deneylerde kalsinasyon sıcaklığının, reaksiyon sıcaklığının, Co miktarının ve reaksiyon süresinin katalizör etkinlik ve seçiciliği üzerindeki etkileri incelendi. En uygun kalsinasyon sıcaklığı 700°C olarak belirlenen 1.4%Pt-1.25%Co-1.25%Ce monolit katalizörün CO oksidasyonu için en yüksek etkinliği, 170°C sıcaklıkta ve mol bazında yüzde bir CO, yüzde bir O_2, yüzde 60 H_2 ve inert He içeren girdi bileşiminde yüzde 100'e varan CO dönüşmesi ile verdiği görüldü. Monolit katalizörler hazırlanırken gerçekleşen etkin madde yüklemeleri ve katalizör bileşimleri İndüktif Eşleştirilmiş Plazma (ICP) analizi ile saptandı. Seramik yapıya düşük miktarlarda etkin madde yüklendiğini gösteren ICP verileri ışığında, monolitik katalizörün bileşimine denk gelen oranlarda etkin madde kullanılarak 1.18%Pt-0.06%Co-1.25%Ce/γ-Al_2O_3 parçacıklı katalizörleri hazırlandı, akışlı mikroreaktörde 90-150°C sıcaklık aralığında ve 100 cm^3 min^{-1} toplam gaz akışı altında seçimli CO oksidasyonu etkinlikleri belirlendi. Parçacıklı katalizörün en yüksek karbon monoksit oksidasyonu etkinliğine 130°C sıcaklıkta ve mol bazında yüzde bir CO, yüzde bir O_2 ve yüzde 60 H_2 ve He içeren girdi bileşiminde %99.4 CO dönüşmesi ile eriştiği görüldü.

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LIST OF SYMBOLS/ABBREVIATIONS

W/F	Residence time
ϵ	Void Fraction
AFC	Alkaline Fuel Cell
ATR	Autothermal Reforming
BCI	Backscattered Composition Imaging
cpsi	Channels per square inch
GC	Gas Chromatograph
ICP	Inductively Coupled Plasma
MCFC	Molten Carbonate Fuel Cell
NMRO	Noble Metal Reducible Oxide
OFA	Open Frontal Area
PAFC	Phosphoric Acid Fuel Cell
PEMFC	Proton Exchange Membrane Fuel Cell
PEFC	Polymer Electrolyte Fuel Cell
POX	Direct Partial Oxidation
PROX	Preferential Oxidation
ppm	Parts per million
SOFC	Solid Oxide Fuel Cell
SR	Steam Reforming
TSA	Total Surface Area
WGS	Water Gas Shift
VOC	Volatile Organic Compounds

1. INTRODUCTION

Hydrogen is an ideal source of chemical energy that can be directly converted to electricity via fuel cells with zero emissions of hazardous species such as volatile organic compounds, nitrogen oxides and carbon oxides (Avcı et al., 2004).

In recent years, chemical and other related industries have given much attention to clean and efficient power generation for various electrical applications which point out the importance of future energy technologies (Kim et al., 2008). At this point, as an alternative power source for generating electricity, fuel cells become important. Nowadays, fuel cells are under intense development because of their high fuel conversion efficiency, environmental compatibility and low emission which meet the strict standards set for air pollution (Marin et al., 2008).

The operation of fuel cells requires an almost pure supply of hydrogen (Önsan, 2007). To get hydrogen on-board in fuel cell-powered vehicles, two options are available a hydrogen storage unit or a fuel processor; but, currently there are several problems associated with a hydrogen storage unit. It is not practical to store and distribute sufficient amounts of H_2 on-board because of the lack of a worldwide infrastructure for transport and distribution of pure hydrogen. In order to overcome these concerns, hydrogen generation via reforming of fossil fuels such as natural gas, LPG or gasoline stands out as a practical route for providing required hydrogen for fuel cells and fuel processors receive attention (Şimşek et al., 2007).

Fuel processors are hydrogen production systems which consist of different units, i.e. the reformer unit, water–gas shift unit and preferential CO oxidation unit (Moreno et al., 2008). In a fuel processor, hydrogen production occurs in three catalytic reactions in series, namely: (i) hydrogen generation by direct or indirect partial oxidation, (ii) water-gas shift reaction which eliminates most of the CO (0.5-1%) and increases concentration of

hydrogen, and (iii) preferential CO oxidation (PROX) that reduces remaining CO to ppm levels (10-50 ppm) in hydrogen-rich streams (Pozdnyakova et al., 2006).

Hydrogen generation to feed PEM (proton exchange membrane) fuel cells starts with reforming reactions that produce CO concentrations around 10-15%, the CO concentration is then reduced to about 1% with the water–gas shift (WGS) reaction. This value is still far beyond the tolerance level of the PEM fuel cell. In order to deal with this problem, another approach, PROX or selective CO oxidation, is used to reduce the CO concentration under a tolerated value (below 50 ppm) which is the simplest and most cost-effective method for removing CO in hydrogen-rich streams from reformed fuels. For the PROX reaction, highly active, stable and selective catalysts are required (Wang et al., 2008).

In the last years, many researches have focused on finding and developing catalysts suitable for PROX, and large numbers of catalysts have been developed (Moretti et al., 2008). Low temperature CO oxidation catalysis has two important aspects which have to occur simultaneously: CO chemisorption and dissociative adsorption of O_2. Therefore, a successful PROX catalyst should include components that will take care of both functions (Trimm and Önsan, 2001). Composite catalysts that contain one or more noble metal as well as one or more reducible metal oxide components are among the most promising catalyst alternatives. Additionally, an efficient PROX catalyst must have high activity and high selectivity for the oxidation of CO, which reduces the H_2 consumption in fuel cells (Lee et al., 2008), but should keep H_2 oxidation to a minimum.

Particulate and monolithic catalysts may be used in the PROX unit of fuel processors. In the case of particulate catalysts, the total catalyst loading required by conventional packed-bed reactors used for reforming, water-gas shift and PROX units of processors feeding hydrogen to PEM fuel cells is of the order of 1.0 kg/kW (Tan et al., 2008). The large catalyst amounts and reactor volumes involved affect the technical feasibility of fuel processors. In addition to the necessity for heat integration, the need for elimination of pore diffusion effects has forced research toward process intensification, i.e. reduction of unit sizes, through the use of structured reactors and engineered catalysts (Önsan, 2007). Among engineered catalysts, the development of monolithic catalysts (initially for catalytic

auto-exhaust converters) is one of the major accomplishments in heterogeneous catalysis and chemical process intensification in recent times (Döker, 2008).

The aim of the present work was to conduct a detailed parametric study of selective CO oxidation using particulate and monolithic Pt-Co-CeO_2 catalysts supported on alumina and to compare their performance in terms of catalyst composition and temperature. In order to achieve this aim, firstly, the most suitable calcination temperature was determined for the monolithic catalyst. In the second step, particulate Pt-Co-CeO_2-Al_2O_3 catalysts and cordierite monolithic Pt-Co-CeO_2-Al_2O_3 catalysts of different compositions were prepared. Thirdly, particulate and cordierite monolithic Pt-Co-CeO_2-Al_2O_3 catalysts were tested for their PROX activity at various temperatures, and the parametric study was finalized by a direct comparison of their PROX performances.

Section 2 involves a literature survey including brief information about fuel cells followed by detailed information about preferential CO oxidation; moreover, the relevant previously reported work on particulate and monolithic catalysts are considered with their preparation methods. Section 3 describes the experimental system and the procedures followed in this study. The results obtained in the experiments are presented and discussed in Section 4, while the conclusions drawn from this work and some recommendations for future work are summarized in Section 5.

2. LITERATURE SURVEY

2.1. Fuel Cells

Energy generation has been known as a major environmental issue, especially for the processes which are used to convert raw materials into energy. The society's growing awareness on environmental issues, particularly for the emission of greenhouse gases, has given rise to significant efforts in developing new clean technologies with a sustainable profile to generate energy (Silva *et al*., 2008). In response to environmental needs, fuel cells were proposed as an alternative power source for generating electricity, and related issues such as hydrogen production and CO clean-up became important. Nowadays, because of their high fuel conversion efficiency, flexibility in size, minimal maintenance requirement reducing life cycle costs of energy production, environmental compatibility and low emission which meet the strict standards set for air pollution, fuel cells are under intense development (Marin *et al.*, 2008). Both industrial R&D departments and academia have been recognized fuel cells as an effective method to produce energy (Cipiti and Recupero, 2009). The applications of fuel cell technology vary from portable/micro power and transportation through to stationary power for buildings and distributed generation. A variety of fuel cells are in different stages of their development (Ghenciu, 2002).

2.1.1. Fuel Cell Background

Fuel cell technology is over 170 years old, since the first fuel cell was demonstrated by Sir William Grove in 1839 (Johnston *et al*., 2005). When he was experimenting on electrolysis of water, he observed that direct current is passed through water to separate it into its hydrogen and oxygen. Afterwards, he discussed that the electrolysis process of water may be reversed whereby hydrogen can be combined with oxygen to generate electric current, which ultimately became the principle of the fuel cell. Efforts on the development of fuel cells were continued until the first direct carbon fuel cell, which was very simple and inexpensive, was built in 1896 by Dr. William W. Jacques (Hackett *et al*., 2007; Johnston *et al*., 2005).

From the 1930s through 1950s Francis Thomas Bacon worked on developing alkaline fuel cells (Johnston *et al*., 2005) and demonstrated a working stack in 1958. Serious interest in fuel cells began from 1960 and onward when the US Space Program (National Aeronautics and Space Administration-NASA) chose fuel cells to provide on board electrical power for spacecrafts (Chaurasia *et al*., 2003). The fuel cell technology was licensed to Pratt and Whitney where it was utilized for the Apollo spacecraft fuel cells (Johnston *et al*., 2005). Moreover, fuel cells furnished power for the Gemini and Apollo spacecrafts and played an important role in the landing of man on the moon (Chaurasia *et al*., 2003). Nowadays in USA, Japan and Germany, many installations are met by fuel cells to produce electricity (Kazim, 2000). Additionally, in different countries all over the world, there are more than 200 units based on fuel cell technology, which are in operation for power generation (Chaurasia *et al*., 2003).

The fuel cell is an electrochemical device which produces energy through electrochemical conversion of the fuel. In principle, a fuel cell operates like a battery; but, unlike a battery, it does not require recharging; electrical energy is produced as long as fuel is supplied to the cell (Johnston *et al*., 2005). Fuel cells consist of an electrolyte material that is sandwiched between two thin electrodes (anode and cathode). The input fuel passes over the anode and oxygen passes over the cathode to generate electricity, water and heat. Every hydrogen molecule splits into H^+ ions and two electrons at the anode whereas two negatively charged oxygen ions are formed from the oxygen molecule by the catalyst at the cathode. Then, while the ions move through the electrolyte toward the oppositely charged electrode (anode), the electrons create an external electrical circuit to provide power. Additionally, at cathode, oxygen reacts with electrons taken from the anode and hydrogen ions form the electrolyte to create water (Song, 2002).

2.1.2. Types of Fuel Cells

Fuel cells can be classified into five groups depending on the type of electrolyte used in the cells:

- Proton exchange membrane fuel cell (PEMFC)
- Alkaline fuel cell (AFC)
- Phosphoric acid fuel cell (PAFC)
- Molten carbonate fuel cell (MCFC)

• Solid oxide fuel cell (SOFC)

The fuel cells listed above have different operating temperatures. The approximate temperature is 353 K for PEMFC, 373 K for AFC, 473 K for PAFC, 923 K for MCFC and 1073 K to 1273 K for SOFC (Ghenciu, 2002).

Compared to the other fuel cell types, PEMFCs possess a series of advantages which make them regarded as the most promising candidates for a wide range of applications that vary from mobile power applications (vehicles) to small stationary power units. A fuel cell system including a fuel processor can utilize the hydrogen from any hydrocarbon fuel, from natural gas to methanol, and even gasoline. As a matter of that fact, hydrogen comes out as a promising carbon-free energy carrier which can be produced from biomass and its derived liquids to generate power by fuel cells (Ghenciu, 2002; Silva *et al*., 2008; Zhou *et al*., 2006).

2.1.3. The PEM Fuel Cell

One of the more common types of fuel cell is the Proton Exchange Membrane Fuel Cell (PEMFC). PEM fuel cells have advantageous features that make them candidates for different applications: low operating temperature, continuous operation at high current density, low weight, high efficiency, compactness, potential for low cost and volume, long stack life, fast start-ups, suitability to discontinuous operation and production of little or no pollutants (Wee and Lee, 2006; Park *et al*., 2009).

The PEMFC consists of an electrolyte membrane sandwiched between an anode (negative electrode) and a cathode (positive electrode). The reaction occurring at the anode and cathode respectively are given in the simplified diagram of a typical PEM fuel cell shown in Figure 2.1.

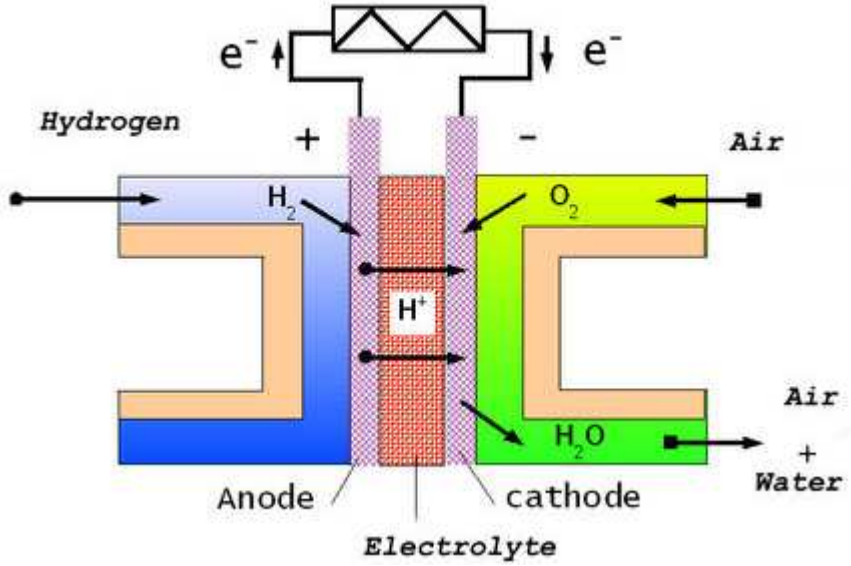

Figure 2.1. Schematic diagram of PEM fuel cells (Technology of Fuel Cell, 2009)

An oxidation half reaction occurs at the anode:

$$H_2\,(g) \rightarrow 2H^+ + 2e^- \qquad (2.1)$$

A reduction half reaction occurs at the cathode:

$$2H^+ + \tfrac{1}{2}\,O_2\,(g) + 2\,e^- \rightarrow H_2O \qquad (2.2)$$

Then the overall fuel cell reaction is:

$$H_2 + \tfrac{1}{2}\,O_2 \rightarrow H_2O \qquad (2.3)$$

Consider the PEM fuel cell given in Figure 2.1. The anode is the electrically negative electrode at which oxidation (loss of electrons) takes place. At the anode, a catalyst is used to separate the hydrogen molecule into a hydrogen protons and hydrogen electrons. On the other hand, at the electrically positive cathode, reduction (gaining of electrons) occurs. Both anode and cathode are composed of platinum particles uniformly supported on carbon particles. The platinum in the electrodes acts as a catalyst to increase the rate of reactions. A solid membrane electrolyte placed between the anode and cathode allows the proton to pass to the cathode. This membrane conducts charged ions, but does not conduct electrons. Hereby, this membrane allows the solution to conduct electricity. The electrons are forced to flow through an external electrical circuit before they reach the cathode. This flow of electrons provides direct current electrical energy (Hoogers, 2003).

Clean CO-free hydrogen devoid of pollutants is the ideal fuel for PEMFCs. Presently, there is no infrastructure available for the storage and distribution of hydrogen. Hence, to

overcome this difficulty, on-board hydrogen production seems the best way to supply the hydrogen required by fuel cells (Cipiti and Recupero, 2009; Jung *et al*., 2008; Simsek *et al*., 2007). Hydrogen for PEMFCs can be produced by on-board fuel processors from liquid hydrocarbon fuels, methanol or natural gas. The process in fuel processor to produce H_2-rich fuel gases is accomplished by a series of catalytic reactions including fuel desulphurization, reforming of fuels, water-gas shift reactions and preferential oxidation of CO. The key feature for successful implementation of direct-hydrogen fuel cell systems during the transition phase to a hydrogen economy is the selection of a suitable fuel processor and fuel combination (Cipiti and Recupero, 2009; Maeda *et al*., 2008).

2.1.4. Hydrogen Production for Fuel Cells

There is a substantial amount of research being conducted for the development of hydrogen production systems. Currently, the most developed and most used technology is the reforming of hydrocarbon fuels in fuel processor (Holladay *et al*., 2009).

Hydrogen for polymer electrolyte fuel cells can be produced in an on-board fuel processor. The absence of hydrogen refuelling infrastructure and problems concerning hydrogen storage has led to the development of fuel processors which can convert available fuels (hydrocarbons and/or alcohols) into hydrogen rich reformate gases via a series of catalytic reactions (Cipiti and Recupero, 2009).

The major chemical processes used for hydrogen production from hydrocarbon fuels are steam reforming (SR), direct partial oxidation (POX) and autothermal reforming (ATR) known also as indirect partial oxidation (Önsan, 2007). The reactions belonging to SR, POX and ATR are given below in detail (Holladay *et al.,* 2009).

$$\text{SR: } C_mH_n + m\,H_2O \rightarrow m\,CO + (m + \tfrac{1}{2}\,n)\,H_2 \qquad \Delta HR>0 \qquad (2.4)$$

$$\text{POX: } C_mH_n + \tfrac{1}{2}\,m\,O_2 \rightarrow m\,CO + \tfrac{1}{2}\,H_2 \qquad \Delta HR<0 \qquad (2.5)$$

$$\text{ATR: } C_mH_n + \tfrac{1}{2}\,m\,H_2O + \tfrac{1}{4}\,m\,O_2 \rightarrow m\,CO + (\tfrac{1}{2}\,m + \tfrac{1}{2}\,n)\,H_2 \qquad \Delta HR\leq 0 \qquad (2.6)$$

Steam reforming reaction shows much promise for the conversion of hydrocarbon fuels to hydrogen which gives a reformate stream with 70%-80% H_2 on a dry basis, whereas POX produces only 35%-45% H_2. However, the resulting gas mixture of the

steam reforming reaction contains a percentage of CO between 5% and 10% which cause poisoning of the fuel cell anode catalyst. To prevent the poisoning, it is necessary to obtain high purity H_2 gas containing less than 50 ppm of CO using various CO removal methods (Marin *et al*., 2008; Önsan, 2007).

Steam reforming, indirect partial oxidation or auto-thermal reforming of hydrocarbon fuels for efficient H_2 production is followed by high- and low-temperature water gas shift (WGS) reactions for maximizing H_2 concentration and lowering CO content in the exit stream of fuel processors with a specified goal (Önsan, 2007).

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \Delta HR<0 \qquad (2.7)$$

The water–gas shift reaction is mildly exothermic and thermodynamically limited. Therefore, high CO conversions can be obtained only at low temperatures (Park *et. al*., 2009). The CO content is reduced by employing the WGS reaction down to levels below one percent (Marin *et al.*, 2008).

Since platinum, anode catalyst of PEMFC, is prone to be poisoned in the presence of small amounts of CO in the hydrogen stream, carbon monoxide should be removed to a trace-level. In order to achieve the upper CO limit of 10-50 ppm required, an additional purification step is needed after the low-temperature water gas shift reaction (Marin *et al*., 2008). Preferential oxidation of CO (PROX) is carried out to reduce the CO content down to ca. 50 ppm, which is the maximum allowable CO level that will not have a deactivating effect on the fuel cell electro-catalysts (Lopez *et al*., 2008).

The PROX reaction is the selective catalytic oxidation of CO in hydrogen rich reformate using oxygen with air injection (Cheekatamarla *et al*., 2005). The CO in the exit stream of the water–gas shift reactor can further be removed by PROX conducted over suitable oxidation catalysts with oxygen being supplied externally to the reactor.

In practice, CO content is reduced during PROX but the oxygen fed to the system also reacts with the hydrogen molecules (Chung and Yeh, 2008):

$$2CO + O_2 \rightarrow 2CO_2 \qquad \Delta H_R <0 \qquad (2.8)$$

$2H_2 + O_2 \rightarrow 2H_2O$ $\Delta H_R < 0$ (2.9)

The catalytic PROX process aims to achieve almost 100% conversion of CO to CO_2 with minimal H_2 oxidation (Önsan, 2007). Therefore, effective catalysts that offer a compromise between catalytic performance and cost of catalysts should be developed to eliminate CO selectively from hydrogen-rich streams to get pure H_2 (Liu *et al*., 2008a). Different catalysts are used for this purpose in the PROX unit of a fuel processor.

2.2. Preferential Carbon Monoxide Oxidation in Hydrogen-Rich Streams

The ideal fuel for PEM fuel cells is pure hydrogen with less than 50 ppm carbon monoxide. Size, weight, cost and technical limitations make it difficult to store hydrogen in necessary quantity and density; therefore the hydrogen gas needs to be generated on site by a series of reactions fuel processors. On-board fuel processors are being developed to provide hydrogen-rich streams to the proton exchange membrane fuel cell for mobile applications. Since the anode catalyst has low tolerance for CO, 10–50 ppm, and the WGS conversion of reformate streams of gasoline and other hydrocarbon fuels generally produce 1–2% of CO, the additional PROX step is carried out which is expected to achieve an overall CO conversion higher than 99.5% for reducing the CO level to less than 50 ppm. As the oxidation reaction is exothermic, multistage PROX systems with interstage cooling or water injections between stages can be used, with the catalyst usually being coated on monolithic supports (Ahluwalia *et al*, 2005 ; Ghenciu, 2002; Holladay, 2009).

The PROX reactions are given in Equation 2.8 and Equation 2.9. The goal in these reactions is the oxidation of CO to CO_2 without simultaneously oxidizing H_2 to H_2O. The $H_2 + O_2$ reaction of Equation 2.9 is more exothermic and favored at high temperatures. So, selective PROX catalysts which are active at low temperatures and resistant to deactivation by the CO_2 and H_2O present in the feed are needed (Gomez-Cortes *et al.*, 2008).

Packed bed reactors can be used for PROX reactions. However, in the case of large scale PROX systems, packed bed reactors have several concerns such as pressure drop within catalyst layer, pore diffusion effects, temperature gradients and hot spots due to the high exothermicity of oxidations of CO and H_2. Nowadays, these issues have increased the

interest in microreactors due to their principal benefits including fast transfers of heat and mass, high surface to volume ratio and decrease of volume (Kim *et al.*, 2008).

2.3. PROX Catalysts

The CO content of hydrogen feed to PEM fuel cells must be kept below 50 ppm for their proper operation, which can be achieved by using catalysts that can oxidize CO selectively in the presence of excess hydrogen. Several catalysts were prepared and tested for selective CO oxidation, and the effects of different parameters such as catalyst composition, catalyst pre-treatment and catalyst preparation methods on the CO oxidation activity of these catalysts have been investigated (Derekaya *et al.*, 2009).

In general, a suitable PROX catalyst must adsorb CO and provide sites for activated oxygen while suppressing hydrogen adsorption. Because CO is adsorbed on the metal sites, the active surface is fully covered by CO which means that oxygen can not be adsorbed on the metal surface and should be activated on different sites, either on a reducible support or on partially oxidized patches. In this way, oxygen can diffuse to interface sites and then react with the components on adjacent metal/metal oxide sites (Pozdnyakova *et al*., 2006).

- For an efficient PROX reaction, the catalyst must have (Lee *et al*., 2008; Zhao *et al*., 2008):
- High CO oxidation activity at low temperatures,
- High selectivity for CO oxidation against the undesired H_2 oxidation that will decrease overall process efficiency,
- Relatively wide temperature range for achieving CO conversions greater than 99% as the PROX unit is to be placed between the low temperature WGS reactor and the fuel cell,
- Good resistance to deactivation caused by the CO_2 and H_2O in the feed.

In 1960s, Engelhardt developed the first catalysts which were commercialized under the name of “Selectoxo” to reduce CO concentration to an acceptable level for the iron ammonia synthesis catalysts without oxidizing H_2 (Marino *et al.*, 2008). Then Selectoxo^{TM} catalysts were used in the early- to mid-1970s for the purpose of increasing the production

rate of ammonia plants (Roberts *et al.,* 2003). The original Selectoxo^{TM} catalysts consisted of γ-alumina tablets which contained 0.3–0.5 wt% Pt promoted with a base metal oxide. Since then, catalysts containing Pt alone and in combination with other metals are in use and several different catalytic formulations have been tested in PROX reactions (Liu *et al.,* 2008a). The reported promising catalysts for PROX can be divided into three groups: (i) nano-gold catalysts, (ii) supported noble metal catalysts such as Au, Pt, Pd or Rh and (iii) base metal oxides catalysts focusing on CuO-CeO_2 (Guo *et al.,* 2008).

For gold catalysts, the breakthrough experimental results of Hutchings and Haruta were reported in 1985 and 1987 which showed that highly dispersed gold nano-particles supported on selected metal oxides can effectively oxidize carbon monoxide with a very high reaction rate at much lower temperatures (at sub-ambient temperatures such as 200 K) as compared to the more conventional Pt-based catalysts (Avgouropoulos *et al.*, 2008). Although high activity at low reaction temperatures is favorable for improving the cold-start properties in fuel cell systems, it is hard to reduce the CO content below 10 ppm over nano-gold catalysts due to their high activities for hydrogen oxidation (Guo *et al*., 2008).

Noble or rare metal catalysts such as Au, Pt, Rh and Ru often present a promising choice with their excellent catalytic performance in PROX reactions; however, they are expensive (Liu *et al.*, 2008a). Oh and Sinkevitch (1993) published the first general work on PROX by testing a variety of catalytic materials, including noble metals such as Pt, Pd, Rh, and Ru and base metals such as Co/Cu, Ni/Co/Fe, Ag, Cr, Fe, and Mn in a feed containing CO, H_2, and O_2 in order to identify alternate catalysts which are more effective than currently used Pt/Al_2O_3 in selectively oxidizing CO in the presence of excess H_2. Platinum, rhodium and ruthenium were found to be the most appropriate catalysts for PROX reactions achieving nearly complete CO conversion to CO_2. The optimum reaction temperature was found to be l00°C for Rh and Ru, and around 170°C for Pt.

Trimm and Önsan (2001) indicated that supported platinum based catalysts play an important role in elimination of CO in hydrogen-rich streams. Pt/Al_2O_3 catalysts promoted with cobalt, ceria, or both cobalt and ceria, also have great potential for CO removal (İnce *et al.*, 2005). Kim *et al.* (2008) studied Pt/Al_2O_3 catalysts by adding various promoters to enhance the activity of the catalyst and found that Co-promoted Pt/Al_2O_3 catalyst reduced outlet CO concentration in a wider temperature range when compared to Pt/Al_2O_3 catalyst;

besides, cobalt addition enhanced catalytic performance to a great extent and residual CO concentration began to decrease rapidly at low temperatures.

Non-precious metal-based catalysts, mainly CuO–CeO_2, have been proposed as one of the best candidates for preferential removal of CO from reformate fuels (Avgouropoulos *et al*., 2008b). These catalysts can operate between 100 and 200 °C with high selectivity, are also very stable under reaction conditions and can tolerate high CO_2 and H_2O concentrations. Compared to Pt-group-based catalysts, non-precious metal-based catalysts exhibit superior activity; on the other hand, although precious metal catalysts are less active, they are much more selective and stable. (Avgouropoulos *et al.*, 2008b; Liu *et al.*, 2008b). Guo and Liu (2008) stated that metal oxides catalysts, which mainly concentrate on CuO-CeO_2, were promising catalysts for partial oxidation of CO and that the catalytic performance of Co_3O_4-CeO_2 catalysts can effectively be improved by MnO_x modification. Co-Ce-Mn mixed oxides catalyst with proper Co:Ce:Mn ratio was found to be a promising candidate for CO removal from hydrogen-rich gases.

2.3.1. Platinum Catalysts

Different catalyst formulations, generally a high platinum group metal loading on high surface area supports, were used for PROX, based on the high activity required to remove CO while maintaining a high CO oxidation selectivity. The formulations comprise of Pt or promoted Pt, Ru, Pd, alloys of Pt–Sn or Pt–Ru, or Rh on alumina or on molecular sieves. Among these catalyts, Pt-based catalysts appear to offer the best results over a larger temperature interval and have been the most studied (Ghenciu, 2002).

Souza *et al.* (2007) studied the effect of support material on Pt catalysts for total and selective oxidation of CO. During the experiments, Pt catalysts supported over alumina, silica, zirconia and ceria were tested in total (H_2-free streams) and selective (H_2-rich streams) oxidation of CO. It was reported that zirconia supported Pt catalyst showed higher activity for total CO oxidation with 100% CO conversion at 150°C and Pt/Al_2O_3 presented slower activation reaching 100% CO conversion at 220°C. For selective CO oxidation, although ceria and zirconia-supported catalysts were active at lower temperatures, CO conversions obtained were lower than those on alumina and silica-supported catalysts: 100% at 140°C for Pt/Al_2O_3 and 200 °C for Pt/SiO_2, against 58% at 100°C for Pt/CeO_2 and

62% at 130°C for Pt/ZrO_2. Moreover, the higher CO conversions of Pt catalysts supported on silica and alumina were also reflected in their higher selectivities to CO_2 formation, especially at temperatures above 100°C.

Manasilp and Gulari (2002) demonstrated a similar behavior for Pt/Al_2O_3 catalyst. Alumina-supported Pt catalysts with 1-2 wt% Pt loading were prepared by the single-step sol–gel technique. The experiments were carried out in a temperature range of 110-250°C with a gas composition of 1% CO, 1% O_2, 65% H_2 and He as balance. At 110°C, the CO conversions were 15 and 20% over 1wt% and 2wt% Pt catalysts, respectively. Increasing the temperature to 170°C increased CO conversion from 20 to 80% for 2 wt% Pt/Al_2O_3 and from 15 to 55% for 1 wt% Pt/Al_2O_3. On the other hand, increasing the temperature further to 210°C resulted in a dramatic drop in CO conversion to 12 and 10%, respectively for both catalysts. It was reported that the addition of water vapor to the feed had a significant positive effect which decreased the activation energy for both CO and hydrogen oxidation, thus, conversion was increased significantly without changing the selectivity. Unlike the positive effect of water vapor, CO_2 in the feed had a detrimental effect on the activity of the catalysts. This effect can be due either to the reverse water gas shift reaction, or to the formation of carbonates on the support or to an increase in the effective surface concentration of CO by dissociative adsorption of CO_2.

The partial CO oxidation activity of Pt/Al_2O_3 catalysts at low oxygen concentrations can be improved by increasing the oxygen supply to Pt sites. This can be accomplished through O_2 storage components like CeO_2. It is suggested that CeO_2 promotes CO oxidation by employing lattice oxygen whereby oxygen can be supplied to Pt from CeO_2 even in low-oxygen concentration environments (Özkara and Aksoylu, 2003).

Ayastuy *et al.* (2006) tested Pt/CeO_2 catalyst for selective CO oxidation in H_2-rich environments and reported that the Pt/CeO_2 catalyst prepared by impregnation showed high activity for CO oxidation at very low temperatures (80°C) compared to Pt/Al_2O_3 catalysts (175°C) which makes these catalyst viable for selective oxidation of CO in the temperature range at which PEMFC operate. The effect of CO_2 and H_2O on CO oxidation behavior was also studied, and the presence of CO_2 was found to slightly activate the catalyst while steam inhibited the catalyst activity. Moreover, water gas shift reaction contribution to CO oxidation was found negligible in the temperature range 25–200°C.

2.3.2. Ceria Catalysts

$CuO\text{-}CeO_2$ catalysts exhibit higher activity in the partial oxidation of CO reactions compared to other conventional copper-based catalysts. Therefore, $CuO\text{-}CeO_2$ catalysts which offer a good compromise between catalytic performance and cost can be considered as promising catalysts for PROX. Preparation methods of $CuO\text{-}CeO_2$ catalysts have a critical influence on their PROX performance, and different preparation methods have been reported up to now.

Coprecipitated $CuO\text{-}CeO_2$ catalysts synthesized by Kim *et al.* (2003) with a BET specific surface of 91 m^2/g showed superior performance for PROX and succeeded in reducing the CO content to less than 100 ppm at temperatures below 170°C for a feed of 1% CO, 1% or 1.25% O_2, 50% H_2 in the presence of H_2O and CO_2.

On the other hand, Avgouropoulos *et al*. (2005) investigated the difference between $CuO\text{-}CeO_2$ catalysts prepared by using coprecipitation, citratehydrothermal, urea-nitrates combustion and impregnation methods. They found that the combustion-prepared sample exhibited the best catalytic performance, followed by the citratehydrothermal-prepared sample. The impregnated sample was found to be the least active for PROX.

Liu *et al*. (2008b) investigated the influence of preparation methods (i.e, impregnation, coprecipitation and inverse coprecipitation) on PROX over $CuO\text{-}CeO_2$ catalysts and the catalysts were characterized by BET, XPS, XRD, UV Raman and TPR techniques. The results showed that the catalysts prepared by coprecipitation had smaller particle sizes, well-dispersed CuO_x species, more oxygen vacancies and were most active in preferential CO oxidation. CO conversion of the catalyst prepared by coprecipitation was 99% at 120°C, while CO conversions of catalysts prepared by inverse coprecipitation and impregnation did not reach 99% in all reaction temperature ranges. Inverse coprecipitation greatly depressed the catalytic performance of $CuO\text{-}CeO_2$ catalysts and caused the growth of $CuO\text{-}CeO_2$ particles because of the pH difference of the precipitation process.

Derekaya *et al*. (2009) examined ceria supported CuO catalysts for selective CO oxidation in excess hydrogen. PROX activities of 25/25/50 $CuO/Co_3O_4/CeO_2$, 5/95 CuO/CeO_2 and 50/50 CuO/CeO_2 catalysts were tested and catalysts prepared by the co-precipitation method gave the highest surface areas. All catalysts were characterized by BET surface area measurement, N_2 physisorption, SEM micrographs and X-ray diffraction. The PROX reaction was carried out between the 110°C and 210°C. Among the catalysts, the 5/95 CuO/CeO_2 gave the highest stable CO conversion and selectivity. The effect of catalyst pretreatment on CO oxidation was also investigated for 5/95 CuO/CeO_2, calcined at three different calcination temperatures: 600°C, 700°C and 800°C. All catalysts gave low CO conversion at low reaction temperatures; but after 150°C, CO conversions rose above 70%. The catalyst calcined at 600°C gave the highest CO conversion of 100% at 200°C. All catalysts had high selectivity to CO oxidation with the catalyst calcined at 800°C gaving 100% selectivity between 100°C and 200°C reaction temperatures. The selectivity of catalysts calcined at 600°C and 700°C increased with increasing temperature and these catalysts gave 95% selectivity at 200°C. Furthermore, deactivation studies showed that the catalyst calcined at 700°C protected its activity and selectivity at a reaction temperature of 200°C for 24 hours.

A kinetic study was conducted by Moreno *et al*. (2008) for CO oxidation over CuO/CeO_2 catalysts in the presence of excess H_2 in a temperature range appropriate for the operation of the PROX unit in the H_2 production process for PEM fuel cells applications. The CuO/CeO_2 catalyst (1 wt% Cu) was prepared by incipient wetness impregnation of the support (ceria) with a $Cu(NO_3)_2.3H_2O$ solution and subsequent calcination at 550°C for 5 hours. In the experiments, the feed gas stream was a mixture of 50% H_2, 1–2.5% CO, 1–4% O_2 and N_2 as balance. The integral reactor experiments demonstrated that CO can be completely removed from the H_2-rich stream working in a wide operation temperature window, from 160°C to 220°C. Since the CO oxidation rate was found to be independent of O_2 partial pressure, it was not necessary to consider the hydrogen consumption profile in the calculation of the theoretical CO conversion profile.

2.3.3. Cobalt Catalysts

The catalysts used for catalytic CO preferential oxidation usually consist of noble metals, Cu–Ce, supported CuO or other base metal oxides. Although it appears that cobalt

is highly active for CO oxidation, only a few studies focusing on cobalt-containing catalysts have been reported.

In order to understand the effect of cobalt, Kang *et al.* (2003) prapared CoO_x/CeO_2 composite catalysts with various cobalt loadings and tested CO oxidation in stoichiometric CO and O_2 mixtures. CO oxidation was investigated over 10 wt% cobalt oxide-containing catalysts like CoO_x/CeO_2 and various other supports. CoO_x/CeO_2 composite catalyst was shown to be superior compared to the other systems such as CoO_x/γ-Al_2O_3, CoO_x/SiO_2, CoO_x/TiO_2 and CoO_x/Zeolite-Y, since the contact of two types of materials, CoO_x and CeO_2, gave rise to a highly active catalyst. The activity and stability of CoO_x/CeO_2 catalysts with various cobalt loadings were studied under feed stream conditions of 1% CO and 0.5% O_2 in N_2. The activity of CoO_x/CeO_2 composite catalysts increased with cobalt loading from 5 to 15 wt% then remained constant at higher loadings of 15–20 wt%. Moreover, experiments indicated that carbon dioxide retention contributed to the small activity decay rates observed. CoO_x/CeO_2 composite catalysts showed good resistance to water vapor poisoning due to the strong interaction between the two catalyst components. Catalyst characterization studies, X-ray diffraction (XRD) and temperature-programmed reduction (TPR) showed that proper cobalt loading (15 wt%) can lead to better dispersion of cobalt oxide and the finely dispersed CoO_x species with higher valence state mainly contribute to the catalytic activity.

Zhao *et al.* (2008) studied preferential oxidation of CO in excess H_2 to investigate the effects of metal oxide supports on PROX performance of cobalt catalysts. Catalysts with 10 wt% cobalt on various metal oxide supports (ZrO_2, CeO_2, SiO_2, Al_2O_3 and TiO_2) were prepared by wet impregnation. Co/ZrO_2 had higher cobalt dispersion and more sites for CO adsorption than the other materials and also had the highest rate of CO conversion during the PROX reaction. Cobalt dispersion on Co/ZrO_2 was only slightly higher than on Co/SiO_2 and Co/Al_2O_3. Additionally, temperature programmed reaction studies and steady-state measurements showed that CO was preferentially oxidized to CO_2 at temperatures below 175°C, but as the temperature was increased, the rate of the competing H_2 combustion reaction led to a decline in CO conversion. At temperatures near 250°C, the methanation reaction also began to play an important role in CO conversion as the cobalt species began to reduce from a more oxidized form.

Yung *et al*. (2007) discussed the activity of Co/ZrO_2 for CO oxidation to CO_2 in excess oxygen. The catalysts with 10 wt% cobalt supported on different metal oxides were prepared by incipient-wetness impregnation. Mechanistic studies on CO oxidation in excess O_2 (without H_2) identified cobalt as being active for CO oxidation. Activity tests showed that CO conversion could be obtained at temperatures as low as 20°C. There is no loss of activity in time-on-stream studies, indicating that the catalyst (Co/ZrO_2) is stable in the experimental oxidizing conditions used. Moreover, catalyst characterization by thermogravimetric analysis, temperature-programmed techniques, X-ray photoelectron spectroscopy, and laser Raman spectroscopy showed that after calcination Co_3O_4 is present on monoclinic ZrO_2. It was reported that Co_3O_4 is active for preferential oxidation of CO and the catalyst was considered as a good candidate since Co_3O_4 was shown to be active for CO oxidation and is less expensive than Au or Pt. However, reduction of the bulk metal oxide to metallic Co could occur under the excess H_2 which may lead to deactivation.

The participation of cobalt in the Co-Al skeleton was observed by Özkara *et al.* (2005) for all coprecipitated samples. The effect of metal loading on structural properties and low temperature CO oxidation activity of coprecipitated Co/Al_2O_3 catalysts was studied. During the experiments, Co/Al_2O_3 catalysts containing 2.4, 9.9, 13.3, 16.8 and 36 wt% Co were prepared by coprecipitation of the hydroxides of cobalt and aluminum from the corresponding nitrates reacting in a basic solution. Reduced cobalt/alumina catalysts were characterized using ESEM-EDXS to get information on their microstructural and metal dispersion properties. At low cobalt loadings, it is observed that the cobalt metal suspended on alumina integrates into the skeletal structure. The SEM figures showed that at a cobalt loading of 16.8 wt%, excess Co cannot incorporate into the skeletal structure and starts to form Co agglomerates. Additionally, the results indicated that TSA (total surface area) has a maximum value at 13.3 wt% Co loading. In other words, it can be said that Co plays a direct role in the formation of the skeletal structure of the coprecipitated Co/Al_2O_3 catalyst. An increase in TSA is possible up to ca. 15 wt% Co loading. On the other hand, at higher loadings, excess Co forms clusters on the catalyst surface that block the pores of the catalyst; at the same time, excess Co forms its own porous structure. The catalysts prepared were evaluated for their CO oxidation performances. It was reported that 16.8 wt% Co/Al_2O_3 displayed the best catalytic performance, since the catalyst did not lose its activity and stayed stable with a CO conversion of 100% at 373 K. Additionally, it was noted that conversions started to decrease after 30 minutes-on-stream for some samples,

because the site ratio for CO and O_2 adsorption was not optimal for stable CO oxidation performance. The active sites for oxygen adsorption may be covered by unused CO on the surface which leads to a scarcity of sites for oxygen adsorption.

2.3.4. Alumina-Supported Catalysts

The Pt/Al_2O_3 catalyst received much attention in the past for selective CO oxidation because of its high catalytic activity at 170–230ºC. However, this catalyst does not show good performance at lower temperatures which meet PEMFC requirements. Researchers have reported that the addition of non-precious metals to Pt/Al_2O_3 catalysts improved its ability to preferentially oxidize CO at low temperatures.

Liu *et al.* (2008a) studied Ce-promoted $Pt/\gamma\text{-}Al_2O_3$ catalysts for PROX under a H_2-rich atmosphere. Catalysts prepared by co-deposition-precipitation and sequential deposition-precipitation methods were tested. The co-deposition-precipitation method was found to be more efficient in preparing highly active Ce-promoted $Pt/\gamma\text{-}Al_2O_3$ catalysts. Among the catalysts investigated, $Pt\text{-}Ce/\gamma\text{-}Al_2O_3$ prepared by co-deposition-precipitation showed the best catalytic performance with maximum CO conversion of 85% at 120ºC which was much better than that over the $Pt/\gamma\text{-}Al_2O_3$ catalyst. Results of catalysts characterization and catalytic activity tests clarified the promoting role of ceria which provides the active oxygen for PROX in H_2-rich atmospheres.

The key for improving the CO oxidation rate is to allow for a non-competitive dual-site mechanism for CO and O_2. New catalyst formulations are being developed towards supplying these catalysts with an additional site for oxygen adsorption by incorporation of a promoter which will directly enhance reaction rates (Ayastuy *et al.*, 2006).

Jain *et al.* (2009) also investigated the catalytic performance of a series of Pt/Al_2O_3 catalysts modified with Cr, Mn, Fe, Co, Ni, Cu and Sn. The promoters were deposited on the surface of 5 wt% monometallic Pt/Al_2O_3 and the catalysts prepared were tested for PROX in hydrogen-rich streams. Additionally, the catalysts were characterized using TEM, EDX, ICP-AES and CO chemisorption to suggest the most successful promoter deposited on the Pt surface. It was reported that the deposition of promoters significantly enhances activity and selectivity even at low promoter loadings (0.15–0.25 wt %) and Fe

and Co promoted catalysts in particular give the highest catalytic activity. On the other hand, Cr promoted Pt/Al_2O_3 has the lowest activity among the other catalysts.

The selective low-temperature CO oxidation over $Pt\text{-}Co\text{-}Ce/Al_2O_3$ catalysts was examined by İnce *et al. (*2003). Catalyts prepared by incipient to wetness co-impregnation technique were investigated in a flow micro-reactor system in hydrogen-rich streams. During the experiments, various combinations of metal loadings and calcination conditions were tested for CO oxidation. 1.4 wt%Pt-1.25 wt%Co-1.25 wt%Ce supported on γ-Al_2O_3 gave 100% CO conversion at 90°C with a feed composition of 1.0% CO, 1.0% O_2, 60% H_2 and balance He. Addition of 25% CO_2 and 10% H_2O into the feed resulted in an increase in the reaction temperature to 110°C where 100% CO conversion was achieved for 300 min time-on-stream. Considering the low operating temperatures and O_2/CO ratios, it was concluded that Pt-Co-Ce catalysts supported on alumina have great commercial potential for CO removal in fuel cell applications.

2.4. Monolithic Catalysts

In heterogeneous catalytic reactions, the chemical reaction occurs on the surface of the solid catalyst; therefore, the catalyst should have high surface area. During catalyst design, low investment cost is considered together with significant energy recovery and space saving. At this point, the development of monolithic catalysts, which have high surface area compared to particulate catalysts, plays an important role making a thinner catalyst layer possible and enhancing the diffusion of reactants toward active catalyst sites. Related scientific literature indicates that the development of monolithic catalysts has been one of the most significant accomplishments in heterogeneous catalysis and catalytic reaction engineering. The word “monolith” originates from the Greek language in which mono means single and lithos means stone. A monolith structure is referred to as a honeycomb structure; but in technical context, it refers to a large uniform block of a single building material (Tomasic *et al.*, 2006; Maeda *et al.*, 2008).

Since their introduction in the mid-1970s, honeycomb-shaped monolithic catalysts have become the standard catalyst shape in most environmental and chemical applications (Boger *et al.*, 2004). The first major application area of the monolithic catalyst was in

automobile exhaust treatment. Other applications of monolithic catalysts became available later such as three-way catalysts, diesel catalysts for the abatement of liquid particulate (soluble organic fraction) and gaseous CO 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 and destruction of volatile organic compounds (VOC) from chemical plants (Avila *et al.*, 2005). The main reason for the success of monoliths in environmental applications is their excellent ratio of pressure drop to geometric surface area. Straight and parallel channels do not hinder gas flow at all and hence the pressure drop across a monolith is extremely low. Compared to other solid structures such as pellets or foams, a considerably lower pressure drop is obtained at a given geometric surface area which is an advantage of monolithic honeycomb structures (Boger *et al.*, 2004).

Basic monolith structure varies in dimension and shape depending on the purpose of use (Tomasic *et al.*, 2006), and honeycoms made of different materials are characterized by the size and geometry of the channel openings (d_h), the void fraction (ϵ) or open frontal area (OFA), and the cell density is usually described by cells per square inch (cpsi) or per square centimeter (Boger *et al.*, 2004); the channels of the monolith may be hexagonal, rectangular or various other shapes.

Different shapes and sizes of monolithic structures composed of a large number of straight and parallel channels that extend throughout the body with different shapes and sizes are shown in Figure 2.2.

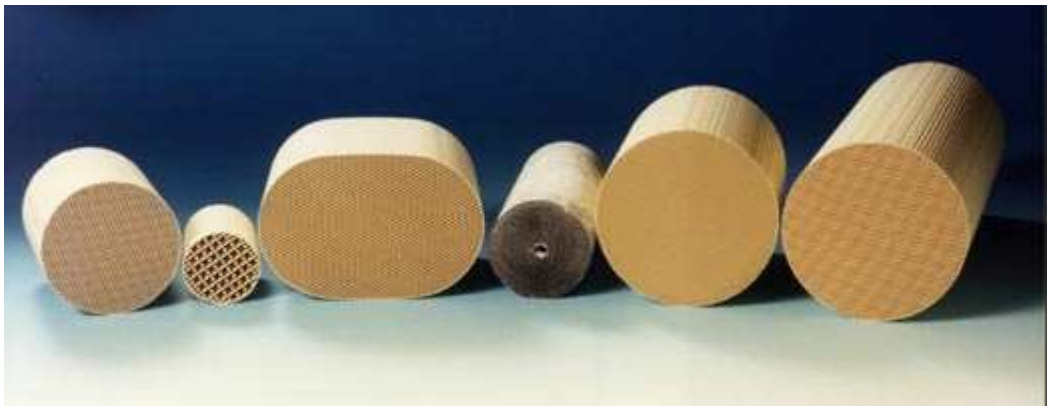

Figure 2.2. Different shapes and sizes of monolithic material (Heiszwolf, 2008)

Monoliths can be classified into two with respect to their basic construction material: monoliths made of (i) ceramic (mainly cordierite) or (ii) metallic materials (stainless steel, metal alloys, etc.) Ceramic and metallic monoliths both have different advantages and disadvantages over each other. Generally, in automobile exhaust purifier systems, ceramic monoliths consisting of a closely packed array of small square cells are used as catalyst supports. Geometric and physical properties of monoliths, such as shape, size of channels, thickness and porosity of the channel wall as well as thickness and microstructure of the deposited catalytic layer depend on specific process constraints (Tomasic *et al.*, 2006).

Monolithic catalysts have numerous advantages over the usual particulate catalysts (Tomasic *et al.*, 2006). Among these advantages are high specific surface, small pressure drop, good interphase mass transfer, much lower resistance to mass transfer by intraphase diffusion through the very thinly deposited catalytic layer, good thermal and mechanical properties, and simplicity of scale up merely by increasing the number of channels.

In heterogeneous catalysis, monoliths are used mostly to support a catalytically active component or as the catalyst itself (if a catalytic component is an integral part of the monolith structure). A monolithic catalyst is generally made by the application of a layer of a catalytically active component or an appropriate support (such as Al_2O_3, SiO_2, ZrO_2, carbon, zeolites, etc.) containing one or more catalytically active components (Pt, Pd, Rh, zeolites, etc.) onto the walls (or inner walls) of the basic, often inert, monolith structure. This process is called “wash-coating”. If the monolith structure is made of the required support material, the catalytically active phase can be coated on the monolith right away. On the other hand, if the monolith is not obtainable in the support material, the desired support material should first be coated on the monolithic substrate. The most important criterion in the selection of the support is that the catalytically active component(s) adhere well to the basic inert monolith structure. This crucial step can be assisted by suitable additives in ceramic monoliths or by proper thermal and/or chemical pretreatment of the metal surface in metallic monoliths.

There are advantages and disadvantages in using ceramic or metallic monoliths. The advantages of metallic over ceramic monoliths are: (i) lower overall volume, (ii) better

mechanical durability, (iii) high thermal conductivity of thin metallic walls (in the order of 0.04–0.05 mm) facilitating quick attainment of operating temperatures while minimizing emission of gaseous pollutants during cold start phase of engines, (iv) practical design options for improving heat and mass transfer and preventing accumulation of backpressure (Tomasic *et al.*, 2006). The major benefit of ceramic monoliths is the ease with which various supports and/or catalyically active materials can be coated onto their surface.

The application of a support layer to ceramic monolith structures is accomplished by different methods that may be listed as (i) colloidal coating where the support particles are in colloidal solution, (ii) sol-gel coating where the support is dissolved in the liquid phase, (iii) slurry coating with suspended support particles, and (iv) other less frequently used specific procedures (Döker, 2008).

After the application of the support layer, or wash-coat, by one of the techniques listed above, catalytically active component(s) are deposited by conventional methods such as impregnation, ion exchange, precipitation or co-precipitation (Madhusoodana *et al.*, 2001; Tomasic *et al.*, 2006). In some cases, the catalytically active component and support material may be coated simultaneously on the monolith structure to achieve the required porosity, good mechanical properties and high dispersion of the catalytically active component. Some catalysts, such as zeolites, do not need a specific support material and can be coated directly on the monolithic structure (Döker, 2008).

During the last decade, ceramic monoliths with straight channels were considered as suitable supports for PROX reactions, since the geometric surface area of the ceramic monoliths is much larger than particulate catalysts that make a thinner catalyst layer and enhance the diffusion of reactants toward active catalyst sites. Furthermore, the high open area also results in a low heat capacity that provides a rapid response to changes in the operating conditions of the fuel processor for PEFCs. Despite these potential advantages, only a few papers, including those of Korotkikh and Farrauto (2000), Roberts *et al*. (2003), Ahluwalia *et al.* (2005), Zhuo *et al.* (2006), Maeda *et al*. (2008), Zeng and Liu (2008) have reported work on monolithic PROX catalysts so far.

Particulate Pt catalysts promoted with a metal oxide are shown to have good activity and selectivity for preferential CO removal in a H_2-rich stream in fuel processing

applications. Enhanced activity is due to the presence of the metal oxide promoter, which provides adsorption sites for O_2 adsorption and dissociation. Therefore, the metal oxide promoter eliminates the normal inhibition observed in the oxidation of CO on Pt catalysts.

In order to study the activity of monolithic PROX catalysts, Korotkikh and Farrauto (2000) prepared a γ-alumina supported 5 wt%Pt catalyst promoted with a base metal oxide which was later crushed to powder form and deposited onto a cordierite monolith structure. The samples were studied in the temperature range 90-150°C. Increasing the reaction temperature from 90°C to 150°C shows a small increase in CO conversion, from 43 to 51%. On the other hand, total O_2 conversion increases more dramatically approaching 100% with the increase in reaction temperature. The increased O_2 conversion is primarily due to an increase in H_2 oxidation as evident by the selectivity decreasing from 80 to 60%. The conversion of CO and O_2 over the promoted Pt monolithic catalyst at 90°C is about 70% at the stoichiometric condition with an O_2/CO ratio of 0.50. Increasing the O_2/CO ratio to 0.75 increases the CO conversion above the 95% level with 65% selectivity. To further understand the performance of this catalyst, a study was conducted with two sets of particulate Pt/γ-Al_2O_3 catalysts of identical Pt loading with and without the promoter oxide respectively. CO conversion is clearly enhanced for the particulate promoted Pt catalyst, and a CO conversion of 68% is obtained as compared to the 13.2% conversion of the particulate unpromoted Pt/γ-Al_2O_3 at 90°C with an O_2/CO ratio of 0.50. The selectivities are comparable at 78 and 82%, respectively, showing that the promoter increases both CO and H_2 oxidation. CO conversion went up to 90% at 90°C and an O_2/CO ratio of 0.75 over the promoted catalyst while it remained constant on the unpromoted Pt/γ-Al_2O_3; selectivities over both catalysts decreased to about 65-66%. In other words, the promoted catalyst performed at higher CO conversion than the unpromoted one while maintaining similar selectivities in the 90–150°C range. When the O_2/CO ratio was increased to 0.75 at 150°C, CO conversion over Pt/γ-Al_2O_3 increased to ca. 27%, but was still less than half the CO conversion on the promoted Pt catalyst which had declined to 62%. The role of the promoter was explained by its ability to provide other sites for dissociative O_2 adsorption. Similar CO conversions and CO oxidation selectivities were obtained over the metal oxide promoted Pt monolith at 90°C and O_2/CO ratios of 0.50-0.75 when feed containing higher CO concentrations was introduced at much lower volume hourly space velocities.

In another study, Roberts *et al*. (2003) synthesized Pt/Al_2O_3 catalysts promoted with Fe and supported on 400 cpsi ceramic straight-channel monoliths which were evaluated in

an adiabatic reactor at a total pressure of 0.20 mPa and inlet temperatures of 80–170°C for preferential oxidation of CO in the presence of excess H_2. Experiments were carried out with an inlet gas composition of 0–1.0% CO, 0–1.0 %O_2, 42% H_2, 9% CO_2, 12% H_2O and N_2 as the balance. The first catalyst evaluated was a ceramic monolith with an Al_2O_3 wash-coat containing 0.5% Pt and 0.005% Fe. Strong inhibition by CO was observed with this catalyst. With a feed gas containing 1% CO and 1% O_2 and at a space velocity of 30,000 h^{-1}, the total O_2 conversion was less than 10% and no significant temperature increase was observed, even with an inlet temperature as high as 170°C, which suggested that both CO and H_2 oxidation were hindered. A series of catalysts were then synthesized with wash-coats containing 5 wt% Pt and different Fe concentrations: 0, 0.05, 0.5 and 1 wt%. The catalyst with a washcoat containing 5 wt% Pt and 0.5 wt% Fe on Al_2O_3 proved to be active and selective for CO conversion. At an inlet temperature of 100°C with 1% CO and 1% O_2 in the feed gas, this catalyst gave 80% CO conversion with a selectivity of about 40%. It was reported that the performance of the 5 wt% Pt-0.5 wt% Fe on Al_2O_3 catalyst appeared to be influenced by external heat and mass transport, especially at low linear velocities which were likely to magnify the effect of the reverse WGS reaction, possibly because of catalyst surface temperatures that were considerably higher than the bulk gas temperature.

Ahluwalia *et al.* (2005) studied CO oxidation over a Pt-based monolithic catalyst; it was the Engelhard Selectra1-PROX I catalyst coated on a 600 cpsi cordierite monolith, 7.62 cm in diameter and 12.7 cm long. The reactor used in the experiments was configured with a single catalyst test section having inlet and outlet flow conditioning stages for providing uniform flow to the catalyst. Experiments showed that it was feasible to conduct selective CO oxidation on a noble-metal catalyst coated on a ceramic monolith at 100°C to produce PEMFC quality hydrogen. Moreover, it was demonstrated that the selectivity for CO oxidation is a function of inlet CO concentration and oxygen stoichiometry; CO oxidation selectivity always decreases with increasing oxygen stoichiometry at constant inlet CO concentration.

Four monolithic catalysts, Pt, Pd, Rh and Ru supported on cordierite monoliths coated with γ-Al_2O_3 were investigated for selectively oxidation of CO by Zhuo *et al.* (2006). Experiments were carried out at atmospheric pressure in a quartz tubular reactor with a reaction mixture consisting of 1% CO, 1% O_2, 50% H_2, 20% CO_2 and N_2 as the balance. Pt/Al_2O_3 was found to be the most promising candidate for selective CO oxidation

in hydrogen-rich gases. Additionally, the Pt/Al_2O_3 monolithic catalyst exhibited very stable performance in the durability test. The sequence of activities for CO oxidation over Pt group metals were observed as follows: Pt>Rh>Ru>Pd. The effects of the presence of H_2O and CO_2 on catalyst performance were also examined. H_2O in the feed enhanced the preferential oxidation of CO, while CO_2 retarded the reaction. When H_2O and CO_2 were both added to the feed, the combined effect was positive at temperatures below 180°C while their effect above 180°C was similar to the effect observed for CO_2 alone.

Maeda *et al*. (2008) studied 4 wt% Pt-0.5 wt% Fe/mordenite catalysts coated on 400 cpsi ceramic straight-channel monoliths for the preferential oxidation of CO in hydrogen-rich gas streams, in the 100-300°C temperature range. Conventional ion-exchange method was used to prepare the Pt-Fe/M powders that were coated on a 400 cpsi cordierite ceramic monolith, 1.2 cm in diameter and 1.5 cm in length. In feed gas containing 1% CO, 1% O_2, with the balance H_2, at temperatures ranging from 100°C to 130°C, CO conversion reached almost 100% with an outlet CO concentration of less than 10 ppm. In other words, the monolithic catalyst was able to meet the 10 ppm target level of CO concentration, even at low O_2/CO ratios and high space velocities in a single-stage reactor. Additionally, even in a synthetic reformate gas (1% CO, 1% O_2, 15% H_2O, 20% CO_2, balance H_2) was used, the monolithic catalyst exhibited excellent activity, reducing the CO concentration to less than 100 ppm. There was no detected change in the outlet CO concentration during 500 hours of operation, which was promising for practical applications.

Zeng and Liu (2008) investigated the role of additives on the PROX performance of $CuO–CeO_2/Al_2O_3$/FeCrAl monolithic catalysts that were prepared by *in situ* combustion method and characterized using SEM, XRD and TPR techniques. FeCrAl honeycombs with cell densities of 400 cpsi were chosen as the metallic supports. Then, $CuO–CeO_2$ and $CuO–Ce_{0.9}M_{0.1}O_2$ (M = Nd and Zr) were loaded onto FeCrAl. The results of catalytic performance tests revealed that the reducibility and dispersion state of CuO in the $CuO–CeO_2/Al_2O_3$/FeCrAl is modified by the inclusion of Nd or Zr, which decrease the activity for hydrogen oxidation and increase oxygen selectivity for CO oxidation in H_2-rich gases. At a reaction temperature of 105°C, the activity of $CuO–CeO_2/Al_2O_3$/FeCrAl is nearly the same as $CuO–Ce_{0.9}Nd_{0.1}O_2$,/Al_2O_3/FeCrAl and $CuO\text{-}Ce_{0.9}Zr_{0.1}O_2/Al_2O_3$/FeCrAl catalysts. Complete CO oxidation is obtained in the reaction temperature range of 165–205°C over $CuO–Ce_{0.9}Nd_{0.1}O_2/Al_2O_3$/FeCrAl and $CuO–Ce_{0.9}Zr_{0.1}O_2/Al_2O_3$/FeCrAl, while temperature

range is 165–185°C for CuO–CeO_2/Al_2O_3/FeCrAl. The order of CO conversions obtained at 205°C suggested that the addition of Nd or Zr and FeCrAl support in the catalysts increased CO conversion. It was also found that the good heat transfer ability of the FeCrAl support can depress reverse WGSR effectively, which is beneficial for CO removal from hydrogen-rich gases via selective oxidation.

Döker (2008) investigated the preparation methods used for monolithic catalysts and developed a preparation procedure for cordierite monolithic Pt-Co-Ce-Al_2O_3 catalyst used for the preferential oxidation of CO in a hydrogen-rich environment. In a comparative study, the monoliths were wash-coated with alumina using three different methods: colloidal coating, slurry coating and aluminum nitrate coating. Metal precursor solutions containing Pt, Co and Ce were then impregnated over alumina wash-coated monoliths. Afterwards, total surface area measurements, environmental scanning electron microscopy (ESEM) and optical microscopy were employed to characterize the catalysts prepared. The most promising catalyst preparation method was found to be colloidal coating and the highest surface area of wash-coated monolithic catalysts was achieved by this method among the three wash-coating methods studied. Colloidal alumina coated and Pt-Co-Ce impregnated monolithic catalysts were tested in a micro-reactor flow system under a total flow of 100 cm^3 min^{-1} in the 383-443 K temperature range. At 443 K, the monolithic catalyst was found to exhibit the highest catalytic activity with CO oxidation approaching 100 percent, even with feed containing 1% CO, 1% O_2, 60 % H_2 and helium as balance.

2.5. Preparation of Monoliths

Generally, three steps can be distinguished for converting a bare ceramic monolithic body into a proper catalyst for conducting reactions (Vergunst *et al*., 2001):

- Coating a monolith with a catalyst support material,
- Deposition of the active phase on a monolithic support,
- Drying of the support.

2.5.1. Coating a Monolith with a Catalyst Support Material

A bare monolithic structure can be coated with a catalyst support layer to increase the BET surface area of the monolith and to have a support material which has a better interaction with the active catalyst material. The process of coating or loading a ceramic monolithic catalyst with a support material is mostly called washcoating. The general methodology of washcoating has been discussed by Nijhuis *et al*. (2001).

During the washcoating, monolith which is cut into desired width, length and height is first immersed into a washcoating solution or slurry for a short period. The monolith is removed from the liquid and most liquid is shaken out. The liquid remaining in the channels of monolith is gently blown out by pressurized air. Then, the monolith is dried in the horizontal position in oven or microwave, being rotated continuously around its axis, to prevent gravity from causing an uneven washcoat distribution. Dry monolith is weighed to determine the amount of catalyst support material that has been taken up. Finally, the coating is fixated to the monolith by a high-temperature calcination step. These stepwise procedures are continued until the desired weight increase is achieved. This procedure can be repeated after calcination or the monolith can be dipped into washcoating solution again after drying before calcination. The disadvantage of repeated coating without intermediate calcination is that the part of the coat layer deposited in a first dip dissolves in the second dip and, therefore, the coated amount does not increase as much as when the monolith has been calcined first. Furthermore, skipping the intermediate calcination results in shorter preparation time (Nijhuis *et al*., 2001).

When coating monolithic bodies, the adherence of the coating on the monolithic structure is very important. In particular, incorrectly prepared slurry coatings can be lost quite easily. Different techniques are available for depositing a catalyst support coat layer onto a monolithic body (Nijhuis *et al*., 2001):

- Colloidal coating
- Sol–gel coating
- Slurry coating
- Polymer coating

2.5.1.1. Coating Using Colloidal Solutions. Colloidal coating using a colloidal solution of the washcoat material is the easiest way to put a washcoat layer on a monolithic substrate.

The active phase is usually applied together with a high surface area support material, e.g., γ-alumina, to achieve good dispersion of the catalyst species (Bager, 2004). Colloidal solutions of silica and alumina are readily available. Other solutions are also available on demand. A typical procedure for coating a monolith in this manner is to submerge the dry monolith in the colloidal coating solution for a few seconds. The excess liquid on the monolith walls is shaken out and the liquid still remaining in the channels is gently blown out by using pressurized air. Complete removal of the remaining liquid phase requires a drying process. Monoliths are dried horizontally at room temperature while continuously being rotated around their axes. Finally, monoliths are calcined in air (Nijhuis *et al*., 2001).

2.5.1.2. Sol–Gel Coating. The sol-gel process is a wet-chemical technique widely used recently in the fields of materials science and ceramic engineering where the liquid phase contains secondary support precursors. The interest in sol-gel processing can be traced in the mid-1880s with the observation that the hydrolysis of tetraethyl orthosilicate (TEOS) led to the formation of SiO_2 under acidic conditions (Hench and West, 1990).

In the sol–gel procedure, the liquid phase contains secondary support precursors. This method is applied by hydrolytic procedure based on hydrolysis of the appropriate alkoxides in the presence of either an acid or a base, followed by polycondensation in the next step (Tomasic *et al.*, 2006):

$$M(OR)_n + nH_2O \rightarrow M(OH)_n + nROH \quad (M= Al, Si, Ti, Zr) \qquad (2.10)$$

$$-M-OH + HO-M'- \rightarrow -M-O-M'- + H_2O \qquad (2.11)$$

The advantage of sol-gel coating is that the coating can easily reach all pores in the cordierite support (Nijhuis *et al*., 2001).

2.5.1.3. Slurry Coating. In slurry coating of monolithic substrates, the coat layer is primarily deposited on the channel walls of the support. The main advantages of this method are that the diffusion distance to the active catalyst species for the reactants flowing through the channels is shorter and that the maximum loading of the coating is not limited by the monolith macropore volume. Slurry coating is usually carried out with slurry of particles of a size comparable to the larger macropores of the support material (typically a few micrometers) (Nijhuis *et al*., 2001).

2.5.1.4. Other Coating Methods. Polymerization coating of carbon is the other method for coating a monolith with a catalyst support material. Carbon is regarded as the third most used catalyst support material after silica and alumina, but it has limited application. Due to the inertness of the carbon material, possible coating options are limited when using carbon on a support. Compared to the other support materials, silica and alumina, carbon has a small physical interaction between support and coating. At this point, the most suitable way to link the carbon coating to the support is to deposit it in the pores and cracks of the support, using a pore-filling procedure (Nijhuis *et al*., 2001). Carbon does have advantages over other types of support. These advantages are its stability in acidic and basic media, its lower tendency to react with the active phase, and its more inert nature compared to other support materials (Nijhuis *et al*., 2001).

2.5.2. Deposition of the Active Phase on a Monolithic Support

The application of an active phase to a monolithic support is the following step after coating in the preparation of a catalyst. For monolithic catalysts, the active phase loading, dispersion and distribution are very important. Due to the lower catalyst content of a monolithic structure per unit reactor volume compared to a packed bed reactor, the active phase should be highly active. This can be achieved by a high loading, a high dispersion, and a uniform active phase distribution over the geometric surface area of the monolithic support (Vergunst *et al.*, 2001). There are different methods to apply active phase precursors to pre-shaped monolithic support. These may be listed as impregnation, ion-exchange and deposition-precipitation methods (Vergunst *et al.*, 2001).

2.5.2.1. Deposition of the Active Phase by Impregnation. Impregnation is the simplest way to deposit a metal on a monolith. Focusing on impregnation, two methods are distinguished for conventional catalyst supports: pore volume or dry impregnation (incipient wetness) and wet impregnation. In pore volume impregnation, a liquid volume equal to the pore volume of the catalyst support is used. For monolithic structures, dry impregnation is quite difficult, as it is hard to supply the monolith with the exact amount of liquid corresponding to its pore volume, where the liquid will have to travel a long distance to reach all the pores. If dry impregnation is used, external parts of the monoliths may contain excess

liquid while the center can remain dry which causes an uneven distribution of the active phase on monolith (Vergunst *et al.*, 2001).

In the case of wet impregnation, excess liquid is used. Firstly, the amount of liquid that a monolith can adsorb must be determined. The metal precursor is dissolved in the liquid so the concentration of metal in the liquid to be taken up by the monolith will produce the desired metal loading. A dry monolith is immersed into precursor solution, removed and excess liquid blown out. The dipping procedure should be carried out in as short a time as is practically feasible to prevent an excess of metal adsorbing on the support to prevent an uneven distribution of metal on the monolithic structure, especially if the metal precursor shows a significant interaction with the support. After impregnation, the procedure is continued immediately with drying step before the solvents start to evaporate after the monolith is removed from the liquid. Additionally, it is useful to keep the wet monoliths in a horizontal position while continuously being rotated to prevent gravity from causing the liquid to flow to one side of the monolith (Vergunst *et al.*, 2001).

2.5.2.2. Deposition of the Active Phase by Ion Exchange. Ion-exchange is a commonly applied method for deposition of the active phase. In this method, the support is put into a solution containing the metal salts in either positively or negatively charged complexes. These complexes can adsorb on (or react with) surface groups of the support. For example, platinum can be put on an alumina support by using chloroplatinic acid (H_2PtCl_6). Many other metal complexes used in ion-exchange metal depositions, such as ammonium hexachlororuthenate (IV) on alumina, adsorb much more slowly on the support and require ion-exchange for a few hours to obtain 1 wt% loading, and there is a risk of maldistribution for these cases. The advantage of an ion-exchange deposition method is that the metal interacts with the support and metal maldistribution problems during drying will not occur easily. However, if the interaction between the metal and support is not strong enough, the metal may move and the drying rate influences metal distribution (Vergunst *et al.*, 2001).

2.5.2.3. Deposition of the Active Phase by Deposition–Precipitation. Deposition–precipitation method is another method used for applying the active phase on a monolithic support. It is based on the formation of an insoluble catalyst precursor complex and the procedure is performed as follows: A soluble metal and a precipitating agent are present in the impregnation solution together with the monolithic support. Urea is frequently used as

the precipitating agent for deposition. By heating this mixture to sufficiently high temperature (>333 K), the pH increases homogeneously throughout the solution, and the following chemical reactions take place (Vergunst *et al.*, 2001).

$$H_2N–CO–NH_2(aq) + 3H_2O \rightarrow CO_2(g) + 2NH_4(aq) + 2OH\ (aq) \quad (2.12)$$

$$Ni_2\ (aq) + 2OH\ (aq) \rightarrow Ni(OH)_2(s) \quad (2.13)$$

2.5.3. Drying of supports

The last step for monolith preparation is the drying of the support. Proper deposition procedures for metals on monoliths are followed by a drying procedure to remove the solvent from the catalyst. Then, the monolithic catalysts are ready to use.

3. EXPERIMENTAL PROCEDURES

3.1. Materials

3.1.1. Chemicals

The chemicals used in catalyst preparation and their properties are given 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
Cerium (III) nitrate hexahydrate	$Ce(NO_3)_3.6H_2O$	Extra Pure	Merck	434.23
Tetraammineplatinum (II) nitrate	$Pt(NH_3)_4(NO_3)_2$	Research	Aldrich	387.21
Cobalt nitrate hexahydrate	$Co(NO_3)_2.6H_2O$	Extra Pure	Merck	291.04
Aluminium Oxide	Al_2O_3	Extra Pure	ZeochmEU	101.96

3.1.2. Gases and Liquids

The high purity reaction gases and liquids used in this experimental study are listed with their applications and specifications in Table 3.2 and Table 3.3 respectively. CO_2, H_2 and He gases were supplied by Birleşik Oksijen Sanayi (BOS) while CO was supplied by HABAŞ Company.

Table 3.2. Gases used in the catalyst activity measurements

Gas/Standard	Application	Specification
Carbon monoxide	Reactant	99.0% HABAŞ
O_2/He mixture	Reactant	70.3 vol. % O_2 in He BOS
Hydrogen	Reactant	99.99% BOS
Helium	Reactant (Inert)	99.99% BOS
Helium	GC Carrier	99.99% BOS

Table 3.3. Liquids used in the catalyst activity measurements

Liquid	Application	Specification
Water	Cleaning	Distilled
Acetone	Cleaning	99.85 vol. %

3.2. The Experimental Set-Up

The experimental systems may be grouped into three:

- *Catalyst preparation systems*: These systems were used for preparation of the particulate catalyst by impregnation method and coating of the monolithic catalyst with alumina followed by co-impregnation method for active metal loading.
- *Micro-reactor flow system*: Catalytic activity tests were conducted in this system consisting of automated reactant flow unit and a temperature controlled reactor.
- *Product analysis system*: This system was connected to the micro-reactor flow system and comprised a gas sampling unit, a gas chromatograph and data processor for determining concentrations of feed gases and reaction products on line.

3.2.1. Catalyst Preparation Systems

In the experimental work, two different catalysts were prepared for conducting a comparative study between particulate and monolithic catalysts. After preparation of particulate and monolithic catalyst, they were used in the selective oxidation of CO.

3.2.1.1. Particulate Catalyst Preparation System. The system for particulate catalyst preparation makes use of a Retsch UR1 ultrasonic mixer, a vacuum pump, a vacuum flask, a beaker, a Masterflex computerized-drive peristaltic pump and silicone tubing for wetness impregnation method. Specific details are discussed in the catalyst preparation procedure section while the schematic diagram of the setup used for incipient wetness impregnation method is presented in Figure 3.1.

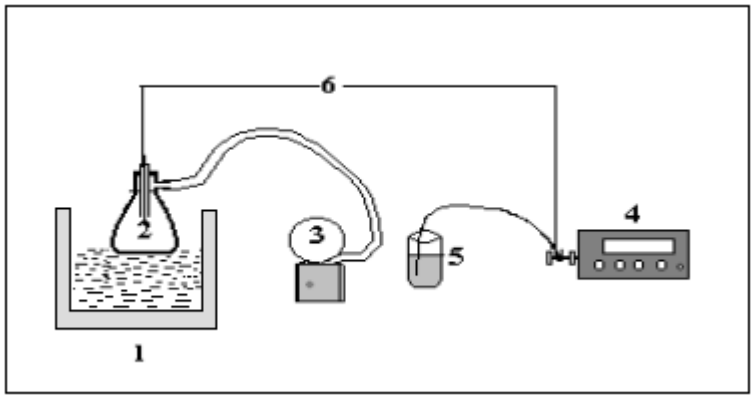

Figure 3.1. The impregnation system: 1.Ultrasonic mixer, 2.Vacuum flask, 3.Vacuum pump, 4.Peristaltic pump, 5.Beaker, 6.Silicone tubing (Uğuz, 2007)

3.2.1.2. Monolithic Catalyst Preparation System. Monolithic catalysts were prepared by using two different systems for wash-coating and impregnation. The alumina wash-coating system consisted of a magnetic mixer, a beaker, a compressor and a microwave oven. The system is presented in Figure 3.2 in detail.

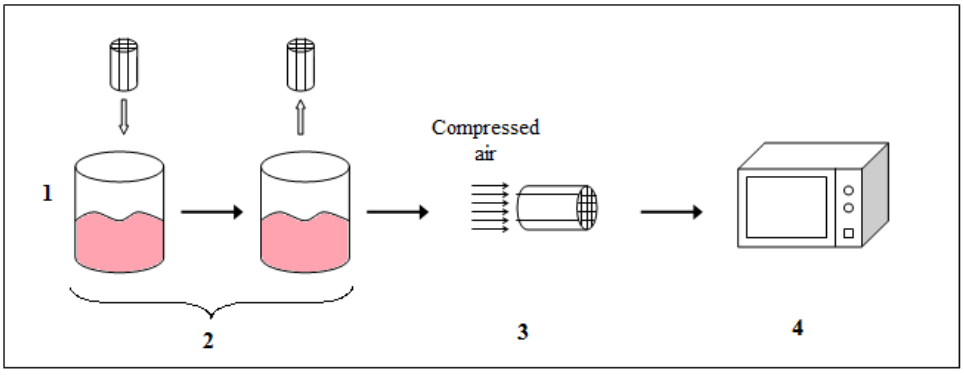

Figure 3.2. The alumina wash-coating system: 1. Beaker, 2.Dipping Procedure, 3. Compressed Air Flow, 4. Microwave Oven (Döker, 2008)

After wash-coating, the monolithic catalysts were co-impregnated with a precursor solution containing active metal salts (Figure 3.3). The impregnation system consisted of a vacuum flask, a glass tube, a vacuum pump, a peristaltic pump and silicone tubing.

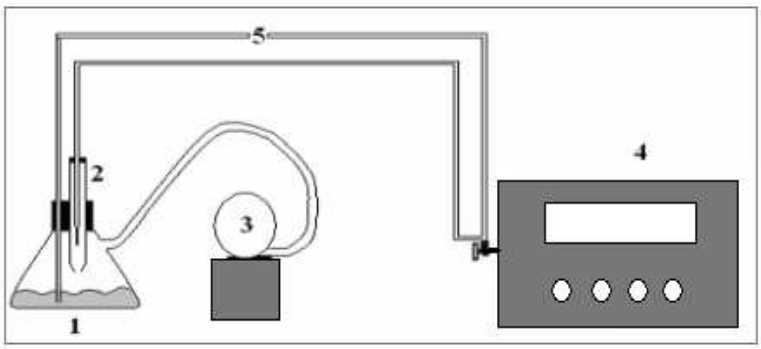

Figure 3.3. The impregnation system: 1. Vacuum Flask, 2.Glass tube, 3.Vacuum pump, 4.Peristaltic pump, 5.Silicone tubing (Döker,2008)

3.2.2. Microflow Reactor System

In the micro-reactor flow system, 1/2", 1/4" and 1/8" OD stainless steel fittings and research grades of pure CO, H_2, He gases and O_2/He mixture are used. The reaction gases were passed through copper tubing. These gases were introduced into the reactor via four Brooks 5850E mass flow controllers which controls the flow rates of these gases. The flow meter set values were controlled by the 4-Channel Brooks 0154 control panel. On-off valves were placed in front of mass flow controllers to protect them from possible back-pressure fluctuations. For all reaction gases, 30 psi was used as the input pressure to the flowmeters to get best performance.

All gases, after being metered and mixed, were allowed to flow through the reaction segment. During the experiments carried out by particulate catalysts, a down-flow 1/4" stainless steel fixed-bed reactor 58 cm in length was used. For monolithic catalyst samples, the reaction segment consisted of an 11.5 mm ID (1/2" OD) stainless steel fixed-bed down-flow micro-reactor 55 cm in length, placed in 2.4 cm ID x 40 cm furnace controlled to ±0.1 K by a Shimaden FP-21 programmable temperature controller. The influence of particulate

and monolithic catalyst on the partial oxidation of CO was studied using constant gas compositions under different temperatures at atmospheric pressure. The temperature was measured with a 1/16" K- type stainless steel sheathed thermocouple placed adjacent to the center point of the catalyst bed just outside the reactor with 55 cm length. Reactor is longer than the furnace to facilitate manipulation during catalyst charging or recharging. Reactions were carried out at temperatures above 100^{o}C; hence, in order to prevent heat loss and maintain stable temperature profile during reaction, the spaces between inlet and outlet of the reactor-furnace system were insulated by glass wool.

During the reaction tests, the catalyst bed was placed in the center of the reactor tube, in the constant temperature region of the furnace, as shown in the Figure 3.4.

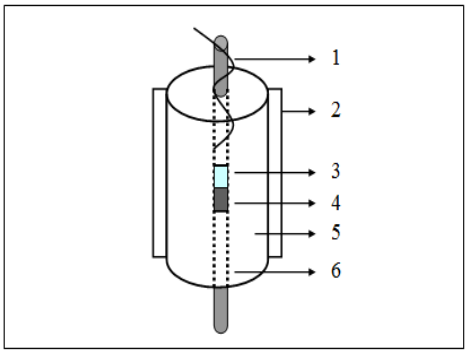

Figure 3.4. Schematic diagram of the reactor and furnace system: 1. Thermocouple, 2. Ceramic wool insulation, 3. Catalyst, 4. Catalyst bed, 5. Furnace, 6. Reactor (Döker, 2008)

3.2.3. Product Analysis System

PROX reactions involve two separate oxidation reactions. These are the oxidation of hydrogen and the oxidation of carbonmonoxide. The aim of this thesis was to selectively convert 100% of CO to CO_2, as required in the PROX unit of a fuel processor.

In the reactant and product sampling section, the reactant mixture entering or the product leaving the reactor were passed through two on-off valves either to the gas chromatograph sampling unit which has a calibrated one cm^3 sample loop for analysis or to the soap bubble meter for measuring the flow rate of the effluent.

After the reaction section, a cold trap was used to condense the water, which is a product of selective CO oxidation. The cold trap consisted of an ice box and coiled tubing to increase contact time of flow through a cold environment.

Reactant and product streams were analyzed using 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 3.4.

Table 3.4. 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 cm^3/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 schematic diagram of micro-reactor flow and product analysis system used in the selective CO oxidation experiments is shown in Figure 3.5. Micro-reactor flow and product analysis system consist of mass flow controllers that control the flow of reaction and carrier gases, temperature controller, reactor, furnace which provides the desired reaction temperature, bubble flowmeter, condenser and gas chromatograph. During the reactions reactor is placed in the furnace. With the help of bubble flowmeter the flow of gases can be calibrated.

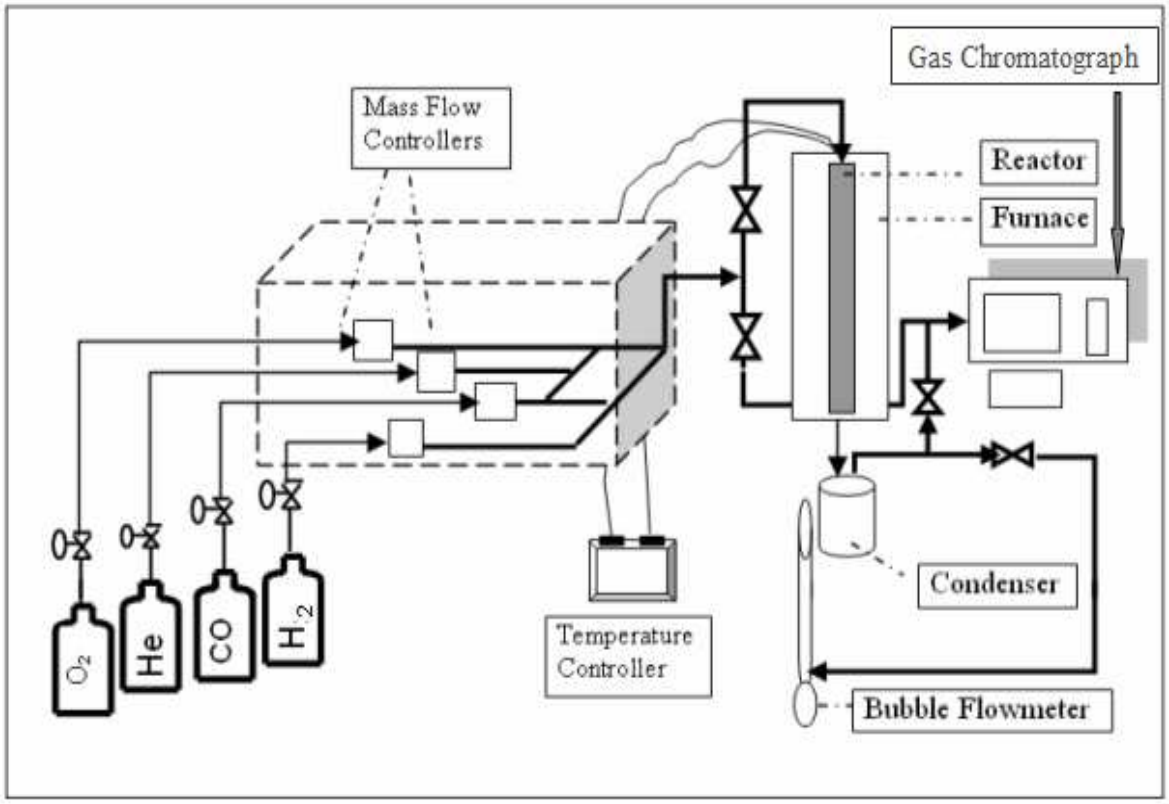

Figure 3.5. The schematic diagram of micro-reactor flow and product analysis system (Döker, 2008)

3.3. Catalyst Preparation Procedure

In the experimental study conducted, the particulate and monolithic catalysts were prepared individually.

3.3.1. Particulate Catalyst Preparation

The Pt-Co-Ce/Al_2O_3 catalysts were prepared by incipient to wetness impregnation to obtain catalysts which had 1.18 weight per cent Pt, 0.06 weight per cent Co and 1.25 weight per cent of Ce. The preparation procedure had four parts. These parts are:

- Evacuating the support
- Contacting the support with the precursor solution
- Drying of slurry
- Calcination

Alumina support was crushed and sieved into 45-60 mesh size (344 -255 μm), dried in a furnace at 105^{o}C for 1 hour and then calcined in a muffle furnace at 450°C for 5 hours prior to impregnation (Uğuz, 2007).

Five grams of calcinated support was placed in a vacuum flask and kept under vacuum for 30 min to remove the air in the support pores which could prevent penetration of the precursor solution. This process was accompanied by mixing in a Retsch UR 1 ultrasonic mixer. The impregnation system used is shown in Figure 3.1 (Uğuz, 2007).

All the metal salts were dissolved in 1.21 cm^3 of water per gram of alumina support, which is the amount of water to wet one gram alumina. The aqueous precursor solution was fed to the vacuum flask at a flow rate of 0.5 cm^3/min via silicone tubing using a Masterflex computerized-drive peristaltic pump .The slurry was mixed under vacuum by an ultrasound mixer to maintain uniform impregnation. Impregnated support was mixed for an additional 90 min. The slurry obtained was dried at 115°C overnight (16 hours). Then all catalyst was calcined in air at 400°C for 2 hours (Uğuz, 2007).

3.3.2. Monolithic Catalyst Preparation

3.3.2.1. Pretreatment of Monolithic Supports. The commercial cordierite monolithic support, Corning Celcor thin-wall substrate, was cut in cylinders of 11 mm diameter and 20 mm length before coating. The diameter of the monoliths was decided according to the inner diameter of the 1/2" stainless steel tubing used in constructing the micro-reactor.

After the monoliths were cut in cylinders with the desired dimensions, they were washed by acetone and dried in microwave oven for 50 minutes at 180 W in order to open the pores of cordierite support and remove the impurities caused by handling (Döker, 2008).

3.3.2.2. Wash-coating with Alumina. The experimental setup shown in Figure 3.2 was used for the wash-coating of monoliths with colloidal alumina solutions. There are different ways to wash-coat monoliths. Döker (2008) indicated that the most promising monolithic catalyst preparation method was colloidal coating. Therefore, monolith wash-

coating was done by using a colloidal solution of the wash-coat material. Colloidal solutions of alumina are commercially available; in preparing monoliths, 20 weight per cent colloidal alumina solutions from Alpha Aesar were used (Döker, 2008).

The pretreated monolith samples 20 mm in length and 11 mm in diameter were used as the structure for wash-coating. Firstly, weighed monoliths were dipped vertically into the colloidal alumina solution for two minutes. After immersion, the slurry in the monolith channels was removed by gentle blowing of pressurized air. Then, the wet monoliths were dried in microwave for 50 minutes at 180 W and weighed. This stepwise procedure, immersion into aluminum oxide dispersion followed by blowing and drying, was repeated until a 13-15 weight per cent increase was obtained on each monolith sample. The wash-coated monoliths were calcined in air at 600°C, 700°C or 800°C for two hours in a muffle furnace, with a temperature ramp of 2.5°C min^{-1} in order to fixate the wash coat on the monolith structure (Döker, 2008).

3.3.2.3. Impregnation Method. The experimental setup designed by Döker (2008) and modified as a part of this study (Figure 3.3) was used for the preparation of Pt-Co-Ce catalysts supported on alumina wash-coated monoliths by an impregnation procedure including four steps. These are:

- Contacting the support with the precursor solution
- Evacuating the channels by compressed air
- Drying
- Calcination

For wet impregnation, one alumina wash-coated cordierite monolith was placed in an open-ended glass tube that was fixed into a vacuum flask by a plastic cork and kept under vacuum during the addition of precursor solution as shown in Figure 3.3. The precursor solution contained equivalents of 1.4wt% Pt-1.25wt% Co-1.25wt% Ce. With the help of a peristaltic pump and a vacuum pump, the precursor solution was dripped into the monolith sample continuously and was forced to drip into the vacuum flask. A Masterflex computerized-drive peristaltic pump was used to feed and circulate the precursor solution to the vacuum flask with a rate of 5 cm^3 min^{-1} via silicone tubing. The precursor solution

was firstly put into the vacuum flask and one end of silicone tubing was dipped into the precursor solution. After the precursor solution was added, the vacuum pump and peristaltic pump were operated simultaneously. The other end of the silicone tubing was used to feed the precursor solution to the open-ended glass tube in which a monolith is placed. When the first droplet of the precursor solution dripped, the impregnation time was started. Döker (2008) studied three different impregnation durations. It was concluded that 15 minutes can be selected as a suitable impregnation period for Pt-Co-Ce catalysts to be used in preferential CO oxidation; therefore, co-impregnation of metals was continued for 15 minutes in the present experimental studies. After impregnation, the impregnated monoliths were firstly dried in a microwave oven operated at 180 W for 50 minutes; then calcined overnight (16 hours) at 550°C to establish active components on the monolith. Prepared monolithic catalysts were stored in a desiccator (Döker, 2008).

3.4. Catalytic Activity Measurements

All catalysts were reduced before the reaction and kept under He flow until the reaction test was conducted. The reduction program is presented in Table 3.5.

Table 3.5. Reduction program for the Pt-Co-Ce/Al_2O_3 catalyst

Segment Number	Starting and End Temperatures	Segment Gas
First Segment	Heating from 298 to 673 K with a heating rate 2.5 ºC min^{-1}	He with flow rate of 50 cm^3 min^{-1}
Second Segment (Reduction)	Keeping constant at 673 K for 2 h	H_2 with flow rate of 50 cm^3 min^{-1}
Third Segment	Flushing at 673 K for 1 h to clean the catalyst surface	He with flow rate of 50 cm^3 min^{-1}
Fourth Segment	Overnight cooling down to 298 K	He with flow rate of 25 cm^3 min^{-1}

All the reaction experiments were carried out in the micro-reactor flow system given in Figure 3.5. The reduced catalysts were tested under a total flow of 100 $cm^3\ min^{-1}$ using reaction temperatures in 110-170°C range for monolithic catalyst samples, and 90-150°C for particulate catalyst samples. Prior to reaction, all catalysts were heated from ambient temperature to the reaction temperature under a stream of 50 $cm^3\ min^{-1}$ helium. Then, the He flow was turned off, and the reaction mixture was turned on. The data were taken with 30 minute intervals at 30, 60, 90 and 120 minutes-time-on-stream. After 120 minutes, the data analysis for reactants in the feed was made.

The summary of the reaction conditions are given in Table 3.6 and Table 3.7 for particulate and monolithic catalyst respectively.

Table 3.6. Reaction conditions for catalytic activity tests on particulate catalyts

Parameter	Value
Catalyst Particle Size	45-60 mesh size (344-255μm)
Catalyst Amount	0,25 g
Reaction Temperature	90-150°C
Reactant Total flow rate	100 $cm^3 min^{-1}$
Feed Composition (vol %)	1%CO, 1%O_2, 60%H_2, 38%He
W/F Ratio	2.5 mg min cm^{-3}

Table 3.7. Reaction conditions for catalytic activity tests on monolithic catalyts

Parameter	Value
Catalyst Amount	250 mg
Reaction Temperatures	110-170°C
Reactant Total Flow	100 $cm^3\ min^{-1}$
Feed Composition (vol %)	1%CO, 1%O_2, 60%H_2, 38%He
W/F Ratio	2.5 mg min cm^{-3}

4. RESULTS AND DISCUSSION

Recently, there have been studies on the behavior of platinum, ceria, cobalt and alumina catalysts prepared with different types of supports for PROX reaction (Chapter 2).

The present study aims to provide a direct comparison between the PROX performances of particulate and monolithic Pt-Co-Ce-Al_2O_3 catalysts. Colloidal alumina coated, Pt-Co-Ce impregnated monolithic catalysts and corresponding particulate Pt-Co-Ce-Al_2O_3 catalyts were prepared and tested in a micro-reactor flow system under 100 cm^3 min^{-1} total feed flow containing 1% CO, 1% O_2 and 60% H_2 (by volume) in inert helium to find the effect of calcination temperature, reaction temperature and time on stream behaviour of catalyts. The effect of cobalt loading was also tested in monolith samples.

The PROX activity of each catalyst was expressed in terms of the percentage of CO converted using the Equation 4.1,

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

$[CO]_{in}$ and $[CO]_{out}$ are the carbon monoxide concentrations in the reactor feed and effluent respectively.

The oxygen conversion and selectivity were defined and calculated as in Equation 4.2 and Equation 4.3.

$$O_2 \text{ conversion } (\%) = \frac{[O_2]_{in} - [O_2]_{out}}{[O_2]_{in}} \times 100 \tag{4.2}$$

$$\text{Selectivity Towards CO } (\%) = \frac{0.5 \times \left([CO]_{in} - [CO]_{out}\right)}{[O_2]_{in} - [O_2]_{out}} \times 100 \tag{4.3}$$

Although, the selectivity and stability are also important for catalyst optimization, CO conversion shapes the main lines in this study; because for fuel cell applications, the CO content of hydrogen feed should be under 10 ppm.

The reactor outlet stream composition was measured at 30-minute intervals for two hours for CO conversion calculation. In time-on-stream studies for possible deactivation, some of the experiments were carried on for 4 hours.

4.1. Selective CO Oxidation on Monolithic Catalysts

Since the introduction of honeycomb-shaped monolithic catalysts in the mid-1970s, they have been used in environmental and chemical applications. During the last decade, ceramic monoliths with straight channels were considered as suitable supports for PROX reactions which have high surface area, small pressure drop, good interphase mass transfer, thermal and mechanical properties compared to particulate catalysts (Tomasic *et al.*, 2006). Despite the advantages, only few papers have reported work on monolithic PROX catalysts so far, and direct comparisons between particulate and monolithic catalysts are scarce.

In a study conducted by Döker (2008), the preparation methods used for monolithic catalysts were investigated and a preparation procedure for cordierite monolithic Pt-Co-Ce-Al_2O_3 catalyst was developed. It was reported that colloidal coating of alumina was the most promising wash-coating method for catalyst preparation among slurry coating and aluminum nitrate coating. The most suitable impregnation period of the active phase onto the alumina wash-coated monoliths was selected as 15 minutes for Pt-Co-Ce catalysts to be used in preferential CO oxidation. Additionally, the feed composition of 1vol% CO, 1vol% O_2 and 60vol% H_2 with He as balance (which is the most likely feed composition for the PROX unit in a fuel processor) showed superior performance compared to the feed composed of 2% CO, 2% O_2 and 60% H_2 with He as balance. These results constituted the starting point of the present study.

4.1.1. The Effect of Calcination Temperature

The effect of calcination temperature on the CO conversion performance of colloidal alumina wash-coated, Pt-Co-Ce impregnated monolithic catalyst samples was investigated. Three different calcination temperatures were examined: 600°C, 700°C and 800°C, and the PROX reactions for testing the effect of calcination temperature were carried out at two different reaction temperatures, 130°C and 150°C, with a feed composition of 1%CO,

1%O_2, 60% H_2 and He as balance. The reduction time prior to reaction was 2 hours (according to Table 3.5) for each calcination temperature tested.

Calcination step is necessary for good adherence and fixation of the washcoat to the cordierite. Depending on the washcoat and the catalyst coated, the monolith is generally calcined in air, typically between 400°C and 900°C. Minimum temperature for calcination is 400°C to obtain a good physical interaction between the monolithic structure and the coating; but, usually, higher calcination temperature are needed for fixating the coated particles to the monolithic support (Nijhuis *et al*., 2001).

In the work of Derekaya *et al*. (2009), the effect of catalyst pretreatment on selective oxidation of CO in excess hydrogen was investigated. Ceria supported CuO catalyst, 5/95 CuO/CeO_2, was calcined at three different calcination temperatures, 600°C, 700°C and 800°C. All catalysts gave low CO conversion at low reaction temperatures; but after 150°C, the CO conversion increased above 70%. The highest CO conversion was obtained on the catalyst calcined at 600°C, which gave 100% CO conversion at 200°C.

In the present study, the results obtained at two different reaction temperatures to determine the effect of calcination temperature on CO oxidation are presented in Table 4.1 and Figure 4.1 in terms of CO conversion achieved over alumina wash-coated and 1.4%Pt-1.25%Co-1.25%Ce impregnated monolithic catalyst at 130°C. Similar CO conversion data over alumina wash-coated 1.4%Pt-1.25%Co-1.25%Ce impregnated monolithic catalyst at 150°C are given in Table 4.2 and plotted in Figure 4.2.

It can be interpreted from Figures 4.1 and Figure 4.2 reporting data at two different reaction temperatures that the highest CO conversion was obtained over the catalyst calcined at 700°C among those calcined at 800°C and 600°C. Comparing three different calcination temperatures, monolithic catalyst samples calcined at 600°C showed the lowest catalytic activity with the lowest CO conversion at both reaction temperatures, which is unlike the behavior of the CuO/CeO_2 catalyst studied by Derekaya *et al*. (2009). At 130°C, the maximum CO conversion of 43.6% was achieved over the catalyst calcined at 700^{o}C.

Table 4.1. Effect of calcination temperature on CO conversion over alumina wash-coated 1.4%Pt-1.25%Co-1.25%Ce impregnated monolithic catalyst at 130°C

Time (min)	CO conversion (%)		
	Calcination temperature 800°C	Calcination temperature 700°C	Calcination temperature 600°C
30	35.2	43.6	25.6
60	32.4	38.9	24.1
90	27.7	34.8	17.9
120	23.7	34.6	18.2

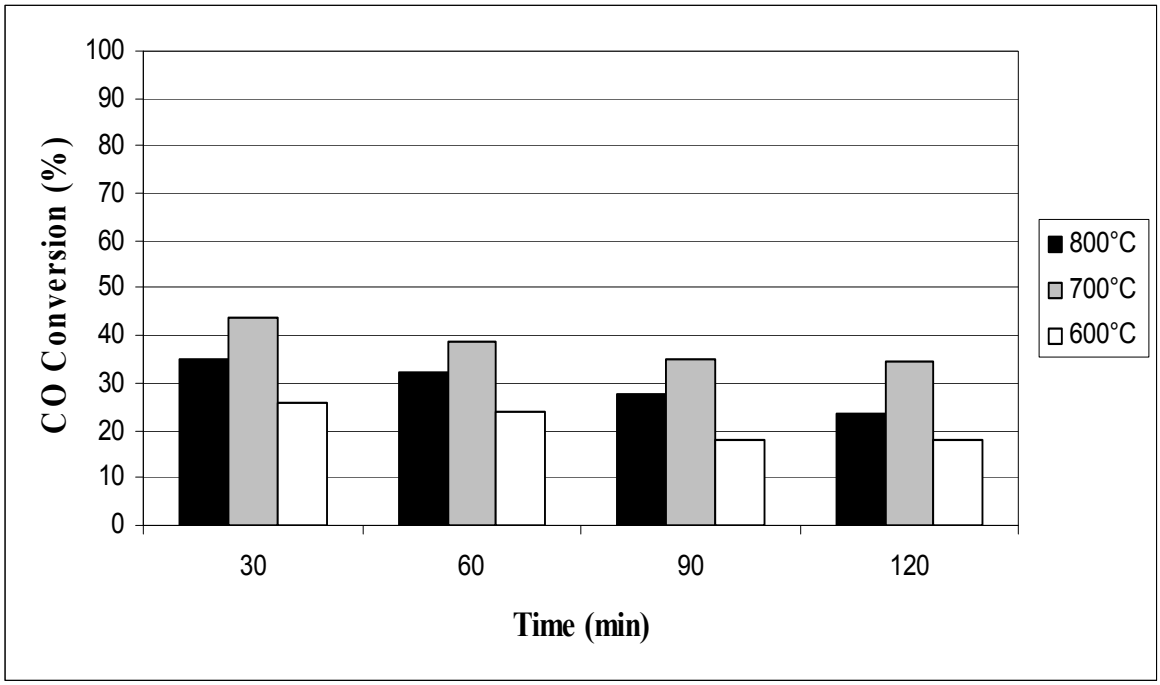

Figure 4.1. Effect of calcination temperature on CO conversion over alumina wash-coated 1.4%Pt-1.25%Co-1.25%Ce impregnated monolithic catalyst at 130°C

Table 4.2. Effect of calcination temperature on CO conversion over alumina wash-coated 1.4%Pt-1.25%Co-1.25%Ce impregnated monolithic catalyst at 150°C

Time (min)	CO conversion (%)		
	Calcination temperature 800°C	Calcination temperature 700°C	Calcination temperature 600°C
30	59.8	64.8	51.9
60	57.1	61.3	49.7
90	53.1	59.2	47.2
120	52.1	58.5	43.9

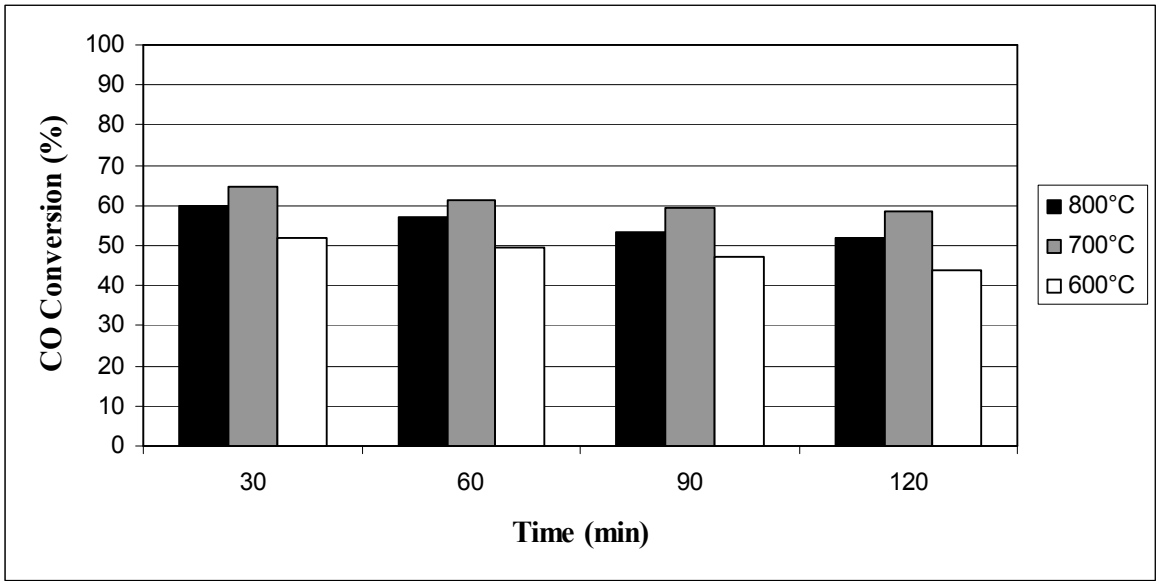

Figure 4.2. Effect of calcination temperature on CO conversion over alumina wash-coated and 1.4%Pt-1.25%Co-1.25%Ce impregnated monolithic catalyst at 150°C

At the same reaction temperature, the catalyst calcined at 600°C gave a CO conversion of 51.9 % at 30th minute. At 150°C, on the other hand, alumina wash-coated and 1.4%Pt-1.25%Co-1.25%Ce impregnated monolithic catalyst calcined at 700°C achieved 64.8% CO conversion at 30th minute which was the maximum value among other

catalyst samples at this reaction temperature. The CO conversion difference between catalysts which were calcined at different temperatures was more significant at the lower reaction temperature of 130^{o}C compared to the higher reaction temperature of 150^{o}C: CO conversion difference among the catalyst calcined at 600°C and 700°C was 18% at 130°C, the value was decreased to 13% at 150°C.

In the report of Nijhuis *et al*. (2001), the typical calcination temperature for alumina was stated as 500°C; but the present experiments showed that CO conversion is at its maximum value with the catalyst calcined at 700°C and, when the calcination temperature is decreased to 600°C, the CO conversion decreases significantly.

These results indicate that, although 700^{o}C is the optimum calcination temperature for alumina wash-coated and 1.4%Pt-1.25%Co-1.25%Ce impregnated monolithic catalyst, the reaction temperatures tested are not high enough to obtain 100% CO conversion, which is the most important criterion for a successful PROX catalyst.

4.1.2. The Effect of Reaction Temperature

The effect of reaction temperature on CO conversion was investigated over colloidal alumina wash-coated and Pt-Co-Ce impregnated monolithic catalysts calcinated at 700°C and 800°C. The feed gas was the standard mixture used in all experiments: 1% CO, 1% O_2 and 60% H_2 with He as balance. The reaction temperatures studied for determining their effect on CO conversion were 110°C, 130°C, 150°C and 170°C. Experiments were carried out for two hours. Table 4.3, Table 4.4, Table 4.5 and Table 4.6 show the CO conversion, O_2 conversion and selectivity results obtained at these reaction temperatures, respectively, for the alumina wash-coated 1.4%Pt-1.25%Co-1.25%Ce impregnated monolithic catalyst calcined at 800°C. CO conversion, O_2 conversion and selectivity values are also plotted in Figure 4.3, Figure 4.4, Figure 4.5 and Figure 4.6, in the same order.

Table 4.3. CO conversion, O_2 conversion and selectivity over alumina wash-coated and 1.4%Pt-1.25%Co-1.25%Ce impregnated monolithic catalyst calcined at 800°C (Reaction temperature: 110°C)

Time (min)	CO Conversion (%)	O_2 Conversion (%)	Selectivity (%)
30	18.2	12.4	60.3
60	16.8	14.8	52.8
90	16.2	16.2	41.6
120	15.3	16.0	40.3

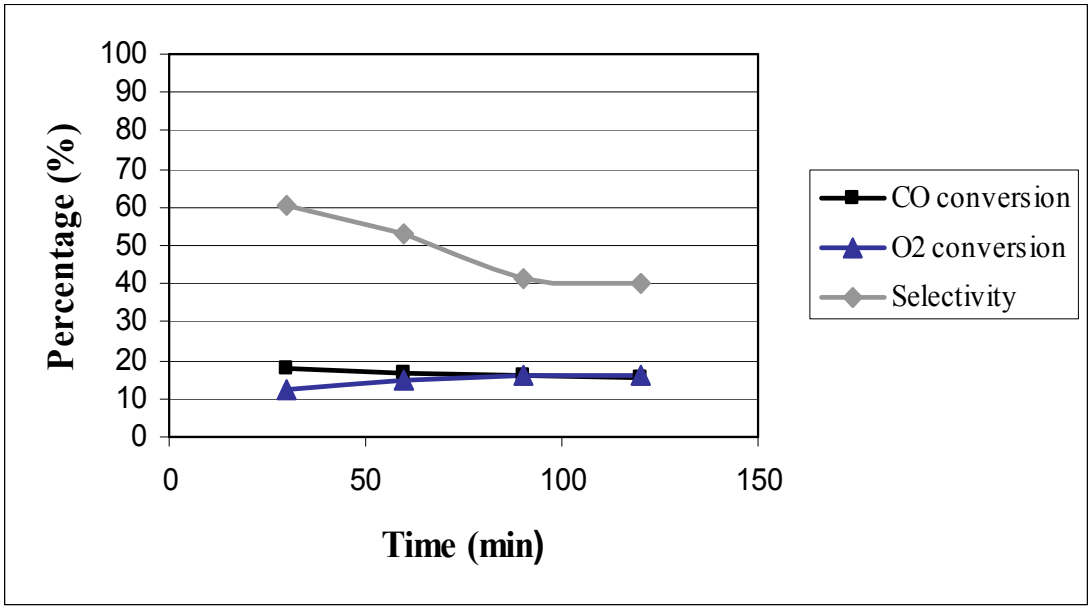

Figure 4.3. CO conversion, O_2 conversion and selectivity over alumina wash-coated and 1.4%Pt-1.25%Co-1.25%Ce impregnated monolithic catalyst catalyst calcinated at 800°C (Reaction temperature: 110°C)

Table 4.4. CO conversion, O_2 conversion and selectivity over alumina wash-coated and 1.4%Pt-1.25%Co-1.25%Ce impregnated monolithic catalyst calcined at 800°C (Reaction temperature: 130°C)

Time (min)	CO Conversion (%)	O_2 Conversion (%)	Selectivity (%)
30	34.2	15.1	49.5
60	32.4	14.5	49.6
90	31.1	13.4	49.7
120	28.9	11.6	49.9

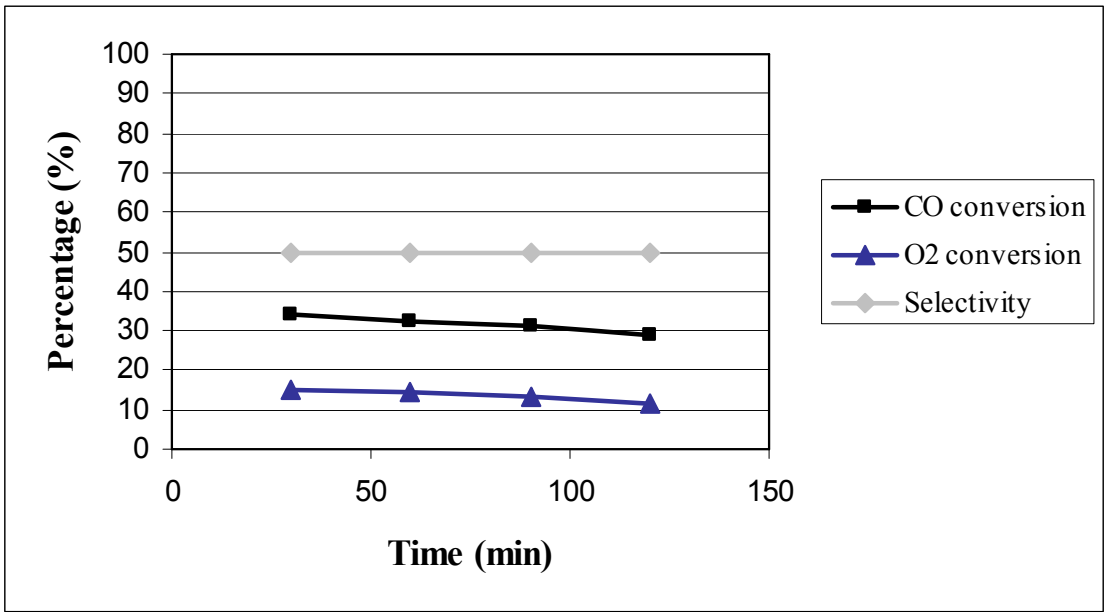

Figure 4.4. CO conversion, O_2 conversion and selectivity over alumina wash-coated and 1.4%Pt-1.25%Co-1.25%Ce impregnated monolithic catalyst catalyst calcinated at 800°C (Reaction temperature: 130°C)

Table 4.5. CO conversion, O_2 conversion and selectivity over alumina wash-coated and 1.4%Pt-1.25%Co-1.25%Ce impregnated monolithic catalyst calcined at 800°C (Reaction temperature: 150°C)

Time (min)	CO Conversion (%)	O_2 Conversion (%)	Selectivity (%)
30	59.8	37.4	78.1
60	57.1	36.6	76.7
90	53.1	41.0	66.4
120	52.9	39.5	62.5

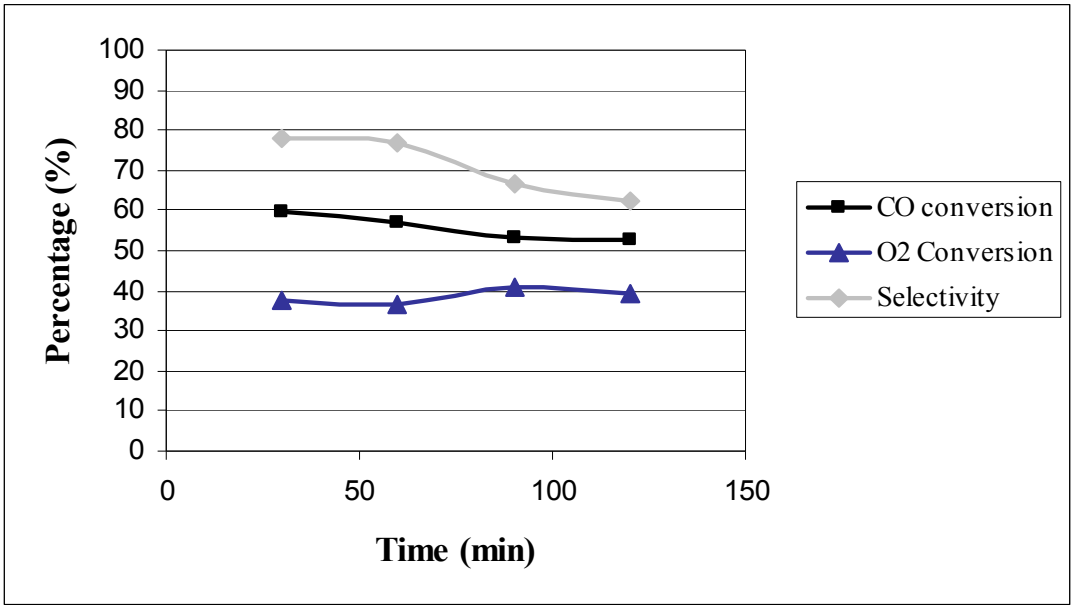

Figure 4.5. CO conversion, O_2 conversion and selectivity over alumina wash-coated and 1.4%Pt-1.25%Co-1.25%Ce impregnated monolithic catalyst catalyst calcinated at 800°C (Reaction temperature: 150°C)

Table 4.6. CO conversion, O_2 conversion and selectivity over alumina wash-coated and 1.4%Pt-1.25%Co-1.25%Ce impregnated monolithic catalyst calcined at 800°C (Reaction temperature: 170°C)

Time (min)	CO Conversion (%)	O_2 Conversion (%)	Selectivity (%)
30	98.7	88.7	55.64
60	98.1	75.0	65.4
90	95.3	69.2	68.8
120	93.6	68.8	68.0

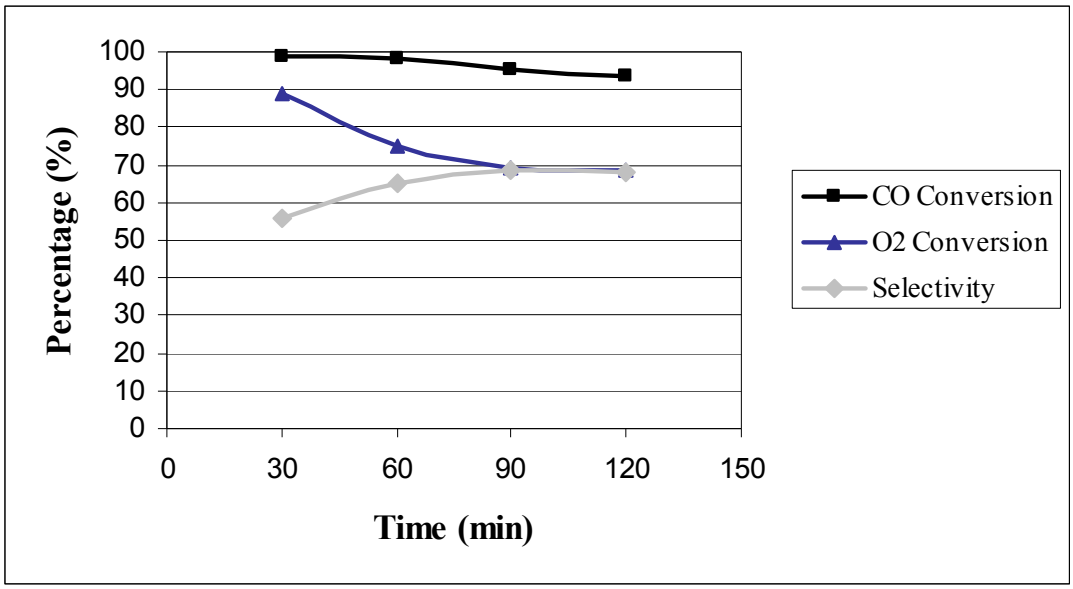

Figure 4.6. CO conversion, O_2 conversion and selectivity over alumina wash-coated and 1.4%Pt-1.25%Co-1.25%Ce impregnated monolithic catalyst catalyst calcined at 800°C (Reaction temperature: 170°C)

Figure 4.3, Figure 4.4, Figure 4.5 and Figure 4.6 indicate that as the temperature increases, the rate of CO oxidation increases and hence we see an increase in both CO and O_2 conversion. The lowest CO conversion and O_2 conversion over alumina wash-coated 1.4%Pt-1.25%Co-1.25%Ce impregnated monolithic catalyst calcined at 800°C is obtained

when the reaction is carried out at 110°C. With the increase of reaction temperature from 110°C to 170°C, CO conversion and O_2 conversion increased remarkably to about 94% and 69%, respectively. According to data, O_2 and CO conversions show a parallel trend with increasing reaction temperature.

Selectivity for CO oxidation has different values at different reaction temperatures. Comparing data collected at 120 min time-on-stream, the lowest selectivity (40.3%) was achieved at 110°C whereas the highest value was obtained at 170°C (68.0%). Considering all reaction temperatures, selectivity is observed to decrease with time-on-stream, but to increase with increasing temperature in contrast to results reported by Liu *et al.* (2008) who reported that with the increase of reaction temperatures, more oxygen was consumed by the reaction with hydrogen, and this caused the decrease of the selectivity of catalyst.

Table 4.7 and Figure 4.7 compare CO conversions achieved at different temperatures over alumina wash-coated 1.4%Pt-1.25%Co-1.25%Ce impregnated monolithic catalyst calcined at 800°C and display the remarkable effect of temperature on catalyst activity.

Table 4.7. CO conversions at different reaction temperatures over alumina wash-coated 1.4%Pt-1.25%Co-1.25%Ce impregnated monolithic catalyst calcined at 800°C

Time (min)	CO Conversion (%)			
	110°C	130°C	150°C	170°C
30	18.2	35.2	59.8	98.7
60	16.8	32.4	57.1	98.1
90	16.2	27.7	53.1	95.3
120	15.3	23.7	52.1	93.6

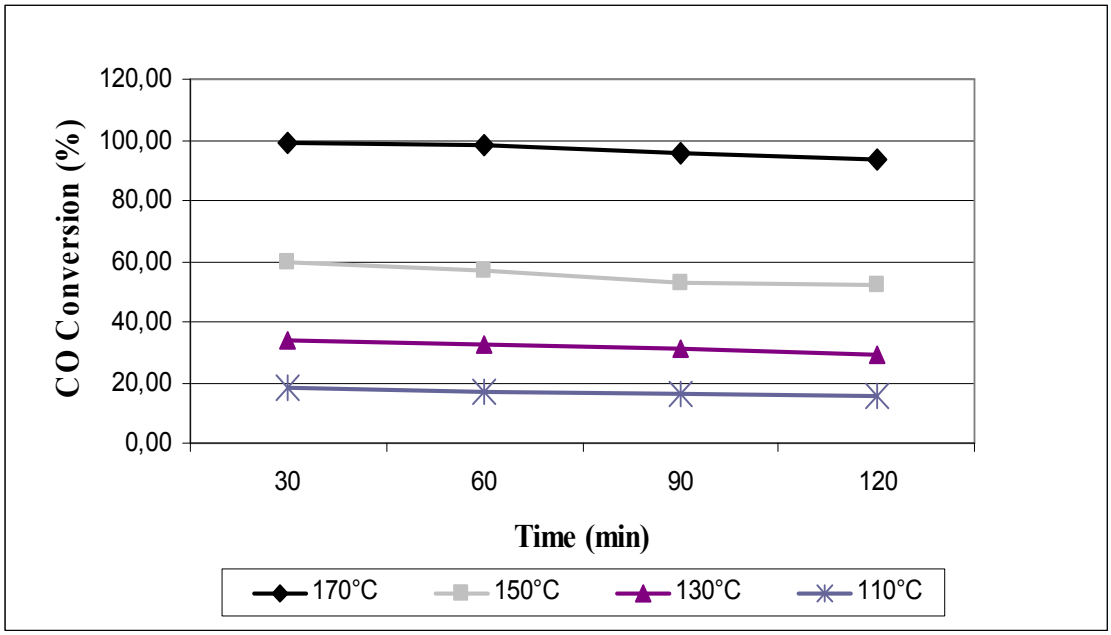

Figure 4.7. Effect of reaction temperature on CO conversion over alumina wash-coated and 1.4%Pt-1.25%Co-1.25%Ce impregnated monolithic catalyst calcined at 800°C

Figure 4.7 shows that CO conversion of PROX increases with increasing temperature and consistent behavior is observed at all reaction temperatures. For the alumina wash-coated and 1.4%Pt-1.25%Co-1.25%Ce impregnated monolithic catalyst calcinated at 800°C, the lowest CO conversion was obtained at 110°C (15.3%) at 120 min time-on-stream. During the increase in temperature from 110°C to 130°C and 130°C to 150°C, the CO conversion increased markedly. At 170°C and 120 min time-on-stream, the CO conversion reached its maximum (93.6%) among other reaction temperatures. These results are supported by the work of Srinivas (2005) who reported that CO conversion for preferential CO oxidation reaction over Pt/γ-Al_2O_3 coated monolithic catalysts increased with temperature until it reached a maximum.

Table 4.8, Table 4.9, Table 4.10 and Table 4.11 show CO conversion, O_2 conversion and CO oxidation selectivity results for alumina wash-coated 1.4%Pt-1.25%Co-1.25%Ce impregnated monolithic catalyst calcined at 700°C for different reaction temperatures. These values are also plotted in Figure 4.8, Figure 4.9, Figure 4.10 and Figure 4.11.

Table 4.8. CO conversion, O_2 conversion and selectivity over alumina wash-coated and 1.4%Pt-1.25%Co-1.25%Ce impregnated monolithic catalyst calcined at 700°C (Reaction temperature: 110°C)

Time (min)	CO Conversion (%)	O_2 Conversion (%)	Selectivity (%)
30	28.6	15.6	87.5
60	27.9	19.6	68.5
90	26.2	24.3	54.4
120	23.4	25.1	50.2

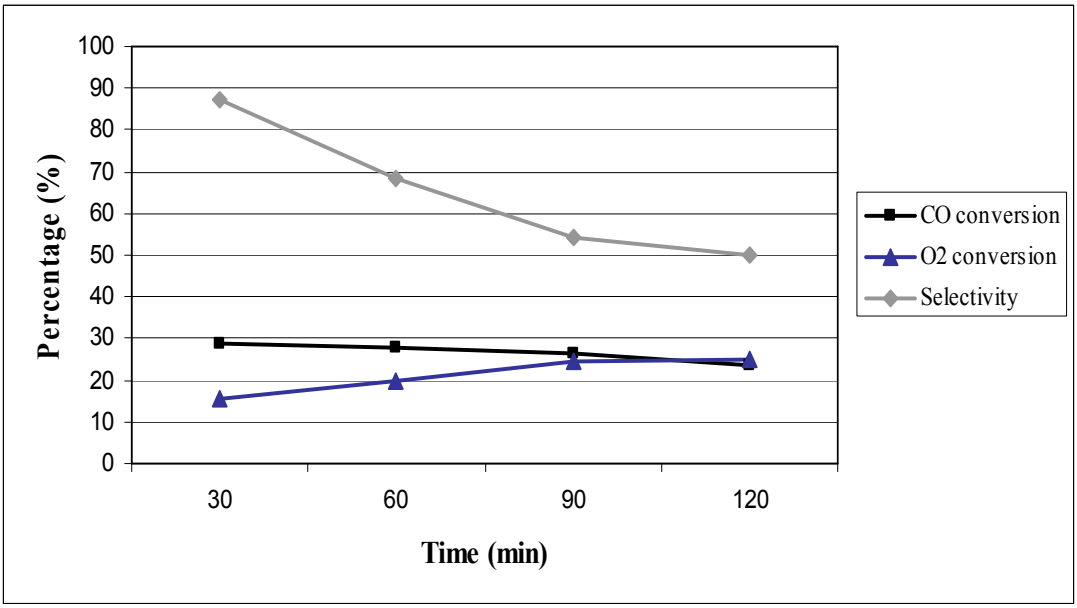

Figure 4.8. CO conversion, O_2 conversion and selectivity over alumina wash-coated and 1.4%Pt-1.25%Co-1.25%Ce impregnated monolithic catalyst catalyst calcined at 700°C (Reaction temperature: 110°C)

Table 4.9. CO conversion, O_2 conversion and selectivity over alumina wash-coated and 1.4%Pt-1.25%Co-1.25%Ce impregnated monolithic catalyst calcined at 700°C (Reaction temperature: 130°C)

Time (min)	CO Conversion (%)	O_2 Conversion (%)	Selectivity (%)
30	46.8	24.1	85.4
60	44.3	23.8	87.1
90	43.2	18.9	90.8
120	41.2	17	93.4

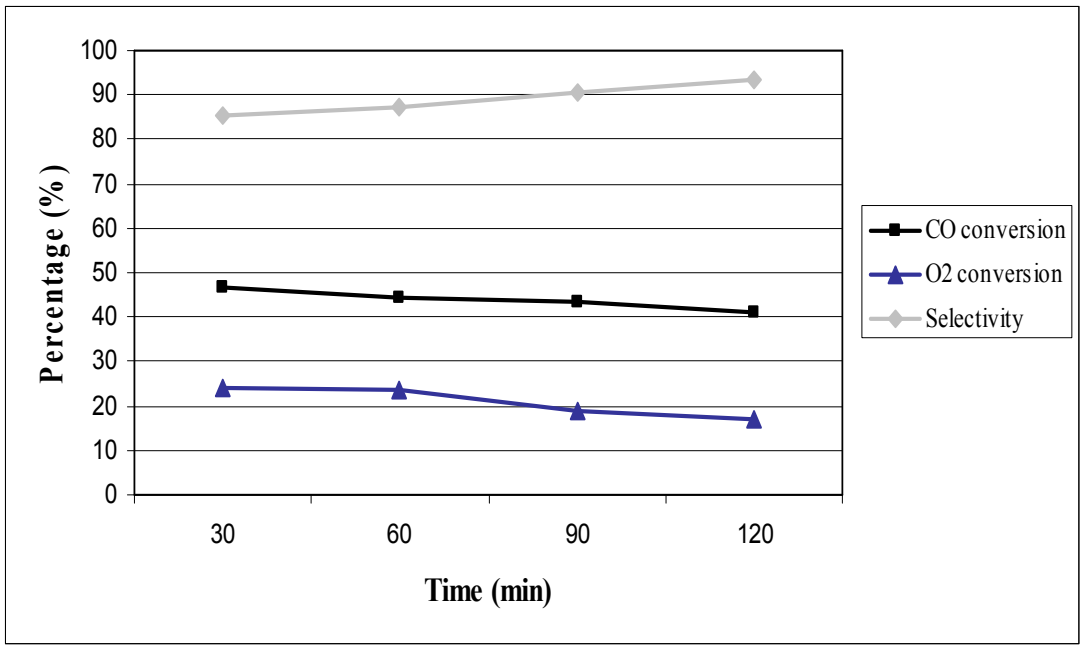

Figure 4.9. CO conversion, O_2 conversion and selectivity over alumina wash-coated and 1.4%Pt-1.25%Co-1.25%Ce impregnated monolithic catalyst catalyst calcined at 700°C (Reaction temperature: 130°C)

Table 4.10. CO conversion, O_2 conversion and selectivity over alumina wash-coated and 1.4%Pt-1.25%Co-1.25%Ce impregnated monolithic catalyst calcined at 700°C (Reaction temperature: 150°C)

Time (min)	CO Conversion (%)	O_2 Conversion (%)	Selectivity (%)
30	65.5	49.5	37.6
60	61.2	46.0	39.4
90	56.0	41.4	48.1
120	57.1	42.3	51.1

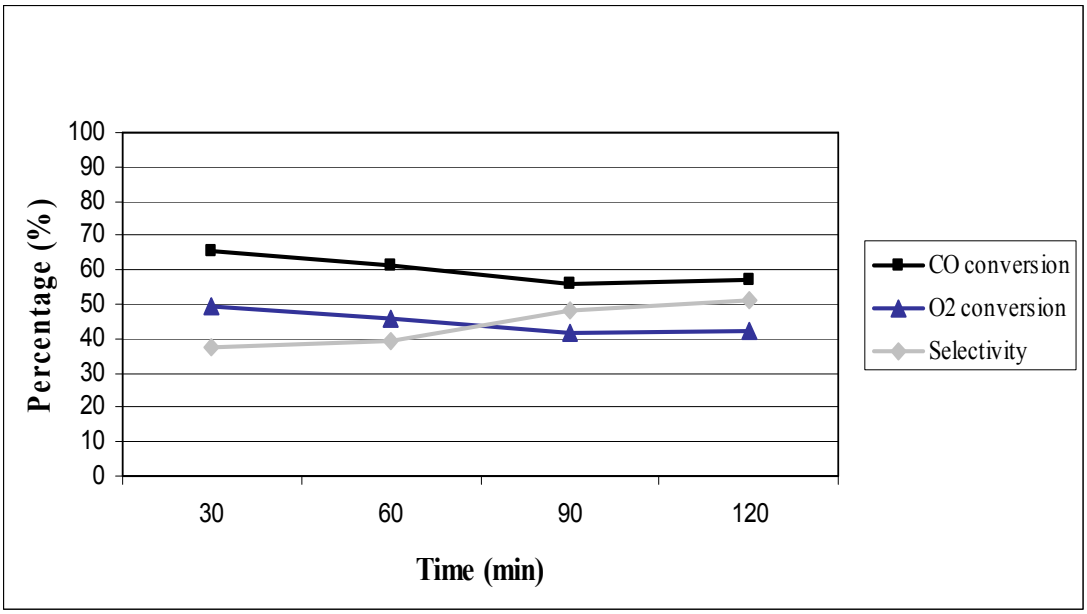

Figure 4.10. CO conversion, O_2 conversion and selectivity over alumina wash-coated and 1.4%Pt-1.25%Co-1.25%Ce impregnated monolithic catalyst catalyst calcined at 700°C (Reaction temperature: 150°C)

Table 4.11. CO conversion, O_2 conversion and selectivity over alumina wash-coated and 1.4%Pt-1.25%Co-1.25%Ce impregnated monolithic catalyst calcined at 700°C (Reaction temperature: 170°C)

Time (min)	CO Conversion (%)	O_2 Conversion (%)	Selectivity (%)
30	99.8	96.0	45.5
60	99.2	93.1	43.6
90	99.1	89.4	45.3
120	98.4	84.6	48.7

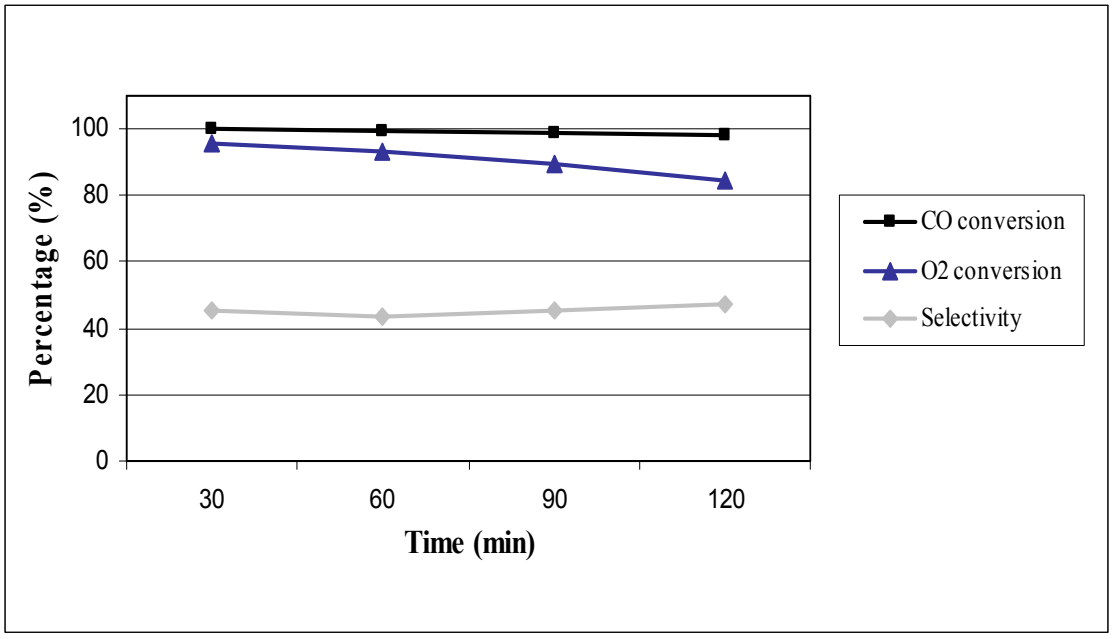

Figure 4.11. CO conversion, O_2 conversion and selectivity over alumina wash-coated and 1.4%Pt-1.25%Co-1.25%Ce impregnated monolithic catalyst catalyst calcined at 700°C (Reaction temperature: 170°C)

Figure 4.8, Figure 4.9, Figure 4.10 and Figure 4.11 show that the increase in reaction temperature resulted in the increase in both CO and O_2 conversion over alumina wash-

coated 1.4%Pt-1.25%Co-1.25%Ce impregnated monolithic catalyst calcinated at 700°C. This behavior is similar to the catalyst calcinated at 800°C. CO conversion increases with increasing temperatures up to 170°C where 99.8% CO conversion is achieved at 30 min time-on-stream, stabilizing at around 99% at 120 min time-on-stream (Table 4.12). In the reaction carried out at 110°C, the lowest CO conversion and O_2 conversion are obtained, and as temperature increases from 110°C to 170°C, both CO and O_2 conversions increase significantly.

Selectivity for CO oxidation in H_2-rich streams is reported to be about 50% at best at high temperatures since nearly half the oxygen is used for H_2 oxidation and O_2 conversions are therefore quite high. The selectivity values calculated at 120 min time-on-stream for reaction temperatures of 110^{o}C, 150°C and 170°C are reasonable, while the unusually high selectivity at 130^{o}C is probably due to a discrepancy in quantitative analysis.

Table 4.12. CO conversions at different reaction temperatures over alumina wash-coated and 1.4%Pt-1.25%Co-1.25%Ce impregnated monolithic catalyst calcined at 700°C

Time (min)	CO conversions (%)			
	110°C	130°C	150°C	170°C
30	28.6	46.8	65.5	99.8
60	27.9	44.3	61.2	99.2
90	26.2	43.2	56.0	99.1
120	22.4	41.2	57.1	98.4

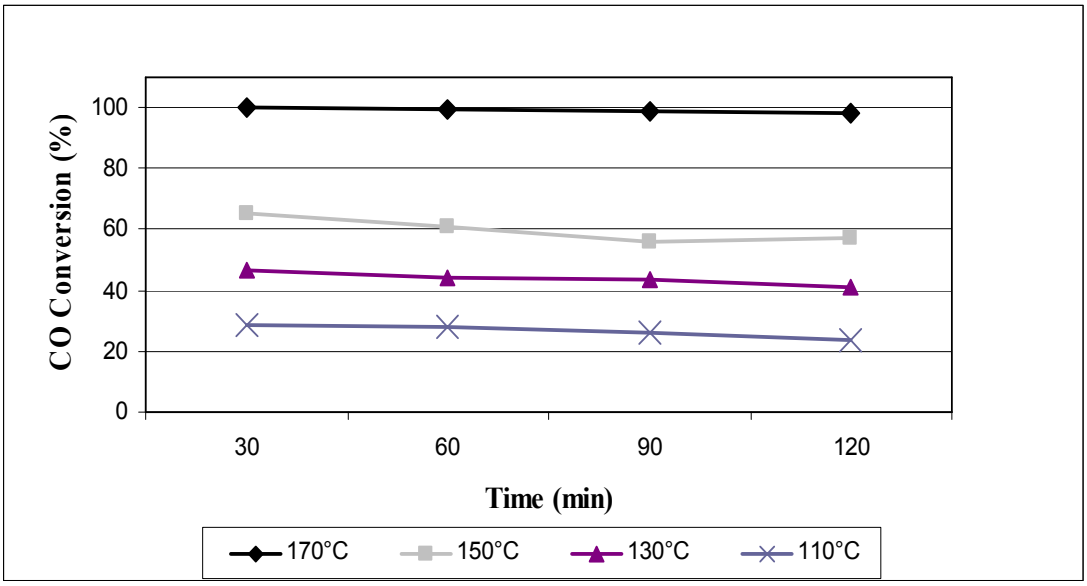

Figure 4.12. Effect of reaction temperature on CO conversion over alumina wash-coated and 1.4%Pt-1.25%Co-1.25%Ce impregnated monolithic catalyst calcined at 700°C

Table 4.12 and Figure 4.12 show the significant effect of temperature on catalyst activity. CO conversion increases with increasing temperature as expected from the previous set of experiments carried out over monolithic catalyst calcined at 800°C. The lowest CO conversion was obtained at 110°C (28.6% at 30 min time-on-stream) over the alumina wash-coated and 1.4%Pt-1.25%Co-1.25%Ce impregnated monolithic catalyst calcined at 700°C. As the reaction temperature increased from 110°C to 150°C, the CO conversion also increased markedly. At 170°C, CO conversion reached its maximum (99.8%) among other reaction temperatures. This may indicate that oxygen adsorption relative to CO adsorption became easier as temperature increased, which resulted in increasing CO conversions with increasing reaction temperature as well as increasing O_2 conversions resulting from both CO and H_2 oxidation.

Uğuz (2007) has used particulate Pt-Co-Ce/Al_2O_3 catalyst in experiments examining the effect of reaction temperature on CO conversion. An average CO conversion of 98.7% was obtained at 80°C, and no deactivation was observed in time-on-stream experiments. At 110°C, CO conversion reached 100%. This clearly indicates that the temperature increase has positive effect on CO conversion, and a similar trend is observed over Pt-Co-Ce/Al_2O_3 monolithic catalyst when the reaction temperature increased.

In all the experiments conducted, CO conversion values stayed constant after 90 min time-on-stream which indicate that the surface concentration of reactants did not change any more at current reaction temperature and catalyst activity becomes stable. Figure 4.13 shows the trend of change in CO conversions at 90 min time-on-stream.

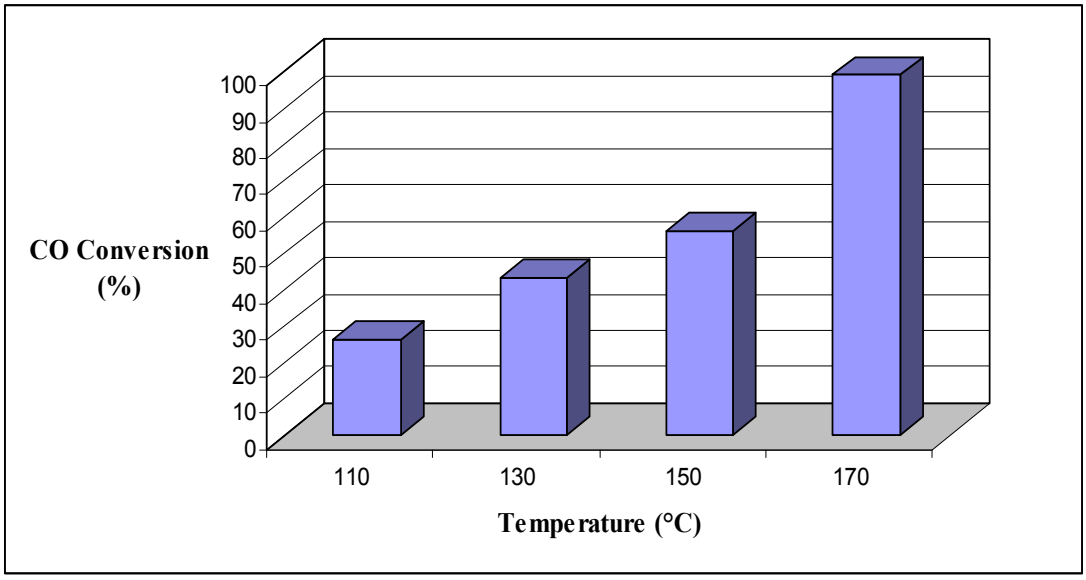

Figure 4.13. CO conversions at 90 minutes time-on-stream over alumina wash-coated and 1.4%Pt-1.25%Co-1.25%Ce impregnated monolithic catalyst calcined at 700°C at different reaction temperatures

From Figure 4.13, it is clear that the increase in reaction temperature resulted in significant increase in CO conversion. At the lowest reaction temperature of 110^{o}C, the lowest CO conversion of 26.2% was obtained; and CO coversion gradually increased to 43.2% at 130^{o}C, to 56.0% at 150^{o}C, and finally, to the maximum CO conversion of 99.1% was achieved at the highest reaction temperature of 170^{o}C.

4.1.3. The Effect of Co Amount

Cobalt is one of the promising promoters for Pt/Al_2O_3 catalysts for selective CO oxidation applications but is difficult to load on monolith structures. Hence, the effect of Co loading on CO oxidation was studied. The reactions were carried out at 130°C using a feed stream composition of 1% CO, 1% O_2, 60% H_2, and He in balance. Ptm weight per cent was set at 1.4 and that of Ce at 1.25 while the weight per cent of Co was varied from 1.25 to 2.5 equivalents in the precursor solution. Catalysts were calcinated at three

different temperatures for comparison. The results are summarized in Table 4.13 and plotted in Figure 4.14.

Table 4.13. CO conversions over monolithic catalyts with different Co percentage at 130°C

Catalyts Composition	Time (min)			
	30	60	90	120
	CO Conversion (%)			
1.4%Pt-1.25%Co-1.25%Ce (Calcination Temperature=800°C)	35.2	32.4	27.7	26.7
1.4%Pt-2.5%Co-1.25%Ce (Calcination Temperature=800°C)	36.9	35.2	31.6	28.1
1.4%Pt-1.25%Co-1.25%Ce (Calcination Temperature=700°C)	46.8	44.3	43.2	41.2
1.4%Pt-2.5%Co-1.25%Ce (Calcination Temperature=700°C)	48.1	46.4	44.2	43.8
1.4%Pt-1.25%Co-1.25%Ce (Calcination Temperature=600°C)	25.6	24.1	19.9	19.1
1.4%Pt-2.5%Co-1.25%Ce (Calcination Temperature=600°C)	33.1	29.6	25.4	25.9

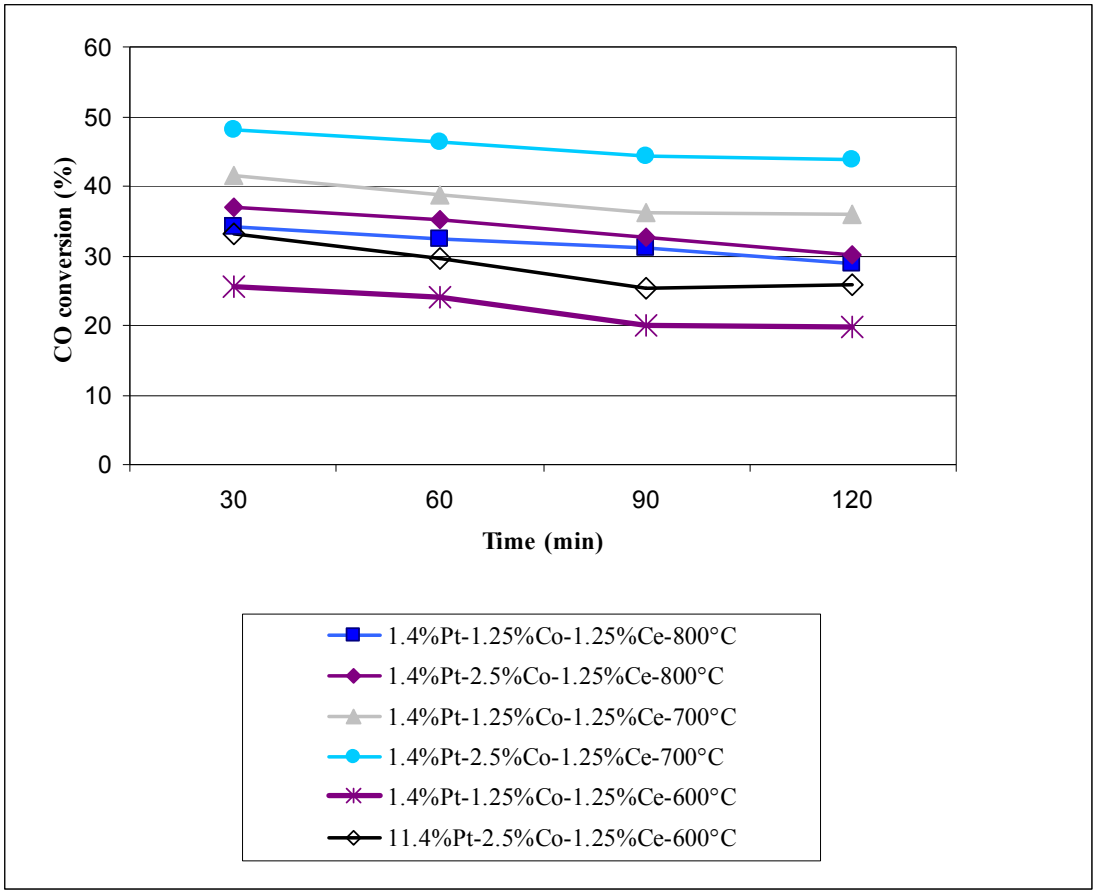

Figure 4.14. CO conversions over monolithic catalyts with different Co percentage at 130°C

According to results given in Table 4.13 and Figure 4.14, the activation trends for all prerapared catalyst were similar. During the first 90 minutes, CO conversion decreased slightly, and after 90 minutes on-stream, catalyst activity was stabilized. The highest CO conversion was obtained at 130°C over the 1.25%Ce-2.5%Co-1.4%Pt catalyst calcined at 700°C. This catalyst was followed by 1.4%Pt-1.25%Co-1.25%Ce catalyst calcined at the same temperature. CO conversions over the two catalysts were quite close to each other: 48.1% over 1.25%Ce-2.5%Co-1.4%Pt and 46.8% over 1.25%Ce-1.25%Co-1.4%Pt. Although the Co amount was doubled, the CO conversion increased slightly.

1.25%Ce-2.5%Co-1.4%Pt and 1.25%Ce-1.25%Co-1.4%Pt catalysts calcined at 800°C came after the catalyst calcined at 700°C, and at 130°C their CO conversions were 36.9% and 35.2 %, respectively. The catalysts calcined at 600°C showed similar behavior. Increasing the Co amount from 1.25% to 2.5%, increased CO conversion from 25.6% to 33.1%, which was more significant than for catalysts calcined at 700°C and 800°C.

Uğuz (2007) carried out experiments over 1.4wt%Pt-1.25wt%Ce/Al_2O_3 with no Co promoter and with 1.4wt%Pt- 1.25wt%Co-1.25wt%Ce/Al_2O_3 catalyst with Co promoter using the same feed stream composition of 1% CO, 1% O_2, 60% H_2, and He in balance. At 80°C, 1.4wt.%Pt-1.25wt.%Ce/Al_2O_3 catalyts gave an average CO conversion of about 13%. With the addition of Co, 98% conversion was achieved at 80°C over 1.4 wt%Pt-1.25 wt%Co-1.25 wt%Ce/Al_2O_3; demonstrating that the addition of Co to Pt-Ce/Al_2O_3 catalyts improves their catalytic activity significantly.

On the other hand, Ko *et al*. (2006) have reported that the effect of Co addition to Pt/Al_2O_3 catalysts that do not contain ceria causes decrease in chemisorbed CO on the catalysts. The amount of chemisorbed CO on Pt-Co/Al_2O_3 catalyts was found to be less than Pt/Al_2O_3 catalyts; but Pt-Co/Al_2O_3 showed better catalytic activity than Pt/Al_2O_3. This enhancement was explained by the formation of bimetallic phase of Pt and Co.

The small changes observed in CO conversion when the amount of Co was doubled are likely to be due to Co deposition capacity of alumina washcoated monolith structure.

4.1.4. The Effect of Time on Stream

Stability of the catalyst is important for actual applications which proceed for a longer duration of time (Wang *et al*., 2008). Time-on-steam (TOS) analysis of the activity for the preferential CO oxidation reaction over the most promising monolithic catalysts, 1.4%Pt-1.25%Co-1.25%Ce and 1.4%Pt-2.5%Co-1.25%Ce monolithic catalyst calcined at 700°C, was carried out for a continuous period of 4 h at a reaction temperature of 130°C and the results are shown in Table 4.14, Table 4.15, Figure 4.15 and Figure 4.16.

Table 4.14. Time-on-steam analysis for PROX reaction at 130^{o}C over alumina wash-coated 1.4%Pt-1.25%Co-1.25%Ce impregnated monolithic catalyst calcined at 700°C

Time (min)	CO Conversion (%)
30	46.8
60	44.3
90	43.2
120	41.2
150	39.5
180	40.8
210	40.4
240	41.6

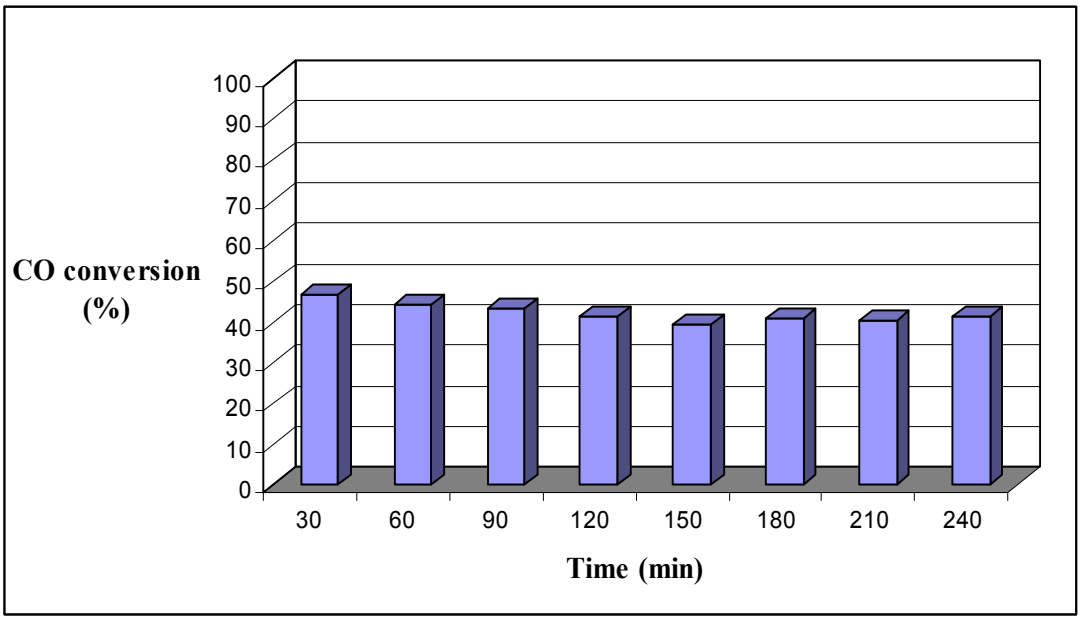

Figure 4.15. CO conversion for PROX reaction at 130 ^{o}C over alumina wash-coated and 1.4%Pt-1.25%Co-1.25%Ce impregnated monolithic catalyst calcined at 700°C for 4 h

Table 4.15. Time-on-steam analysis for PROX reaction reaction at 130°C over alumina wash-coated 1.4%Pt-2.5%Co-1.25%Ce impregnated monolithic catalyst calcined at 700°C

Time (min)	CO Conversion (%)
30	48.1
60	46.4
90	44.2
120	43.8
150	42.7
180	42.9
210	43.1
240	42.3

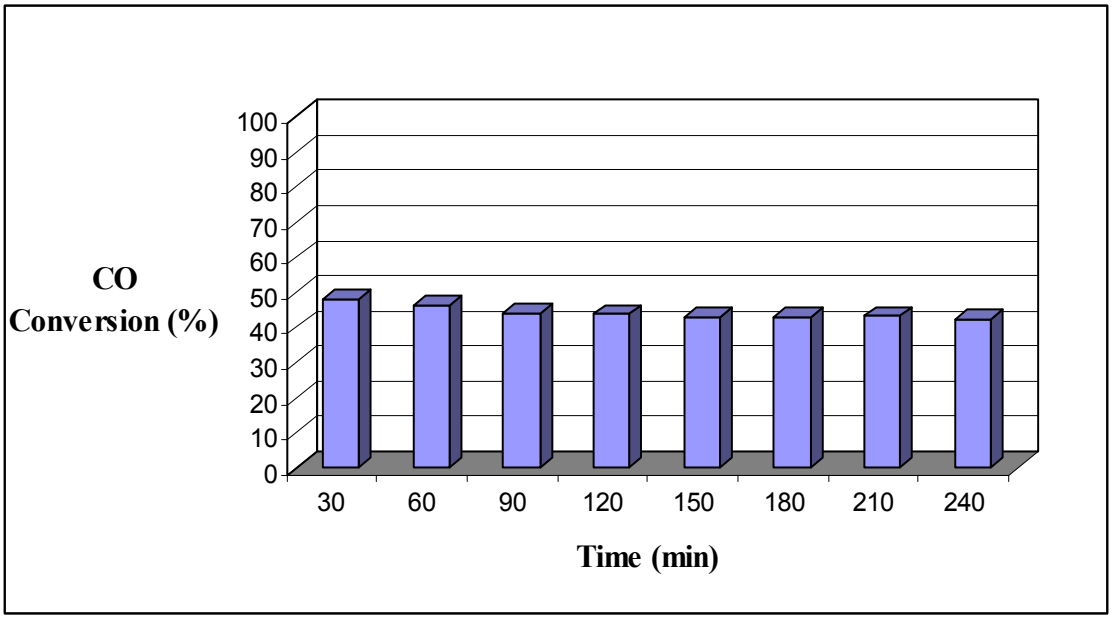

Figure 4.16. CO conversion for PROX reaction at 130°C over alumina wash-coated and 1.4%Pt-2.5%Co-1.25%Ce impregnated monolithic catalyst calcined at 700°C for 4 h

Time-on-steam analysis was used for demonstrating the long-term stability of the monolithic catalyst. For both 1.4%Pt-1.25%Co-1.25%Ce and 1.4%Pt-2.5%Co-1.25%Ce catalysts, there was no outstanding change detected in CO conversion during 240 minutes of operation. The catalysts underwent slight deactivation during the first 90 minutes. After 90 minutes, CO conversions became stable. It was evident that this catalyst exhibits good

stability within a period of 4 h. Under the light of these results, 1.4%Pt-1.25%Co-1.25%Ce and 1.4%Pt-2.5%Co-1.25%Ce monolithic catalysts may be considered as promising for practical applications and have potential for CO removal in fuel cell applications.

4.2. Catalyst Characterization

The Pt and Co loadings on monolithic catalyst samples were determined by Inductively Coupled Plasma (ICP) analysis at TUBITAK to find the fraction of active metals loaded onto the cordierite support and the actual composition of the monolithic alumina wash-coated Pt-Co-CeO_2 catalysts prepared.

4.2.1. Inductively Coupled Plasma (ICP) Analysis

The actual amounts of Pt and Co loaded on colloidal alumina coated monoliths using 15 minute impregnations were determined by Inductively Coupled Plasma (ICP) analysis at TUBITAK.

During the experiments, one monolith is considered to adsorb nearly one cm^3 of water and each monolith was impregnated with an excess of precursor solution, two cm^3 including both 1.4wt%Pt-1.25wt%Co-1.25wt%Ce and 1.4wt%Pt-2.5wt%Co-1.25wt%Ce. After impregnation, the residual metal precursor solution in the vacuum flask was washed with 20 ml distilled water in order to determine the amount of metals left behind. This solution was analyzed by TUBITAK. Table 4.16 and Table 4.17 show the inductively coupled plasma results of residual impregnation solution in terms of concentrations and calculated fractions of Pt and Co metals loaded onto the monolithic catalyst.

Table 4.16. ICP analysis of Pt loadings on monolithic catalysts

Targeted Catalyst	Total Pt added to impregnation solution (g)	Pt in Residual Impregnation Solution (g)	Fraction of Pt Impregnated on Monolith (%)
1.4wt%Pt-1.25wt%Co-1.25wt%Ce	0.002150	0.0003986	81.4
1.4wt%Pt-1.25wt%Co-1.25wt%Ce	0.002335	0.0003275	86.6
1.4wt%Pt-2.5wt%Co-1.25wt%Ce	0.002730	0.0004477	83.5
1.4wt%Pt-2.5wt%Co-1.25wt%Ce	0.002461	0.0003506	85.7

Table 4.17. ICP analysis of Co loadings on monolithic catalysts

Targeted Catalyst	Total Co added to impregnation solution (g)	Co in Residual Impregnation Solution (g)	Fraction of Co Impregnated on Monolith (%)
1.4wt%Pt-1.25wt%Co-1.25wt%Ce	0.001920	0.001796	6.4
1.4wt%Pt-1.25wt%Co-1.25wt%Ce	0.002085	0.002020	3.3
1.4wt%Pt-2.5wt%Co-1.25wt%Ce	0.004861	0.004824	7.5
1.4wt%Pt-2.5wt%Co-1.25wt%Ce	0.004390	0.003999	8.8

There is a difference between the targeted and actual loading of Pt and Co on the monolithic catalyst surface. It has been shown that Pt can load efficiently on the monolithic catalyst whereas Co loading remains under 10% of the targeted amount. For 1.4wt%Pt-1.25wt%Co-1.25wt%Ce catalyst, the average Pt loading was 84.0 % of target value and the average Co loading was 4.8% of target value. In the 1.4wt%Pt-2.5wt%Co-1.25wt%Ce catalyst, the Pt content was kept the same but Co content was doubled. According to the ICP results, the average Pt loading was still 84.6% and Co loading was 8.2% of the target value; i.e. when the Co precursor was doubled, the loading of Co increased from 4.8% to 8.2%. Compared to the Pt loading achieved, the values for Co show that Co cannot load on the monolith efficiently.

4.3. Selective CO Oxidation on Particulate Catalyts

It was evident from the ICP analysis, carried out at TUBITAK to determine the amount of active metals loaded on colloidal alumina wash-coated monoliths, that the actual composition of the monolithic catalyst prepared with the precursor solution targeting a composition of 1.4wt%Pt-1.25wt%Co-1.25wt%Ce on alumina was in fact 1.18wt%Pt-0.06wt%Co-1.25wt%Ce. Therefore, on the basis of ICP results, a 1.18wt%Pt-0.06wt%Co-1.25wt%Ce particulate catalyst was prepared by the method given in Section 3.2.1.1 to match the actual composition of the monolith and to allow direct comparison.

4.3.1. The Effect of Reaction Temperature

The effect of reaction temperature on CO conversion was investigated over 1.18%Pt-0.06%Co-1.25%Ce particulate catalyst. The feed gas was the standard mixture used in all experiments: 1% CO, 1% O_2 and 60% H_2 with He as balance. The reaction temperatures studied for determining their effect on CO conversion were 90°C, 110°C, 130°C and 150°C. Experiments were carried out for two hours. The CO conversions obtained at different reaction temperatures over the particulate 1.18%Pt-0.06%Co-1.25%Ce catalyst are given in Table 4.18. The results are also plotted in Figure 4.17.

Table 4.18. Effect of temperature on CO conversion over the particulate 1.18%Pt-0.06%Co-1.25%Ce catalyst

Time (min)	CO conversions (%)			
	90°C	110°C	130°C	150°C
30	71.9	87.3	99.2	97.7
60	73.2	88.9	99.1	97.9
90	73.1	87.4	99.4	98.2
120	72.4	86.8	98.7	97.5

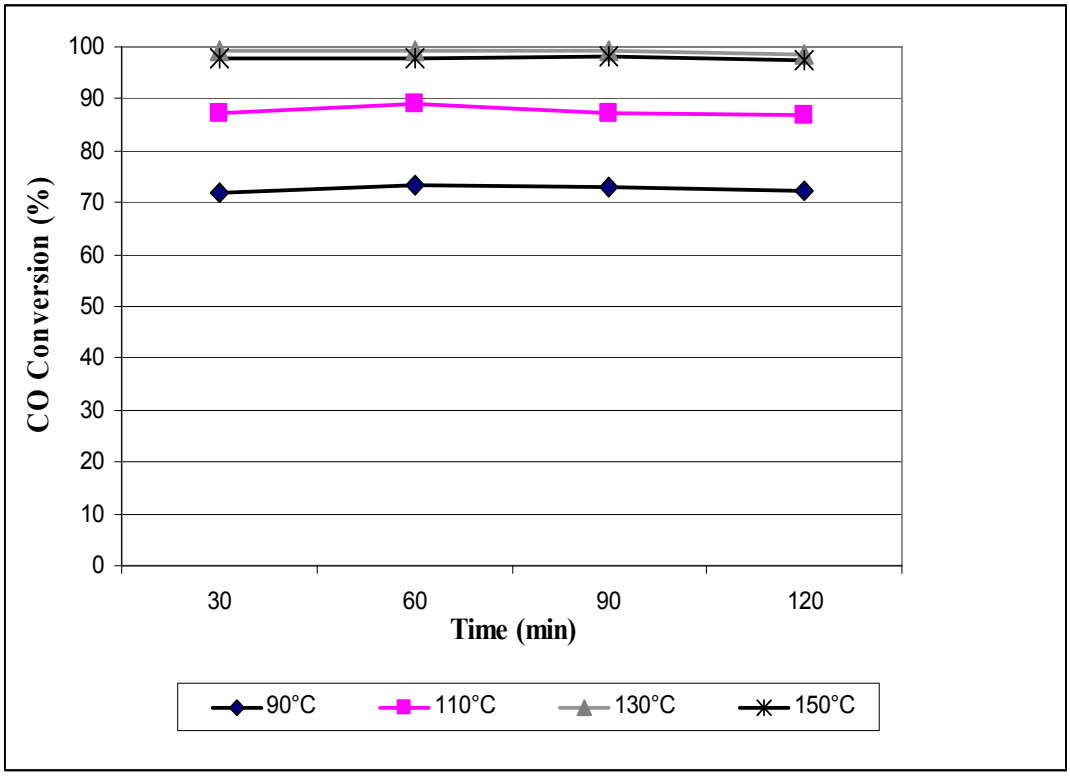

Figure 4.17. Effect of reaction temperature on CO conversion over 1.18%Pt-0.06%Co-1.25%Ce particulate catalyst

Table 4.18 and Figure 4.17 show the significant effect of temperature on catalyst activity. The CO conversion increases with increasing temperature as expected from the previous set of experiments carried out over monolithic catalyst. The lowest CO conversion over 1.18%Pt-0.06%Co-1.25%Ce particulate catalyst was obtained at 90°C (71.9% at 30 min time-on-stream). As the reaction temperature was increased from 90°C to 130°C, the CO conversion also increased markedly. At 130°C and 90 min time-on-stream, CO conversion reached its maximum (99.4%) among other reaction temperatures. CO conversion decreased slightly (98.2%) at 150°C.

İnce *et al.* (2005) used 1.4wt.%Pt-1.25wt.%Co-1.25wt.%Ce/Al_2O_3 particulate catalyst at 80 ˚C. They obtained 100% CO conversion at 60 min time-on-stream with a feed containing 1% CO, 1% O_2, 60% H_2, and He as balance; after 60 min, they observed deactivation. Uğuz (2007) used 1.4wt.%Pt-1.25wt.%Co-1.25wt.%Ce/Al_2O_3 particulate catalyst in experiments to examine the effect of reaction temperature on CO conversion using a feed stream of the same composition. An average CO conversion of 98.7% was obtained at 80°C, and no deactivation was observed in time-on-stream experiments. At

110°C, CO conversion reached 100%. This indicates that the temperature increase has positive effect on CO conversion, and a similar trend is observed over 1.18wt%Pt-0.06wt%Co-1.25wt%Ce particulate catalyst when the reaction temperature increased. The contribution of the Co promoter to catalyst activity is important and is evident from the temperatures at which almost 100% CO conversion is achieved; the particulate catalyst with 0.06wt%Co content gives 99.4% CO conversion at 130^{o}C while the particulate catalyst with 1.25wt%Co content gives 100% CO conversion at 110^{o}C.

5. CONCLUSIONS AND RECOMMENDATIONS

5.1. Conclusions

The purpose of this study was to conduct a parametric study of selective CO oxidation using particulate and monolithic Pt-Co-CeO_2 catalysts supported on alumina. Preferential CO oxidation was studied over monolithic and particulate Pt-Co-Ce-Al_2O_3 catalysts in hydrogen-rich environment to compare their performance in terms of catalyst composition and temperature. In this comparative study, the monoliths were wash-coated with alumina using colloidal coating method. Metal precursor solutions containing 1.4 per cent Pt, 1.25 or 2.5 per cent Co and 1.25 per cent Ce by weight were impregnated over alumina wash-coated monoliths. Colloidal alumina coated and Pt-Co-Ce impregnated monolithic catalysts were tested for the preferential CO oxidation reaction in a micro-reactor flow system in the temperature range of 110-170°C. The effect of calcination temperature, reaction temperature, Co amount and residence time on the activity and selectivity of the monolithic catalyst were examined. The amount of metal loaded on colloidal alumina coated monoliths via 15 minute impregnations was determined on Inductively Coupled Plasma analysis at TUBITAK, which showed that the actual composition of the monolithic catalyst prepared with the precursor solution aiming 1.4wt%Pt-1.25wt%Co-1.25wt%Ce was in fact 1.18wt%Pt-0.06wt%Co-1.25wt%Ce. Therefore, a particulate catalyst with the 1.18wt%Pt-0.06wt%Co-1.25wt%Ce composition was prepared to match the actual composition of the monolith and to allow direct comparison and was tested for preferential CO oxidation in a micro-reactor flow system using reaction temperatures in the 90-150°C range.

The major conclusions obtained in this study can be summarized as follows:

- 700°C is the optimum calcination temperature for alumina wash-coated and 1.4wt%Pt-1.25wt%Co-1.25wt%Ce impregnated monolith catalyst which gave the highest CO compared to catalysts calcined at 600°C and 800°C.
- Reaction temperature has a positive effect on CO conversion, which increases dramatically when the reaction temperature is increased from 110°C to 170°C on

alumina wash-coated 1.4wt%Pt-1.25wt%Co-1.25wt%Ce monolith catalysts calcined at 800°C and 700°C.

- 99.8 % CO conversion is achieved at 170°C on alumina wash-coated 1.4wt%Pt-1.25wt%Co-1.25wt%Ce monolith catalysts calcined at 700°C.
- CO conversion values stay constant and catalyst activity becomes stable after 90 min time-on-stream over monolithic catalysts. Both 1.4wt%Pt-1.25wt%Co-1.25wt%Ce and 1.4wt%Pt-2.5wt%Co-1.25wt%Ce catalysts do not show any appreciable change in CO conversion during 240 minutes of operation.
- ICP analysis shows that the actual composition of monolith catalyst prepared with precursors targeting 1.4wt%Pt-1.25wt%Co-1.25wt%Ce on alumina is in fact 1.18wt%Pt-0.06wt%Co-1.25wt%Ce and that while 84% of the Pt in the impregnation solution is loaded onto the alumina wash-coated monolith, only 4.8% of the Co is loaded. When the Co amount in the precursor solution is doubled according to 2.5wt%Co, fraction of Co actually loaded is also doubled but is only 8.2% of the Co present in the impregnation solution.
- The effect of Co promotion on catalyst activity is evidenced by the temperatures at which almost 100% CO conversion is achieved; the particulate catalyst with 0.06wt%Co content gives 99.4% CO conversion at 130^{o}C while the particulate catalyst with 1.25wt%Co content gives 100% CO conversion at 110^{o}C.
- 100% CO conversion is achieved at 170^{o}C over the colloidal alumina wash-coated monolithic Pt-Co-CeO_2 catalyst prepared in this study while 99.4% conversion is reached at 130^{o}C over the particulate 1.18wt%Pt-0.06wt%Co-1.25wt%Ce/γ-Al_2O_3 catalyst with similar composition.

5.2. Recommendations

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

- The effect of the presence of CO_2 and H_2O in the feed can be investigated since these components are present in the feed entering the PROX reactor in a fuel processor system.

- The impregnation procedure may be adjusted to achieve targeted metal loadings on the monolithic structure.
- Special laboratory reactors which allow temperature measurement inside the channels of monolithic structures can be designed for studying different micro-structured reactors.
- The stability of the catalyst can be tested for industrial use.
- Experiments can be carried out by coating and impregnation on metallic monolith structures.

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