PHYSICAL PROPERTIES AND PREFERENTIAL CO OXIDATION PERFORMANCE OF Pt-Co-Ce/Al_2O_3 CATALYSTS

by

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In the memory of
my lovely
grandma …

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ABSTRACT

PHYSICAL PROPERTIES AND PREFERENTIAL CO OXIDATION PERFORMANCE OF Pt-Co-Ce/Al_2O_3 CATALYSTS

The objective of this study was to examine the effects of design parameters on the physical properties and on preferential CO oxidation (PROX) activity of Pt-Co-Ce/Al_2O_3 catalysts. The major catalyst design parameters considered were the metal loadings of Pt, Co and Ce, calcination temperature and calcination time. Ten different Pt-Co-Ce/Al_2O_3 catalysts were prepared using incipient to wetness impregnation method. The total surface areas, pore volumes, solid and envelope densities of the catalysts were measured in order to investigate the effect of design parameters on physical properties. A realistic gas mixture simulating the exit stream of a typical fuel processor and containing 1% O_2, 1% CO, 60% H_2, 25% CO_2, 10% H_2O and inert He as balance was used in the PROX experiments. Activity tests were performed on five of the ten catalysts studied. CO and O_2 conversions were measured at 30-minute intervals up to two hours.

It was found that Al_2O_3-supported catalysts with Pt loadings between 1.4-1.8 wt%, Co and Ce loadings between 1.25-3.75 wt% and calcined at 450^oC for 2 h all achieve 100% CO conversion with a selectivity of 50% and are successful PROX catalysts. Among the catalysts studied, 1.4%Pt-1.25%Co-1.25%Ce/Al_2O_3 calcined at 450^oC for 2 h is the optimum PROX catalyst since it yields 100% CO conversion both in the presence and in the absence of carbon dioxide and water vapor in the feed.

ÖZET

Pt-Co-Ce/Al_2O_3 KATALİZÖRLERİNİN FİZİKSEL ÖZELLİKLERİ VE SEÇİMLİ CO OKSİDASYONU ETKİNLİKLERİ

Bu çalışmanın ana amacı, katalizör tasarım parametrelerinin Pt-Co-Ce/Al_2O_3 katalizörlerinin fiziksel özelliklerine ve seçimli CO oksidasyonu (PROX) etkinliklerine olan etkilerinin incelenmesidir. Pt, Co ve Ce metallerinin ağırlık yüzdeleri, kalsinasyon sıcaklığı ve kalsinasyon süresi başlıca tasarım parametreleri olarak ele alınmış ve empregnasyon yöntemi kullanılarak on ayrı katalizör hazırlanmıştır. Tasarım parametrelerinin katalizörün fiziksel özelliklerine etkisini belirlemek için, toplam yüzey alanları, gözenek hacimleri, katı ve parçacık yoğunlukları ölçülmüştür. Seçimli CO oksidasyonu deneylerinde girdi olarak tipik bir yakıt işlemcinin çıktısı ile aynı bileşime sahip gerçekçi bir gaz karışımı (1% CO, 1% O_2, 60% H_2, 25% CO_2, 10% H_2O ve inert He) kullanılmıştır. Seçimli CO oksidasyonu deneyleri için hazırlanan on katalizörün beşi seçilerek bu katalizörler üzerinde gerçekleşen CO ve O_2 dönüşmeleri 30-dakika aralıklarla iki saat süreyle ölçülmüştür.

Pt içeriği 1.4-1.8 %(ağırlık), Co ve Ce içerikleri 1.25-3.75 %(ağırlık) aralığında olan ve kalsinasyonu 450^oC de 2 saat süreyle yapılan Al_2O_3-destekli katalizörlerin tümü %100 karbon monoksit dönüşmesini %50 seçimlilikle sağlayan başarılı katalizörleridir. Bunlar arasında, reaktör girdisinde karbon dioksit ve su buharının olduğu ve olmadığı tüm durumlarda %100 karbon monoksit dönüşmesi sağlayan 1.4%Pt-1.25%Co-1.25%Ce/Al_2O_3 katalizörü ekonomik açıdan da optimum olarak belirlenmiştir.

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1. INTRODUCTION

Fuel cells are receiving increased recognition as alternatives to existing power generation technologies. The conversion of the fuel hydrogen to energy takes place without combustion; therefore, the process is highly efficient, clean and quiet. The most promising fuel-cell technology for transport applications appears to be the polymer electrolyte membrane fuel-cell (PEMFC) fueled by hydrogen. In order to avoid storing high pressure H_2 on a vehicle, it has been proposed that hydrogen for PEMFC can be produced in an onboard fuel processor (Trimm and Önsan, 2001).

Current technology imposes that an economically feasible way of producing pure hydrogen has three catalytic processes in series:

- Auto-thermal reforming (ATR) of a hydrocarbon for H_2 production,
- Water-Gas Shift (WGS) reaction to maximize the concentration of H_2 and to lower CO concentration,
- Selective catalytic oxidation of carbon monoxide for removal of the remaining CO from the hydrogen stream.

The fuel cell output and life depends on a number of factors. One factor of great importance is the quality of H_2. It must be virtually free of major poisons such as sulfur and carbon monoxide both of which can be present when the source of H_2 is a hydrocarbon reformer. A second issue is the life of membrane that is damaged by the formation of peroxide intermediates at the cathode and anode. A third issue is the corrosion of the carbon at the cathode. The cost of the precious metals dominates the economics of the system (Farrauto, 2005).

Since the product stream after WGS unit has 1-2 vol% carbon monoxide, which poisons the Pt-anode of the PEM fuel cell even at these small concentrations, the selective oxidation of CO in a H_2-rich atmosphere (PROX) has attracted increasing interest. Due to the technological importance of the PROX reaction various catalysts have been tested and

proposed, including alumina or silica supported Pt, Rh or Ru catalysts, other alumina supported metal or alloy catalysts, zeolite supported Pt catalysts and, more recently, also low-temperature catalysts such as metal oxide supported Au catalysts and Pt-Sn catalysts as well as non-noble metal containing oxide catalysts such as CuO or $CuO\text{-}CeO_2$ catalysts (Han *et al.,* 2004).

The selective CO oxidation reaction takes place in the presence of large amounts of hydrogen that should not be oxidized to water. Selective oxidation of carbon monoxide is an exothermic reaction and is carried out mostly at temperatures below 150 ºC, otherwise CO oxidation selectivity drops with increasing H_2 oxidation (Goerke *et al*., 2004). It is also important to study selective CO oxidation in realistic gas mixtures since CO_2, CO, H_2 and H_2O are all tied together by the water gas shift reaction (Manasilp and Gulari, 2002).

The primary objective of this study is to examine the effects of design parameters on the physical properties and on preferential CO oxidation (PROX) activity of $Pt\text{-}Co\text{-}Ce/Al_2O_3$ catalysts. The major catalyst design parameters to be considered are the metal loadings of Pt, Co and Ce, calcination temperature and calcination time. $Pt\text{-}Co\text{-}Ce/Al_2O_3$ catalysts are prepared using incipient to wetness impregnation method within the region of conditions defined by İnce (2004) and Uysal (2005) for optimum catalyst performance. Physical properties such as total surface area, total pore volume, solid and envelope densities are determined for all catalyst samples with the aim of examining the effects of design parameters on physical properties. Subsequently, activity tests are performed on five of the ten catalysts investigated using hydrogen-rich feed containing both CO_2 and H_2O. The CO and O_2 conversions are determined as a function of time-on-stream, and the selectivities for CO oxidation are calculated.

Chapter 2 includes information about fuel cells, hydrogen production for fuel cells and the catalysts used for hydrogen clean-up. The effect of carbon dioxide and water vapor concentrations on catalyst activity and selectivity and also the physical properties of catalysts are examined in detail. Chapter 3 is about the experimental work conducted in this study. The results obtained in the experiments are presented and discussed in Chapter 4, while the conclusions and recommendations for future work are given in Chapter 5.

2. LITERATURE SURVEY

2.1. Fuel Cell Systems

Fuel cells are considered to be the propulsion system of the near future, since they can produce electricity without polluting the environment, and they possess the necessary specific power, power density and durability to replace conventional internal combustion engines from their current applications (Avgouropoulos *et al.,* 2002). There are five major types of fuel cells which differ in the composition of their electrolytes and are at different stages of development: alkaline fuel cells (AFC), phosphoric acid fuel cells (PAFC), proton-exchange membrane fuel cells (PEMFC), molten carbonate fuel cells (MCFC) and solid oxide fuel cells (SOFC) (Song, 2002).

Polymer electrolyte membrane fuel cells (PEMFCs) have received much attention because they possess characteristics that are essential for transportation applications. They are light in weight, small in size, and have high power density at a relatively low operating temperature (e.g. about 80^{o}C) (Igarashi et al., 1997). Ghenciu (2002) also states that PEM fuel cells (Figure 2.1) possess a series of advantageous features that make them leading candidates for mobile power applications or for small stationary power units:

- Low operating temperature,
- Sustained operation at high current density,
- Low weight, compactness,
- Potential for low cost and volume, long stack life,
- Fast start-up times,
- Suitability to discontinuous operation.

PEM fuel cells work with a polymer electrolyte in the form of a thin, permeable sheet. Efficiency is about 40 to 50 per cent, and operating temperature is about 353 K. Cell outputs generally range from 50 to 250 kW. The solid, flexible electrolyte will not leak or

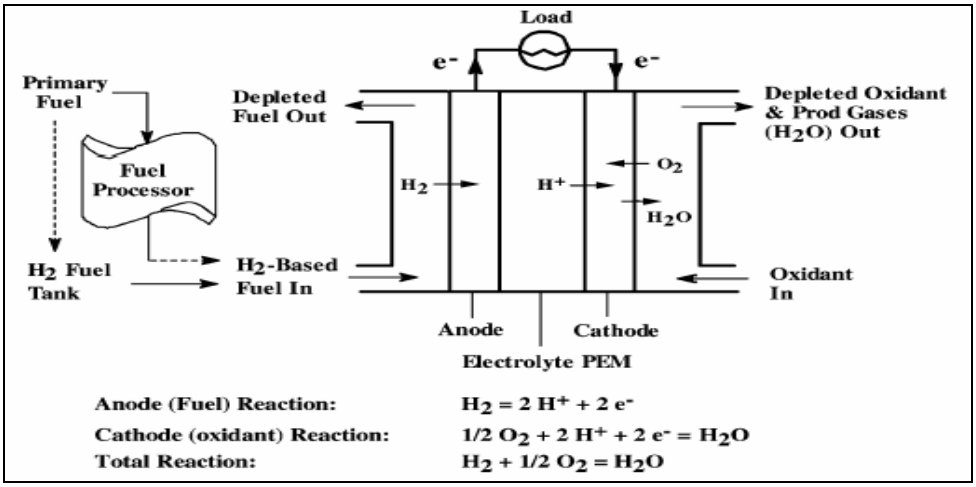

Figure 2.1. Operating concept of a PEMFC (Song, 2002)

crack, and these cells operate at a low enough temperature to make them suitable for homes and cars. The best fuel for PEMFC is hydrogen which must be purified to remove almost all CO, and the Pt catalyst used on both sides of the membrane increases costs. In order to be competitive, studies are being conducted for cost reduction and it seems possible to reach reasonable costs which are 50-75 US$ per kW for mobile applications and around 1500 US$ per kW for stationary combined heat and power (CHP) applications (Ralph and Hards, 1998).

2.2. Hydrogen Production for Fuel Cells

The ideal fuel for efficient performance is pure hydrogen in low temperature fuel cells since it simplifies system integration, maximizes system efficiency, and produces zero harmful emissions. However, hydrogen is not naturally available as a fuel**;** since it is stored in high density in hydrocarbons, processing of hydrocarbon fuels is necessary to extract hydrogen for stationary and mobile fuel cell applications (Sandhua *et al.,* 2005).

In the conventional hydrogen generation processes, the hydrocarbons are converted to hydrogen in the presence of oxidants (air, oxygen or steam), thus resulting in the production of CO_x. As an alternative, the co-production of CO can be avoided if the hydrocarbons are reformed in a step-wise manner. This method involves the catalytic decomposition of hydrocarbons in the first step (which should theoretically be CO_x-free)

followed by catalyst regeneration with steam/air in another step. This two step process when operated in cycles represents a potential CO_x-free route for hydrogen production (in the first step of the process) for fuel cell applications (Choudhary and Goodman, 2002). Hydrogen for automotive PEM fuel cells can also be produced in an on-board fuel processor. The production of hydrogen actually occurs in three steps (Son and Lane, 2001; Trimm and Önsan, 2001):

- Hydrogen is produced by the autothermal reforming of a hydrocarbon (fuel + O_2 + H_2O ↔ CO_x + H_2) where without water it is partial oxidation or without oxygen it is steam reforming.
- The water-gas shift reaction (CO+ H_2O ↔ CO_2 + H_2) eliminates most of the carbon monoxide and also produces more hydrogen.
- Any remaining CO is reduced to ppm levels by preferential oxidation.

Epling *et al*.,(2003) state that the PEMFC anode uses a Pt catalyst which is very sensitive to CO poisoning at its low operating temperature. The Partnership for a New Generation of Vehicles (PNGV) has therefore set a CO target concentration for the fuel processor at 10 ppm. In order to achieve this low CO concentration, the preferential oxidation (PROX) reactor is placed between the shift reactor and the fuel cell anode.

Equations below are the main reactions taking place in autothermal reforming of hydrocarbons. Several routes for reforming fuels to produce syngas have been investigated, analyzed and are employed today in fuel processing: steam reforming (Equation 2.1), catalytic partial oxidation (Equation 2.2), and autothermal reforming (ATR). The choice of reforming route is based on the type of fuel cell, the demands and volume of the system, and heat management strategy. ATR combines oxidation and steam reforming in one single unit, with the exothermic partial oxidation driving the endothermic steam reforming. Heat management can be finely tuned through the steam-to-carbon (S/C) and air-to-fuel (A/F) ratios (Ghenciu, 2002).

$$C_nH_m + nH_2O \rightarrow nCO + (n+m/2)H_2 \quad \Delta H^o_{298} > 0 \tag{2.1}$$

$$C_nH_m + n/2O_2 \rightarrow nCO + m/2H_2 \quad \Delta H^o_{298} < 0 \tag{2.2}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \quad \Delta H^o_{298} = -41.2 \text{ kJ/mol} \tag{2.3}$$

$$CO + 3H_2 \rightarrow CH_4 + H_2O \quad \Delta H^o_{298} = -206{,}2 \text{ kj/mol} \tag{2.4}$$

$$CO + 1/2O_2 \rightarrow CO_2 \quad \Delta H^o_{298} = -283.6 \text{ kj/mol} \tag{2.5}$$

$$H_2 + 1/2O_2 \rightarrow H_2O \quad \Delta H^o_{298} = -243.5 \text{ kj/mol} \tag{2.6}$$

For instance, steam reforming of methane (SRM) is a widely practiced technology for hydrogen production (Rostrup-Nielsen, 1984). The reaction is highly endothermic. Traditional methane steam reforming catalysts for industrial production of hydrogen and synthesis gas are based on nickel/nickel oxide or cobalt compositions on refractory alumina or supports such as magnesium alumina, often promoted with alkali or alkali-earth compounds to accelerate carbon removal (Trimm, 1998), and are less costly than precious metals on alumina. Partial oxidation (Equation 2.2) is much faster reaction than steam reforming, offering therefore the advantage of smaller reactors and higher throughputs.

The water-gas shift (WGS) reaction (Equation 2.3) is a critical step in fuel processors for preliminary CO clean up and additional hydrogen generation prior to the CO preferential oxidation or methanation step (Equation 2.4). WGS units are placed downstream of the reformer to further lower the CO content and improve the H_2 yield. Ideally, the WGS stage(s) should reduce the CO level to less than 5000 ppm. For this equilibrium outlet CO to be obtained from reformate, the WGS catalyst has to be active at low temperatures, 200–280^{o}C, depending on the inlet concentrations in reformate (Ghenciu, 2002). The reaction is moderately exothermic, with low CO levels resulting at low temperatures, however, with favorable kinetics at higher temperatures (Peppley, et al., 1999).

2.3. Hydrogen Clean-up by Selective CO Oxidation

Selective oxidation of CO in hydrogen-rich mixtures is an important reaction in fuel cell technology. The hydrogen used as fuel in PEM fuel cells should be essentially free of CO to avoid poisoning of the Pt anode catalyst (Kim and Lim, 2002). It is known that hydrogen can be supplied by various methods: for example, steam reforming of methanol, hydrocarbons or even bio-ethanol. When hydrogen is produced via the reforming reaction, the product stream is expected to consist of only CO_2 and H_2, but the exit gas always

contains small amounts of CO as a poisoning impurity. Although the CO concentration is reduced via the water gas shift reaction, the product stream still contains 1-2 volume per cent CO. This is because the water gas shift reaction is a reversible equilibrium reaction so that CO cannot be removed completely. Therefore, the fuel processor must be equipped with a CO removal system (Tanaka *et al*., 2003).

Preferential (or selective) oxidation of CO (called PROX) has been recognized as one of the most straightforward and cost-effective methods to achieve acceptable CO concentrations (Martinez-Arias *et al.*, 2006). In the PROX reactor, the following two oxidation reactions are likely to occur (Choi and Stenger, 2004)**:**

$$\text{Desired Reaction} : CO + \tfrac{1}{2} O_2 \longrightarrow CO_2 \quad ; \quad \Delta H^o = -283 \text{ kJ/mol} \qquad (2.7)$$

$$\text{Undesired Reaction} : H_2 + \tfrac{1}{2} O_2 \longrightarrow H_2O \quad ; \quad \Delta H^o = -242 \text{ kJ/mol} \qquad (2.8)$$

The oxidation of hydrogen competes with the oxidation of carbon monoxide. Consequently, one critical point is to find a catalyst that is both highly active and highly selective towards the oxidation of CO to CO_2. The operating temperature should be somewhere in between the low-temperature WGS unit (250–300 ºC) and the temperature of the PEMFC (80-100 ºC). Finally, such a catalyst should be able to operate under transient conditions, as the power demand will vary considerably (Marino *et al*., 2004).

2.4. Catalyst Used for Selective CO Oxidation

The low-temperature selective oxidation of CO in H_2-rich gas streams has recently been reviewed in detail (Trimm, 2005**;** Trimm and Önsan, 2001). It has been pointed out that it is crucial to control O_2/CO ratios and temperatures, as excess O_2 in the reactor may also oxidize the H_2 in the feed to the fuel cell. Therefore, a catalyst that can selectively oxidize CO in the presence of CO_2 and H_2O at the cost of only very small amounts of H_2 oxidation has to be designed. Precious metals supported on or promoted with ceria are identified as most suitable catalysts for PROX, in spite of the cost involved. More specifically, Pt-based catalysts promoted by Co or K appear to be the best choice at present. For careful temperature control, it may be necessary to use two reactors.

Pozdnyakova *et al.,* (2006) have investigated PROX over CeO_2-supported precious metal catalysts and state that several catalytic formulations have so far been tentatively tested in the PROX reaction. Supported noble metals such as Au, Pt, Rh, Ru and the bimetallic Pt-Sn system were found applicable for the reaction.

The catalysts that have been tested for their efficiency in the PROX process can be classified into three general groups in terms of their composition and resulting catalytic properties (Figure 2.2). The first group involves supported noble metal catalysts (mainly Pt) and follows from the first developments conducted by Engelhard researchers in the context of processes related to ammonia production. The currently used PROX systems include this group of catalysts, which have the main drawback (apart from their cost) of relatively low selectivity for CO oxidation; this can be improved by the use of appropriate promoters and/or supports at the operating temperatures concerned (423-473 K). In order to maintain selective CO oxidation, careful temperature control is absolutely necessary**;** and the use of two reactors with inter-stage cooling may be required to avoid extensive heating caused by the exothermic reactions (Trimm, 2005).

A second group involves supported gold (or oxidized gold) catalysts, well known for their outstanding performance for low-temperature CO oxidation, especially in O_2-rich and CO_2-deficient environments (Haruta, 1997). These systems show a high activity for the PROX process with a better match between their activity window and the PEMFC anode operating temperature (353- 403 K). They exhibit, however, poor resistance to CO_2 and H_2O in the reactant mixture. Since Au-based catalysts require an oxidative pretreatment, their stability in H_2 environments is likely to depend on the transformations between the oxide forms of the support material and, hence, on the O_2 level and the temperature (Trimm and Önsan, 2001).

The third group of catalysts under research is related to formulations based on closely interacting copper oxide and ceria (CuO/CeO_2), or structurally related cerium-containing mixed base-metal oxides. These have shown promising properties in terms of activity, selectivity and resistance to CO_2 and H_2O, while being probably most interesting from an economical point of view. The particular ability of the latter class of catalysts for the PROX or related processes has been essentially attributed to the exceptional redox

properties achieved by interfacial sites upon establishment of interactions between both catalyst components (Martinez-Arias *et al.*,2006).

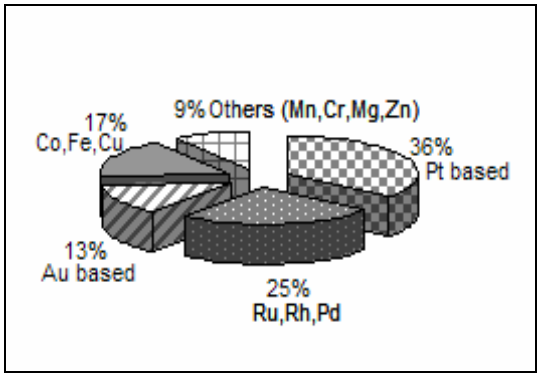

Figure 2.2. Typical formulation of selective CO oxidation catalysts in recent publications (Choi and Stenger, 2004)

2.4.1. Platinum (Pt) Catalysts

Purifying H_2 by selectively oxidizing trace amounts of carbon monoxide over a Pt-based catalyst is not new. The first patent for using a Pt-supported on alumina catalyst to oxidize CO selectively in hydrogen was awarded to Engelhard in 1963. A number of platinum group metal-based catalysts supported on alumina, zeolite or activated carbon have been studied as potential PROX catalysts (Uysal, et al., 2006**;** Uysal, 2005**;** Şimşek, 2005**;** Park, et al., 2004**;** Özkara and Aksoylu, 2003). At low oxygen concentrations in the feed, the selectivity of Pt-based catalysts for CO oxidation in a H_2-rich environment was improved by increasing the oxygen supply to Pt sites via promoters like CeO_2 or SnO_x (Manasilp and Gulari, 2002**;** Son and Lane, 2001).

Pt catalysts can be used for PROX due to their higher activity around 200ºC with lower CH_4 formation rate (Son *et al.*, 2003). Pt-based catalysts tested achieve maximum conversions at approximately 200^{o}C, with a selectivity approaching 40-60% in a 1% CO, 1% O_2, and H_2 balance mixture. The introduction of O_2 into the reactor at different stages enhances this selectivity (Epling *et al.*, 2003).

In order to interpret the bistability in CO oxidation on Pt, one has to understand the mechanism of this reaction (Zhdanov and Kasemo, 2003). The evolution of the concepts in this field can retrospectively be divided into a few periods. Before and during the formative period of surface science, CO oxidation on the Pt-group metals was generally accepted to occur via the following mechanisms:

Reversible CO adsorption

$$CO_{gas} \longleftrightarrow CO_{ads} \tag{2.9}$$

Dissociative O_2 adsorption

$$(O_2)_{gas} \longrightarrow 2O_{ads} \tag{2.10}$$

Langmuir–Hinshelwood (LH) reaction between adsorbed CO and O

$$CO_{ads} + O_{ads} \longrightarrow (CO_2)_{gas} \tag{2.11}$$

Eley–Rideal (ER) reaction between gas-phase CO and adsorbed O

$$CO_{gas} + O_{ads} \longrightarrow (CO_2)_{gas} \tag{2.12}$$

Surface-science-based studies have shown that the ER step actually does not occur.

Temperature and pressure are important variables that can significantly affect surface kinetic parameters and, hence, reaction rate and selectivity. Temperature has an effect on every step of reaction (surface reactions, adsorption, and desorption) whereas pressure can affect the reaction in terms of the driving force to form product. Since CO oxidation is highly exothermic, operating on an industrial scale can result in temperature gradients that affect the local activity and selectivity of the catalyst. At relatively low temperatures (i.e. 90ºC), the Pt surface is predominantly covered with adsorbed CO and the rate of reaction is directly proportional to oxygen partial pressure. The relationship between selectivity and temperature on Pt catalysts is still not clear in open literature (Sirijaruphan *et al*., 2004).

It has been found that the CO oxidation on the Pt/Al_2O_3 catalyst increases with an increase in reaction temperature to a maximum value, then decreases with a trend similar to that of CO oxidation selectivity. This behavior is explained by the fact that CO inhibits

adsorption of H_2 at temperatures below 200^0C. At temperatures higher than 200^0C, CO adsorption is retarded whereas H_2 adsorption is enhanced. This results in the lowering of the CO oxidation selectivity relative to hydrogen oxidation (Sandhu *et al.*, 2005).

Kachlich *et al*. (1997) also reported that the Pt-based catalysts tested achieved maximum conversions at approximately 200 ºC, with a selectivity approaching 40–60 % in 1 % CO, 1 % O_2 and H_2 balance mixture.

Bracchini (in Wang *et al.*, 2006) showed that Pt and Ru supported on active carbon had higher activities in CO selective oxidation when compared to Pt supported on alumina. In contrast to Pt catalysts, Au catalysts are intrinsically more active in terms of CO oxidation than in H_2 oxidation, and their catalytic activity is possibly enhanced by the presence of moisture.

Special catalysts such as Pt supported on zeolite were also proposed for selective oxidation of carbon monoxide in hydrogen-rich fuels (Igarashi *et al*., 1997). The proposed Pt-zeolite catalysts oxidized carbon monoxide much more selectively in a large excess of hydrogen with the addition of low concentrations of oxygen than a conventional alumina-supported Pt catalyst. The selectivity was affected by the supports and oxygen contents in the feed stream. Enhanced selectivity was obtained on Pt-zeolite catalysts by decreasing the oxygen content (nearly 100% selectivity for CO oxidation at 0.05% oxygen in feed). Pt-mordenite showed the highest conversion of carbon monoxide to carbon dioxide among the catalysts examined; this catalyst minimized oxygen addition for complete oxidation of CO in large excess of H_2 by using a two-stage reactor. Furthermore, it had resistance to the addition of water into the feed stream. Pt-mordenite is promising as a practical catalyst for the simple system to remove carbon monoxide from reformed gases and can be substituted for conventional Pt/Al_2O_3 catalysts.

The CO conversions on four noble metal catalysts (Ru, Rh, Pt, Pd, all supported on γ-Al_2O_3) exhibited a maximum with increasing temperature, and the decline in CO conversion observed at higher temperatures was attributed to the water-gas equilibrium leading to increased consumption of the limited O_2 supply by H_2. These results indicate that high-temperature operation is to be avoided because, under such conditions, H_2 is

preferentially removed rather than the CO contaminant. For each noble metal catalyst, there was an optimum O_2 concentration, and O_2 levels beyond the optimum simply increased H_2 oxidation (Trimm and Önsan, 2001).

CO_2 and H_2O present in the feed stream were also found to affect the performance of PROX catalysts. For example, in the case of 2wt%Pt/Al_2O_3, the presence of water vapor in the feed considerably enhanced the CO oxidation reaction in the 383–463 K range where the activation energy for CO oxidation was reduced. On the other hand, the presence of CO_2 in the feed decreased CO oxidation rate as well as oxygen consumption. When both CO_2 and H_2O were present in the feed, not only the rate of CO oxidation increased but also the maximum CO conversion temperature shifted down from 443 K to 423 K, suggesting that the positive effect of water is more dominant than the negative effect of CO_2 [Park, et al., 2004; Manasilp and Gulari, 2002]. On the other hand, in the case of activated carbon supported Pt-SnO_x and Pt-CeO_x, the presence of CO_2 in the H_2-rich feed had a beneficial effect on CO conversion (Şimşek, 2005).

2.4.2. Cerium Oxide (CeO_x) Promoters

Extensive research conducted particularly during the past 10 years has shown that the presence of ceria affects a number of catalytic reactions. Cerium oxide or ceria (CeO_2) may exist in several oxidation states, due to the ease with which the oxidation state changes between +3 and +4. A number of functions have been ascribed to ceria, including the promotion of WGS activity, maintenance of the dispersion of the catalytic metals and stabilization of the surface area of the support. In addition, it also promotes precious metal catalysts for WGS reaction, and because of these beneficial effects, ceria is chosen as the support for Pt and Au-based WGS catalysts (Luengnaruemitchai *et al.,* 2003).

Son (2006) reported that adding a Ce promoter to the alumina-supported Pt catalyst improved the activity and selectivity of CO oxidation in H_2 at 100–200^oC by enhancing the oxygen supply to Pt along with stability. The higher Ce loadings by weight could supply more oxygen to Pt, which yielded higher CO conversion and higher selectivity.

Ceria as an additive in automotive catalysts utilizes its ability to store oxygen. It also improves the dispersion of the noble metal. A number of recent publications have been devoted to ceria-containing catalysts for investigating its chemisorptive, nanostructural and catalytic properties. The determination of the chemisorptive properties of ceria-supported noble metals (NM/CeO_2) is difficult because hydrogen (and oxygen) spillover occurs between the metal and the carrier oxide even at room temperature. The spillover of hydrogen can lead to surface reduction of the support. However, ceria surface area, pretreatment conditions and the use of chlorine-containing metal precursors were shown to have a strong influence on the apparent H/metal or O/metal ratios (Teschner *et al.*, 2001).

Ceria-supported copper catalysts offer a wider temperature window for the operation of the PROX reactor and the PEM fuel cell, compared to costly noble metal based catalysts. It must be remembered at this point that the selectivity towards the CO oxidation on the noble metal catalysts, such as Pt/Al_2O_3, continuously decreases as the temperature increases for $T > 90^oC$. Ceria or ceria–zirconia-supported copper catalysts, independently of the surface area of the support, were shown to be very active for selective CO oxidation. In that case one should note that ceria-based oxides are basic and that the oxygen is very mobile on such supports. Furthermore, it was also postulated that in CuO/CeO_2 catalysts, the presence of CeO_2 increases the dispersion of copper oxide and enhances the redox behavior of the copper ions, and that the presence of copper, in turn, increases the reducibility of ceria. It was also reported that synergetic effects would involve the stabilization by the ceria support of non-stoichiometric metastable copper oxide species formed during the reduction, which species would be highly active for the CO oxidation reaction (Marino *et al*., 2005).

Cerium oxide has been shown to improve the thermal stability of the support and to increase the noble metal dispersion. Moreover, cerium oxide was shown to influence the kinetics of reactions, e.g. the water-gas shift and the CO oxidation reactions, and to have oxygen storage and releasing capacity. The latter means that ceria stores oxygen under oxygen rich conditions, and subsequently releases oxygen under oxygen poor conditions (Oran and Üner, 2004).

Pozdnyakova *et al.* (2006) have also stated that cerium oxide is active in transient oxygen storage, and as a catalyst support, it can promote oxidation even under oxygen-poor conditions. Ceria-supported Pt, Rh and Pd catalysts are also remarkably active in the low-temperature oxidation of CO, and they are able to oxidize carbon monoxide even in the absence of oxygen, as demonstrated by the so-called 'oxygen storage capacity' (OSC) measurements.

It has been reported that water enhances the rate of reaction, and the presence of oxygen is required at temperatures too low for gas phase water-gas shift reactions to occur. Furthermore, it is known that H_2O does not adsorb onto noble metal surfaces but can adsorb on ceria and alumina. The effect of water is essentially a bifunctional reaction path involving CO adsorbed on the noble metal and OH adsorbed on the oxygen storage cells. The bulk diffusion of oxygen in ceria plays a major role in the presence of water (Rajasree *et al*., 2004).

Özkara and Aksoylu (2003) reported that ceria can be an adequate support or promoter for Pt when one has to lower the CO concentration in a hydrogen-rich stream by using the PROX reaction at low temperature and/or with minimum hydrogen loss.

Ceria-supported platinum was found to be active in hydrogen oxidation as well, and therefore cannot be considered as an effective PROX catalyst above 130ºC. Nevertheless, ceria can be considered as a beneficial additive to Pt catalysts supported on other materials (Wootsch *et al*., 2004).

2.4.3. Cobalt Oxide (CoO_x) Promoters

Cobalt is a particularly active metal and possesses high activity for both CO and hydrocarbon oxidation. The supported Co catalyst is as active as the Pt catalyst at high temperatures, and Co could be a good replacement for Pt at operating temperatures above 120 ºC. However, it is inhibited by the other reformate gases, H_2O and CO_2 (Epling *et al*., 2003). At low temperatures, it is inactive for CO oxidation which may be due to its water sensitivity.

Deraz (2002) stated that the addition of Co_3O_4 to the $CuO–Al_2O_3$ system resulted in an increase in the activity of CO oxidation at 600°C, and a decrease was observed in this activity by heating to 800°C. The change in the activity of $CuO–Co_3O_4/ Al_2O_3$ catalysts could be discussed in terms of (i) the concentration of catalytically-active constituents on the uppermost surface layers of the catalyst and (ii) the progressive transformation of the most active constituents into $CuAl_2O_4$ and $CoAl_2O_4$ phases. Co_3O_4 acts as a suitable stabilizer via coating of some of the CuO crystallites, thus hindering their grain growth.

The pre-oxidized cobalt-containing catalysts were found to be very active at low temperatures and showed light-off temperatures around 210 K. This low temperature activity of the cobalt containing catalysts was found to be independent of the presence of platinum. The presence of platinum seems to increase the reduction rate of the cobalt oxide when the temperature exceeds 400 K (Thormahlen *et al.*, 1999).

Park *et al*. (2005) investigated the catalytic activity and selectivity of CO oxidation over the $CuO\text{-}CeO_2/\gamma\text{-}Al_2O_3$ catalyst in excess hydrogen. When Cu-Ce catalyst was further modified with Co as a promoter, the highest activity and selectivity was obtained over the wide temperature windows of 150-220 ^{0}C.

Jansson (2000) stated that the oxidation of CO over Co_3O_4 follows a redox cycle where gas-phase CO adsorbs on a cobalt site, and the adsorbed CO reacts with a lattice oxygen atom forming CO_2 plus an oxygen vacancy, so reducing the oxidation state of the Co site. The following mechanism was proposed for low temperature CO oxidation over $Co_3O_4/\gamma\text{-}Al_2O_3$:

- CO is adsorbed on an oxidized Co site (probably Co^{+3}).
- The adsorbed CO reacts with oxygen linked to the active Co^{+3}, CO_2 is formed and quickly desorbs forming a partially reduced site which may consist of two Co^{+2} ions or may be regarded as an oxygen vacancy.
- The partially reduced site can undergo two different reactions
  i. it can be re-oxidized by gas-phase oxygen to an active Co^{+3} site, or
  ii. CO can adsorb on the site and thus deactivate it.

- CO_2 can react with the oxidized surface to form carbonate species, and the carbonate may exchange oxygen with the surface and be desorbed as CO_2 again.

Disadvantages of cobalt oxide, at high temperatures and in the presence of water, are sintering of the active phase and reaction with alumina supports, leading to formation of the fairly inactive spinal $CoAl_2O_4$ (Törncrona *et al*., 1997).

2.4.4. Aluminum Oxide (Al_2O_3) Support

Many industrial catalysts consist of metals or metal compounds supported on an appropriate support, the basic role of which is to maintain the catalytically active phase in a highly dispersed state. However, it is well documented that the role of the support is not merely that of a carrier; it may actually contribute to catalytic activity and it may react to some extent with other catalyst ingredients during the manufacturing process. Further, the interaction between the active phase and the support phase can affect the catalytic activity. The selection of the support is based on a series of desirable characteristics: inertness; stability under reaction and regeneration conditions; adequate mechanical properties; appropriate physical form for the given reactor; high surface area (which is usually, but not always, desirable); porosity and chemical nature. Among the wide range of possible catalyst support materials, in practice only three combine these characteristics optimally, and they account for most industrial supported catalysts: alumina, silica and carbon, mainly activated carbon (Rodriguez-Reinoso,1997).

Al_2O_3 is an advanced support and its various versions (α, β, γ) optimized for specific processes are produced on an industrial scale (Zdražil, 2003). γ-Al_2O_3 has a large surface area and is widely used as a supporting material for catalysts. If a H_2-selective silica membrane is combined with a γ-Al_2O_3 film which is loaded with a noble metal catalyst, the CO concentration can be decreased to levels below the threshold value (Hasegawa *et al*., 2002).

Al_2O_3 is not regarded as a good support for gold catalysts and is very different from reducible oxides such as FeO_x, NiO_x, and CoO_x (Schubert *et al*., 2001; Haruta, 1996). When gold is supported on Al_2O_3, which is believed to behave as neutral in the reaction

process, only moderately active catalysts are obtained. Therefore, gold catalysts supported on composite MO_x/Al_2O_3 seem to have the possibility to realize the commercialization of high-activity catalysts. It is desirable to develop this kind of $Au/MO_x/Al_2O_3$ catalysts for practicable applications (Wang *et al*., 2003).

2.5. The Effect of CO_2 and H_2O on Selective CO Oxidation

2.5.1. The Effect of CO_2 on Selective CO Oxidation

Adding a small amount of CO_2 generally decreases the catalytic activity of Pt/γ-Al_2O_3, Au/α-Fe_2O_3 and CuO-CeO_2 catalysts for selective CO oxidation. The magnitude of this negative effect depends on the nature of the catalyst. Au/α-Fe_2O_3 was found to be the most sensitive, while the Pt/γ-Al_2O_3 catalyst was the most resistant towards deactivation by CO_2 (Avgouropoulos *et al*., 2002). The presence of CO_2 in the feed stream caused a decrease in the CO oxidation selectivity of Ru/C and Pt/C catalysts, compared to the value in the absence of CO_2 (Snytnikov *et al.,*2003). On the contrary, the addition of CO_2 into the pure H_2-rich feed of the PROX reactor increased CO conversion levels of Pt-SnO_x and Pt-CeO_x catalysts supported on unoxidized or oxidized activated carbon (AC), which is unlike the CO_2 effect observed on PROX catalysts prepared with other support materials (Şimşek, 2005).

Manasilp and Gulari (2002) reported that the presence of realistic amounts of CO_2 in the feed has a detrimental effect on the activity of Pt/alumina catalysts. This can be either due 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 caused by the dissociative adsorption of CO_2.

Coprecipitated gold-ceria catalysts are active in the selective oxidation of CO in H_2-rich streams. Calcination significantly enhances CO conversion whereas selectivity to CO_2 formation does not exceed 40% in any investigated reaction condition. The addition of CO_2 to the reaction stream negatively affects both CO conversion and selectivity to CO_2 formation (Panzera *et al.,* 2004). CO_2 also affects negatively the activity of both uncalcined and calcined Fe_2O_3-supported gold catalysts. CO conversion decreases linearly as the CO_2

concentration increases. However, for CO_2 concentrations higher than 12 per cent, where CO conversion is lower than 20 per cent, CO_2 slightly affects the CO conversion. Likewise, selectivity to CO_2 formation decreases as the CO_2 concentration in the feed increases.

Au-based catalysts lose activity in the presence of CO_2, while CO conversion over the $Pt_{0.5}$ $Al_1Mn_{6.7}Co$ catalyst increases significantly, which is also reflected in the selectivity for CO oxidation**;** the Co-Mn catalyst shows the highest CO oxidation selectivity in the presence of CO_2. Apparently, CO_2 preferentially blocks the sites responsible for H_2 oxidation on this catalyst (Maier and Saalfrank, 2004).

A decreased activity for Au/MnO*x* catalysts in the presence of 15–16% CO_2, is observed. Recently, Schubert et al. showed that both H_2O and CO_2 have pronounced and detrimental effects for this reaction over Au/Fe_2O_3 catalysts (Luengnaruemitchai *et al.,* 2005).

Liu *et al*. (2004) reported that when 20% of CO_2 is added into the feed mixture over the $CuO\text{-}CeO_2$ catalyst, CO conversion decreases while the selectivity increases a little. The conversion of CO reaches nearly 100% and the selectivity is about 90% over the $CuO\text{-}CeO_2$ catalysts in a feed gas containing 1% CO, 20% CO_2, 1–2% O_2 and 50% H_2 in He at 165^{o}C. An adverse effect of CO_2 on CO oxidation is observed only at temperatures below 140^{o}C which is attributed to the strong binding of CO_2 on the ceria surface at these temperatures.

The presence of CO_2 in the anode feed of proton exchange membrane fuel cells can lead to a significant loss in performance. Especially platinum based gas diffusion electrodes are sensitive for CO_2. Due to this effect of CO_2 on fuel cell anodes, complete removal of CO from reformate streams does not guarantee PEM fuel cell performance (Bruijn *et al*., 2002).

The presence of 15% CO_2 in the reactant feed has a negative effect on the performance of $CuO\text{-}CeO_2$ catalysts. It lowers their catalytic activity by approximately one order of magnitude. This is probably due to competitive adsorption of CO and CO_2 on the catalyst surface (Avgouropoulos and Ioannides, 2003).

2.5.2. The Effect of H_2O on Selective CO Oxidation

Han *et al.*, (2004) investigated the influence of water vapor in the feed gas on the PROX characteristics of Rh/MgO, Pt/γ-Al_2O_3 and Ru/γ-Al_2O_3 catalysts. Measurements in idealized reformate with increasing amounts of water in the feed, from 0 to 10 kPa, demonstrated that water has little effect on the catalytic activity and selectivity of all three catalysts. On the other hand, Manasilp and Gulari (2002) reported that the addition of water vapor to the feed has significant positive effect; it reduces the activation energies of both CO oxidation and hydrogen oxidation over Pt/Al_2O_3; thus, the conversion is increased significantly without changing the selectivity. They speculated that this was due to the participation of hydroxyl groups formed by the dissociative adsorption of H_2O on Pt.

Maier and Saalfrank (2004) reported that the addition of 2.2% H_2O resulted in a similar change of catalytic activity and selectivity as did the CO_2. The Co-Mn and Cu-Ce catalysts were strongly deactivated; the Au-catalyst was not affected by water, while the Pt-catalyst showed loss of CO conversion with increasing temperature. Since water as well as CO_2 strongly deactivates noble metal-free catalysts, the effect of both poisons was tested with Au and Pt-containing catalysts both of which were little affected by CO_2 and H_2O.

Addition of H_2O to the hydrogen-rich feed stream decreases the catalytic activity of Cu-Ce/γ-Al_2O_3 and Cu-Ce-Co/γ-Al_2O_3 for selective CO oxidation and the temperature at which 50% conversion of CO is obtained. It is found that the catalytic activity decreases markedly at low temperatures (Park *et al*., 2004).

Over Au/α-Fe_2O_3 catalysts, the addition of water leads to both an increased CO oxidation rate and an increased selectivity compared to CO_2-containing reformate, partly compensating the negative influence of CO_2 on the preferential CO oxidation. The effects of water addition are very sensitive to the reaction temperature. They are very prominent at a reaction temperature of 40ºC, while at 120ºC hardly any differences are observed. This is reflected in the lower activation energy for CO oxidation under these conditions, which is reduced by one-third from about 30 to 20 kJ/mol. The deactivation is slowed down or even reversed by the transformation of carbonate species into thermally less stable bicarbonate

species that are decomposed at a higher rate than carbonates. The effects of CO_2 and H_2O only partly compensate each other (Schubert *et al*., 2004).

Luengnaruemitchai *et al*. (2003) reported that water has a positive effect on Pt/CeO_2 catalysts and a moderate positive effect on the Au/CeO_2 and Au/Fe_2O_3 catalysts. The promoting effect of water vapor on CeO_2 can be explained as oxidation of the CeO_2 support by water. The water in hydroxide form may play an important role as a good oxidant in WGS reaction.

At temperatures below the boiling point of water, the Ag-Co and Ag-Mn composite oxide catalysts lost activity in the presence of large amounts of water vapor with CO_2, but, above the boiling point of water, catalysts gave good activity even for the gas mixture including CO_2. It is possible that pore blockage occurs due to condensation and leads to the coverage of surface centers. Thus, the presence of gas phase CO_2 in the feed depresses the CO oxidation activity of the composite oxide catalyst, but the depression is more severe when CO_2 and water vapor are present together (Güldür and Balıkçı, 2002).

Tanaka *et al*. (2003) have reported that in the case of the Rh/USY catalyst, the effect of steam is very small. CO conversion in the low-temperature range was slightly increased, while the minimum CO concentration was slightly decreased. This result indicates that CO_2 is formed mainly via CO oxidation with O_2. In the case of K-Rh/USY catalyst (K/Rh = 3), steam addition decreased CO conversion in the temperature range below 400 K. In contrast, steam addition increased O_2 conversion in the low-temperature range. This indicates that the presence of steam inhibits CO oxidation and promotes H_2 oxidation slightly. As a result, CO oxidation becomes less preferential by the addition of steam at low-temperature range. However, it is very important that no effect of steam at all is observed in the temperature range higher than 400 K.

It was demonstrated that the moisture in the reactant gas has a significant effect on the activity of the Au/TiO_2 catalyst for CO oxidation. The activity is mainly affected by the amount of moisture adsorbed on the catalyst. The optimum concentration of moisture for the catalytic reaction is about 200 ppm. Enhancement of the reaction rate by moisture is no less than 10 times compared to that for 0.1ppm H_2O. When the concentration of moisture

is about 6000 ppm, the catalytic activity is depressed probably due to the blocking of the active sites (Date and Haruta, 2001).

Generally, the activity of a catalyst is significantly depressed by the presence of water in the feed stream. CO oxidation activity could even be enhanced by water vapor over Au/Fe_2O_3 catalyst while giving the opposite effect over Au/TiO_2 catalysts. The conversion and selectivity show insignicant difference between with and without water indicating that both catalysts could resist to that much water vapor (Luengnaruemitchai *et al*., 2005).

2.6. Catalyst Preparation

Solid catalysts are highly sophisticated products derived from chemicals by means of several different preparation procedures (Perego and Villa, 1997). Catalytic properties of heterogeneous catalysts are strongly affected by every step of the preparation together with the quality of the raw materials. The choice of a laboratory method for preparing a given catalyst depends on the physical and chemical characteristics desired in the final product. Despite the variety of preparation techniques, most of them can be reduced to a series of elementary steps or unit operations. Such unit operations can be classified by:

- the chemical and physical transformations which are implied,
- the scientific laws which govern such transformations based on fundamental inorganic chemistry,
- the operation variables such as temperature, pressure, pH, time, concentration,
- the general characteristics of the products of the operation, and
- the type of apparatus required.

There are several techniques applied in both laboratory and industrial practice for catalyst preparation, like gas and liquid phase deposition, ion exchange, incipient wetness, deposition precipitation, sol–gel, metal introduction into mesoporous materials via in situ synthesis. Catalyst preparation method strongly affects the metal dispersion, which could be crucial for achieving high activity and selectivity (Maki-Arvela, *et al*., 2005).

Since the Pt-Co-Ce/Al_2O_3 catalyst investigated in this work was prepared by the incipient to wetness impregnation, only the impregnation method is briefly discussed here.

2.6.1. Impregnation Method

Impregnation is the procedure whereby a certain volume of solution containing the precursor of the active phase is contacted with the solid support, which, in a subsequent step, is dried to remove the imbibed solvent. Two types of impregnation techniques may be employed; these are incipient to wetness and dipping impregnation, the latter is also termed as wet soaking impregnation (Satterfield, 1991).

In dipping impregnation, an excess of solution is used. After a certain time, the solid is separated and the excess solvent is removed by drying. The composition of the batch solution will change and the release of debris can form a mud which makes it difficult to completely use the solution. The heat of adsorption is released in a short time.

In incipient wetness impregnation, the volume of the solution of appropriate concentration is equal or slightly less than the pore volume of the support. Control of the operation must be rather precise and repeated applications of the solution may be necessary. The maximum loading is limited by the solubility of the precursor in the solution. Advantages of this type of impregnation method are the technical simplicity of the method and its low cost**;** getting controllable and reproducible metal loadings at the end of the impregnation process constitutes the most important feature of the method. The disadvantage of this method is the limited metal loadings by solubility of metal compound; however, this disadvantage can easily be overcome by multiple impregnation steps.

In both methods, the major operating variable is the temperature which influences both the precursor solubility and the solution viscosity and, as a consequence, the wetting time. The concentration profile of the impregnated compound depends on the mass transfer conditions within the pores during impregnation and drying (Campanati *et al*., 2003).

2.7. Catalyst Physical Properties

Most practical catalysts are highly complex materials, and a basic problem is how to correlate catalyst behavior with physical and chemical structure. Some methods of characterization are standardized. These include determination of total surface area, void fraction, pore size distribution and, in some cases, specific metal surface area by selective chemisorption, plus certain mechanical properties (Satterfield, 1991).

2.7.1 Measurement of Surface Area

The standard method for measuring catalyst total surface areas is based on the physical adsorption of a gas on the solid surface. Usually, the amount of N_2 adsorbed at equilibrium at the normal boiling point (−195.8^{o}C) is measured over a range of nitrogen pressures below atmospheric. Under these conditions, several layers of molecules may be adsorbed on top of each other on the surface. The amount adsorbed when one molecular layer is attained must be identified in order to determine the total surface area. The surface area so measured may not be the area effective for catalysis. Only certain parts of the surface, the active centers, may be active for chemisorption of a reactant, while nitrogen may be physically adsorbed on much more of the surface (Smith, 1981).

The most common method of measuring surface area was developed by Brunauer, Emmett and Teller in 1938 (Satterfield, 1991). In essence, the Langmuir adsorption isotherm is extended to multilayer adsorption. As in the Langmuir approach, the rate of evaporation is considered to be equal to the rate of condensation for the first layer, and the heat of adsorption is taken to be independent of coverage. For layers beyond the first, the rate of adsorption is taken to be proportional to the fraction of the lowest layer still vacant. The rate of desorption is taken to be proportional to the amount present in that layer. The heat of adsorption for all layers except the first layer is assumed to be equal to the heat of liquefaction of the adsorbed gas. Summation over an infinite number of adsorbed layers gives the final expression:

$$\frac{P}{V(P_o - P)} = \frac{1}{V_m C} + \frac{(C-1)P}{V_m C P_o} \tag{2.13}$$

where V is the volume of gas adsorbed at pressure P (in cm^3); V_m is the volume of gas adsorbed in monolayer (in cm^3); P_o is the saturation pressure of adsorbate gas at the experimental temperature (in mmHg); C is a constant related exponentially to the heats of adsorption and liquefaction of the gas; and P is the partial pressure (in mmHg). A plot of $P/V(P_o-P)$ versus P/P_o yields a straight line, both V_m and C can be calculated from the slope and intercept of this line.

The surface area of the catalyst may then be calculated from V_m if the average area occupied by an adsorbed molecule is known. The volume, V_m can be converted to the number of molecules adsorbed and is used in the following equation. The total surface area S is calculated from this equation:

$$S = \frac{NA_g V_m}{V} \tag{2.14}$$

where N is the Avagadro number (6.02×10^{23} molecules/gmole); A_g is the cross sectional area of each adsorbed gas molecule (16.2×10^{-20} m^2/molecule for nitrogen gas); V is the molar volume of the gas at reference conditions (cm^3/gmole).

2.7.2. Measurement of Total Pore Volume

A direct and simple method of determining the total volume of the pores is by measuring the increase in weight when the pores are filled with a liquid of known density. The liquid should preferably be of low molecular weight so that fine pores are filled. Water or various hydrocarbons may be used satisfactorily. However, the method is limited in accuracy and more accurate results are obtained by the mercury-helium method, which is based on the fact that mercury does not wet most surfaces and, therefore, does not penetrate most pores at atmospheric pressure and also adsorption of helium gas is negligible at room temperature (Satterfield, 1991).

The other method for measuring the distribution of pore volumes is the nitrogen-adsorption experiment (Smith, 1981). All the void volume is filled with adsorbed and condensed nitrogen; then a desorption isotherm is established by lowering the pressure in

increments and measuring the amount of nitrogen evaporated and desorbed for each increment. Since the vapor pressure of a liquid evaporating from a capillary depends on the radius of the capillary, these data can be plotted as volume desorbed versus pore radius. Thus, this procedure gives the distribution of pore volumes.

2.7.3. Catalyst Density Measurement

Solid density can be determined from the helium-mercury measurements. The volume of helium displaced by a sample of catalyst is measured; then the helium is removed, and the volume of mercury that is displaced is measured. Since mercury will not fill the pores of most catalysts at atmospheric pressure, the difference in volumes gives the pore volume of the catalyst sample. The volume of helium displaced is a measure of the volume occupied by the solid material. From these and the weight of the sample, the density of the solid phase, ρ_s, can be obtained.

Agglomeration of porous catalysts gives a pellet containing two void regions: small void spaces within the individual particles and larger spaces between particles. The void spaces within the primary particles are commonly termed micropores, and the void regions between particles are called macropores (Smith, 1981). The density of both the solid part and the micropore of the catalyst together is called envelope (apparent) density, ρ_p.

3. EXPERIMENTAL WORK

3.1. Materials

3.1.1. Chemicals

All the chemicals used for catalyst preparation and catalyst characterization in this study are listed in Table 3.1.

Table 3.1. Chemicals used in catalyst preparation

Chemicals	Formula	Grade	Source	Molecular Weight (g/mole)
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
Cerium(III) nitrate hexahydrate	$Ce(NO_3)_3.6H_2O$	Extra Pure	Merck	434.23
Aluminium Oxide	γ-Al_2O_3	Extra Pure	Zeochm EU	101.96

3.1.2. Gases and Liquids

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

Table 3.2. Applications and specifications of the gases used

Gas	Application	Specification
Carbon monoxide	Reactant, GC calibration	99.999% HABAŞ
Oxygen in helium	Reactant, GC calibration	70.3% BOS
Carbon dioxide	Reactant	99.99% BOS
Hydrogen	Reactant, Reducing agent	99.99% BOS
Helium	Reactant (Inert)	99.99% BOS
Helium	GC Carrier	99.99% BOS
Helium	AccuPyc	99.99% HABAŞ
Helium	BET	99.99% BOS
Nitrogen	BET	99.99% BOS

Table 3.3. Applications and specifications of the liquids used

Liquid	Application	Specification
Nitrogen	BET Surface Area	HABAŞ
Water	Reactant, cleaning	Distilled

3.2. Experimental Setup

The experimental systems used in this present work can be described in essentially four groups:

1) Catalyst preparation system; used for catalyst preparation by impregnation method,
2) Catalyst Characterization Systems; which are used for determining the surface area, pore volume and densities of the prepared catalysts,
3) Microreactor flow system; which is used for catalytic activity tests,
4) Product analysis system; which is connected to the microreactor flow system and consists of a gas sampling section, a gas chromatograph and a data processor.

3.2.1. Catalyst Preparation System

Catalysts were prepared by impregnation method using the system presented in Figure 3.1. The support placed in vacuum flask was impregnated with an aqueous solution of precursor. Precursor solution was prepared in the beaker and pumped by the peristaltic pump through the silicone tubing.

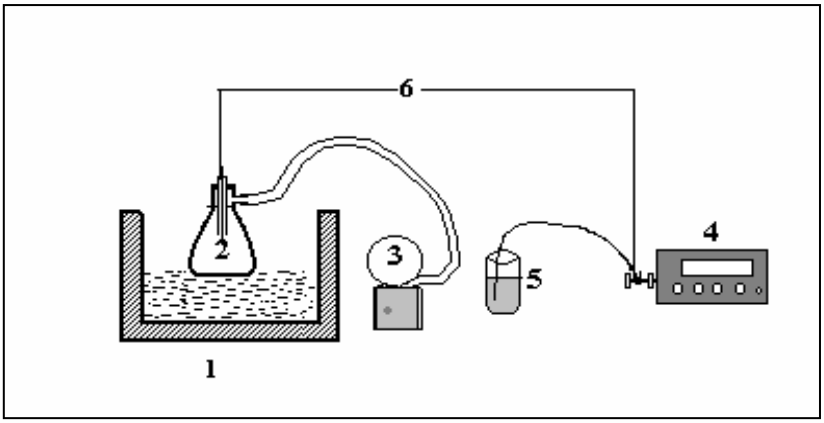

Figure 3.1. The impregnation system: 1. Ultrasonic mixer 2. Vacuum flask 3. Vacuum pump 4. Peristaltic pump 5. Beaker 6. Silicone tubing

The experimental set-up shown in Figure 3.1 was used for the preparation of the alumina-supported Pt, Co, and Ce catalysts used in this study by the incipient wetness impregnation method. The metal content, calcination temperature and calcination time values corresponding to these catalysts are listed in Table 3.4.

Incipient wetness impregnation method used in this study consists of the four steps described below:

i. Evacuating the suppport
ii. Contacting the support with the precursor solution
iii. Drying
iv. Calcination.

Table 3.4. The list of the catalysts prepared by impregnation

Metal Content (in grams)			Calcination Temperature (^oC)	Calcination Time (hr)
$Pt(NH_3)_4(NO_3)_2$	$Ce(NO_3)_3.6H_2O$	$Co(NO_3)_2.6H_2O$		
0.1390	0.5810	0.9260	450	2
0.1390	0.5810	0.9260	500	3
0.1790	0.3870	0.6170	450	2
0.1390	0.3870	0.6170	450	2
0.1390	0.3870	0.6170	450	3
0.1790	0.3870	0.6170	500	3
0.1390	0.3870	0.6170	500	2
0.1390	0.3870	0.6170	500	3
0.1390	0.1937	0.3087	450	2
0.1390	0.1937	0.3087	500	3

Commercial γ-alumina support was crushed and sieved into 45-60 mesh size (344-255 μm) and calcined at 450 ºC for 5 hours prior to impregnation. Five grams of support was placed in a vacuum flask and kept under vacuum both before and during the addition of the precursor solution. Since trapped air in the pores of the support could prevent complete penetration of the precursor solution, the vacuum pump was used to remove the trapped air and to give a uniform distribution of the active component. Before impregnating the solution, the support material was mixed under vacuum with an ultrasonic mixer for half an hour.

All the metal salts were dissolved in 1.21 cm^3 of water per gram of alumina support. Aqueous precursor solution was fed to the vacuum flask at a flow rate of 0.5 cm^3/min via silicone tubing. A Masterflex computerized-drive peristaltic pump was used to feed the solution. The slurry was mixed under vacuum by an ultrasonic mixer to maintain uniform distribution of the precursor solution. After the addition of precursor solution, the slurry was mixed under vacuum for an additional 90 min by the ultrasonic mixer. The final slurry obtained was dried in an electric oven at 115^{o}C overnight (16 hours).

Pt-Co-Ce/Al_2O_3 catalyst was then calcined at 450ºC or 500^{o}C for 2 or 3 hours depending on the specific experiment (Table 3.4).

3.2.2. Catalyst Characterization Systems

Most practical catalysts are highly complex materials, and a basic problem is how to correlate catalyst behavior with physical and chemical structure. The following are instrumental techniques and most of them require expensive and elaborate apparatus and a high degree of sophistication.

3.2.2.1. Total Surface Area Measurement. A constant-pressure dynamic apparatus, Micromeritics Flowsorb II 2300, was used for the determination of the total surface areas of the catalysts prepared and used in this study. The schematic diagram of the device used is given in Figure 3.2.

Total surface area of the catalyst sample was determined by nitrogen adsorption from N_2–He mixtures using a multipoint technique together with the BET equation.

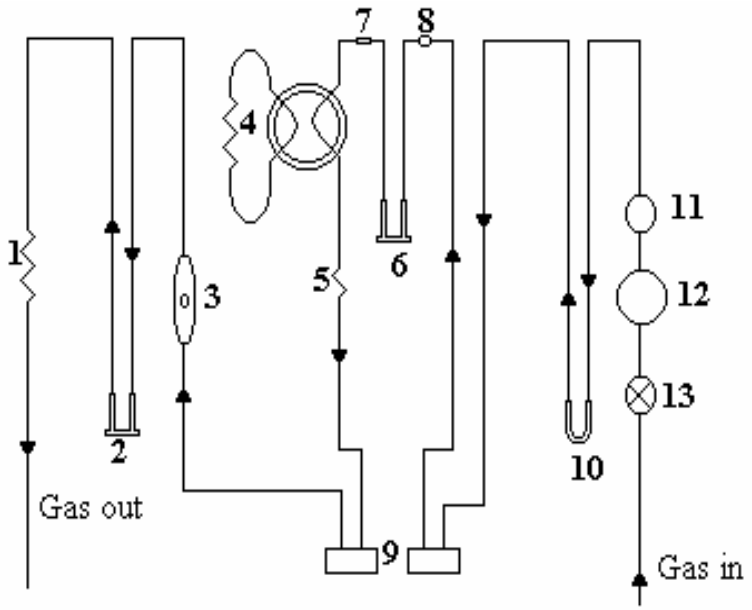

Figure 3.2. Schematic diagram of the BET equipment: 1. Back diffusion restrictor 2. Degas 3. Flowmeter 4. Long path 5. Short path 6. Test sample 7. Filter 8. Septum 9. Matched thermal conductivity cells 10. Cold trap 11. Flow adjustment valve 12. Differential flow controller 13. On-off valve

The sample was dried and degassed at 523 K for two and a half hours and then cooled to room temperature. The Flowsorb II 2300 unit was calibrated by injecting one milliliter of nitrogen at ambient conditions, calculating the corresponding volume of gas at standard conditions and setting the instrument to indicate thereafter adsorbed and desorbed gas volumes at standard conditions. Then a flow of the measuring gas (5 per cent to 25 per cent nitrogen-helium mixture) was allowed to pass over the sample at liquid nitrogen temperature of 77.4 K and to equilibrate. After the adsorption equilibrium was established as indicated by the threshold lamp, the temperature of the sample was raised to ambient temperature and the amount of nitrogen desorbed was measured by the thermal conductivity detector. This nitrogen adsorption-desorption procedure was repeated at least four times with different nitrogen-helium gas mixtures. In this study, the total surface area measurements were made with N_2-He gas mixtures for four different gas compositions. These compositions are given in Table 3.5. Helium was used as an inert to adjust the amount of required N_2.

Table 3.5. Scales of N_2-He gas mixtures and percentage of N_2.

Cases	N_2%	Channel 1 (N_2)	Channel 2 (He)
1	25.0	3	9
2	21.7	2.5	9
3	18.2	2	9
4	14.3	1.5	9

The total surface area was calculated from the BET equation by using software supplied by Micromeritics Inc. The adsorbed amount of gas was determined by weighing the sample in the test tube before and after the measurement. Given data on volume adsorbed versus pressure, the BET equation provides a reliable means whereby total surface area can be determined. The total surface area was calculated from Equations 2.13 and 2.14 by using the software supplied by Micromeritics Inc. together with the Flowsorb 2300 unit.

3.2.2.2. Total Pore Volume Measurement. The total pore volume measurement with the Flowsorb 2300 unit requires the determination of the volume of gas which, when condensed as a liquid, is taken up by the sample from the 95% N_2-5% He mixture at liquid nitrogen temperature.

The sample is first dried and degassed at 250^{o}C for two and a half hours and then cooled to room temperature. The Flowsorb 2300 unit is calibrated by injecting ten milliliters of nitrogen at ambient conditions, calculating the corresponding volume of gas at standard conditions and setting the instrument to indicate thereafter adsorbed and desorbed volumes at standard conditions. The sample is first saturated using 100 per cent nitrogen and then equilibrated with a 95% N_2-5% He gas mixture at liquid nitrogen temperature. The quantity of gas desorbed from this latter equilibration establishes the total pore volume.

3.2.2.3. Solid Density Measurement The AccuPyc 1330 Pycnometer was used to determine density and volume by measuring the pressure change of helium in a calibrated volume. The chamber temperature is also reported at the end of the requested runs. The analysis measures sample volume, from which density can be derived automatically if the sample weight has been entered. The pycnometer uses helium (99.995 % pure or better) to provide rapid, accurate analysis. The cylinder containing helium was fitted with a gas regulator set for 20-22 psig. A known amount of catalyst was placed into the sample holder.

There are two cells in the equipment, called the sample cell and the expansion cell, which are connected to each other via a valve. Both cells are expanded to atmospheric pressure P_A and temperature T_A. When the valve is closed the cell pressure becomes P_1. The mass balance equation is:

$$P_1 (V_{CELL} - V_{SAMPLE}) = n_C R T_A \quad (3.1)$$

The equation for the expansion volume is:

$$P_A V_{EXP} = n_E R T_A \quad (3.2)$$

When the valve is opened, the pressure comes to equilibrium at P_2.

$$P_2 (V_{CELL} - V_{SAMPLE} + V_{EXP}) = n_C R T_A + n_E R T_A \quad (3.3)$$

From Equations (3.1) and (3.2) and making rearrangements like $P_G = P - P_A$, where P_G is the gauge pressure, the sample volume is found to be:

$$V_{SAMPLE} = \frac{V_{EXP}}{\frac{P_{1g}}{P_{2g}} - 1} \quad (3.4)$$

3.2.2.4. Envelope Density Measurement. The GeoPyc 1360 system is a compact bench-top unit that determines the envelope density. Envelope density is the mass of an object divided by its volume, where the volume includes that of its pores and small cavities.

To begin an analysis, the operater places a weighed quantity of sample in the sample chamber, inserts a plunger part-way into the chamber, then mounts the chamber/ plunger assembly on the instrument. After a short series of prompts, the consolidation force, sample weight and other parameters are instructed and the automatic analysis begins.

The consolidation force is the force with which the sample is compressed during analysis. An exact force is selected at the start of each analysis. During analysis, the plunger is driven into the sample chamber while the chamber is agitated. The agitation causes the sample to consolidate as uniformly as possible while the plunger moves forward. When the desired force is reached, the volume of the sample is measured. The distance the plunger moves into the chamber is the actual measurement with which calculations are made. The distance is measured by the number of steps moved by the stepper motor that drives the plunger. The plunger actually moves 2.6458×10^{-4} cm with each motor pulse.

The volume is determined by the difference in how far the plunger is driven into a cylinder containing only the medium and then when the sample is added. The depth of the

plunger, C, is converted to volume by a conversion factor, v, which is found from a sample of known volume. The volume is:

$$V = (C_{MEDIUM} - C_{SAMPLE})v \tag{3.5}$$

3.2.3. Microreactor Flow System

The microreactor flow system designed and constructed for conducting the selective CO oxidation experiments is shown in Figure 3.3.

1/4″ and 1/8″ OD stainless steel or brass tubing and fittings were used in the system. Research grade gases (pure helium, pure hydrogen, carbon monoxide and oxygen in helium) from pressurized cylinders were passed, if necessary, through silica gel traps before entering the system. Flow rates of the pure He, pure H_2, pure CO and O_2/He mixture were controlled by calibrated Aalborg DFC digital mass flow controllers. The gas flow rates were set via Aalborg 4PROC 4-Channel Command Module.

After mixing, all gases were sent into the reaction section which consists of a 4 mm. ID stainless steel fixed-bed down-flow micro-reactor located in a 2.4 cm ID x 40 cm furnace controlled to 0.5 ± K by a Shimaden FP-21 programmable temperature controller. The total length of the reactor was 53 cm, which is longer than the furnace tube so that the fittings of the reactor can be kept out of the furnace to facilitate manipulation during catalyst charging or recharging. The catalyst bed was placed in the center of the reactor which was located in the constant-temperature region of the furnace (about five centimeters in height). The reaction temperature was measured by a 1/16″ K type stainless steel sheathed thermocouple at the central point of the furnace and adjacent to the catalyst bed. Another K-type sheathed thermocouple that was placed in the center of the furnace was used for controlling the furnace temperature.

Silane treated glass wool supplied from Applied Science Laboratories Inc. was used to hold the catalyst bed in fixed position. Ceramic wool was placed at the top and the bottom ends of the furnace to prevent heat loss for maintaining a stable reaction

temperature. In the reactant and product sampling section, the reactant mixture entering or the product leaving the reactor were passed through two ON-OFF valves to either the GC sampling unit which has a calibrated one milliliter sample loop for analysis or to the soap bubble-meter for measuring the flow rate of the effluent at the ambient temperature.

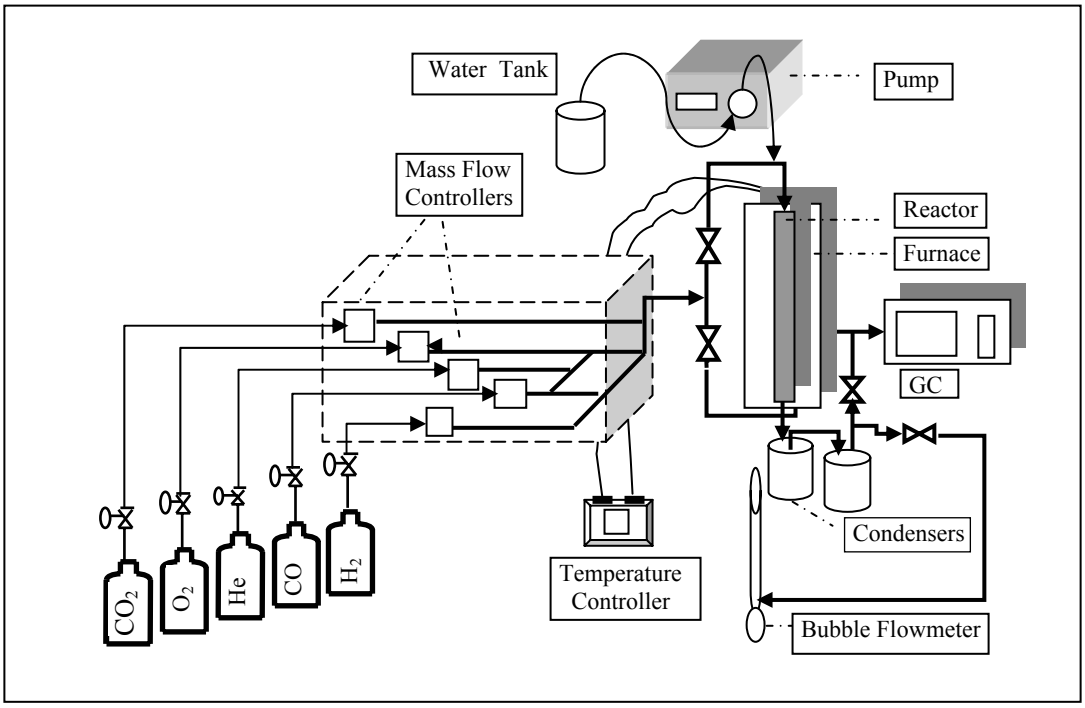

Figure 3.3. The micro-reactor flow system

3.2.4. Product Analysis System

Temperature-controlled and programmable gas chromatograph (ATI UNICAM 610 Series), equipped with a Thermal Conductivity Detector (TCD) and ATI UNICAM 4815 Computing Integrator was used for the analysis of the products. CTR I concentric column was used for detecting the feed and the remaining reactant gases after the reaction. Analysis conditions are given in Table 3.6.

Table 3.6. Reactant and product gas analysis conditions

Column Type	CTR I (Packed Concentric Column)
Outer Column Packing	Activated Molecular Sieve
Inner Column Packing	Porous Polymer Mixture
Column Oven Temperature	303 K
Carrier Gas	Helium
Carrier Gas Flow Rate	35 ml/min
Detector Type	Thermal Conductivity
Detector Current	120 mA
Filament Temperature	513 K (Low Sensitivity)
Detector Oven Temperature	413 K
Injector Oven Temperature	323 K

3.2.5. Catalytic Activity Measurements

All catalysts were reduced by H_2 before the reaction took place and kept under He flow until the reaction test was performed. The reduction program used is given in Table 3.7.

Activity tests took place in the micro-reactor flow system presented in Section 3.2.3. Freshly reduced catalysts were packed in a fixed bed micro-reactor.

The catalytic activity tests for selective CO oxidation in hydrogen rich streams with CO_2 and H_2O were conducted with a feed containing 1% CO, 1%O_2, 60% H_2, 10% H_2O, 25% CO_2 and He as balance. Total flow rate was kept at 100 cm^3/min for all reactions.

Table 3.7. Reduction program of the Pt-Co-Ce/Al_2O_3 catalyst

Segments	Starting and End Temperatures	Segment Gas
First Segment	Heating from 25 ºC to 375 ºC with a heating rate 2.5 ºC/min	He with flow rate of 50 ml/min
Second Segment (Reduction)	Keeping constant at 375 ºC for 3h	H_2 with flow rate of 50 ml/min
Third Segment	Flushing at 375 ºC for 1h to clean the catalyst surface	He with flow rate of 50 ml/min
Fourth Segment	Overnight cooling down to 25 ºC	He with flow rate of 25 ml/min

Catalyst weight was 250 mg in all reactions. The micro-reactor was first heated from the ambient temperature to 110^{o}C under a stream of 50 cm^3/min helium. Then, the He flow was turned off, and the reaction mixture was turned on. Data were taken at 30-minute intervals for 2 hours, followed by cooling the system to the ambient temperature. The summary of the reaction conditions is listed in Table 3.8.

Table 3.8. Reaction conditions used in selective CO oxidation experiments

Parameter	Value
Catalyst Particle Size	45-60 mesh size (344-255μm)
Catalyst Amount	250 mg
Reduction Conditions	At 375 ^{o}C for 3 hours (50 ml/min H_2)
Reaction Temperature	110 ^{o}C
Reactant total flow rate	100 ml/min
W/F Ratio	2.5 mg.min/ml

4. RESULTS AND DISCUSSION

Maximization of CO conversion in H_2-rich gas streams is the primary objective of PROX in fuel cell applications for obtaining clean CO-free hydrogen. Selective CO oxidation over the Pt-Co-Ce/Al_2O_3 catalyst was previously studied in the absence of carbon dioxide and water vapor by İnce (2004); later, the effects of introducing CO_2 and/or H_2O into the feed stream were investigated by Uysal (2005). The catalyst composition that gave 100% CO conversion was found to be 1.4%Pt-1.25%Co-1.25%Ce/Al_2O_3.

In the present work, ten different Pt-Co-Ce/Al_2O_3 catalysts were prepared by changing several preparation variables within the region of conditions defined by İnce (2004) and Uysal (2005) for optimum catalyst performance. Physical properties such as total surface area, total pore volume, solid and envelope densities were determined for all catalyst samples with the aim of examining the effects of design parameters on physical properties and on catalytic activity. The major catalyst design parameters considered were the metal loadings of Pt, Ce and Co, calcination temperature and calcination time. Subsequently, activity tests were performed on five of the ten catalysts investigated using hydrogen-rich feed containing both CO_2 and H_2O, and CO conversions were measured at 30-minute intervals up to two hours. CO conversion and selectivity for CO oxidation were calculated as follows:

$$\text{CO conversion (\%)} = \frac{[CO]_{in} - [CO]_{out}}{[CO]_{in}} x100 \tag{4.1}$$

$$O_2 \text{ conversion (\%)} = \frac{[O_2]_{in} - [O_2]_{out}}{[O_2]_{in}} x100 \tag{4.2}$$

$$\text{CO oxidation selectivity (\%)} = \frac{0.5x([CO]_{in} - [CO]_{out})}{[O_2]_{in} - [O_2]_{out}} x100 \tag{4.3}$$

4.1. Effects of Metal Content on the Physical Properties

4.1.1. Effect of Pt Content

The effect of the amount of Pt on catalyst physical properties was analyzed by changing the per cent Pt content, keeping all other design parameters constant. The effect of Pt loading on physical properties of the catalysts are given in Tables 4.1 and 4.2. These results are plotted in Figure 4.1. Total surface areas of other catalysts prepared are presented in Table A.1 of Appendix A.

Table 4.1. Effect of Pt loading on physical properties (calcination at 450 ^{o}C, 2 h)

Exp	Pt%	Ce%	Co%	ρ_p (g cm^{-3})	ρ_s (g cm^{-3})	TSA (m^2 g^{-1})	PV (cm^3 g^{-1})
3	1.8	2.5	2.5	0.79	1.73	148± 5	0.14
4	1.4	2.5	2.5	0.80	1.68	152± 4	0.13

Table 4.2. Effect of Pt loading on physical properties (calcination at 500 ^{o}C, 3 h)

Exp	Pt%	Ce%	Co%	ρ_p (g cm^{-3})	ρ_s (g cm^{-3})	TSA (m^2 g^{-1})	PV (cm^3 g^{-1})
6	1.8	2.5	2.5	0.74	1.76	134± 4	0.13
8	1.4	2.5	2.5	0.74	1.68	160± 5	0.15

Both Tables 4.1 and 4.2 show that the small change in Pt loading does not affect ρ_p or PV (0.14±0.01 cm^3/g) while a small increase is indicated in ρ_s with increasing Pt content. Although the TSA differences in Table 4.1 are within experimental error, those in Table 4.2 clearly indicate 10-15% decrease in TSA with increasing Pt loading at higher calcination temperature and longer calcination time.

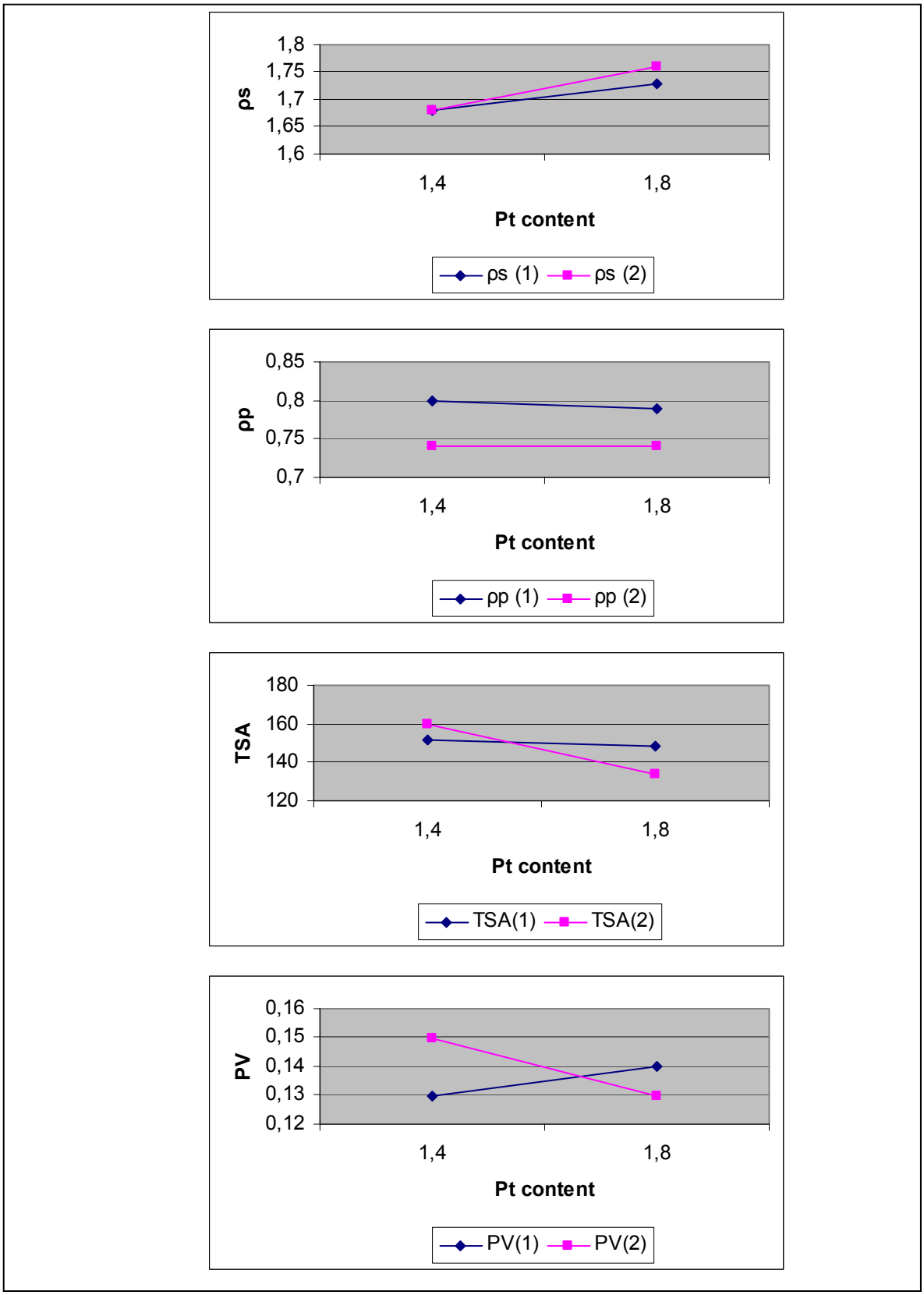

Figure 4.1. The effect of Pt loading on physical properties; (1) and (2) indicate calcination conditions in Tables 4.1 and 4.2, respectively.

4.1.2. Effect of Ce and Co Contents

The effect of Ce-Co content on the physical properties of the catalysts was studied by using three levels of Ce-Co loadings and keeping all other design parameters constant. The results obtained are presented in Tables 4.3 and 4.4, and are plotted in Figure 4.2.

Table 4.3. Effect of Co-Ce loading on physical properties (calcination at 450 ^{o}C, 2 h)

Exp	Pt%	Ce%	Co%	ρ_p (g cm^{-3})	ρ_s (g cm^{-3})	TSA (m^2 g^{-1})	PV (cm^3 g^{-1})
1	1.4	3.75	3.75	0.80	1.66	160±9	0.14
4	1.4	2.50	2.50	0.80	1.68	152± 4	0.13
9	1.4	1.25	1.25	0.80	1.67	141± 4	0.13

Table 4.4. Effect of Co-Ce loading on physical properties (calcination at 500 ^{o}C, 3 h)

Exp	Pt%	Ce%	Co%	ρ_p (g cm^{-3})	ρ_s (g cm^{-3})	TSA (m^2 g^{-1})	PV (cm^3 g^{-1})
2	1.4	3.75	3.75	0.88	1.65	209±6	0.17
8	1.4	2.50	2.50	0.74	1.68	160±5	0.15
10	1.4	1.25	1.25	0.84	1.57	132±6	0.13

The ρ_p and ρ_s values obtained for catalysts calcined at 450^{o}C for 2 h are almost the same with some variation due to experimental error, while TSA values show a gradual increase with increasing Co-Ce content accompanied by a slight increase in PV. These trends in TSA and PV are accentuated when the calcination temperature and time are increased to 500^{o}C and 3 h, respectively (Table 4.4).

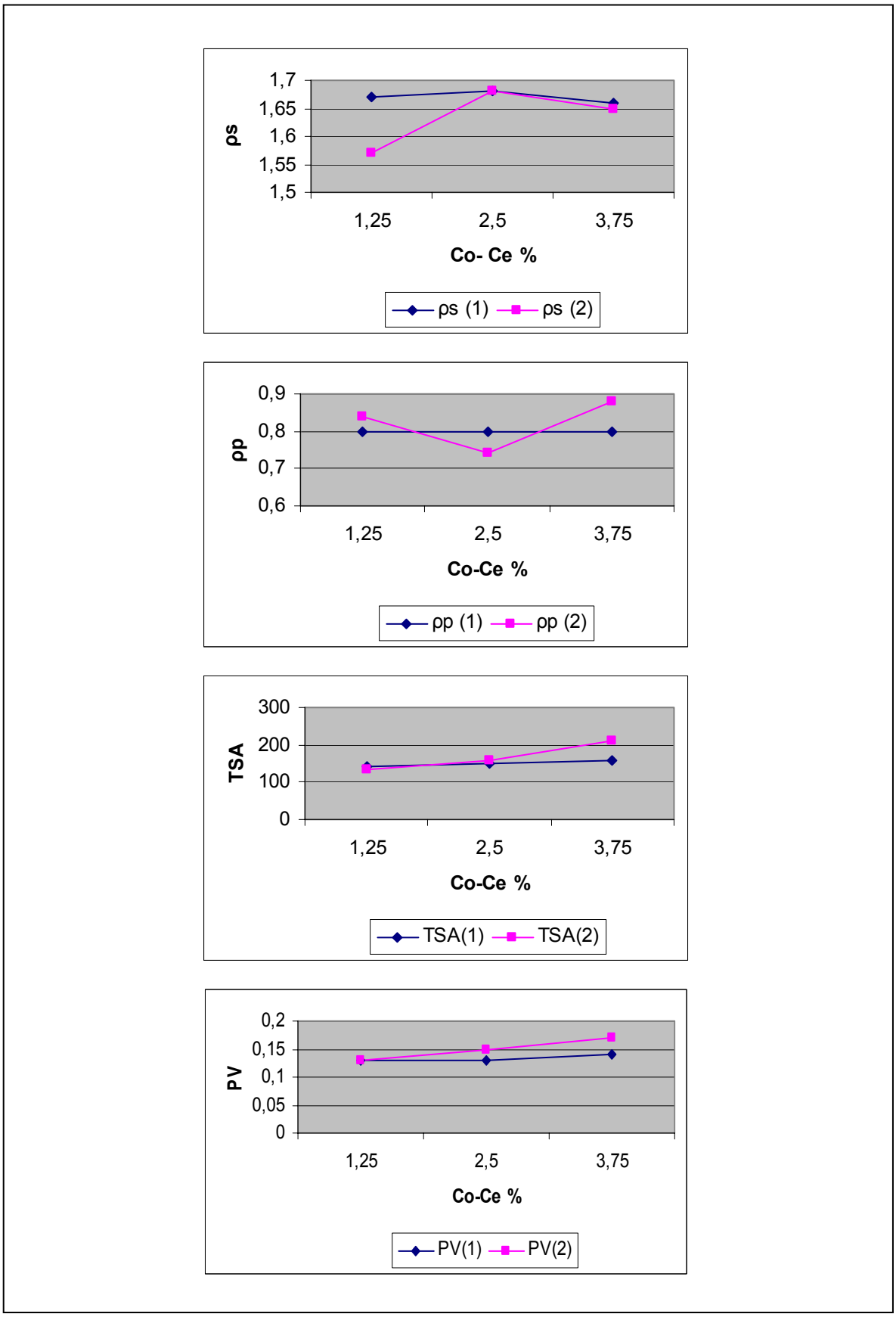

Figure 4.2. The effect of Co-Ce loading on physical properties; (1) and (2) indicate calcination conditions in Tables 4.3 and 4.4, respectively.

4.2. Effect of Calcination Conditions

4.2.1. Effect of Calcination Temperature

The calcination parameters greatly affect the mechanical properties of solid catalysts. The calcination of particles at high temperatures increases crystallinity, decreases surface and bulk defects (Salmi *et al*., 2004). These changes are reflected in the physical properties that are of importance in catalytic activity. For example, calcination at high temperatures leads to a decrease in the total surface area of the particles. The effect of calcination conditions on physical properties of 1.4%Pt-2.5%Co-2.5%Ce/Al_2O_3 was studied at two calcination temperatures using two calcination times (Tables 4.5 and 4.6, and Figure 4.3).

Table 4.5. Effect of calcination temperature on physical properties (calcination time: 2 h)

Exp	Pt%	Ce%	Co%	Calcination Temp (^oC)	ρ_p (g cm^{-3})	ρ_s (g cm^{-3})	TSA (m^2 g^{-1})	PV (cm^3 g^{-1})
4	1.4	2.5	2.5	450	0.80	1.68	152±4	0.13
7	1.4	2.5	2.5	500	0.78	1.66	130±6	0.15

Table 4.6. Effect of calcination temperature on physical properties (calcination time: 3 h)

Exp	Pt%	Ce%	Co%	Calcination Temp (^oC)	ρ_p (g cm^{-3})	ρ_s (g cm^{-3})	TSA (m^2 g^{-1})	PV (cm^3 g^{-1})
5	1.4	2.5	2.5	450	0.81	1.70	178±3	0.12
8	1.4	2.5	2.5	500	0.74	1.68	160±5	0.15

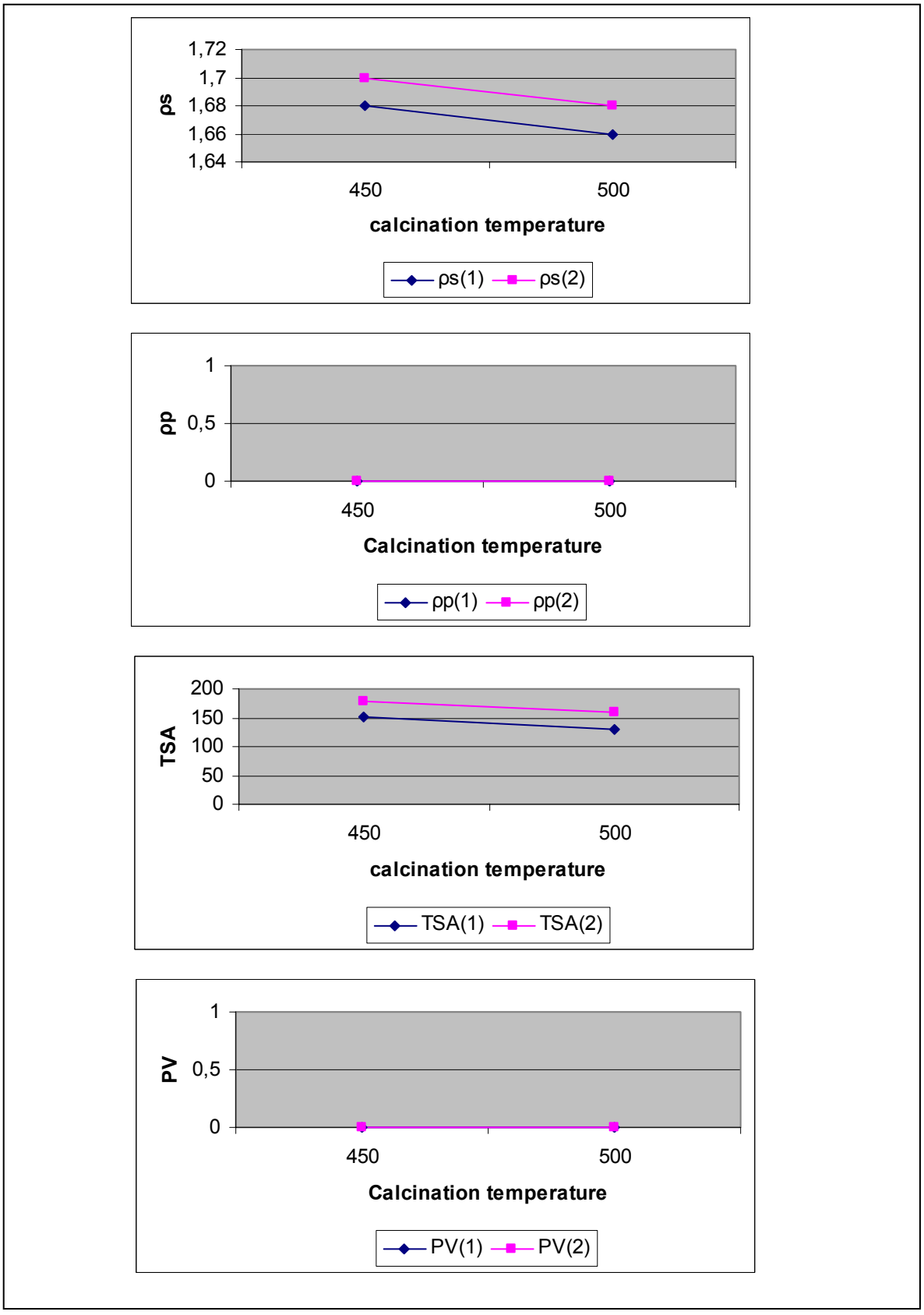

Figure 4.3. Effect of calcination temperature on physical properties; (1) and (2) indicate calcination conditions in Tables 4.5 and 4.6, respectively.

4.2.2. Effect of Calcination Time

The effect of calcination time was studied for 1.4%Pt-2.5%Co-2.5%Ce/Al_2O_3 at two temperatures. The physical properties measured are presented in Tables 4.7 and 4.8 and also plotted in Figure 4.4. The results indicate that the envelope density, ρ_p, the solid density, ρ_s, and pore volume, PV, are not changed by increasing the calcination time from 2 h to 3 h. At both calcination temperatures, however, the total surface area TSA is increased by 15-20% when the calcination period is longer; this effect is somewhat more significant at the higher calcination temperature of 500^{o}C.

Table 4.7. Effect of calcination time on physical properties (calcination temp: 450 ^{o}C)

Exp	Pt%	Ce%	Co%	Calcination Time (h)	ρ_p (g cm^{-3})	ρ_s (g cm^{-3})	TSA (m^2 g^{-1})	PV (cm^3 g^{-1})
4	1.4	2.5	2.5	2	0.80	1.68	152±4	0.13
5	1.4	2.5	2.5	3	0.81	1.70	178±3	0.12

Table 4.8. Effect of calcination time on physical properties (calcination temp: 500 ^{o}C)

Exp	Pt%	Ce%	Co%	Calcination Time (h)	ρ_p (g cm^{-3})	ρ_s (g cm^{-3})	TSA (m^2 g^{-1})	PV (cm^3 g^{-1})
7	1.4	2.5	2.5	2	0.78	1.66	130±6	0.15
8	1.4	2.5	2.5	3	0.74	1.68	160±5	0.15

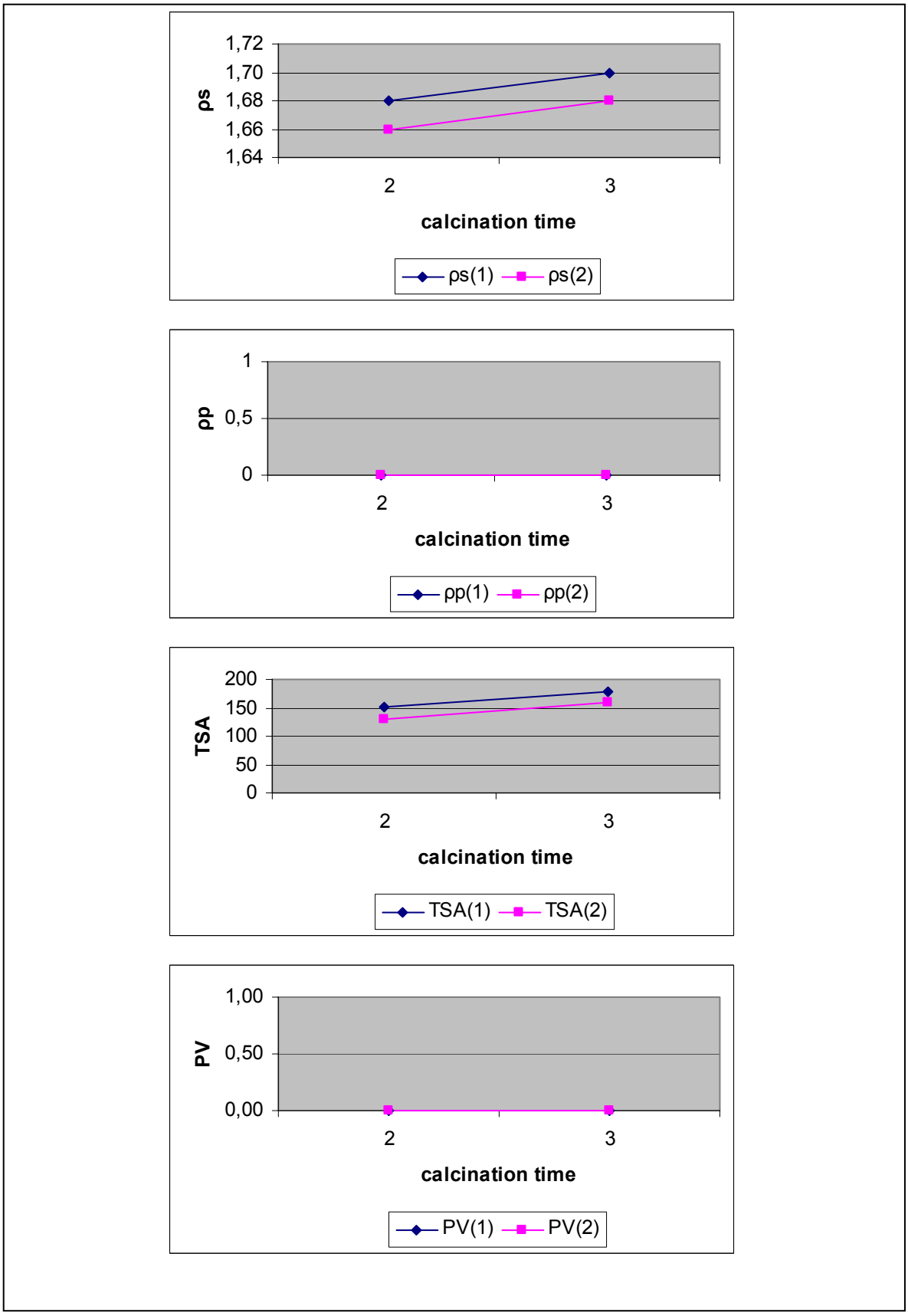

Figure 4.4. Effect of calcination time on physical properties of 1.4%Pt-2.5%Co-2.5%Ce/Al_2O_3; (1) and (2) indicate calcination conditions in Tables 4.7 and 4.8, respectively.

4.3. Effect of Design Parameters on the Activity of the Catalysts

İnce (2004) carried out an experimental design strategy for determining the optimum design parameters for selective CO oxidation over Pt-Co-Ce/Al_2O_3 catalysts in the absence of carbon dioxide and water vapor. The catalysts were prepared using incipient to wetness impregnation, and the effects of weight percentages of Pt, Co and Ce as well as the effects of calcination temperature and time were investigated as design parameters. The optimum design parameters were found as 1.4 weight per cent Pt, 1.25 weight per cent Co, 1.25 weight per cent Ce and calcination at 450 ºC for 2 hours. The effect of reaction conditions were also investigated, and it was found that 100 per cent CO conversion can be achieved at 90ºC at 24000 cm^3/g-h space velocity with a feed composition of 1 per cent oxygen, 1 per cent carbon monoxide, 60 per cent hydrogen and balance helium using 100 cm^3/min total flow rate. These results were taken as the starting point for the present study.

In this work, the effects of (i) the presence of CO_2 and H_2O in the feed, (ii) preparation variables such as calcination temperature and time, and (iii) metal content in terms of Pt, Co and Ce on the selective CO oxidation performance of Pt-Ce-Co/Al_2O_3 catalysts were studied. Ten catalyst samples were prepared using the incipient to wetness impregnation method, five of which were later selected for PROX reaction tests.

4.3.1. Effect of Calcination Conditions

The effects of preparation variables on PROX activity were first examined for two catalyst samples with 1.4 wt % Pt-1.25 wt % Co-1.25 wt % Ce/Al_2O_3 composition one of which was calcined at 450^{o}C for 2 hours and the other at 500^{o}C for 3 hours. The CO and O_2 conversions as well as the selectivities for CO oxidation are presented in Table 4.9 as a function of time-on-stream.

The experimental results show that catalyst samples calcined under milder conditions (450^{o}C, 2 h) exhibited incomplete CO conversion (98%) and complete O_2 conversion at short reaction times where the selectivity for CO oxidation was 49%. At longer reaction times, and up to 2 h on stream, both CO and O_2 conversions were 100%, which means that some hydrogen was also oxidized**.** CO and H_2 oxidation stoichiometries indicate that the

selectivity for each oxidation reaction was 50%, and that all the O_2 in excess of the 0.5 gmol required for oxidizing 1.0 gmol of CO was used up in H_2 oxidation.

Table 4.9. Effect of calcination conditions on the catalytic activity of 1.4%Pt-1.25%Co-1.25%Ce/Al_2O_3 (Feed Composition: 1% CO, 1% O_2, %10 H_2O, %25 CO_2, %60 H_2 and He as balance, F/W=24000 cm^3/g.h, T=110^oC)

Reaction Time (min)	30 minutes			60 minutes			90 minutes			120 minutes		
Calcination Conditions	[a]X_{CO} (%)	[b]X_{O2} (%)	[c]S_{CO} (%)	X_{CO} (%)	X_{O2} (%)	S_{CO} (%)	X_{CO} (%)	X_{O2} (%)	S_{CO} (%)	X_{CO} (%)	X_{O2} (%)	S_{CO} (%)
450^oC,2h	98	100	49	100	100	50	100	100	50	100	100	50
500^oC,3h	100	99	51	90	91	46	90	86	52	88	85	52

[a]CO conversion, [b]O_2 conversion, [c]CO oxidation selectivity

On the other hand, catalyst samples calcined under the relatively more severe conditions of 500^oC and 3 h, started out with 100% and 99% CO and O_2 conversion, respectively, at short contact times. However, the results reported in Table 4.9 show that both CO and O_2 conversions gradually declined down to 88% and 85%, respectively, at the end of the two hours on stream; the selectivity for CO oxidation was 52% at this time.

Since preferential CO oxidation in H_2-rich streams is primarily conducted for PEM fuel cell applications where the major requirement is to lower the CO content to levels below 10 ppm, a successful PROX catalyst must achieve a CO conversion of at least 99.99%. One may conclude that 1.4 % Pt-1.25 % Co-1.25 % Ce/Al_2O_3 calcined at 450^oC for 2 h meets this requirement for a realistic feed mixture containing 1%CO, 1%O_2, 10% H_2O, 25% CO_2 and 60% H_2 with inert He as balance. This is also in agreement with the findings of İnce (2004) for selective CO oxidation in H_2-rich feed in the absence of CO_2 and H_2O.

During calcinations, the catalyst should be heated under controlled conditions to a temperature at least as high as will be necessary to remove bond water or carbon dioxide, to allow changes in pore size distribution, active phase generation, surface conditioning and stabilization of mechanical properties. At calcination temperatures of 500°C or above, γ-alumina can react with the metal oxide to form a metal aluminate, $MeAl_2O_4$, which may be relatively unreactive. The active component that is most likely to form an aluminate in the catalysts used in the present work is cobalt.

4.3.2. Effect of Catalyst Composition

On the basis of the results reported in the section above, the 1.4 wt % Pt-1.25 wt % Co-1.25 w t% Ce/Al_2O_3 catalyst calcined at 450°C for 2 h was taken as the central point for optimum performance in selective CO oxidation in H_2-rich feed containing CO_2 and H_2O. In order to determine a suitable interval in which catalyst composition can be changed without losing the required activity level of 100% CO conversion, Pt, Co and Ce loadings were varied in a relatively narrow range. The results of reaction tests conducted at 110°C over catalysts with 4 different compositions are presented in Table 4.10.

Table 4.10. Effect of catalyst composition on catalytic activity
(Feed Composition: 1% CO, 1% O_2, %10 H_2O, %25 CO_2, %60 H_2
and He as balance, F/W=24000 $cm^3/g.h$, T=110°C)

	30 minutes			60 minutes			90 minutes			120 minutes		
Pt/Co/Ce (wt%)	[a]X_{CO} (%)	[b]X_{O2} (%)	[c]S_{CO} (%)	X_{CO} (%)	X_{O2} (%)	S_{CO} (%)	X_{CO} (%)	X_{O2} (%)	S_{CO} (%)	X_{CO} (%)	X_{O2} (%)	S_{CO} (%)
1.4/3.75/3.75	100	100	50	100	100	50	100	100	50	100	100	50
1.8/2.50/2.50	100	97	52	100	100	50	100	100	50	100	100	50
1.4/2.50/2.50	100	98	51	100	100	50	100	100	50	100	100	50
1.4/1.25/1.25	98	100	46	100	100	50	100	100	50	100	100	50

Since the 1.0 wt % Pt-2.50 wt % Co-2.50 wt % Ce/Al_2O_3 catalyst gave considerably lower CO conversions (ca. 40%) in the absence of CO_2 and H_2O in the feed (İnce, 2004), only the Pt contents above 1.0 wt % were tested keeping the Co and Ce loadings constant**:** 1.4 wt % Pt-2.50 wt % Co-2.50 wt % Ce/Al_2O_3 and 1.8 wt % Pt-2.50 wt % Co-2.50 wt % Ce/Al_2O_3. Table 4.10 shows the CO and O_2 conversions as well as the CO oxidation selectivities of the two catalysts as a function of time-on-stream. In both cases, CO conversions are 100% at all times while the O_2 conversion is slightly lower only at short reaction times, leading to 50% CO oxidation selectivity. It may be said that 100% CO conversion is maintained in catalysts containing 1.4–1.8 wt% Pt, and, since Pt is the most expensive component of the catalyst, the lower Pt loading is to be preferred.

In the second set of experiments, the Co and Ce loadings of the catalyst were varied between 1.25-3.75 wt% while keeping the Pt content constant at 1.4 wt%. The results of selective CO oxidation tests presented in Table 4.10 clearly indicate that all three catalysts, i.e. 1.4 wt % Pt-1.25 wt %Co-1.25wt%Ce/Al_2O_3, 1.4wt%Pt-2.50wt%Co-2.50wt%Ce/Al_2O_3 and 1.4wt%Pt-3.75wt%Co-3.75wt%Ce/Al_2O_3, give 100% conversion of CO and O_2, and the corresponding selectivity is 50%. Hydrogen is also oxidized in an amount equal to CO.

A selectivity level of 50% is acceptable in this work, since it indicates (a) that 100% CO conversion is achieved, which is crucial for PROX reactors, and (b) that only 1% H_2 is consumed from a feed containing 60% H_2. Therefore, the Al_2O_3-supported catalysts containing1.4-1.8 wt% Pt and 1.25-3.75 wt% Co and 1.25-3.75 wt% Ce are successful PROX catalysts. The ideal catalyst would be one giving 100% CO conversion and incomplete O_2 conversion, leading to selectivity levels between 50-100%; this would mean that little or no H_2 is oxidized during the PROX process.

5. CONCLUSIONS AND RECOMMENDATIONS

5.1. Conclusions

The purpose of this study was to examine the effects of design parameters on catalyst physical properties and on catalytic activity. Platinum content (wt% Pt), cobalt content (wt% Co), ceria content (wt% Ce), calcination temperature (T) and calcination time (t) were selected as catalyst design parameters. In the present work, Pt-Co-Ce/Al_2O_3 catalysts previously optimized in the absence of carbon dioxide and water vapor by İnce (2004) and later tested by Uysal (2005) in the presence of CO_2 and/or H_2O in the feed stream were further investigated. Ten different Pt-Co-Ce/Al_2O_3 catalysts were prepared using incipient to wetness impregnation method. The total surface areas, pore volumes, solid and envelope densities of the catalysts were measured in order to investigate the effect of design parameters on physical properties. A realistic gas mixture similar to the exit stream from a fuel processor and containing 25% CO_2 and 10% H_2O together with 1% O_2, 1% CO and 60% H_2 was balanced with inert gas and used in the PROX experiments. Activity tests were performed on five of the ten catalysts investigated. CO and O_2 conversions were measured at 30-minute intervals up to two hours. The following conclusions can be drawn from the studies conducted:

- Small increases in the Pt loading do not affect the pore volume, PV, or the envelope density, ρ_p, while a decrease is observed in the total surface area, TSA, and a small increase in the solid density, ρ_s.
- TSA values show a gradual increase with increasing Co-Ce content accompanied by a slight increase in PV for catalysts calcined at 450^{o}C and 2 h. These trends in TSA and PV are accentuated when the calcination temperature and time are increased to 500^{o}C and 3 h, respectively. The ρ_p and ρ_s values obtained for catalysts calcined under both conditions are almost unaffected by changes in the Co-Ce content
- Increasing the calcination temperature decreases TSA and a small increase is observed in PV. There is no significant effect of calcination temperature on ρ_p or ρ_s.
- The envelope density, ρ_p, the solid density, ρ_s, and pore volume, PV, are not changed by increasing the calcination time from 2 h to 3 h. At both calcination temperatures, however, the total surface area TSA is increased by 15-20% when the calcination

period is longer; this effect is somewhat more significant at the higher calcination temperature of 500^{o}C.

- It can be concluded that 1.4%Pt-1.25%Co-1.25%Ce/Al_2O_3 catalyst calcined at 450^{o}C for 2 h achieves a CO conversion of 100% in a realistic feed mixture containing 1%CO, 1%O_2, 10% H_2O, 25% CO_2 and 60% H_2 with inert He as balance. This is also in agreement with the results obtained in the absence of CO_2 and H_2O.
- Al_2O_3-supported catalysts with Pt loadings between 1.4-1.8 wt%, Co and Ce loadings between 1.25-3.75 wt% and calcined at 450^{o}C for 2 h all achieve 100% CO conversion with a selectivity of 50% and are successful PROX catalysts.
- Among the catalysts studied, 1.4%Pt-1.25%Co-1.25%Ce/Al_2O_3 calcined at 450^{o}C for 2 h is the optimum PROX catalyst since it yields 100% CO conversion both in the presence and in the absence of carbon dioxide and water vapor in the feed.

5.2. Recommendations

The recommendations for further work are as follows:

- Since platinum metal is costly, Pt loadings below 1.4 wt% must be tested to determine the lowest possible Pt content that gives 100% CO conversion. Other less expensive metals may also be evaluated as alternatives for platinum.
- The catalysts must be tested at lower contact times to obtain lower CO and O_2 conversions that will allow better comparison of different catalyst compositions and calcinations conditions.
- The optimum catalyst should be tested for its long-term stability by time-on-stream experiments conducted under realistic feed conditions in order to prepare the activity loss profiles required for industrial use.
- The changes in the physical properties of the alumina support under different calcinations conditions must be studied to see their contribution to overall catalyst structure.

Table A.1. Total surface areas of some Pt-Co-Ce/Al_2O_3 catalysts prepared

Metal Content					
$Pt(NH_3)_4(NO_3)_2$	**$Ce(NO_3)_3.6H_2O$**	**$Co(NO_3)_2.6H_2O$**	**Calci.temp (^oC)**	**Calci.Time (hr)**	**TSA ($m^2\ g^{-1}$)**
0.099	0.775	0.617	500	3	120+/-7
0.099	0.387	0.000	500	3	225+/-3
0.099	0.387	0.617	500	1	317+/-3
0.099	0.387	0.617	500	3	299+/-10
0.099	0.387	0.617	500	3	154+/-28
0.060	0.194	0.309	550	2	200+/-11
0.060	0.194	0.309	450	4	194+/-16
0.060	0.581	0.926	550	2	150+/-10
0.099	0.387	1.235	500	3	246+/-8
0.099	0.387	0.617	500	3	154+/-12
0.139	0.581	0.926	450	2	211+/-17
0.139	0.194	0.926	550	2	164+/-1
0.099	0.387	0.617	600	3	199+/-13
0.099	0.387	0.617	500	3	122+/-12
0.099	0.000	0.617	500	3	230+/-12
0.139	0.194	0.926	450	4	249+/-10
0.139	0.581	0.309	450	4	83+/-2
0.060	0.194	0.926	450	2	248+/-13
0.179	0.387	0.617	500	3	219+/-8
0.060	0.581	0.309	450	2	277+/-15
0.139	0.194	0.309	450	2	262+/-15
0.020	0.387	0.617	500	3	271+/-20
0.060	0.581	0.309	550	4	167+/-9
0.099	0.387	0.617	400	3	257+/-15
0.060	0.581	0.926	450	4	258+/-18
0.139	0.194	0.309	550	4	149+/-8
0.139	0.581	0.926	550	4	93+/-61
0.099	0.387	0.617	500	5	117+/-16
0.139	0.581	0.309	550	2	243+/-13
0.060	0.194	0.926	550	4	332+/-1

REFERENCES

Avgouropoulos, G. and T. Ioannides, 2003, "Selective CO Oxidation over $CuO-CeO_2$ Catalysts Prepared via the Urea–Nitrate Combustion Method", *Applied Catalysis A: General,* Vol. 244, pp. 155-167.

Avgouropoulos, G., T. Ioannides, C. H. Papadopoulou, J. Batista, S. Hocevar and H. K. Matralis, 2002, "A Comparative Study of $Pt/\gamma-Al_2O_3$, $Au/\alpha-Fe_2O_3$ and $CuO-CeO_2$ Catalysts for the Selective Oxidation of Carbon Monoxide in Excess Hydrogen", *Catalysis Today,* Vol. 75, pp. 157-167.

Bruijin F. A., D. C. Papageorgopoulos, E. F. Sitters, G. J. M. Janssen, 2002, "The influence of carbon dioxide on PEM fuel cell anodes", *Journal of Power Sources*, Vol. 110, pp. 117-124.

Campanati, M., G. Fornasari and A. Vaccari, 2003, "Fundamentals in the Preparation of Heterogeneous Catalysts", *Catalysis Today,* Vol. 77, pp. 299-314.

Choi, Y. and H. G. Stenger, 2004, "Kinetics, Simulation and Insights for CO Selective Oxidation in Fuel Cell Applications", *Journal of Power Sources*, Vol. 129, pp. 246-254.

Choudhary, T. V. and D. W. Goodman, 2002, "CO-free Fuel Processing for Fuel Cell Applications", *Catalysis Today*, Vol. 77, pp. 65-78.

Date, M. and M. Haruta, 2001, "Moisture Effect on CO Oxidation over Au/TiO_2 Catalyst", *Journal of Catalysis,* Vol. 201, pp. 221-224.

Deraz N-A. M., 2002, "Surface and catalytic properties of Co_3O_4-doped $CuO-Al_2O_3$ catalysts", *Colloids and Surfaces A: Physicochemical and Engineering Aspects ,* Vol. 207, pp. 197-206.

Epling, W. S., P. K. Cheekatamarla and A. M. Lane, 2003, "Reaction and Surface Characterization Studies of Titania-Supported Co, Pt and Co/Pt Catalysts for the Selective Oxidation of CO in H_2-Containing Streams", *Chemical Engineering Journal*, Vol. 93, pp. 61-68.

Farrauto, R. J., 2005, "Introduction to solid membrane fuel cells and reforming natural gas for production of hydrogen", *Applied Catalysis B: Enviromental,* Vol. 56 pp. 3-7.

Ghenciu, A. F., 2002, "Review of Fuel Processing Catalysts for Hydrogen Production in PEM Fuel Cell Systems", *Current Opinion in Solid State and Materials Science*, Vol. 6, pp. 389-399.

Goerke, O., P. Pfeifer and K. Schubert, 2004, "Water Gas Shift Reaction and Selective Oxidation of CO in Microreactors", *Applied Catalysis A: General,* Vol. 263 pp. 11-18.

Güldür, Ç. and F. Balıkçı, 2002, "Selective Carbon Monoxide Oxidation over Ag-Based Composite Oxides", *International Journal of Hydrogen Energy*, Vol. 27, pp. 219-224.

Han, Y. F., M. J. Kahlich, M. Kinne and R. J. Behm, 2004, "CO Removal from Realistic Methanol Reformate via Preferential Oxidation-Performance of a Rh/MgO Catalyst and Comparison to Ru/γ-Al_2O_3, and Pt/γ-Al_2O_3", *Applied Catalysis B: Environmental*, Vol. 50, pp. 209-218.

Haruta, M., 1997, "Size and support dependency in the catalysis of gold ", Catalysis Today, Vol. 36, pp. 153-166.

Hasegawa, Y., A. Ueda, K. Kusakabe and S. Morooka, 2002, "Oxidation of CO in Hydrogen-Rich Gas Using a Novel Membrane Combined with a Microporous SiO_2 Layer and a Metal-Loaded γ-Al_2O_3 Layer", *Applied Catalysis A: General*, Vol. 225, pp. 109-115.

Igarashi, H., H. Uchida, M. Suzuki, Y. Sasaki and M. Watanabe, 1997, "Removal of Carbon Monoxide from Hydrogen-Rich Fuels by Selective Oxidation over Platinum Catalyst Supported on Zeolite", *Applied Catalysis A: General*, Vol. 159, pp. 159-169.

İnce, T., 2004, *Low Temperature Oxidation of Carbon Monoxide over Pt-CeO_2-Co_3O_4/Al_2O_3 Catalyst in H_2-Rich Streams*, M. S. Thesis, Boğaziçi University.

Jansson, J., 2000, "Low temperature CO oxidation over Co_3O_4/Al_2O_3", *Journal of Catalysis*, Vol. 194, pp. 55-60.

Kahlich, M., J. H. A. Gasteiger and R. J. Behm, 1997, "Kinetics of the Selective CO Oxidation in H_2-Rich Gas on Pt/Al_2O_3", *Journal of Catalysis*, Vol. 171, pp. 93-105.

Kim, D. H. and M. S. Lim, 2002, "Kinetics of Selective CO Oxidation in Hydrogen-Rich Mixtures on Pt/Alumina Catalysts", *Applied Catalysis A: General*, Vol.224, pp. 27-38.

Liu, Y., Q. Fu and M. F. Stephanopoulos, 2004, "Preferential Oxidation of CO in H_2 over CuO-CeO_2 catalysts", *Catalysis Today*, Vol. 93-95, pp. 241-246.

Luengnaruemitchai, A., D. T. K. Thoa, S. Osuwan and Erdogan Gulari, 2005, "A Comparative Study of Au/MnO_x and Au/FeO_x Catalysts for the Catalytic Oxidation of CO in Hydrogen Rich Stream", *International Journal of Hydrogen Energy*, in press.

Luengnaruemitchai, A., S. Osuwan and E. Gulari, 2004, "Selective Catalytic Oxidation of CO in the Presence of H_2 over Gold Catalyst", Inter*national Journal of Hydrogen Energy*, Vol. 29, pp. 429-435.

Luengnaruemitchai, A., S. Osuwan and E. Gulari, 2003, "Comperative Studies of Low-Temperature Water Gas Shift Reaction over Pt/CeO_2, Au/CeO_2, and Au/Fe_2O_3 Catalysts", *Catalysis Communications*, Vol. 4, pp. 215-221.

Maier, W. F. and J. Saalfrank, 2004, “Discovery, Combinatorial Chemistry and a New Selective CO Oxidation Catalyst”, *Chemical Engineering Science,* Vol. 59, pp. 4673-4678.

Maki-Arvela P., J. Hajek, T. Salmi, D. Yu. Murzin, 2005, “Chemoselective hydrogenation of carbonyl compounds over heterogeneous catalysts”, *Applied Catalysis A:General*, Vol. 292, pp. 1- 49.

Manasilp, A. and E. Gulari, 2002, “Selective CO Oxidation over Pt/alumina Catalysts for Fuel Cell Applications”, *Applied Catalysis B: Environmental*, Vol. 37, pp. 17-25.

Marino, F., C. Descorme and D. Duprez, 2004, “Noble Metal Catalysts for the Preferential Oxidation of Carbon Monoxide in the Presence of Hydrogen (PROX)”, *Applied Catalysis B: Environmental*, Vol. 54, pp. 59-66.

Marino, F., C. Descorme and D. Duprez, 2005, “Supported Base Metal Catalysts for the Preferential Oxidation of Carbon Monoxide in the Presence of Excess Hydrogen (PROX)”, *Applied Catalysis B: Environmental*, Vol. 58, pp. 175–183.

Martinez-Arias, A., A. B. Hungria, G. Munuera, D. Gamarra, 2006, “Preferential oxidation of CO in rich H_2 over CuO/CeO_2: Details of selectivity and deactivation under the reactant stream”, *Applied Catalysis B: Enviromental,* Vol. 65, pp. 207-216.

Oran, U. and D. Üner, 2004, “Mechanisms of CO Oxidation Reaction and Effect of Chlorine Ions on the CO Oxidation Reaction over Pt/CeO_2 and $Pt/CeO_2/\gamma\text{-}Al_2O_3$ Catalysts”, *Applied Catalysis B: Environmental,* Vol. 54, pp. 183-191.

Özkara, Ş. and A. E. Aksoylu, 2003, "Selective Low Temperature Carbon Monoxide Oxidation in H_2-Rich Gas Streams over Activated Carbon Supported Catalysts", *Applied Catalysis A: General*, Vol. 251, pp. 75-83.

Panzera, G., V. Modafferi, S. Candamanoa, A. Donato, F. Frusteri, P.L. Antonucci, 2004, "CO Selective Oxidation on Ceria-Supported Au Catalysts for Fuel Cell Application" *Journal of Power Sources*, Vol. 135, pp. 177–183.

Park, J. W., J. H. Jeong, W. L. Yoon and Y. W. Rhee, 2004, "Selective Oxidation Of Carbon Monoxide in Hydrogen-Rich Stream over Cu-Ce/γ-Al_2O_3 Catalysts Promoted With Cobalt in a Fuel Processor for Proton Exchange Membrane Fuel Cells", *Journal of Power Sources*, Vol. 132, pp. 18-28.

Park, J. W., J. H. Jeong, W. L. Yoon, C. S. Kim, D. K. Lee, Y. K. Park and Y. W. Rhee, 2005, "Selective Oxidation of CO in Hydrogen-Rich Stream over Cu-Ce Catalyst Promoted with Transition Metals", *International Journal of Hydrogen Energy,* Vol. 30, pp. 209-220.

Peppley, B. A., J. C. Amphlett, L. M. Kearns, R. F. Mann, 1999, " Methanol Steam Reforming on Cu/ZnO/Al_2O_3. Part I: A Comprehensive Kinetic Model", *Applied Catalysis A: General*, Vol. 179, pp. 31-49.

Perego, C. and P. Villa, 1997, "Catalyst Preparation Methods", *Catalysis Today,* Vol. 34, pp. 281-305.

Pozdnyakova, O., D. Teschner, A. Wootsch, J. Kröhnert, B. Steinhauer, H. Sauer, L. Toth, F. C. Jentoft, A. Knop- Gericke, Z. Paal, R. Schlögl, 2006, "Preferential CO Oxidation in hydrogen (PROX) on ceria-supported catalysts, part I: Oxidation state and surface species on Pt/CeO_2 under reaction conditions", *Journal of Catalysis,* Vol. 237, pp. 1-16.

Rajasree, R., J. H. B. J. Hoebink and J. C. Schouten, 2004, "Transient Kinetics of Carbon Monoxide Oxidation by Oxygen over Supported Palladium/Ceria/Zirconia Three-Way Catalysts in the Absence and Presence of Water and Carbon Dioxide", *Journal of Catalysis*, Vol. 223, pp. 36-43.

Ralph, T. R. and G. A. Hards, 1998, “Powering the Cars and Homes of Tomorrow”, *Chemistry and Industry,* Vol. 9, pp. 337-342.

Rodriguez-Reinoso, F., 1998, “The Role of Carbon Materials in Heterogeneous Catalysis”, *Carbon*, Vol. 36, pp. 159-175.

Rostrup-Nielsen, J. R., 1984, "Catalytic Steam Reforming" *Catalysis Science and Technology*; Andersen, J.R., Boudart, M., Eds.; Springer-Verlag, New York, Vol. 5, pp 1-117.

Salmi M., N. Tkachenko, V. Vehmanen, R. J. Lamminmaki, S. Karvinen, H. Lemmetyinen, 2004, “The effect of calcination on photocatalytic activity of TiO_2 particles: femtosecond study”, *Journal of Photochemistry and Photobiology A: Chemistry,* Vol. 163, pp. 395-401.

Sandhu, S. S., Y.A. Saif and J.P. Fellner, 2005, “A Reformer Performance Model for Fuel Cell Applications”, *Journal of Power Sources,* Vol. 140, pp. 88-102.

Satterfield, C. N., 1991, Heterogenous Catalysis in Industrial Practice, McGraw-Hill, USA.

Schubert, M. M., A. Venugopal, M. J. Kahlich, V. Plzak and R. J. Behm, 2004, “Influence Of H_2O and CO_2 on the Selective CO Oxidation in H_2-Rich Gases over Au/α-Fe_2O_3”, *Journal of Catalysis*, Vol. 222, pp. 32-40.

Sirijaruphan, A., J. G. Goodwin and R. W. Rice, 2004, “Effect of Fe Promotion on the Surface Reaction Parameters of Pt/γ-Al_2O_3 for the Selective Oxidation of CO”, *Journal of Catalysis,* Vol. 224, pp. 304-313.

Sirijaruphan, A., J. G. Goodwin and R. W. Rice, 2004, “Effect of Temperature and Pressure on the Surface Kinetic Parameters of Pt/γ-Al_2O_3 during Selective CO Oxidation”, *Journal of Catalysis,* Vol. 227, pp. 547-551.

Smith, J. M., Chemical Engineering Kinetics, McGraw-Hill, Singapore, 1981.

Son, I. H., 2006, "Study of Ce-Pt/γ-Al_2O_3 for the selective oxidation of CO in H_2 for application to PEFCs: Effect of gases", *Journal of Power Sources*, Vol. 124, pp. 415-419.

Son, I. H. and A. M. Lane, 2001, "Promotion of Pt/γ-Al_2O_3 by Ce for Preferential Oxidation of CO in H_2", *Catalysis Letters*, Vol. 76, pp. 151-154.

Son, I. H., A. M. Lane and D. T. Johnson, 2003, "The Study of the Deactivation of Water Pretreated Pt/γ-Al_2O_3 for Low Temperature Selective CO Oxidation in Hydrogen", *Journal of Power Sources*, Vol. 124, pp. 415-419.

Song, C., 2002, "Fuel Processing for Low-Temperature and High-Temperature Fuel Cells: Challenges, and Opportunities for Sustainable Development in the 21st Century", *Catalysis Today,* Vol. 77, pp. 17-49.

Syntnikov, P. V., V. A. Sobyanin, V.D. Belyaev, P. G. Tsyrulnikov, N. B. Shitova and D. A. Shylyapin, 2003, "Selective Oxidation of Carbon Monoxide in Excess Hydrogen over Pt-, Ru- and Pd-supported Catalysts", *Applied Catalysis A: General,* Vol. 239, pp. 149-156.

Şimşek, E., 2005, Preferential CO Oxidation Over Activated Carbon Supported Noblemetal Reducible Oxide Catalysts, M. S. Thesis, Boğaziçi University, Istanbul.

Tanaka, H., S. Ito, S. Kameoka, K. Tomishige and K. Kunimori, 2003, "Catalytic Performance of K-promoted Rh/USY Catalysts in Preferential Oxidation of CO in Rich Hydrogen", *Applied Catalysis A: General,* Vol. 250, pp. 255-263.

Teschner D., A. Wootsch, T. Röder, K. Matusek, Z. Paal, 2001, "Ceria as a new support of noble metal catalysis for hydrocarbon reactions: chemisorption and catalytic studies", *Solid State Ionicss,* Vol. 141-142, pp. 709-713.

Thormahlen, P., M. Skoglundh, E. Fridell and B. Andersson, 1999, "Low-Temperature CO Oxidation over Platinum and Cobalt Oxide Catalysts", *Journal of Catalysis,* Vol. 188, pp. 300-310.

Törncrona, A., M. Skoglundh, P. Thormählen, E. Fridell and E. Jobson, 1997, "Low Temperature Catalytic Activity of Cobalt Oxide and Ceria Promoted Pt and Pd: Influence of Pretreatment and Gas Composition", *Applied Catalysis B: Environmental,* Vol. 14, pp. 131-145.

Trimm, D. L. and Z. İ. Önsan, 2001, "Onboard Fuel Conversion for Hydrogen Fuel Cell Driven Vehicles", *Catalysis Reviews-Science and Engineering*, Vol. 43 (1&2), pp. 31-84.

Uysal, G., 2005, Effect Of Carbondioxide and Water vapor on selective carbon monoxide oxidation over Pt- based catalysts, M. S. Thesis, Boğaziçi University, Istanbul.

Wang, D., Z. Hao, D. Cheng, X. Shi and C. Hu, 2003, "Influence of Pretreatment Conditions on Low-Temperature CO Oxidation over $Au/MO_x/Al_2O_3$ Catalysts", *Journal of Molecular Catalysis A: Chemical,* Vol. 200, pp. 229-238.

Wang, J. H., J. I. Zhu, J. C. Zhang, L. F. Song, J.Y. Hu, S. L. Ong, W. J. Ng, 2006, "Selective oxidation of CO in hydrogen-rich mixtures and kinetics investigation on platinum- gold supported on zinc oxide catalysts", *Journal of Power Sources,* Vol. 155, pp. 440-446.

Zhdanov, V. P. and B. Kasemo, 2003, "The Effect of Oxide Formation on Bistability in CO Oxidation on Pt", *Journal of Catalysis,* Vol. 220, pp. 478-485.

Zdrazil M., 2003, "MgO-supported Mo, Co-Mo and Ni-Mo sulfide hydrotreating catalysts", *Catalysis Today,* Vol. 86, pp. 151-171.