EFFECTS OF PROMOTERS ON SELECTIVE CO OXIDATION IN HYDROGEN-RICH STREAMS OVER Pt/Al_2O_3 CATALYSTS

by

Kamuran Erdem Uğuz

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APPROVED BY:

Assoc. Prof. Ramazan Yıldırım .....…….....
(Thesis Supervisor)

Prof. Ayşe Nilgün Akın .....…….....

Prof. Ahmet Erhan Aksoylu .....…….....

DATE OF APPROVAL: ……

to my family

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ABSTRACT

EFFECTS OF PROMOTERS ON SELECTIVE CO OXIDATION IN HYDROGEN-RICH STREAMS OVER Pt/Al_2O_3 CATALYSTS

The objective of this study was to investigate the second promoter effects on Pt-X-Ce/Al_2O_3 and Pt-Co-Y/Al_2O_3 catalyst for selective CO oxidation. Seven promoters were tested in two groups; Ni, K and Co as one group (as X) were coupled with ceria, while Ce, Mg, Mn, Fe and Zr as second goup (as Y) were coupled with Co.

All catalyst prepared by wetness impregnation method with 1.25wt.% promoter and 1.4 or 0.7%wt.% platinum. Three different gas streams are used for experiments; one without CO_2 and H_2O, one with 25% CO_2 but no H_2O and with both 25% CO_2 and 10% H_2O. All the feed streams contained 1% CO, 1% O_2, 60% H_2, and He as balance.

Co is found to be the best second promoter for Pt-X-Ce/Al_2O_3 catalyst at 80 and 110 ˚C for 1.4 wt.% Pt in the absence of CO_2 and H_2O. For Pt-Co-Y/Al_2O_3, Fe and Mn addition decreased the CO conversion, where the others has no significant effect at 80 ˚C. At 110 ˚C second promoter has increased the conversion rate to 100% from 97-98%.

Then the tests over Pt-Co-Y/Al_2O_3 catalysts were also performed using 0.7 wt.% Pt. at 110 ˚C for all reaction streams. At 110 ˚C, all catalysts exhibit promosing activities, except Fe and Zr containing ones. Among these tests Pt-Co-Mg/Al_2O_3 was found to be slightly better than others.

The increases of temperature to 130 ˚C did not increase the conversion, on the contrary it decreased CO conversion in all catalysts. However, the increase of Pt content to1 wt.% which is tested in Pt-Co-Mg/Al_2O_3 at 110 ˚C resulted 100% CO conversion for 2 hours period without any deactivation in the presence of CO_2 and H_2O in the feed.

ÖZET

HİDROJENCE ZENGİN GAZ KARIŞIMLARDA CO OKSİDASYONU KATALİZÖRÜ Pt/Al_2O_3 ÜZERİNDE GELİŞTİRİCİLERİNİN ETKİLERİ

Bu çalışmanın amacı CO oksidasyonu için ikinci geliştiricilerin Pt-X-Ce/Al_2O_3 ve Pt-Co-Y/Al_2O_3 üzerindeki etkileri incelendi. Yedi farklı geliştirici iki farklı grupta kullanıldı. İlk grubu oluşturan Ni, K, Co Ce'nin yanında ikinci bir geliştirici olarak kullanılırken (X), Ce, Mg, Mn, Fe, Zr ikinci grup olarak Co varlığında kullanıldı(Y).

Katalizörler her birinden 1.25 ağırlık yüzdesi geliştirici ve 1.4 veya 0.7 ağırlık yüzdesi platin içerecek şekilde emdirme yöntemi ile hazırlandı. Deneylerde üç farklı gaz karışımı kullanıldı; CO_2 ve H_2O içermeyen, %25 CO_2 içeren ve hem %25 CO_2 hemde %10 H_2O içeren. Bütün akımlarda %1 CO, %1 O_2, %60 H_2 ve balans olarak He kullanıldı.

CO_2 ve H_2O olmayan gaz karışımında 80 ve 110 ˚C'de yapılan ve 1.4 Pt ağırlık yüzdesinde kullanılan Pt-X-Ce/Al_2O_3 katalizörlerinde için en iyi ikinci geliştiricinin Co olduğu anlaşılmıştır. Fe ve Mn eklenmesi CO dönüşümünü azaltırken, diğerlerinin 80 ˚C'de belirgin bir etkisi olmamıştır. 110 ˚C'de ise bütün geliştiricilerin CO dönüşümünü %97-98'den %100'e arttırdığı gözlenmiştir.

Pt-Co-Y/Al_2O_3 katalizörleri için testler Pt yüzdesi 0.7'ye düşürülerek de yapılmış 110 ˚C'de, CO_2 ve H_2O varlığında, Zr ve Fe içeren dışındakiler %100'e yakın sonuçlar vermişlerdir. Bu testlerde, Pt-Co-Mg/Al_2O_3 en iyi sonucu vermiştir.

Sıcaklığın 130 ˚C'ye çıkartılması dönüşümü artırmadığı, hatta bütün katalizörlerde biraz düşürdüğü gözlenmiştir. Pt içeriğinin ağırlıkça %1'e çıkartılması Pt-Co-Mg/Al_2O_3 katalizörünün 110 ˚C'de CO_2 ve H_2O varlığında iki saat boyunca %100 CO dönüşümü verdiği saptanmıştır.

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LIST OF SYMBOLS/ABBREVIATIONS

ΔH°	Enthalpy of the reaction at the standart conditions
AFC	Alkaline Fuel Cell
ATR	Autothermal Reforming
DRIFTS	Diffuse Reflectance Infrared Fourier Transform Spectroscopy
MCFC	Molten Carbonate Fuel Cell
NMRO	Noble Metal Reducible Oxide
OSC	Oxygen Storage Capacity
PEMFC	Proton Exchange Membrane Fuel Cell
PNGV	Partnership for A New Generation of Vehicles
PEM	Polymer Electrolyte Membrane
PROX	Preferential Oxidation
SDC	Samaria-Doped Ceria
SEM	Scaning Electron Microscopy
SPFC	Solid Polymer Fuel Cell
SOFC	Solid Oxide Fuel Cell
TEM	Transmission Electron Microscopy
TPR	Temperature Programmed Reduction
XRD	X-Ray Diffraction

1. INTRODUCTION

Today, more than 85% of total energy needed is provided from the fossil fuels such as natural gas, petroleum and coal (Energy, 2007). Due to limited amount of the fossil fuels, the low efficiency of the fossil fuel applications and the concerns for the environment, the search for new energy sources and new technologies has become an important task. Fuel cells are among the promising pollution-free energy conversion technologies of the future and hence they have recently attracted many researchers.

A fuel cell is a device that converts chemical energy to electricity without polluting the environment. H_2 is used as a fuel in this system with O_2, producing electricity and water. A fuel cell consists of an electrolyte (a conductor of charged particles) between an anode (negatively charged electrode) and a cathode (a positively charged electrode).

The main problem for fuel cell application to over come, is the need for CO free H_2 as the fuel, because the anode catalyst, which is generally Pt, loses its efficiency drastically at even 10 ppm CO in the inlet fuel. For Pt-Ru alloy catalysts that concentration may reach to 100 ppm (Ito *et al.,*2004).

One of the hydrogen production is autothermal reforming of hydrocarbon, followed by water gas shift reaction to lower CO concentration, which also produce additional H_2.

The typical composition of gas stream after WGS reactor is 45-75 volume per cent H_2, 15-25 volume per cent CO_2, 0.5-2 volume per cent CO, a few per cent H_2O and N_2, where even 0.5 volume per cent CO is still poisoning for Pt (Petterson *et al*., 2001). There are several methods used to reduce the amount of CO under 10 ppm such as palladium-based membrane purification, catalytic methanation, and selective catalytic CO oxidation. Among these methods, selective catalytic carbon monoxide oxidation is the most promising one, due to its simplicity and low cost (Kahlich *et al*. 1997).

The catalyst used in selective CO oxidation should be effective between 80 ˚C and 200 ˚C which are the temperatures for WGS and PEM fuel cell. Another important aspect for a good catalyst is the high selectivity toward CO oxidation to prevent undesired H_2

oxidation. Also the catalyst should not lose its efficiency in the presence of CO_2 and H_2O since these two are also part of feed gas.

To date, the proposed catalysts generally contain the platinum group metals (Pt, Rh, Ru) on alumina and zeolite supports, or gold-based catalysts. Although, these metals have good activity for CO oxidation, they are rare, expensive, and lose their activity at high temperatures (Trimm and Önsan, 2001; Park et al., 2004).

To lower the cost, overcome the activity loss in CO_2 presence, and increase the stability, the oxides of metals such as ceria, cobalt, iron, nickel, potassium are used as the promoter. The idea behind using promoters is to combine Pt's activeness and promoters properties such as oxygen storage capacity, and durability.

Besides the metals, promoters and supports, the preparation process is also very important in the catalytic activity. The precipitation, impregnation, ion exchange and sol-gel methods can be used for catalyst preparation. Among these methods, the impregnation of porous support materials with solutions of active components is the best-known one, especially for preparing supported noble metal catalysts (İnce, 2004)

The impregnation method is simply impregnating of porous support materials with a solution of active components. If a second noble metal with or without a promoter is going to be employed, impregnation can be done as co-impregnation or sequential impregnation. The impregnated catalysts have many advantages; their pore structure and specific surface area are largely determined by the supporting material, controlled metal loading, and reproducibility.

The objective of this thesis is to investigate different promoters for Pt/Al_2O_3 catalyst for selective CO oxidation. Seven different promoters are used for experiments; Ceria, Cobalt, Nickel, Potassium, Magnesium, Manganese, Iron. Mostly these promoters used as couples, only $Pt\text{-}Co/Al_2O_3$ and $Pt\text{-}Ce/Al_2O_3$ were prepared for comparison. All catalysts were prepared by impregnation method. A microreactor flow system is used for the catalytic activity measurements.

The proceeding chapter, chapter 2, contains a literature survey on fuel cells, catalytic selective CO oxidation, and further survey on platinum, promoters and alumina as a support. Chapter 2 also contains information about impregnation method. Chapter 3 presents the experimental work performed. The results and the discussion are given in the 4^{th} chapter while chapter 5 contains the conclusions drawn from the present study and recommendations for future work.

1. LITERATURE SURVEY

2.1. Fuel Cells

A fuel cell is an energy conversion device that is two or three times more efficient than an internal combustion engine in converting fuel to power. Internal combustion engine efficiency is limited by Carnot Cycle. The fuel cell, on the other hand, provides highly efficient conversion of chemical energy into electrical energy without any pollutants. There are several possible applications for fuel cells ranging from portable power and transportation through to stationary power for buildings (Chang, 2004).

A variety of fuel cells under development for the different of applications are:

- Solid polymer fuel cells (SPFC), or more common name proton-exchange membrane (PEM) fuel cells operating at 80 ˚C,
- Alkaline fuel cells (AFC) operate at ~ 100 ˚C,
- Phosphoric acid fuel cells (PAFC) operate at ~ 200 ˚C,
- Molten carbonate fuel cells (MCFC) ,operation temperature ~ 650 ˚C,
- Solid oxide fuel cells (SOFC) for high temperature operation, 800- 1100 ˚C.

All fuel cells have the same basic operating principle. An input fuel (usually hydrogen) is catalytically reacted (electrons removed from the fuel elements) in the fuel cell to create an electric current. The input fuel passes over the anode (negatively charged electrode) where it catalytically splits into electrons and ions, and oxygen passes over the cathode (positively charged electrode). The electrons go through an external circuit to serve an electric load while the ions move through the electrolyte toward the oppositely charged electrode. At the cathode, the ions are combined to create by-products, primarily water. Depending on the input fuel and electrolyte, different chemical reactions will occur (Song, 2002).

According to Ghenciu (2002), PEM fuel cells have various advantages like low operating temperature, low weight, low cost and low volume, long stack life, fast start up times and suitability to discontinuous operation for the transportation applications.

In the center of the PEM fuel cell there is a polymer electrolyte membrane. The negative ions are rigidly held in the structure on the membrane, where the positive ions contained within the membrane are mobile and thus free to carry positive charge though the membrane. In PEM, hydrogen ions are the positive ones, they move only one way from anode to cathode. With this movement current will be produced (Chang, 2004).

The ideal fuel for PEM fuel cells is pure hydrogen. The hydrogen is ionized to protons and electrons at the anode of the cell. Protons migrate through a membrane to the cathode where reaction takes place to produce water (Figure 2.1). Overall, fuel is oxidized electrochemically and each cell produces approximately 0.6-0.7 eV electricity (Trimm and Önsan, 2001). The reactions at the anode and the cathode, respectively, are:

$H_2 \Leftrightarrow 2H^+ + 2e^-$ (anode reaction)	(2.1)
$O_2 + 4e^- + 4H^+ \Leftrightarrow 2H_2O$ (cathode reaction)	(2.2)

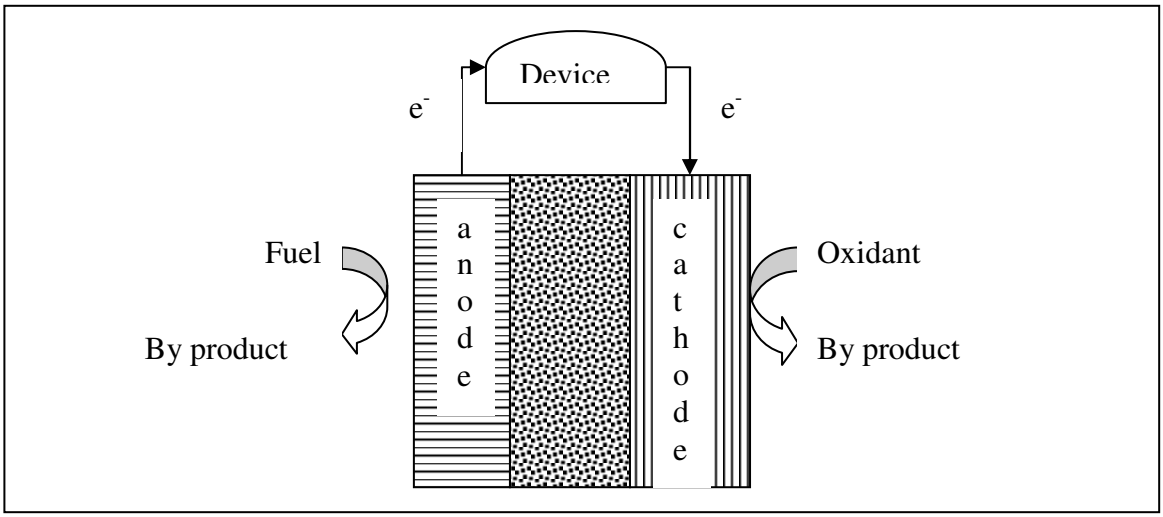

Figure 2.1. Schematic diagram of PEM fuel cell

The problem that needs to be overcome is producing pure H_2 (CO-free) on-board for transportation vehicles applications and on site of small applications like houses and offices because the hydrogen is difficult to store and distribute. Therefore, the hydrogen gas should be generated on site and on demand, by reforming available fuels such as natural gas, gasoline, propane and methanol, which is generally achieved in three steps as summarized in Figure 2.2 (Son and Lane, 2001):

- Hydrogen production by autothermal reforming of the hydrocarbon. Several routes for reforming fuels to produce syngas: steam reforming (Reaction 2.3), catalytic partial oxidation (Reaction 2.4), and autothermal reforming (ATR). ATR combines oxidation and steam reforming in one single unit, with the exothermic partial oxidation driving the endothermic steam reforming.

$C_nH_m + nH_2O \rightarrow nCO + (n+m/2)H_2 \quad \Delta H^0_{298} > 0$	(2.3)
$C_nH_m + n/2O_2 \rightarrow nCO + m/2H_2 \quad \Delta H^0_{298} < 0$	(2.4)

- The water gas shift reaction which eliminates most of the carbon monoxide producing additional hydrogen.

$CO + H_2O \Leftrightarrow CO_2 + H_2$	(2.5)

- After WGS CO concentration decreases to 0.5-1 per cent, however, the CO content has to be further reduced to 10 ppm with CO oxidation. Several Approaches are currently applied: CO preferential oxidation, catalytic methanation and Pd-membrane separation (Trimm and Önsan, 2001; Ghenciu, 2002).

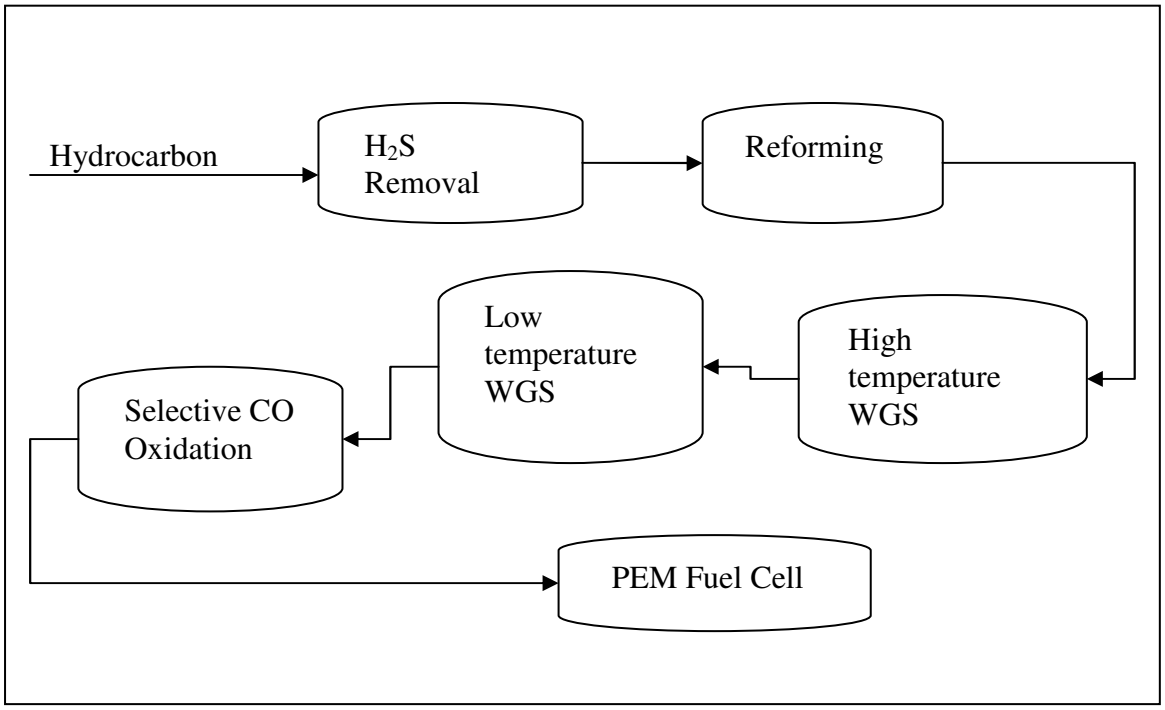

Figure 2.2. Schematic diagram of fuel processing sequence for fuel cell

2.2. Selective CO Oxidation in H_2-Rich Streams

Among the various available methods for removing CO from H_2-rich streams, the selective catalytic oxidation of CO with molecular oxygen is the most straightforward, simple and cost effective (Avgouropoulos *et al*., 2002). For the academic community, this reaction is of interest due to richness of its spatio-temporal kinetics exhibiting bistability, oscillations, and the pattern formation (Carlsson *et al.,* 2005).

As mentioned before, the carbon monoxide concentration at the outlet stream of a reformer or water-gas shift unit is approximately one mole per cent that is set by the thermodynamic equilibrium of water-gas shift reaction. Since the tolerance limit of PEM to CO concentration is 10 ppm, the efficiency of catalytic selective CO oxidation should be over than 99.9 per cent.

There are three possible ways to oxidize CO in H_2 rich stream. The first possibility is to find a catalyst that absorbs only CO not H_2, so the reaction will be 100 per cent selective to CO. Another way is to find reaction temperature that only CO oxidation reaction can

take place. The last possibility is to find a catalyst that both oxidize CO and H_2, but kinetic parameters lead to preferential oxidation of CO at the cost of only small amounts of H_2 oxidation (Trimm and Önsan, 2001).

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

- High CO oxidation activity,
- High selectivity with respect to the undesired H_2 oxidation. The ideal case is to be inactive for oxidation of H_2,
- Activity between the temperature region defined by the temperature level of the low-temperature shift reactor unit (~200 ˚C) and that of the H_2-PEM fuel cell (~80 ˚C),
- Tolerance towards the presence of CO_2 and H_2O in the feed.

In the reaction stage, the oxygen-carbon monoxide ratio and reaction temperature are very important for effective CO oxidation. The amount of oxygen to be injected for selective CO oxidation is critical, because excess O_2 usage can lead to hydrogen oxidation. Therefore, a catalyst that uses only stoichiometric amounts of oxygen is favorable for selective CO oxidation. Also the reaction temperature is important for selectivity, because high reaction temperatures promote H_2 oxidation (Kahlich *et al*. 1997).

Many researchers investigate various catalyst systems with different support, noble metal, promoter and preparation methods. Among several supports and active metals, platinum as the active metal and the alumina as support are used the most extensively in the researches for selective CO oxidation reaction.

In recent years, there has been a considerable interest in the use of catalyst, which contains both noble metal and metal oxides. Nobel Metal Reducible Oxide (NMRO) catalyst each are having two active sites seem to provide a promising choice for effective carbon monoxide oxidation. NMRO catalysts are produced by using one or two metals like Pt, Pd, Au, Ag, Ru with metal oxide like SnO_2, MnO_x, SnO_2, Fe_2O_3, CeO_x and distributing them over a support such as Al_2O_3 or SiO_2. Interaction across the metal-oxide interface

have been suggested to be important, as carbon monoxide absorbed on the metal reacts with oxygen associated with the oxide (Kang *et al*., 2003).

The low temperature noble metal reducible oxide catalyst must exhibit strong metal support interaction, because neither the noble metal nor the reducible oxide alone can catalyze carbon monoxide oxidation at temperatures <100 ˚C. One or more of three types of synergetic interaction between the two catalysts components are said to be responsible for the high efficiency observed at low temperatures (Trimm and Önsan, 2001):

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

2.2.1. Platinum

Using Pt-based catalyst for purifying H_2 is not a new; Engelhard took the first patent for selectively oxidizing CO in hydrogen by Pt/alumina catalyst in 1963. Researches are generally focused on alumina-supported noble metals (Pt, Ru, Rh, and Pd) and zeolite supported platinum (Snytnikov *et al.,* 2003).

Zhdanov and Kasemo (2003) stated that CO oxidation on the Pt-group metals was generally accepted to occur via the following mechanisms:

- Reversible CO adsorption:

$CO_{gas} \Leftrightarrow CO_{ads}$	(2.6)

- Dissociative O_2 adsorption:

$(O_2)_{gas} \rightarrow 2O_{ads}$	(2.7)

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

$CO_{ads} + O_{ads} \rightarrow (CO_2)_{gas}$	(2.8)

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

$CO_{gas} + O_{ads} \rightarrow (CO_2)_{gas}$	(2.9)

According to Carlsson *et al*. (2004); CO is adsorbed associatively and starts to be desorbed rapidly above about 350 K, while O_2 is adsorbed dissociatively above about 100 K and desorbed associatively above 720 K. CO diffuses rapidly over the surface and reacts with O to yield CO_2, which is immediately desorbed into the gas phase (CO_2 is desorbed at 95 K).

The work done by Mariño *et al.* (2004) shows that, among the noble metals they studied, the platinum was shown to be active in the oxidation of carbon monoxide in the presence of large excess in hydrogen. However, with increasing reaction temperature, the undesired hydrogen oxidation reaction also proceeds in competition with the oxidation of CO. Furthermore, since the oxygen activation takes place easily on these metals, the hydrogen oxidation rate is also accelerated when the oxygen concentration in the feed increases.

Igarashi *et al*. (1997) investigated Pt supported on alumina and A-type, mordenite and x-type zeolites. Pt/A-zeolite catalyst showed higher CO oxidation selectivity as compared to Pt/Al_2O_3 obtained at similar conversion levels. Subsequent studies involving a series of catalysts (Pt/A, Pt/mordenite, Pt/X, Pt/Al_2O_3) showed that the Pt/mordenite catalyst required the least amount of excess oxygen for the complete conversion of CO (1 per cent) in presence of excess of hydrogen. The selectivity for CO oxidation versus H_2 oxidation follows the order of zeolite A > mordenite > zeolite X > alumina. The use of a two-stage reactor further increased the effectiveness of the Pt/mordenite catalyst. Also, the catalyst performance was not significantly influenced by the presence of water in the feed stream.

Many researchers state that low oxygen concentration minimizes hydrogen oxidation. In the light of this, selectivity of Pt/alumina catalyst for CO oxidation can be improved by using O_2 storage components as promoter for reaction.

2.2.2. Cerium Oxide (CeO_x)

According to Dabill *et al.* (1978); in order to initiate the oxidation reaction in a mixture of H_2, CO and O_2 adsorbed carbon monoxide should be removed from the surface of catalyst to allow the dissociative adsorption of oxygen. This can be accomplished by using a promoter.

The CO oxidation reaction on Pt-CeO_2/Al_2O_3 may consist of the formation of CO_2 via reduction of the interfacial ceria by CO absorbed on Pt, and noncompetitive Langmuir-Hinshelwood mechanism is assumed on the metal/oxide interface. CeO_2 has also been proposed as a direct source of oxygen, and in this way oxidation reactions proceed at the metal-support interface (Serre *et al*., 1993).

In addition to its oxygen storage capability, CeO_2 also prevents alumina from sintering at high temperature and improves the dispersion and thermal stability of noble metals (Park and Ledford, 1998).

According to Nunan *et al*. (1992) there is a direct interaction between Pt and CeO_2, which led to large improvements in the performance of catalyst after the catalyst activation with synthetic exhaust gas. They reported that activation of catalyst was due to the reduction of the noble metals and surface ceria. Also, Serre *et al*. (1993) found that with a reductive pre-treatment, the reactivity of platinum-ceria on alumina catalysts improved significantly. They attributed this to the beneficial effect of the ceria to Pt^0-CeO_2 sites localized at the Pt-Ce interface. But after oxidation, these sites were believed to be deactivated by the formation of PtO_2-CeO_2 sites, and then the reaction took place only on Pt^0 sites.

Özkara and Aksoylu (2003) reported that ceria can be used as support 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 a minimum hydrogen loss. Unfortunately, ceria-supported platinum was found to be too active in hydrogen oxidation as well, and cannot be considered as an effective PROX catalyst above 130 ˚C. Nevertheless, ceria can be considered as a beneficial additive to supported Pt catalyst (Wootsch *et al*., 2001).

2.2.3. Cobalt Oxide (CoO_x)

Due to its high CO oxidation activity in CO-O_2 mixtures even at ambient temperature, cobalt oxide is used in this reaction widely. It was shown that Co_3O_4/Al_2O_3 with pre-oxidized cobalt oxide has high CO oxidation activity even without a noble metal. The main reason for this is that the CO is unable to block the cobalt oxide surface from O_2 absorption as it does on platinum. However, in the presence of water and hydrocarbons the activity of cobalt oxide decreases significantly (Thormählen *et al*., 1999).

Jansson *et al.* (2001) proposed the following mechanism for CO oxidation reaction on Co_3O_4/Al_2O_3 without the presence of hydrogen.

- CO is absorbed on the cobalt oxide surface,
- The absorbed CO reacts with activated oxygen already present on the cobalt oxide surface. The produced CO_2 is then desorbed from surface, also carbonate species might be formed as an intermediate,
- The reduced cobalt is deoxidized by gas phase oxygen or it is further reduced by CO, thus deactivating the site,
- CO_2 can be absorbed on the surface and from surface carbonate species.

Mergler *et al*. (1996) and Hatura *et al*. (1993) suggested similar mechanisms with Pt or Au containing catalyst. According to them, CO is absorbed on Pt or Au site, while oxygen is supplied by CoO_x. The reaction between CO_{ads} and O_{ads} takes place either in the interface between Pt with or Au with CoO_x. The oxygen-spillover to the Pt or Au sites is also possible.

Törncrona *et al*. (1997) studied the promoting effect of cobalt oxide on Pt. According to their study, CO starts to be desorbed from cobalt sites at about 100 ˚C and create

vacancy for oxygen absorption and subsequent reaction between CO and O_2. When the oxygen atoms are present and close to the interface between Pt and Co, the reaction may spillover to Pt by reaction with CO adsorbed on Pt. Törncrona *et al.* (1997) suggest that the reaction starts on Co and spills over to Pt, where more rapid light off takes place.

2.2.4. Magnesium Oxide (MgO_x)

Magnesium oxide, which has a rock salt type structure, has been used as a support material for the metal catalysts. The (1 0 0) plane is regarded as the most stable surface of MgO, which is a neutral plane composed of stoichiometric Mg^{2+} cations and O^{2-} anions. Magnesium oxide exhibits a high surface basicity by virtue of the presence of O^{2-} ions, which can easily capture the protons. Also, it possesses weak basic sites that can be assigned to the surface Mg^{2+} ions. In order to suppress this surface basicity, a number of alternative magnesium oxides have been synthesized in recent years using various procedures including the thermal decomposition of precursors and the sol-gel technique. The characteristic feature of Pt/MgO may provide the potential application to selective oxidation systems with unique performance, possibly assisted by coexisting or added H_2O in the catalytic processes. (Asakura *et al.,* 1999).

According to Cho *et al*. (2006) by addition of Mg to Pt/Al_2O_3 catalyst, the concentration of low basicity sites increases with the occurrence of medium basicity sites, where there are no medium basicity sites in Pt/Al_2O_3. The main advantage of the low basicity sites is, CO_2 desorption occurs in lower temperatures in low basicity sides than medium and high basicity sites.

CO_2 has three different desorption temperature stages:

- Low basicity sites where, CO_2 is desorbed between 80-140 ˚C,
- Medium basicity sites where, CO_2 desorption take place between 160-240 ˚C,
- High basicity sites where, desorption temperature rises over 300 ˚C.

Also Cho *et al*. (2006) found that Pt on Pt-Mg/Al_2O_3 is more reduced than that on Pt /Al_2O_3, also Pt^0 of Pt-Mg/Al_2O_3 is found to be very stable.

Grisel and Nieuwenhuys (2001) found that addition of MgO to Al_2O_3 resulted in good reproducibility of manufacturing catalyst with highly dispersed Au phase.

2.2.5. Nickel

Ko *et al*. (2006) found that addition of Ni to Pt/Al_2O_3 increased the CO conversion and the CO_2 selectivity at low temperature with respect to Pt/Al_2O_3. Ko *et al*. (2006) also found that the CO chemisorption decreased from 34.8 to 23.9 $\mu mol/g_{cat}$ by adding Ni to Pt/Al_2O_3. This illustrates that Ni addition decreases the active sites for CO chemisorption. According to their XRD and TPR results, the catalytic activity increased due to the formation of bimetallic phase of Pt and Ni.

2.2.6. Manganese Oxide (MnO_x)

MnO_x is reported as a high oxygen storage capacity compound. It has been studied in oxidation reaction mainly as support. Also, MnO_x-doped Pt catalysts have been studied for automotive industry for pollution control and CO oxidation. It has not been much subjected to PROX reaction as promoter.

The research done by Grisel and Nieuwenhuys (2001) showed that Au/MnO_x/Al_2O_3 has lower CO oxidation activity than Au/Al_2O_3. The main reason for decreasing activity is the bigger Au particle size in Au/MnO_x/Al_2O_3 than Au/Al_2O_3. However, Au/MnO_x/MgO/Al_2O_3 catalyst exhibit higher CO oxidation activity than Au/MgO/Al_2O_3 even the Au particle sizes are found to be quite similar. In these catalysts MgO was used to stabilize the Au particle size, it was suggested that MnO_x was able to supply O for CO oxidation reaction via Mars and van Krevelen type mechanism which created the activity difference:

$Mn\text{-}O + CO_{ads} \rightarrow Mn\text{-}\square + CO_2$	(2.7)

$Mn\text{-}\square + O_2 \rightarrow Mn\text{-}O + O_{ads}$	(2.8)
$O_{ads} + Mn\text{-}\square \rightarrow Mn\text{-}O$	(2.9)
$O_{ads} + CO_{ads} \rightarrow CO_2$	(2.10)

The MnOx-Pt/Al_2O_3 has higher reducibility than Pt/Al_2O_3 and MnO_x/Al_2O_3. This is probably related to the capacity of MnO_x to provide O_2 for reaction. The promotion of effect of MnO_x was found to be very noticeable at low temperature and low excess of oxygen. This supports the mechanism in which the promoter (MnO_x) activates the oxygen required for reaction: at low temperatures, as Pt metal is completely covered by CO, the oxygen is activated at the interface, whereas at higher temperatures the oxygen can also be activated on Pt sites. (Ayastuy *et al*., 2006).

2.2.7. Zirconium Oxide (Zr_2O)

The zirconium is generally used as support in oxidation reactions due to its oxygen storage capacity. The reducible metal oxides like ZrO_2, presented higher activities in CO oxidation reaction, as a support for Pt, because of the different reaction mechanism than alumina and silca based catalysts. In reducible metal oxides, the non-competitive Langmuir-Hinshelwood mechanism occurs on the metal/oxide interface: CO absorbed on the Pt surface reacts with the oxygen atom that spillover from the support surface. Although, ZrO_2 exhibits higher catalytic activity than alumina and silica in CO oxidation reaction, the activity decreases dramatically in selective CO oxidation where H_2 oxidation competes with CO oxidation. In ZrO_2, CO desorption much more easily than alumina or silica support. High CO desorption rate cause high H_2 absorption rate which cause a lower conversion and selectivity (Souza *et al*., 2007).

ZrO_2 is also used with CeO_2 as co-support in the form of $Ce_xZr_{1-x}O_2$. The main reason for adding ZrO_2 is to enhance the oxygen storage capacity of CeO_2. Addition of ZrO_2 to CeO_2 increases the reducibility of the support.

2.2.8. Potassium Carbonate (K_2CO_3)

Addition of alkali metal ions to noble metal can affect the CO and O_2 adsorption properties. The effects of alkali metal ion depend on its basicity strength. The alkali metals with strong basicity enhance the CO oxidation activity. Addition of K with the molar ratio of K/Pt= 10 ratio boosts the catalytic activity for selective CO oxidation. The TOF of K-Pt/Al_2O_3, when K/Pt is 10, is 10 times higher than of Pt/Al_2O_3 alone. It has been reported that the OH group can promote CO oxidation on Pt and, it is believed that the OH group coverage amount increased with K and Pt interaction (Minemura *et al*., 2006).

Tanaka *et al*. (2003) reported that the addition of potassium to Rh/SiO_2 enhances the activity and selectivity of CO oxidation due to the basicity of potassium. Potassium is a strong basic, therefore it can supply electron Pt and this electron makes CO adsorption strong. This can be related to the promotion of CO oxidation in H_2-rich gas.

2.2.9. Iron Oxide

It is widely accepted that CO oxidation on Pt metal follows a competitive Langmuir-Hinshelwood mechanism, where CO and O compete for Pt site. In selective CO oxidation, H_2 also compete with CO for oxidation. Addition of Fe oxide to Pt/Al_2O_3 creates a dual site non-competitive reaction conditions. Fe oxide is an active oxygen supplier; it can provide necessary oxygen for reaction so the oxygen does not have to compete for Pt site with CO. Addition of Fe oxide to Pt/Al_2O_3 has no effect on the size and distribution of Pt metals. Fe oxide also interacts with Pt metal surface strongly leading to an electron rich Pt metal surface (Liu *et al*., 2002).

Sirijaruphan *et al*. (2004) found that Fe oxide addition has no effect on BET surface area of Pt/Al_2O_3. The search also suggests that there is a change in reaction order with addition of Fe oxide to Pt/Al_2O_3. For Pt/Al_2O_3, the oxygen adsorption can be rate controlling step due to the competitive Langmuir-Hinshelwood mechanism. In the presence of Fe, however, the oxygen is preferable adsorbed on the Fe sites. Therefore, the rate has little or no dependence on oxygen concentration.

Addition of Fe oxide to Pt/Mordenite improves both CO conversion and selectivity. In temperature region of ≤200˚ C, the Pt-Fe/M exhibits 100% CO conversion with stoichiometric amount of O_2, where, Pt/M maximum conversion is 80% (Watabane *et al*., 2003).

2.2.10. Aluminum Oxide (Al_2O_3) Support

Many industrial catalysts consist of metals or metal compounds supported on an appropriate support; the basic role of a support is to maintain the catalytically active phase in a highly dispersed state (Rodriguez-Reinoso, 1998).

The aim of using support is mainly to spread out the expensive catalyst ingredient such as platinum for its most effective use, or a means of improving the mechanical strength of an inherently weak (metal/active phase) catalyst.

Although, the support is generally described as an inert substance, it can also contribute to the catalytic activity, depending upon the reaction type and conditions (Satterfield, 1991). The support selection is mainly done according to its desirable characteristics, such as the followings:

- A support must have desirable mechanical properties, including attrition resistance, hardness, and strength.
- It should be stable under the reaction and the regeneration conditions.
- It should provide the necessary surface area.
- The support must supply the porosity, including the average pore size and the pore-size distribution. The high area implies the fine pores, but the relatively small pores may become plugged in the catalyst preparation, especially if the high loadings are sought.
- It should be cheap.
- It should be inert or provide the active sites for activity or the strong metal/support interaction depending on reaction.

The alumina, silica, carbon (mainly activated carbon) supports combine these characteristics optimally (Özkara, 2002).

The γ-alumina and η-alumina, which are also called active aluminums, are the most important transition oxides for catalytic applications. γ-alumina is especially used for applications where the high surface area and the high thermal and mechanical stability are required.

For the noble metal-based catalysts, mostly the alumina is preferred as support. These catalysts are used for hydrogenation or oxidation reaction. Also γ-alumina is used as the catalyst in its native from in alcohol dehydration reaction and Claus process.

The active alumina is much more widely used in catalytic applications than the silca and the carbon since it is not only an excellent support, but it is also very active as a catalyst in its own right for several applications (Ertl *et al*., 1999).

2.4. Catalyst Preparation Method: Impregnation

The catalyst preparation method has strong effects on the activity of the catalyst. The chemical and physical properties of a catalyst are determined by the history of the preparation procedure (Satterfield, 1999).

The catalyst preparation may be considered as combination of several different unit operations each of which has important effect on the properties of the catalyst produced. Common preparation methods for supported catalysts are multi-step processes consisting of following steps (Kılaz, 1999).

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

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

Among these preparation methods impregnation is one of the best known. Generally the impregnation method is used for preparing supported catalyst with expensive active compounds such as noble metals on a support like Al_2O_3. The impregnation is both simple and effective method of producing a catalyst, and it contains of following steps:

- Precipitation of support
- Washing and drying
- Shaping the support
- Impregnation with solutions of the active component or components
- Drying
- Decompositon (calcinations)
- Activation

In the impregnation process, the active components with thermally unstable anions like nitrates, acetates, carbonates and hydroxides are used. The active component or components are dissolved in a solvent, which is usually water. The support is immersed in this solution under the precisely defined conditions (such as concentration, mixing rate, temperature, time etc.). Depending on production conditions, the selective adsorption of active components occurs on the surface or in the interior parts of the support resulting a non-uniform distribution.

To achieve the best possible impregnation, the air in the pores of the support should be removed by evacuation or support is treated with gases such as CO_2 or NH_3 prior to impregnation. Evacuation before the impregnation gives more uniform distribution of active component(s).

After the impregnation of the support by a solution of active component(s), the catalyst is dried and then calcined. The drying process must be carried out by a mild

thermal treatment in a temperature range of 350 K to 500 K. The aim of this drying step is to remove the solvent used in impregnation step. The speed of drying process in conjunction with the pore structure has a profound effect on metal compound distribution in a catalyst pellet (Bülbül, 1999).

Calcination is a heat treatment in an oxidizing atmosphere at a temperature slightly higher than the intended operating temperature of the catalyst. During calcination, the numerous processes can occur that alter the catalyst in such ways as the formation of new components by solid-state reactions, the transformation of amorphous regions into crystalline regions, and the modification of the pore structure and mechanical properties. In case of the supported metal catalysts, the calcination resulted to the formation of metal oxides as catalyst precursors, and these must be reduced to the metals. Hence, the next step is reduction, and it can be performed with H_2, CO, or milder reduction agents such as alcohol vapor. In some cases, reduction of catalyst can be carried out in the reactor prior to process start-up.

Two types of impregnation techniques may be employed. These are incipient to wetness and dipping impregnation, which is also termed as wet soaking impregnation.

2.4.1. Incipient to Wetness Impregnation

This method is usually used for the preparation of controlled metal loading on catalysts for the supports, which have low adsorption of metal precursors. The solution containing a calculated amount of metal compound is added in an amount just sufficient to fill up the pore volume if the support is pelletized. If it is in powder form, then the amount of the solution should be larger than pore volume.

The wetness impregnation method is simple and low cost method that is easy to control. The high reproducibility is another important advantage of the wetness impregnation. Limited metal loading due to solubility of metal precursors can be considered as disadvantage; however, this disadvantage can be overcome by multiple impregnation steps.

2.4.2. Dipping Impregnation

The support is immersed in a solution of metal compound in this type impregnation. Before that, the support can be pre-saturated with a solution (wet impregnation) or can be used dry (capillary impregnation) for desired active component profile in the support particles. The slurry is stirred for a predetermined time and filtered; and the product is dried, calcined and reduced prior to reaction.

The metal loading of catalysts prepared by dipping impregnation is governed by the concentration of adsorption sites on the surface of support. Therefore, it's not possible to prepare a supported catalyst with a predetermined metal loading by this method.

2.4.3. Advantages of Impregnation Compared to Other Methods

The catalysts prepared by impregnation method have many advantages when compared with catalysts prepared by other methods such as precipitation. The impregnated catalysts' pore structure and specific surface area are largely determined by the support. Since the support materials are available in all desired ranges of surface area, porosity, shape, size and mechanical stability, the impregnated catalysts can be tailor-made with respect to the mass transport properties. The impregnation is preferred especially in preparing supported noble metal catalysts.

3. EXPRERIMENTAL WORK

3.1. Materials

3.1.1. Chemicals

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

Table 3.1. Chemicals used in catalyst preparation

Chemicals	Formula	Grade	Source	Molecular Weight (g/mole)
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
Mangan(II)nitrate Tetrahydrate	$Mn(NO_3)_2.4H_2O$	Extra Pure	Merck	251.01
Zirconyl nitrate Hydrate	N_2O_7Zr	Extra Pure	Fluka	231.23
Magnesium nitrate Hexahydrate	$Mg(NO_3)_2.6H_2O$	Extra Pure	Merck	256.41
Nickel(II) nitrate hexahydrate	$Ni(NO_3)_2.6H_2O$	Extra Pure	Merck	290.81
Cerium(III) nitrate hexahydrate	$Ce(NO_3)_2.6H_2O$	Extra Pure	Merck	434.23
Iron(III) nitrate nonahydrate	$Fe(NO_3)_2.9H_2O$	Extra Pure	Merck	341.6
Potassium Carbonate	K_2CO3	Extra Pure	Merck	138.21
Aluminium Oxide	Al_2O_3	Extra Pure	ZeochmEU	101.96

3.1.2. Gases and Liquids

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

Table 3.2. Applications and specifications of the gases used

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

Table 3.3. Applications and specifications of the liquids used

Liquid	Application	Specification
Water	Reactant, cleaning	Distilled

3.2. The Experimental Set-Up

The experiment set-up consists of three parts:

- Catalyst Preparation System: in which, catalysts prepared by impregnation method,
- Microreactor System: in which, the catalytic activity tests are done,
- Analysis System: in which, a mass spectrometer employed.

3.2.1. Catalyst Preparation System

In catalyst preparation system Retsch UR1 ultrasonic mixer, a vacuum pump, a vacuum flask, a beaker, a Masterflex computerized-drive peristaltic pump and silicone tubing were employed for wetness impregnation method (Figure 3.1).

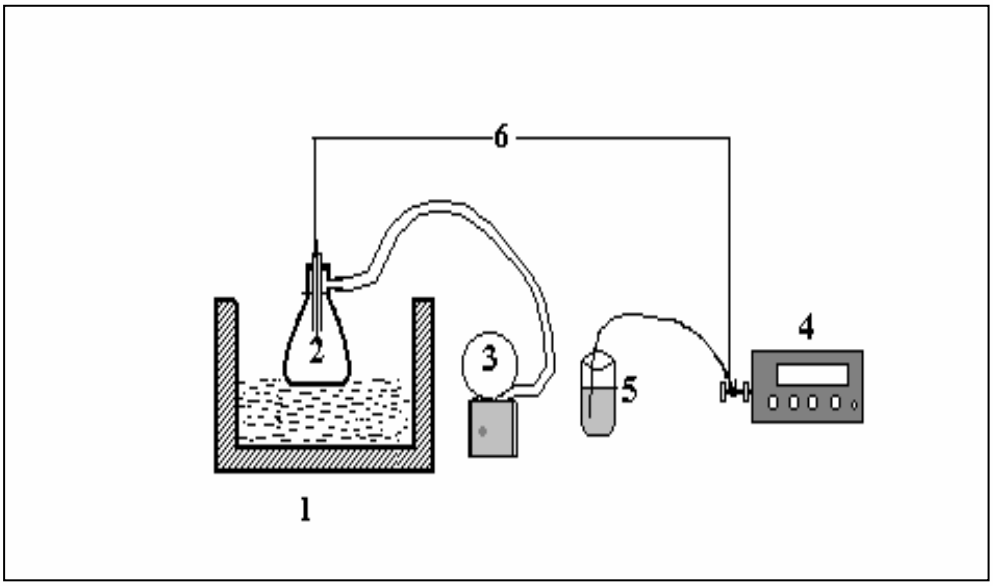

Figure 3.1. The impregnation system: 1. Ultrasonic mixer 2. Vacuum flask 3. Vacuum pump 4. Peristaltic pump 5. Beaker 6. Silicone tubing

3.2.2. Microflow Reactor System

1/4″, 1/8″, and 1/16″ OD stainless steel and copper tubing with brass and stainless steel fittings were used in the system. The reaction gases pass though the copper tubings and the flows were controlled by Brooks 5850 E mass flow controller. The flow meters set values were controlled by 4-Channel Brooks 0154 control panel. For all reaction gases, 30 psi was used as the input pressure to the flowmeters to get best performance.

After flow controller segment, the gases were mixed and sent to reaction segment in include a down-flow 4 mm ID× 58.5 cm stainless steel fixed-bed reactor placed in 2.4 cm ID× 50 cm furnace controlled to 0.5± K with Shimaden FP-21 programmable temperature controller (Figure 3.2). The K-type sheathed thermocouple was placed at the midst of the catalyst outside the microreactor. The fitting of the reactors, which were outside the

furnace, were isolated by ceramic wool to prevent heat loss and maintain stable reaction conditions.

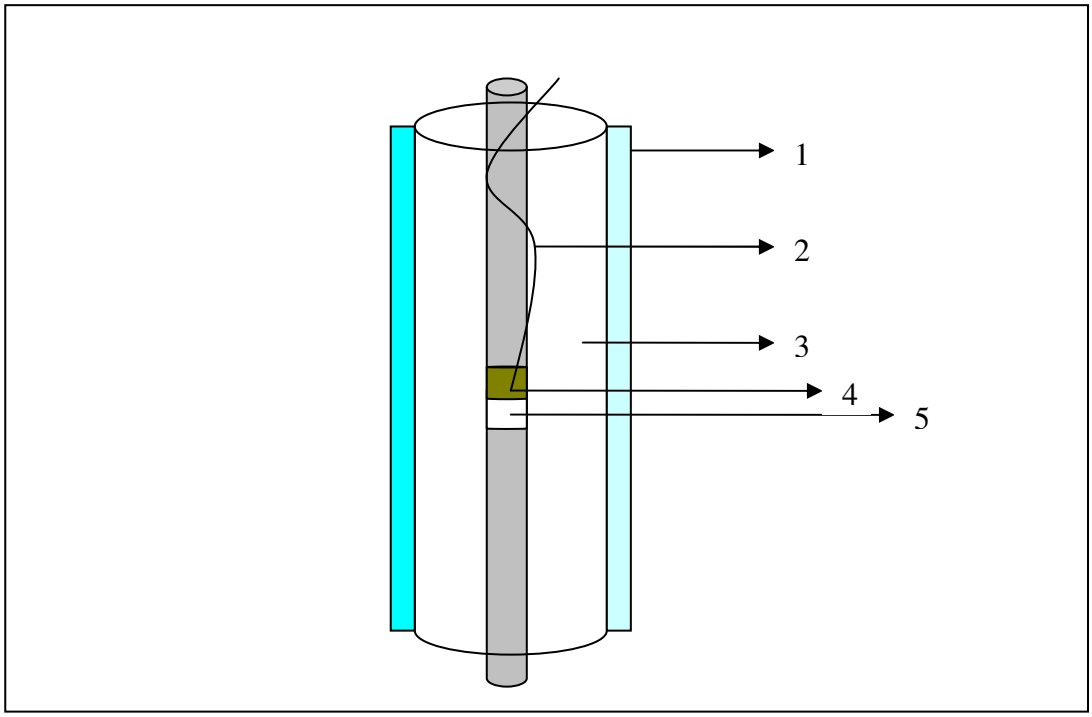

Figure 3.2. Reactor and furnace system: 1.Ceramic wool insulation 2.Thermocouple 3.Furnace 4.Catalyst 5.Catalyst bed

The Jasco PU-2080 Plus HPLC pump was used for water pumping. Distillated water was used for all reactions. The water was added after all reaction gases were mixed. The reaction gases were passed though heated stainless steel tubing, in order to get the necessary energy to vaporize the water. The temperature was controlled by Dixell single stage digital controller XT110C. For heating the stainless tubing, Seres heating type was used with ceramic wool isolation.

3.2.3. Product Analysis System

After the reaction section a cold trap was used to condense the water, which wass product of selective CO oxidation. The cold trap consisted of an ice box and coiled tubing to increase contact time of flow through a cold environment. The product streams were analyzed using a Hiden Hal 210 mass spectrometer connected to a personal computer and employing MASoft software.

The entire microflow reaction system is presented in Figure 3.3.

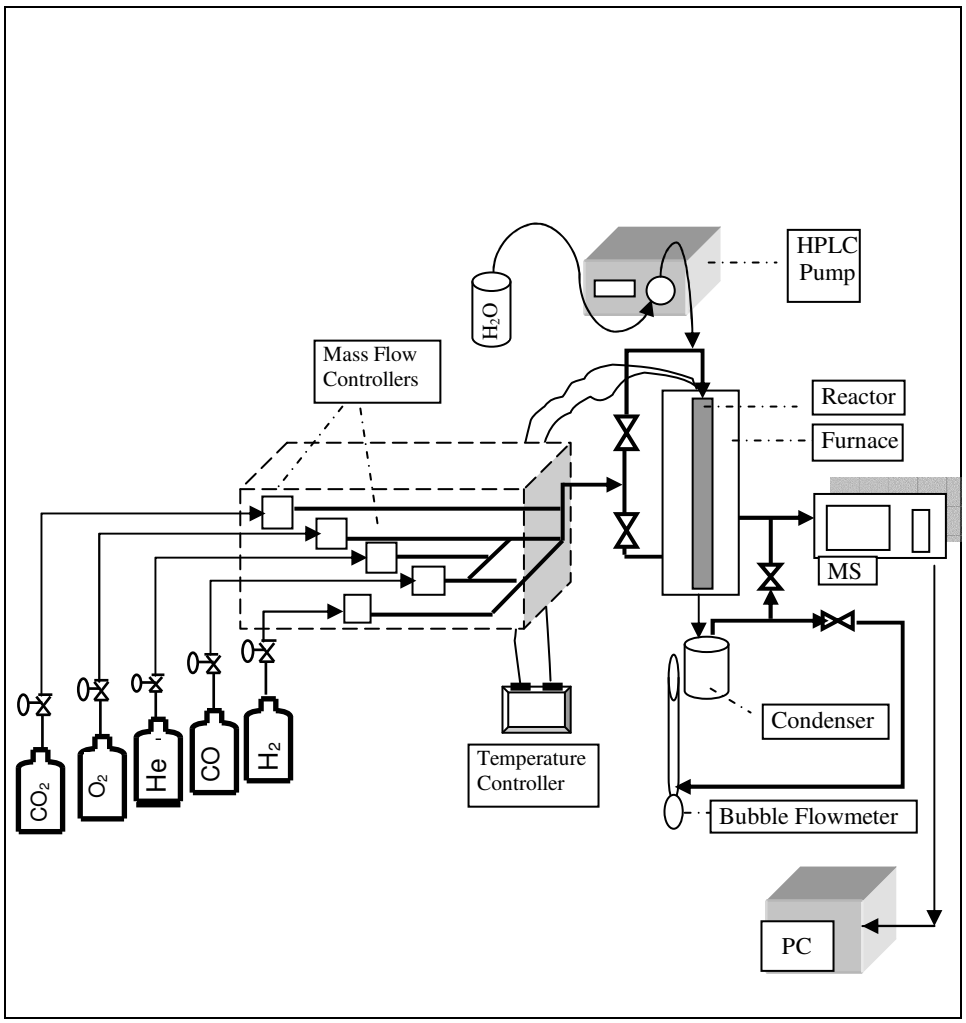

Figure 3.3. The microreactor flow and product analysis system

3.3. Catalyst Preparation

The catalyst was prepared by incipient to wetness impregnation. It contained either 1.4 weight per cent or 0.7 weight per cent Pt, 1.25 weight per cent of each promoter; Ce, Co, Ni, Mn, Mg, K, Zr, Fe. The experimental setup shown in Figure 3.1 was used for catalyst preparation. The procedure had four steps:

- Evacuating the support
- Contacting the support with the precursor solution
- Drying
- Calcination.

Alumina support was crushed and sieved into 45-60 mesh size (344 -255 μm). It was calcined at 450 ˚C for 5 hours prior to impregnation. Five grams of support was placed in a vacuum flask and kept under the vacuum for 30 min so that the trapped air in pores of the support that could not prevent penetration of the precursor solution. This was accompanied by mixing in Retsch UR 1 ultrasonic mixer.

All the metal salts were dissolved in 1.21 ml of water per gram of alumina support, which is the amount of water to wet one gram alumna. The aqueous precursor solution was fed to the vacuum flask at a flow rate of 0.5 ml/min via silicone tubing. A Masterflex computerized-drive peristaltic pump was used to feed the solution. The slurry was mixed under vacuum by an ultrasound mixer to maintain uniformity of impregnation. The impregnated support was mixed for additional 90 min. The slurry obtained was dried at 115 ˚C overnight (16 hours). Then all the catalysts are calcined in the air using the procedure summarized in Table 3.4 depending on the promoter used.

Table 3.4. Calcination procedures of catalysts

Catalyst	Calcination Temperature	Calcination Time

Pt-Co/Al_2O_3	400 ˚C	2 hours
Pt-Co-Ce/Al_2O_3	400 ˚C	2 hours
Pt-Co-Mg/Al_2O_3	400 ˚C	4 hours
Pt-Co-Fe/Al_2O_3	300 ˚C	2 hours
Pt-Co-Mn/Al_2O_3	400 ˚C	5 hours
Pt-Co-Zr/Al_2O_3	400 ˚C	2 hours
Pt-Ce/ Al_2O_3	400 ˚C	2 hours
Pt-K-Ce/ Al_2O_3	500 ˚C	1 hour
Pt-Ni-Ce/ Al_2O_3	450 ˚C	2 hours

3.4. Catalytic Activity Measurements

All catalysts were reduced before the reaction, and kept under He flow until the reaction test was performed. All cobalt containing catalysts have the same reduction procedure except Pt-Mn-Co/Al_2O_3. The reduction program can be seen for each catalyst in in table Table 3.5 through Table 3.9.

Table3.5. Reduction program for Pt- Co-X/Al_2O_3 catalyst (X=Mg, Fe, Zr, Ce, or none)

Segments	Starting and End Temperatures	Segment Gas
First Segment	Heating from 25 ˚C to 400 ˚C with a heating rate 2.5 ºC/min	He with flow rate of 50 ml/min
Second Segment (Reduction)	Keeping constant at 400 ˚C for 2h	H_2 with flow rate of 50 ml/min
Third Segment	Flushing at 400 ˚C for 1h to clean the catalyst surface	He with flow rate of 50 ml/min
Fourth Segment	Overnight cooling down to 25 ˚C	He with flow rate of 25 ml/min

Table 3.6. Reduction program for Pt-Co-Mn/Al_2O_3 catalyst

Segments	Starting and End Temperatures	Segment Gas

First Segment	Heating from 25 ˚C to 400 ˚C with a heating rate 2.5 ˚C/min	He with flow rate of 50 ml/min
Second Segment (Reduction)	Keeping constant at 400 ˚C for 2h	H_2 50 ml/min, He 50 ml/min with total flow rate of 100ml/min
Third Segment	Flushing at 400 ˚C for 1h to clean the catalyst surface	He with flow rate of 50 ml/min
Fourth Segment	Overnight cooling down to 25 ˚C	He with flow rate of 25 ml/min

Table 3.7. Reduction program for Pt-Ce/Al_2O_3 catalyst

Segments	Starting and End Temperatures	Segment Gas
First Segment	Heating from 25 ˚C to 500 ˚C with a heating rate 2.5 ˚C/min	He with flow rate of 50 ml/min
Second Segment (Reduction)	Keeping constant at 500 ˚C for 2h	O_2 with flow rate of 50 ml/min for 1 hour than H_2 with flow rate of 50 ml/min for 1 hour
Third Segment	Flushing at 500 ˚C for 1h to clean the catalyst surface	He with flow rate of 50 ml/min
Fourth Segment	Overnight cooling down to 25 ˚C	He with flow rate of 25 ml/min

Table 3.8. Reduction program for Pt-K-Ce/Al_2O_3 catalyst

Segments	Starting and End Temperatures	Segment Gas
First Segment	Heating from 25 ˚C to 500 ˚C	He with flow rate of

	with a heating rate 2.5 ˚C/min	50 ml/min
Second Segment (Reduction)	Keeping constant at 500 ˚C for 1h	H_2 with flow rate of 50 ml/min
Third Segment	Flushing at 500 ˚C for 1h to clean the catalyst surface	He with flow rate of 50 ml/min
Fourth Segment	Overnight cooling down to 25 ˚C	He with flow rate of 25 ml/min

Table 3.9. Reduction program for Pt-Ni-Ce/Al_2O_3 catalyst

Segments	Starting and End Temperatures	Segment Gas
First Segment	Heating from 25 ˚C to 150 ˚C with a heating rate 2.5 ˚C /min	He with flow rate of 50 ml/min
Second Segment (Reduction)	Keeping constant at 150 ˚C for 1h	H_2 with flow rate of 50 ml/min
Third Segment	Flushing at 150 ˚C for 1h to clean the catalyst surface	He with flow rate of 50 ml/min
Fourth Segment	Overnight cooling down to 25 ˚C	He with flow rate of 25 ml/min

The activity tests took place in the microreactor flow system shown in Figure 3.3. The reduced catalysts were exposed to the different reaction mixtures in different temperatures. Prior to reaction, all the catalysts were heated from ambient temperature to reaction temperature under a stream of 50 ml/min helium. Then, the He flow was turned off, and the reaction mixture was turned on. The data are taken continuously with Hiden Hal 201 mass spectrometer.

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

- First set consist of 60 ml/min H_2, 38 ml/min He, 1 ml/min CO, and 1 ml/min O_2 in the absence of CO_2 and H_2O.

- The second set includes CO_2 at 25 ml/min flow rate, where He flow rate decreased to 13 ml/min keeping all the other the same as the first set.
- In the last set, 10 ml/min H_2O added to second set, which 60 ml/min H_2, 3 ml/min He, 1 ml/min CO, and 1 ml/min O_2, 25 ml/min CO_2, 10 ml/min H_2O.

The reactions were done under three different temperatures 80, 110, and 130 ˚C. The summary of the reaction conditions are given in Table 3.10, the results are presented and discussed in chapter 4.

Table 3.10. Reaction conditions for catalytic activity test

Parameter	Value
Catalyst Particle Size	45-60 mesh size (344-255µm)
Catalyst Amount	0,25 g
Reaction Temperature	80, 110, 130 ˚C
Reactant Total flow rate	100 ml/min
W/F Ratio	2.5 mg.min/ml

4. RESULTS AND DISCUSSION

Thirteen catalysts were prepared and tested to study the effects of promoters and Pt content. The conversions and selectivity were defined and calculated as follows:

$\text{CO conversion } (\%) = \frac{[CO]_{in} - [CO]_{out}}{[CO]_{in}} \times 100$	(4.1)
$O_2 \text{ conversion } (\%) = \frac{[O_2]_{in} - [O_2]_{out}}{[O_2]_{in}} \times 100$	(4.2)
$\text{Selectivity Towards CO } (\%) = \frac{0.5 \times ([CO]_{in} - [CO]_{out})}{[O_2]_{in} - [O_2]_{out}} \times 100$	(4.3)

The reactor outlet stream was measured continuously and the data taken in every 10 minute were used for the conversions and selectivity calculations. The results obtained for all the reaction conditions were discussed in the following sections.

Although, the selectivity and stability are also the important aspects of catalyst optimization; the CO conversion shapes the main borders in this work since the CO content of hydrogen feed should be under 10 ppm for fuel cell applications, hence Pt content and the promoter selection were decided according to the CO conversion, only.

In the previous study done by İnce *et al*. (2005) for selective CO oxidation over Pt-Co-Ce/Al_2O_3, Pt weight per cent, Co weight per cent, Ce weight per cent, calcination time, and calcination temperature were taken as the design parameters. They found that 1.4wt.%Pt-1.25wt.%Co-1.25wt.%Ce/Al_2O_3 exhibits 100% CO conversion at 110 ˚C for gas stream; 1% CO, 1% O_2, 60% H_2, 25% CO_2, 10% H_2O, and He as balance. According to their results Pt-Co-Ce/Al_2O_3, in given weight per cents, is a promising catalyst for selective CO oxidation.

4.1. Selective CO Oxidation in the Absence CO_2 and H_2O

4.1.1. 1.4wt.%Pt- 1.25wt.%X-1.25wt.%Ce/Al_2O_3 (X= None, K, Ni, Co) at 80 ˚C

The first study was replacing Co with the some other potential metals in the Pt-Co-Ce/Al_2O_3 catalyst optimized by İnce *et al.* (2005). The reactions were carried out at 80 ˚C first using a feed stream composition of 1% CO, 1% O_2, 60% H_2, and He in balance (in the absence of CO and water). In all catalysts Pt per cent was set to be 1.4 while the promoters' weight per cent was 1.25. A Pt-Ce/Al_2O_3 catalyst was also prepared and tested as a base for comparisons. The results for this Pt-Ce/Al_2O_3 catalyst are given in Table 4.1.

Table 4.1. Conversion and selectivity results for Pt-Ce/Al_2O_3 at 80 ˚C

Time (min)	% CO conversion	%O_2 conversion	% Selectivity
0	12.1	9.2	65.5
10	12.6	9.5	66.3
20	13.0	9.9	65.6
30	13.0	10.4	62.5
40	13.2	10.7	61.6
50	13.5	10.7	63.1
60	13.6	10.7	63.3
70	13.6	10.5	64.6
80	13.6	10.4	65.5
90	13.8	10.6	65.3
100	13.5	10.2	66.2
110	13.7	10.3	66.8
120	13.6	9.9	68.4

The conversion was about 13 per cents which is in agreement with the results of İnce *et al.*(2005), where they obtained 14.7% maximum conversion at 90 ˚C with 1wt.%Pt-2.5wt.% Ce/Al_2O_3. Son (2006) was also reported that the light off temperature of 1wt.%Pt-

1wt.% Ce/Al_2O_3 is 150 ˚C, and less than 100 ˚C the conversion is under 10 per cent which is quite close to our results.

The cobalt is known as a promising promoter for Pt/Al_2O_3 catalyst for selective CO oxidation applications Ko *et al*. (2006). As it can be seen from Table 4.2, the addition of Co improved the catalytic activity significantly. İnce *et al*. (2005) used 1.4wt.%Pt-1.25wt.%Co-1.25wt.%Ce/Al_2O_3 at 80 ˚C, and they obtain 100% CO conversion for 60 min, than they observed a deactivation with the feed composition 1% CO, 1% O_2, 60% H_2, and He as balance. In our catalyst, there was no deactivation occurs, although, 100% CO conversion could not be reached.

Table 4.2. Conversion and selectivity results for Pt-Co-Ce/Al_2O_3 at 80 ˚C

Time (min)	% CO conversion	% O_2 conversion	% Selectivity
0	98.5	100	49.3
10	98.6	100	49.3
20	98.5	100	49.3
30	98.5	100	49.3
40	98.6	100	49.3
50	98.6	100	49.3
60	98.6	100	49.3
70	98.7	100	49.3
80	98.7	100	49.3
90	98.7	100	49.4
100	98.8	100	49.4
110	98.8	100	49.4
120	98.8	100	49.4

According to Ko *et al*. (2006) the effect of Co addition to Pt/Al_2O_3 decreases of chemisorbed CO on catalysts. The amount of chemisorbed CO on Pt-Co/Al_2O_3 is less than Pt/Al_2O_3, but Pt-Co/Al_2O_3 had better catalytic activity than Pt/Al_2O_3. This enhancement was explained by the formation of bimetallic phase of Pt and Co. Ko *et al*. (2006) obtained

20% CO conversion at 80 ˚C with 1wt.%Pt-3wt.%Co/Al_2O_3 catalyst with the feed containing 1% CO, 1% O_2, 80% H_2, 2% H_2O.

The addition of alkali metal ions to noble metal can affect the CO and O_2 adsorption properties. The effect of alkali metal is strongly related to the basicity strength of alkali metal ion (Minemura *et al*., 2006). The potassium was also tested as the alkali metal promoter to Pt-Ce/Al_2O_3, which exhibit promising results in literature. Its effects, however, was quite limited in this study as shown in Table 4.3.

Table 4.3. Conversion and selectivity results for Pt-K-Ce/Al_2O_3 at 80 ˚C

Time (min)	%CO conversion	%O_2 conversion	Selectivity
0	14.3	13.3	53.8
10	15.0	13.6	55.2
20	16.2	15.2	53.3
30	15.0	14.3	52.5
40	14.0	13.9	50.4
50	13.6	13.1	51.9
60	13.0	12.6	51.6
70	12.8	12.5	51.2
80	12.6	12.5	50.4
90	12.6	12.4	50.8
100	12.2	11.4	53.5
110	12.1	11.3	53.5
120	11.8	11.3	52.2

According to the results obtained by Ito *et al*.(2004) and Minemura *et al*. (2006), the promoting effect of alkali ion on the selective CO oxidation can be explained with two possible ways . The first one is that it can promote CO oxidation by changing the binding energies of adsorbed oxygen. The second one is the role of hydroxyl group (OH), which is formed from H_2 and O_2. Although, the promoting mechanism of OH groups over alkali

promoted Pt catalyst is not clear yet, the possible explanation is; the increasing OH coverage due to interaction of these groups with potassium.

The results obtained by Ito *et al.*(2004) and Minemura *et al*. (2006) showed that the optimum molar ratio of K/Pt and K/Rh is very important on catalytic activity. For K-Pt/Al_2O_3 Minemura *et al*. (2006) found that the best performance obtained with K/Pt=10, where according to Ito *et al.* (2004) it is 3 for K/Rh.

However, in our case there is no activity change observed with addition of K at 80 ˚C. It can be due to low reaction temperature or the molar ratio as it is mentioned above.

Nickel, is the last promoter that was coupled with ceria. There are limited researches that used nickel as promoter to selective CO oxidation. As can be seen from the experimental results in Table 4.4., the use of nickel did not improve the CO conversion either.

However Ko *et al*. (2006) found that Ni impregnation to Pt/Al_2O_3 caused an improvement in CO conversion. Although the active sites for CO chemisorption were decreased with Ni addition, the amount of chemisorbed CO on Pt/Al_2O_3 and Pt-Ni/Al_2O_3 were 34.8µmol/g_{cat} and 23.9µmol/g_{cat}, respectively, Pt-Ni/Al_2O_3 exhibits better catalytic activity than Pt/Al_2O_3. Ko *et al*. (2006) suggest that a new metal oxide composed of Pt and Ni was formed in the calcinations step. They observed a very small amount of H_2 consumption till 1000 K for Ni-promoted Pt/Al_2O_3. They reached 40% conversion at 80 ˚C using 1wt.%Pt –1.5wt.%Ni/Al_2O_3 catalyst with a gas stream of 1% CO, 1% O_2, 80% H_2, 2% H_2O, which is quite similar to the conditions used in this work..

Table 4.4. Conversion and selectivity results for Pt-Ni-Ce/Al_2O_3 at 80 ˚C

Time (min)	% CO conversion	% O_2 conversion	% Selectivity
0	15.5	13.7	56.0
10	15.0	13.8	54.0
20	13.8	13.4	52.0
30	13.4	13.0	52.0
40	12.8	12.6	51.0
50	12.2	12.3	51.0
60	12.0	12.0	51.0
70	11.5	11.4	51.0
80	10.8	10.7	51.0
90	10.8	10.7	51.0
100	10.5	10.5	50.0
110	10.0	10.2	50.0
120	10.0	10.0	50.0

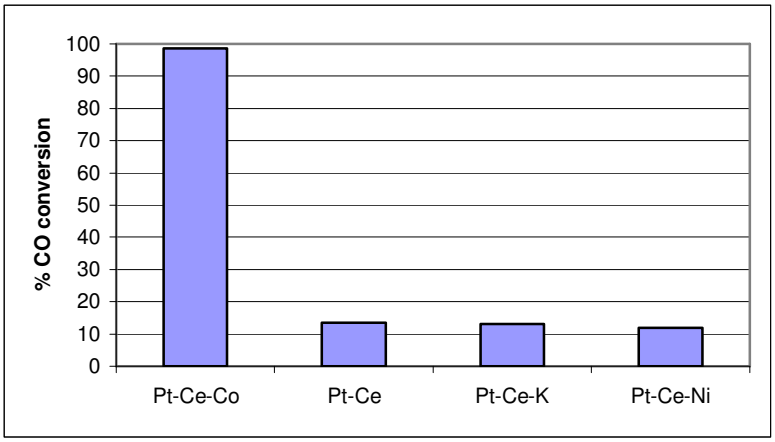

Figure 4.1. CO conversion at the 60th minute for Pt-X-Ce/Al_2O_3 at 80 ˚C

Figure 4.1 indicating that only Co addition improve the catalytic performance of Pt-Ce/Al_2O_3 significantly at 80 ˚C. However, that performance is not sufficient for the fuel cell applications.

4.1.2. 1.4wt.%Pt-1.25wt.%X-1.25wt.%Ce/Al_2O_3 (X= None, K, Ni, Co) at 110 ˚C

This time the temperature increased to 110 ˚C to see the effect of the promoter on CO conversion with the change of temperature with same feed stream that used at 80 ˚C (water and CO_2 free).

Again the first experiments were done with Pt-Ce/Al_2O_3 for comparison, and the results are given in Table 4.5. As it can be seen from Table 4.5 and Table 4.1 there is no significant activity difference between 80 and 110 ˚C for Pt-Ce/Al_2O_3 catalyst.

This result supported by the work of Son (2006), it was reported that 10% CO conversion obtained over 1wt.%Pt-1wt.%Ce/Al_2O_3 at 110 ˚C. Also, according to results of Son (2006) the light off temperature for 1wt.%Pt-1wt.%Ce/Al_2O_3 is 150 ˚C, which again supports our results.

Table 4.5. Conversion and selectivity results for Pt-Ce/Al_2O_3 at 110 ˚C

Time (min)	% CO conversion	% O_2 Conversion	% Selectivity
0	16.1	17.1	46.6
10	15.3	16.4	46.8
20	14.9	15.1	49.6
30	14.7	13.7	53.5
40	14.7	12.7	57.9
50	14.1	11.8	59.9
60	14.1	10.9	64.7
70	13.9	10.2	68.5
80	13.9	10.1	69.3
90	13.8	9.6	71.4
100	13.5	9.6	70.4
110	13.4	9.3	71.6
120	13.3	9.3	71.7

Than Pt-Co-Ce/Al_2O_3 was tested at 110 ˚C, and 100% conversion was obtained at all the value of time on stream as it was also found by İnce et al (2005). This clearly indicates that Pt-Co-Ce/Al_2O_3 has the best performance among the catalysts tested in this study at the condition studied so far (Table 4.6).

Ko *et al*. (2006) obtained 75% CO conversion at 110 ˚C with 1wt.%Pt-3wt.%Co/Al_2O_3 catalyst using the feed containing 1% CO, 1% O_2, 80% H_2, 2% H_2O. The TPR results by Suh *et al*. (2005) support the formation of bimetallic phase between Pt and Co. According to TPR results, no peaks corresponding to the reduced cobalt species were observed with Pt-Co/Al_2O_3, meaning that the Co atoms were located around Pt species and interacted with them. They obtain 100% CO conversion over a wide temperature range of temperature (25-175 ˚C) with 1wt.%Pt-1.8wt.% Co/Al_2O_3 using 0.0011% CO, 0.00099% O_2, 1.01% H_2, and N_2 balance as feed stream.

Table 4.6. Conversion and selectivity results for Pt-Co-Ce/Al_2O_3 at 110 ˚C

Time (min)	% CO conversion	% O_2 Conversion	% Selectivity
0	100	100	50.0
10	100	100	50.0
20	100	100	50.0
30	100	100	50.0
40	100	100	50.0
50	100	100	50.0
60	100	100	50.0
70	100	100	50.0
80	100	100	50.0
90	100	100	50.0
100	100	100	50.0
110	100	100	50.0
120	100	100	50.0

There was also activity enhancement observed with the addition of K to Pt-Ce/Al_2O_3 at 110 ˚C, like Co addition. However, the CO conversion only increased from 13% to 70%, where it is not sufficient for the fuel cell applications. Moreover, a deactivation observed after 80 min reaction time.

Minemura *et al.* (2006) studied K-promoted Pt/Al_2O_3 with different molar ratios. They reported that the CO conversion is under 50% at 100 ˚C with 2wt.%Pt loading at the K/Pt molar ratio of 4.5, which is the same as ours.

According to Tanaka *et al*. (2003) the light off temperature for K-promoted Rh catalyst was 100 ˚C, which supports our activity increase.

Table 4.7. Conversion and selectivity results for Pt-K-Ce/Al_2O_3 at 110 ˚C

Time (min)	% CO conversion	% O_2 Conversion	% Selectivity
0	70.9	100	35.5
10	70.1	100	35.1
20	71.0	100	35.5
30	71.5	100	35.8
40	72.0	100	36.0
50	72.5	100	36.3
60	73.0	100	36.5
70	73.0	100	36.5
80	73.0	100	36.5
90	60.0	100	30.0
100	57.0	100	28.5
110	57.0	100	28.5
120	57.0	100	28.5

Although, it seems Pt-Ce-K/Al_2O_3 is superior than Pt-K/Al_2O_3 and Pt-Ce/Al_2O_3, the maximum conversion was still 70% with less than 50% selectivity.

Like Co and K containing catalysts, the temperature increase has positive effect on CO conversion for Pt-Ni-Ce/Al_2O_3 catalyst. About 92% CO conversion was obtained at 110 ˚C, compare to the 13% in Pt-Ce/Al_2O_3. Ko *et al*. (2006) also obtained 90% conversion with 1wt.%Pt–1.5wt.%Ni/Al_2O_3 at 110 ˚C, with feed containing 1% CO, 1% O_2, 80% H_2, 2% H_2O, indicating that ceria has no significant effect in the presence of Ni at 110 ˚C at the conditions used.

Table 4.8. Conversion and selectivity results for Pt-Ni-Ce/Al_2O_3 at 110 ˚C

Time (min)	% CO conversion	% O_2 Conversion	% Selectivity
0	92.5	99.9	46.3
10	92.6	100	46.3
20	92.6	99.9	46.9
30	92.7	99.9	46.4
40	92.9	99.9	46.5
50	92.5	99.9	46.3
60	92.3	99.9	46.2
70	92.1	99.9	46.1
80	92.0	100	46.0
90	92.0	99.9	46.1
100	92.3	100	46.2
110	92.7	99.9	46.4
120	92.6	100	46.3

The CO conversion obtained at the 60 minutes time on stream at 110 ˚C for all catalysts tested are given in Figure 4.2 for comparison. Although, the results suggest that the Ni and K may also reach 100% conversion under some other conditions, Co is definitely the most appropriate promoter under the conditions studied. Hence Co was used as the first promoter in the remaining part of the study, which is about the effects of the potential second promoter as an alternative to Ce.

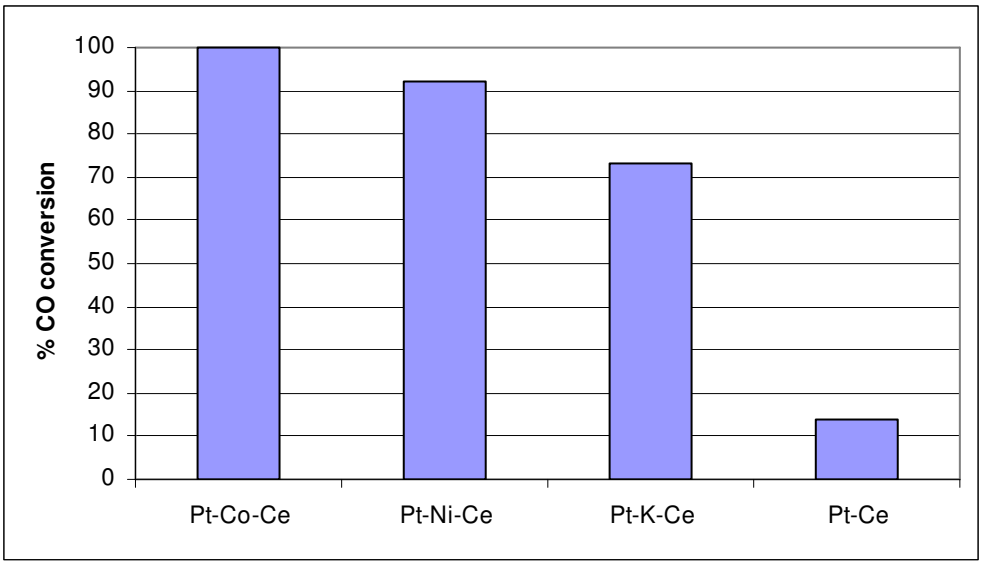

Figure 4.2. CO conversions at the 60th minute for Pt-X-Ce/Al_2O_3 at 110 ˚C

4.1.3. 1.4wt.%Pt-1.25wt.%Co-1.25wt.%X/Al_2O_3 (X= None, Ce, Fe, Mg, Mn, Zr) at 80 ˚C

In this part of the thesis, the selective CO oxidation was carried out replacing Ce with various alternatives at 80 ˚C using a feed stream composition of 1% CO, 1% O_2, 60% H_2, and He in balance.

First of all, a Pt-Co/Al_2O_3 catalyst was prepared as basis. Even at 80 ˚C Pt-Co/Al_2O_3 exhibits promising performance reaching over 99% CO conversion after 40 minute reaction time (Table 4.9).

According to Thormählen *et al*. (1999) the main reason for the higher activity of Co containing catalysts was the surface coverage dependent sticking coefficients for CO and O_2. CO seemed unable to block the cobalt surface from O_2 adsorbtion as it did on Pt.

Table 4.9. Conversion and selectivity results for Pt-Co/Al_2O_3 at 80 ˚C

Time (min)	% CO conversion	% O_2 Conversion	% Selectivity
0	98.7	100	49.4
10	98.8	100	49.4
20	98.9	100	49.4
30	99.0	100	49.5
40	99.0	100	49.5
50	99.0	100	49.5
60	99.0	100	49.5
70	99.1	100	49.5
80	99.1	100	49.5
90	99.1	100	49.5
100	99.1	100	49.6
110	99.2	100	49.6
120	99.4	100	49.6

Although the conversion over Pt-Co/Al_2O_3 is promising; it is still not sufficient for the fuel cell applications, where the CO concentration should be under 10 ppm level. This problem could be solved by adding another promoter to Pt-Co/Al_2O_3. Obviously Ce is the first choice since it is the second promoter in our starting catalyst Pt-Co-Ce/Al_2O_3. The results obtained in this catalyst were already presented in Table 4.2, indicating about 98-99% CO conversion.

Although CeO_2 has been widely suggested because of its promoting effect for CO oxidation by employing lattice oxygen (Son and Lane, 2001), it has no significant contribution to Pt-Co/Al_2O_3 under the conditions studied. This is; however, understandable since the, ceria is not active under 100 ˚C (Son, 2006).

In the light of the results obtained by Cho *et al*. (2006) and Grisel and Nieuwenhuys (2001), magnesium was used as the second promoter in Pt-Co/Al_2O_3.

Table 4.10. Conversion and selectivity results for Pt-Co-Mg/Al_2O_3 at 80 ˚C

Time (min)	% CO conversion	% O_2 conversion	% Selectivity
0	98.6	99.9	49.4
10	98.8	100	49.3
20	98.8	100	49.3
30	98.9	99.8	49.5
40	99.0	99.9	49.5
50	99.0	99.6	49.7
60	99.0	99.8	49.6
70	98.9	99.6	49.6
80	98.9	99.5	49.7
90	98.6	99.1	49.7
100	98.5	99.1	49.7
110	98.4	98.7	49.8
120	98.0	98.0	49.9

Cho *et al*. (2006) measured the basicity of Pt/Al_2O_3 and Pt-Mg/Al_2O_3 by means of CO_2 TPD. They found that Mg containing catalyst has the sites with lower basicity than Pt/Al_2O_3, which CO_2 desorbed within the range of 80-140 ˚C. That means, in Mg containing catalyst, CO_2 desorbs from the surface in low temperatures than non-containing Pt/Al_2O_3. It prevents CO_2 accumulation on catalyst surface even in low reaction temperatures.

According to Grisel and Nieuwenhuys (2001) addition of MgO to Al_2O_3 resulted in good reproducibility of highly dispersed Au catalyst Au/MgO/Al_2O_3. They also suggested that MgO might merely to stabilize small Au particles throughout the preparation and oxidation experiments.

However, there is no significant conversion change was obtained with addition of Mg to Pt-Co/Al_2O_3 as it can be seen from Table 4.10. This can be due to low reaction temperature since Cho *et al*. (2006) reported the light off temperature for Pt-Mg/Al_2O_3 as

125 ˚C. Like the other catalysts, the selectivity is also 50% in Pt-Co-Mg/Al_2O_3 throughout the reaction time.

Another alternative for the second promoter is manganese. Similar to CeO_2, MnO_x is also reported as a high oxygen storage capacity compound. However, there are only a few reported researches on MnO_x doped catalyst for PROX reaction (Ayastuy *et al*., 2006).

Table 4.11. Conversion and selectivity results for Pt-Co-Mn/Al_2O_3 at 80 ˚C

Time (min)	% CO conversion	% O_2 conversion	% Selectivity
0	53.9	44.2	60.9
10	50.2	41.2	60.9
20	47.4	38.6	61.4
30	45.1	37.2	60.6
40	43.4	35.6	60.9
50	41.9	34.7	60.3
60	40.6	33.8	60.0
70	39.4	32.8	60.0
80	38.3	32.1	59.6
90	37.2	31.5	59.0
100	36.5	30.8	59.3
110	36.0	30.2	59.6
120	36.0	30.2	59.6

The results for Pt-Co-Mn/Al_2O_3 are given in Table 4.11. It is clear that addition of Mn to Pt-Co/Al_2O_3 has decreased the CO conversion significantly. This is supported by Ayastuy *et al*. (2006) reporting that the low Mn containing (Mn wt%≤2) MnO_x/Pt/Al_2O_3 is less effective than Pt/Al_2O_3 over wide temperature range. There are two possible explanations for the low conversion. First, it is possible that Pt-Mn and Pt-Co interactions have some inhibiting effects on each other. The other reason may be the CO_2 adsorbtion on the surface of the catalyst due to low temperature.

The iron is also widely used as promoter and support for selective CO oxidation reaction. For instance Sirijaruphan *et al.* (2004) used 5wt.%Pt-0.5wt.%Fe/Al_2O_3 for selective CO oxidation. According to their results Fe addition did not change the BET surface area of the catalysts where absorbed CO amount decreased from 127 to 77 µmol CO/g_{cat}. The initial CO oxidation rate for Fe-promoted and non-promoted are 48.2 and 8.3 µmol CO/g_{cat}.s respectively. It is clear from the results of Sirijaruphan *et al.* (2004) Fe addition improve the CO oxidation activity of Pt/Al_2O_3.

Our results given in Table 4.12 supports this idea considering that CO conversion decreased slightly with the addition of Fe.

Table 4.12. Conversion and selectivity results for Pt-Co-Fe/Al_2O_3 at 80 ˚C

Time (min)	% CO conversion	% O2 conversion	% Selectivity
0	94.8	100	47.4
10	95.0	100	47.5
20	95.3	100	47.6
30	95.5	100	47.8
40	95.8	100	47.9
50	95.9	100	47.9
60	96.1	100	48.0
70	95.9	100	48.0
80	96.1	100	48.1
90	96.1	100	48.1
100	96.1	100	48.1
110	96.0	100	48.0
120	96.0	100	48.0

Kotobuki *et al*. (2006) obtained less than 10 per cent CO conversion with 4wt.%Pt-0.5 wt.% Fe/Al_2O_3 at 100 ˚C using sticohometric amount of O_2. The maximum conversion was 35 per cent at 200 ˚C.

The possible explanation of activity decrease by addition of Fe is given by Liu *et al.* (2002). They found that Fe prefers to interact with Pt rather than alumina. Since Co has also strong interaction with Pt, it is possible that Co and Fe may inhibit the interactions of each other.

The last alternative as second promoter is zirconium. The zirconium generally is used as support for selective CO oxidation reaction. Recently ZrO_2 coupled with CeO_2 as support in the form of $Ce_xZr_{1-x}O_2$ was reported by Ayastuy *et al.*(2006), suggesting that ZrO_2 enhances the oxygen storage capacity of CeO_2 by increasing the oxygen vacancies of the support due to high oxygen mobility in the solid solution.

Table 4.13. Conversion and selectivity results for Pt-Co-Zr/Al_2O_3 at 80 ˚C

Time (min)	% CO conversion	% O_2 conversion	% Selectivity
0	98.5	99.9	49.3
10	98.6	99.8	49.4
20	98.8	99.9	49.5
30	98.9	100	49.5
40	98.9	100	49.5
50	99.0	100	49.5
60	99.0	99.2	49.9
70	97.3	94.9	51.3
80	90.5	85.5	52.9
90	82.0	73.6	55.7
100	75.5	63.7	59.2
110	70.6	56.7	62.2
120	67.1	51.6	65.0

However, the addition of Zr did not improve our results as given in Table 4.13. On the contrary, there was a rapid deactivation of the catalyst, after one hour reaction time, which can be associated with low CO_2 desorption at 80 ˚C.

The CO conversion at the 60th minute time on stream for the six catalysts tested in this section is summarized in Figure 4.3. All the promoters except Mn appear to have a potential. It should be noted that, however, the catalyst containing Zr lost its activity after 60 minutes. Figure 4.4 was also presented to stress this fact.

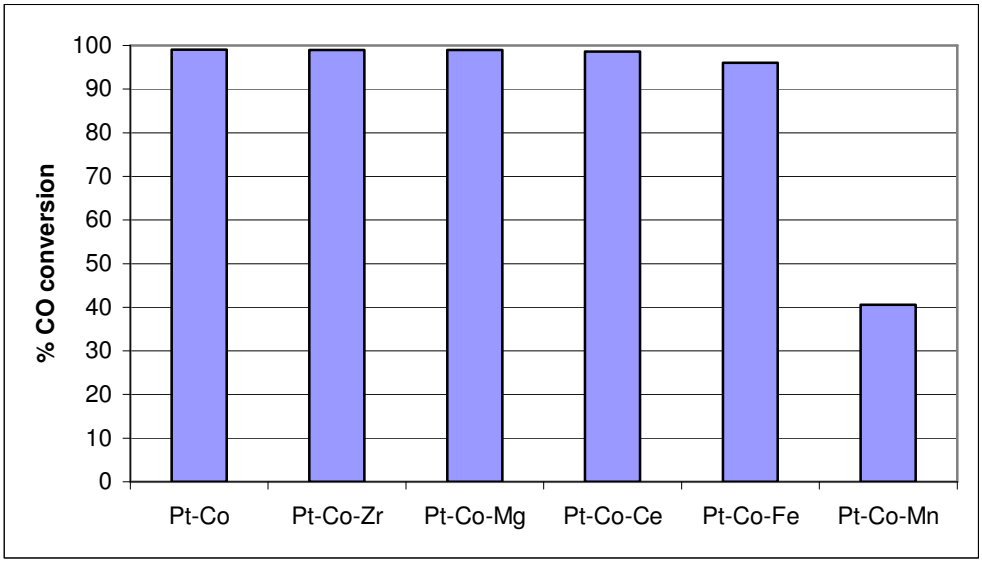

Figure 4.3. CO conversion at the 60th minute for Pt-Co-X/Al_2O_3 at 80 ˚C

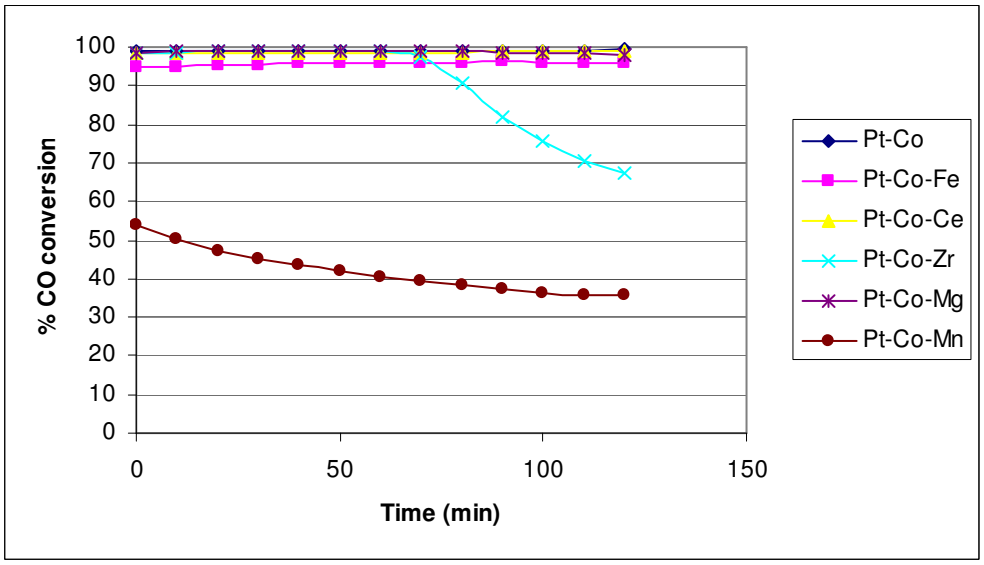

Figure 4.4. CO conversion comparison for Pt-Co-X /Al_2O_3 at 80 ˚C

4.1.4. 1.4wt.%Pt-1.25wt.%Co-1.25wt.%X/Al_2O_3 (X= None, Ce, Fe, Mg, Mn, Zr) at 110 ˚C

This time the temperature increased to 110 ˚C to see the effect of the promoter on CO conversion with the change of temperature with same feed stream that used at 80 ˚C (water and CO_2 free).

Pt-Co/Al_2O_3 again was tested first for the comparison, resulted about 96-98% conversion as shown in Table 4.14. Apparently increasing temperature from 80 to 110 ˚C has no significant effect on the CO conversion for as Table 4.9 and Table 4.14 compared.

According to Suh *et al*. (2005) there is also no significant activity change for Pt-Co/Al_2O_3 with 1wt.%Pt and 1.8wt.%Co loading over a wide temperature range 25-175 ˚C with feed stream 0.1% H_2, 0.01% CO, 0.0099% O_2.

Table 4.14. Conversion and selectivity results for Pt-Co/Al_2O_3 at 110 ˚C

Time (min)	% CO conversion	% O_2 Conversion	% Selectivity
0	96.7	100	48.3
10	96.7	100	48.4
20	97.1	100	48.5
30	97.4	100	48.7
40	97.6	100	48.8
50	97.7	100	48.9
60	97.8	100	48.9
70	98.0	100	49.0
80	98.1	100	49.0
90	98.1	100	49.1
100	98.2	100	49.1
110	98.3	100	49.1
120	98.3	100	49.1

On the other hand, CO conversion was reached to 100% for all catalysts contain two promoters for all the time on streams tested at 110 ˚C (Table 4.15). This suggests that all the second promoters tested enhanced the effects of Co.

It should be also noted that the oxygen was totally consumed in all tests meaning about 1.6% hydrogen was also oxidized. Although the hydrogen oxidation is undesired reaction, it can be tolerated at this level since the first concern for the fuel cell applications is to reduce the CO concentration in the feed to 10 ppm.

Table 4.15. Conversion and selectivity results for Pt-Co-X /Al_2O_3 at 110 ˚C (X=Ce, Mn, Mg, Fe, Zr)

Time (min)	% CO conversion	% O_2 Conversion	% Selectivity
0	100	100	50.0
10	100	100	50.0
20	100	100	50.0
30	100	100	50.0
40	100	100	50.0
50	100	100	50.0
60	100	100	50.0
70	100	100	50.0
80	100	100	50.0
90	100	100	50.0
100	100	100	50.0
110	100	100	50.0
120	100	100	50.0

The good way to understand the activity differences among Fe, Mg, Mn, Zr, Ce is to decrease Pt amount from 1.4wt.% to 0.7wt.%.

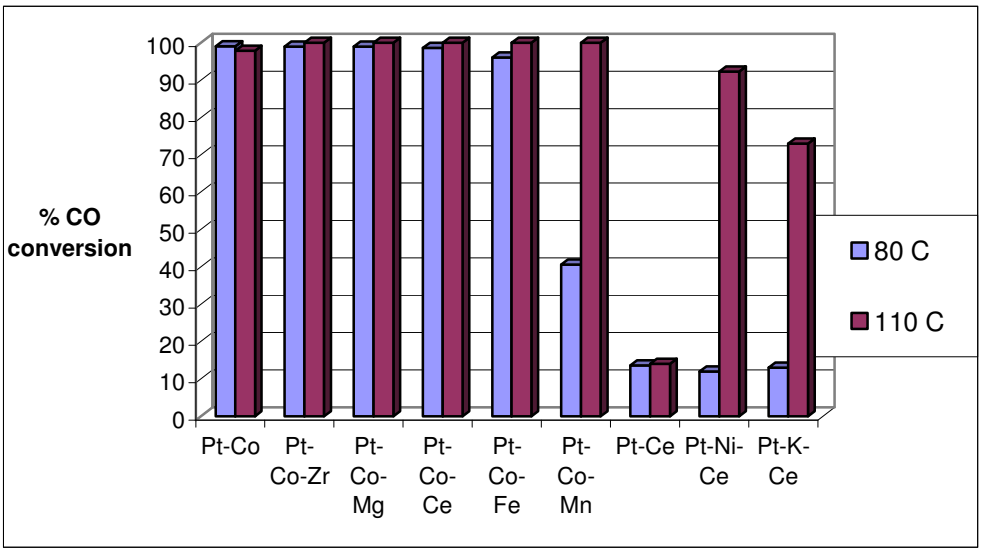

Figure 4.5. CO conversions at the 60th minute for Pt-Co-X/Al_2O_3 and Pt-X-Ce/ Al_2O_3 at 110 and 80 ˚C

4.1.5. 0.7wt.%Pt-1.25wt.%Co-1.25wt.%X/Al_2O_3 (X= None, Ce, Fe, Mg, Mn, Zr) at 110 ˚C

In this part of the thesis, 0.7wt.%Pt containing catalysts was tested by fixing Co as the first promoter and changing the other. The promoter amounts were also kept the same as in the case of 1.4wt.%Pt containing catalysts. 110 ˚C is selected as the reaction temperature because even 1.4wt.%Pt containing catalysts could not reach 100% conversion at 80 ˚C, indicating the new catalyst will not result full conversions either. Besides the actual feed to PEM fuel cell will contain some amount of water, hence the CO removal should be at a temperature above 100 ˚C to prevent the condensation of water.

The experiments were started with Pt-Co/Al_2O_3 catalyst as the bases, and the results that shown in Table 4.16 were obtained.

Table 4.16. Conversion and selectivity results for Pt-Co /Al_2O_3 at 110 ˚C (0.7wt.%Pt)

Time (min)	% CO conversion	% O_2 Conversion	% Selectivity
0	99.0	100	49.5
10	99.0	100	49.5
20	99.0	100	49.5
30	99.1	100	49.5
40	99.1	100	49.5
50	99.1	100	49.6
60	99.1	100	49.6
70	99.3	100	49.6
80	99.3	100	49.6
90	99.3	100	49.6
100	99.3	100	49.7
110	99.3	100	49.7
120	99.3	100	49.7

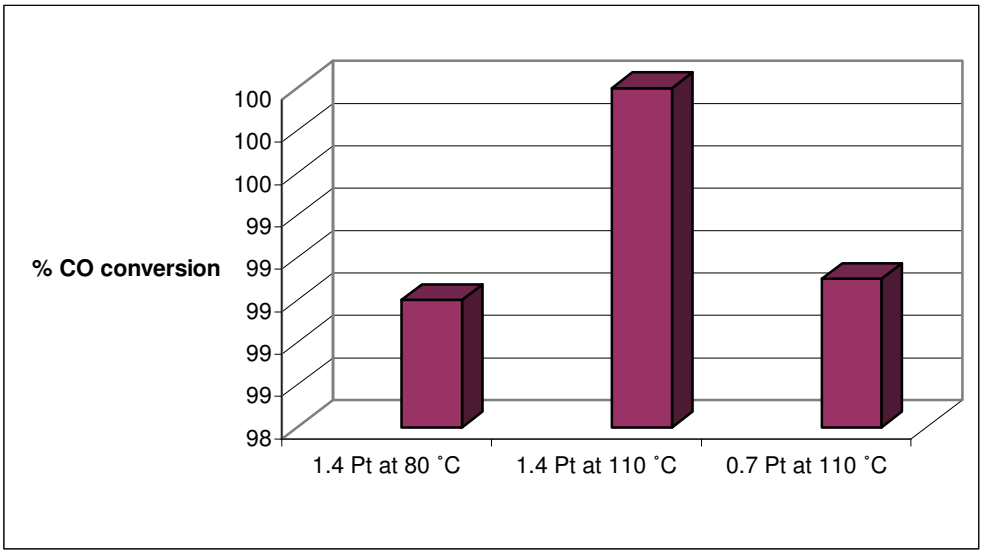

Figure 4.6. Comparison of Pt-Co/Al_2O_3 catalysts at the 60th minute

The decrease in the Pt amount has no significant effect on CO conversion as Table 4.16 and Table 4.14 was compared. The apparent slight increase with decreasing Pt content could be attributed to the experimental error. The selectivity towards CO is still 50%, which means undesired H_2 oxidation still occurs.

The results obtained for Pt-Co-Ce/Al_2O_3 with 0.7wt.% Pt content in Table 4.17 while the CO conversion at the 60 minute were compared with the results obtained 1.4wt.%Pt at 110 ˚C and 80 ˚C in Figure 4.7. Although CO conversion was quite high at even the Pt content reduced to half, it was not 100% as required for the fuel cell application.

Table 4.17. Conversion and selectivity results for Pt-Co-Ce/Al_2O_3 at 110 ˚C (0.7wt.%Pt)

Time (min)	% CO conversion	% O_2 Conversion	% Selectivity
0	98.2	100	49.1
10	98.2	100	49.1
20	98.4	100	49.2
30	98.5	100	49.3
40	98.6	100	49.3
50	98.6	100	49.3
60	98.7	100	49.4
70	98.7	100	49.4
80	98.7	100	49.4
90	98.8	100	49.4
100	98.8	100	49.4
110	98.8	100	49.4
120	98.8	100	49.4

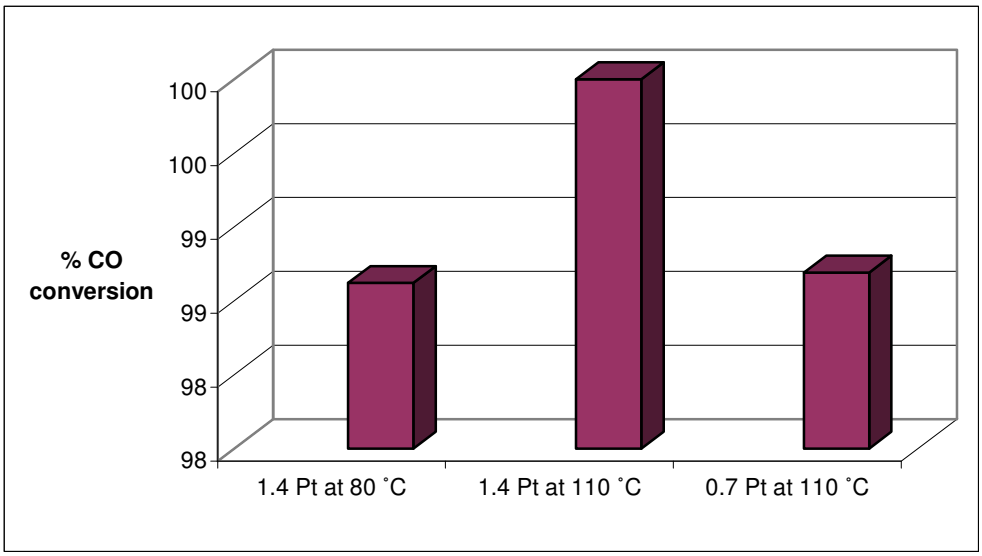

Figure 4.7. Comparison of Pt-Co-Ce/Al_2O_3 catalysts at the 60th minute

Next, Ce was replaced with Mg in the presence of 0.7wt.%Pt. The conversion and selectivity results Table 4.18. The CO conversion was again compared with the results obtained with 1.4 % Pt catalyst at 80 and 110 ˚C in Figure 4.8.Decreasing the Pt content to 0.7 decreased the CO conversion slightly (2 per cent) as shown in Table 4.18. There was still 100% oxygen conversion for 0.7wt.%Pt, meaning low selectivity towards CO (Table 4.18).

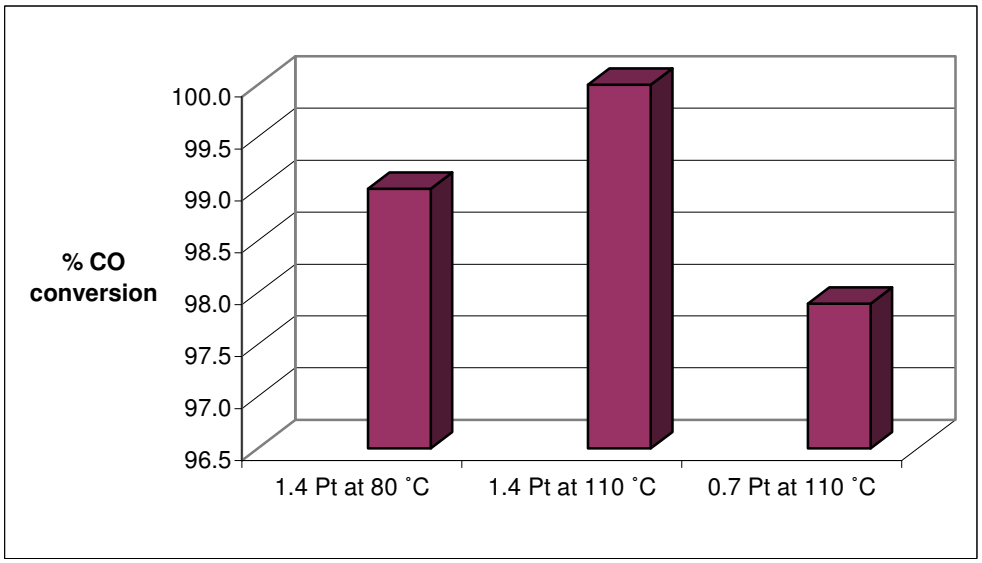

Figure 4.8. Comparison of Pt-Co-Mg/Al_2O_3 catalysts at the 60th minute

Table 4.18. Conversion and selectivity results for Pt-Co-Mg/Al_2O_3 at 110 ˚C (0.7wt.%Pt)

Time (min)	% CO conversion	% O_2 Conversion	% Selectivity
0	97.0	100	48.5
10	97.4	100	48.7
20	97.6	100	48.8
30	97.7	100	48.8
40	97.7	100	48.9
50	97.8	100	48.9
60	97.9	100	48.9
70	97.9	100	49.0
80	97.9	100	49.0
90	97.9	100	49.0
100	98.0	100	49.0
110	98.0	100	49.0
120	98.0	100	49.0

The results are given in Table 4.19 and CO conversion at the 60^{th} min compared with the results obtained over 1.4wt%Pt catalyst for Pt-Co-Mn/Al_2O_3. The activity of the catalyst was slightly decreased with decreasing Pt percent.

This decrease in CO conversion is negligible considering that the Pt content of the catalyst decreased to the half of its starting point. This makes the Pt-Co-Mn/Al_2O_3 a. promising choice for CO oxidation in the hydrogen rich streams.

Table 4.19. Conversion and selectivity results for Pt-Co-Mn /Al_2O_3 at 110 ˚C (0.7wt.%Pt)

Time (min)	% CO conversion	% O_2 Conversion	% Selectivity
0	97.5	100	48.8
10	97.6	100	48.8
20	97.7	100	48.8
30	97.8	100	48.9
40	97.9	100	48.9
50	98.0	100	49.0
60	98.0	100	49.0
70	98.0	100	49.0
80	98.0	100	49.0
90	98.3	100	49.1
100	98.7	100	49.4
110	98.7	100	49.4
120	98.8	100	49.4

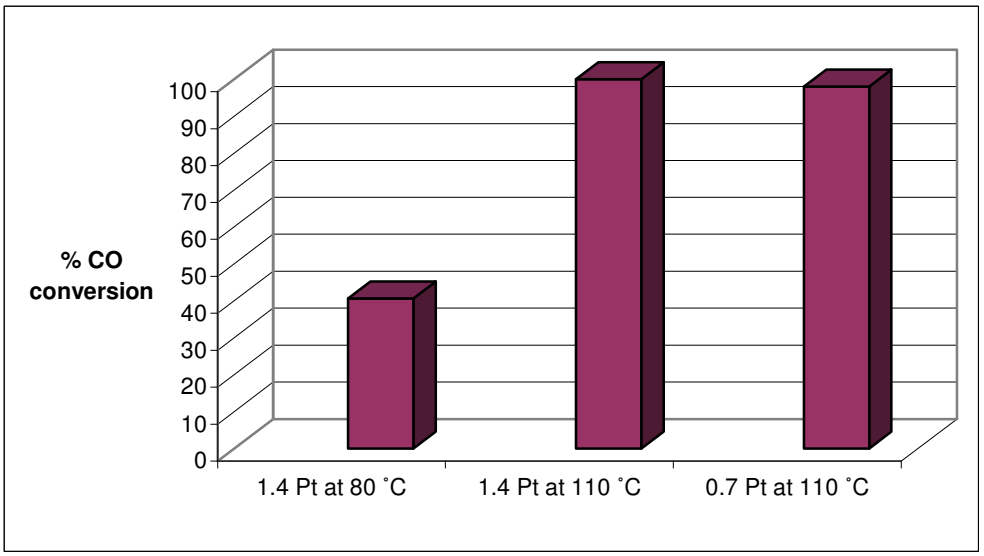

Figure 4.9. Comparison of Pt-Co-Mn/Al_2O_3 catalysts at the 60th minute

The results for Pt-Co-Fe/Al_2O_3 is given in Table 4.20 and Figure 4.10.

As mentioned for 1.4 Pt containing Pt-Co-Fe/Al_2O_3, Liu *et al*. (2002) suggests that, Fe prefers Pt rather than alumina. So when Pt amount decreased from 1.4wt.% to 0.7wt.% the competition between Co and Fe enhanced for Pt sites, which caused activity decreasing. Moreover, selectivity decreased from 50% to 41%, which cause more hydrogen loss due to hydrogen oxidation.

Table 4.20. Conversion and selectivity results for Pt-Co-Fe /Al_2O_3 at 110 ˚C (0.7wt.%Pt)

Time (min)	% CO conversion	% O_2 Conversion	% Selectivity
0	80.1	100	40.0
10	80.7	100	40.3
20	80.8	100	40.4
30	81.1	100	40.6
40	81.1	100	40.6
50	81.7	100	40.8
60	82.0	100	41.0
70	82.3	100	41.2
80	82.8	100	41.4
90	83.3	100	41.7
100	83.3	100	41.7
110	83.4	100	41.7
120	83.4	100	41.7

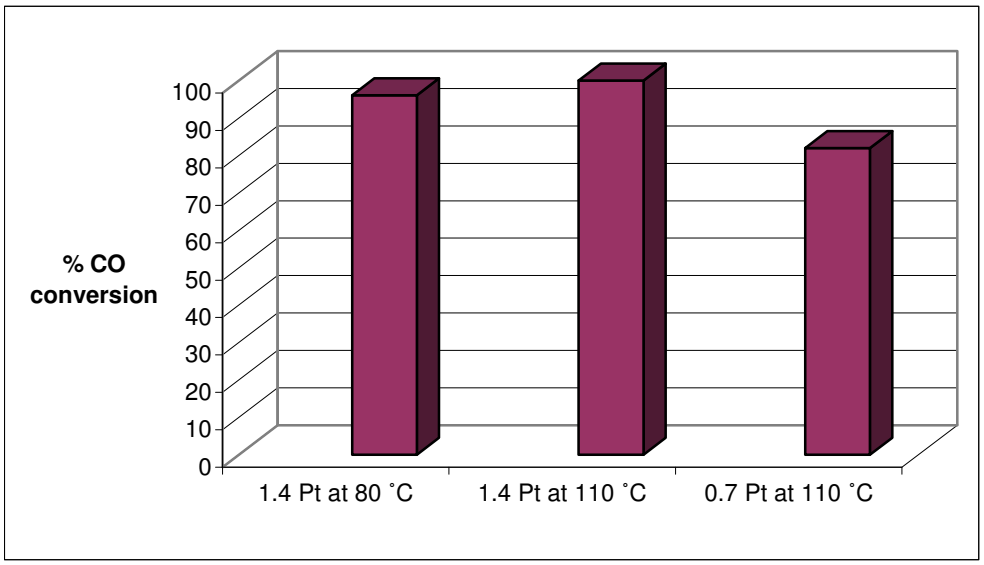

Figure 4.10. Comparison of Pt-Co-Fe/Al_2O_3 catalysts at the 60th minute

Finally, Pt-Co-Zr/Al_2O_3 was tested with 0.7wt.%Pt, and it was found that it is the least active catalysts among the catalysts tested with the CO conversion of less than 50%, making this catalyst one of the less promising choice. (Table 4.14 and Table 4.21).

Table 4.21. Conversion and selectivity results for Pt-Co-Zr /Al_2O_3 at 110 ˚C (0.7wt.%Pt)

Time (min)	% CO conversion	% O_2 Conversion	% Selectivity
0	54.4	57.6	47.0
10	50.4	53.7	46.9
20	48.2	52.2	46.1
30	46.2	52.4	44.0
40	46.0	52.8	43.5
50	45.0	51.7	43.5
60	43.7	52.8	41.4
70	44.0	51.5	42.8
80	44.5	53.5	41.6
90	43.0	55.0	39.2
100	42.0	56.4	37.2
110	41.7	58.4	35.7
120	41.2	60.3	34.2

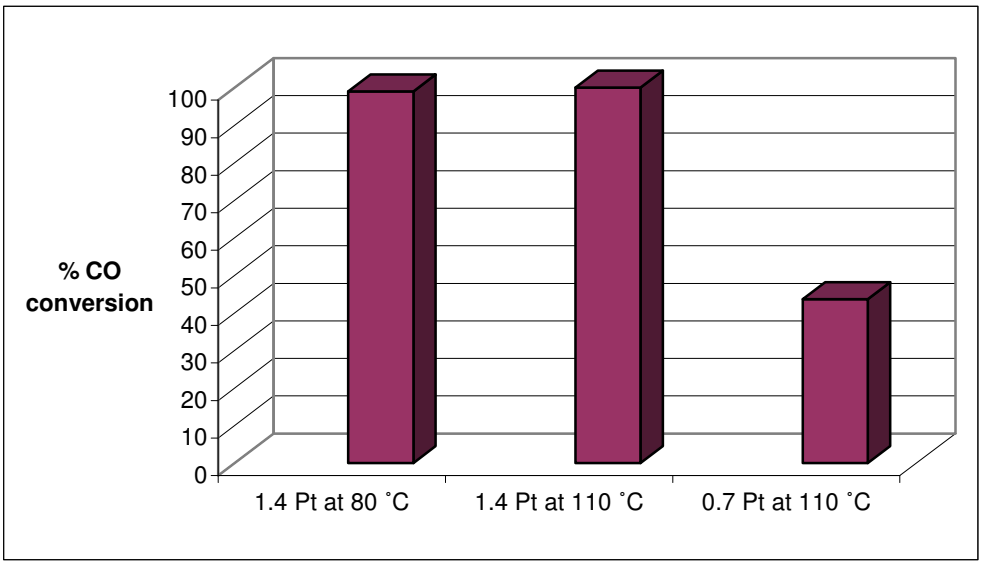

Figure 4.11. Comparison of Pt-Co-Zr/Al_2O_3 catalysts at the 60 min

4.2. Selective CO Oxidation in the Presence of CO_2

In real conditions, the gas stream contains 20-25% CO_2 after WGS reactor. A decrease in CO conversion is expected in the presence of CO_2. Then the catalyst were tested in the presence of 25% CO_2 keeping O_2, CO and H_2 content of feed constant, and adjusting the balance He. The possible effect of CO_2 on selective CO oxidation is that it can cause reverse water gas shift reaction, which produce CO by consuming H_2.

$CO_2 + H_2 \leftrightarrow CO + H_2O$	(4.1)

Again the first experiment was done with Pt-Co/Al_2O and results are given in Table 4.22. By addition of CO_2 the CO conversion is decreased with 7 per cent (Figure 4.12). That means our catalyst is active for reverse water gas shift reaction. However, Ko *et al.* (2006) did not observed any activity decrease for Pt-Co/Al_2O_3 with addition of CO_2.

Table 4.22. Conversion and selectivity results for Pt-Co/Al_2O_3 at 110 ˚C with CO_2 (0.7wt.%Pt)

Time (min)	% CO conversion	% O_2 Conversion	% Selectivity
0	92.6	100	46.3
10	92.4	100	46.2
20	92.5	100	46.2
30	92.6	100	46.3
40	92.8	100	46.4
50	92.8	100	46.4
60	93.0	100	46.5
70	93.1	100	46.6
80	93.3	100	46.7
90	93.4	100	46.7
100	93.3	100	46.6
110	93.5	100	46.7
120	93.3	100	46.7

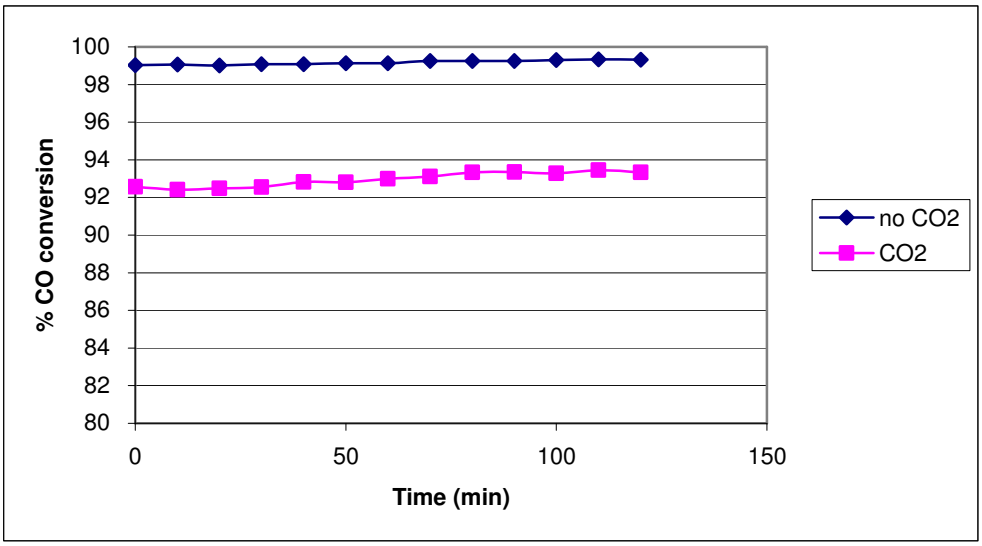

Figure 4.12. CO conversion comparison for Pt-Co/Al_2O_3 with CO_2 and without CO_2 in the feed stream (0.7wt.%Pt)

The effect of CO_2 on Pt-Co-Ce /Al_2O_3 was less pronounced than Pt-Co/Al_2O_3. Conversion decreased only 4 per cent. Unlike the experiments done without any CO_2, cerium addition has positive effect on CO conversion. The results are given in Table 4.23.

According to İnce *et al*. (2005) at 90 ˚C addition of 25% CO_2 causes a continuous decrease of CO conversion with time-on-stream for Pt-Co-Ce/Al_2O_3. At 30 min. the conversion dropped to about 85% decreases to 33% at 120 min, where without CO_2 100% conversion is obtained. At 110 ˚C, however, CO conversion remained 100% for 120 min. It seems that the equilibrium of CO oxidation is shifted towards CO in the presence of a high concentration of CO_2 as the product, which is balanced back with the increasing temperature. However, for longer reaction time, the activity dropped to 71% after 180 min. İnce *et al*. (2005) results are supporting ours, there is no activation decrease during the reaction time for our Pt-Co-Ce/Al_2O_3 catalyst as seen in Figure 4.16.

Table 4.23. Conversion and selectivity results for Pt-Co-Ce/Al_2O_3 at 110 ˚C with CO_2 (0.7wt.%Pt)

Time (min)	% CO conversion	% O_2 Conversion	% Selectivity
0	94.0	100	47.0
10	94.0	100	47.0
20	94.0	100	47.0
30	94.0	100	47.0
40	94.3	100	47.2
50	94.1	100	47.0
60	94.4	100	47.2
70	94.4	100	47.2
80	94.5	100	47.3
90	94.5	100	47.3
100	94.7	100	47.3
110	94.6	100	47.3
120	94.5	100	47.3

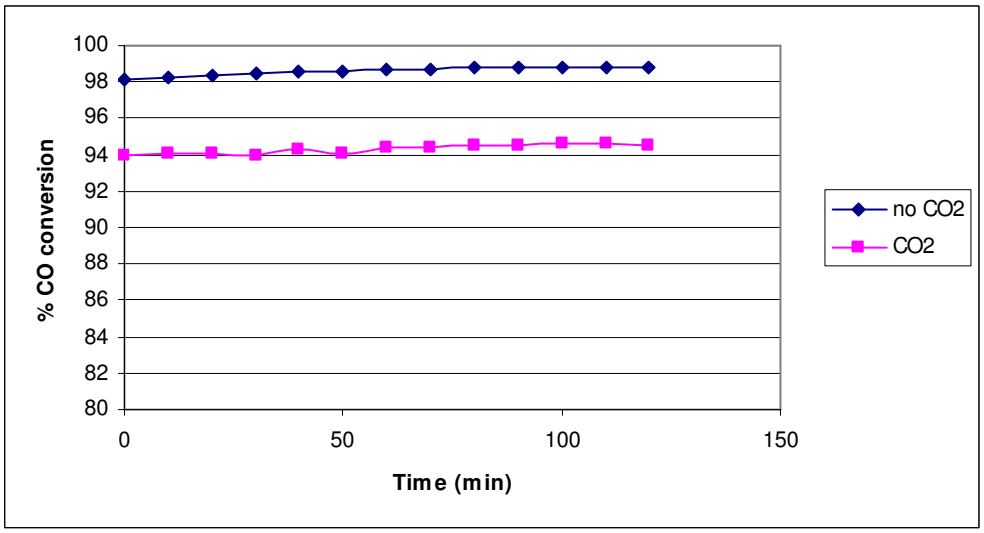

Figure 4.13. CO conversion comparison for Pt-Co-Ce/Al_2O_3 with CO_2 and without CO_2 in the feed stream (0.7wt.%Pt)

Table 4.24 contains the results for Pt-Co-Mg/Al_2O_3 catalyst with CO_2 in the feed stream. The effects of CO_2 addition to the feed on Pt-Co-Mg/Al_2O_3 was also about 3-4 per cent decrease as in the case of Pt-Co-Ce/Al_2O_3 (Figure 4.17).

This is quite small compare to the result obtained by Cho *et al*. (2006). At their work the activity lost for Pt-Mg/Al_2O_3 with addition of 20 vol.% was about 23% 100 ˚C in the presence of 1.0% CO, 0.75% O_2, 65% H_2 and rest He.

Table 4.24. Conversion and selectivity results for Pt-Co-Mg /Al_2O_3 at 110 ˚C with CO_2 (0.7wt.%Pt)

Time (min)	% CO conversion	% O_2 Conversion	% Selectivity
0	92.0	100	46.0
10	92.9	100	46.4
20	92.4	100	46.2
30	92.7	100	46.3
40	92.9	100	46.4
50	92.9	100	46.5
60	93.4	100	46.8
70	93.2	100	46.6
80	93.3	100	46.7
90	93.8	100	46.9
100	93.9	100	47.0
110	94.0	100	47.0
120	94.0	100	47.0

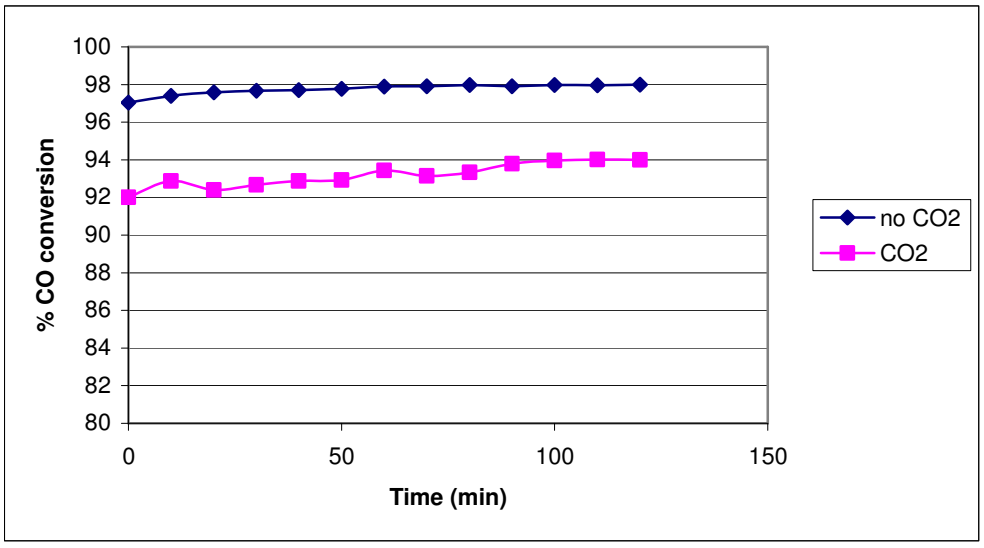

Figure 4.14. CO conversion comparison for Pt-Co-Mg/Al_2O_3 with CO_2 and without CO_2 in the feed stream (0.7wt.%Pt)

The CO conversion decreased more significantly in Pt-Co-Mn/Al_2O_3 when the 25% CO_2 added to the feed (Table 4.25). The decrease in activation was about 7-8% compare to 3-4% decreases in other catalysts (Figure 4.18).

Table 4.25. Conversion and selectivity results for Pt-Co-Mn /Al_2O_3 at 110 ˚C with CO_2 (0.7wt.%Pt)

Time (min)	% CO conversion	% O_2 Conversion	% Selectivity
0	89.5	100	44.7
10	89.6	100	44.8
20	90.0	100	45.0
30	90.1	100	45.1
40	90.4	100	45.2
50	90.3	100	45.2
60	90.4	100	45.2
70	90.5	100	45.2
80	90.2	100	45.1
90	89.6	100	44.8
100	89.7	100	44.9
110	90.0	100	45.0
120	90.0	100	45.0

This is supported by the fact the presence of MnO_x modifies the catalyst behavior substantially when CO_2 added: the temperature for maximum CO conversion is shifted to higher values (Ayastuy *et al.,* 2006).

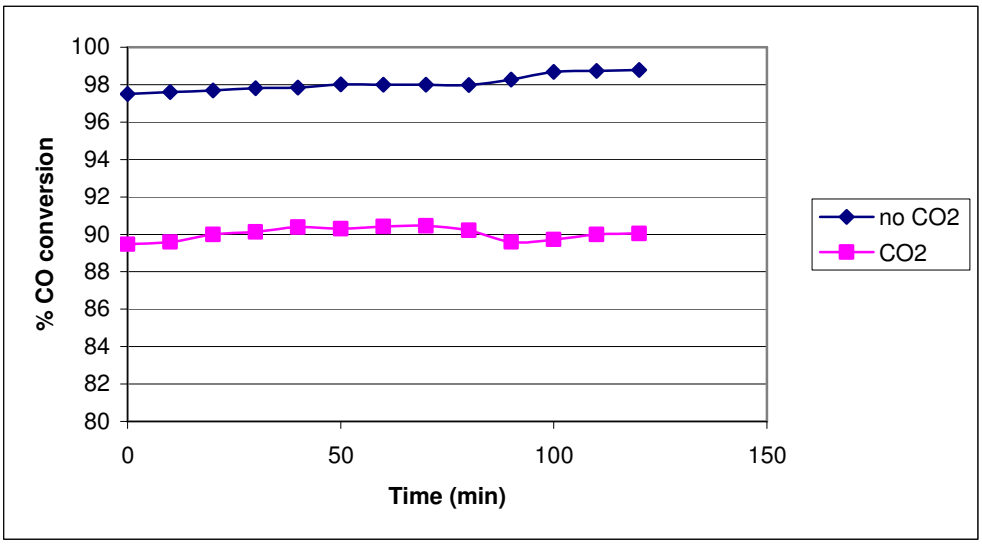

Figure 4.15. CO conversion comparison for Pt-Co-Mn/Al_2O_3 with CO_2 and without CO_2 in the feed stream (0.7wt.%Pt)

Like Pt-Co-Mn/Al_2O_3, the Pt-Co-Fe/Al_2O_3 catalyst was also affected by the CO_2 addition significantly. As shown in Table 4.26 and Figure 4.16 CO conversion decreased to 65%, which is more than 10% lower than the value obtained in the absence of CO_2. The O_2 conversion, on the other hand was still 100% making the selectivity lower.

According to results obtained by Kotobuki *et al*. (2006) CO_2 addition to gas stream hardly affects to the CO oxidation reaction on Pt-Fe/Mordenite catalyst. This means that activity of the catalyst was very poor to the reverse water-gas shift reaction, where CO_2 reacts with H_2O and produce CO. In the light off that, it is possible that our Pt-Co-Fe/Al_2O_3 catalyst is active for reverse water gas shift reaction at 110 ˚C.

Table 4.26. Conversion and selectivity results for Pt-Co-Fe/Al_2O_3 at 110 ˚C with CO_2 (0.7wt.%Pt)

Time (min)	% CO conversion	% O_2 Conversion	% Selectivity
0	66.0	100	33.0
10	66.3	100	33.2
20	65.5	100	32.8
30	65.2	100	32.6
40	65.1	100	32.6
50	65.5	100	32.7
60	65.6	100	32.8
70	65.8	100	32.91
80	66.3	100	33.1
90	66.5	100	33.2
100	66.4	100	33.2
110	67.0	100	33.5
120	67.3	100	33.6

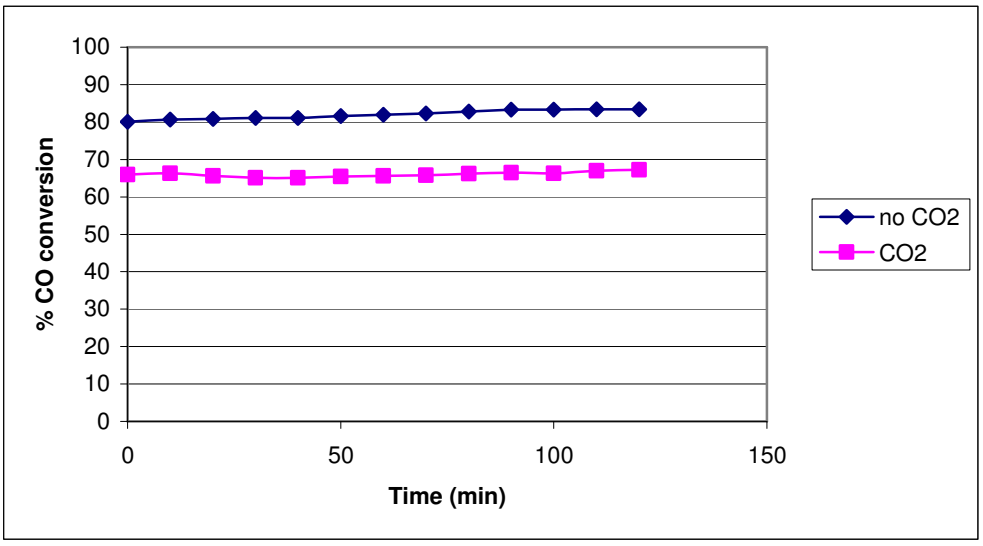

Figure 4.16. CO conversion comparison for Pt-Co-Fe/Al_2O_3 with CO_2 and without CO_2 in the feed stream (0.7wt.%Pt)

The CO conversion value for all the catalyst tested in the presence of CO_2 is summarized in Figure 4.17. The conversion was dropped in all the cases as expected. The decrease was more dramatic for the Fe containing catalysts. The other trend observed was that the relative activity of the catalysts was not changed with the addition of CO_2.

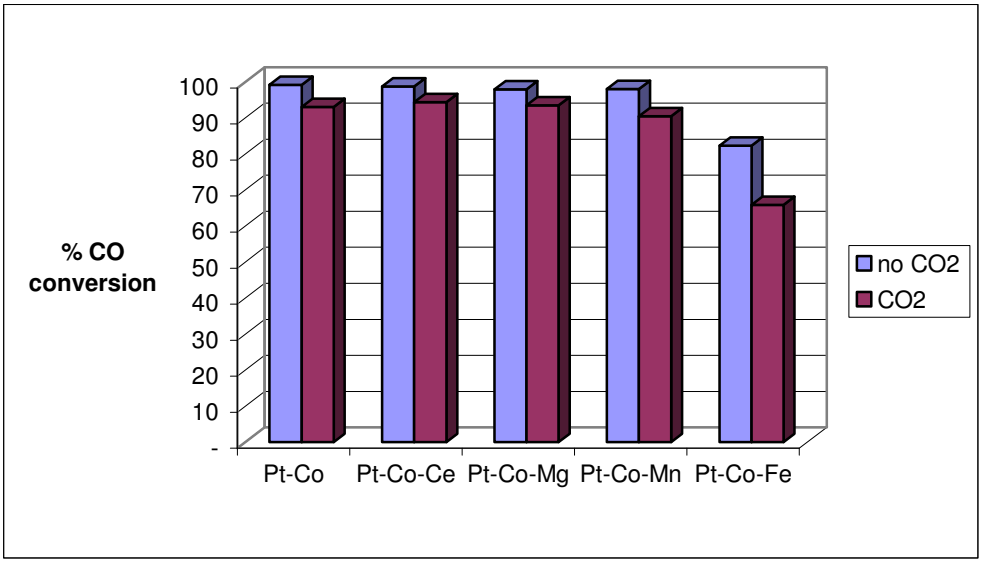

Figure 4.17. CO conversion comparison of Pt-Co-X/Al_2O_3 for gas stream with CO_2 and without CO_2 at 110 ˚C (0.7wt.%Pt)

4.3. Selective CO Oxidation in the Presence of CO_2 and H_2O

In this section the effect of 10% water vapor investigated since these components will be in the actual feed stream at about 10%. It is expected that the water addition will improve the CO conversion due to formation of OH group on the surface of the catalyst. These OH groups on the surface are facilitating CO removal (Manasilp *et al.,* 2002). Another reason for activity enhancement has been explained that the presence of water helps to remove CO by leading some water-gas shift activity.

The conversion and selectivity results for Pt-Co/Al_2O_3 are given in Table 4.27. Although, the water vapor addition improved the CO conversion, this improvement was not sufficient to balance the inverse effects of CO_2, hence the conversion was not as high as the value obtained in the absence of both CO_2 and water vapor (Figure 4.21).

Table 4.27. Conversion and selectivity results for Pt-Co/Al_2O_3 at 110 ˚C with CO_2 and H_2O (0.7wt.%Pt)

Time (min)	% CO conversion	% O_2 Conversion	% Selectivity
0	94.7	100	47.4
10	94.9	100	47.5
20	95.1	100	47.5
30	95.2	100	47.6
40	95.3	100	47.7
50	95.3	100	47.7
60	95.4	100	47.7
70	95.4	100	47.7
80	95.0	100	47.5
90	95.8	100	47.9
100	95.8	100	47.9
110	95.8	100	47.9
120	95.9	100	47.9

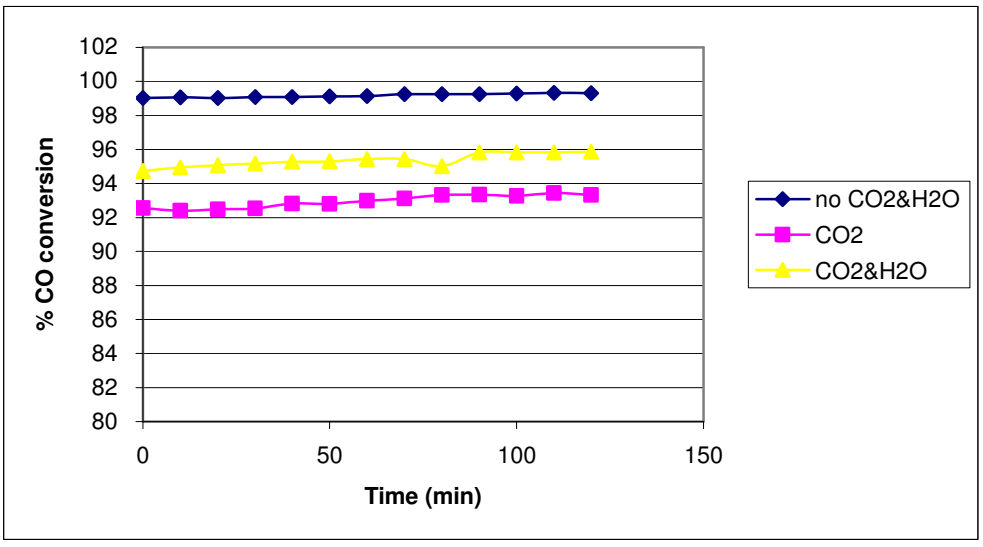

Figure 4.18. CO conversion for Pt-Co/Al_2O_3 catalyst with feed streams without CO_2&H_2O, with CO_2, and with CO_2&H_2O (0.7wt.%Pt)

Apparently the water gas shift activity and other effects of water vapor were not realized in this catalyst.

In the Table 4.28 the conversion and selectivity results are given for Pt-Co-Ce/Al_2O_3 catalyst. Similar to Pt-Co/Al_2O_3 the water has a significant positive effect of water on CO conversion over Pt-Co-Ce/Al_2O_3, however, that was also not sufficient to fully recover the inhibiting effect of CO_2 as illustrated in Figure 4.22.

İnce *et al*. (2005) found that the water vapor has positive effect on CO conversion on the 1.4wt.%Pt-1.25wt.%Co-1.25wt.%Ce/Al_2O_3. The water vapor prevents activity decrease due to addition of CO_2 to reaction stream for a long reaction periods (300 min). The CO conversion decrease to 71% after 180 min without water vapor, with water vapor the CO conversion kept at 100% for 300 min. Apparently 0.7.wt%Pt was not sufficient to produce a similar effects.

Table 4.28. Conversion and selectivity results for Pt-Co-Ce /Al_2O_3 at 110 ˚C with CO_2 and H_2O (0.7wt.%Pt)

Time (min)	% CO conversion	% O_2 Conversion	% Selectivity
0	96.0	100	48.0
10	96.0	100	48.0
20	96.0	100	48.0
30	95.8	100	47.9
40	96.0	100	48.0
50	95.9	100	48.0
60	96.1	100	48.0
70	96.6	100	48.3
80	96.8	100	48.4
90	97.0	100	48.5
100	97.0	100	48.5
110	97.6	100	48.8
120	98.1	100	49.0

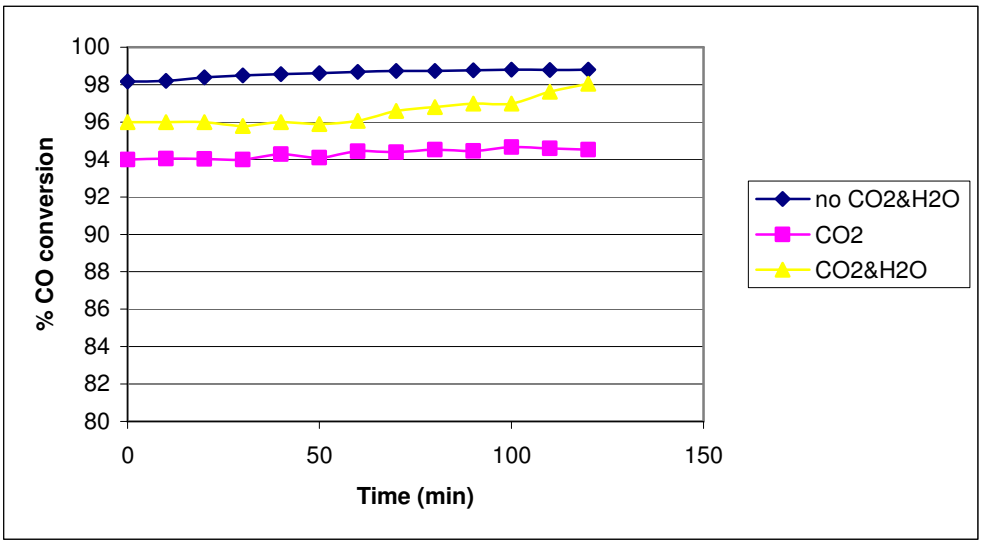

Figure 4.19. CO conversion for Pt-Co-Ce/Al_2O_3 catalyst with feed streams without CO_2&H_2O, with CO_2, and with CO_2&H_2O (0.7wt.%Pt)

For Pt-Co-Mg/Al_2O_3 the positive effect of water vapor was more pronounced than the other catalysts (Table 4.29). The CO conversion decreased up to 98.5% after 100 min reaction time, where at the same reaction time it was 93.97% for the gas stream containing 25% CO_2 and no H_2O. This is a conversion value that is slightly higher than the conversion obtained in the absence of both CO_2 and water indicating that water could eliminate the inverse effects of CO_2.

Table 4.29. Conversion and selectivity results for Pt-Co-Mg /Al_2O_3 at 110 ˚C with CO_2 and H_2O (0.7wt.%Pt)

Time (min)	% CO conversion	% O_2 Conversion	% Selectivity
0	96.5	100	48.3
10	96.5	100	48.3
20	97.0	100	48.5
30	97.0	100	48.5
40	97.1	100	48.6
50	97.2	100	48.6
60	97.2	100	48.6
70	97.3	100	48.6
80	97.1	100	48.6
90	98.4	100	49.2
100	98.5	100	49.3
110	98.5	100	49.3
120	98.6	100	49.3

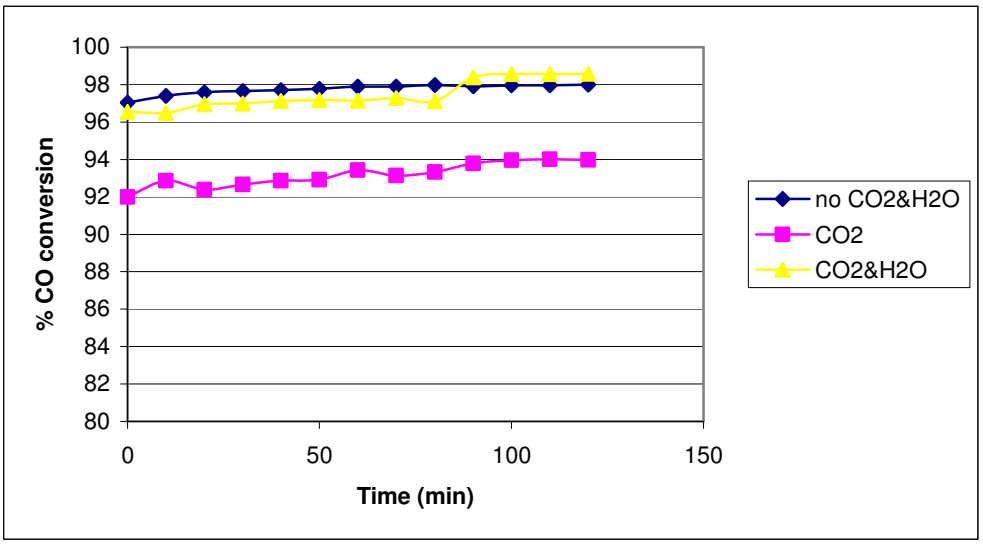

Figure 4.20. CO conversion for Pt-Co-Mg/Al_2O_3 catalyst with feed streams without CO_2&H_2O, with CO_2, and with CO_2&H_2O (0.7wt.%Pt)

Similarly Cho *et al.* (2006) found that addition of 2% volume water vapor to feed stream increased the CO conversion from 94.6% (with 20% CO_2) to 98.0%. However, increasing the amount of water vapor has negative effect on CO conversion; addition of 10% volume water vapor decreased the CO conversion to 87.9% at same condition for Pt-Mg/Al_2O_3.

Even water addition was not as effective as in the Pt-Co-Mg/Al_2O_3 catalyst, for Pt-Co-Mn/Al_2O_3 water recovered the CO_2 effect on CO conversion (Table 4.30). The CO conversion increased up to 97.8% after water vapor addition where it was 90% for CO_2 containing catalyst.

However, according to Ayastuy *et al*. (2007) 5% water vapor addition to MnO_x/Pt/Al_2O_3 has no significant effect on conversion for Mn content less than 2 wt.%. With increasing Mn content in catalyst water vapor shows a detrimental effect on conversion.

Table 4.30. Conversion and selectivity results for Pt-Co-Mn/Al_2O_3 at 110 ˚C with CO_2 and H_2O (0.7wt.%Pt)

Time (min)	% CO conversion	% O_2 Conversion	% Selectivity
0	97.0	100	48.5
10	97.1	100	48.6
20	97.2	100	48.6
30	97.2	100	48.6
40	97.3	100	48.7
50	97.4	100	48.7
60	97.0	100	48.6
70	97.4	100	48.7
80	97.3	100	48.6
90	97.3	100	48.7
100	97.0	100	48.5
110	97.7	100	48.9
120	97.7	100	48.9

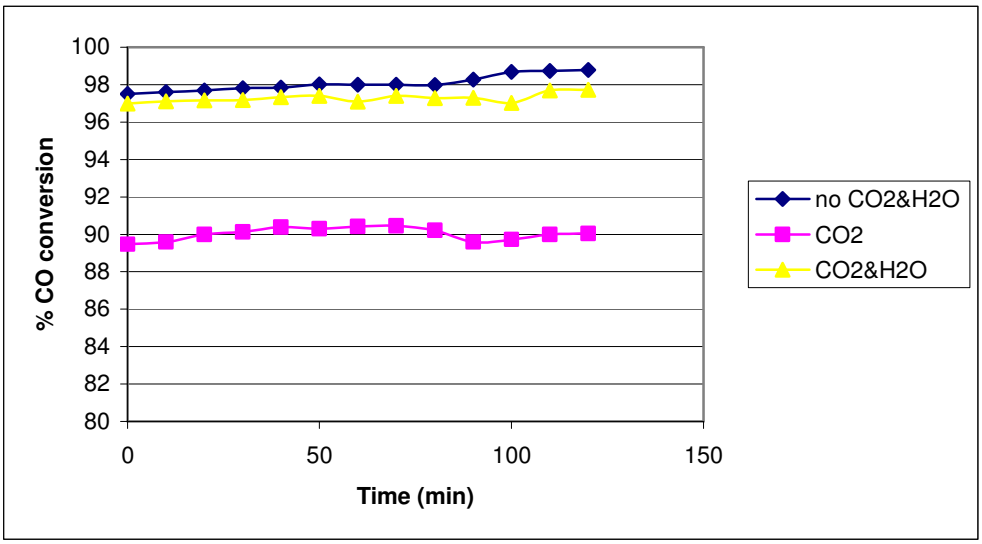

Figure 4.21. CO conversion for Pt-Co-Mn/Al_2O_3 catalyst with feed streams without CO_2&H_2O, with CO_2, and with CO_2&H_2O (0.7wt.%Pt)

The conversion and selectivity results for Pt-Co-Fe/Al_2O_3 in the presence of water and CO_2 are given in Table 4.31. It is clear that addition of water vapor increased the CO conversion; however, conversion was still under 80% which is not applicable for fuel cell applications (Figure 4.25)

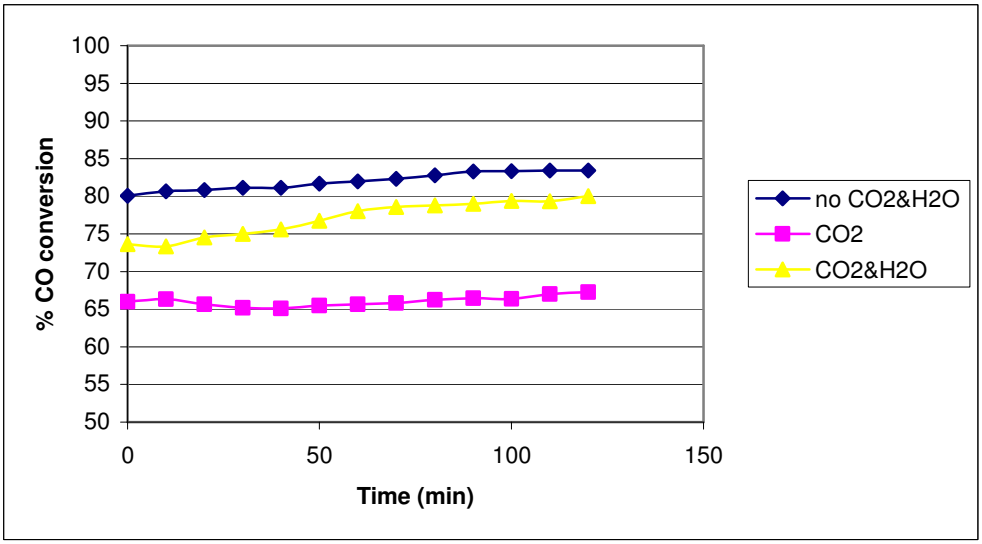

Figure 4.22. CO conversion for Pt-Co-Fe/Al_2O_3 catalyst with feed streams without CO_2&H_2O, with CO_2, and with CO_2&H_2O (0.7wt.%Pt)

Table 4.31. Conversion and selectivity results for Pt-Co-Fe/Al_2O_3 at 110 ˚C with CO_2 and H_2O (0.7wt.%Pt)

Time (min)	% CO conversion	% O_2 Conversion	% Selectivity
0	73.6	100	36.8
10	73.3	100	36.7
20	74.5	100	37.3
30	75.0	100	37.5
40	75.6	100	37.8
50	76.7	100	38.4
60	78.0	100	39.0
70	78.6	100	39.3
80	78.8	100	39.4
90	79.0	100	39.5
100	79.4	100	39.7
110	79.3	100	39.7
120	80.0	100	40.0

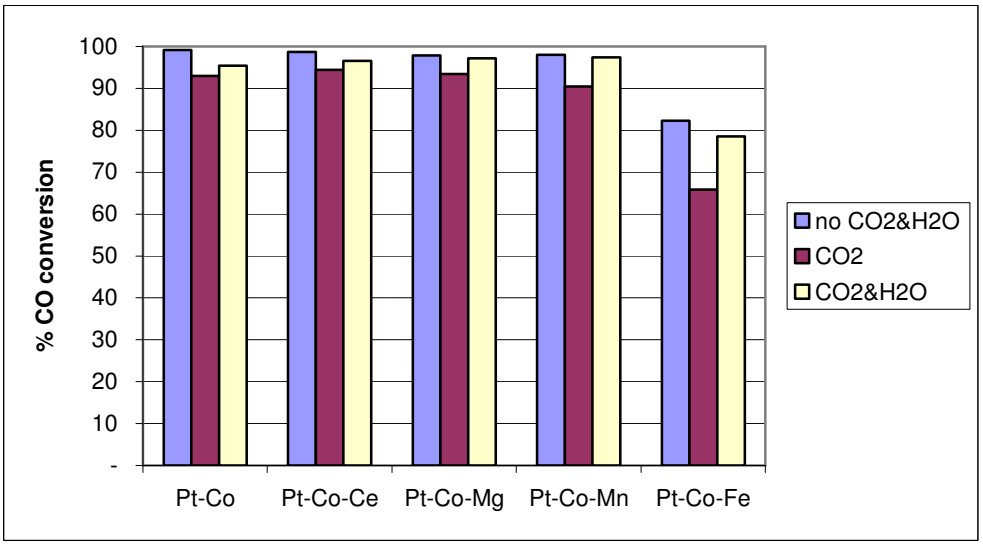

Figure 4.23. Catalysts comparison for 0.7wt.%Pt containing at 110 ˚C at the 60th minute

The CO conversion obtained at the 60th minute time on stream was summarized in Figure 4.23 for all the catalyst tested in the absence of CO_2 and water, in the presence of CO_2 only, and in the presence of both CO_2 and water.

It is clear that CO_2 had inverse affects in all the catalysts, and these effects were partially balanced with the addition of water.

4.3.1. Selective CO oxidation at 130 ˚C with 0.7wt.%Pt in the Presence of CO_2 and H_2O

The addition of Ce, Mg and Mn as a second promoter seem to improve the activity slightly in the actual feed conditions (in the presence of CO_2 and water) as discussed in section 4.3 and summarized in Figure 4.24. However the results were not yet sufficient for the fuel cell applications, hence all the catalysts (with 0.7wt.%Pt) were also tested at 130 ˚C in the presence of CO_2 and water.

Table 4.32 contains the results for Pt-Co/Al_2O_3.and the increase in the temperature did not improve the CO conversion (Figure 4.24). On the contrary, it causes a slight decrease (about 1%) which may be contributed to the experimental error.

Suh *et al.* (2005) also found that with increasing temperature after 100 ˚C, CO conversion decreases for Pt-Co/Al_2O_3. Another research done by Ko *et al*. (2006), on the other hand, showed that the maximum conversion obtained at 120 ˚C for Pt-Co/Al_2O_3, and the activity decrease occurs at higher temperatures.

Table 4.32. Conversion and selectivity results for Pt-Co/Al_2O_3 at 130 ˚C with CO_2 and H_2O (0.7wt.%Pt)

Time (min)	% CO conversion	% O_2 Conversion	% Selectivity
0	95.0	100	47.5
10	95.0	100	47.5
20	94.5	100	47.3
30	94.3	100	47.2
40	95.0	100	47.5
50	95.0	100	47.5
60	95.0	100	47.5
70	95.0	100	47.5
80	94.8	100	47.4
90	94.2	100	47.1
100	94.7	100	47.2
110	94.7	100	47.4
120	94.4	100	47.2

A similar activity lost was also observed over Pt-Co-Ce/Al_2O_3 catalysts when the temperature increased to 130 ˚C (see Figure 4.24 for the comparison with the results at 110 ˚C). Apparently the negative effects of temperature increases on Co was combined with the negative effects on Ce as observed by (Son, 2006) although they observation was after 200 ˚C.

Table 4.33. Conversion and selectivity results for Pt-Co-Ce/Al_2O_3 at 130 ˚C with CO_2 and H_2O (0.7wt.%Pt)

Time (min)	% CO conversion	% O_2 Conversion	% Selectivity
0	94.6	100	47.3
10	94.5	100	47.2
20	94.7	100	47.4
30	94.8	100	47.4
40	95.0	100	47.5
50	95.0	100	47.5
60	95.3	100	47.7
70	95.6	100	47.8
80	95.7	100	47.9
90	95.6	100	47.8
100	95.3	100	47.6
110	95.7	100	47.9
120	95.3	100	47.7

For Pt-Co-Mg/Al_2O_3 the conversion and selectivity results are given in Table 4.34. A significant activity decreased observed with increasing temperature for Pt-Co-Mg/Al_2O_3 as shown in the Figure 4.24 as the other catalysts.

Cho *et al*. (2006) also observed activity decrease for Pt-Mg/Al_2O_3 after 160 ˚C for feed stream containing 20% CO_2 and 2% H_2O.

Table 4.34. Conversion and selectivity results for Pt-Co-Mg/Al_2O_3 at 130 ˚C with CO_2 and H_2O (0.7wt.%Pt)

Time (min)	% CO conversion	% O_2 Conversion	% Selectivity
0	87.5	100	43.8
10	89.3	100	44.6
20	90.2	100	45.1
30	90.0	100	45.0
40	90.2	100	45.1
50	90.5	100	45.2
60	90.2	100	45.1
70	90.3	100	45.1
80	90.4	100	45.2
90	90.3	100	45.2
100	90.2	100	45.1
110	90.4	100	45.2
120	90.3	100	45.2

The experiment results for Pt-Co-Mn/Al_2O_3 at 130 ˚C are given in Table 4.35. As it can be seen from Figure 4.24 CO conversion was slightly decreased again with increasing temperature. Ayastuy *et al*. (2006) also observed the decreasing CO conversion with increasing temperature after 140 ˚C for MnO_x/Pt/Al_2O_3. However, they found that the activity change with temperature highly depends on Mn content. In higher Mn content activity decrease is more pronounced than the lower Mn content catalysts.

Table 4.35. Conversion and selectivity results for Pt-Co-Mn/Al_2O_3 at 130 ˚C with CO_2 and H_2O (0.7wt.%Pt)

Time (min)	% CO conversion	% O_2 Conversion	% Selectivity
0	91.7	100	45.9
10	91.8	100	45.9
20	91.3	100	45.7
30	91.4	100	45.7
40	92.9	100	46.5
50	92.2	100	46.1
60	92.0	100	46.0
70	92.9	100	46.5
80	92.9	100	46.4
90	92.9	100	46.5
100	92.2	100	46.1
110	91.2	100	45.6
120	92.9	100	46.5

Table 4.36 contains the conversion and selectivity results for Pt-Co-Fe/Al_2O_3. As can be seen from Figure 4.24 it is clear that activity decreases was the most dramatic over this catalyst as CO conversion dropped from 80% to 55% at the 60^{th} minute.

Table 4.36. Conversion and selectivity results for Pt-Co-Fe/Al_2O_3 at 130 ˚C with CO_2 and H_2O (0.7wt.%Pt)

Time (min)	% CO conversion	% O_2 Conversion	% Selectivity
0	51.3	100	25.7
10	51.2	100	25.6
20	51.3	100	25.7
30	51.5	100	25.8
40	51.5	100	25.8
50	53.3	100	26.7
60	54.3	100	27.1
70	54.5	100	27.3
80	55.3	100	27.6
90	56.6	100	28.3
100	56.9	100	28.4
110	57.5	100	28.8
120	58.1	100	29.0

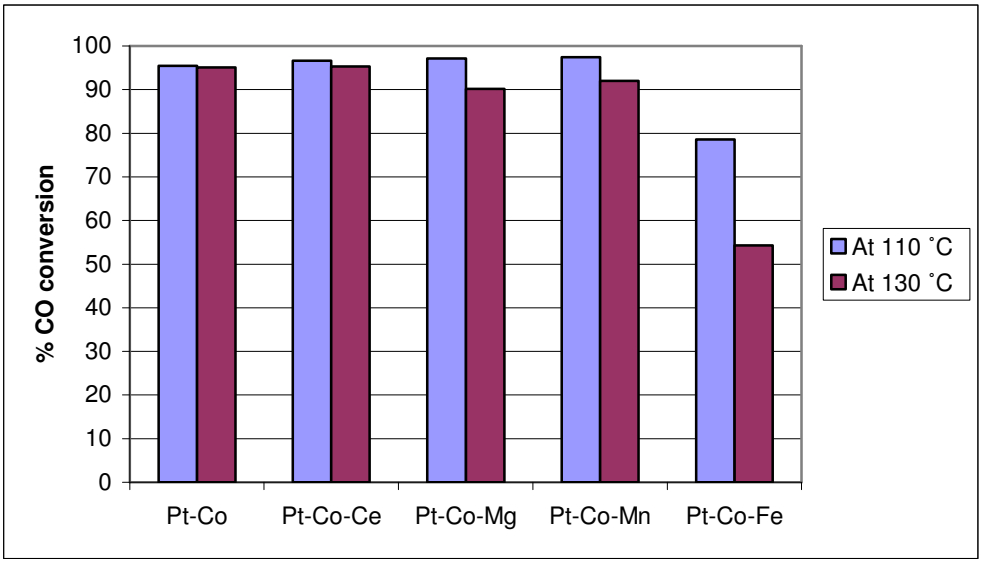

Figure 4.24. CO conversion comparison between 110 ˚C and 130 ˚C at the 60th minute (0.7wt.%Pt)

As a summary, the increasing temperature did not give the expected higher conversion any of the catalysts containing 0.7wt.%Pt. Another possible solution for increasing the conversion is to increase the Pt content.

4.3.2. Selective CO Oxidation for 1wt.%Pt- 1.25wt.%Co- 1.25wt.%Mg/Al_2O_3 at 110 ˚C

According to results obtained in the previous section, the Pt-Co-Mg/Al_2O_3 seems to be slightly better than the others. Hence this catalyst was prepared using 1wt.%Pt and tested at 110 ˚C with feed stream contains both CO_2 and H_2O. Table 4.37 contains the conversion and selectivity results for this catalyst indicating 100% CO conversion at all the time on streams up to 120 minutes. This results make the Pt-Co-Mg/Al_2O_3 as a promising choice since 1wt.%Pt contain can be still considered as low compare to many catalysis suggested in the literature.

Table 4.37. Conversion and selectivity results for Pt-Co-Mg/Al_2O_3 at 110 ˚C with CO_2 and H_2O (1wt.%Pt)

Time (min)	% CO conversion	% O_2 Conversion	% Selectivity
0	100	100	50
10	100	100	50
20	100	100	50
30	100	100	50
40	100	100	50
50	100	100	50
60	100	100	50
70	100	100	50
80	100	100	50
90	100	100	50
100	100	100	50
110	100	100	50
120	100	100	50

5. CONCLUSIONS AND RECOMMENDATIONS

5.1. Conclusions

The purpose of this work was to investigate the second promoter effect on Pt-Ce/Al_2O_3 and Pt-Co/Al_2O_3 for selective CO oxidation reaction considering the promising results obtained using Pt-Co-Ce/Al_2O_3 in a previous study (İnce *et al.,* 2005). All catalysts were prepared using impregnation method containing 1.25wt.% promoter(s) and 0.7 or 1.4wt.%Pt. The Co, Ni and K were used as the first promoter (as addition to Ce) while Ce Mg, Mn, Fe, and Zr were tried as the second promoter (in addition to Co). The desired result was to create a catalyst that is capable of 100% CO conversion with reasonable selectivity with a reaction temperature range between 80 and 200 ˚C. The conclusions drawn were summarized in three group based on the reaction gas stream used.

The conclusions of the experiments using gas streams containing 1% CO, 1% O_2, 60% H_2 and balance He (in the absence of CO_2 and H_2O);

- Only 1.25wt.% Co addition to 1.4wt.%Pt-1.25wt.%Ce/Al_2O_3 improved the CO conversion at 80 ˚C, while Ni and K addition was proven to be ineffective. At 110 ˚C, on the other hand all K or Ni addition improves the activity significantly, however with only Co addition 100% CO conversion was obtained.
- The addition of 1.25wt.% Ce, Mg, Mn, Fe or Zr to 1.4wt.%Pt-1.25wt.%Co/Al_2O_3 had no effects on conversion at 80 ˚C. However, at 110 ˚C all produced 100% CO conversion, where for 1.4wt.%Pt-1.25wt.%Co/Al_2O_3 catalyst's maximum conversion was 98.3%, indicating that the second promoters have some positive impacts.
- For 0.7wt.%Pt containing catalysts Co was set to be the one of the promoter and the effects of Ce, Mg, Mn, Fe or Zr is investigated, due to low conversions of K and Ni. The experiments done at 110 ˚C, addition of Fe and Zr had negative effect on conversion, where the others have no significant effect.

The conclusions of the experiments using gas streams containing 1% CO, 1% O_2, 60% H_2, 25% CO_2 and balance He (in the absence H_2O);

- In all catalysis containing 0.7wt.%Pt and 1.25wt.% of promoter(s), CO conversion decreased with addition of CO_2. In Fe containing catalysts, the decreased was more pronounced than the others ones.
- 0.7wt.%Pt-1.25wt.%Co-1.25wt.%Ce/Al_2O_3 showed slightly better activity for selective CO oxidation than the other catalysis.

The conclusions of the experiments using gas streams containing 1% CO, 1% O_2, 60% H_2, 25% CO_2, 10% H_2O and balance He;

- The addition of H_2O increased conversion in all catalysts containing 0.7wt.%Pt and 1.25wt.% of promoter(s).
- The H_2O addition had recovered the negative effect of CO_2 only over 0.7wt.%Pt-1.25 wt.%Co-1.25wt.%Mg/Al_2O_3 catalyst. However, the conversion was still below the desired 100% although it was close (98.5%).
- The increase of reaction temperature to 130 ˚C did not improve the CO conversion. At the contrary the conversion decreased in all the all catalysts..
- 1wt.%Pt-1.25wt.%Co-1.25wt.%Mg/Al_2O_3 produced 100% CO conversion at 110 ˚C, and it was found be good candidate for CO oxidation in hydrogen rich stream for the fuel cell applications.

5.2. Recommendations

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

- As mentioned in Chapter 2 catalyst preparation is an important factor for catalytic activity. Sequential impregnation can be employed instead of co-impregnation method, especially for 0.7wt.% Pt containing catalyst.
- The temperature programmed reduction test should be employed in order to find the best reduction temperature.

- To understand the surface parameters, BET surface area, XRD, TEM, and SEM tests should be done.
- The stability of the catalysis should be tested for industrial use. The optimum catalyst obtained, should be tested in industrial scales using reactors at real sizes.

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