KINETICS OF LOW TEMPERATURE CO OXIDATION OVER ACTIVATED CARBON SUPPORTED Pt-SnO_x CATALYSTS

by

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to my family

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ABSTRACT

KINETICS OF LOW TEMPERATURE CO OXIDATION OVER ACTIVATED CARBON SUPPORTED Pt-SnO_x CATALYSTS

This experimental study comprises a kinetic study of low-temperature CO oxidation both in the absence and presence of H_2 over air-oxidized activated carbon supported 1wt.%Pt-0.25wt.%SnO_x catalyst prepared by the sequential impregnation method. Kinetic experiments were conducted at 383 K and atmospheric pressure, and different sets of CO and O_2 concentrations each at different space times and catalyst loadings were used. Molar reactant concentrations in the feed were varied between 1-10 per cent CO and 1-4 per cent O_2 in the absence of hydrogen. The effect of the presence of H_2 in the feed on CO oxidation rates was also investigated. In preferential CO oxidation experiments, the H_2 concentrations used were between 10-45 per cent.

Experimental rate data were used to estimate kinetic parameters of the power law model by using the method of initial rates. The investigation of power law kinetics gave reaction orders of 0.87 and 0.13 with respect to carbon monoxide and oxygen, respectively, and a reaction rate constant of 1.37 $\mu mol.mg^{-1}.min^{-1}.atm^{-1}$ at 383 K. The variance of experimental error was found to be 0.017 $(\mu mol.g^{-1}.s^{-1})^2$ for this rate expression, and the agreement between experimentally measured and model predicted rates was good. Finally, the addition of H_2 to the feed did not alter reaction kinetics, but an almost four fold enhancement was observed in CO oxidation rates over 1wt.%Pt-0.25wt.%SnO_x/AC2 at all the feed H_2 concentrations studied.

ÖZET

AKTİF KARBON DESTEKLİ Pt-SnO$_x$ KATALİZÖRÜ ÜZERİNDE DÜŞÜK SICAKLIK KARBON MONOKSİT OKSİDASYONU KİNETİĞİ

Bu deneysel araştırma, ardışık emdirilme yöntemiyle hazırlanmış ve hava ile yükseltgenmiş aktif karbon destekli ağırlıkça 1%Pt-0.25%SnO$_x$ içeren katalizör üzerinde hidrojenin varlığında ve yokluğunda yapılan düşük sıcaklık karbon monoksit oksidasyonu kinetik çalışmasını içermektedir. Kinetik deneyler 383 K sıcaklıkta ve atmosferik basınç altında yapılmış, kinetik ölçümlerde farklı karbon monoksit ve oksijen yüzdeleri ile her bir derişim için farklı reaktörde kalma süreleri ve katalizör miktarları kullanılmıştır. Hidrojenin yokluğunda yapılan deneylerde, beslemedeki molar reaktant derişimleri karbon monoksit için yüzde bir ile on, oksijen için ise yüzde bir ile dört arasında değiştirilmiştir. Ayrıca reaktör girdisinde hidrojen bulunmasının karbon monoksit oksidasyon hızlarına etkisi de araştırılmıştır. Seçimli karbon monoksit oksidasyonu deneylerinde kullanılan hidrojen yüzdeleri 10-45 arasındadır.

Deneysel hız verileri kullanılarak üssel hız denkleminde yer alan kinetik parametreler başlangıç hızları yöntemi ile hesaplanmıştır. Karbon monoksit ve oksijenin reaksiyon mertebeleri sırasıyla 0.87 ve 0.13, 383 K sıcaklığındaki reaksiyon hız sabiti ise 1.37 $\mu mol.mg^{-1}.dk^{-1}.atm^{-1}$ olarak belirlenmiştir. Bu hız ifadesi için deneysel hata varyansı 0.017 $(\mu mol.g^{-1}.s^{-1})^2$ olarak bulunmuş olup deneysel olarak ölçülen ve kinetik parametrelerle yeniden hesaplanan hızlar arasındaki uyum iyidir. Reaktör girdisine yüzde 10-45 oranında hidrojen eklenmesi, ağırlıkça 1%Pt-0.25%SnO$_x$/AC2 katalizörü üzerindeki reaksiyon kinetiğini değiştirmemekle birlikte ölçülen CO oksidasyonu hızlarını yaklaşık dört kat arttırmıştır.

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LIST OF SYMBOLS/ABBREVIATIONS

C_i	Concentration of component i
E_a	Activaton energy
F_i	Flow rate according to component i
k_i^b	Rate constant of backward reaction of step i
k_i^f	Rate constant of forward reaction of step i
k_i	Rate constant of reaction step i
K_i	Adsorption constant of component i
N	Number of experiments
p	Parameter values
P_i	Partial pressure of component i
R	Universal gas constant
$-r_i$	Reaction rate according to component i
S_i	Adsorption site of component i
S	Selectivity
T	Temperature
W_{cat}	Weight of catalyst
W/F	Space time
x_i	Conversion of component i
$\Delta H°$	Enthalpy of the reaction at the standart conditions
$\theta_{O\bullet}$	Coverage of adsorbed oxygen on ceria sites
α	Reaction order with respect to carbon monoxide
β	Reaction order with respect to oxygen
σ^2	Variance of experimental error
AC	Activated Carbon
AFC	Alkaline Fuel Cell
ATR	Autothermal Reforming
DMFC	Direct Methanol Fuel Cell

ELS	Electronic Lodgment Service
ER	Eley-Rideal
GC	Gas Chromatograph
LHHW	Langmuir-Hinshelwood-Hougen-Watson
MCFC	Molten Carbonate Fuel Cell
NMRO	Noble Metal Reducible Oxide
PAFC	Phosphoric Acid Fuel Cell
PEFC	Polymer Electrolyte Fuel Cell
PEM	Proton-Exchange Membrane
PEMFC	Proton Exchange Membrane Fuel Cell
PGM	Platinum Group Metals
PO	Partial Oxidation
PROX	Preferential Oxidation
ppm	Parts per million
r-WGS	Reverse Water-Gas Shift Reaction
SEM	Scanning Electron Misroscopy
SOFC	Solid Oxide Fuel Cell
SPFC	Solid Polymer Fuel Cells
SR	Steam Reforming
TCD	Thermal Conductivity Detector
TOF	Time of Flight
TOS	Time-on-Stream
TPO	Thermal Programmed Oxidation
UHV	Ultra High Vacuum
WGS	Water-Gas Shift Reaction

1. INTRODUCTION

Hydrogen can play a major role in future energy system. The individual parts of hydrogen energy system such as production, delivery, storage, and conversion are closely interrelated. Among them, hydrogen storage is one of the bottlenecks for the applications in mobile systems (Züttel, 2003). Although the catalytic control of automotive engine emissions is well established (Matsumoto, 2004), the limits of the technology are such that increasingly harsh legislative demands can only be met by alternative approaches to the problem. One favored technology is based on fuel cells (Farrauto, 2005; Ruettinger *et al.,* 2003), which are about twice as efficient as the internal combustion engine and produce little or no primary pollutants (CO_2, NO_x, hydrocarbons). The most successful fuel cells are those powered by hydrogen. As a result, attention has been focused on the conversion of presently available hydrocarbon fuels to hydrogen, either on board a vehicle or at a service station (Trimm and Önsan, 2001).

Hydrogen can be produced from hydrocarbon fuels or alcohols by various reforming processes. The product streams of reforming processes usually contain mixtures of hydrogen, carbon monoxide, carbon dioxide and steam. The carbon monoxide level in the gas has to be reduced to a level below 20 ppm in order to avoid poisoning of the catalyst at the fuel cell electrodes (Song, 2002; Armor, 1999). Conventionally, this is achieved by a multi-step purification train including high and low temperature water gas shift (WGS) reactors and a preferential oxidation reactor (PROX) or a methanation unit for the removal of carbon oxides (Song, 2002; Trimm, 2005).

The fuel cell operates at around 80-100°C. Thus, the preferred temperatures for removal of CO are in the region of 80-120°C (Trimm and Önsan, 2001). The preferential oxidation of CO in a H_2-rich atmosphere has attracted increasing interest because of its application in Polymer Electrolyte Membrane Fuel Cell (PEMFC) technology, for the removal of CO from fuel gases produced by reforming processes (Lemons, 1990; Kawatsu, 1998). CO impurity contained in the reformer gas (60-65 per cent H_2, 10-15 per cent H_2O, 1-2 per cent CO, rest CO_2) is known to poison commonly used anode catalysts (e.g. Pt, Pt-Ru) and decrease the efficiency of the fuel cell to an unacceptable level (Gottesfeld, 1990).

Golunski (1998) has described the CO oxidation unit in several stages, most probably to avoid the risk of overheating due to the exothermicity of the reaction. CO levels were reduced from >2 per cent to 10 ppm at the expense of 6 per cent of the hydrogen output.

Much effort has been directed to the kinetics of CO oxidation. Both Eley-Rideal (gaseous CO reacting with adsorbed oxygen) and Langmuir-Hinshelwood (adsorbed CO reacting with adsorbed oxygen) mechanisms have been used, with early work favoring the Eley-Rideal (ER) mechanism. Currently, Langmuir-Hinshelwood mechanism is favored (Salomons *et al*., 2007). The experimental data published and the models proposed to correlate the data have been summarized. Most models are of the Langmuir-Hinshelwood type, and the analysis of the kinetic data indicate that the rate limiting step is the surface reaction between the adsorbed species (Shalabi *et al*., 1996).

One promising catalyst used for low-temperature CO oxidation is Pt/SnO_2, with or without promoters (Herz *et al.*, 1993; Hoflund *et al.,* 1995). Low-temperature CO oxidation over oxidized and non-oxidized activated carbon supported Pt-SnO_x catalysts has been studied in order to characterize these catalysts and to determine their activity in low-temperature CO oxidation (Aksoylu *et al*., 2000b). Later, a series of activated carbon supported Pt-SnO_x and Pt-CeO_x catalysts were studied for determining their catalytic properties and activity for selective CO oxidation (PROX) in hydrogen-rich streams (Özkara and Aksoylu, 2003; Şimşek *et al*., 2007). Kinetic measurements on preferential CO oxidation in a H_2-rich atmosphere (PROX) over a bimetallic, carbon supported PtSn catalyst revealed high activity and CO oxidation selectivity at temperatures as low as 0-80 °C which was superior to commercial Pt/Al_2O_3 (Schubert *et al*., 2001). The kinetics of low-temperature CO oxidation was studied over 1wt%Pt-0.25wt%SnO_x supported on HNO_3-oxidized activated carbon (AC3) using a wide range of CO and O_2 concentrations (Baltacıoğlu *et al*., 2007). On the other hand, kinetics of low-temperature CO oxidation was also studied over air-oxidized activated carbon (AC2) supported Pt-CeO_x catalyst both in the presence and in the absence of hydrogen (Gülyüz, 2007).

The aim of this work was to study the kinetics of low-temperature CO oxidation over air-oxidized activated carbon (AC2) supported 1wt%Pt-0.25wt%SnO_x to find out the effect of support pretreatment on catalyst performance. Kinetic studies have been conducted in the initial rates region at a temperature of 383 K using pure and mixed feed experiments in the same range as those used for the 1wt%Pt-0.25wt%SnO_x/AC3 catalyst. A power function rate expression has thus been established with experimentally determined reaction orders with respect to the reactants. Effect of the presence of H_2 in the feed has also been investigated.

Chapter 2 contains literature survey including information about fuel cells and H_2 production followed by detailed information about low-temperature CO oxidation as well as preferential CO oxidation in the presence of hydrogen. Plausible mechanisms for low-temperature CO oxidation are also summarized in Chapter 2. The experimental procedures used in the present study are presented in Chapter 3. The results obtained in the experiments and related discussions can be found in Chapter 4. Finally, Chapter 5 consists of the conclusions drawn from the present study and recommendations for future work.

2. LITERATURE SURVEY

2.1. Fuel Cells

Fuel cells are a viable alternative for clean energy generation (Gray and Petch, 2000; Edwards *et al.*, 1998). They have seen remarkable progress in the last decade and are being developed for transportation, as well as for both stationary and portable power generation. The advances in fuel cells and their supporting technology have been spurred by the recognition that these electrochemical devices have the potential for both high efficiency and lower emissions (McNutt and Johnson, 1999).

Fuel cell systems being considered for stationary applications range from large central power stations, to distributed-power generators that can be used in buildings and residences in urban areas, to small systems located in remote areas. The inclination of central power plants toward fuel cell systems is driven by the need to improve efficiency and durability (fuel cell systems will have fewer moving parts) and to lower emissions. Higher energy efficiency itself will lead to a reduction in carbon dioxide emissions, to which many countries committed themselves at the global warming conferences (UN Framework Convention on Climate Change) in Kyoto, Japan (1992) and Buenos Aires, Argentina (1998). Fuel cells will also lower such atmospheric pollutants as carbon monoxide, nitrogen oxides (NO_x), and sulfur oxides (SO_x) (Ahmed and Krumpelt, 2001).

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

- Solid polymer fuel cells (SPFC), also known as proton-exchange membrane (PEM) fuel cells operating at 80 °C,
- Alkaline fuel cells (AFC) operating at ~100 °C,
- Phosphoric acid fuel cells (PAFC) for ~200 °C operation,
- Molten carbonate fuel cells (MCFC) operating at ~650 °C,
- Solid oxide fuel cells (SOFC) for high temperature operation, 800-1100 °C,
- Proton exchange (or polymer electrolyte) membrane fuel cells (PEMFC),

- Direct methanol fuel cells (DMFC),
- Regenerative fuel cells,
- Zinc air fuel cells,
- Protonic ceramic fuel cells (PCFC).

While the higher temperature fuel cells (MCFC and SOFC) are being demonstrated for central power plants, polymer electrolyte fuel cells (PEFCs) predominate among the smaller power generators being developed for residential units and for propulsion power in automobiles. Its low operating temperature enables the PEFC to start up and provide electric power very quickly, an essential requirement in automotive use, and one of the major reasons why it was selected for automotive propulsion power (Ahmed and Krumpelt, 2001).

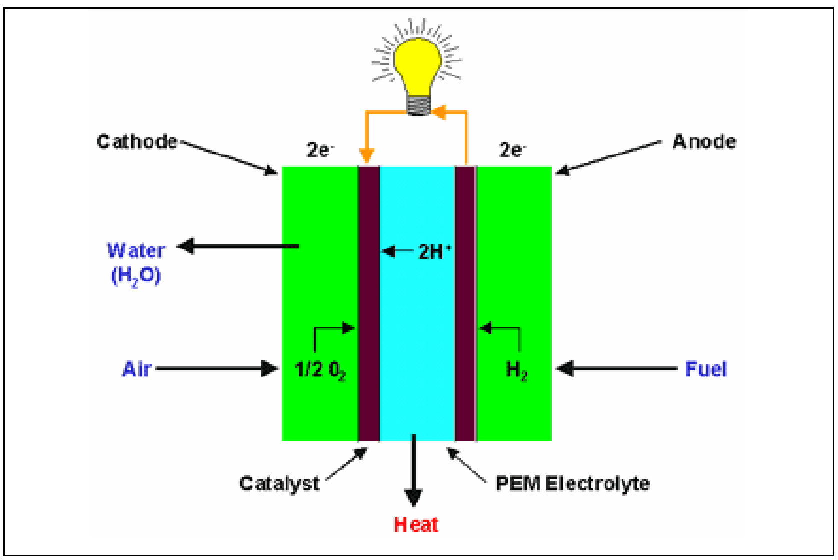

Figure 2.1. Image of PEM fuel cell (Fuel Cell, 2007)

Since proton exchange membrane fuel cell (PEMFC) is clean, quiet, energy efficient, modular, and capable of quick start-up, it appears to be the most promising fuel cell technology. The core of the fuel cell comprises two electrodes (anode and cathode) separated by a polymer exchange membrane. Each electrode is coated on one side with a catalyst, which causes the hydrogen fuel to separate into free electrons and protons (positive hydrogen ions) at the anode. The free electrons are conducted in the form of usable electrical current through an external circuit. The protons migrate through the membrane electrolyte to the cathode, where the catalyst causes the protons to combine with oxygen from the air and electrons from the external circuit to form water and heat.

Overall, fuel is oxidized electrochemically and each cell produces approximately 0.6-0.7 eV only (Trimm and Önsan, 2001). The reactions at the anode and the cathode, respectively, are:

$$H_2 \leftrightarrow 2H^+ + 2e \text{ (anode process)} \tag{2.1}$$

$$O_2 + 4e + 4H^+ \leftrightarrow 2H_2O \text{ (cathode process)} \tag{2.2}$$

2.2. H_2 Production

Hydrogen would be the ideal fuel for most fuel cells. On the other hand, there is not yet an infrastructure for wide distribution of hydrogen. Consequently, numerous research groups in the world are actively involved in fuel processing for on-site (stationary) or on-board (mobile) production of synthesis gas and hydrogen for fuel cells. Hydrocarbon fuels, such as natural gas and gasoline, have wide distribution network and thus are promising as fuels for on-board and on-site production of synthesis gas and hydrogen for fuel cells. However, they often contain sulfur compounds that need to be removed, because sulfur can poison the catalysts in fuel processing train and in electrodes. The reformate from hydrocarbon reforming at high temperatures also contain high concentrations of carbon monoxide that must be removed or converted prior to use in low-temperature fuel cells, particularly proton-exchange membrane fuel cells (Katikaneni *et al.*, 2002).

The production of hydrogen occurs in three steps:

- Hydrogen is usually produced by autothermal reforming (ATR) of a hydrocarbon (fuel+$H_2O \leftrightarrow CO_x + H_2$), where without water it is partial oxidation (POX) and without oxygen it is steam reforming (SR) (Son and Lane, 2001). Depending on the type of anode the CO concentration in the hydrogen feed must be under 1-100 ppm (Wootsch *et al.*, 2004).

- The homogeneous water-gas shift (WGS) reaction ($CO + H_2O \leftrightarrow CO_2 + H_2$) has been employed for 40 years in industrial processes for H_2 production (Lei *et al.,* 2005; Rhodes *et al.,* 1995). The role of the WGS reaction is to increase the H_2 yield and to decrease the CO concentration (Rhodes *et al.,* 1995; Keiski *et al.*, 1996). It is essential to adjust $CO{:}H_2$ ratio to the desired value (Trimm, 2005). The gas at the outlet of a reformer and water gas shift reactor typically contains 45-75 vol. per cent H_2, 15-25 vol. per cent CO_2, a few vol. per cent H_2O, traces of unconverted fuel and, unfortunately, 0.5-1 vol. per cent CO (Sedmak *et al.*, 2004). This amount of CO is still high and needs to be removed (Pozdnyakova *et al.*, 2006a).

- A final reaction for CO preferential oxidation (CO-PROX: $CO + 0.5O_2 \rightarrow CO_2$) is capable to completely remove the CO down to a limit of 20 ppm (Trimm, 2005).

2.3. Carbon Monoxide Removal

Many studies have shown the negative effect of carbon monoxide on the performance of the polymer electrolyte membrane fuel cells (Kim and Lim, 2002). Trace amounts of CO in the H_2-PEMFC deteriorate the efficiency of the fuel cell Pt catalyst via CO poisoning, accelerated at CO levels higher than 50 ppm CO. While more CO-tolerant fuel cell catalysts are being developed, efforts in developing catalysts to selectively remove the 0.5–1 per cent CO from the H_2-rich reformate prior to reaching the fuel cell are continuing (Acres *et al.*, 1997; Gunner *et al.,* 1999; Rohland and Plzak, 1999).

Reduction to ppm levels can be achieved in several ways. One obvious route is to diffuse hydrogen through a Pd/Ag membrane (McCabe and Mitchell, 1987), but this requires a high-pressure differential and fairly high temperatures. It is also expensive. By analogy with the ammonia synthesis train, carbon monoxide could be methanated, but this consumes 3 molecules of hydrogen per molecule of CO and results in the emissions of methane—an unwanted greenhouse gas. Methanation of carbon dioxide could also occur. As a result, attention has been focused on selective oxidation of carbon monoxide, which has to be achieved in the presence of CO_2 and H_2O, with minimum H_2 oxidation (Trimm and Önsan, 2001). Among these, preferential oxidation (PROX) is the lowest cost method to reduce CO to the desired level without excessive hydrogen consumption (Ghenciu, 2002).

The fuel conversion system involves a partial oxidation process coupled to or followed by a water–gas shift system. Exit gas temperatures required to achieve reasonably low concentrations of CO from the water–gas shift are of the order of 150–250°C. The fuel cell operates at ~80–100°C. Thus, the preferred temperatures for removal of CO are of the order of 80–100°C (Trimm and Önsan, 2001).

2.3.1. Low-Temperature CO Oxidation

The oxidation of CO is a most important reaction in emission control, particularly in the cleanup of vehicle emissions (Armor, 1992).

PROX catalysts need to be active and selective; the catalyst should oxidize 0.5–1 per cent CO to less than 50 ppm without oxidizing a large amount of hydrogen at the selected process temperature, usually between the outlet temperature of the WGS reactor and the inlet temperature of the fuel cell (~80 °C). The reformate containing mostly hydrogen, its oxidation leads to a decrease in the overall fuel efficiency. Depending on the nature of the catalyst, the water produced through hydrogen oxidation may affect catalyst activity. The lower the selectivity of the process, the higher the required ratio O_2/CO has to be in order to completely oxidize CO to CO_2 (Ghenciu, 2002).

This is true for most conventional catalysts, which are not active at low temperatures and low O_2/CO ratios because O_2 and CO compete for the same sites. O_2 adsorption has more severe site requirements in that it must dissociate. Under these conditions, CO adsorption dominates the metal surface and prevents O_2 adsorption and surface reaction.

Over base–metal oxide catalysts, on the other hand, O_2 is held too strongly to be displaced by CO at low temperatures. Thus, an efficient low-temperature CO oxidation catalyst should accommodate both CO chemisorption and the simultaneous dissociative adsorption of O_2. This has suggested the use of composite materials with different components, each having activity for one or other of these functions (Herz *et al.*, 1993).

In recent years, there has been a considerable interest in the use of catalysts, which contain both metals and metal oxides. Nobel Metal Reducible Oxide (NMRO) catalysts 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 a metal oxide like SnO_2, MnO_x, Fe_2O_3, CeO_x and distributing them over a support such as Al_2O_3 or SiO_2. Interactions across the metal-oxide interface have been suggested to be important, as carbon monoxide adsorbed on the metal reacts with oxygen associated with the oxide (Kang *et al.*, 2003). The noble metal chemisorbs CO and the reducible oxide provides sites that dissociatively adsorb O_2. Since CO and O_2 do not compete for the same adsorption sites, the inhibition of low-temperature CO oxidation by CO is eliminated (Akın *et al*., 2001).

Low-temperature noble metal reducible oxide catalysts 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 synergistic interaction between the two catalyst components may be responsible for the high efficiency observed at low temperatures (Trimm and Önsan, 2001).

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

2.3.2. Low-Temperature CO Oxidation in H_2-Rich Gas Streams

The low-temperature CO oxidation has been reviewed and it is documented in the literature, however, the number of publications on the selective CO oxidation in the presence of H_2 has only recently increased as a result of the interest in PEM fuel cell technology (Ghenciu, 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).

Removing carbon monoxide in a hydrogen rich stream is a critical issue and an unavoidable problem when hydrocarbons are used as the hydrogen source for fuel cells. Among the various methods to remove CO selectively, catalytic oxidation is considered as one of the most plausible and economical options (Choi and Stenger, 2004). It consists of a catalytic process aiming to selectively convert CO to CO_2 with air injection in the presence of large amounts of H_2 (around 50 vol. per cent) that must be oxidized in as much as possible limited amounts (Caputo *et al*., 2006).

In the CO selective oxidation reaction system, two oxidation reactions occur. The desired reaction is CO oxidation and the undesired one is the water formation (Choi and Stenger, 2004). In an oxygen deficient atmosphere in a PROX reactor, carbon monoxide can be formed again by the reverse water–gas shift reaction (r-WGS) (Kolb *et al*., 2007). Also, in addition to the reactions of CO and H_2 oxidation, it is also necessary to consider the reverse water gas shift reaction in the kinetic model of the PROX reactor (Choi and Stenger, 2004).

$$H_2O + CO \leftrightarrow CO_2 + H_2 \quad \Delta H^o = -\ 41.1\ \text{kJ/mol} \tag{2.3}$$

There are three obvious possibilities that can be considered. It may be possible to find a catalyst that adsorbs CO but not H_2, and hence favors selective oxidation of CO. It may be possible to operate at a temperature where CO is oxidized and H_2 is not. Finally, it may be possible to find a catalyst where both CO and H_2 are oxidized, but kinetic parameters lead to preferential CO oxidation at the cost of only small amounts of H_2 oxidation (Trimm and Önsan, 2001).

Water content is one of the most critical factors in the PROX reaction and is very important for proper operation of the fuel cell stack. Contradictory viewpoints still exist as to whether water acts positively for CO oxidation or not. Many research groups have reported that water enhances the CO oxidation reaction for a certain range of temperatures. Choi and Stenger (2004) reported that the CO conversion and selectivity enhanced by the addition of water when the reactor temperature is above 200 °C. Their simulations showed that the reverse WGS is most likely the cause of this enhancement. On the other hand, Korotkikh and Farrauto reported that the addition of small amounts of water (3 mol per cent) decreased the CO conversion. Grisel and Nieuwenhuys (2001) and Avgouropoulos *et al.* (2002) also reported that H_2O had a detrimental effect on the CO oxidation activity of Au based catalyst (Choi and Stenger, 2004).

2.3.3. Catalysts Used for Carbon Monoxide Removal

The catalysts for CO selective oxidation can be classified into three categories as shown in Figure 2.2 which summarizes 30 recent publications. The most commonly used formulation is platinum or other precious metals on alumina, and at temperatures around 200 ºC. Lastly, several common transition metals have been investigated to find a more economical CO selective oxidation catalyst (Choi and Stenger, 2004).

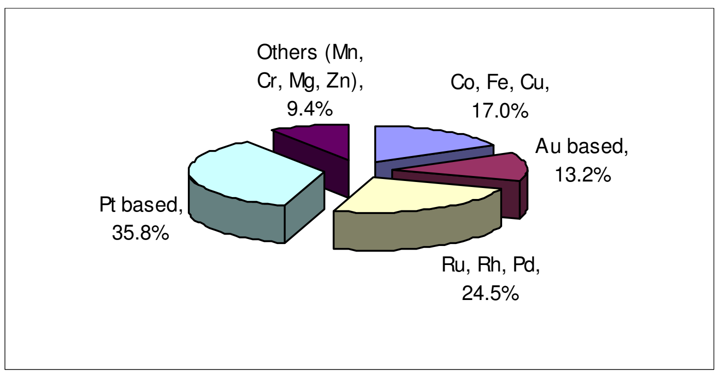

Figure 2.2. Typical formulation of CO selective oxidation catalysts in the 30 recently published papers (Choi and Stenger, 2004)

Based on the high activity required to remove CO while maintaining a high CO oxidation selectivity, catalyst formulations used for PROX involve, in general, a high PGM loading on high surface area supports, and are operated at relatively low temperature, 80–200 °C. Formulations comprise of Pt or promoted Pt, Ru, Pd, alloys of Pt–Sn or Pt–Ru, or Rh on alumina or on molecular sieves, or, more recently, Au catalysts (Ghenciu, 2002).

Research published by a number of laboratories on Au catalysts for several applications suggested that gold catalysts are potential candidates for commercial applications, more so for CO selective oxidation than for WGS, based on the lower operation temperature in the case of the former. Results reported by several groups on the performance of Au formulations for PROX agree on the very high selectivities obtained at low temperature (Ghenciu, 2002).

Au/MnO_2 has been suggested to be a promising catalyst with high longterm CO oxidation activity. Gardner *et al.* (1991) have shown that coprecipitated Au/MnO_x catalysts are about five times more active than Pt/SnO_x catalysts prepared by deposition–precipitation (Trimm and Önsan, 2001).

Among the catalysts, Pt appears to offer the best results over a larger temperature interval and have been the most studied (Ghenciu, 2002).

2.3.3.1. Platinum (Pt) Catalysts. Platinum possesses high resistance to chemical attack, excellent high-temperature characteristics, and stable electrical properties. All these properties have been exploited for industrial applications. Platinum does not oxidize in air at any temperature, but can be corroded by cyanides, halogens, sulfur, and caustic alkalis. The catalytic properties of the six platinum family metals are outstanding. For this catalytic property, platinum is used in catalytic converters, incorporated in automobile exhaust systems, as well as tips of spark plugs (Platinum, 2007).

One promising catalyst used for low-temperature CO oxidation is Pt/SnO_2, with or without promoters (Herz *et al.*, 1993). Because Pt/SnO_2 has much higher catalytic activity for CO oxidation than either Pt or SnO_2 alone, a synergetic interaction involving separate but complementary sites on the Pt and SnO_2 phases or at the Pt–SnO_2 interface clearly exists (Trimm and Önsan, 2001).

The nature, temperature, and duration of pretreatment affect the subsequent catalytic activity of Pt/SnO_2. A relatively mild reductive pretreatment using CO or H_2 at temperatures between 125°C and 225°C for about 1 h increased catalytic activity relative to no pretreatment or pretreatment with air or inert gas. Reduction at 125°C led to conversion of Pt oxides to $Pt(OH)_2$, whereas reduction at 225°C led to reduction to Pt periods was found to result in an initial fall in the CO_2 yield that persisted for hours or days before the higher steady-state yield was reached (Schryer *et al.*, 1990).

Low-temperature oxidation of CO over alloy type Sn–Pt/SiO_2 catalysts with different Sn/Pt ratios has been investigated at different CO partial pressure using thermal programmed oxidation (TPO) technique and time on stream (TOS) experiments. The introduction of tin into platinum strongly increased the activity of the catalyst. The activity had a maximum, which depended on both the Sn/Pt (at./at.) ratio and the CO partial pressure (Margitfalvi *et al.*, 2002).

In addition to the abundant literature on Pt/SnO_2, Mergler *et al.* (1996) have studied a number of Pt/SiO_2 catalysts promoted by metal oxides other than SnO_2. They described the CO oxidation behavior of Pt/SiO_2, Pt/CoO_x/SiO_2, and Pt/MnO_x/SiO_2 catalysts and compared them with commercially available Pt/Al_2O_3, Pt/Rh/Al_2O_3, and Pt/CeO_x/Al_2O_3. The order in CO oxidation activity after a reductive pretreatment was found as Pt/CoO_x/SiO_2 >Pt/MnO_x/SiO_2 > Pt/CeO_x/Al_2O_3 > Pt/Al_2O_3 > Pt/Rh/Al_2O_3 > Pt/SiO_2. It was shown that the addition of metal oxides such as CoO_x and MnO_x to a standard Pt/SiO_2 catalyst does not change Pt particle size. The results suggest that MnO_x and CoO_x are active components of Pt-based catalysts in both CO oxidation and NO reduction reactions (Trimm and Önsan, 2001).

Choi and Stenger (2004) reported the activity of the in house platinum catalyst with varying Pt loadings (1.6, 0.55 and 0.19 per cents Pt). As expected, the activity directly increased with platinum amount over this range of Pt loadings. However, the high loading platinum catalyst (1.6 per cent) showed the poorest selectivity at higher temperatures.

Pt itself is active both in hydrogen and CO oxidation, and an obvious reaction route is that products of these reactions, CO_2 and H_2O, desorb from Pt. The selectivity is determined only by the competitive adsorption of CO, H_2, and O_2 (Pozdnyakova *et al.*, 2006a). Pt/Al_2O_3 has been the most studied PROX catalyst because of its high CO conversion and stability at moderate temperatures (~200°C). Kahlich *et al.* (1997) investigated the kinetics of CO oxidation on Pt /Al_2O_3 under integral and differential conditions and found that on 0.5% Pt /Al_2O_3, the presence of hydrogen actually increases the rate of CO oxidation.

Korotkikh and Farrauto (2002) investigated the CO selective oxidation at low temperature in a H_2 stream in the absence of CO_2, on a monolithic support. For the same metallization, the Fe-promoted catalyst performed at higher conversion than the unpromoted formulation, 5% Pt /γ-Al_2O_3 , while maintaining the selectivity at 90- 150 °C (Liu *et al.*, 2002).

It is suggested that CeO_2 promotes CO oxidation by employing lattice oxygen, which implies that improvement in oxygen supply to Pt from CeO_2 in low-oxygen-concentration environments is probable. Son and Lane (2001) found that addition of Ce improved CO conversion and selectivity significantly by increasing the O_2 supply to Pt.

Rhodium is a common catalyst used for oxidation reactions and one of the candidates for the CO PROX reaction. Although Rh is used for automotive catalysts, there are very few papers addressing CO selective oxidation for Pt–Rh bimetallic catalysts. Cai *et al.* (1996) reported the synergist effects of Pt–Rh alloy particle at certain conditions for CO oxidation. However, that work was when hydrogen was not a feed component (Choi and Stenger, 2004).

2.3.3.2. Tin Oxide (SnO_x) Promoters. The catalytic effect of adsorbed Sn on CO oxidation is generally accepted. It is often ascribed to a facilitated adsorption of OH either on Sn atoms or close to them on neighboring Pt. Others favor the interpretation that Sn changes the electronic properties and thereby lowers the adsorption strength of adsorbed CO or increases its oxidation rate (Massong *et al.*, 2000).

Determining the oxidation state of tin and the chemical nature of tin oxide formed by oxidation reactions at Sn and alloyed-Sn/TM surfaces has been the subject of numerous studies and is still controversial. The tin oxide formed has been identified previously as SnO, SnO_2, a mixture of SnO and SnO_2, an intermediate oxide phase (first identified by Cox and Hoflund (1985) using ELS), and a phase different from SnO or SnO_2 (Padova *et al.*, 1994).

Bond *et al*. (1976) suggested that spillover of both CO and atomic oxygen from metal site to the support SnO_2 is responsible for the enhanced activity and about 2 per cent Pd is sufficient to cover the entire surface of SnO_2 (Kulshreshtha and Gadgil, 1997).

Pt/SnO_2 supported catalysts have been demonstrated in extensive studies to be good catalysts for low-temperature CO oxidation (Schryer *et al.*, 1990). The use of tin as the second metal in Pt-based catalysts on supports like silica, alumina, carbon, graphite, activated carbon, has found application in different catalytic reactions like CO oxidation, selective hydrogenation and CO_2 reforming of CH_4 (Stagg *et al.,* 1998).

The presence of excess SnO_2 on the surface cause activity loss, since Sn or SnO_x species may cover the available Pt surface after reduction, thus preventing CO chemisorption (Hoflund *et al*., 1995; Akın *et al*., 2001).

2.3.4. Catalyst Support

Many industrial catalysts consist of metals or metal compounds supported on an appropriate support, the basic role of which is to maintain the catalytically active phase in a highly dispersed state (Rodriguez-Reinoso, 1998). Also, a support can be described as an inert substance that provides a means of spreading out an 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 (Satterfield, 1991).

The support chosen for a catalyst has a critical impact on catalyst activity, selectivity and ease of catalyst recycling. The support can impart an acidic or basic environment for the active catalyst component. The selection of a support is based on its desirable characteristics such as the following (Satterfield, 1991):

- A support must have desirable mechanical properties including attrition resistance, hardness, and comparative strength.
- It should be stable under reaction and regeneration conditions.
- It should provide enough surface area to guarantee targeted dispersion of active phases. High surface area is usually, but not always, desirable.

- The support must supply porosity, including average pore size and pore-size distribution. High area implies fine pores, but relatively small pores may become plugged in catalyst preparation, especially if high loadings are sought.
- It should have low cost.
- It should either be inert or provide active sites for activity or strong metal/support interaction depending on the reaction.

In the literature it has been proposed that the surface chemistry of the support determines the precursor/support interaction and hence the reducibility of the species formed (Román-Martínez *et al.,* 1993). The main goal of oxidation is to obtain a more hydrophilic surface with a relatively large number of oxygen containing surface groups (Aksoylu *et al.*, 2000a).

2.3.4.1. Carbon Materials. The use of carbon in catalysis is continuously increasing. Its application as a catalyst support offers several advantages. Carbon is cheap and is relatively inert material. After an activation process, a porous network is developed which gives very high surface areas to activated carbon (Gandia and Montes, 1994).

Moreover, the varieties of available forms (e.g. graphite, carbon black, activated carbon, activated carbon fibers, carbon nanotubes and carbon molecular sieves) make carbon materials very attractive as catalysts or supports for metal catalysts (Chen *et al.*, 2006). Among them, activated carbon and carbon black are the carbon materials of choice for most carbon-supported catalysts (Rodriguez-Reinoso, 1998).

Activated carbon is a microcrystalline, nongraphitic form of carbon that has been processed to develop internal porosity. This porosity yields the surface area that provides the ability to adsorb gases and vapors from composite gases and dissolved or dispersed substances from liquids (Roy, 1995). Activated carbon has the highest volume of adsorptive porosity of any material known to man. Important physical properties of activated carbon are surface area, product density, mesh size, abrasion resistance and ash content. High surface area and a well developed porosity are essential for achieving large metal dispersions, which usually results in a high catalytic activity (Fraga *et al*., 2002;

Rodriguez-Reinoso, 1998). “Molecular plates” in activated carbon form the lattice for entrapment of impurities.

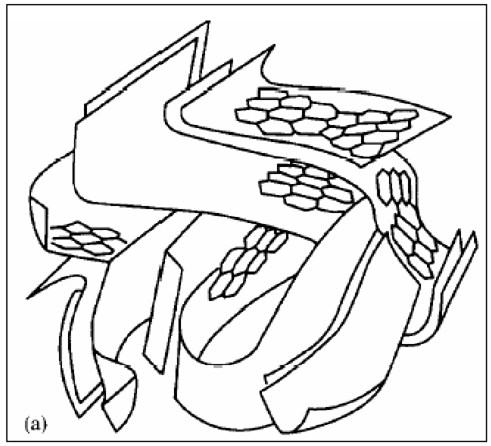

Figure 2.3. Schematic representation of the structure of activated carbon (Rodriguez-Reinoso, 1998)

The use of activated carbon (AC) as a catalyst support material has been fueled by its unique properties like stability in both acidic and basic media, easy recovery of precious metals when supported on AC, very high thermal resistance and the possibility of changes in its textural and surface chemical properties as well as the introduction of carefully controlled process parameters during its production to ensure reproducible characteristics (Rodriguez-Reinoso, 1998; Auer *et al.*, 1998).

Although, carbon is considered to be an inert material in comparison with other catalyst supports, its surface is not as inert as expected due to the formation of active sites by the presence of heteroatoms (O, H and N). In terms of catalyst preparation, the presence of oxygen bearing groups is of great interest. Most of the chemical properties of activated carbon come from the incorporation of oxygen during its production, forming oxides, i.e. carboxylic, phenolic, lactonic and etheric groups which are responsible both for the acid/base and the redox properties of activated carbons. In the literature, it has been proposed that the surface chemistry of the support determines the precursor/support interaction and hence the reducibility of the species formed (Aksoylu *et al.*, 2000a).

In spite of the unique properties mentioned, activated carbon has a main disadvantage as a catalyst support: it can not be used in gas phase oxidation above 500 K (Rodriguez-Reinoso, 1998). Keeping in mind the beneficial effects of the modifications via support pre-treatments, preparation methods and metal ratios on the catalytic properties, as well as the temperature limit in oxidation reactions, the use of activated carbon supported catalysts might be adequate for the low-temperature CO oxidation (Aksoylu *et al*., 2000b). In the literature, studies on CO oxidation both in the absence and in the presence of H_2 (preferential oxidation) over activated carbon supported catalysts were reported.

One of the bimetallic combinations that have been tested on carbon and activated carbon supports is the Pt-Sn system (Coloma *et al.*, 1996; Aksoylu *et al.*, 2000a).The results indicate the beneficial use of AC supports rich in surface oxygen bearing groups, which lead to the formation of Pt-rich alloys without an additional oxidation step of the catalyst after reduction (Aksoylu *et al*., 2000b).

Selective oxidation of CO in a H_2-rich gas stream was investigated over a series of Pt-Ce and Pt-Sn catalysts supported on activated carbon (AC). In order to study the effect of AC surface chemistry on the catalytic performance of AC supported catalysts, three types of activated carbon, namely (i) grinded and HCl washed activated carbon (AC1), (ii) air-oxidized form of AC1 (AC2), and (iii) HNO_3 oxidized form of AC1 (AC3), were prepared and used as catalyst supports. Between these catalysts, the highest activity, ca. 80 per cent CO conversion, is obtained on 0.25% SnO_x-1% Pt/AC2 (Özkara and Aksoylu, 2003).

Preferential CO oxidation over activated carbon, supported catalysts in H_2-rich gas streams containing CO_2 and H_2O was investigated by Şimşek *et al*. (2007). 1%Pt-0.25% SnO_x supported on HNO_3-oxidized AC stands out as a potential candidate for commercial use in PROX since it yields 100 per cent CO conversion under realistic feed conditions. 1 %Pt-1% CeO_x catalysts prepared by sequential or co-impregnation and supported on air-oxidized AC also give 100 per cent CO conversion in H_2-rich feed containing (CO_2+H_2O) during extended run times and hence hold promise as PROX catalysts (Şimşek *et al.*, 2007).

The higher CO conversions obtained in the presence of CO_2 over catalysts with oxidized activated carbon supports can be attributed to their unique properties; oxidative pretreatments enhance the construction of surface oxygen bearing groups that provide anchoring sites for metallic precursors as well as for metals and thus increase the dispersion of Pt metallic crystallites on activated carbon supports (Aksoylu *et al*., 2001).

2.4. Catalyst Preparation

Catalyst preparation process is frequently described as an art. Catalyst preparation is crucial in the sense that the chemical and physical properties of a catalyst are determined by the total history of its preparation procedure (Satterfield, 1991). The most common catalyst preparation techniques are;

- Impregnation,
- Precipitation,
- Deposition,
- Sol-Gel.

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

- Distributing a precursor compound over the support surface by a catalyst preparation technique;
- Drying and calcinations of the catalyst;
- By reduction, transformation of the precursor compound into the active metallic phase.

One of the best-known methods for catalyst preparation is the impregnation of porous support materials with solutions of active components. In impregnation process, 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 precisely defined conditions (such as concentration, mixing rate, temperature, time etc.). Depending on production conditions, selective adsorption of active components occurs on the surface or in the interior parts of the support resulting a nonuniform distribution (Bülbül, 1999).

After impregnation of the support by a solution of active component(s), the catalyst is dried and then calcined. Drying process must be carried by a mild thermal treatment in a temperature range of 350 K to 500 K. The aim of this drying step is to remove 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).

Two types of impregnation techniques may be employed. These are incipient to wetness and dipping impregnation, which is also termed as wet soaking impregnation. Incipient to wetness is usually used for the preparation of the catalysts with controlled metal loading and for those supports which have low adsorption capacity for metal precursors, while dipping impregnation can be applied if the precursor is likely to interact with the support. In the case of incipient wetness, an amount of solution containing a calculated quantity of the metal compound is added just sufficient to fill up the pore volume (Kılaz, 1999). Advantages of incipient to wetness are the technical simplicity of the method, low cost, getting controllable and reproducible metal loadings at the end. The disadvantage of this method is limited metal loadings by solubility of metal compound. But, this disadvantage can be overcome by multiple impregnation steps (İnce, 2004).

The catalysts prepared by impregnation method have many advantages when compared with catalysts prepared by other methods, such as precipitation. Impregnated catalysts’ pore structure and specific surface area largely determined by the support. Since support materials are available in all desired ranges of surface area, porosity, shape, size and mechanical stability, impregnated catalysts can be tailor-made with respect to mass transport properties. Impregnation is preferred especially in preparing supported noble metal catalysts (İnce, 2004).

2.4.1. Calcination and Reduction

In catalyst preparation, calcination and reduction represent the final operations. In general, the dried catalyst is calcined and activated at temperatures at least as high as those used in the reaction. Calcination is generally carried out in oxidizing atmospheres and several processes, such as loss of chemically bound water or carbon dioxide, changes in pore size distribution, active phase generation, surface conditioning and stabilization of mechanical properties occur during calcination (Kılaz, 1999).

The final activation of a supported metal catalyst consists of the transformation of the metal precursor or its oxide into metallic state by reduction, usually in hydrogen and sometimes in carbon monoxide. Phase transformations, sintering of the catalytic component and strong interaction between the metal and the support may occur depending on the reduction temperature and the nature of active phase(s) and support. Therefore, reduction can result in distinctly different catalytic performance even with the same calcined catalyst precursor (Satterfield, 1991).

2.5. Kinetics of CO Oxidation

Most recent papers are focused on catalyst formulation, characterization, and basic performance such as activity and selectivity of CO. Few papers have investigated the kinetics and rate expressions of the reactions involved (Choi and Stenger, 2004). The supported catalysts used for low-temperature CO oxidation are quite complex; thus, determining how they function has been difficult, even though CO oxidation is a relatively simple catalytic reaction (Oh and Hoflund, 2007).

Kahlich *et al.* (1997) investigated the kinetics of CO oxidation on Pt /Al_2O_3 under integral and differential Pt conditions and found that on 0.5% Pt /Al_2O_3, the presence of hydrogen actually increases the rate of CO oxidation. In trying to find a correlation between CO surface coverage and selectivity, the authors proposed a mechanism similar to that of CO oxidation in the absence of H_2 , 'low-rate branch' vs. 'high-rate branch' (Kahlich *et al*., 1997). A high rate branch where the CO surface concentration is very small, occurs at high temperatures and/or λ values (oxidizing conditions), and a low rate branch in which the surface is predominantly covered with adsorbed CO, occurs at low temperatures and/or λ values (reducing conditions). The process parameter λ is defined as:

$$\lambda = \frac{2C_{O_2}}{C_{CO}} = \frac{2P_{O_2}}{P_{CO}} \quad (2.4)$$

Langmuir-Hinshelwood mechanism was proposed for both cases. The low rate branch is associated with a reaction order approaching -1 for P_{CO} and close to +1 for P_{O_2} (CO desorption limited), while the high rate branch exhibits a reaction order of +1 for P_{CO} and zero for P_{O_2}. More recent studies dealing with high-pressure CO oxidation on single-crystalline platinum metals and supported Pt-catalysts come to similar conclusions, indicating that the reaction mechanism of CO oxidation under UHV and high pressure conditions are essentially identical (in the absence of mass transport effects) (Kahlich *et al.*, 1997).

Assuming that the addition of H_2 to the CO/O_2 mixture does not fundamentally alter the CO oxidation mechanism, one would expect the reaction to occur in the low rate branch, i.e., on a surface predominantly covered with adsorbed CO (CO_{ads}) at conditions which prevail in the PROX process on Pt/ γ -Al_2O_3, i.e., at temperatures below 250 ^oC and $\lambda \leq 2$, where λ is shown in Equation (2.4) (Kahlich *et al.*, 1997).

Schubert *et al.* (2001) studied kinetic measurements on preferential CO oxidation in a H_2-rich atmosphere (PROX) over a bimetallic, carbon supported PtSn catalyst. It revealed a high activity and selectivity already at low temperatures (0-80 °C), superior to a commercial Pt/A_2O_3 system. Also, they compared the reaction mechanism for CO oxidation on PtSn with that on another low temperature CO oxidation catalyst, on Au/Fe_2O_3. The latter catalyst is very different from PtSn in that on the Au surface CO adsorption is much weaker, leading to a very low steady state CO coverage at operating temperatures between 40 and 80 °C (Ma, 1995). On the other hand, despite the low CO coverage, oxygen adsorption on Au is practically not possible because of the very low sticking coefficient for dissociative oxygen adsorption on Au (Trimm, 1983).

The kinetics of CO oxidation by oxygen in the 0–80°C temperature interval on Al_2O_3-supported Pt/SnO_2 catalysts was studied by Grass and Lintz (1997). The results of rate measurements and titration experiments indicated that the chemisorption of CO is restricted to Pt, whereas oxygen is adsorbed both on Pt and SnO_2. At low CO concentrations, the reaction was first order in CO, whereas at high CO and O_2 concentrations, it is zero order in both CO and O_2. The sharp decrease between the two domains is typical and was explained by the transition from an oxygen-covered surface to a CO-covered one (Trimm and Önsan, 2001).

2.5.1. Suggested Mechanisms and Rate Expressions for CO Oxidation

The main questions arising from the scientific point of view are the understanding of the reaction mechanism and the kinetics of CO oxidation (Schmal *et al.,* 2005). On the other hand, mechanisms of heterogeneous catalysis are complex (Minh and Brown, 2006). Langmuir–Hinshelwood (LH) kinetics is the most commonly used kinetic expression to explain the kinetics of the heterogeneous catalytic processes (Kumar *et al.,* 2007).

For precious metal catalysts, several different kinetic rate expressions have been reported. Amphlett *et al.* (1996) developed a simple first-order rate expression for CO oxidation on a platinum/alumina catalyst as follows:

$$r_{CO} = k_{CO} C_{CO} \left(mol.s^{-1}.kg^{-1} \right) \tag{2.5}$$

$$k_{CO} = 0.026 \exp\left(-\frac{1000}{T} \right) (m^3.s^{-1}.kg^{-1}) \tag{2.6}$$

Kahlich *et al.* (1997) derived a different kinetic expression. According to this kinetic expression, the reaction rate of CO can be determined with reaction orders of –0.42 for CO and +0.82 for O_2 and an activation energy of 71 kJ mol^{-1}. According to these reaction orders, it was suggested the selective CO oxidation reaction occurs in the low-rate branch that means the Pt surface is thought to be completely covered by CO, with dissociative O_2 adsorption being the rate limiting step. They obtained the rate expression by applying the power law:

$$-r_{CO} = k \left(P_{CO} \right)^{0.4} \left(\frac{2P_{O_2}}{P_{CO}} \right)^{0.82} \tag{2.7}$$

Kahlich *et al.* (1999) also studied the Au/α-Fe_2O_3 catalyst and found positive reaction orders for both CO and O_2 at the reaction temperature of 80°C. It has been demonstrated that due to its high activity and selectivity Au/α-Fe_2O_3 is a very attractive catalyst for selective CO oxidation in fuel cell applications. In simulated reformer gas and at 80°C the kinetics of selective CO oxidation on Au/α-Fe_2O_3 can be expressed by simple powerlaw functionality over wide ranges of CO partial pressures (0.025–1.5 kPa) and, values (0.5–20). The reaction orders with respect to p_{CO} (α_{CO}) and p_{O2} (α_{O2}) were 0.55 and 0.27, respectively. The apparent activation energy for CO oxidation was determined to 31 kJ/mol. The reaction order α_{CO} is strongly temperature dependent, due to the weak adsorption of CO on the gold particles.

Also, Kim and Lim (2002) used a similar rate expression as follows:

$$-r_{CO}, TOF = 1.4\times10^{8}\exp\left(\frac{-78}{RT}\right)\left(P_{CO}\right)^{-0.51}\left(P_{O_2}\right)^{0.76} \tag{2.8}$$

For another approach, Venderbosch *et al.* (1998) (Equation (2.9)) found the parameters of the Langmuir–Hinshelwood (LH) expression using a downhill-simplex minimization method and experimental data.

$$r(c,T) = \frac{k_p{}^0 \exp(-E_a / RT)c_{CO}c_{O_2}}{\left(1 + K_a{}^0 \exp(\Delta H_{ads} / RT)c_{CO}\right)^2} \tag{2.9}$$

Finally, Sedmak *et al.* (2003) evaluated two LH type rate expressions for the Cu-CeO based catalyst shown in Equation (2.10) and (2.11).

$$r_{CO} = \frac{k_{CO}k_{O_2}P_{CO}\left(P_{O_2}\right)^n}{0.5k_{CO}P_{CO} + k_{O_2}\left(P_{O_2}\right)^n} \tag{2.10}$$

$$r_{CO} = \frac{k_L K_L P_{CO}\left(P_{O_2}\right)^m}{1 + K_L\left(P_{CO}\right)^n} \tag{2.11}$$

Akın *et al.* (2001) suggested two alternative reaction paths for CO oxidation over Pt-SnO_2/γ-Al_2O_3 in the absence of CO_2 and H_2O in the feed. On the basis of the kinetic analysis, they found the most plausible mechanism to be CO oxidation at the Pt/SnO_2 interface between adjacently chemisorbed CO and O_2, with the reversible dissociative adsorption of O_2, being the rate-determining step. The mechanism was given as follows:

$$\text{(i)}\ \ CO + \blacksquare \underset{k_1^b}{\overset{k_1^f}{\Leftrightarrow}} CO\blacksquare \tag{2.12}$$

$$\text{(ii)}\ \ O_2 + 2* \underset{k_2^b}{\overset{k_2^f}{\Leftrightarrow}} 2O* \tag{2.13}$$

$$\text{(iii)}\ CO\blacksquare + O* \xrightarrow{k_3^f} CO_2 + \blacksquare + * \tag{2.14}$$

where "■" refers to the Pt sites, and "*" refers to the SnO_2 sites. The following rate expression is obtained using the concept of the most abundant reactive surface species and hence neglecting the surface concentration of oxygen in the adsorption term:

$$-r_{CO} = \frac{kP_{O_2}}{(1 + K_1 P_{CO})^2} \tag{2.15}$$

Oran and Uner (2004) investigated the reaction orders of CO and O_2 over the Pt/CeO_2 catalysts in the absence of CO_2 and H_2O in the feed. The orders of CO and O_2 were found as -1 and 0, respectively that indicated a CO poisoned mechanism. They suggested that over the Pt/CeO_2 catalyst, reaction proceeds through the adsorbed CO and oxygen adatoms which are first dissociatively adsorbed on ceria surface and than reverse-spilled over the platinum surface where, the reverse spill over oxygen adatom to platinum surface is the rate-determining step and CO is the most abundant surface species. The surface reactions were depicted as follows:

$$\text{(i)}\ \ CO + \blacksquare \underset{k_1^b}{\overset{k_1^f}{\Leftrightarrow}} CO\blacksquare \tag{2.16}$$

$$\text{(ii)}\ \ O_2 + 2\bullet \xrightarrow{k_2^f} 2O\bullet \tag{2.17}$$

$$\text{(iii)}\ \ O\bullet + \blacksquare \xrightarrow{k_3^f} O\blacksquare + \bullet \tag{2.18}$$

(iv) $CO■ + O■ \xrightarrow{k_4^f} CO_2 + 2■$ (2.19)

where "■" refers to the Pt sites, and "●" refers to the ceria sites. As a result, the reaction rate takes the following form:

$$r_{CO_2} = \frac{k_2^f \theta_{O\bullet}}{1 + K_1 P_{CO}} \tag{2.20}$$

where "$\theta_{O\bullet}$" is the surface coverage of oxygen over ceria. Reaction mechanisms for low-temperature CO oxidation in H_2 rich streams were also investigated as well as the low-temperature CO oxidation.

There are various studies of CO oxidation on Pd/SnO_2 and Pt/SnO_2 catalysts. A synergism is observed in these studies; but there is no general agreement concerning its origin. There are several explanations of the observed synergism. Bond *et al.* (1977) propose a bifunctional mechanism based on the spillover of both carbon monoxide and oxygen from the noble metal to tin dioxide. Sheintuch *et al.* (1989) also consider a bifunctional mechanism but restrict the spillover to CO. The explanation of Schryer *et al.* (1991) is based on the existence of a new phase—a platinum–tin alloy. Finally, Gangal *et al.* (1990) introduce the hypothesis that the adsorption of the reactants leads to a local temperature increase of the platinum particles, promoting the reaction on adjacent SnO_2 sites.

Grass and Lintz (1997) studied the kinetics of the oxidation of carbon monoxide by oxygen on alumina supported Pt/SnO_2 catalysts. The combined rate and titration experiments lead them to conclude that in the zero order domain, where on pure platinum catalysts the oxidation is inhibited by the coverage of the noble metal by adsorbed CO, the reaction is sustained in the case of SnO_2-containing catalysts due to the adsorption of oxygen on SnO_2. This oxygen subsequentially diffuses to the noble metal particles to react with adsorbed CO via the normal Langmuir–Hinshelwood step. Therefore the following tentative mechanism was proposed. They started with the generally accepted elementary reaction sequence in the CO oxidation on platinum, that is, molecular adsorption and desorption of carbon monoxide (Ertl, 1983),

$$CO + S_{Pt} \leftrightarrow CO\text{–}S_{Pt} \ , \qquad (2.21)$$

dissociative adsorption and molecular desorption of oxygen,

$$O_2 + 2S_{Pt} \leftrightarrow 2O\text{–}S_{Pt} \ , \qquad (2.22)$$

and the reaction of both adsorbed species,

$$CO\text{–}S_R + O\text{–}S_R \leftrightarrow CO_2 + 2S_R \ , \qquad (2.23)$$

where S_{Pt} designates an adsorption site on platinum and S_R means a site where the reaction takes place.

As the measurements have shown that oxygen equally adsorbs on and desorbs from tin dioxide, the following corresponding step is included:

$$O_2 + 2S_{SnO2} \leftrightarrow 2O\text{–}S_{SnO2} \ , \qquad (2.24)$$

The Langmuir–Hinshelwood reaction is possible only if the reacting species can migrate toward each other. As carbon monoxide cannot adsorb on SnO_2, its mobility is limited to the platinum surface:

$$CO\text{–}S_{Pt} + S_R \leftrightarrow CO\text{–}S_R + S_{Pt} \ , \qquad (2.25)$$

Finally, oxygen can migrate on both surfaces; we do not need the differentiation between SnO_2 or Pt sites and may write (Grass and Lintz, 1997)

$$O\text{–}S + S_R \leftrightarrow O\text{–}S_R + S \qquad (2.26)$$

The activity of the PtSn catalyst at 80 °C is reached only at 150 °C by the Pt catalyst. This reactivity can be compared with that of another low temperature PROX catalyst, Au/Fe_2O_3, where under identical conditions (80 °C) a TOF of 0.7 s^{-1} was determined (Kahlich *et al.,* 1999). For CO oxidation on the chemically rather similar Pt/SnO_2 catalyst, lower, by about one order of magnitude activities, were reported for similar reaction conditions, however, in the absence of H_2 (see Table 2.1). Similar to Pt/Al_2O_3, an increase was noted in CO oxidation activity for the PtSn catalyst, by a factor of 2-3, in the presence of H_2 (Kahlich *et al.,* 1997). Nevertheless, a difference by a similar factor still remains, which must reflect a genuine difference between the PtSn and the Pt/SnO_2 catalysts. Only for higher reactant concentrations presented in Table 2.1, were activities of comparable magnitude observed (Schubert *et al.,* 2001).

Table 2.1. Comparison of published literature data for CO oxidation at atmospheric pressure in the absence of H_2 on similar catalysts ([a] With 8% CO_2 added
[b] Evaluated at high conversion) (Schubert *et al.,* 2001)

System	T (°C)	P_{CO} (kPa)	P_{O_2} (kPa)	r_{co} (10^{-5}.mol.s^{-1}.g_{Pt}^{-1})
0.98% $Pt\text{-}SnO_2/\alpha\text{-}Al_2O_3$	60	0.8	1	2.2
2.8% $Pt\text{-}SnO_2/SiO_2$	35	1	0.5	0.4[a]
0.46% Pt-SnO_2/Cordierite	60	1	6	1.7
3% $Pt\text{-}SnO_2$	150	1.6	1.8	3.7
2% $Pt\text{-}SnO_2$	75	5	5	11[b]
2.7% $Pt\text{-}Sn/SiO_2$	50	16	8	13[b]

3. EXPERIMENTAL WORK

3.1. Materials

3.1.1. Chemicals

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

Table 3.1. Chemicals used in catalyst preparation

Chemicals	Formula	Grade	Source	Molecular Weight ($g.mol^{-1}$)
Hexachloroplatinic acid	$H_2PtCl_6.6H_2O$	Extra pure	Carlo Erba	517.92
Tin(IV)chloride	$SnCl_4.5H_2O$	Extra Pure	Riedel-de Haën	350.5
Activated Carbon	C	ROX 0.8	NORIT	12
Hydrochloric Acid	HCl	Research	Merck	36.46

3.1.2. Gases

All of the gases used in this study are listed with their applications and specifications in the Table 3.2 and were obtained from BOS Company, Istanbul, Turkey.

Table 3.2. Applications and specifications of the gases used

Gas/Standard	Application	Specification
Nitrogen	Catalyst preparation	99.99% BOS
Dry air	Catalyst preparation	99.99% BOS
Carbon monoxide	Reactant, GC calibration	99.99% BOS
70.3 vol. % oxygen in helium	Reactant	BOS
Carbon dioxide	Reactant	99.99% BOS
Hydrogen	Reactant, reducing agent	99.99% BOS
Helium	Reactant (Inert)	99.99% BOS
Helium	GC Carrier	99.99% BOS
Helium	Catalyst preparation	99.99% BOS

3.2. Experimental Setup

This study includes catalyst preparation, reaction tests and kinetic studies. The experimental systems used can be classified in three groups:

- Catalyst preparation system: Sequential impregnation method is used in this system.
- Microreactor flow system: This system consists of automated reactant flow system and a temperature controlled reactor.
- Product analysis system: Microreactor flow system is connected to this system. It consists of a gas sampling section, a gas chromatograph and a data processor. The gas chromatograph is used for determining concentrations of feed gases and reaction products on line.

3.2.1. Catalyst Preparation System

Activated carbon supported 1wt.%Pt-0.25wt.%SnO_x catalyst was prepared by sequential impregnation method using the system presented in Figure 3.1 in this study.

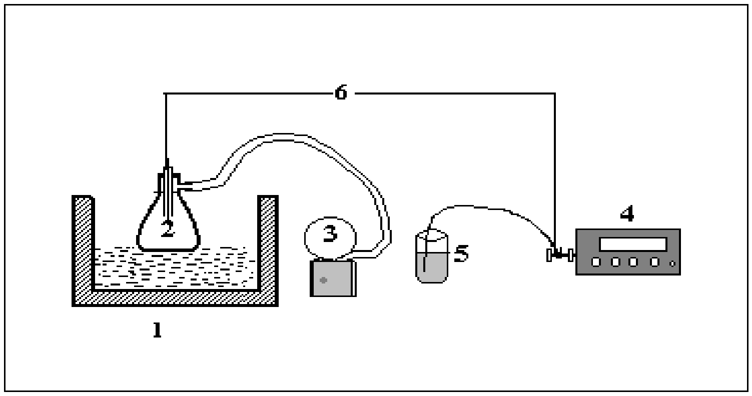

Figure 3.1. The impregnation system: 1.Ultrasonic mixer 2.Vacuum flask 3.Vacuum pump 4.Peristaltic pump 5.Beaker 6.Silicone tubing (Akın, 1996)

3.2.2. Catalytic Reaction System

In the system, 1/4" and 1/8" OD stainless steel or brass tubing and fittings and research grades of pure CO, H_2, He gases and O_2/He mixture were used. Four Brooks 5850E mass flow controllers were used to control the flow rates of these gases. All gases, after being mixed, were sent into the reaction section which consists of a four mm. ID stainless steel fixed-bed down-flow microreactor located in a 2.4 cm ID x 40 cm furnace controlled to ±0.5 K by a Shimaden FP-21 programmable temperature controller. The total length of the reactor was 55 cm, which is longer than the furnace to facilitate manipulation during catalyst charging or recharging. In the constant temperature region of the furnace, the catalyst bed was placed in the middle of the reactor tube. A 1/16" K- type stainless steel sheathed thermocouple is placed adjacent to the middle point of the catalyst bed just outside the microreactor. In order to prevent heat loss and maintain stable temperature profile, the spaces between inlet of the reactor-furnace and the outlet of the reactor-furnace were closed by ceramic wool. In the reactant and product sampling section, the reactant mixture entering or the product leaving the reactor were passed through two on-off valves to either the gas chromatograph sampling unit which has a calibrated one ml sample loop for analysis or to the soap bubble meter for measuring the flow rate of the effluent at the ambient temperature.

The microreactor flow and product analysis system used in the preferential CO oxidation experiments is shown in Figure 3.2.

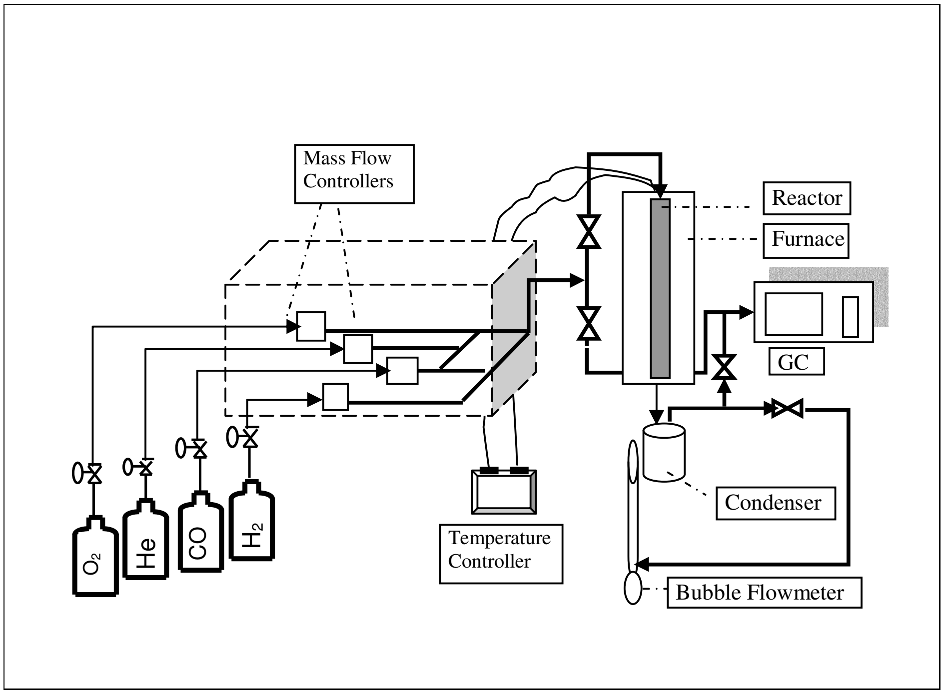

Figure 3.2. The microreactor flow and product analysis system

3.2.3. Product Analysis System

Reactant and product streams were analyzed using an ATI UNICAM 610 Series, temperature-controlled and programmable gas chromatograph equipped with a thermal conductivity detector (TCD), ATI UNICAM 4815 Computing Integrator and CTR I concentric column. Reactant and product gas analysis conditions are given in Table 3.3.

3.3. Catalyst Preparation

The sequential impregnation method was used to prepare the activated carbon supported catalyst which contained 1 wt.%Pt and 0.25 wt.%SnO_x. A commercial activated carbon (AC) was used as a support after washing with HCl and further oxidation with a N_2- dry air mixture for the enhancement of its textural and surface chemical characteristics.

Table 3.3. Reactant and product gas analysis conditions

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

3.3.1. Pretreatment of the Support

The commercial activated carbon supplied by Norit ROX was crushed and sieved into 45-60 mesh size (344-255 μm) and exposed to the thermal and chemical pretreatments indicated below prior to being used as support.

Firstly, activated carbon material was treated with 200 ml of 2N HCl acid solution to remove some ash content and accompanying sulfur. This treatment was carried out in a Soxhlet apparatus. Approximately 15 g of the commercial activated carbon held by a cellulosic cup was placed in an extraction unit. Extraction process was continued under reflux for 12 h, after which the slurry was rinsed with 250 ml distilled water and washed again inside the Soxhlet apparatus for six hours to remove HCl remaining on the support surface. Finally, the slurry was dried at 388 K overnight. This support was called AC1.

AC1 support was oxidized in a down-flow reactor according to a procedure which involves heating the AC1 from room temperature to 723 K at 10 K/min heating rate under 150 ml/min N_2 flow, keeping it at 723 K for 10 h under the flow of 150 ml/min N_2 + 50 ml/min dry air mixture and cooling the sample down to the room temperature under the flow of 150 ml/min N_2. Finally, these procedures gave the air-oxidized AC support which is called the second type of AC support, AC2.

3.3.2. Preparation of Pt-SnO_x/AC2 Catalyst

The experimental setup shown in Figure 3.1 was used for the preparation of the air-oxidized activated carbon (AC2) supported 1%Pt-0.25%SnO_x catalyst. The impregnation procedure contains three steps. These are:

- Evacuation of the support,
- Contacting it with the precursor solution,
- Drying.

For incipient wetness impregnation, five grams of AC2 was placed in a vacuum flask and kept under vacuum both before and during the addition of precursor solutions. Thus, trapped air in pores of the support that could prevent penetration of the precursor solution was eliminated. The vacuum pump was used to remove the trapped air and to give a uniform distribution of the active component. Before impregnating the precursor solution, the support material was mixed in an ultrasonic mixer for 25 minutes.

A Masterflex computerized-drive peristaltic pump was used to feed the precursor solution to the vacuum flask at a rate of 5 mL/min via silicone tubing. The slurry was mixed by the ultrasound mixer during the impregnation in order to maintain uniform distribution of the precursor solutions. After the precursor solution was added, the slurry was ultrasonically mixed for an additional 90 minutes. The thick slurry obtained was then dried at 115^{o}C overnight.

Bimetallic Pt-SnO_x/AC catalyst with 1 wt.% Pt and 0.25 wt.% SnO_x loadings was prepared by sequential impregnation (Sn+Pt). Firstly, acidic aqueous tin chloride solution was impregnated and it was followed by heat treatment under He flow at 673 K and lastly the aqueous hexachloroplatinic acid solution was impregnated. After each impregnation step, the sample was dried overnight at 115^{o}C and then stored in a dessicator.

Activated carbon supported Pt-SnO_x catalysts were previously prepared in the laboratory by Özkara (2002) with sequential impregnation in which impregnation of acidic aqueous tin chloride solution was followed by heat treatment under He flow at 673 K and then by impregnation of aqueous hexachloroplatinic acid solution in order to make characterization and performance tests for CO oxidation, and these catalysts were used by Şimşek (2005) for investigating effect of CO_2 and (CO_2+H_2O) on CO oxidation in H_2-rich feed. In this study, the hexachloroplatinic acid solution was also impregnated in the same manner after the heat treatment under He flow at 673 K.

3.3.3. Reductive Pretreatment

Table 3.4. Reduction program for Pt-SnO_x/AC2 catalyst

Segments	Starting and End Temperatures	Segment Gas
First	Heating from 293 K to 393 K with a heating rate 10 K/min	He with flow rate of 50 $ml.min^{-1}$
Second	Keeping constant at 393 K for 20 min	He with flow rate of 50 $ml.min^{-1}$
Third	Heating from 393 K to 673 K with a heating rate 10 K/min	He with flow rate of 50 $ml.min^{-1}$
Fourth (Calcination)	Keeping constant at 673 K for 2 hours	He with flow rate of 50 $ml.min^{-1}$
Fifth (Reduction)	Keeping constant at 673 K for 2 hours	H_2 with flow rate of 50 $ml.min^{-1}$
Sixth	Sweeping at 673 K for 1 hour	He with flow rate of 50 $ml.min^{-1}$

In order to obtain high catalytic activities, a pretreatment involving the reduction of the active metals from the oxide states formed during calcinations to the metallic state is required prior to the reaction, since catalysts in their oxide forms of the precious metal are usually inactive for the reactions (Baltacıoğlu, 2007).

The presence and decomposition of oxygen bearing groups can contribute to strong and extensive Pt-SnO_x interaction during the reduction procedure through a reduction-oxidation cycle. Studies have shown that reduction using pure hydrogen flow at 673 K for 2 h is a suitable procedure for pretreating the bimetallic Pt-Sn catalyst (Aksoylu *et al.,* 2000b). The temperature program used for the reductive pretreatment of the 1 wt.% Pt-0.25 wt.% SnO_x/AC2 is given in Table 3.4.

3.4. Kinetic Experiments

The CO oxidation reaction on Pt-SnO_x/AC2 catalyst was studied over a relatively wide range of CO concentrations at a temperature of 383 K. Kinetic experiments involved different sets of CO and O_2 concentrations each measured at different space times and catalyst loadings. Molar reactant concentrations in the feed were varied between 1-10 per cent CO and 1-4 per cent O_2 in the absence of hydrogen. In preferential CO oxidation experiments, the H_2 concentrations used were between 10-45 per cent in order to investigate the effect of the presence of H_2 in the feed on CO oxidation rates.

The reaction conditions for the catalyst in the presence of H_2 and in the absence of H_2 are given in Tables 3.5 and 3.6, respectively.

Table 3.5. Reaction conditions of preferential CO oxidation over 1wt.%Pt-0.25wt.%SnO_x/AC2 in the presence of H_2

Exp. No	T_{rxn} (°C)	Total Flow ($ml.min^{-1}$)	Weight of Catalyst (mg)	Feed Composition (%) with He as Balance		
				CO	O_2	H_2
21	110	150	200	5	2	10
22	110	150	200	5	2	20
23	110	150	200	5	2	30
24	110	150	200	5	2	45

Table 3.6. Reaction conditions of CO oxidation over 1wt.%Pt-0.25wt.%SnO_x/AC2 in the absence of H_2

Exp. No	T_{rxn} (ºC)	Total Flow ($ml.min^{-1}$)	Weight of Catalyst (mg)	Feed Composition (%) with He as Balance		
				CO	O_2	H_2
1	110	150	150	1	1	-
2	110	150	100	2	1	-
3	110	150	150	3	1	-
4	110	175	150	3	1	-
5	110	150	150	3	1.5	-
6	110	175	150	3	1.5	-
7	110	175	150	4	2.5	-
8	110	200	200	4	2.5	-
9	110	150	150	4	2	-
10	110	150	200	4	2	-
11	110	200	100	5	2.5	-
12	110	200	150	5	2.5	-
13	110	150	150	5	2	-
14	110	150	200	5	2	-
15	110	200	130	8	4	-
16	110	200	200	8	4	-
17	110	200	100	10	4	-
18	110	175	100	10	4	-
19	110	200	150	10	4	-
20	110	200	250	10	4	-

4. RESULTS AND DISCUSSION

The results obtained in low-temperature CO oxidation over 1wt.% Pt-0.25wt.% SnO_x catalysts supported on AC1, AC2 and AC3 and tested in a H_2-free feed stream have clearly shown that the AC3-supported catalyst prepared by sequential impregnation exhibited the highest activity (Aksoylu *et al*., 2000b). Later, Özkara (2002) studied selective oxidation of CO in a H_2-rich gas stream over various HNO_3- and air-oxidized AC supported 1wt.%Pt-0.25wt.%SnO_x catalysts, and among these catalysts, the highest activity of about 80 per cent CO conversion was obtained over 1wt.%Pt-0.25wt.%SnO_x/AC2. Effects of the addition of CO_2 and water to the reactor feed were later studied by Şimşek (2005) using the same catalysts. It was found that both 1wt.%Pt-0.25wt.%SnO_x/AC3, with the HNO_3-oxidized AC support, and 1wt.%Pt-1wt.%CeO_x/AC2, with the air-oxidized AC support, give 100 per cent CO conversion in the presence of CO_2 or (CO_2+H_2O) in the feed.

In the present work, the kinetics of low-temperature CO oxidation over air-oxidized activated carbon (AC2) supported 1wt.%Pt-0.25wt.%SnO_x was studied over a fairly wide range of CO concentrations (1-10 per cent) at feed ratios of P_{O_2}/P_{CO} = 0.33-1.0 in the initial rate region and at a constant temperature of 383 K. The effect of H_2 on CO oxidation was also investigated by varying its concentration at the expense of diluent helium while keeping the CO and O_2 concentrations constant in the feed. This study focuses on the determination of a power-function rate expression for low-temperature CO oxidation.

CO conversion (X_{CO}), O_2 consumption (X_{O2}) and selectivity for CO oxidation in excess hydrogen (S_{CO}) are defined as follows:

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

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

$$S_{CO}(\%) = \frac{0.5([CO]_{in} - [CO]_{out})}{[O_2]_{in} - [O_2]_{out}} \times 100 \qquad (4.3)$$

The catalyst mass-based reaction rates in the kinetic measurements, ($-r_{CO}$), can be calculated from the conversion versus residence time ($W_{cat} / F_{CO_{in}}$) data as follows:

$$-r_{CO} = \frac{x_{CO} F_{CO_{in}}}{W_{cat}} \qquad (4.4)$$

where x_{CO} is CO conversion, $F_{CO_{in}}$ is CO flow rate in the feed in ml.min^{-1} converted to μmol.min^{-1}, W_{cat} is catalyst weight in mg and ($-r_{CO}$)is the reaction rate in μmol.mg^{-1}.min^{-1}. The space time (mg.min.μmol^{-1}) is defined as the ratio of mass of catalyst (W_{cat}) to the molar flow rate of carbon monoxide ($F_{CO_{in}}$) at the reactor inlet. The parameter λ used in the presentation of experimental results was defined by Equation 2.4 given in Section 2.5.

In a kinetic study, the use of the differential method of data analysis to determine reaction orders and specific reaction rates is clearly one of the easiest, since it requires only one experiment. However, other effects, such as the presence of a significant reverse reaction or inhibition by products, could render the differential method ineffective. In these cases, the method of initial rates can be used to determine reaction orders and the specific rate constant. In the method of initial rates, a series of experiments are carried out at different initial reactant concentrations. The initial rate can be calculated by differentiating the data and extrapolating back to zero time (Fogler, 1999). In the present work, kinetic measurements were carried out at 383 K at suitable ($W_{cat} / F_{CO_{in}}$) in order to obtain low CO conversion levels that are required for the application of the initial rates method.

4.1. Kinetic Analysis of Low-Temperature CO Oxidation

The air-oxidized activated carbon supported catalyst, 1wt.%Pt-0.25wt.%SnO_x/AC2, was studied first in terms of its low-temperature CO oxidation behavior in the absence of H_2 in the feed stream. Experimental conditions are listed in Table 4.1. The kinetic experiments were conducted at atmospheric pressure and a constant temperature of 383 K by using various CO and O_2 concentrations in the feed at different O_2/CO molar ratios (λ = 0.67-2.0) and space times (0.12-2.45 mg.min.μmol^{-1}). The aim of the experiments conducted was the determination of reaction orders with respect to CO and O_2.

Table 4.1. Experimental conditions of low-temperature CO oxidation and PROX

Parameters	**CO Oxidation**	**PROX**
Temperature, K	383	383
Catalyst, mg	100-250	200
Total Flow, ml.min^{-1}	150-200	150
CO, mol%	1-10	5
O_2, mol%	1-4	2
H_2, mol%	0	10-45
Inert Balance	He	He
Time-on-stream, min	90	90

CO conversions obtained at 90 minutes time-on-stream (TOS) over fresh catalyst samples were used in the kinetic calculations. Representative fractional CO conversions obtained at 30, 60, 90 and 120 min are shown in Figure 4.1 for O_2/CO inlet ratios of 0.33 and 0.5 at W/F_{CO} values of 0.81 and 0.82 mg.min.μmol^{-1}, respectively. In each set of experiments, CO conversion (X_{CO}) data taken at constant feed composition by varying space time (W/F_{CO}) were used to confirm the linear change characteristic of the initial rates region; data with linear regression constants 98 per cent or better were used in the subsequent individual rate calculations. This is demonstrated for several experiments in Appendix A. The CO conversions obtained in 20 duplicate experiments over the 1wt.%Pt-

0.25wt.%SnO_x/AC2 catalyst at 383 K with CO, O_2 and balance He in the feed are given in Table 4.2.

Initial rates of CO consumption were individually extracted from intrinsic kinetic data obtained in 20 experiments run under conditions where maximum CO conversions were kept ≤ 10 per cent. Seven different CO concentrations and five different O_2 concentrations corresponding to five different λ values were used, and each feed composition was tested at 1-4 different space times.

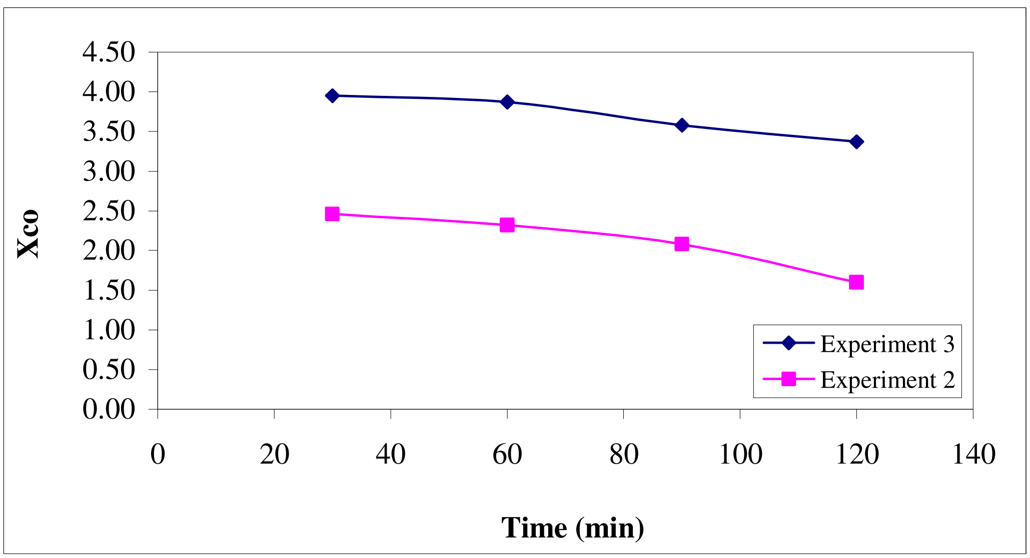

Figure 4.1. Fractional CO conversion versus time for experiments 2 and 3 conducted under conditions defined in Table 4.2

Table 4.2. CO conversions over 1wt.%Pt-0.25wt.%SnO_x/AC2 with He as balance in the absence of H_2 at 383 K

Exp. No	CO %	O_2 %	λ	O_2/CO	F_T (ml.min^{-1})	W_{cat} (mg)	Fractional conversion at 90 min TOS
							x_{CO}
1	1	1	2	1	150	150	0.0367
2	2	1	1	0.5	150	100	0.0208
3	3	1	0.67	0.33	150	150	0.0358
4	3	1	0.67	0.33	175	150	0.0220
5	3	1.5	1	0.5	150	150	0.0303
6	3	1.5	1	0.5	175	150	0.0241
7	4	2.5	1.25	0.625	175	150	0.0323
8	4	2.5	1.25	0.625	200	200	0.0388
9	4	2	1	0.5	150	150	0.0250
10	4	2	1	0.5	150	200	0.0304
11	5	2.5	1	0.5	200	100	0.0160
12	5	2.5	1	0.5	200	150	0.0253
13	5	2	0.8	0.4	150	150	0.0280
14	5	2	0.8	0.4	150	200	0.0375
15	8	4	1	0.5	200	130	0.0200
16	8	4	1	0.5	200	200	0.0245
17	10	4	0.8	0.4	200	100	0.0151
18	10	4	0.8	0.4	175	100	0.0167
19	10	4	0.8	0.4	200	150	0.0224
20	10	4	0.8	0.4	200	250	0.0380

4.1.1. Rate Calculations

The following power-function rate expression is used for describing the kinetics of low-temperature CO oxidation over 1wt.%Pt-0.25wt.%SnO_x/AC2 in the initial rate region:

$$(-r_{co})_o = k\,(P_{co})^{\alpha}\,(P_{o_2})^{\beta} \tag{4.5}$$

The determination of the reaction rates is firstly required to obtain the rate parameters. CO conversion and W/F_{CO} data given in Table 4.2 were used together with Equation 4.4 to determine the reaction rates. The flow rates of CO and O_2 were converted to concentrations in mole per cent which were equivalent to reactant partial pressures as the operation pressure was atmospheric. The resulting rate versus partial pressure data given in Table 4.3 were processed using nonlinear regression analysis. The Levenberg-Marquardt algorithm provided in the computer software POLYMATH 5.1 was used in order to estimate the parameters, k, α and β of Equation 4.5.

The Levenberg-Marquardt algorithm is an iterative technique that locates the minimum of a function that is expressed as the sum of squares of nonlinear functions (Equation 4.6). The sum of the squared differences of the measured reaction rates, $(-r)_m$, and the calculated reaction rates, $(-r)_c$, for N experiments (=20) and p parameter values (=3) is defined as variance of experimental error given by the following equation:

$$\sigma^2 = \sum_{i=1}^{n} \frac{\left[(-r)_{im} - (-r)_{ic}\right]^2}{(N - p)} \tag{4.6}$$

The equation that best fits the experimental data can be determined by comparing the variance of the experimental error (σ^2) for each model and selecting the equation with a smaller one (Fogler, 1999). A model with smaller variance (Equation 4.6) is likely to represent the data more accurately than a model with larger values of this indicator.

Table 4.3. Partial pressures of CO and O_2 and calculated initial rates over 1wt.%Pt-0.25wt.%SnO_x/AC2 in the absence of H_2, T = 383 K

Experiment No	Partial Pressures (atm)		$W_{cat} / F_{CO\,in}$ (mg.min.μmol^{-1})	$(-r_{co})_o$ (μmol.mg^{-1}.min^{-1})
	CO	O_2		
1	0.01	0.01	2.45	0.0149
2	0.02	0.01	0.82	0.0250
3	0.03	0.01	0.81	0.0442
4	0.03	0.01	0.7	0.0314
5	0.03	0.015	0.81	0.0374
6	0.03	0.015	0.7	0.0344
7	0.04	0.025	0.52	0.0621
8	0.04	0.025	0.61	0.0636
9	0.04	0.02	0.61	0.0410
10	0.04	0.02	0.81	0.0375
11	0.05	0.025	0.24	0.0667
12	0.05	0.025	0.37	0.0684
13	0.05	0.02	0.49	0.0570
14	0.05	0.02	0.65	0.0577
15	0.08	0.04	0.2	0.1000
16	0.08	0.04	0.3	0.0820
17	0.1	0.04	0.12	0.1259
18	0.1	0.04	0.14	0.1193
19	0.1	0.04	0.18	0.1244
20	0.1	0.04	0.3	0.1267

The reaction orders with respect to CO (α) and O_2 (β) were determined as 0.87 and 0.13, respectively, using POLYMATH computer software. The reaction rate constant, k, was determined as 1.37 μmol.mg^{-1}.min^{-1}.atm^{-1}. Consequently, the power-function rate expression for low-temperature CO oxidation over air-oxidized activated carbon supported 1wt.%Pt-0.25wt.%SnO_x/AC2 catalyst at 383 K in the initial rate region can be given as:

$$\left(-r_{co}\right)_o = 1.37\left(P_{co}\right)^{0.87}\left(P_{o_2}\right)^{0.13} \tag{4.7}$$

The variance of experimental error is found to be 0.017 (µmol.g^{-1}.s^{-1})^2 for this rate expression. The fit between experimentally measured and model predicted rates is reasonably good with a mean squared error of 0.96; this is demonstrated in Figure 4.2 which takes into account all individual rates used in the non-linear regression analysis.

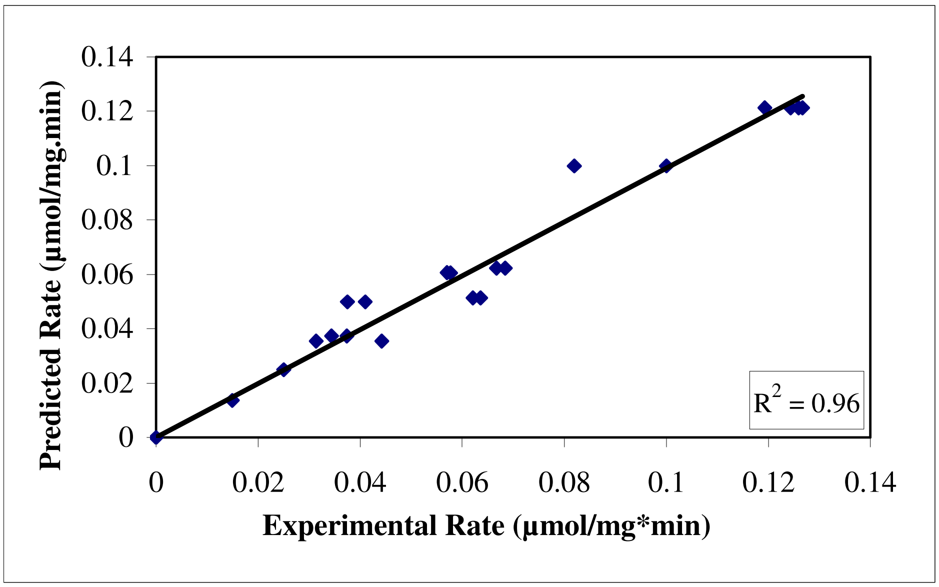

Figure 4.2. Experimental rates versus calculated rates of low-temperature CO oxidation over 1 wt.%Pt-0.25wt.%SnO_x/AC2

Two reaction regimes have been described for CO oxidation studies over supported Pt catalysts. The first one shows that the surface is primarily covered with CO, which is expected to prevail at low temperatures and/or reducing conditions (lower λ values), and the second regime shows that the surface concentration of CO is rather small, which is likely to occur at higher temperatures and/or oxidizing conditions (higher λ values). The first regime controlled by the intrinsic reaction kinetics is characterized by negative reaction orders approaching unity for carbon monoxide and positive reaction orders close to one for oxygen. On the other hand, the second regime is characterized by positive reaction orders close to unity for CO and almost zero order for O_2 (Kahlich *et al.*, 1997). In general, negative orders in CO imply that the Pt surface is effectively saturated by CO whereas positive reaction orders mean that the CO coverage is considerably below saturation under the reaction conditions and, therefore, a decrease in CO partial pressure will also decrease the reaction probability for CO oxidation (Schubert *et al.*, 1999).

Since oxygen can adsorb on both Pt and SnO_2 sites while CO chemisorbs only on Pt, the drastic change between the two regimes is generally attributed to the shift from an oxygen-covered surface to a CO-covered one. The mechanistic suggestion is that SnO_2 provides suitable sites for dissociative oxygen adsorption. On the other hand, over oxidized AC supports, an association occurs at the atomic level upon extensive reduction leading to the formation of PtSn and/or Pt_3Sn alloys which are also proposed as efficient catalysts or active sites for CO oxidation (Aksoylu *et al.,* 2000a). The Pt-rich Pt_3Sn alloy can adsorb oxygen more readily than either the Pt or the PtSn alloy sites. The activity of Pt-Sn/AC catalysts in CO oxidation reaction is, therefore, strongly affected by the surface chemistry of the support, the preparation method of the catalyst, the Pt:Sn ratio and the reduction procedure applied (Aksoylu *et al.,* 2000b).

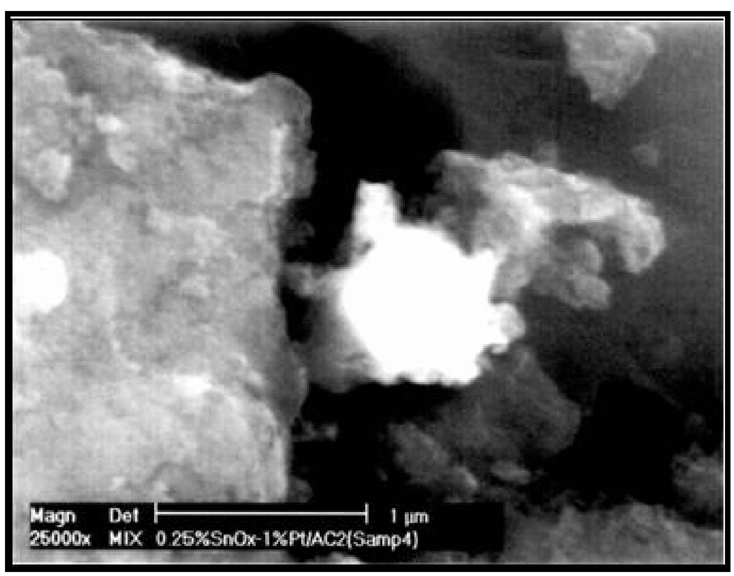

Figure 4.3. SEM image of 1wt.%Pt-0.25wt.%SnO_x/AC2 (Özkara, 2002)

Sequential impregnation of Sn and Pt precursors, with Sn being introduced first, and reduction with H_2 at 673 K both facilitate the formation of active Pt and Pt-rich alloy sites (Aksoylu *et al.,* 2000b). The SEM image of the 1wt.%Pt-0.25wt.%SnO_x/AC2 catalyst prepared by sequential impregnation and reduced at 673 K is shown in Figure 4.3 in which it can be observed that the active sites are placed very close to each other (Özkara, 2002).

Kahlich *et al*. (1997) have reported that the kinetics of CO oxidation over Pt/SiO_2 studied by Cant *et al*. (1978) at 150^oC gave reaction orders with respect to CO and O_2 as −0.2 and 0.9, respectively. Gülyüz (2007) studied the kinetics of low-temperature CO oxidation over 1wt.%Pt-1wt.%CeO_x/AC2 and obtained reaction orders of −0.29 and 1.07 with respect to CO and O_2, respectively. Both studies have stated that the first regime mentioned above is prevalent, i.e. the positive reaction order close to unity with respect to oxygen obtained in these studies implies that relatively weak adsorption of oxygen is involved. On the other hand, Baltacıoğlu *et al*. (2007) have studied CO oxidation over 1wt.%Pt-0.25wt.%SnO_x/AC3 and found a positive reaction order close to unity (0.96) with respect to CO and a negative reaction order (-0.31) for O_2, implying an oxygen-covered surface with weak adsorption of CO. In the present study, the positive reaction order close to unity (0.87) obtained for carbon monoxide also implies that relatively weak adsorption of CO is involved. Comparison of the reaction orders with respect to CO (α) and O_2 (β) between the three AC-supported catalysts is presented in Table 4.4.

The HNO_3-oxidized AC support, AC3, has a high concentration of oxygen-bearing surface groups, mainly carboxylic acid groups, which impart an acidic nature to the support and provide a high concentration of anchoring sites for the metal precursors (Aksoylu *et al.,* 2000a). During reduction, some of these groups decompose, thus assisting the formation of Pt_3Sn alloy sites adjacent to Pt sites via a reduction-oxidation cycle. Since the formation of Pt-rich alloy sites is generally higher when AC3 support is used, stronger oxygen adsorption and weaker CO adsorption on the Pt-SnO_x/AC3 catalyst were observed when compared to the Pt-SnO_x/AC2 catalyst.

The adsorption strength of CO on Pt_3Sn alloy sites is lower compared to that on Pt sites, which implies enhanced resistance by Pt_3Sn against CO poisoning. The decrease in the overall adsorption strength of CO is caused by (i) the decrease in the number of possible adsorption sites, since CO cannot adsorb on Sn-incorporated sites, and (ii) the electronic modification of Pt sites by the Sn present in the neighborhood, which results in a reduction of the CO adsorption strength on Pt sites (Baltacıoğlu *et al.,* 2007).

Table 4.4. Comparison of the reaction orders of three AC-supported catalysts with respect to CO (α) and O_2 (β)

Catalyst	α	β	Reference
1wt.%Pt-0.25 wt.%SnO_x/AC3	0.96	-0.31	Baltacıoğlu *et al.*, 2007
1wt.%Pt-0.25 wt.%SnO_x/AC2	0.87	0.13	Present work
1 wt.%Pt-1 wt.%CeO_x/AC2	-0.29	1.07	Gülyüz, 2007

The positive reaction order close to unity (0.87) obtained for CO in the present kinetic study implies that the CO coverage on metallic sites is significantly below saturation while that of oxygen is relatively high as indicated by its reaction order of 0.13 which is quite close to zero. A possible explanation of these results can be the surface chemistry of the support and the presence of some Pt-rich Pt_3Sn alloy sites close to Pt sites.

4.2. Effect of H_2 on Low-Temperature CO Oxidation

Preferential CO oxidation in H_2-rich streams is a promising method for H_2 clean-up in fuel processor/fuel cell systems. When the AC supported catalysts were tested for their low-temperature PROX activity in a H_2-rich stream containing 1 mol per cent CO, 1 mol per cent O_2 and 60 mol per cent H_2, the 1wt.%Pt-0.25wt.%SnO_x/AC2 catalyst gave the highest CO conversion of 81 per cent with a CO oxidation selectivity of 41 per cent, indicating the beneficial effect of the thermally stable oxygen-bearing surface groups of the air-oxidized AC support (Özkara and Aksoylu, 2003). In the present work, the effects of the presence of H_2 on CO conversions and CO oxidation rates were tested in the initial rates region. The effect of H_2 on the CO oxidation rate over 1wt.%Pt-0.25wt.%SnO_x/AC2 was also assessed by comparing the results with kinetic data for CO oxidation in the absence of H_2. Low-temperature CO oxidation was studied at 383 K in the presence of 5 per cent CO, 2 per cent O_2 using a fixed total flow rate of 150 ml.min^{-1} with different H_2 concentrations and balance He and a fixed catalyst loading of 200 mg. Reactant conversions and the selectivity for CO oxidation in H_2-containing feed streams are presented in Table 4.5. The selectivity for CO oxidation is defined as the amount of oxygen consumed in CO oxidation divided by the total amount of oxygen consumed, taking into consideration the λ value and the reaction stoichiometry.

Table 4.5. CO and O_2 conversions and selectivity for CO oxidation in the presence of H_2 ($\lambda = 0.80$; T = 383 K; W/F_{CO} = 0.65 mg.min.μmol^{-1}; time-on-stream = 90 min)

Exp. No	CO %	F_{CO} (ml.min^{-1})	O_2 %	F_{O_2} (ml.min^{-1})	H_2 %	F_{H_2} (ml.min^{-1})	fractional conversions at 90 min TOS		
							x_{CO}	x_{O_2}	Sco (%)
14	5	7.5	2	3	0	0	0.037	0.031	-
21	5	7.5	2	3	10	15	0.123	0.159	97
22	5	7.5	2	3	20	30	0.142	0.241	75
23	5	7.5	2	3	30	45	0.158	0.422	46
24	5	7.5	2	3	45	67.5	0.149	0.407	45

In the present work, the addition of H_2 into the feed increased both CO and O_2 conversions. In the absence of H_2, CO conversion was 3.7 per cent and with 10 mol per cent H_2 in the feed, the enhancement in the CO conversion was almost three fold, namely 12.3 per cent and in the O_2 conversion was found five fold, namely 15.9 per cent. The selectivity obtained for CO oxidation was remarkably high, 97 per cent. As the H_2 in the feed was gradually increased up to 45 mol per cent, CO conversions remained almost constant which was accompanied by a rapid increase in O_2 conversion from 15.9 per cent to 40.7 per cent in the same interval at a space time of 0.65 mg.min.μmol^{-1}. When H_2 amount was increased to 20 per cent, the selectivity for CO oxidation decreased slightly. However, when the H_2 concentration was increased from 10 to 45 mol per cent, the selectivity for CO oxidation decreased from 97 per cent to 45 per cent. These results are presented in Table 4.5 and plotted in Figures 4.4 and 4.5.

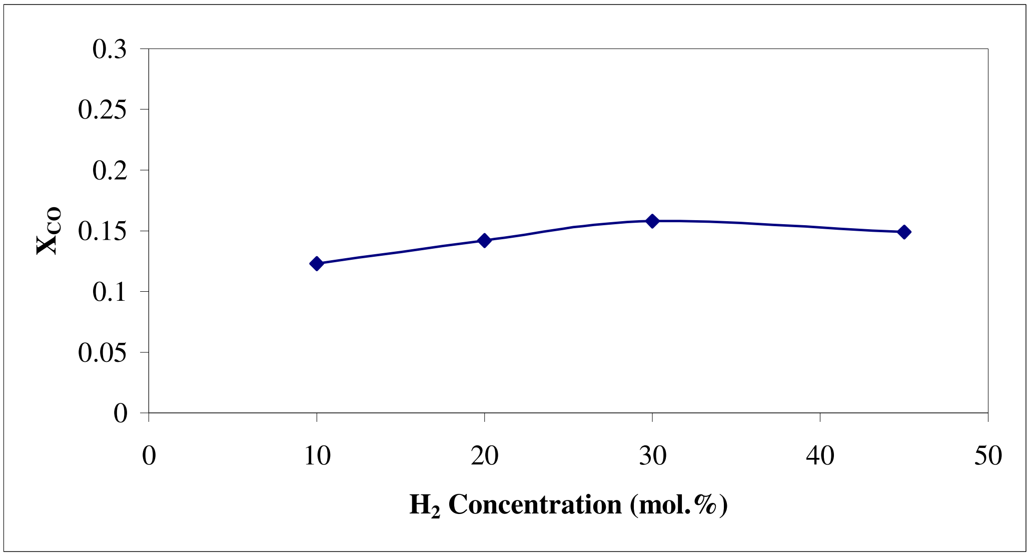

Figure 4.4. Effect of H_2 concentration on CO conversion over 1wt.%Pt-0.25wt.%SnO_x/AC2 at 383 K (5 mol% CO, 2 mol% O_2 and balance He)

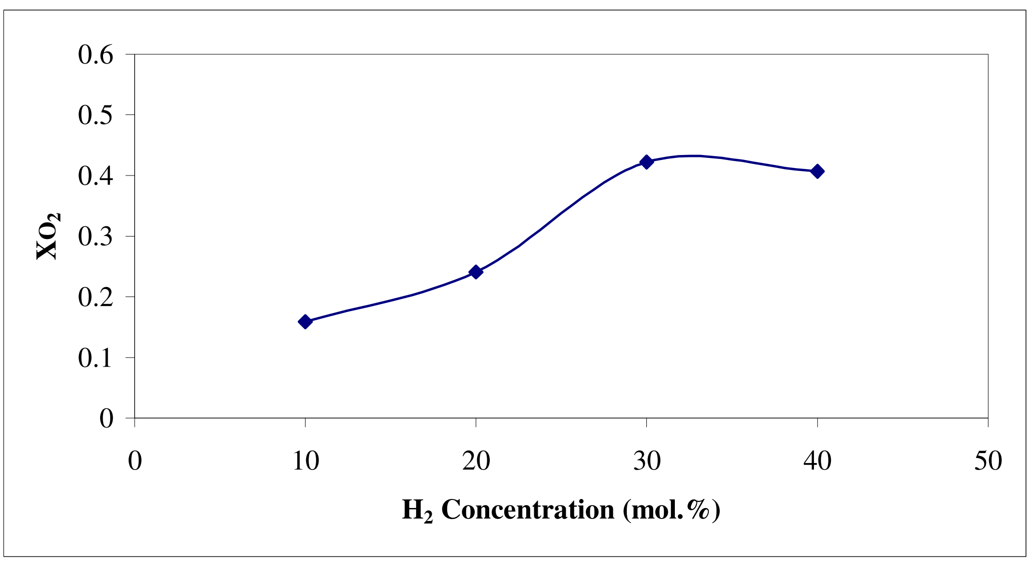

Figure 4.5. Effect of H_2 concentration on O_2 conversion over 1wt.%Pt-0.25wt.%SnO_x/AC2 at 383 K (5 mol% CO, 2 mol% O_2 and balance He)

It is assumed that the addition of hydrogen to a feed containing CO and O_2 does not essentially change the mechanism of CO oxidation over the catalyst (Baltacıoğlu *et al.*, 2007). In fact, Schubert *et al.* (2001) confirmed that the surface coverage of CO was still close to its saturation value at the reaction temperature in PROX studies conducted over carbon supported bimetallic PtSn catalysts. In the present work, the enhancement in the CO oxidation rate over 1wt.%Pt-0.25wt.%SnO_x/AC2 with the addition of H_2 into the feed stream is almost four fold at H_2 concentrations between 10-45 mol per cent which are typical of the H_2 concentrations existing in the inlet stream of the PROX reactor located in a fuel processor. A plausible explanation may be that the interaction of H_2 with oxygen-bearing surface groups, and/or with the oxygen species adsorbed on Pt, Pt/Sn and Pt_3Sn sites, diminishes the oxidizing conditions provided by the AC2 support and releases some of the active metallic sites for CO adsorption which, in turn, leads to the H_2-induced increase measured in CO oxidation rates. The effect of H_2 content in the feed on CO oxidation rates at 383 K over 1wt.%Pt-0.25wt.%SnO_x/AC2 is presented in Figure 4.6. The results show that the CO oxidation rate is unaffected by increases in H_2 content above 10 volume per cent. Therefore, a new rate expression is not necessary. These results may provide an insight on the role of different active sites in the CO oxidation mechanism.

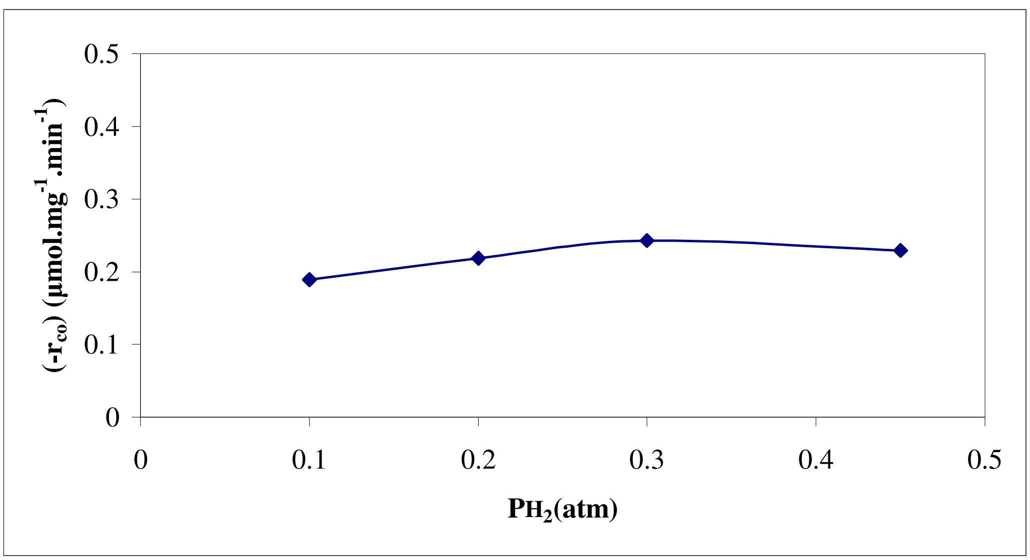

Figure 4.6. Effect of H_2 partial pressure on CO oxidation rates

In the presence of large quantities of hydrogen at 383 K, the conversion and reaction rate of CO may be stable because of hydrogen oxidation. This would be consistent with the work of Baltacıoğlu *et al.* (2007) who studied PROX over the Pt-SnO_x/AC3 catalyst at low temperatures. On the other hand, Gülyüz (2007) found that both the conversion and oxidation rate of CO decrease in PROX studies over the Pt-CeO_x/AC2 catalyst. In both of these studies, hydrogen dependence does not appear in the rate expression for low temperature CO oxidation. In the latter case, the decrease in CO conversion may be caused by the strong adsorption of CO on the Pt surfaces where H_2 adsorption as well as competing reactions ($H_2 + ½ O_2 \rightarrow H_2O$) may also occur due to the high concentration of H_2 in the reactants stream. One possible mechanism may be that CO strongly adsorbs onto a Pt site, then H_2 reacts with the adsorbed CO to form H_2O, leaving behind carbon on the surface; O_2 may then react with that carbon to re-form adsorbed CO. Clearly, there is a competition between CO adsorption, reaction of H_2 with adsorbed CO or O_2 or both, and the ability for the O_2 to react with the carbon to form CO_2 and subsequently desorb to free the site for another reaction (Gülyüz, 2007).

5. CONCLUSIONS AND RECOMMENDATIONS

5.1. Conclusions

The kinetics of low temperature CO oxidation over the air-oxidized activated carbon supported 1wt.%Pt-0.25wt.%SnO_x/AC2 catalyst prepared by sequential impregnation was investigated at 383 K using a relatively wide range of CO and O_2 concentrations. Intrinsic kinetic data were obtained in the initial rates region in the absence of H_2. Preferential CO oxidation was also investigated in order to determine the effect of H_2 on CO oxidation rates using varying H_2 concentrations in the feed at constant residence time. The following conclusions may be drawn:

- A simple power-law rate equation with reaction orders of 0.87 for CO and 0.13 for O_2 can describe low temperature CO oxidation over 1wt.%Pt-0.25wt.%SnO_x/AC2 at 383 K in the absence of H_2. The results indicate that the reaction takes place on a surface that is predominantly covered by adsorbed oxygen with relatively weak CO adsorption. A plausible explanation of these results can be provided by the surface chemistry of the support and the presence of the PtSn and Pt-rich Pt_3Sn alloy sites on which the adsorption strength of O_2 is high.

- The addition of H_2 into the feed increases both CO and O_2 conversions. The increase in the CO oxidation rate over 1wt.%Pt-0.25wt.%SnO_x/AC2 with the addition of H_2 into the feed stream is almost four fold at H_2 concentrations between 10-45 mol per cents. The enhancement effect of H_2 in the feed stream on CO oxidation rates is the same above 10 volume per cent, regardless of the amount of H_2.

5.2. Recommendations

According to the results of the present study, the following points are thought worthwhile for future studies on the kinetics of low-temperature CO oxidation both in the absence and presence of H_2:

- Several experiments at different temperatures can be performed to calculate the activation energy of the CO oxidation reaction. With the results of these experiments, the effect of temperature on the mechanism over activated carbon supported Pt-SnO_x catalyst can be investigated.

- Effect of the presence of excess hydrogen on kinetic experiments can be further investigated at various initial concentrations of CO and O_2. These studies can be beneficial to find out if changes in the reaction orders with respect to CO and O_2 are likely and also to gain further insight into the contribution of the AC surface to the catalytic reaction over Pt-SnO_x.

- Effects of the presence of CO_2 and H_2O in the feed on CO oxidation kinetics can be studied, since these components are present in the feed entering the PROX reactor in a fuel processor system. These studies will be useful in the design of PROX reactors.

APPENDIX A: CONVERSION VERSUS RESIDENCE TIME GRAPHS

Carbon monoxide conversion versus residence time (mg.min.μmol^{-1}) graphs for the low-temperature CO oxidation in the absence of H_2 were illustrated as follows.

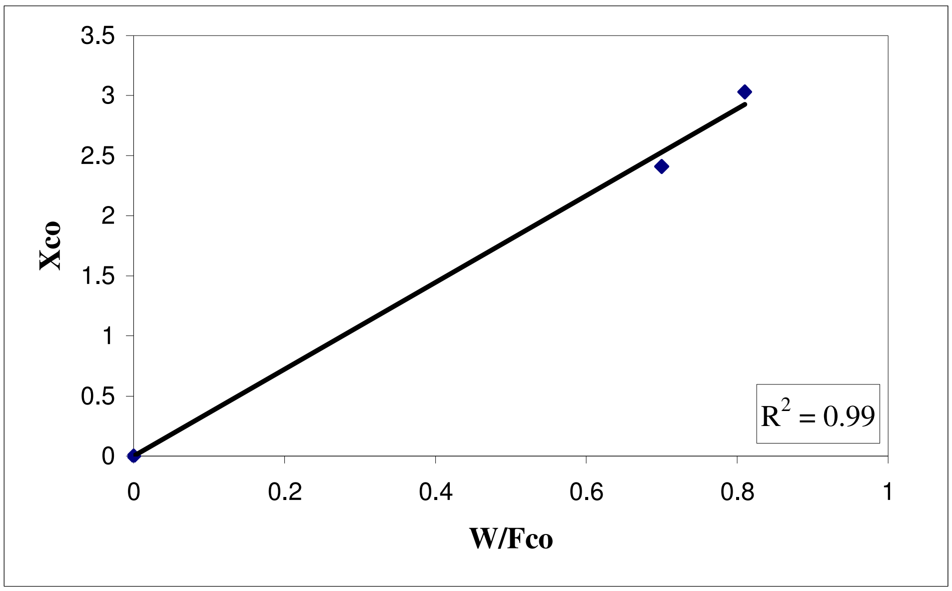

Figure A.1. Fractional CO conversion vs. residence time graph of experiments 5 and 6

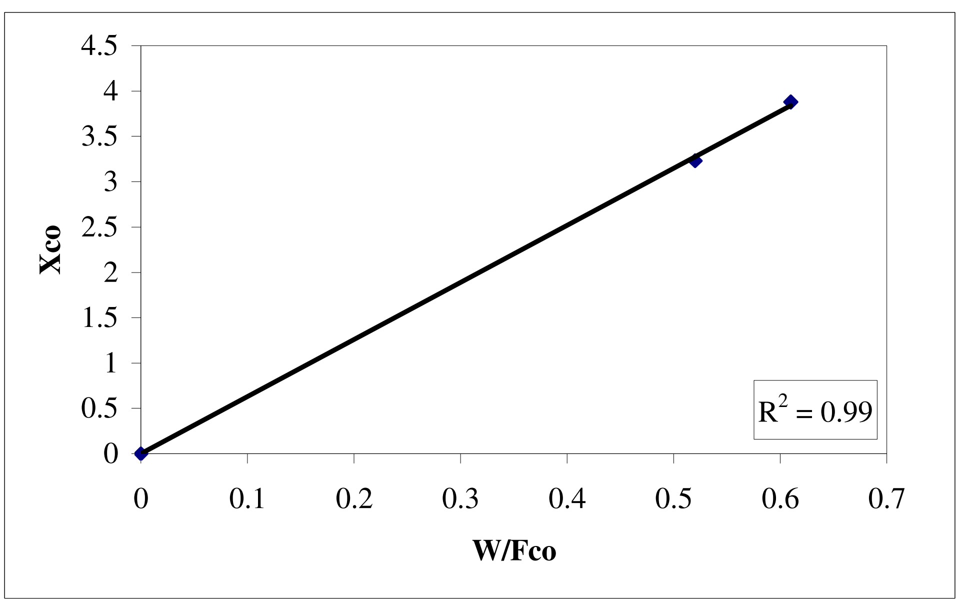

Figure A.2. Fractional CO conversion vs. residence time graph of experiments 7 and 8

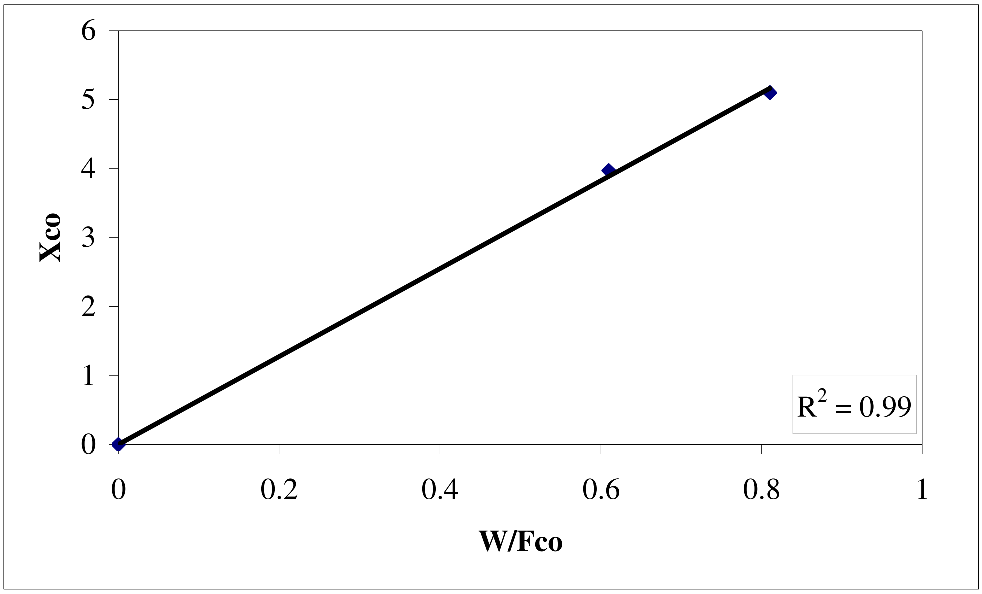

Figure A.3. Fractional CO conversion vs. residence time graph of experiments 9 and 10

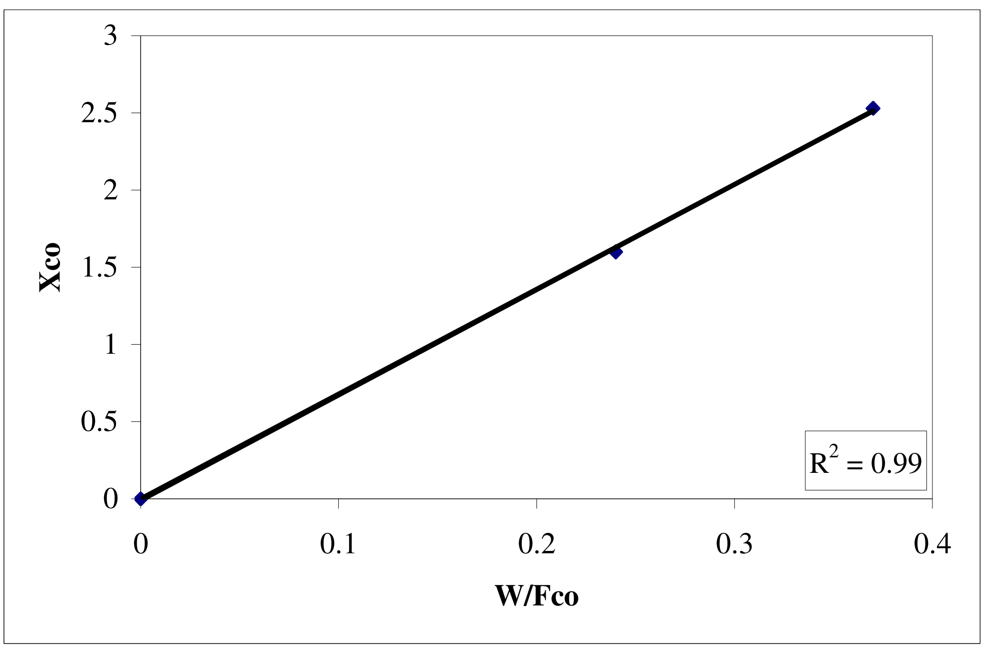

Figure A.4. Fractional CO conversion vs. residence time graph of experiments 11 and 12

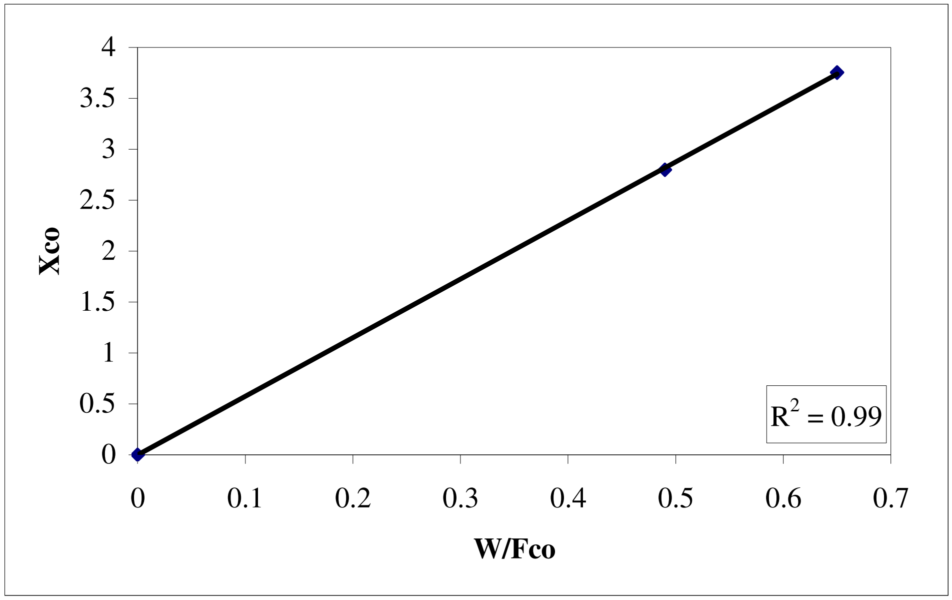

Figure A.5. Fractional CO conversion vs. residence time graph of experiments 13 and 14

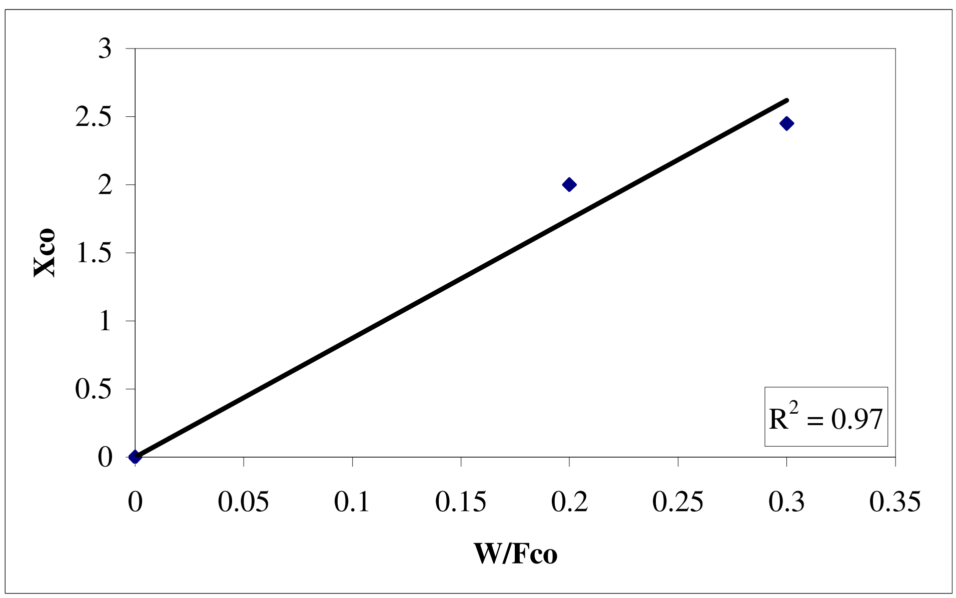

Figure A.6. Fractional CO conversion vs. residence time graph of experiments 15 and 16

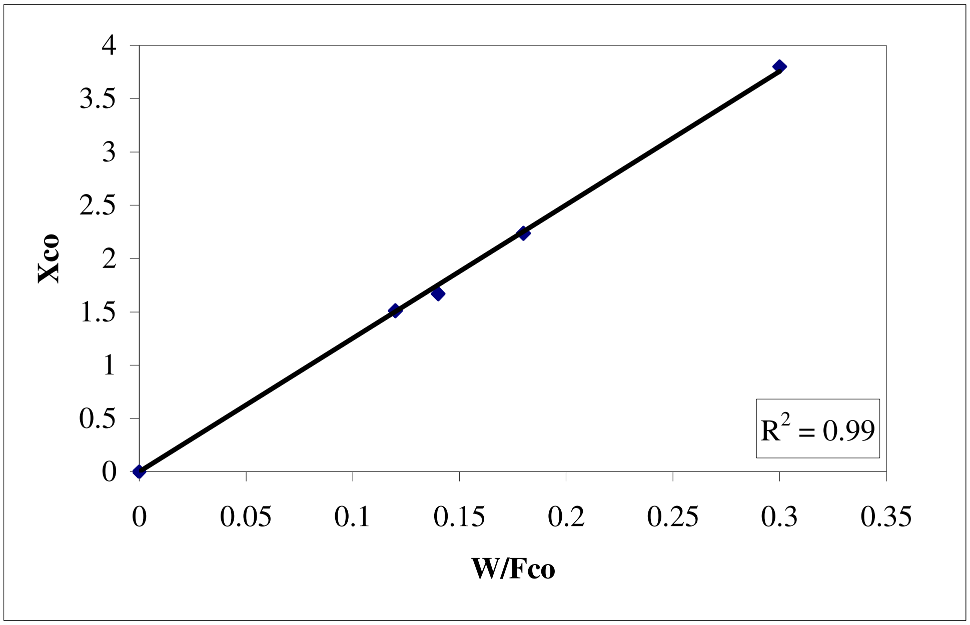

Figure A.7. Fractional CO conversion vs. residence time graph of experiments 17-20

Table A.1. The calculated rate data with using the fractional CO conversion vs. residence time graphs

Experiment No	Partial Pressures (atm)		$W_{cat} / F_{CO\,in}$ (mg.min.μmol^{-1})	x_{CO}	$(-r_{CO})_o$ (μmol.mg^{-1}.min^{-1})
	CO	O_2			
1	0.01	0.01	2.45	0.0367	0.0136
2	0.02	0.01	0.82	0.0208	0.0249
3	0.03	0.01	0.81	0.0358	0.0354
4			0.7	0.022	
5	0.03	0.015	0.81	0.0303	0.0374
6			0.7	0.0241	
7	0.04	0.025	0.52	0.0323	0.0513
8			0.61	0.0388	
9	0.04	0.02	0.61	0.025	0.0498
10			0.81	0.0304	
11	0.05	0.025	0.24	0.016	0.0623
12			0.37	0.0253	
13	0.05	0.02	0.49	0.028	0.0606
14			0.65	0.0375	
15	0.08	0.04	0.2	0.02	0.0998
16			0.3	0.0245	
17	0.1	0.04	0.12	0.0176	0.1213
18			0.14	0.0167	
19			0.18	0.0224	
20			0.3	0.038	

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