PREFERENTIAL OXIDATION PERFORMANCE OF Pt-Sn/AC CATALYSTS

by

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ABSTRACT

PREFERENTIAL OXIDATION PERFORMANCE OF Pt-Sn/AC CATALYSTS

Preferential low temperature CO oxidation was studied to find out the effect of H_2O, CO_2, CH_4 and O_2 to CO ratio in the feed stream. Moreover the effect of temperature is also studied on 1% Pt-0.25%Sn/AC. The AC was HCl washed first and then oxidized with HNO_3. Selective CO oxidation experiments were conducted for two sets of feed streams, with and without methane: 1% CO, 1% O_2, 60% H_2 and balance He; 1% CO, 1.25% O_2, 60% H_2 and balance He; 1% CO, 1% O_2, 60% H_2, 10% CO_2, 15% H_2O and balance He; and lastly with 1% CO, 1.25% O_2, 60% H_2, 10% CO_2, 15% H_2O and balance He. In the second part, 3% CH_4 is added to the feed streams and the experiments were repeated. 250 mg catalyst is used, with 100 ml/min feed flow rate, the W/F ratio is kept constant throughout the study. Catalyst activities were tested with a Thermo 48i CO analyzer with 1 pbm sensitivity and GC at 135-125-115 and 110 ˚C.

The results obtained from the study showed that the CO conversion levels generally increase with the increase in O_2:CO ratio. The negative effect of CO_2 can be offset by the addition of H_2O or via changing the reaction temperature or increasing the O_2:CO ratio. Temperature is found to be inversely proportional with CO conversion. Methane addition lowered the catalytic activity at higher temperatures but did not have any significant effect at lower temperatures. The best results were obtained at the feed stream concentrations of 1% CO, 1.25% O_2, 60% H_2 and balance He. The conversion percentage was 95 per cent at 110 ˚C. Most important result is obtained under the realistic methane containing feed of 1% CO, 1.25% O_2, 60% H_2, 10% CO_2, 15% H_2O, 3% CH_4 and balance He. It is found that under the realistic fuel processor conditions CO conversion values were equal to the base case of 1% CO, 1% O_2, 60% H_2 and balance He. 88% CO conversion is achieved.

ÖZET

AKTIF KARBON DESTEKLI PLATIN KALAY KATALIZÖRLERININ TERCIHLI KARBONMONOKSIT OKSIDASYON PERFORMANSI

Bu çalışmada, besleme akımındaki H_2O, CO_2, CH_4 ve O_2 miktarlarının, tercihli CO oksidasyonuna etkisi çalışıldı. Ayrıca sıcaklık değişiminin 1% Pt-0.25%Sn/AC katalizöründeki etkisi de çalışıldı. Aktif karbon, başta hidroklorik asitle yıkanmış ve nitrik asitle okside edilmiştir. Tercihli CO oksidasyonu, besleme akımında metan gazının varlığı göz önünde bulundurularak iki ayrı deney seti olarak ele alındı: İlk deney setinde, 1% CO, 1% O_2, 60% H_2 ve 38% He, 1% CO, 1.25% O_2, 60% H_2 ve 37.75% He; 1% CO, 1% O_2, 60% H_2, 10% CO_2, 15% H_2O ve 13% He; ve son olarak 1% CO, 1.25% O_2, 60% H_2, 10% CO_2, 15% H_2O ve 12.75% He, besleme akımları olarak kullanıldılar. İkinci deney setinde bütün akımlar 3% CH_4 eklenerek ve takiben helyum akışlarından 3% azaltılarak tekrarlandı. Her deneyde 100 ml/dk akış altında 250 mg katalizör kullanıldı. Katalizör ağırlığının, akışa miktarına oranı bütün deneylerde sabit tutuldu. Katalizör aktivitesi, hassasiyeti milyarda 1 parça kadar yüksek olan Thermo 48i marka CO analizörü ve gaz kromatografisi ile 135, 125, 115 ve 110 derece sıcaklıklarında ölçüldü.

Bu çalışmada elde edilen sonuçlar, CO dönüşümünün, O_2:CO oranı ile arttığını gösterdi. CO_2' nin negatif etkisinin ise, besleme akımına su buharı eklenerek, reaksiyon sıcaklığı değiştirilerek veya O_2:CO oranını arttırılarak bertaraf edilebileceği gözlemlendi. Besleme akımına metan gazı katkısının, katalizör aktivitesini yüksek sıcaklıklarda düşürdüğü ama düşük sıcaklılarda hiç etkilemediği gözlemlendi. En iyi sonuç 1% CO, 1.25% O_2, 60% H_2 ve 37.75% He ile 95% dönüşüm oranı ile 110 derece sıcaklıkta gözlemlendi. En önemli sonuç ise, metan katkılı 1% CO, 1.25% O_2, 60% H_2, 10% CO_2, 15% H_2O, 3% CH_4 ve 9.75% He ihtiva eden besleme akımında elde edildi. Bu realistik besleme akımındaki CO dönüşümü oranının, ilk besleme akımındaki ile eşit ve 88% olduğu bulundu.

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1. INTRODUCTION

Depletion of fossil fuel reserves, and environmental problems caused by conventional energy production methods make search for finding alternative energy production routes utilizing renewable sources one of the most interested areas of research. Fuel Cells are major candidate for future energy production due to their heightened efficiency and low emission levels. They are long lived, generate almost no noise, and since they do not have a heat generation step, they are unaffected by the thermodynamic constraints of efficiency. A variety of fuel cells have been developed using different electrolytes. The PEMFC fuel cells operating with hydrogen are found to be the most suitable candidate for small scale applications like automobile propulsion, heat engines, and small scale energy generators. Its advantages are high power density, quick response, compactness and modularity due to the ease of using fuel cell stacks. (Ahmet and Krumpelt 2001; Avcı 2003)

Pure hydrogen feed is the optimum fuel for the PEMFCs. However transporting and distributing hydrogen is very challenging due to its low molecular weight. Alternative methods are preferred to storing hydrogen in pressurized tanks. Carbon nanotubes have been found promising for non pressurized hydrogen storage (Sarkar and Banerjee 2004). [2] The hydrogen storage capacity reached in the reported literature and technological reports is still well below the specifications of US department of energy, i.e. 6,5 % by weight and 63kg/m3 density. Therefore, storing pure hydrogen feed vehicles is currently not economically feasible.

Another practical solution for having hydrogen is producing it on board from easily stored hydrocarbons via fuel processing. A fuel processor unit produces hydrogen generally through series of three reactions; autothermal reforming, high and low temperature shift reaction and, finally, the preferential oxidation. Autothermal reforming has been accepted as the most efficient reforming reaction for small scale applications. In autothermal reforming, a portion of the fuel is burned to supply necessary heat for the endothermic steam reforming reaction, which produces hydrogen. The effluent of reformer has 10% CO. The CO concentration at the exit of WGS reactors drops down to 1-2%. The following preferential CO oxidation step (PROX) is necessary since most widely used fuel cell catalysts are prone to carbon monoxide poisoning; for example, platinum based cathode catalysts require carbon monoxide levels as low as 10ppm for stable operation (Dudfield et al., 2000). Therefore, PROX aims to reduce carbon monoxide levels from 1% to below 10 ppm. Hydrogen oxidation must be as low as possible. Hydrogen oxidation would lead to wasting the fuel gas and more water disposal problems in the PEMFC. Thus the carbonmonoxide/hydrogen selectivity is also a major objective. PROX is an essential step in hydrogen production to be used in fuel processors.

Desired reaction : $CO + \frac{1}{2} O_2 \rightarrow CO2$ $\Delta H = -67{,}6$ kcal/mol

Undesired Reaction: $H_2 + \frac{1}{2} O_2 \rightarrow H_2O$ $\Delta H = -58{,}6$ kcal/mol

In order to avoid the use of heat exchangers, PROX temperature should be ideally around 100˚C. On the other hand, temperature values as high as 130˚C can be also preferred due to favorable selectivity at elevated temperatures.

Most conventional CO oxidation catalysts require high temperatures to operate. Low temperature CO catalysis has two important aspects which have to occur simultaneously, i.e. CO chemisorption and dissociative adsorption of O_2. Therefore the catalyst should have separate components to take care of both functions simultaneously. (Trimm and Önsan, 2001)

It is imperative in every catalytic study to determine the noble metal which can selectively catalyze the reaction. The most encountered form of catalysts for the low temperature CO oxidation consists of a noble metal, a metal oxide or zeolite and the support material.

Activated Carbon (AC) is renowned for his high surface area (500 m^2 per gram) and can be used in fiber form for CO oxidation as support. (Bulushev et al., 2004) The surface of the activated carbon consists of many porous different layers, and these layers are prone to modification by chemical means. The textural and chemical properties of the AC surface can be changed to better suit the reaction. AC is stable over a large pH rate. It is stable even in high temperatures, although the carbon bulk is considered inert; its surface has free H, N and O groups, of which especially O groups are important for oxidation. (Aksoylu et al., 2000a)

Platinum is the traditional catalyst noble metal for CO oxidation however Au shows greater activity at low temperatures. Although Platinum based catalysts are very active, they are very susceptible to CO poisoning, metal oxide SnO_x addition gives it more CO resistance

Pt-Sn over air oxidized and nitric acid etched activated carbon has been tried for PROX reactions previously by Şimşek et al. 2006. 100% CO conversion has been reached with the addition of CO2 gas and water to the feed. CO2 and water are also the product of the Water Gas shift Reactions which are directly upstream of the PROX reactor in an on board fuel processor, the reported catalyst was successful. However the product analysis was done by Gas Chromatoghraphy which has a maximum of 100 ppm sensitivity. In this work, it is aimed to fine tune the Pt-Sn over nitric acid etched activated carbon to the PROX reaction and analyze the product gas with a Thermo 48c CO Analyzer. The sensitivity of the CO analyzer is about 0.1 ppm and only with this analysis, it can be seen whether the CO conversion level is suitable (below 10 ppm) for a real application.

The set of experiments for this work is selected to be on 1%Pt-0.25SnO_x/AC sequentially impregnated. Activity tests for this catalyst were performed by Özkara (2002) with a stream composition of 1% CO, 1% O_2, 60% H_2 and inert He. Afterwards they are tested for realistic feed conditions by Şimşek et al. (2007) under realistic PROX feed conditions of 1% CO, 1% O_2, 60% H_2, 15% CO_2, 10% H_2O and inert He. In this work the selected feed conditions are started from 1% CO, 1% O_2, 60% H_2 and inert He, effect of CO_2 and water in the feed will be tested along with the effect of hydrocarbon addition to the feed. The product stream will be tested on CO concentration with 0.1 ppm sensitivity.

Chapter 2 in the report gives general information about the importance of the fuel cells, the position of the PROX reactor within this system and the important aspects of the CO oxidation in the fuel cell. Moreover the relevant previously worked catalysts will be considered, along with the importance of bimetallization. The effect of the water vapor and carbondioxide addition to selectivity and activity will be examined. Experimental work will be explained in detail on Chapter 3. The results will be discussed in the 4th Chapter and the conclusions that are drawn from the work will be given in the 5th Chapter.

2. LITERATURE SURVEY

2.1. Fuel Cells

Fuel Cells are devices which convert chemical energy stored in a fuel to electrical energy; in that sense they are galvanic cells but not batteries. The Fuel cell operation is continuous whereas the batteries die after a certain amount of time. Conversion of electrical energy to mechanical energy is much more efficient than normal fuel consumption methods where the chemically stored energy is converted to mechanical energy through heat. Therefore, all combustion engines are limited by the thermodynamic constraints of efficiency; the fuel cells however, are not. A great amount of funding is currently flowing into the fuel research to meet the objectives set by the United States Department of Energy. Over the past years most automobile companies developed their own prototype hydrogen vehicles to reduce the carbondioxide emissions. There are many types of fuel cells under development which are intended for use in different applications;

- Proton Exchange Membrane or Polymer Exchange Membrane (PEM) type fuel cells operate at relatively low temperatures of 80˚C. They are compact in size have high electric production per unit volume and are tolerant to transient operations mode. These types of fuel cells combined with electric motors are the most suitable candidates for replacing the gasoline engines for mobile applications.

- Alkali fuel cells operate with compressed hydrogen and oxygen; they use KOH as electrolyte and operate at 150-200˚C. Their pure hydrogen requirement and platinum catalysts make them too expensive.

- Molten carbonate fuel cells use molten salts as electrolyte and operate at 650˚C. Although its nickel based catalysts are not too expensive, its required temperature is too high for mobile applications and home use.

- Phosphoric acid fuel cells operate at 150-200˚C, they have good CO tolerance, however platinum catalysts are still needed and all of the casing must be able to withstand the corrosive acid.

- Solid oxide fuel cells use solid metal oxides as the electrolyte; they operate at about 1000˚C. This type of fuel cells are currently being considered for stationary applications, its waste heat can also be used to produce more electricity. (Smithsonian Institute)

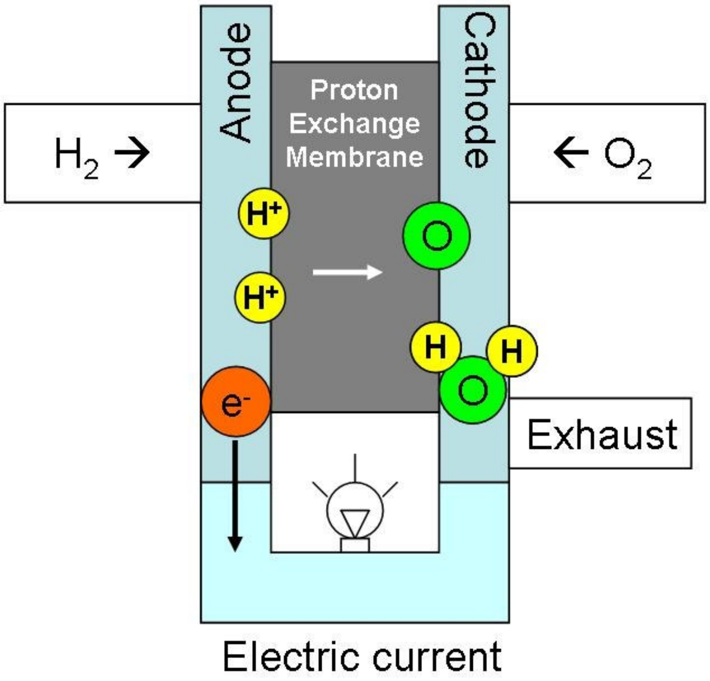


Figure 2. 1 PEM Fuel Cell Schematic

Platinum based catalysts are widely used and very successful in running the reduction reaction at the cathode and much progress has been achieved in reducing the Pt loadings. (Gasteiger et. al., 2004) However the platinum catalysts are easily fouled by the CO. In order to prevent CO poisoning, the PEM feed must contain less than 10 ppm CO.

2.2. On Board Hydrogen Production for Mobile Applications

Pure hydrogen feed is the best fuel for the fuel cells but storing hydrogen in feasible quantities still pose a problem. Therefore, producing hydrogen on board via fuel processor, which is a device having catalytic reactors in series for producing hydrogen from easy-to-store hydrocarbons, and using it as the feed for the fuel cell is a plausible short term solution for fuel cell powered vehicles.

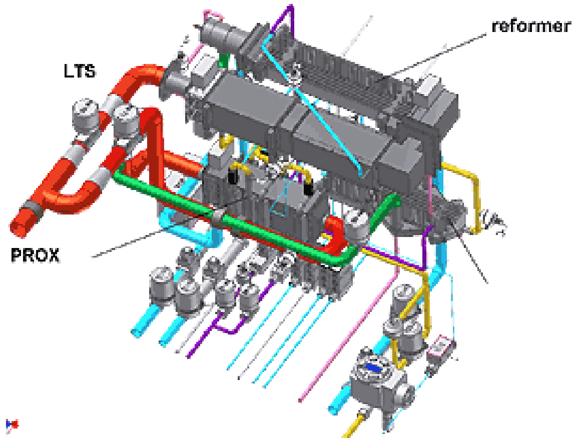


Figure 2. 2 A prototype fuel processor

The fuel is converted into hydrogen in the reformer section of the processor via autothermal reforming of the gas. Depending on the type and fuel of the processor, the product stream of the reformers contains 3-10 per cent CO, 40-75 per cent H_2, 5-15 per cent CO_2, 15- 30 per cent H_2O and 0-25 per cent N_2. The water gas shift reactions (HTS and LTS) reduce the CO content down to 1 per cent. However this 1 per cent needs to be further oxidized, since CO levels as low as 10 ppm is needed to prevent catalyst poisoning in the fuel cells. (Trimm and Önsan, 2001)

2.3. Reactions in a Fuel Cell Processor

Steam reforming of hydrocarbons is an old and viable method for hydrogen production (Equation 2.3.1). The reaction is highly endothermic; this is why Steam Reforming is combined with partial oxidation of methane, in Autothermal reformers for which some of the fuel is burnt via partial oxidation (equation 2.3.2) to provide the necessary energy for the reforming reaction. (Defalco et. al. 2007)

$$C_nH_m + H_2O \rightarrow nCO+(n+m/2)H_2 \ \Delta H^{\circ}_{298}>0 \qquad (2.3.1)$$

$$C_nH_m + n/2O_2 \rightarrow nCO+(m/2)H_2 \ \ \Delta H^{\circ}_{298}<0 \qquad (2.3.2)$$

Water gas shift reactors are placed downstream of the autothermal reformers and provide the initial CO cleanup (Equation 2.3.3) and additional hydrogen via utilizing bond breakage of the water molecule. (Equation 2.3.4). The water gas shift catalyst should be active at relatively low temperatures of 200 – 280˚C.

$$CO + H_2O \rightarrow CO_2 + H_2 \ \Delta H^{\circ}_{298}= 41.2 \text{ kj/mol} \qquad (2.3.3)$$

Preferential oxidation, as the name implies, is performed for cleaning up the remaining CO (Equation 2.3.4) while oxidizing as little hydrogen as possible. (Equation 2.3.5) Aiming to have high energy efficiency in combined fuel processor - fuel cell system, the PROX catalyst should operate at temperatures as low as 120˚C with fast kinetics.

$$CO + \tfrac{1}{2}\ O_2 \rightarrow CO_2 \ \ \Delta H^{\circ}_{298}= -283.6 \text{ kj/mol} \qquad (2.3.4)$$

$$H_2 + \tfrac{1}{2} O_2 \rightarrow H_2O \ \Delta H^{\circ}_{298}= -243.5 \text{ kj/mol} \qquad (2.3.5)$$

2.4. CO Oxidation

2.4.1. PROX Catalysts

Platinum, palladium and ruthenium are favorable metals due to their high activity and selectivity for CO oxidation. Cheaper substitutes like tin and copper can also be used to catalyze the reaction; however, due to the low catalyst loadings, this is considered as a secondary aim. Most of the noble metal catalysts start to activate around 170˚C. O_2 and CO compete for the same sites on the catalyst at lower temperatures; during the competitive adsorption CO chemisorps to the surface and prevents O_2 disassociation on the surface. Alternatively, at low temperatures O_2 can be held too strongly by the surface thereby preventing displacement by CO depending on the active metal used. Thus an effective PROX catalyst has to simultaneously provide the conditions for CO chemisorption and dissociative adsorption of O_2. (Trimm and Önsan, 2001)

Gold based catalysts have shown promising results due to their activity in CO oxidation and better selectivity compared to Pt based catalysts. Additionally gold catalysts are resistant to water present in realistic feed conditions. Cameron et. al. (2003) report that with increasing platinum and palladium prices, gold is the cheaper noble metal. Since catalyst cost per kW/h poses a major problem for the fuel cells, gold would bring a much appreciated decrease in fuel cell costs. Gold is also used in PROX catalysts successfully. Kahlich et. al. (1998) experimented with Au/Fe_2O_3 and found that at 80˚C its activity and selectivity is comparable by the commercial platinum based PROX catalyst $Pt/\gamma{-}Al_2O_3$. The reported energy for CO oxidation was 31 kj/mol and the reaction orders were 0.55 and 0.27. Additionally the selectivity was also not affected by the amount of CO in the stream. However although the oxygen conversions were as high as 75% for CO oxidation, it was not suitable for the fuel cells since nearly 99.9% conversion is aimed. Panzera et. al.(2004), report conversions as high as 99% at 120˚C, with 5% Au loading on cerium oxide pre calcined at 500˚C. On the other hand however pre-calcination also lowers the CO_2 selectivity of the catalyst and 5% Au loading amounts to higher costs than 1% Platinum loadings. Rossignol et. al.(2004), worked with gold catalysts on three different supports, Al_2O_3, TiO_2, ZrO_2 of a temperature range between 25 and 450˚C. They achieved complete conversions with titanium oxide supports at 350˚C and reported that TiO_2 is the best support for gold catalysts. This has first been proposed by Haruta et. al. (1996) and is confirmed with oncoming studies. Gardner et al. used co-precipitated 20% Au/CeOx at 75˚C with negligible activity losses; Lyn and Flytzani-Stephanopoulos (2006) achieved complete CO oxidation at ambient temperature on a Au0.05[Ce(La)]0.95Ox catalyst. However, the hydrogen oxidation becomes significant over 80˚C. Luengnaruemitchai et. al. (2004) have found out that the activity and selectivity of the gold based catalysts are strongly dependant on the selected preparation method. Au/Ceria catalyst prepared by co-precipitation method was the most active among the ones prepared by impregnation, co-precipitation and sol-gel methods. Dekkers et al. (1999) showed an increase in catalytic activity for PROX on silica- and alumina-supported Au samples with subsequently impregnated 10% CeOx. At 2002 Bera and Hegde managed to have complete CO oxidation below 200˚C over thermally treated Au/CeOx. PROX reactions inside a compact fuel processor cannot have the additional expense and complication of heat exchangers; therefore, the catalysts must be active at temperatures lower than 130˚C.

As pretreatment of catalysts gained such importance, Echigo and Tabata performed experiments on pretreated Ru/Al_2O_3 with heating the catalyst under H_2/N_2 gas flow. They were tested catalysts in the reaction also without pretreatment. The CO level in the product stream was reported under 10 ppm around 90-140˚C for the pretreated sample and 155-180˚C for the one not pretreated. Pd/Al_2O_3 in the presence of oxygen at 130˚C lacks selectivity but Pd based catalysts are also applicable. For example Pd/CeO_2 catalysts are found to be active for PROX reaction in both under presence and absence of oxygen (Bekyarova et al 1998; Bedrane et al 2002). Chang et al. (2008), inspected over 150 catalyst systems and deemed 4 of them promising, i.e. $Pt\text{-}Co/Al_2O_3$, Pt/Al_2O_3, Au/Fe_2O_3, and $CuO\text{-}CeO_2$. Further investigation of these catalysts in differential reactors, where heat and mass transfer effects are negligible, yielded that the original Pt/Al_2O_3 is the best candidate for the PEM fuel cells. However, it is interesting to note that, the $CuO\text{-}CeO_2$ association was found to be more selective and thermally stable than Au or Pt based catalysts. This system is important due to its economical advantage led by the use of copper instead of platinum group precious metals. Moretti et al (2007) used ceria modified alumina as the support and found a thermally selective catalyst with good activity. Work is continuing on this system with the current main interest on the catalyst nanostructure.

Noble metals are not the sole option for CO oxidation, gold is cheaper than platinum and palladium, and copper based catalysts are much cheaper. Gomez – Cortez et. al. (2008) reported total conversion between 125-130˚C with different loadings of CuO over two types of CeO_2 supports. Low cost of copper allows for high loadings such as 3% - 6%. Copper on high surface area cerium oxide achieved high conversion values and acceptable selectivity values. At higher temperatures, around 150˚C, the catalyst deactivated to lower conversions and selectivity values. Catalyst preparation is vital to PROX success. Chen et. al. (2007) used CuO/Ce_x over $Zr_1{-}xO_2.Al_2O_3$, the addition of aluminum increased the dispersion of the metal over the support. Zirconia addition to CeO_2 increased the activity of the catalyst by activating the mobility of the lattice hydrogen. They experimented with different amounts of dopants and found that 7% CuO/ $Ce_{0.9}Zr_{0.1}O_2.Al_2O_3(20\%)$ is a competitive candidate in PROX with nearly 100% conversion at 370 K and a very high selectivity value, 100%, at the same temperature. The catalyst goes a slight deactivation after 1 hr and settles at 98% conversion. PROX is a widely researched subject and the alloys are also investigated. According to Papavasiliou (2006), Cu-Mn catalysts show favorable characteristics and catalytic properties for the production and purification of hydrogen.

2.4.2. Pt Catalysts

Pt/Al_2O_3 was proposed by Engelhard in 1963 to oxidize carbonmonoxide under excess hydrogen. Atalik and Uner (2006) investigated this catalyst's PROX activity at a temperature range from 100˚C to 350˚C with different active metal loadings. Catalyst with higher loadings, like 0.83 weight per cent, peaked at 40-45% conversion at 200˚C after which the catalyst deactivated slightly. The same trend is observed also for the catalysts with lower loadings, but they were activated at even higher temperatures. PROX reactor of a fuel processor used in combined fashion with a fuel cell demand far stricter CO conversion levels at lower temperatures. Suh et al, 2004, compared the noble metal catalysts nicely; the study showed that Ru/Al_2O_3 is more active than Pt/Al_2O_3 but methanation, which occurs as the side reaction on Ru, results in hydrogen consumption. Rh/Al_2O_3, Pd/ Al_2O_3, and Au/Al_2O_3 cannot oxidize carbon monoxide more efficiently than conventionally used Pt/Al_2O_3. Bisset et al. (2005) and Kahlich et al. (1997) investigated the kinetics of Pt/Al_2O_3 and have developed a satisfactory model for the reaction on Pt/Al_2O_3 catalysts. Cho and Stenger (2006) evaluated the rate expression for the reaction over the noble catalysts (Pt, Rh, Pt-Fe, Pt-Rh) supported on γ–Al_2O_3. Another work from Luengnaruemitchai et al. (2007) was over zeolite supported Pt catalysts for a hydrogen rich CO stream. Addition of carbondioxide and water are also observed; CO_2 had no significant effect on the catalyst activity and selectivity. Water, on the other hand, lowered the selectivity of Pt on Zeolite. The catalyst having 1 per cent weight load reached complete conversion around 220˚C with a maximum selectivity of 80%. It was better in terms of activity than the traditional Pt/Al_2O_3 and had much higher selectivity. Pt/CeO_2 is another promising catalyst for PROX reactions. Monyanon et. al. (2006) prepared Pt/CeO_2, Au/CeO_2 with single step sol gel method. Among 1 per cent weight metal loaded catalysts, Pt based catalyst showed a conversion peak of 80 per cent at 90˚C, the gold based catalyst activated at 150˚C and reached 70% conversion. The selectivities showed similar trends. Ayastuy et. al. (2006) investigated the effect of the reaction parameters on the conversion of CO. In the experiments which were conducted at 80, 100 and 120˚C, the catalyst showed lower conversions with increasing temperature for the non realistic feed of 60% hydrogen, 1% CO and 1% oxygen. The addition of CO_2 and water reduced the conversions at 80˚C, but the conversions increased at 100 and 120˚C, complete conversion was achieved at 100˚C with 5% CO_2 and 5% water in the feed. At the complete conversion the selectivity was 50% since the oxygen/CO ratio was in the feed 2:1 stochiometrically.

Pt over SnO_2 catalysts gave much promising results in CO oxidation and can operate under 100˚C. It should be noted that temperature catalysis is avoided to prevent the usage of heat exchangers inside the fuel processor and the selectivity. Hydrogen starts to get selectively oxidized over CO at increased temperatures. The activity of Pt/SnO_2 catalyst is greater than both of Pt and Sn catalysts. This clearly indicates that there is a synergetic interaction between Pt and Sn, and shows that Pt and Sn have either complementary sites for the reaction, or the Pt-Sn interface is particularly suitable for the oxidation. High temperature reduction leads to pure Pt metal whereas low temperature reduction around 125˚C leads to platinic bases. (Trimm and Önsan, 2001)

2.4.3. Bimetallic Pt Catalysts

Considering oxygen and carbonmonoxide require separate sites on the catalyst support, Pt/SnO_x benefits from the chemisorption on tin. This leads to the prospect of bimetallic catalysts; promoter metals may enhance the activity of the catalysts.

Kotobuki et al 2006 have shown that complete CO conversion at relatively high temperatures ca. 150˚C, with Pt-Fe alloy over mordenite is possible under with realistic feed conditions. In this bifunctional mechanism, CO adsorbs on Pt and Fe sites act as in the dissociative-adsorption sites, where the oxygen atom and CO reacts to CO_2. Pt supported on Zeolites and TiO_2 also yielded even better results than Pt/Al_2O_3 according to Ruth et al. Son et al. (2000) managed to increase the activity and selectivity of Pt/Al_2O_3 by water vapor pretreatment; it has been hypothesized that this is caused through the size reduction of platinum particles. Guerrero at al, (2007) experimented with an unusual promoter, niobium, on Pt/Al_2O_3. Addition of 5% niobium increased the activity of the original catalyst significantly; total conversion reached ca. 150˚C. Platinum supported on Niobium oxide did not give satisfactory results in terms of conversion, however its CO/H_2 selectivity was near 100%. Niobium is a relatively cheap metal, which enables working with high loadings. Kim et. al. (2007) prepared Al_2O_3 microchannel reactors and doped them with Pt and Cobalt promoters.. Selectivities near 30-40% reached with high percent activities, but the temperature was in the range of 225-250˚C. Monyanon et. al. (2006) experimented with PtAu/CeO_2 with 1% loadings, and achieved 90% conversion at ca. 90˚C, with 55% selectivity.

The success of the Pt/SnO_2 clued that Pt-Sn interface is very suitable for CO oxidation, which is natural for the bimetallic Pt- Sn catalysts to be examined. Schubert et al. (2001) reported that, Pt-Sn system over carbon supports achieved much higher selectivity and activity than Pt/Al_2O_3. The CO oxidation's desorption limits are lifted for this catalyst and the spectroscopic studies showed that CO and H_2 compete for Pt sites, while O_2 adsorbs mainly on Sn sites. (Choudhary and Goodman, 2002)

2.5. Catalyst Supports

Earlier catalysts were designed without supports, like the iron based catalyst of the Bosch – Haber process. As the technology improved, more valuable metals, made the catalyst cost substantial. Since the reactions depend almost solely on the surface properties, methods of maximizing catalyst surface area per gram of used noble metal gained importance. This lead to the use of catalyst supports. Supports are generally classified as inert and much cheaper substances which introduce a means of spreading of the active metal. However supports are in no way unimportant. Catalyst supports are known to react with noble metals to increase or decrease its activity. (Satterfield, 1991) A support should have the following characteristics:

- High material strength resilience to attrition and corrosion effects.
- High surface area to enable dispersion for the active phase.
- High porosity values and cracked layers if possible
- Low Cost

The most common PROX support is the aluminum oxide however carbon materials also have many advantages. This work focuses on the activated carbon supports and their properties.

2.5.1. Activated Carbon

Activated carbon consists of many overlapping layers, which contribute to a high surface area of above 500 m^2 per gram. Carbon is pyrolyzed at 900˚C prior to use and is therefore highly resistant to high temperatures. Its surface consists of a porous network with many meso and micropores. Carbon Black, graphite, metal covered carbons and glassy carbon are other examples. Activated carbon is selected as the support for many catalytic applications. (Rodriguez-Reinoso, 1998)

Carbon is active in both acidic and basic media. It allows the recovery of the active metal which is very important for industrial applications from an economical point of view. Activated carbon can be burnt off after the catalyst is spent. This would enable recycling of the active metal. Activated carbon’s surface can be enhanced or changed via different treatment methods. Its textural properties are relatively easier to be changed in order to suit the needs of the targeted catalytic reaction this property widens the usage of active carbon.

Carbon is used as support for noble metals in hydrogenation reactions of fuel cell catalysts, in the large scale production of vinyl acetate and chloride, as filter material in gas masks due to its property of adsorbing hazardous gases on its surface and oxidation of hazardous gases. Carbon’s structure enables it to selectively oxidize hazardous gases via chemisorption. This natural tendency makes it a suitable candidate for the PROX reaction. (Lee and Misono, 1999)

The primary role of the support is to finely disperse and stabilize small metallic particles and thus provide access to a much larger number of catalytically active atoms than in the corresponding bulk metal even when the latter is ground to a fine powder. Thus, the most important parameters for the catalyst manufacturer and the user of a catalyst are the porosity and the pore size distribution of the activated carbon as well as its surface area. Additional important parameters are the particle size distribution of a powder or granulate, the attrition resistance and the ash content. Activated carbons formed must also exhibit sufficient high crush strength. Together with the surface chemistry of the activated carbon, these factors strongly influence the performance of the activated carbon supported catalysts. (Auer et al., 1998)

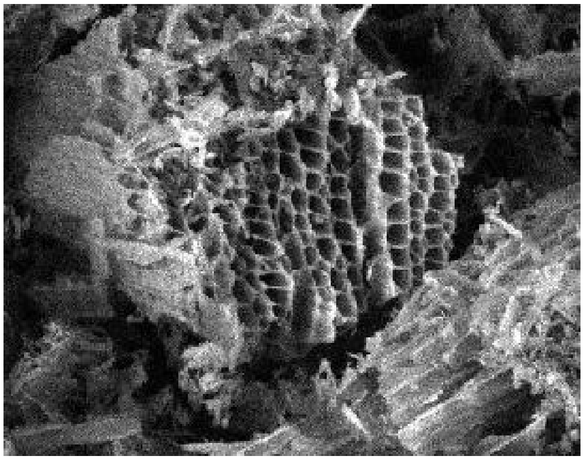
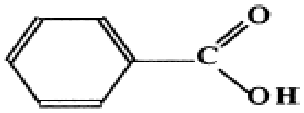
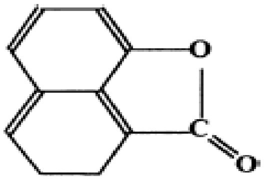
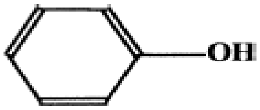
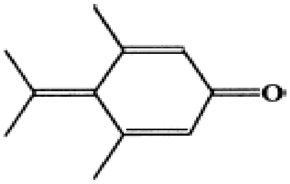
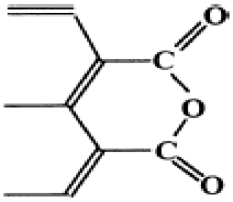
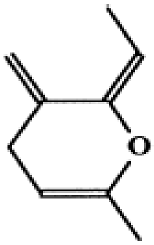
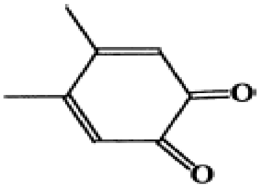


Figure 2.3. An activated carbon gas filter

Activated carbon looks like crumpled paper with a high amount of pores. (Figure 2.3) It usually has very few hydrogen and oxygen groups bonded on its surface. 15% of active carbon consists of mineral content, which is named as ash. The surface interactions of the activated carbon with the noble metal are very important for catalysis. Most of the treatments consist of removing or modifying the surface oxygen groups of the activated carbon.

The functional groups on the carbon surface are mostly oxygen bearing surface groups namely, phenolic groups, lactonic groups, etheric groups and carboxylic groups. These groups are responsible for the acid/base behavior and the redox properties of the activated carbon, since the carbon itself is generally inert. Surface groups may hinder or help the chemisorption the active metals during catalyst preparation. For some catalysts these groups function as nucleation sites for the noble metal. Thus, it comes down to preparing the surface for the reaction by rooting out dysfunctional surface groups. Oxygenation of the carbon surface can be achieved via reaction with the oxygen carrying molecules like carbondioxide, ozone nitrious and/or nitric oxides. Table 2.1 shows the temperature programmed desorption/decomposition (TPD) tests of the corresponding groups.

Table 2.1. TPD results for the Activated Carbon Functional Groups Aksoylu et. al. (2000a)

Type of group	Name	Species released	Peak T [21]
	Carboxylic	CO_2	ca. 510 K
	Lactone	CO_2	ca. 940 K
	Phenol	CO	ca. 905 K
	Carbonyl	CO	ca. 1080 K
	Anhydride	$CO + CO_2$	ca. 820 K
	Ether	CO	ca. 973 K
	Quinone	CO	ca. 1080 K

Much of the underlying theory on the active carbon is still not understood, however a variety of pretreatments showed different effects and results this enables the active carbon surface to be tailored according to the need. The experimental works have showed that:

- Carbon is resistant to heat due to pyrolyzation in its production procedure;
- Not being a metal oxide, it remains stable at a large pH interval both in basic and acidic media;
- Cost of carbon is cheaper than most metal oxides;
- Its surface can be tailored to suit the needs of the catalyst;
- Active phase can be recycled via burning off the carbon .

Increasing the oxygen groups is important for PROX catalysts. Carbon is hydrophobic in its elementary form. Hydrophobic surfaces repulse carbonmonoxide and reduce the catalytic activity. The functional oxygen groups however are hydrophilic due to their polarity by hydrogen bonding interactions. Since carbonmonoxide is polar whereas carbondioxide is not, a polar surface would attract carbonmonoxide and repulse the product of the reaction (carbondioxide), which is ideal for activity. Therefore, increasing the hydrophilic groups; with as much oxygen as possible should be the aim of the activated carbon pretreatment for the PROX reactions. (Aksoylu et al. 2000a)

2.6. Pt-Sn Catalysts over Activated Carbon Support

Treating the activated carbon surface to increase the oxygen bearing groups is a viable way to enhance the catalyst activity. Aksoylu et. al. (2000) treated the activated carbon with nitric acid and doped Pt-Sn via co- and sequential impregnation methods. TPD profiles showed that the concentration of oxygen bearing groups are increased more than ten times, when compared to raw activated carbon. 100% conversion is reached with 1% Pt - 0.25% Sn on AC catalyst prepared by sequential impregnation. Özkara and Aksoylu (2003) experimented with the same active metal loadings of 1% Pt and 0.25% Sn on air oxidized active carbon. The feed was rich in hydrogen and oxygen. O_2:CO loading in the feed was 1:1 stoichometrically. 80 per cent CO conversion is achieved along with 100% O_2 conversion.

Şimşek et. al. (2007) investigated the catalyst further. The activity of 1% Pt 0.25% Sn over acid etched activated carbon is analyzed at 150˚C under hydrogen rich feed. The conversion was 41%. The exit stream of the WGS reactor in the fuel processor usually contains 15 per cent CO_2 by volume, therefore presence of CO_2 should be analyzed. In the presence of 15 per cent CO_2, conversion percentages are found as 95 per cent for 1%Pt-0.25%Sn over HCl washed activated carbon support (AC1). For 1%Pt-0.25%Sn over HCl washed and air oxidized carbon support (AC2) the conversion is found to be 89 per cent. Finally for 1%Pt-0.25%Sn over HCl washed and nitric acid oxidized activated carbon support (AC3), the conversion was 100 per cent. Addition of 10 per cent H_2O to the feed stream changed the conversion percentages to 72 per cent, 74 per cent and 100 per cent for AC1, AC2 and AC3 respectively. Further analysis is needed for lower temperatures which are more suitable for the PROX processor operation. Since a PROX processor feed stream will most likely contain unburnt hydrocarbons from previous steps in the processor hydrocarbons should be added to the feed stream to realistically simulate fuel processor conditions. The PEM fuel cells operate at temperatures close to 80˚C and PROX reactions are preferred to occur at temperatures close to 105-110˚C.

3. EXPERIMENTAL WORK

The experimental work for the thesis can be summarized as follows. See Figure 3.1.

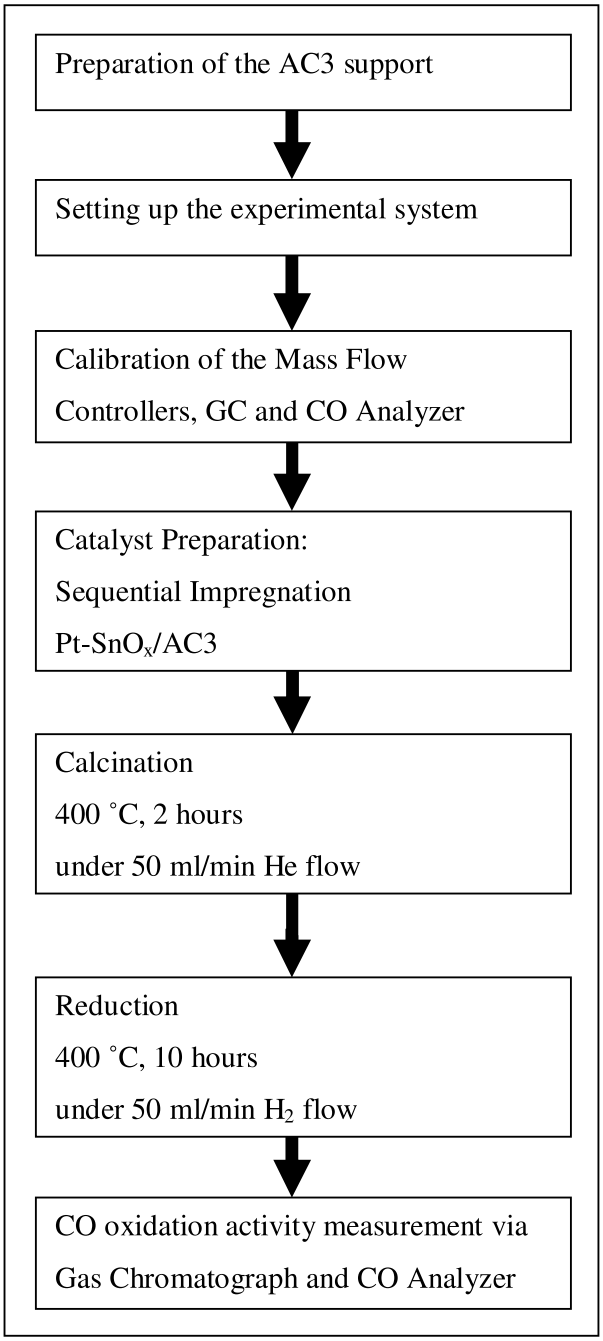


Figure 3.1. A Schematic diagram of the experimental work done in this study

3.1. Materials

3.1.1. Chemicals

The catalysts that were tested in this study were prepared in the scope of the previous study performed by Şimşek (2006). 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/mole)
Hexachloroplatinic(IV)acid hexahydrate	$H_2PtCl_6.6H_2O$	Extra pure	Merck	517.9
Tin(IV)chloride	$SnCl_4.5H_2O$	Extra pure	Riedel-de Haën	350.5
Activated carbon	C	ROX 0.8	NORIT	12
Nitric Acid	HNO_3	Research	Merck	63.0
Hydrochloric acid	HCl	Research	Merck	36.5

3.1.2. Gases and Liquids Used

All of the gases used in this study were supplied by BOS (Birleşik Oksijen Sanayii) Company, Istanbul, Turkey. Table 3.2 gives the specifications and the use of these gases.

Table 3.2. Specifications and applications of the gases and standards used

Gas/Standard	Specification	Application
Carbon monoxide	99.999% BOS	GC calibration, Reactant
Oxygen	99.999% BOS	GC calibration, Reactant
Carbon dioxide	99.999% BOS	Reactant
Helium	99.99% BOS	Reactant
Methane	99.99% BOS	Reactant
Hydrogen	99.99% BOS	Reactant, reducing agent
Helium	99.99% BOS	GC carrier

Table 3.3. Specifications and applications of the liquids used

Liquid	**Specification**	**Application**
Water	Distilled	Aqueous solutions, Reactant

3.2. The Experimental Set-Up

There are mainly three systems which were used in this study;

(i) AC preparation system which was used for the preparation of HNO_3 – oxidized AC support

(ii) Catalyst preparation system which was used in the preparation of sequentially impregnated Pt-Sn/AC3 catalysts

(iii) Reaction test system which was used in the catalytic performance tests. The reaction test system includes three sub units, namely reactant stream preparation unit, temperature controlled reactor and the analysis block including a CO analyzer and a GC.

3.2.1. Catalyst Preparation System

The system used for catalyst preparation by sequential impregnation technique includes a Retsch UR1 ultrasonic mixer, a vacuum pump, a buchner flask and a MasterFlex computerized-drive peristaltic pump.

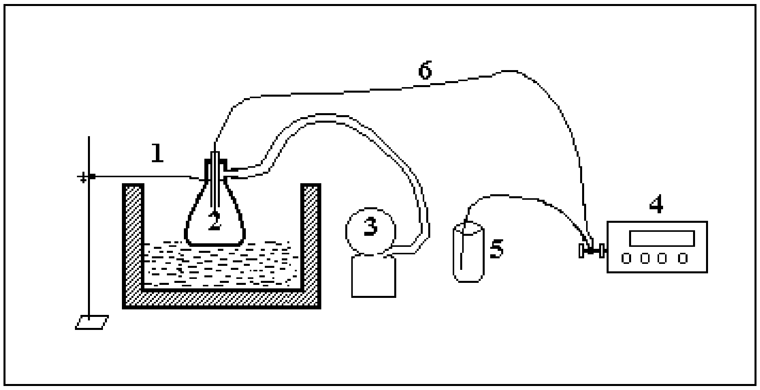


Figure 3.2. The impregnation system: 1. Ultrasonic mixer 2. Vacuum flask 3. Vacuum pump 4. Peristaltic pump 5. Beaker 6. Silicone Tubing

3.2.2. Catalytic Reaction System

The catalytic reaction system designed and constructed in CATREL has three sections:

- Feed preparation section
- Reactor section
- Product analysis section

Feed preparation section, which is stationed before the reactor, consists of mass flow control systems, 1/4", 1/8" and 1/16" stainless steel tubes and fittings for feeding liquid water and gaseous species, i.e. helium, hydrogen, oxygen, carbondioxide, carbonmonoxide and methane. Water is fed to the system with an Agilent 1200 series HPLC pump at constant flow rates. The 1/16” tube, through which water was allowed to flow and the lines between the water inlet and the reactor are kept above 100°C with a 2 m heating tape to enable vaporisation. The heating tape is controlled by an Omron E5AN PID controller with ± 3K sensitivity. The high purity gases are supplied by pressurized cylinders and their pressures are reduced via BOS 5850E model gas regulators to 1.5-2 atmospheres. The gases are passed through calibrated Brooks mass flow controllers. Two Brooks CC1A10 series control boxes are used to regulate the gas flows. On-off valves were placed in front of the mass flow controllers to protect them from possible back-pressure fluctuations.

It was possible to divert flow using three way valves: The feed gases could be diverted to the bypass line, so that feed composition could be analyzed using the gas chromatograph and the CO analyzer. Another three way valve was used for diverting the flow to the bypass vent line for establishing steady state flow and mixing of the steam and other gaseous reactants prior to the reaction.

The reactants, metered and mixed in the feed section, were allowed to flow through the reaction section. This section was composed of a 50 cm x 2.4 cm ID tube furnace controlled to ± 0.5 K by a Eurotherm 3216 programmable temperature controller and a 1/4" stainless steel fixed-bed microreactor. The reactor was also constructed in CATREL and its length was selected to be 60 cm so that it was longer than the furnace.

During the reaction tests, the catalyst bed was placed in the center of the reactor. The reaction temperature was controlled and measured by a 20-gauge wire K type sheathed thermocouple (insulation material: ceramic fiber braid) that was placed in the center of the furnace. The position of the reactor and hence catalyst bed was adjusted to coincide with the constant-temperature zone of vertical tube furnace. Silane-treated glass wool (Alltech Associates Inc.) was used to hold the catalyst bed in a fixed position. Ceramic glass wool insulations were placed in top and bottom ends of the reactor furnace to prevent heat loss from the furnace and to provide a good temperature profile.

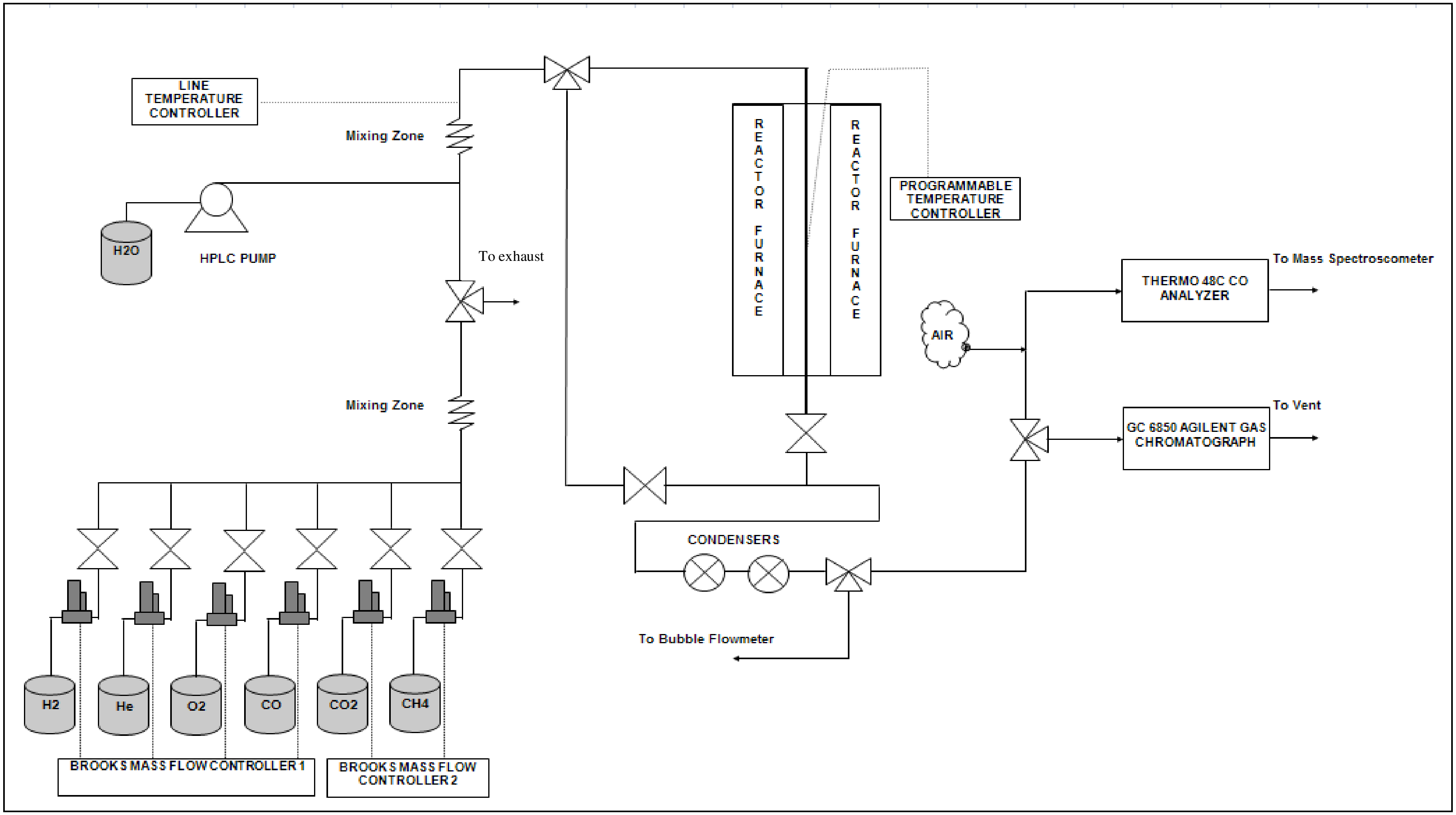


Figure 3.3. Flowsheet of the microreactor system

3.2.3. Product Analysis Systems

PROX experiments involve only two separate oxidation reactions. Oxidation of hydrogen and oxidation of the carbonmonoxide. Therefore the product gas needs to be tested only in terms of oxygen and carbonmonoxide concentrations.

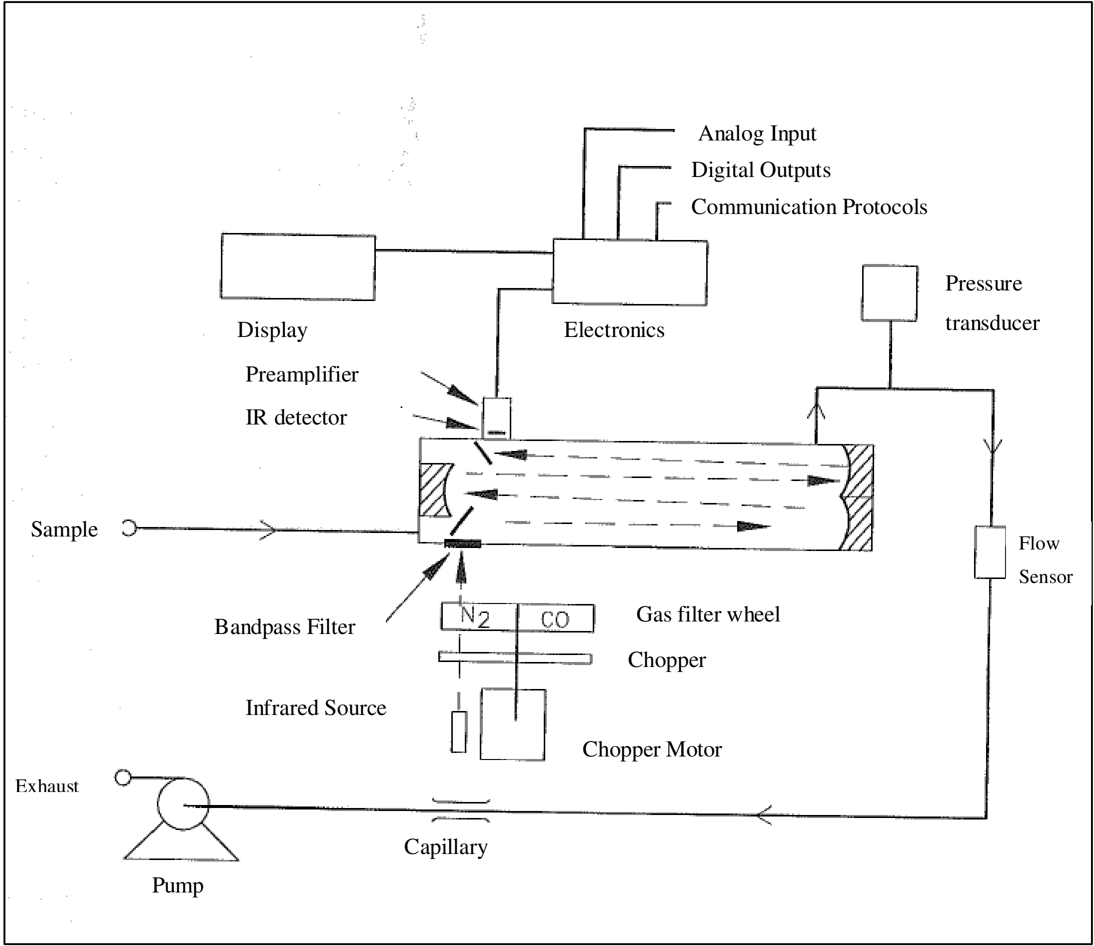


Figure 3.4. Schematic of the CO analyzer

CO analyzer operates on the principle that CO absorbs infrared radiation at a wavelength of 4.6 microns. Infrared absorption is a non linear measurement technique therefore, it is necessary to transform the basic analyzer signal into a linear output. The CO analyzer uses and internally stored calibration curve to accurately linearize the instrument. This calibration curve limits the CO analyzers upper concentration range to 10000 ppm.

The experiments were conducted within the range of 10 - 1000 ppm, which is well below the upper limit (Table 3.4). The operation diagram of the CO analyzer is given in Figure 3.5. The sample flows through an optical bench. Radiation from an infrared source is chopped then passed through a gas filter alternating between CO and N_2. The radiation then passes through a narrow bandpasss interference filter and enters the optical bench where absorption by the sample gas occurs. The infrared radiation then exits the optical bench and falls on an infrared detector. The CO gas filter acts to produce a reference beam which cannot further be attenuated by CO in the sample cell. The N_2 side of the filter wheel is transparent to the infrared radiation and therefore produces a measurement beam which can be absorbed by CO in the cell. The chopped detector signal is modulated by the alternation between the two gas filters with an amplitude related to the concentration of CO in the sample cell. Other gases do not cause modulation of the detector signal since they absorb and measure beams equally. Therefore the system responds specifically to CO.

Agilent 6850C equipped with a Thermal Conductivity Detector (TCD) is used to analyze the product gas. An Alltech CTR1 column with the outer packing material of 6ft x 1/4" Packed with Activated Molecular Sieve and with the inner packing material of 6ft x 1/8” porous polymer mixture. Analysis conditions are given below in Table 3.5.

Table 3. 4. CO analyzer specifications

Range	0-1 to 10000 ppm
Zero Roise	0.02 ppm RMS (30 second averaging time)
Lower Detectable Limit	0.04 ppm
Zero Drift	<0.1 ppm
Span Drift	±1 % full-scale
Response Time	60 seconds (30 second averaging time)
Linearity	±1% of full-scale ≤1000 ppm
	±2.5% of full-scale > 1000 ppm
Sample Flow Rate	1.0 LPM
Operating Temperature	20- 30˚C (may be safely operated over the range of 0-45˚C)

Table 3.5. Reactant and product gas analysis conditions

Column Type	CTR I (Packed Concentric Column)
Outer Column Packing	Activated Molecular Sieve
Inner Column Packing	Porous Polymer Mixture
Column Oven Temperature	353 K
Carrier Gas	Helium
Carrier Gas Flow Rate	20 ml/min
Detector Type	Thermal Conductivity
Detector Current	120 mA
Front Detector Temperature	493 K
Front Inlet Temperature	393 K
Auxillary Temperature	323 K

3.3. Catalyst Preparation

The activated carbon supported catalysts were prepared by incipient wetness impregnation method previously used by Özkara (2002). The catalysts prepared by impregnation method. 1% Pt- 0.25% Sn over Activated Carbon 3 catalyst was used for experiments.

3.3.1. Pretreatment of the AC Support

Commercial activated carbon supplied by NORIT was crushed and sieved into 45-60 mesh size (344-255μm) and exposed to different thermal and chemical pretreatments indicated below prior to being used as support:

- Firstly, activated carbon material was treated with 200 ml of 2 N HCl of 200 ml acid solution to remove some ash content and Sulfur accompanied with it. This treatment was carried out in a Soxhlet apparatus. Approximately 15 g of commercial activated carbon was placed in an extraction unit held by a cellulosic cup. Extraction process was continued under reflux for 12 hours. The slurry was then rinsed with 250 ml distilled water and washed again for 6 hours inside the Soxhlet apparatus to remove HCl remaining on the support surface. Finally, the slurry was dried at 115°C overnight. This support is called AC1.

- AC1 support was oxidized in a down flow reactor, heating it from room temperature up to 450°C under the flow of 15 ml/min N_2 with 10°C/min heating rate. It was kept at 450°C under the flow of 150 ml/min N_2-50 ml/min dry air mixture for 10 hours and was cooled down to room temperature under the flow of 150 ml/min N_2. This procedure gave the second type of AC support called AC2. AC2 catalysts are not reported in this work.
- 15 g of AC1 was put into a round bottom flask containing 350 ml of 5 N HNO_3 solution. This flask was heated up under total reflux for 3 hours. Afterwards, the oxidized sample was rinsed with boiling distilled water for 2 hours. The rinsing procedure was repeated 3 times, and then the slurry was dried at 115°C overnight. The third type of AC support thus obtained is called AC3.

3.3.2. Impregnation

The experimental set-up shown in Figure 3.2 was used for catalyst preparation by the incipient to wetness impregnation. Incipient wetness impregnation method that was used in the study consists of three parts:

- Evacuating the support,
- Contacting the support with the precursor solution, and
- Drying.

For incipient to wetness impregnation, five grams of activated carbon was placed in the vacuum flask and kept under vacuum both before, during and after the addition of precursor solutions. Since trapped air in the pores of the support could prevent penetration of the solutions, vacuum pump was used to remove the trapped air and to give a uniform distribution of the active component. Before impregnating the solution, the support material was mixed with ultrasonic mixer for 25 min.

A Masterflex computerized-drive peristaltic pump was used to feed the precursor solution to the vacuum flask at a rate of 0.5 mL/min via slicone tubing. The slurry was mixed by an ultrasound mixer during the impregnation in order to maintain uniform distribution of the precursor solutions. After the precursor solution was added, the slurry was ultrasonially mixed for additional 90 min. The thick slurry obtained was dried at 115˚C overnight.

3.4. Selective CO Oxidation

3.4.1. Catalyst Activation

The results obtained in the scope of the study conducted by Özkara (2002) showed that reduction at 673 K results in densely populated active sites placed very close to each other. Here, reduction temperature for Pt-Sn/AC3 catalyst was also chosen as 673 K. The activated carbon supported catalyst was calcined in situ under He with flow rate of 50 ml/min at 673 K for 2 hours and then reduced by H2 with flow rate of 50 ml/min for 10 hours prior to the reactions. The reduction time length is obtained from the study of Aksoylu (2000) Temperature procedure is given in Table 3.6.

Table 3.6. Temperature program for the in situ pretreatment activated carbon supported catalysts

Segments	Starting and End Temperatures	Segment Gas
First	Heating from 293 K to 393 K with a heating rate of 10 K/min	He with flow rate of 50 ml/min
Second	Keeping constant at 393 K for 10 min	He with flow rate of 50 ml/min
Third	Heating from 393 K to 573 K with a heating rate of 10 K/min	He with flow rate of 50 ml/min
Fourth	Heating from 573 K to 673 K with a heating rate of 10 K/min	He with flow rate of 50 ml/min
Fifth (Calcination)	Keeping constant at 673 K for 2 hrs	He with flow rate of 50 ml/min
Sixth (Reduction)	Keeping constant at 673 K for 10 hrs	H2 with flow rate of 50 ml/min
Seventh	Sweeping at 673 K for 1 hrs	He with flow rate of 50 ml/min

3.4.2. Catalytic Activity Measurements and the Experiments

All the reactions were conducted in the micro reactor system given in the flow sheet Figure 3.2. The total flow rate is kept constant at 100 ml/min and the catalyst loading was 0.25g. The weight of the catalyst over the flow rate ratio (W/F) is therefore kept constant through all the experiments. The reaction temperatures were taken at 4 steps 135/125/115/110°C. Refer to table 3.8 for reaction conditions. The ratio of oxygen to carbondioxide is taken as 2:1 stochiometrically and 2,5:1 stochiometrically. The effect of carbondioxide and water addition was tested with 15% CO_2 and 10% water addition to the feed. The possible effect of the unburnt hydrocarbons to the reaction was also tested with 3 per cent methane in the feed. Refer to table 3.8 for a complete list of catalytic activity measurements for the 1% Pt-0.25% Sn/AC3 catalyst.

Table 3.7. Reaction conditions for catalytic activity tests

Parameter	Value
Catalyst Particle Size (mesh size)	45-60 (344-255μm)
Catalyst Amount (mg)	250
Reduction Temperature (^{o}C)	400
Reaction Temperature (^{o}C)	135, 125, 115, 110
Reaction Total Flow Rate (ml.min^{-1})	100
W/F_{CO} Ratio (mg.min.μmol^{-1})	0.25

After the catalyst preparation steps, the catalyst was isolated in pure helium (inert) atmosphere and the feed gases were sent through the bypass line. Thus the feed gases would not start to react before the flow reaches steady state. The CO analyzer collects real time data, therefore steady state was assumed to be achieved after the CO readings stay constant for more than 5 minutes. The CO analyzer is designed to work in an open atmosphere and therefore it is calibrated according to the laboratory's ambient atmosphere. The trace amount of CO from the atmosphere is the base set value for the CO analyzer. Notice that between summer and winter months the CO content in the atmosphere changes due to heating issues; however, the base line is observed to change by only 50 pbm. Thus, it is safe to neglect the trace amount of CO in the air. The inlet flow rate of the CO analyzer was 1.089 l/min. The make - up stream of the CO analyzer was provided by air. The CO analyzer readings, which do not reflect the exact concentration of CO in the feed stream due to dilution with air, were corrected accordingly for finding the CO concentration in the reactor exit. Refer to Figure 3.4 for the Block diagram of the CO analyzer and eqn 3.4 for the CO concentration in the feed.

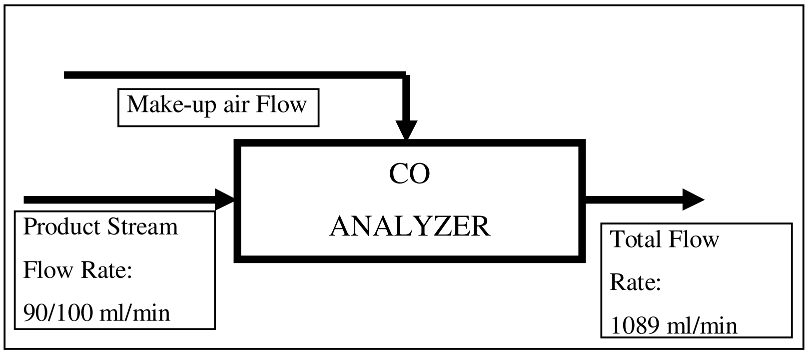


Figure 3. 5. Block diagram for the CO analyzer

$$\text{CO in the product stream} = \frac{\text{What is read on the CO analyzer} \times 1089}{100} \tag{3.1}$$

The initial temperature for the reaction was selected as 135˚C and the data for 125-115-110˚C are collected after the activation at 135˚C. The concentration of CO in the feed stream was calculated by Eqn 3.1 and corresponds to 926 ppm, this value is read with ±2 % accuracy from the CO analyzer before the reaction starts. All of the CO concentration graphs were drawn according to Eqn 4.1.

Table 3.8. A summary of the experimental conditions for the 1%Pt-0.25%Sn/AC3 Catalyst

	Temperature in˚C	**O_2:CO Ratio**	**CO Flow Rate ml/min**	**H_2 Flow Rate ml/min**	**He Flow Rate ml/min**	**CH_4 Flow Rate in ml/min**	**$H_2O_{(g)}$ Flow Rate in ml/min**	**CO_2 Flow Rate in ml/min**
Exp1	135	1	1	60	38	0	0	0
Exp2	125	1	1	60	38	0	0	0
Exp3	115	1	1	60	38	0	0	0
Exp4	110	1	1	60	38	0	0	0
Exp5	135	1.25	1	60	37.75	0	0	0
Exp6	125	1.25	1	60	37.75	0	0	0
Exp7	115	1.25	1	60	37.75	0	0	0
Exp8	110	1.25	1	60	37.75	0	0	0
Exp9	135	1	1	60	14	0	10	15
Exp10	125	1	1	60	14	0	10	15
Exp11	115	1	1	60	14	0	10	15
Exp12	110	1	1	60	14	0	10	15
Exp13	135	1.25	1	60	13.75	0	10	15
Exp14	125	1.25	1	60	13.75	0	10	15
Exp15	115	1.25	1	60	13.75	0	10	15
Exp16	110	1.25	1	60	13.75	0	10	15
Exp17	135	1	1	60	36	3	0	0
Exp18	125	1	1	60	36	3	0	0
Exp19	115	1	1	60	36	3	0	0
Exp20	110	1	1	60	36	3	0	0
Exp21	135	1.25	1	60	35.75	3	0	0
Exp22	125	1.25	1	60	35.75	3	0	0
Exp23	115	1.25	1	60	35.75	3	0	0
Exp24	110	1.25	1	60	35.75	3	0	0
Exp25	135	1	1	60	11	3	10	15
Exp26	125	1	1	60	11	3	10	15
Exp27	115	1	1	60	11	3	10	15
Exp28	110	1	1	60	11	3	10	15
Exp29	135	1.25	1	60	10.75	3	10	15
Exp30	125	1.25	1	60	10.75	3	10	15
Exp31	115	1.25	1	60	10.75	3	10	15
Exp32	110	1.25	1	60	10.75	3	10	15

4. RESULTS AND DISCUSSION

This study aims to determine the effects of various reaction parameters to the performance, i.e. activity and selectivity of 1%Pt-0,25%Sn/AC3 catalyst. The reaction parameters were selected as temperature, oxygen flow rate in the feed, presence of water vapor and carbondioxide in the feed and, lastly, presence of a hydrocarbon (methane) in the feed including CO_2 and water vapor. The activated carbon had been treated with nitric acid in order to increase the amount of oxygen bearing groups, specifically carboxylic groups, on the support surface. The catalysts were prepared by sequential impregnation for which Sn precursor was impregnated first. This sequence enables stabilized Sn species to disperse on the catalyst surface. The tin species on the surface may lead the Pt particles to create the Pt-Sn (1:1) alloy, whenever the dispersion of both metallic species and their stochiometry surface allows.

In the performance tests CO oxidation and PROX for hydrogen rich streams tests were performed first. These tests were followed by PROX under the presence of CO_2 and water vapor; for the given temperature interval, CO_2 and water addition affected the catalyst activity in a negative way. This can be explained by the PROX reaction over the catalyst follows a reversible reaction path especially for very low CO concentrations. Although the Agilent 6850 gas chromatograph showed no CO peaks for the lower temperatures, Thermo CO Analyzer shows exact conversion rates with 95 per cent as maximum at 110˚C. All the reported reaction tests were conducted in 110-135˚C temperature range; it should be noted that CO conversion level increased with a decrease in temperature except the tests conducted at 105˚C, for selected samples of the limited number of tests conducted at 105˚C are not reported.

4.1. Catalysts Characterization

Reduction procedure is one of the most important features of the Pt-Sn catalyst. The procedure affects the interaction between metal precursors and species. Characterization test of the catalyst used in this study was performed in the previous works by Özkara and Aksoylu (2003). The calcination and reduction temperature is selected to be 673K, same as the previous work of Şimşek (2006). This temperature enables adequate dispersion of the active metallic centers on the catalyst. The catalyst was calcined at 400°C under He flow for stabilizing the precursors and the metals. The reduction was conducted for 10 hrs. The preliminary experiments showed that the catalyst surface might not have been stabilized after 2 hours of calcination; in these unreported experiments, the catalyst activity ramped up continuously at a high rate and did not stabilize. With 10 hour reduction procedure, the activities showed a ramp up behaviour during reaction tests, however the activity was generally stabilized after two-three hours of reaction.

4.2. Catalyst Activity Tests

PROX catalyst must have high activity values along with high selectivity to CO formation in order to reach high activity and selectivity necessary for H_2 purification. The feed stream to a PROX reactor is H_2 rich and contains CO_2, H_2O as well as unused hydrocarbons. The activity and selectivity values were calculated using Eqn 4.1-2-3.

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

$$O_2 \text{ conversion (\%)} = \frac{[O2]_{in} - [O2]_{out}}{[O2]_{in}} x100 \tag{4.2}$$

$$\text{CO selectivity (\%)} = \frac{0.5x([CO]_{in} - [CO]_{out})}{[O2]_{in} - [O2]_{out}} x100 \tag{4.3}$$

The amount of liquid water used in the experiments was calculated as follows:

$$V_{Steam(H_2O)} = \frac{V_{Liquid(H_2O)} \times \rho_{H_2O} \times R \times T}{MW_{H_2O} \times P} \tag{4.4}$$

where ρ=1000 g.L^{-1}; P=1 atm; R=0.082 L.atm.mol^{-1}.K^{-1}; T=298 K and MW_{H2O}=18 g.mol^{-1}.

The reaction pathway proposed in the literature supports that there is only one type of site which can adsorb both CO and O for monometallic catalysts. For bimetallic systems and systems including alloy(s) as the active sites generally may have specific sites for O and CO adsorption. In any case CO oxidation reaction takes place between adsorbed O and adsorbed CO to form CO_2. (Aksoylu et. al., 2000). The claims about the rate limiting step are contradictory in the related literature. Theoretically, desorption of CO_2 occurs immediately above 300K since CO_2 has a linear non-polar structure which does not bond well with the metal surface. For some groups of catalysts, the adsorption of oxygen, which competes for the same adsorption sites with CO, can be inhibited by strong CO adsorption; there, all the metal surface may get covered with CO leaving no more vacant sites for oxygen adsorption and, thus the catalyst activity decreases drastically. Low activity values for the monometallic PROX catalysts are attributed to this inhibition especially at low temperatures. Addition of promoters like Sn, to monometallic Pt enhance the activity of the catalyst under realistic feed conditions of high H_2, CO_2, H_2O and unburnt hydrocarbon presence. It is reported that one promising catalyst used for low-temperature CO oxidation is Pt-SnO_x with or without promoters. Pt-SnO_x is found to have significantly higher catalytic activity for CO oxidation at low temperatures than either Pt or SnO_x alone (Akın et al., 2001).

4.3. Preliminary Tests

Preliminary tests were conducted in order to test the stability of the micro reactor system, and the test conditions for performance tests. Early tests showed that the catalyst had a tendency to activate over time, i.e. has a pre-activation occurred as the reaction test progresses. Therefore the reduction step with H_2 was extended from two hours (Şimşek, 2006) to 10 hrs. The catalysts with two hour reduction time did not stabilize after four hours time on stream during performance tests. With 10 hours of reduction, it was observed that the activity of the catalyst stabilized after two to three hours time on stream. Upon the stabilisation, the activity values remained fairly constant even after the temperature changes in reaction temperature level during the tests.

The Thermo 48i CO analyzer is capable of reading real time data during the reaction. Note that catalyst also remained stable and active after even 15 hours of operation full time-on stream test including temperature progression with 10˚C decreasing steps. For guaranteeing there was no activity loss during reaction temperature changes, in a preliminary test the activity data was taken only at 125˚C, the results were compared with the experiment for which the catalyst was kept at 135˚C for 5 hours and then the temperature was brought down to 125˚C. Refer to Figure 4.1 and Table 4.1 for the comparison of the CO conversion results.

Table 4.1. Comparison of CO activation percentages for 1%Pt-0.25%SnO_x/AC3 catalyst. Constant temperature case and temperature step changed case

Reaction Time in min	Constant Temperature CO Conversion	Temperature Step Change CO Conversion
1	2.85	2.78
30	58.67	54.77
60	66.97	64.47
90	70.02	68.79
120	71.40	71.39
150	72.10	72.88
180	72.51	73.86
210	72.90	74.76
240	73.18	75.38

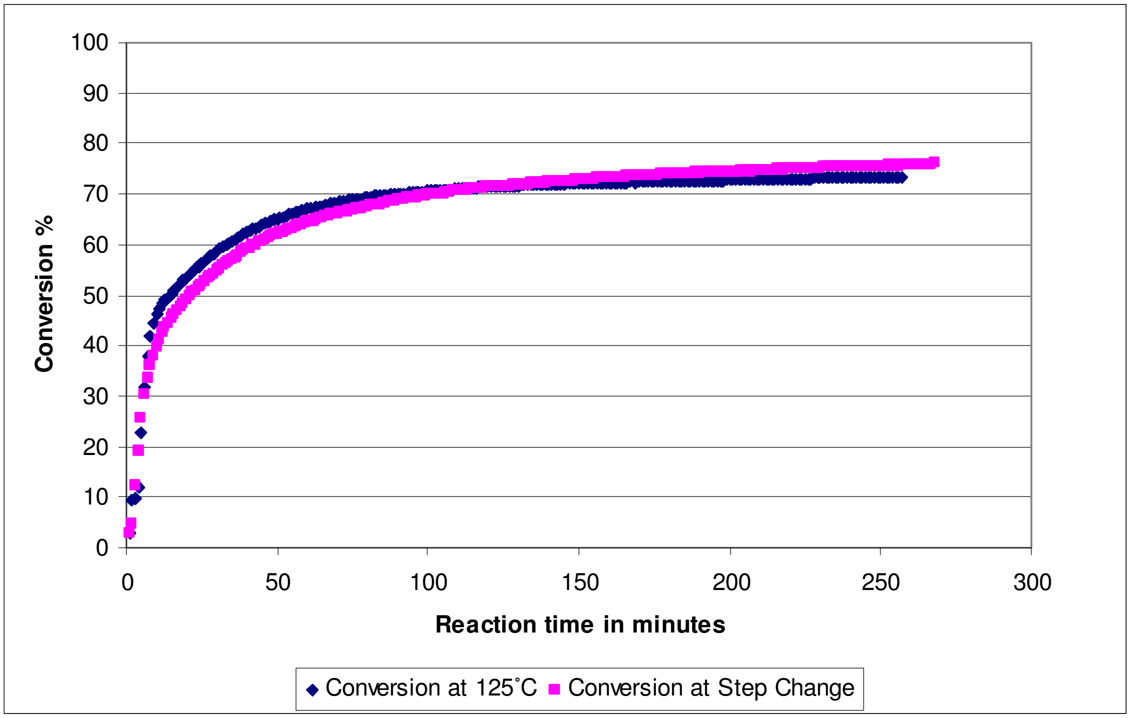


Figure 4.1. Comparison of CO oxidation activities for 1%Pt-0.25%SnO_x/AC3 at constant temperature and temperature step changed case

4.4. Selective CO Oxidation Activity of Sequentially Impregnated 1% Pt-0.25% SnO_x/AC Catalysts

CO oxidation experiments of the Pt-SnO_x/AC catalysts were performed by Özkara (2002) using a feed stream composition of 1% CO, 1%O_2, 60% H_2 and inert He as balance. Şimşek drove the study further and tested the catalyst under realistic feed conditions of % CO, 1% O_2, 60% H_2, 15% CO_2, 10% H_2O and inert He. Both studies are performed at 150˚C. In this study, the reaction parameters were changed and the reactor effluent was analyzed by highly sensitive (1 ppb) CO analyzer. The reaction temperature was changed between 110-135˚C. Refer to table 3.8 for the whole list of experiments and experimental conditions.

4.4.1. Effect of Temperature on CO Oxidation Activity for H_2 Rich Feed with O_2:CO ratio of 1:1

The reaction was kept at 135˚C for at least 4 hours for every set of reactions in order to ascertain stability in the catalyst activation. The first 2 hours of reaction can be regarded as the time that passes for the reaction to reach a steady state. Refer to Figure 4.2 and table 4.2 for the activation under the feed flow

Table 4.2. CO oxidation activity and selectivity data for 1%Pt-0.25SnO_x/AC3 catalyst for a feed composition of 1% CO, 1% O_2, 60% H_2 and balance He at 135˚C (Experiment #1)

Reaction Time in min	CO Amount in ppm	% CO Conversion	% CO Selectivity
1	900	2.78	1.39
30	419	54.77	27.39
60	329	64.47	32.24
90	289	68.79	34.40
120	265	71.39	35.70
150	251	72.88	36.44
180	242	73.86	36.93
210	234	74.76	37.38
240	228	75.38	37.69

The catalyst started to activate with a decreasing rate as the reaction proceeds. Figure 4.2 shows the time - on - stream activity profile stabilizes right below 80 per cent conversion. This increase in conversion might be attributed to pre activation period involving the stabilization of surface concentration of reacting species. Towards the reaction steady state, conversion values were stabilized, which may indicate that surface concentration of reacting species did not change any more at the current temperature level.

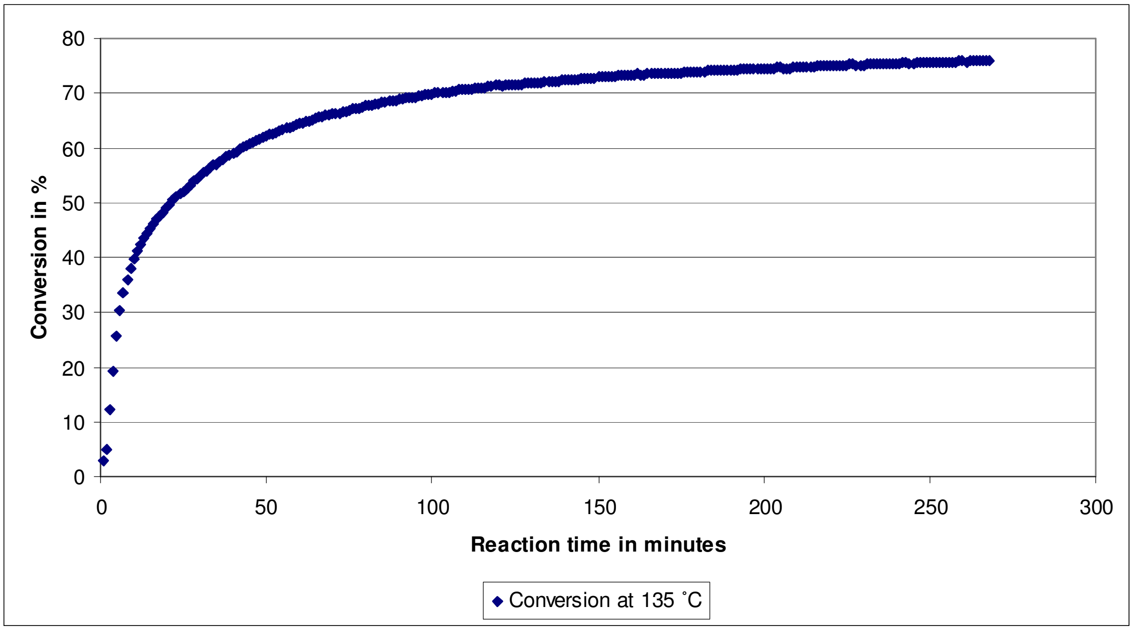


Figure 4.2. CO oxidation activity for 1%Pt-0.25SnO_x/AC3 catalyst for a feed composition of 1% CO, 1% O_2, 60% H_2 and balance He at 135˚C (Experiment #1)

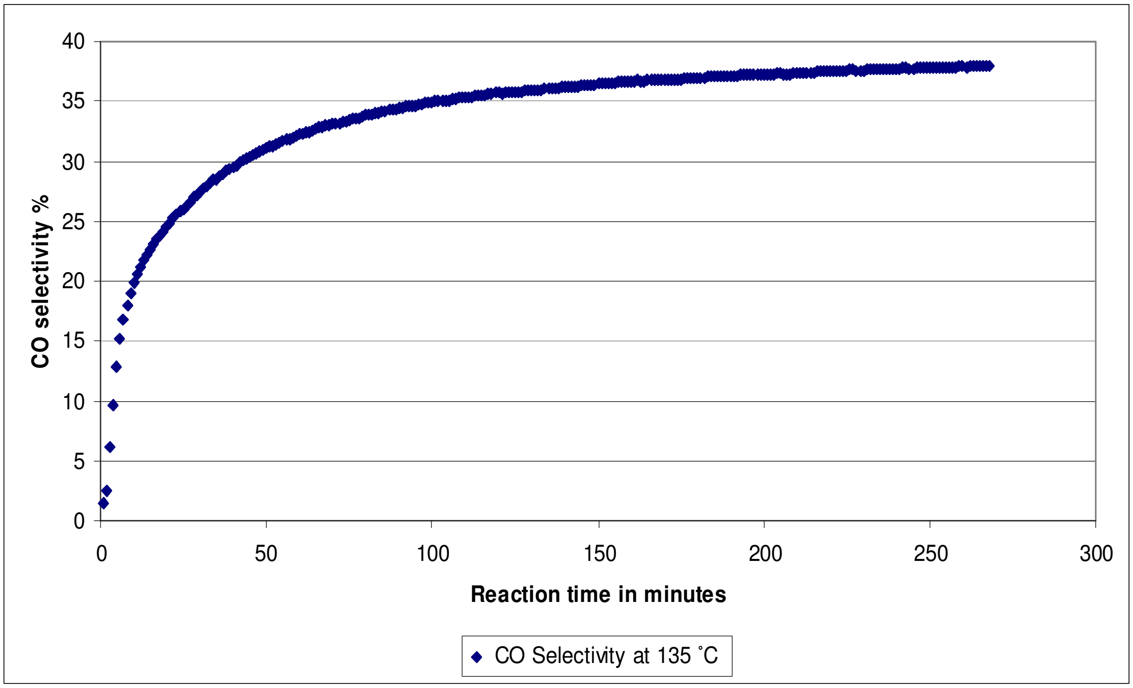


Figure 4.3. CO Selectivity CO oxidation selectivity for 1%Pt-0.25SnO_x/AC3 catalyst for a feed composition of 1% CO, 1% O_2, 60% H_2 and balance He at 135˚C (Experiment #1)

Table 4.3. CO oxidation activity and selectivity data for 1%Pt-0.25SnO_x/AC3 catalyst for a feed composition of 1% CO, 1% O_2, 60% H_2 and balance He at 125°C (Experiment #2)

Reaction Time in min	CO Amount in ppm	% CO Conversion	% CO Selectivity
1	228	75.37	37.68
15	195	78.96	39.48
30	190	79.46	39.73
45	187	79.76	39.88
60	184	80.10	40.05
75	180	80.47	40.24
90	178	80.75	40.37
105	176	81.02	40.51
120	173	81.32	40.66

Table 4.4. CO oxidation activity and selectivity data for 1%Pt-0.25SnO_x/AC3 catalyst for a feed composition of 1% CO, 1% O_2, 60% H_2 and balance He at 115°C (Experiment #3)

Reaction Time in min	CO Amount in ppm	% CO Conversion	% CO Selectivity
1	185	80.07	40.04
15	143	84.55	42.28
30	144	84.40	42.20
45	144	84.41	42.21
60	144	84.49	42.24
75	142	84.63	42.31
90	141	84.82	42.41
105	138	85.05	42.52
120	137	85.20	42.60

Table 4.5. CO oxidation activity and selectivity data for 1%Pt-0.25SnO_x/AC3 catalyst for a feed composition of 1% CO, 1% O_2, 60% H_2 and balance He at 110˚C (Experiment #4)

Reaction Time in min	CO Amount in ppm	% CO Conversion	% CO Selectivity
1	145	84.29	42.15
15	108	88.30	44.15
30	111	88.03	44.02
45	111	87.97	43.99
60	111	87.96	43.98
75	112	87.96	43.98
90	111	88.00	44.00
105	111	87.98	43.99
120	109	88.18	44.09

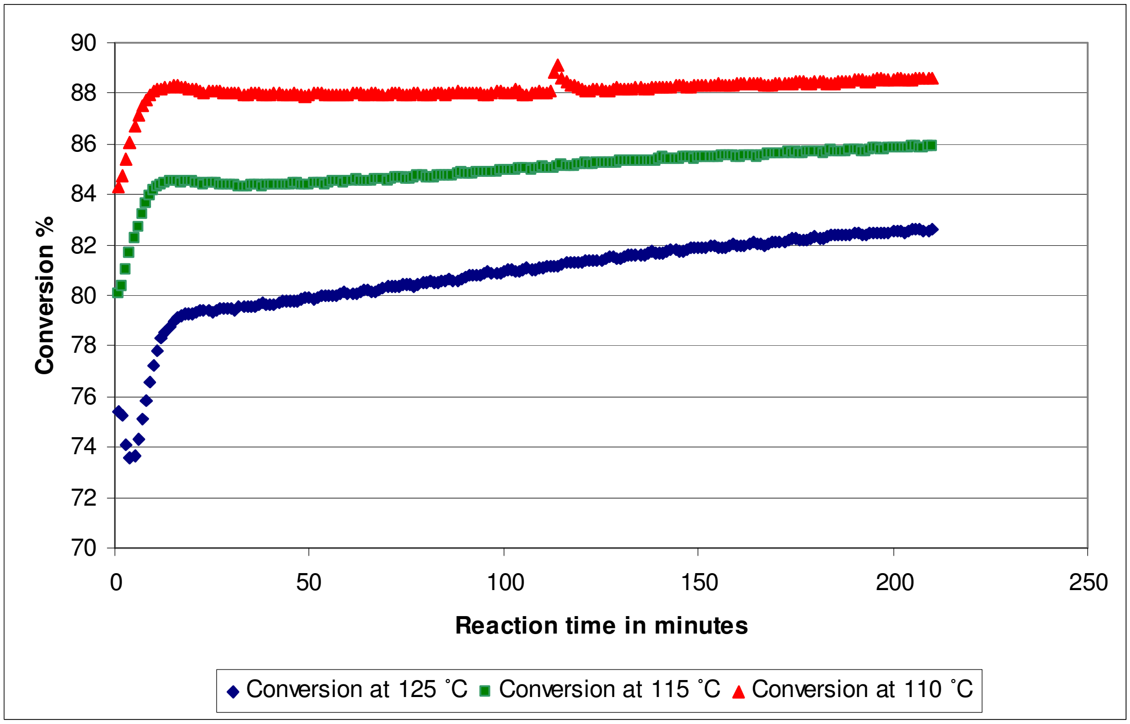


Figure 4.4. CO oxidation activity for 1%Pt-0.25SnO_x/AC3 catalyst for a feed composition of 1% CO, 1% O_2, 60% H_2 and balance He at 135-125-115°C (Experiment #2-3-4)

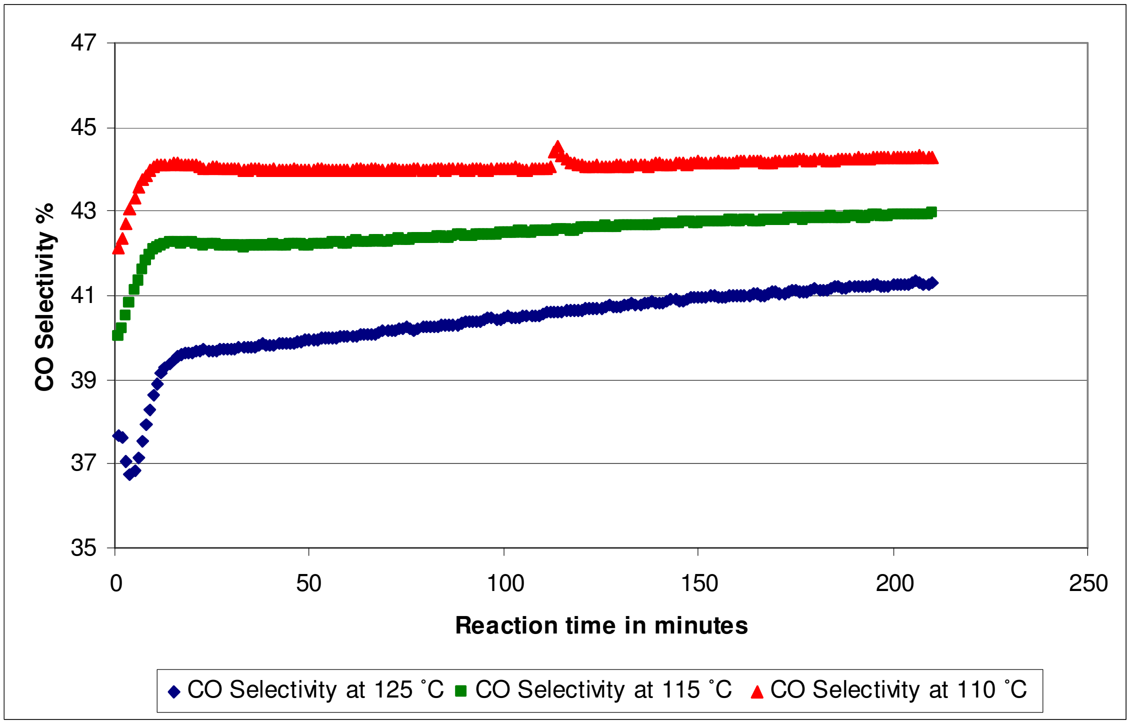


Figure 4.5. CO selectivity for 1%Pt-0.25SnO_x/AC3 catalyst for a feed composition of 1% CO, 1% O_2, 60% H_2 and balance He at 135-125-115˚C (Experiments #2-3-4)

After the decreasing 4 hour reaction at 135˚C, the catalyst activity was safely assumed to be stabilized, and the decreasing temperature progression begins from 135˚C to 125˚C initially. The catalyst undergoes a slight activation at 125˚C. This may indicate that oxygen adsorption relative to that of CO became easier as the temperature decreases. This resulted in an increase in the CO conversion values. The conversion increases by 7 per cent to near 82 per cent. This trend continues with Experiment # 3 and #4 where the temperature was decreased by two 10˚C and one 5˚C steps, as can be seen in Tables 4.3, 4.4 and 4.5. Figure 4.4 shows a comparison of CO conversion obtained at different temperatures. It is clear that CO conversion increases with decreasing temperature. The CO analyzer readings were checked with the GC and the CO amounts are given in Table 4.6. It should be noted that GC readings also showed the same trend; however, the GC readings gave higher CO conversion values. The Agilent 6850 GC sensitivity to CO concentrations is between 100-200 ppm according to the specifications of the manufacturer. As the conversions near 100 per cent, the GC started to deviate from CO analyzer. This is expected especially with the CTR- 1 column, whose large diameter makes the GC much less sensitive than the CO analyzer. It should be noted that Thermo 48i CO analyzer's sensitivity is on ppb basis and is therefore more accurate.

Table 4.6. Gas chromatograph data for CO oxidation activity and selectivity for 1%Pt-0.25SnO_x/AC3 catalyst for a feed composition of 1% CO, 1% O_2, 60% H_2 and balance He at 135-125-115-110˚C (Experiments #1-2-3-4)

	Temperature in˚C	% CO Conversion by GC	% Oxygen Conversion by GC	% CO Selectivity by GC
Exp #1	135	87.49	100	43.75
Exp #2	125	90.52	100	45.26
Exp #3	115	93.30	100	46.65
Exp #4	110	95.48	100	47.74

The main purpose of the GC is to analyze the oxygen content of the product stream. No oxygen peak was encountered during the experiments and the oxygen concentration in the product stream can be assumed to be zero. The CO selectivities show the parallel trends with CO conversions as can be seen in Figures 4.3 and 4.5.

4.4.2. Effect of Increasing O to CO Ratio for Hydrogen Rich Feed Free from H_2O, CO_2 and CH_4

Figure 4.2 and 4.4 show CO conversions for 1.25:1 stochiometric O_2 to CO. Experiments #5-8 investigate the effect of oxygen concentration on the reaction by increasing the O_2 to CO molar feed ratio to 1.25:1. Figure 4.6 shows the CO conversion percentages for experiment #5.

Table 4.7. CO oxidation activity and selectivity data for 1%Pt-0.25SnO$_x$/AC3 catalyst for a feed composition of 1% CO, 1.25% O_2, 60% H_2 and balance He at 135˚C (Experiment #5)

Reaction Time in min	CO Amount in ppm	% CO Conversion	% CO Selectivity
1	552	40.39	16.16
30	418	54.86	21.94
60	349	62.31	24.92
90	301	67.49	27.00
120	265	71.38	28.55
150	234	74.73	29.89
180	213	77.00	30.80
210	198	78.62	31.45
240	186	79.91	31.97

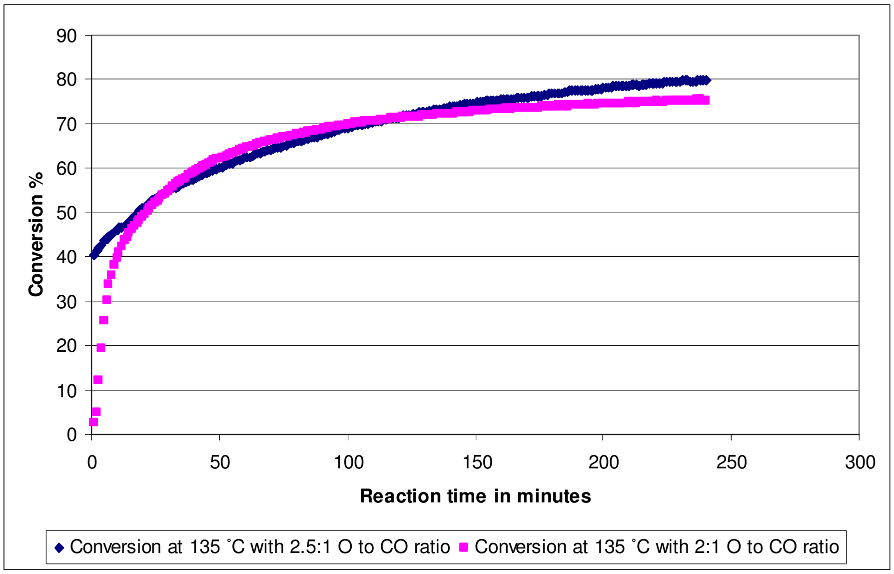


Figure 4.6. Comparison of CO oxidation activity for 1%Pt-0.25SnO$_x$/AC3 catalyst for feed compositions of: (i) 1% CO, 1.25% O_2, 60% H_2 and balance He at 135˚C (ii) 1% CO, 1% O_2, 60% H_2 and balance He at 135˚C (Experiments #1 and #5)

The catalyst undergoes a activation similar to that observed in experiment #1. However, it should be noted that, the catalyst activity in experiment #1 starts from 2 per cent CO conversion in the first minute and ramps up from that point on. In the experiment #5, on the other hand there was more oxygen in the feed stream and the initial conversion was 40 per cent, and ramped up from that point. This can be explained by the relation between the relative strengths of adsorption of CO and O and their concentrations in the gaseous stream. For lower O_2 concentrations in the gaseous feed, time necessary for the build-up of surface oxygen concentration is far greater than that for higher O_2 concentration case; as the O_2 concentration increases, O and CO surface concentrations reach their stable points rapidly and, resultantly, pre-activation period was shortened. Compared to the 75 per cent CO conversion in experiment #1, the case with 1.25:1 oxygen ratio has 79 per cent conversion at 135˚C. This increase in conversion can be explained simply by the reaction kinetics. Oxygen is a reactant and increasing its concentration also increases the conversion ratios. Trimm and Önsan (2001) support that PROX is surface reaction limited; the effect of oxygen on the CO conversion is in agreement with this claim. Tables 4.8-4.10 show the conversion and selectivity percentages as the reaction proceeds and Figure 4.7 compares conversion values at different temperatures.

Table 4.8. CO oxidation activity and selectivity data for 1%Pt-0.25SnO_x/AC3 catalyst for a feed composition of 1% CO, 1.25% O_2, 60% H_2 and balance He at 125˚C (Experiment #6)

Reaction Time in min	CO Amount in ppm	% CO Conversion	% CO Selectivity
1	179	80.67	32.27
15	109	88.21	35.28
30	105	88.67	35.47
45	103	88.93	35.57
60	101	89.06	35.62
75	99	89.33	35.73
90	97	89.56	35.82
105	94	89.83	35.93
120	92	90.11	36.05

Table 4.9. CO oxidation activity and selectivity data for 1%Pt-0.25SnO$_x$/AC3 catalyst for a feed composition of 1% CO, 1.25% O$_2$, 60% H$_2$ and balance He at 115˚C (Experiment #7)

Reaction Time in min	CO Amount in ppm	% CO Conversion	% CO Selectivity
1	103	88.89	35.56
15	68	92.71	37.08
30	66	92.84	37.14
45	64	93.10	37.24
60	63	93.15	37.26
75	63	93.16	37.26
90	62	93.28	37.31
105	60	93.47	37.39
120	60	93.50	37.40

Table 4.10. CO oxidation activity and selectivity data for 1%Pt-0.25SnO$_x$/AC3 catalyst for a feed composition of 1% CO, 1.25% O$_2$, 60% H$_2$ and balance He at 110˚C (Experiment #8)

Reaction Time in min	CO Amount in ppm	% CO Conversion	% CO Selectivity
1	69	92.51	37.00
15	45	95.13	38.05
30	46	95.03	38.01
45	45	95.04	38.02
60	45	95.04	38.01
75	46	94.97	37.99
90	46	95.05	38.02
105	46	95.06	38.03
120	45	95.12	38.05

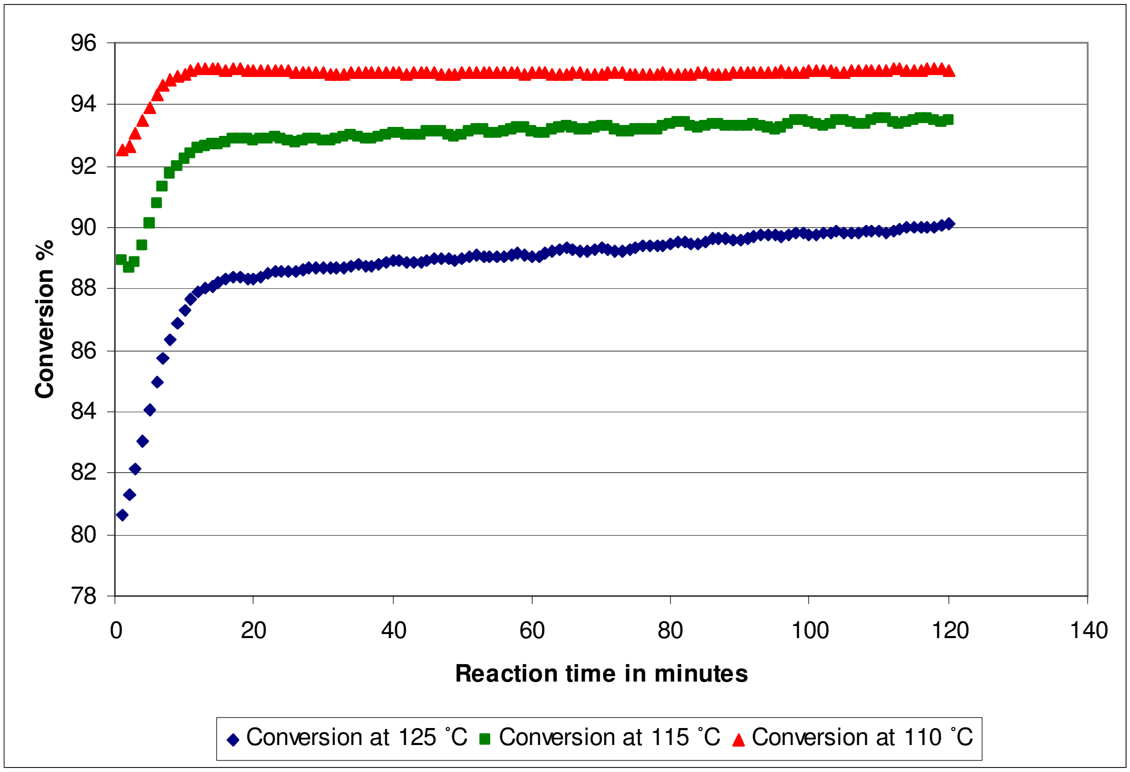


Figure 4.7. CO oxidation activity for 1%Pt-0.25SnO_x/AC3 catalyst for a feed composition of 1% CO, 1.25% O_2, 60% H_2 and balance He at 125-115-110˚C (Experiments #6-7-8)

The CO conversion percentages increased with decreasing temperature, as expected from the previous set of experiments. At 110˚C the conversions were as high as 95%. All of the oxygen was spent (Table 4.11); therefore, the selectivity values decreased compared to experiments #1-4. The GC detected no CO in the feed but, as explained in the previous section, this does not mean that complete conversion took place; it was rather a result directly related with GC sensitivity. The GC could not detect CO concentrations as low as 400-500 ppm with a high diameter concentric column under the analysis conditions applied. Marino et. al. (2008) experimented with CuO-CeO_2 catalysts with increasing the oxygen ratios and found that increasing O:CO ratio has a positive effect on the CO conversion while decreasing the selectivity of the catalyst. Kahlich et. al. (1999) determined the reaction orders for Au/a-Fe_2O_3, it is found that hydrogen oxidation and CO oxidation occur separately and the reaction order for oxygen concentration is positive.

Parallel to the results given in the literature, CO conversion level increased with the increase in O_2 concentration in the feed for Pt-Sn/AC3.

Table 4.11. Gas chromatograph data for CO oxidation activity and selectivity for 1%Pt-0.25SnO_x/AC3 catalyst for a feed composition of 1% CO, 1.25% O_2, 60% H_2 and balance He at 135-125-115-110˚C (Experiments #5-6-7-8)

	Temperature in˚C	% CO Conversion by GC	% Oxygen Conversion by GC	% CO Selectivity by GC
Exp #5	135	85.65	100	34,26
Exp #6	125	100	100	40
Exp #7	115	100	100	40
Exp #8	110	100	100	40

The oxygen conversion was 100% in throughout experiments #5-8 according to table 4.11 and no methane formation is observed.

4.3.3. Effect of Water and CO_2 Addition on PROX Activity for Hydrogen Rich Feed with O_2:CO ratio of 1:1

Şimşek (2006) reported that addition of 15% CO_2 and 10% water to the feed increased PROX activity of Pt-Sn/AC3 catalyst. A realistic PROX feed should surely contain CO_2 and water, thus the effect of their addition to the feed stream must be observed. According to the reaction kinetics, addition of the reaction product to the feed would decrease the catalyst performance; however,Pt-Sn/AC3 catalyst offers unique set of properties, which are beneficial for PROX; those are:

i. The catalyst has very well dispersed active phases Pt and Pt_3Sn, all over the support; very high dispersion is led by the surface chemistry of AC3 support, which is very rich in oxygen bearing groups, especially carboxylic acid groups, forming anchoring sites for the metal precursors and metallic species. (Aksoylu et. al., 2000)

ii. AC3 support is very rich in carboxylic acid groups which decomposes during high temperature activation steps, i. e. calcination and reduction, and facilitates formation of Pt_3Sn alloy sites besides pure Pt sites. Pt_3Sn alloy has lower E_{ads} for CO adsorption, meaning it is tolerant to CO poisoning. (Manasilp et. al., 2002)

iii. Sn-including sites of Pt_3Sn can selectively adsorb oxygen and for specific sites for oxygen adsorption. (Gülmen et. al., 2006)

iv. Adsorbed O and CO on Pt_3Sn sites are in closed proximity, partially eliminating necessary O transfer for Pt-Sn/AC3 system. (Gülmen et. al., 2006) (Sümer et. al., 2006)

v. Pt sites on Pt-Sn/Ac still needs O transfer. Through the support surface which may be blocked by mobile CO_2; on the other hand, since AC has many free surface carbon left uncoordinated upon decomposition of AC surface groups and can easily stabilize CO_2 and limit its surface mobility.

vi. OH^- groups formed on the surface may facilitate CO removal from especially monometallic Pt sites. (Manasilp et. al., 2002)

However, the previous experiments (experiments #1-8) support that the limiting step in PROX for Pt-Sn based catalysts, is the surface kinetics. Therefore, water's ability to ease the mass transfer would not have a positive effect on the catalyst but its effect of slowing down the surface reaction is expected to reduce the activity. At that point, relatively lower temperature levels in this study, between 110- 135˚C, compared to Şimşek et. al.(2007), at 150˚C, should be mentioned. Figures 4.8 and 4.9 show that, the PROX activity of the catalyst was not affected by the addition of water and CO_2 to the feed stream.

Table 4.12. CO oxidation activity and selectivity data for 1%Pt-0.25SnO_x/AC3 catalyst for a feed composition of 1% CO, 1% O_2, 60% H_2, 10% H_2O, 15% CO_2 and balance He at 135˚C (Experiment #9)

Reaction Time in min	CO Amount in ppm	% CO Conversion	% CO Selectivity
1	904	2.33	1.17
30	394	57.48	28.74
60	316	65.87	32.94
90	268	71.04	35.52
120	254	72.61	36.31
150	237	74.43	37.22
180	237	74.36	37.18
210	227	75.47	37.74
240	227	75.54	37.77

The increasing activity level trend in response to a decrease in reaction temperature did not change with the addition of CO_2 and water to the feed. No oxygen or methane concentration is encountered in the product stream (Refer to table 4.16). The CO selectivity of the reaction did not increase; since the conversion levels stayed almost the same, the selectivity of the reaction remained almost constant. CO_2 and water addition to the feed did not have a significant impact on the conversion levels. Ayastuy et. al. (2006) report that, with Pt/CeO_2 catalysts, addition of CO_2 has a negative impact for conversion, whereas addition of water has a positive effect. It can be said that possible negative effects of CO_2, which should be limited on Pt-Sn/AC due to the reasons explained above, were offset by the water addition for Pt-Sn/AC3.

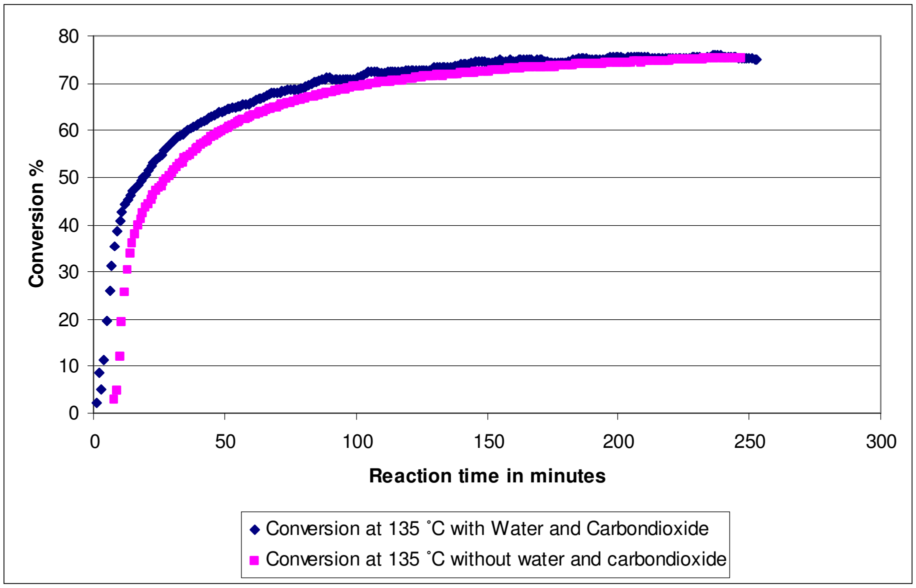


Figure 4.8. Comparison of CO oxidation activity for 1%Pt-0.25SnO$_x$/AC3 catalyst for feed compositions of: (i) 1% CO, 1% O_2, 60% H_2, 10% H_2O, 15% CO_2 and balance He at 135˚C (ii) 1% CO, 1% O_2, 60% H_2 and balance He at 135˚C (Experiments #1 and #9)

Table 4.13. CO oxidation activity and selectivity data for 1%Pt-0.25SnO$_x$/AC3 catalyst for a feed composition of 1% CO, 1% O_2, 60% H_2, 10% H_2O, 15% CO_2 and balance He at 125˚C (Experiment #10)

Reaction Time in min	CO Amount in ppm	% CO Conversion	% CO Selectivity
1	244	73.70	36.85
15	181	80.46	40.23
30	175	81.09	40.55
45	171	81.56	40.78
60	176	81.03	40.52
75	180	80.58	40.29
90	163	82.43	41.22
105	156	83.19	41.60
120	151	83.67	41.83

Table 4.14. CO oxidation activity and selectivity data for 1%Pt-0.25SnO$_x$/AC3 catalyst for a feed composition of 1% CO, 1% O_2, 60% H_2, 10% H_2O, 15% CO_2 and balance He at 115˚C (Experiment #11)

Reaction Time in min	CO Amount in ppm	% CO Conversion	% CO Selectivity
1	160	82.73	41.36
15	150	83.78	41.89
30	135	85.43	42.72
45	139	85.04	42.52
60	140	84.90	42.45
75	146	84.21	42.10
90	146	84.22	42.11
105	143	84.61	42.31
120	143	84.50	42.25

Table 4.15. CO oxidation activity and selectivity data for 1%Pt-0.25SnO$_x$/AC3 catalyst for a feed composition of 1% CO, 1% O_2, 60% H_2, 10% H_2O, 15% CO_2 and balance He at 110˚C (Experiment #12)

Reaction Time in min	CO Amount in ppm	% CO Conversion	% CO Selectivity
1	156	83.10	41.55
15	128	86.21	43.10
30	124	86.63	43.32
45	123	86.68	43.34
60	124	86.60	43.30
75	115	87.59	43.80
90	116	87.52	43.76
105	113	87.80	43.90
120	113	87.85	43.93

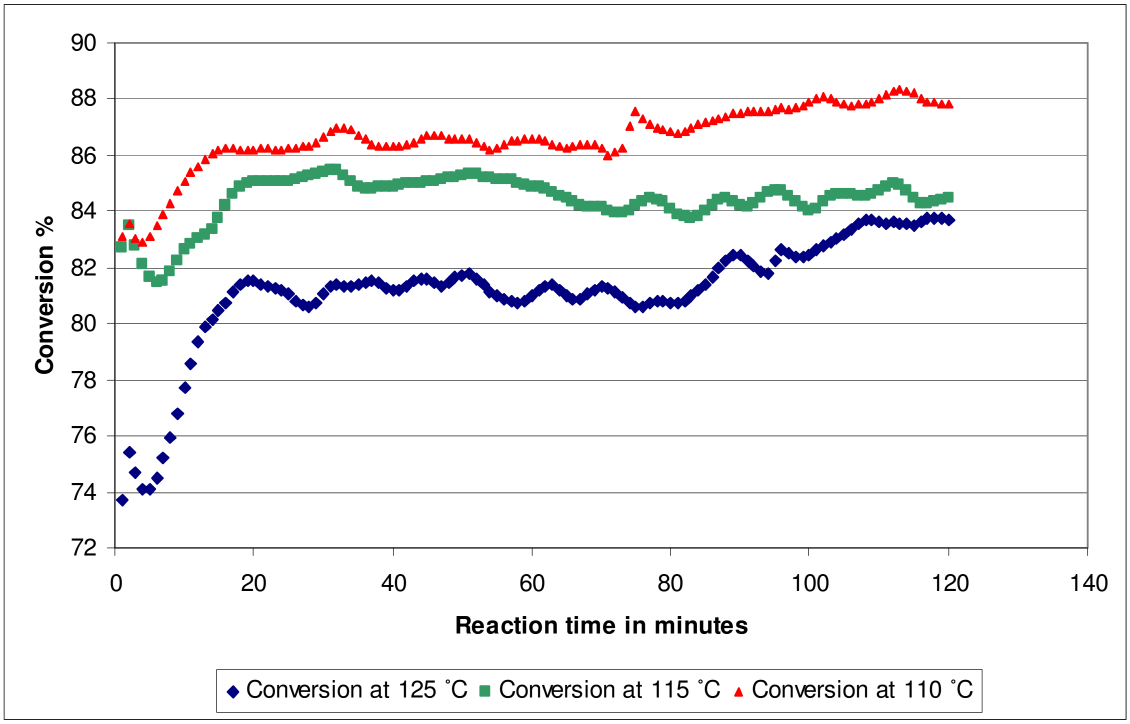


Figure 4.9. CO oxidation activity for 1%Pt-0.25SnO$_x$/AC3 catalyst for a feed composition of 1% CO, 1% O$_2$, 60% H$_2$, 10% H$_2$O, 15% CO$_2$ and balance He at 125-115-110˚C (Experiments #10-11-12)

Table 4.16. Gas chromatograph data for CO oxidation activity and selectivity for 1%Pt-0.25SnO$_x$/AC3 catalyst for a feed composition of 1% CO, 1% O$_2$, 60% H$_2$, 10% H$_2$O, 15% CO$_2$ and balance He at 135-125-115-110˚C (Experiments #9-10-11-12)

	Temperature in˚C	% CO Conversion by GC	% Oxygen Conversion by GC	% CO Selectivity by GC
Exp #9	135	74.93	100	37.47
Exp #10	125	84.65	100	42.32
Exp #11	115	87.04	100	43.52
Exp #12	110	89.31	100	44.65

4.4.4. Effect of O to CO Ratio in the feed for Hydrogen Rich, H_2O and CO_2 containing, CH_4 Free Feed Stream

The oxygen amount in the feed stream was increased to observe its effect on the CO conversion. Addition of CO_2 and water to the feed stream under 1:1 oxygen to CO ratio did not have any significant effect on the CO conversion; the occasional 1 per cent deviation can be attributed to the statistical uncertainty. On the other hand, increasing the oxygen concentration in the feed in the absence of water and CO_2, significantly increases the CO conversion up to 95 per cent. Under the light of those previous results, it might be assumed that increasing the oxygen amount would also increase the activity of the catalyst for a feed containing water vapor and CO_2. However, as indicated in Figure 4.10, CO conversion levels dropped significantly to 69 per cent in experiment #13 from the conversion value of 75 per cent in experiment #9.

Table 4.17. CO oxidation activity and selectivity data for 1%Pt-0.25SnO_x/AC3 catalyst for a feed composition of 1% CO, 1.25% O_2, 60% H_2, 10% H_2O, 15% CO_2 and balance He at 135°C

(Experiment #13)

Reaction Time in min	CO Amount in ppm	% CO Conversion	% CO Selectivity
1	870	6.07	2.43
30	395	57.36	22.95
60	340	63.30	25.32
90	313	66.16	26.46
120	302	67.38	26.95
150	294	68.29	27.31
180	290	68.72	27.49
210	287	69.04	27.62
240	283	69.47	27.79

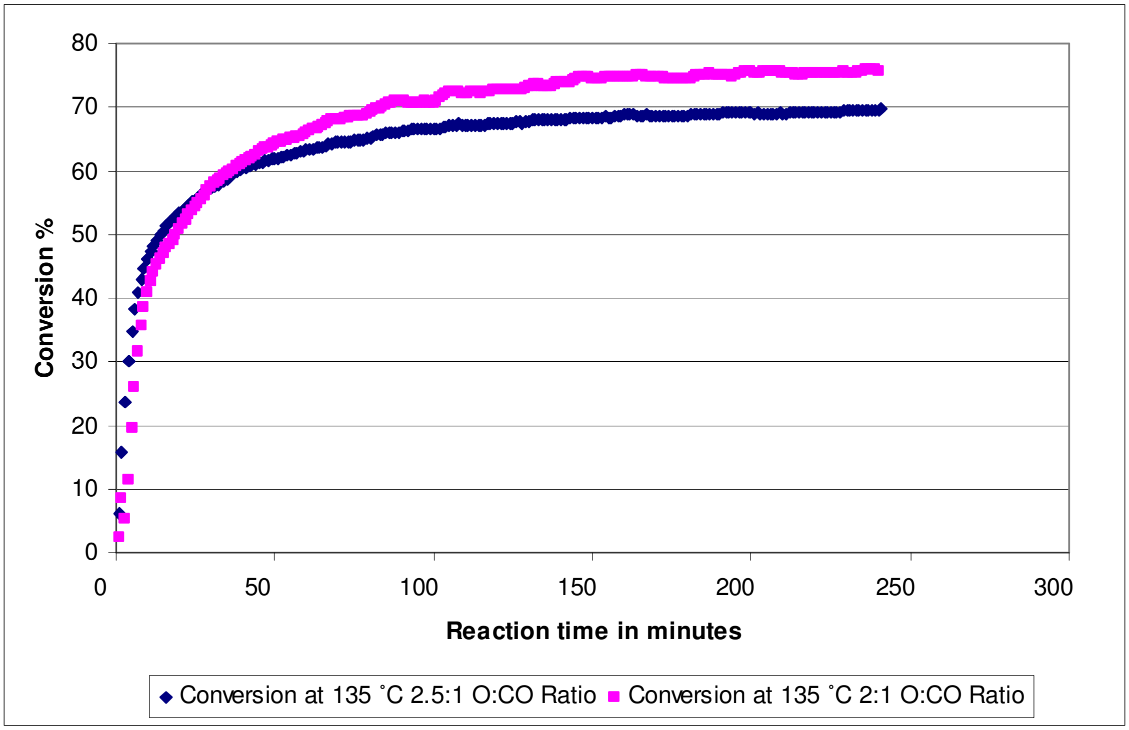


Figure 4.10. Comparison of CO oxidation activity for 1%Pt-0.25SnO_x/AC3 catalyst for feed compositions of: (i) 1% CO, 1.25% O_2, 60% H_2, 10% H_2O, 15% CO_2 and balance He at 135˚C (ii) 1% CO, 1% O_2, 60% H_2, 10% H_2O, 15% CO_2 and balance He at 135˚C (Experiments #9 and #13)

Although the activation trend stayed the same as in the previous sets, it should be noted that the curve has near 0 per cent CO conversion initially for the both sets, set #9 and #13. In set #5 for which there was an oxygen to CO ratio of 1.25:1, the catalyst conversion was at 40 per cent initially and ramped up from there. This might indicate that the surface O and CO concentrations reached their stable levels rather sluggishly in the presence of water and CO_2

Table 4.18. CO oxidation activity and selectivity data for 1%Pt-0.25SnO_x/AC3 catalyst for a feed composition of 1% CO, 1.25% O_2, 60% H_2, 10% H_2O, 15% CO_2 and balance He at 125˚C (Experiment #14)

Reaction Time in min	CO Amount in ppm	% CO Conversion	% CO Selectivity
1	259	72.01	28.80
15	270	70.88	28.35
30	271	70.72	28.29
45	277	70.09	28.04
60	282	69.54	27.82
75	286	69.15	27.66
90	287	69.04	27.61
105	289	68.83	27.53
120	295	68.19	27.28

Table 4.19. CO oxidation activity and selectivity data for 1%Pt-0.25SnO_x/AC3 catalyst for a feed composition of 1% CO, 1.25% O_2, 60% H_2, 10% H_2O, 15% CO_2 and balance He at 115˚C (Experiment #15)

Reaction Time in min	CO Amount in ppm	% CO Conversion	% CO Selectivity
1	324	65.00	26.00
15	269	71.00	28.40
30	268	71.01	28.40
45	276	70.17	28.07
60	283	69.44	27.78
75	287	68.99	27.59
90	290	68.65	27.46
105	293	68.39	27.36
117	293	68.31	27.32

Table 4.20. CO oxidation activity and selectivity data for 1%Pt-0.25SnO$_x$/AC3 catalyst for a feed composition of 1% CO, 1.25% O_2, 60% H_2, 10% H_2O, 15% CO_2 and balance He at 110˚C (Experiment #16)

Reaction Time in min	CO Amount in ppm	% CO Conversion	% CO Selectivity
1	323	65.13	26.05
15	275	70.25	28.10
30	282	69.56	27.82
45	286	69.10	27.64
60	289	68.79	27.52
75	289	68.75	27.50
90	289	68.74	27.50
105	293	68.38	27.35
120	294	68.24	27.30

The tests conducted at different reaction temperatures showed that the conversion was not dependent on the temperature for this experimental set. Figure 4.11 clearly shows that after one hour time on stream, CO conversion stabilizes around 68 per cent, which was also the CO conversion level for 135˚C. It is interesting to point out that, under high oxygen amounts, the catalyst activity was increased as was in the case of experiments #5-8. On the other hand, addition of CO_2 and water without increasing the oxygen amount did not have any effect on the catalyst conversion (experiments #9-12). However, increasing the oxygen concentration under the presence of water and CO_2, decreased the catalytic performance. Since the catalyst conversion does not increase with the decrease in temperature for this condition, the loss of activity based on CO conversion was higher in lower temperatures, when compared to the previous cases like experiments #2,3 and #4.

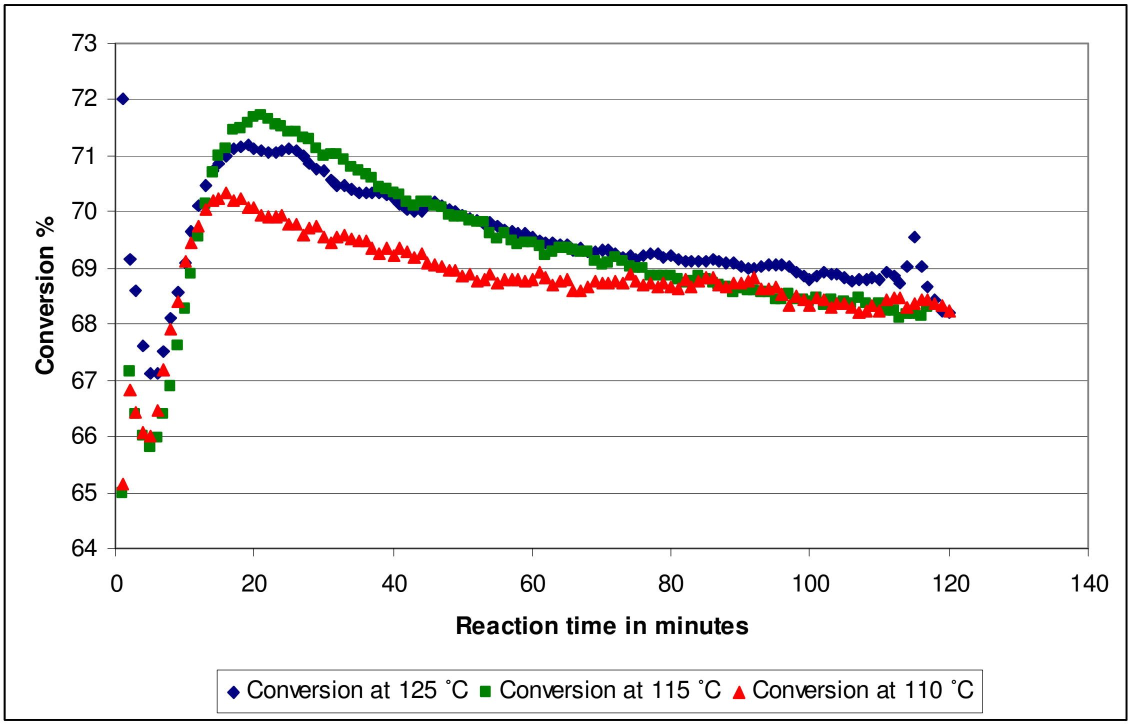


Figure 4.11. CO oxidation activity for 1%Pt-0.25SnO$_x$/AC3 catalyst for a feed composition of 1% CO, 1.25% O_2, 60% H_2, 10% H_2O, 15% CO_2 and balance He at 125-115-110˚C (Experiments #14-15-16)

Table 4.21. Gas chromatograph data for CO oxidation activity and selectivity for 1%Pt-0.25SnO$_x$/AC3 catalyst for a feed composition of 1% CO, 1.25% O_2, 60% H_2, 10% H_2O, 15% CO_2 and balance He at 135-125-115-110˚C (Experiments #13-14-15-16)

	Temperature in˚C	% CO Conversion by GC	% Oxygen Conversion by GC	% CO Selectivity by GC
Exp #13	135	68.00	100	27.20
Exp #14	125	65.10	100	26.04
Exp #15	115	63.79	100	25.52
Exp #16	110	63.92	100	25.57

4.4.5 Effect of Methane Addition to Hydrogen Rich, H_2O and CO_2 free, 1:1 O_2 to CO Feed Stream

In a real fuel processor system, a fuel that is easier to store than hydrogen will be used to produce a hydrogen rich feed. Natural gas, which consists mostly of methane, is the most promising candidate (Trimm and Önsan 2001) as the fuel processor feed. After the Autothermal Reforming and the High and Low temperature water gas shift reactions, a small amount of unreacted methane would also be present in the feed to the PROX reactor, regardless of hydrocarbon feed used. Therefore, the effect of this unreacted methane on the reaction conversion and selectivity was investigated. Table 4.21 and Figure 4.12 show the CO conversion data for methane addition.

Table 4.22. CO oxidation activity and selectivity data for 1%Pt-0.25SnO_x/AC3 catalyst for a feed composition of 1% CO, 1% O_2, 60% H_2, 3% CH_4 and balance He at 135˚C (Experiment #17)

Reaction Time in min	CO Amount in ppm	% CO Conversion	% CO Selectivity
1	890	3,89	1,95
30	562	39,35	19,68
60	505	45,47	22,74
90	476	48,56	24,28
120	452	51,15	25,57
150	436	52,94	26,47
180	420	54,65	27,33
210	403	56,50	28,25
240	387	58,20	29,10

According to Figure 4.12 methane addition lowers the catalyst conversion by a considerable amount ca. 15 per cent at 135˚C. Methane can oxidize with oxygen to give water and carbon dioxide and this decrease may lead to a decrease in CO conversion; methane might compete with hydrogen and CO for the available oxygen. As the reaction temperature decreases, the activity of the catalyst increases like in the previous cases.

However, for the experiments with methane in the feed stream, this increase occurs at a greater rate. At 125˚C, the conversion difference between the feeds with and without methane was 7 per cent. At 115˚C, methane addition lowered the CO conversion only by 1-2 per cent. Lastly, at 110˚C, the CO conversion values were equal for both cases. Refer to Figure 4.13 and Tables 4.23-24-25 for the conversion values. This trend supports the possibility of methane oxidation, since methane oxidation rate would diminish greatly with decreasing temperature. At 110˚C methane addition has no effect on the conversion levels.

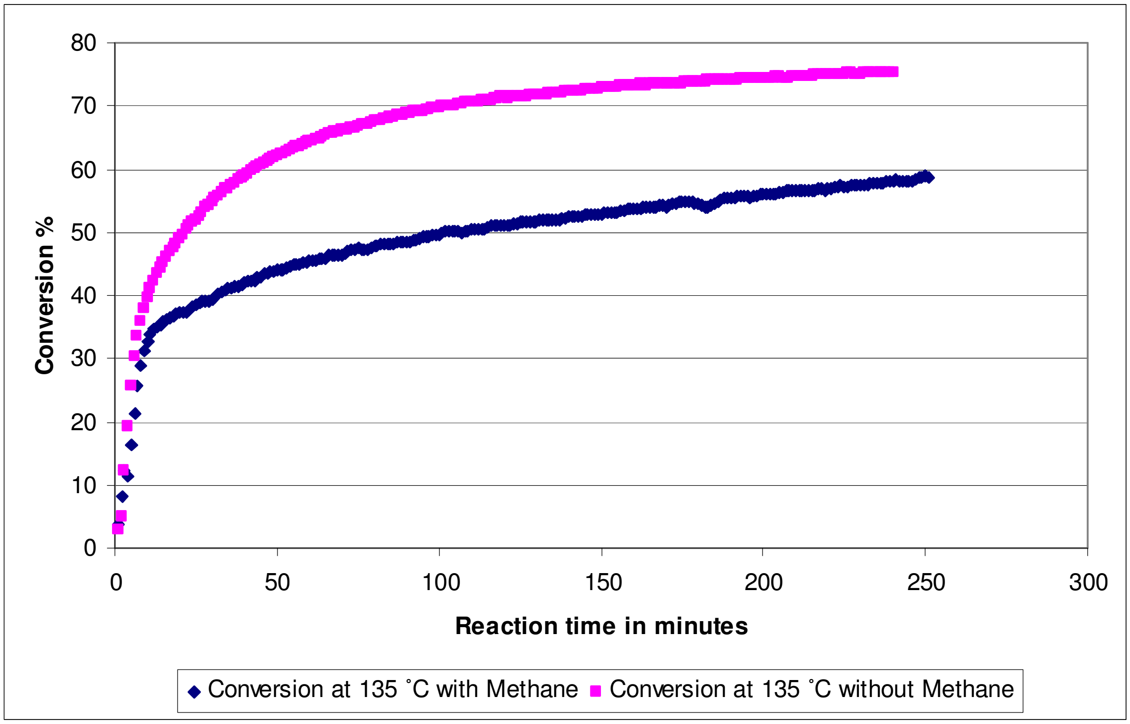


Figure 4.12. Comparison of CO oxidation activity for 1%Pt-0.25SnO$_x$/AC3 catalyst for feed compositions of: (i) 1% CO, 1 % O_2, 60% H_2, 3% CH_4 and balance He at 135˚C (ii) 1% CO, 1% O_2, 60% H_2 and balance He at 135˚C (Experiments #1 and #17)

Table 4.23. CO oxidation activity and selectivity data for 1%Pt-0.25SnO$_x$/AC3 catalyst for a feed composition of 1% CO, 1% O$_2$, 60% H$_2$, 3% CH$_4$ and balance He at 125˚C (Experiment #18)

Reaction Time in min	CO Amount in ppm	% CO Conversion	% CO Selectivity
1	353	61,90	30,95
15	309	66,62	33,31
30	299	67,75	33,87
45	289	68,74	34,37
60	284	69,30	34,65
75	278	70,01	35,01
90	271	70,73	35,36
105	261	71,85	35,93
120	238	74,34	37,17

Table 4.24. CO oxidation activity and selectivity data for 1%Pt-0.25SnO$_x$/AC3 catalyst for a feed composition of 1% CO, 1% O$_2$, 60% H$_2$, 3% CH$_4$ and balance He at 115˚C (Experiment #19)

Reaction Time in min	CO Amount in ppm	% CO Conversion	% CO Selectivity
1	238	74,27	37,13
15	189	79,57	39,79
30	178	80,79	40,40
45	173	81,28	40,64
60	168	81,84	40,92
75	165	82,13	41,07
90	158	82,95	41,47
105	154	83,38	41,69
120	151	83,69	41,84

Table 4.25. CO oxidation activity and selectivity data for 1%Pt-0.25SnO$_x$/AC3 catalyst for a feed composition of 1% CO, 1% O_2, 60% H_2, 3% CH_4 and balance He at 110˚C (Experiment #20)

Reaction Time in min	CO Amount in ppm	% CO Conversion	% CO Selectivity
1	162	82,48	41,24
15	117	87,41	43,70
30	114	87,67	43,84
45	112	87,87	43,93
60	110	88,12	44,06
75	108	88,37	44,19
90	106	88,54	44,27
105	104	88,82	44,41
120	102	88,99	44,50

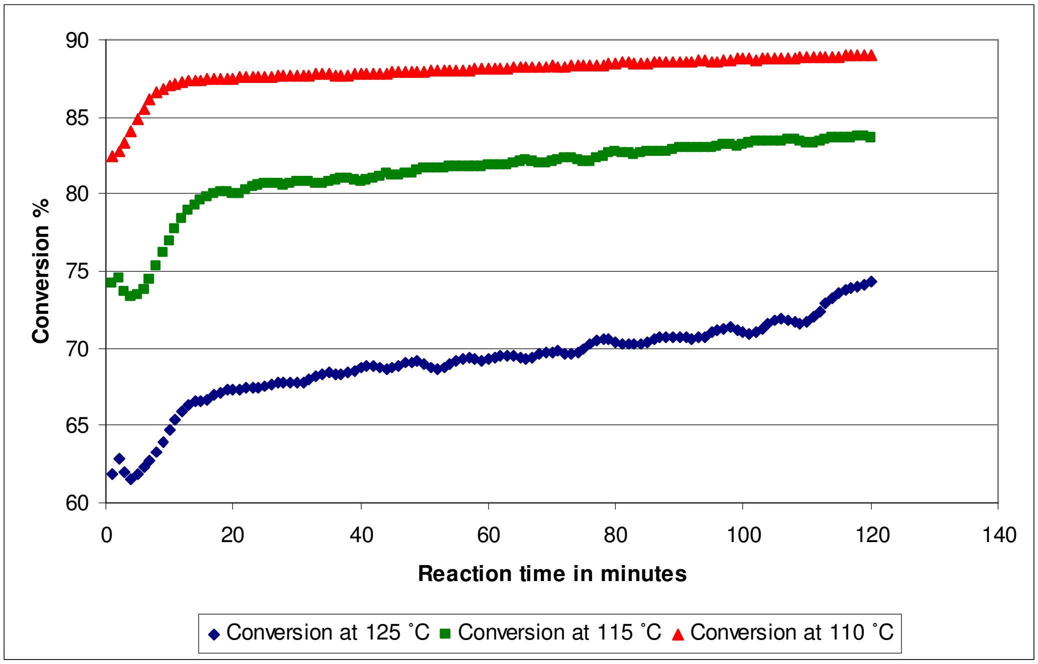


Figure 4.13. CO oxidation activity for 1%Pt-0.25SnO$_x$/AC3 catalyst for a feed composition of 1% CO, 1% O_2, 60% H_2, 3% CH_4 and balance He at 125-115-110˚C (Experiments #18-19-20)

Table 4.26. Gas chromatograph data for CO oxidation activity and selectivity for 1%Pt-0.25SnO_x/AC3 catalyst for a feed composition of 1% CO, 1% O_2, 60% H_2, 3% CH_4 and balance He at 135-125-115-110˚C (Experiments #17-18-19-20)

	Temperature in˚C	% CO Conversion by GC	% Oxygen Conversion by GC	% CO Selectivity by GC
Exp #17	135	64.59	100	32.30
Exp #18	125	78.64	100	39.32
Exp #19	115	88.61	100	44.31
Exp #20	110	90.34	100	45.17

No oxygen is encountered in the feed stream, (Table 4.26) thus it is safe to assume that the CO selectivity of oxygen is one half of the CO con*version. Remaining oxygen may have reacted with methane or hydrogen, but regardless of what it reacted with, the CO selectivity remains constant. For the CO conversions GC data are also in agreement with the CO analyzer results with a margin of ±5 per cent.

4.4.6. Effect of O_2 to CO ratio in the Hydrogen Rich Feed Including Methane and Free from H_2O and CO_2

Increasing the oxygen concentration in the feed stream had a positive effect on the CO conversion for the experiments without methane. The conversion percentages rose from 75 per cent to 80 per cent for CO. Same trend was observed in the experiments with methane in the feed stream; the CO conversion was increased by more than 10 per cent (Figure 4.14). Methane oxidation uses 3 moles of oxygen per each mole of methane; therefore, even small amounts of oxidized methane can reduce the oxygen considerably. Increasing the oxygen amount attributes to a larger increase in conversion levels for the experiments which have methane in the feed, compared to those experiments which do not. However the overall CO conversion levels of the methane containing experiments at high temperatures (Experiments #17-18-19 and 21-22-23) are lower than their methane free counterparts (Experiments #1-2-3 and 5-6-7).

Table 4.27. CO oxidation activity and selectivity data for 1%Pt-0.25SnO$_x$/AC3 catalyst for a feed composition of 1% CO, 1.25% O$_2$, 60% H$_2$, 3% CH$_4$ and balance He at 135˚C (Experiment #21)

Reaction Time in min	CO Amount in ppm	% CO Conversion	% CO Selectivity
1	884	4.55	1.82
30	626	32.40	12.96
60	387	58.24	23.30
90	339	63.38	25.35
120	321	65.37	26.15
150	305	67.05	26.82
180	293	68.33	27.33
210	284	69.37	27.75
240	272	70.58	28.23

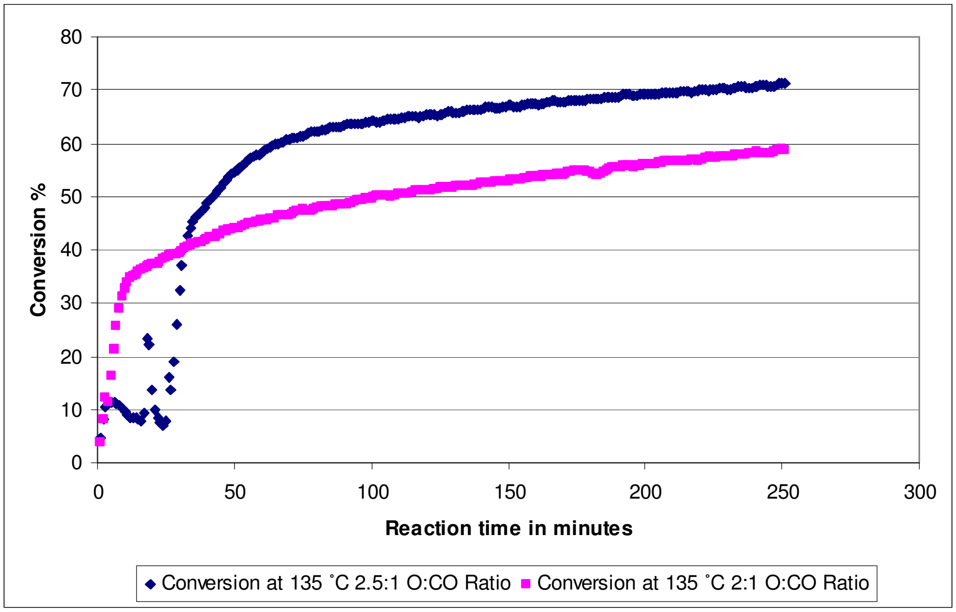


Figure 4.14. Comparison of CO oxidation activity data for 1%Pt-0.25SnO$_x$/AC3 catalyst for feed compositions of: (i) 1% CO, 1.25 % O$_2$, 60% H$_2$, 3% CH$_4$ and balance He at 135˚C (ii) 1% CO, 1% O$_2$, 60% H$_2$, 3% CH$_4$ and balance He at 135˚C (Experiments #17 and #21)

Table 4.28. CO oxidation activity and selectivity data for 1%Pt-0.25SnO_x/AC3 catalyst for a feed composition of 1% CO, 1.25% O_2, 60% H_2, 3% CH_4 and balance He at 125°C (Experiment #22)

Reaction Time in min	CO Amount in ppm	% CO Conversion	% CO Selectivity
1	269	70.92	28.37
15	302	67.44	26.98
30	301	67.54	27.02
45	296	68.00	27.20
60	287	68.99	27.60
75	285	69.21	27.68
90	277	70.13	28.05
105	275	70.31	28.12
120	271	70.78	28.31

Table 4.29. CO oxidation activity and selectivity data for 1%Pt-0.25SnO_x/AC3 catalyst for a feed composition of 1% CO, 1.25% O_2, 60% H_2, 3% CH_4 and balance He at 115°C (Experiment #23)

Reaction Time in min	CO Amount in ppm	% CO Conversion	% CO Selectivity
1	254	72.59	29.03
15	316	65.87	26.35
30	311	66.38	26.55
45	303	67.28	26.91
60	292	68.52	27.41
75	281	69.65	27.86
90	270	70.83	28.33
105	257	72.28	28.91
120	248	73.22	29.29

Table 4.30. CO oxidation activity and selectivity data for 1%Pt-0.25SnO$_x$/AC3 catalyst for a feed composition of 1% CO, 1.25% O_2, 60% H_2, 3% CH_4 and balance He at 110˚C (Experiment #24)

Reaction Time in min	CO Amount in ppm	% CO Conversion	% CO Selectivity
1	244	73.67	29.47
15	222	76.02	30.41
30	209	77.44	30.97
45	196	78.78	31.51
60	184	80.18	32.07
75	172	81.39	32.55
90	161	82.58	33.03
105	153	83.50	33.40
120	144	84.40	33.76

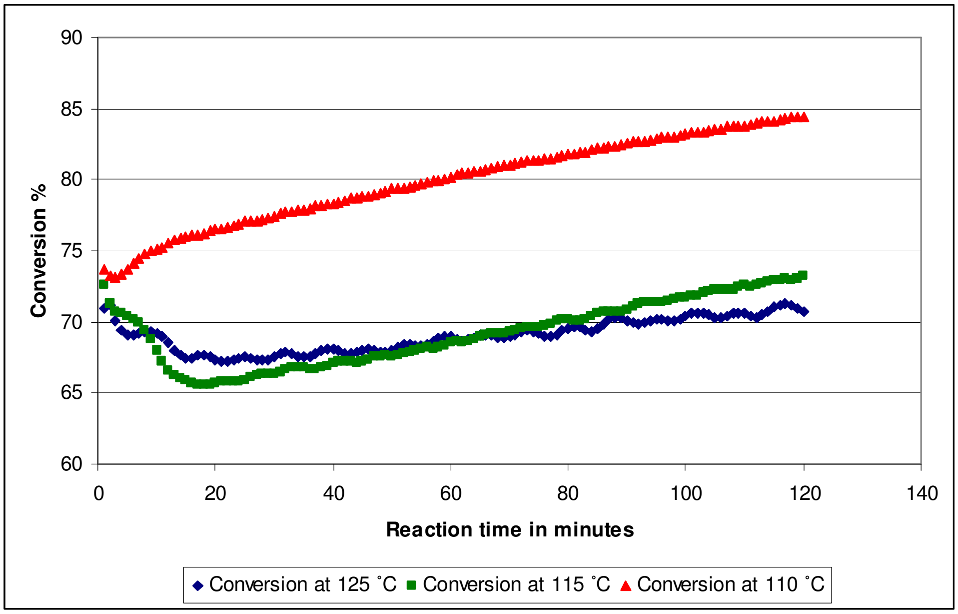


Figure 4.15. CO oxidation activity for 1%Pt-0.25SnO$_x$/AC3 catalyst for a feed composition of 1% CO, 1.25% O_2, 60% H_2, 3% CH_4 and balance He at 125-115-110˚C (Experiments #22-23-24)

Experiments #21-22-23-24 show a different temperature dependency. Conversion percentages remain constant at 135-125 and 115˚C, but conversion reaches 85 per cent at 110˚C compared to the 73 per cent of the previous temperatures. The GC data corresponds with the CO analyzer results (Table 4.31).

Table 4.31. Gas chromatograph data for CO oxidation activity and selectivity for 1%Pt-0.25SnO_x/AC3 catalyst for a feed composition of 1% CO, 1.25% O_2, 60% H_2, 3% CH_4 and balance He at 135-125-115-110˚C (Experiments #21-22-23-24)

	Temperature in˚C	% CO Conversion by GC	% Oxygen Conversion by GC	% CO Selectivity by GC
Exp #21	135	70.35	100	28.14
Exp #22	125	70.05	100	28.02
Exp #23	115	74.12	100	29.65
Exp #24	110	85.29	100	34.12

4.4.7. Effect of Water and CO_2 Addition to Hydrogen Rich 2:1 O:CO ratio, Methane Containing Feed Stream

In order to simulate the realistic feed conditions of a PROX reactor, the feed stream is designed to have methane, water, CO_2, hydrogen and oxygen at the same time. This feed stream reduced CO conversions achieved over Pt-Sn/AC3 drastically down to 45 per cent at 135˚C. Table 4.32 and Figure 4.16 show 15 per cent decrease in catalyst performance with the addition of water and CO_2.

Table 4.32. CO oxidation activity and selectivity data for 1%Pt-0.25SnO_x/AC3 catalyst for a feed composition of 1% CO, 1% O_2, 60% H_2, 10% H_2O, 15% CO_2 3% CH_4 and balance He at 135˚C (Experiment #25)

Reaction Time in min	CO Amount in ppm	% CO Conversion	% CO Selectivity
1	827	10.71	5.35
30	677	26.90	13.45
60	604	34.82	17.41
90	565	39.00	19.50
120	544	41.28	20.64
150	529	42.85	21.42
180	519	43.99	22.00
210	509	45.03	22.52
240	503	45.68	22.84

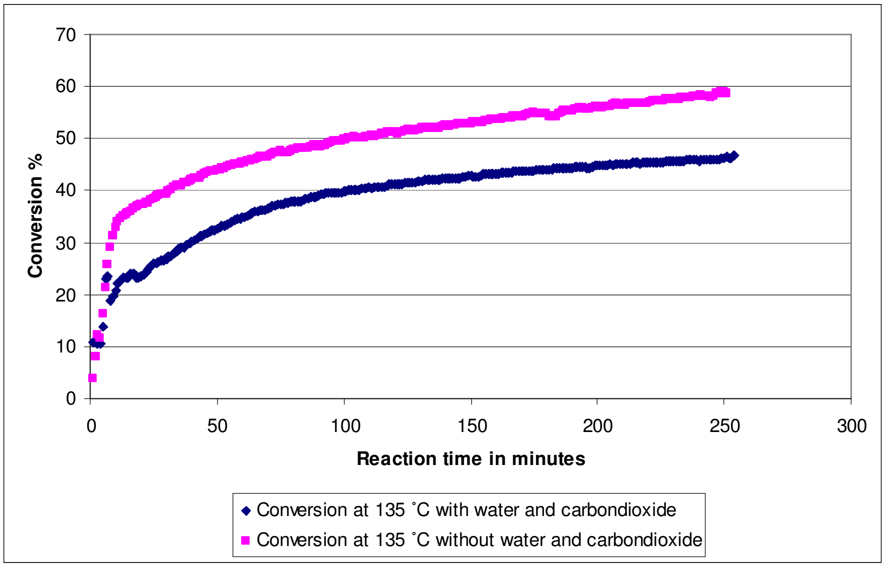


Figure 4.16. Comparison of CO oxidation activity data for 1%Pt-0.25SnO_x/AC3 catalyst for feed compositions of: (i) 1% CO, 1 % O_2, 60% H_2, 10% H_2O, 15% CO_2, 3% CH_4 and balance He at 135˚C (ii) 1% CO, 1% O_2, 60% H_2, 3% CH_4 and balance He at 135˚C (Experiments #17 and #25)

Table 4.33. CO oxidation activity and selectivity data for 1%Pt-0.25SnO$_x$/AC3 catalyst for a feed composition of 1% CO, 1% O_2, 60% H_2, 10% H_2O, 15% CO_2 3% CH_4 and balance He at 125˚C (Experiment #26)

Reaction Time in min	CO Amount in ppm	% CO Conversion	% CO Selectivity
1	522	43.65	21.82
15	499	46.13	23.06
30	494	46.66	23.33
45	490	47.13	23.56
60	486	47.57	23.78
75	478	48.34	24.17
90	473	48.88	24.44
105	470	49.25	24.62
120	470	49.29	24.65

Table 4.34. CO oxidation activity and selectivity data for 1%Pt-0.25SnO$_x$/AC3 catalyst for a feed composition of 1% CO, 1% O_2, 60% H_2, 10% H_2O, 15% CO_2 3% CH_4 and balance He at 115˚C (Experiment #27)

Reaction Time in min	CO Amount in ppm	% CO Conversion	% CO Selectivity
1	491	47.03	23.51
15	457	50.64	25.32
30	454	50.98	25.49
45	444	52.05	26.03
60	448	51.58	25.79
75	444	52.01	26.01
90	441	52.39	26.20
105	436	52.88	26.44
120	433	53.26	26.63

Table 4.35. CO oxidation activity and selectivity data for 1%Pt-0.25SnO_x/AC3 catalyst for a feed composition of 1% CO, 1% O_2, 60% H_2, 10% H_2O, 15% CO_2 3% CH_4 and balance He at 110˚C (Experiment #28)

Reaction Time in min	CO Amount in ppm	% CO Conversion	% CO Selectivity
1	452	51.18	25.59
15	414	55.27	27.64
30	413	55.43	27.72
45	410	55.70	27.85
60	410	55.71	27.86
75	405	56.21	28.11
90	400	56.80	28.40
105	396	57.19	28.60
120	396	57.19	28.60

Experiment #17 included methane but not CO_2 or water, and it showed a steep increase in activity with decreasing temperature; same trend was also observed with realistic feed conditions, the decrease in temperature increased conversion percentages by ca. 13 per cent. The GC results do not correspond with the data obtained from the CO analyzer at this point.

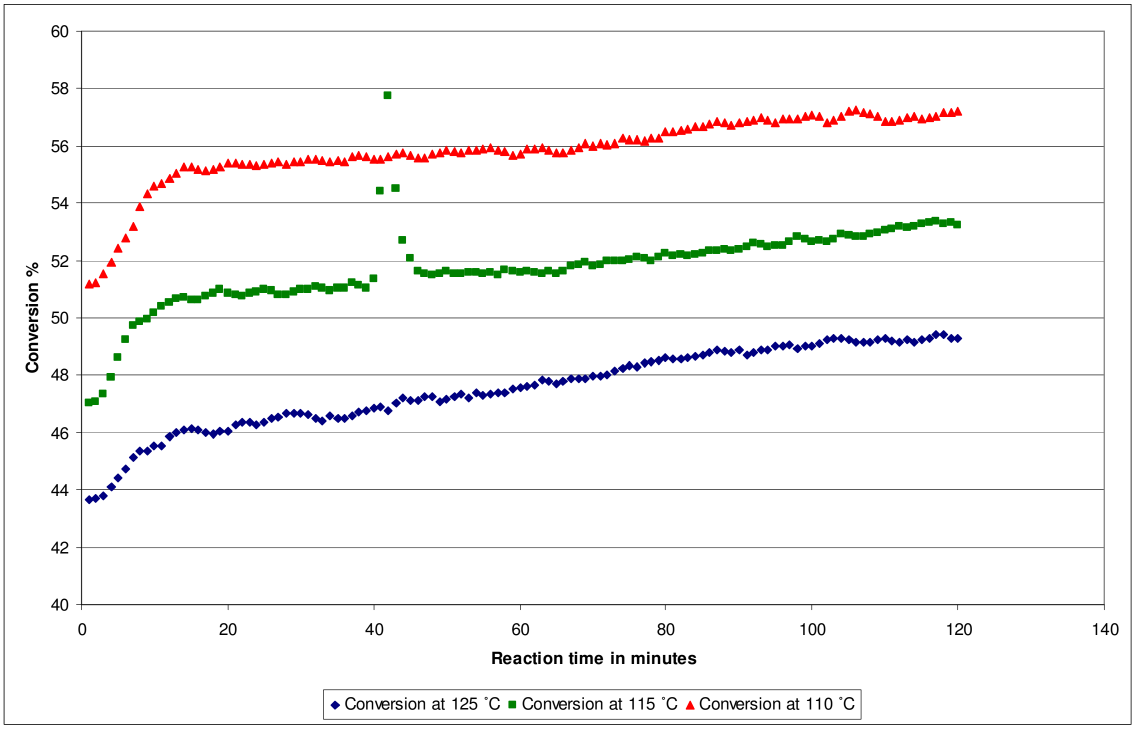


Figure 4.17. CO oxidation activity for 1%Pt-0.25SnO$_x$/AC3 catalyst for a feed composition of 1% CO, 1% O_2, 60% H_2, 10% H_2O, 15% CO_2, 3% CH_4 and balance He at 125-115-110˚C (Experiments #26-27-28)

Table 4.36. Gas chromatograph data for CO oxidation activity and selectivity for 1%Pt-0.25SnO$_x$/AC3 catalyst for a feed composition of 1% CO, 1% O_2, 60% H_2, 10% H_2O, 15% CO_2, 3% CH_4 and balance He at 135-125-115-110˚C (Experiments #25-26-27-28)

	Temperature in˚C	% CO Conversion by GC	% Oxygen Conversion by GC	% CO Selectivity by GC
Exp #25	135	33.53	100	16.76
Exp #26	125	57.65	100	28.82
Exp #27	115	56.12	100	28.06
Exp #28	110	51.18	100	25.59

4.4.8. Effect of O to CO Ratio for Hydrogen Rich Feed Stream Containing CH_4, H2O and CO_2

The realistic feed conditions yielded very poor CO conversion levels upon the addition of methane. It was observed in the previous experiments and also in the literature, that increasing O_2:CO ratio has a positive impact on the CO conversion levels. Figure 4.18 shows a tremendous change in conversion levels with the increase in the O:CO ratio. CO conversion increased by ca. 30 per cent at 135˚C. The oxygen conversion level was 100 per cent for both O_2 concentrations. Therefore it may be assumed that oxygen reacts with methane when its concentration is low and furtherly added oxygen reacts with CO to form CO_2.

Table 4.37. CO oxidation activity and selectivity data for 1%Pt-0.25SnO_x/AC3 catalyst for a feed composition of 1% CO, 1.25% O_2, 60% H_2, 10% H_2O, 15% CO_2 3% CH_4 and balance He at 135˚C (Experiment #29)

Reaction Time in min	CO Amount in ppm	% CO Conversion	% CO Selectivity
1	871	5.89	2.35
30	419	54.77	21.91
60	360	61.12	24.45
90	319	65.56	26.22
120	292	68.49	27.40
150	262	71.69	28.68
180	250	73.02	29.21
210	232	74.90	29.96
240	222	75.99	30.40

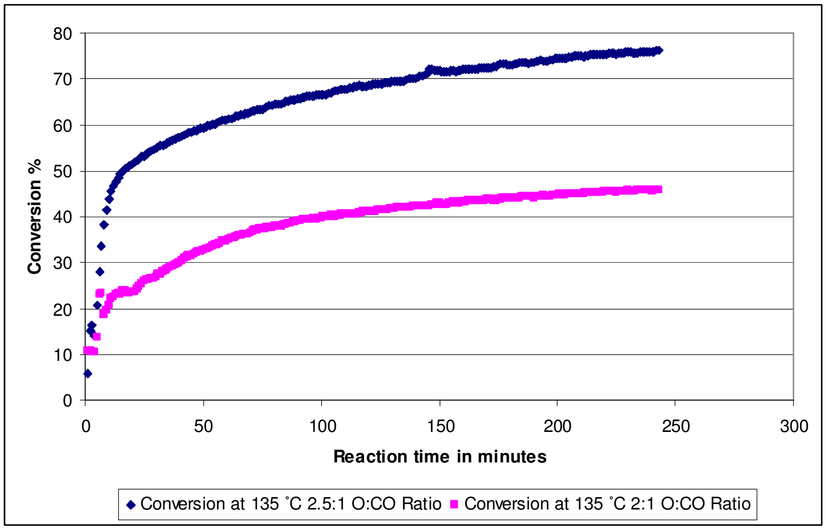


Figure 4.18. Comparison of CO oxidation activity data for 1%Pt-0.25SnO$_x$/AC3 catalyst for feed compositions of: (i) 1% CO, 1.25 % O_2, 60% H_2, 10% H_2O, 15% CO_2, 3% CH_4 and balance He at 135˚C (ii) 1% CO, 1% O_2, 60% H_2, 10% H_2O, 15% CO_2 3% CH_4 and balance He at 135˚C (Experiments #25 and #29)

Table 4.38. CO oxidation activity and selectivity data for 1%Pt-0.25SnO$_x$/AC3 catalyst for a feed composition of 1% CO, 1.25% O_2, 60% H_2, 10% H_2O, 15% CO_2 3% CH_4 and balance He at 125˚C (Experiment #30)

Reaction Time in min	CO Amount in ppm	% CO Conversion	% CO Selectivity
1	234	74.74	29.89
15	196	78.83	31.53
30	183	80.21	32.08
45	172	81.44	32.58
60	163	82.35	32.94
75	161	82.56	33.03
90	157	83.02	33.21
105	153	83.50	33.40
120	149	83.96	33.58

Table 4.39. CO oxidation activity and selectivity data for 1%Pt-0.25SnO_x/AC3 catalyst for a feed composition of 1% CO, 1.25% O_2, 60% H_2, 10% H_2O, 15% CO_2 3% CH_4 and balance He at 115˚C (Experiment #31)

Reaction Time in min	CO Amount in ppm	% CO Conversion	% CO Selectivity
1	162	82.51	33.00
15	131	85.80	34.32
30	130	85.92	34.37
45	128	86.22	34.49
60	125	86.52	34.61
75	121	86.91	34.76
90	118	87.24	34.90
105	116	87.52	35.01
120	111	87.96	35.18

Table 4.40. CO conversion and selectivity data for experiment #3 CO oxidation activity and selectivity data for 1%Pt-0.25SnO_x/AC3 catalyst for a feed composition of 1% CO, 1.25% O_2, 60% H_2, 10% H_2O, 15% CO_2 3% CH_4 and balance He at 110˚C (Experiment #32)

Reaction Time in min	CO Amount in ppm	% CO Conversion	% CO Selectivity
1	127	86.23	34.49
15	120	87.07	34.83
30	118	87.21	34.88
45	116	87.49	35.00
60	112	87.85	35.14
75	109	88.18	35.27
90	107	88.45	35.38
105	105	88.69	35.47
120	101	89.13	35.65

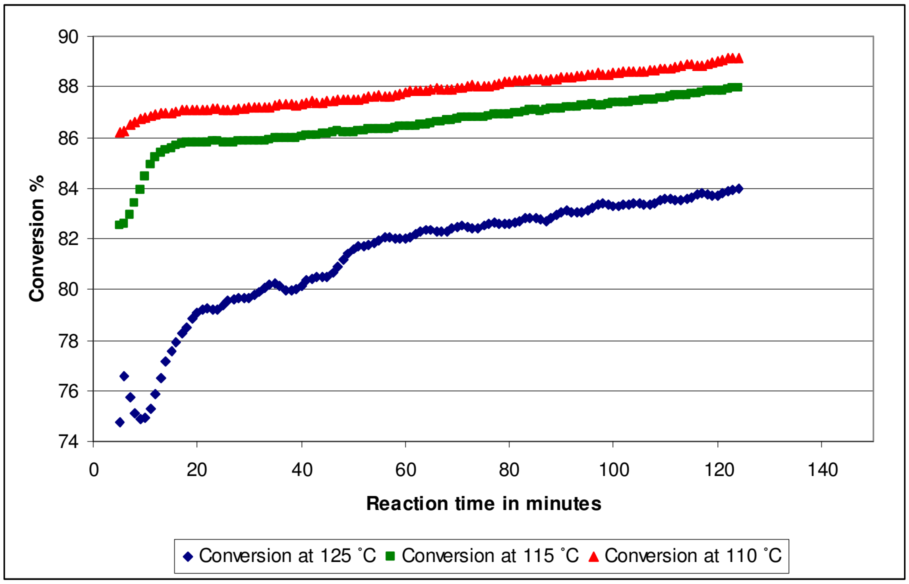


Figure 4.19. CO oxidation activity for 1%Pt-0.25SnO_x/AC3 catalyst for a feed composition of 1.25% CO, 1% O_2, 60% H_2, 10% H_2O, 15% CO_2, 3% CH_4 and balance He at 125-115-110˚C (Experiments #30-31-32)

Temperature dependency of the catalyst was as expected; decrease in temperature increased CO conversion, and the rate of increase was similar to the base case experiment. (Experiment #1).

Table 4.41. Gas chromatograph data for CO oxidation activity and selectivity for 1%Pt-0.25SnO_x/AC3 catalyst for a feed composition of 1.25% CO, 1% O_2, 60% H_2, 10% H_2O, 15% CO_2, 3% CH_4 and balance He at 135-125-115-110˚C (Experiments #29-30-31-32)

	Temperature in˚C	% CO Conversion by GC	% Oxygen Conversion by GC	% CO Selectivity by GC
Exp #25	135	70.39	100	28.15
Exp #26	125	80.85	100	32.34
Exp #27	115	87.15	100	34.86
Exp #28	110	88.92	100	35.57

Table 4.42. Experimental results

	Temperature in˚C	**Oxygen Flow Rate ml/min**	**CO Flow Rate in ml/min**	**Methane Flow Rate in ml/min**	**Water Flow Rate in ml/min**	**CO_2 Flow Rate in ml/min**	**% O_2 Conversion**	**% CO Selectivity**	**% CO Conversion**
Exp1	135	1.00	1.00	0	0	0	100	37.69	75.38
Exp2	125	1.00	1.00	0	0	0	100	40.66	81.32
Exp3	115	1.00	1.00	0	0	0	100	42.60	85.20
Exp4	110	1.00	1.00	0	0	0	100	44.09	88.18
Exp5	135	1.25	1.00	0	0	0	100	31.97	79.91
Exp6	125	1.25	1.00	0	0	0	100	36.05	90.11
Exp7	115	1.25	1.00	0	0	0	100	37.40	93.50
Exp8	110	1.25	1.00	0	0	0	100	38.05	95.12
Exp9	135	1.00	1.00	0	10	15	100	37.77	75.54
Exp10	125	1.00	1.00	0	10	15	100	41.83	83.67
Exp11	115	1.00	1.00	0	10	15	100	42.25	84.50
Exp12	110	1.00	1.00	0	10	15	100	43.93	87.85
Exp13	135	1.25	1.00	0	10	15	100	27.79	69.42
Exp14	125	1.25	1.00	0	10	15	100	27.28	68.19
Exp15	115	1.25	1.00	0	10	15	100	27.32	68.31
Exp16	110	1.25	1.00	0	10	15	100	27.30	68.24
Exp17	135	1.00	1.00	3	0	0	100	29.10	58.20
Exp18	125	1.00	1.00	3	0	0	100	37.17	74.34
Exp19	115	1.00	1.00	3	0	0	100	41.84	83.96
Exp20	110	1.00	1.00	3	0	0	100	44.50	88.99
Exp21	135	1.25	1.00	3	0	0	100	28.23	70.58
Exp22	125	1.25	1.00	3	0	0	100	28.31	70.78
Exp23	115	1.25	1.00	3	0	0	100	29.29	73.22
Exp24	110	1.25	1.00	3	0	0	100	33.76	84.40
Exp25	135	1.00	1.00	3	10	15	100	22.84	45.68
Exp26	125	1.00	1.00	3	10	15	100	24.65	49.29
Exp27	115	1.00	1.00	3	10	15	100	26.63	53.26
Exp28	110	1.00	1.00	3	10	15	100	28.60	57.19
Exp29	135	1.25	1.00	3	10	15	100	30.40	75.99
Exp30	125	1.25	1.00	3	10	15	100	33.58	83.96
Exp31	115	1.25	1.00	3	10	15	100	35.18	87.96
Exp32	110	1.25	1.00	3	10	15	100	35.65	89.13

5. CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Preferential oxidation of CO under H_2 rich atmosphere was studied to find out the effect of water, carbondioxide, oxygen concentration and methane content in the feed stream. The experiments were conducted at 135-125-115 and 110˚C over 1% Pt- 0.25% Sn supported on HNO_3 oxidized form of activated carbon.

- The catalyst activated constantly during the reaction runs at fixed temperature a decreasing rate; even on 20 hour stability runs, the catalyst continued to activate.
- 10 hours of reduction under 50 ml H_2 flow at 400˚C resulted in a relatively more stable catalyst activity compared to those reduced for 2 hours under the same flow conditions. The CO conversion levels started higher and increased at a lower rate during the reaction.
- Throughout the experiments no oxygen is encountered in the product stream and oxygen conversion was found to be 100 per cent in all cases.

The results obtained for different feed conditions for 1% Pt-0.25%SnO_x/AC3 catalysts are as follows:

- The catalyst was tested under hydrogen rich CO and oxygen containing atmosphere, 88 per cent conversion was reached for this base case experiment.
- Increasing the oxygen amount in the feed has a positive effect on the CO conversions generally, except the case where CO_2 and water are fed to the reactor in the presence of methane where it caused a decrease in CO conversion with methane present in the feed stream. The increase caused by introduction of oxygen changes between 3 per cent to 30 per cent.
- Water and CO_2 addition to the feed stream did not have any effect on the CO conversion percentages when the O_2:CO ratio was 1:1. The deactivation caused by CO_2 is offset by water’s surface washing effect through formation of surface OH.

When water and CO_2 are fed to the reactor under 2.5:1 O:CO ratio, the CO conversion levels dropped to 68 per cent and became independent of temperature.

- Methane addition to the base hydrogen rich stream resulted in a decrease in CO conversion at high temperatures (135°C), but as the temperature neared 110°C, methane addition is found to have no negative effect on the CO conversion.
- Further addition of water and CO_2 to the feed stream containing methane resulted in a drastic decrease of 20 per cent in the CO conversion levels as well as selectivities. However when the O_2:CO ratio is increased to 1.25:1, CO conversion levels became same with the base case CO conversions.

The effect of temperature on the CO conversions is as follows:

- Decreasing the temperature yielded an increase in the CO conversion levels for most cases(3-10 per cent). One exception is the experiment set where water and CO_2 are fed to the reactor in the absence of methane and 1.25:1 O_2:CO ratio. CO conversion levels remained constant throughout the temperature range for the corresponding feed conditions.
- Temperature dependency of CO conversion percentages became stronger for the tests conducted with methane containing feed streams. It is found that higher temperatures were not favorable when there is methane in the feed, but as the temperature decreased, CO conversion levels became on par with the methane-free feed streams.
- Highest CO conversion is reached at 110°C, in the absence of water, CO_2 and methane. 1.25:1 O_2:CO ratio is used and the conversion reached was ca. 95 per cent.
- Most significant result is achieved under the realistic feed of 10 per cent water, 15 per cent CO_2, 3 per cent methane, 60 per cent hydrogen, 1.25 per cent oxygen, 1 per cent CO and make up helium for a total of 100 ml/min feed stream. 250 mg 1% Pt-0.25%SnO_x/AC3 yielded 89.13 per cent CO conversion with 35.65 per cent selectivity at 110°C.

5.2 Recommendations

Considering the results obtained in this study, following ideas are suggested for future studies on preferential CO oxidation under realistic feed conditions.

- The reaction flow system could be modified to enable the usage of the MS (mass spectrometer), in the current situation, the product stream is sent to MS after it passes through the CO analyzer. CO analyzer requires the product stream to be mixed with air. Air has nitrogen which has a molecular weight of 28. The molecular weight of CO is also 28, thus making it impossible to get accurate readings for CO concentrations on MS. Moreover high oxygen content of the air along with its impurities would decrease the sensitivity of the analysis drastically. The flow path should be redesigned to enter MS first. MS uses a very small amount of the product gas for analysis thus, the stream may be considered unaffected. The product stream would then mix with air and continue to CO analyzer. With the utilization of the MS, low concentration substituents of the product stream like oxygen and methane could be read more accurately, since the CTR-1 column is not sensitive enough to measure oxygen or methane amounts in the product stream.
- After the modification mentioned above has been made, the analysis would also show methane content before and after the experiment as well as a more accurate reading for the remaining oxygen after the reaction. This would clarify whether methane oxidation is taking place, and if it is, to what extent methane oxidizes at what temperature.
- Condensation of water is done via metallic condensers and ice cubes during the experiment, although the experiments are conducted with utmost caution, condensation via putting ice cubes in a box is a batch process, which disturbs the continuity of the product stream. The product stream cools and contracts when the ice cubes are added, and more air enters the CO analyzer, since the CO analyzer's inlet flow is kept constant. The result is a momentary decrease in CO concentration, which reflects to the conversion as a conversion "peak" (Figure 5.1) which subsides after approximately five minutes as the stream gets to steady state. A continuous cooler would make the experimental data free of water and free of kinks or peaks at the same time.

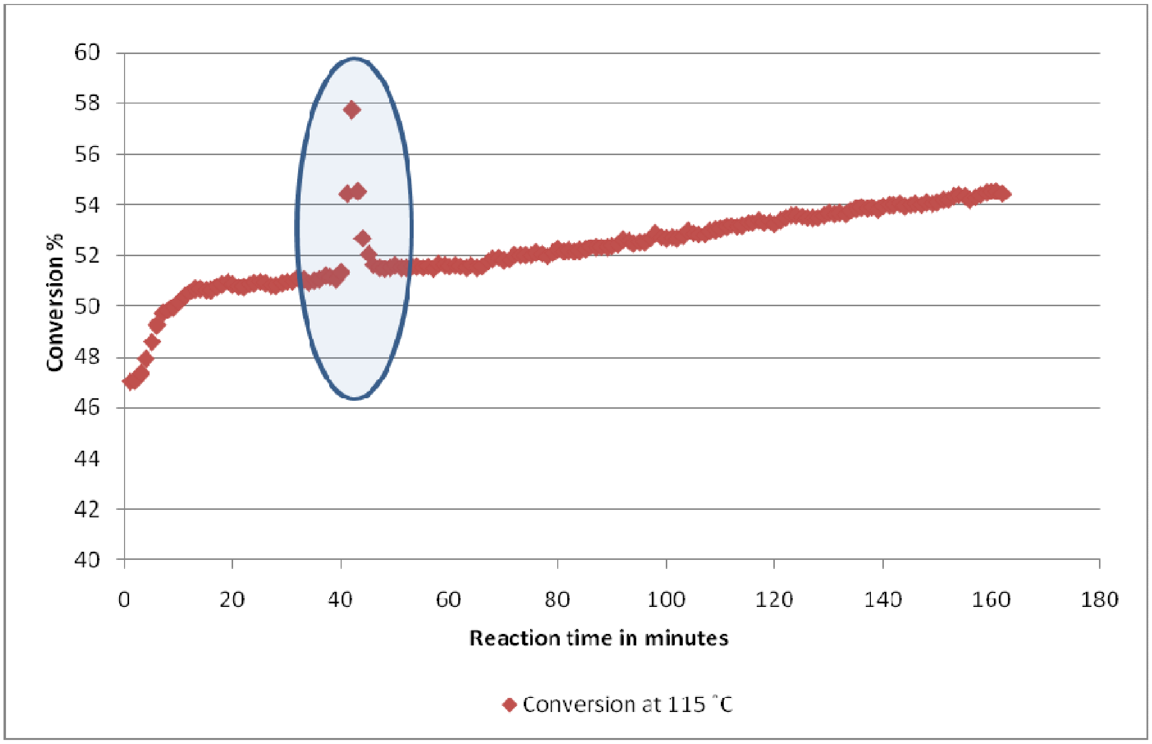


Figure 5.1. The peak in the CO conversion data for experiment #27, resulting from the addition of ice cubes to the condenser.

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