Low Temperature CO Oxidation for Fire Escape Mask Application Using Microfibrous Entrapped Catalyst

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Abstract

Prime reason for deaths in fire is not the fire itself but poisoning caused due to carbon monoxide. It has been reported by the American Medical Association that, every year 2100 deaths and 10000 injuries occur due to CO poisoning. The research work undertaken here deals with development of high contacting efficiency microfibrous entrapped catalysts to remove carbon monoxide for fire escape mask application. Microfibrous materials are a special class of catalysts that entrap micro-sized (10-250 micron) catalyst particles in micron sized (2-20 micron) wires. This approach enables high contacting efficiency with lower pressure drop. This paper presents development of catalyst, the multiplicity of steady states in CO oxidation as observed in microfibrous beds and hysteresis effects. Preliminary results indicating compliance of performance of the catalyst bed with EN 403 standards.

Keywords: Fire escape mask; microfibrous entrapped catalyst; Oxidation, hysteresis, multiplicity

Introduction

It has been long known that removal of carbon monoxide is a difficult task. The reason why carbon monoxide removal has been found to be difficult lies in its physical and chemical properties. Due to its low boiling point and critical temperature, adequate adsorption at ordinary temperature is not possible. Due to its very low solubility in all solvents makes it impossible to be removed by physical absorption under any condition. Chemically CO is very inert at room temperature. The only known means so far is to oxidize carbon monoxide by means of a very powerful oxidizing agent such as platinum, palladium etc. Due to many important applications of low temperature carbon monoxide oxidation process, it has received considerable attention over a period of time. Moreover the simplistic appearance of the reaction, yet complex behavior observed in this reaction, became subject of investigations. The reaction has significant applications in control of emission in automotive exhaust gases, environmental clean up and a gamut of industrial applications of significant economic importance. The reaction can be written as follows:

$CO + 0.5O_2 \rightarrow CO_2$

Many catalysts which are active for this process under different conditions are very well known. There still exists a need for developing a better catalyst that would be active for longer time and would be tolerant to moisture and impurities in reacting gases. Moreover effective contacting pattern between the catalyst surface and reacting gases always plays a key role in catalytic reactions. Microfibrous materials are a means of better contacting efficiency as smaller size of catalyst particles can be used at lower pressure drop.

As it is well known, the main cause of life casualties in fire is Carbon monoxide poisoning rather than the fire itself. Carbon monoxide is often referred to as the “Silent Killer”. Carbon monoxide causes about 2100 deaths per year and about 10000 physical injuries [1].

Carbon monoxide can be lethal at a concentration of more than 400 ppm. Depending upon cases, fire can contain as high as 3600 ppm of carbon monoxide. Other places where it is possible to get poisoned by carbon monoxide are, ship boiler rooms due to defective ventilation, fires below deck in and out, manufacture of power and illuminating gas, coal mining, certain classes of copper mining, wherever explosives are being used in enclosed spaces, leaky flues, exhaust gases from explosive engines and places where coal fires are employed in case of improper ventilation. The catalyst developed here can be very effective to remove CO from the breathing air by incorporating it into gas mask or breathing apparatus. Following section describes standards for Carbon Monoxide Removal for fire escape mask application.

Testing standards and Test Protocols

For suitability of escape only respirators, European Standards Institute [2], NIOSH (National Institute of Occupational Safety and Health) [3] and ANSI (American National Standards Institute)/ISEA (International Safety Equipment Association) [4] have published different testing standards that these have to comply in order to be suitable for commercial use.

EN 403 Standards

Table 1 shows the details of European EN 403 standards. These standards were proposed and accepted by European Union in 1993. Since then, America also followed the same standards. Recently new standards are being proposed.

Table 1: EN 403 Standards Details

Test Agent	Test gas Conc. In air (ppm)	Breakthrough Conc. (ppm)
Propenal (acrolein)	100	10.5
Hydrogen Chloride (HCl)	1000	5
Hydrogen Cyanide	400	10
Carbon Monoxide	2500	200[a]

[a]: Time weighted average over 10 min.

NIOSH Standards

NIOSH standards were published in March 2003 as attachment A to CFR 42.84. Table 2 lists the details of NIOSH CBRN (Chemical, Biological, Radioactive and nuclear) with CO standards.

Table 2: NIOSH Standards Details

Test Agent	Test gas Conc. In air (ppm)	Breakthrough Conc. (ppm)
Ammonia	1250	25
Cyanogen Chloride	150	2
Cyclohexane	1300	10
Formaldehyde	250	10
Hydrogen Cyanide	470	10
Hydrogen Sulfide	500	30
Nitrogen Dioxide	100	1
Phosgene	125	1.25
Phosphine	150	0.5

Test Agent	Test gas Conc. In air (ppm)	Breakthrough Conc. (ppm)
Sulfur Dioxide	750	5
Carbon Monoxide[c]	3600	402.5[b]

[b]: Time weighed average over the one time use of canister
[c]: For a flow rate of 64 LPM (equivalent to breathing flow rate)

ANSI/ISEA 110-2003 Standards

The mask should be active minimum for 15 minutes while removing 3090 ppm CO down to less than 200 ppm instantaneous at room temperature and 90% relative humidity of the feed and for category 7 removing 5150 ppm CO down to less than 200 ppm instantaneous at room temperature as well as zero deg C, and 90% relative humidity of the feed.

Experimental

Figure 1 shows the schematic of catalyst testing set-up. Carbon monoxide and air are fed to the reactor by means of mass flow controllers. Reactor is 50 mm diameter glass reactor. The catalyst is loaded in the reactor and is supported by means of glass wool plug. A thermocouple at the center of the catalyst bed monitors the temperature. The gases after the reaction flow to a detector for monitoring CO concentration at the exit. The detector is RAE CO ppm level infra-red detector. The reaction set-up has heating or cooling jackets depending upon the need.

Microfibrous Support Preparation

Microfibrous catalyst support is prepared by wet-lay processing followed by pre-oxidation and sintering at high temperature in presence of hydrogen. Detailed preparation process has been published in literature [5]. Slurry is made out of mixture of cellulose and nickel fibers in water. This slurry when poured with catalyst support particles into paper making machine yields the pre-form. This pre-form is then subjected to flowing air at about 400 ^{0}C to remove the cellulose. The material then is subjected to reductive environment at around 900 ^{0}C to sinter the fibers. Figure 2 shows the sintered microfibrous entrapped silica. The fiber size used is 4 and 8 μ nickel fibers. Silica particle size is 150-250 μ.

Preparation of Catalysts

Catalysts are prepared by means of conventional impregnation technique. The support is properly dried before impregnation to remove any moisture that can possibly be present inside the pores. The promoter is then impregnated onto the support. The impregnated material is then dried at 100 ^{0}C for about 24 hours and is then subjected to calcinations at 400 ^{0}C. The same process is repeated for noble metal impregnation. Depending upon the catalyst, pre-reduction is used as a treatment.

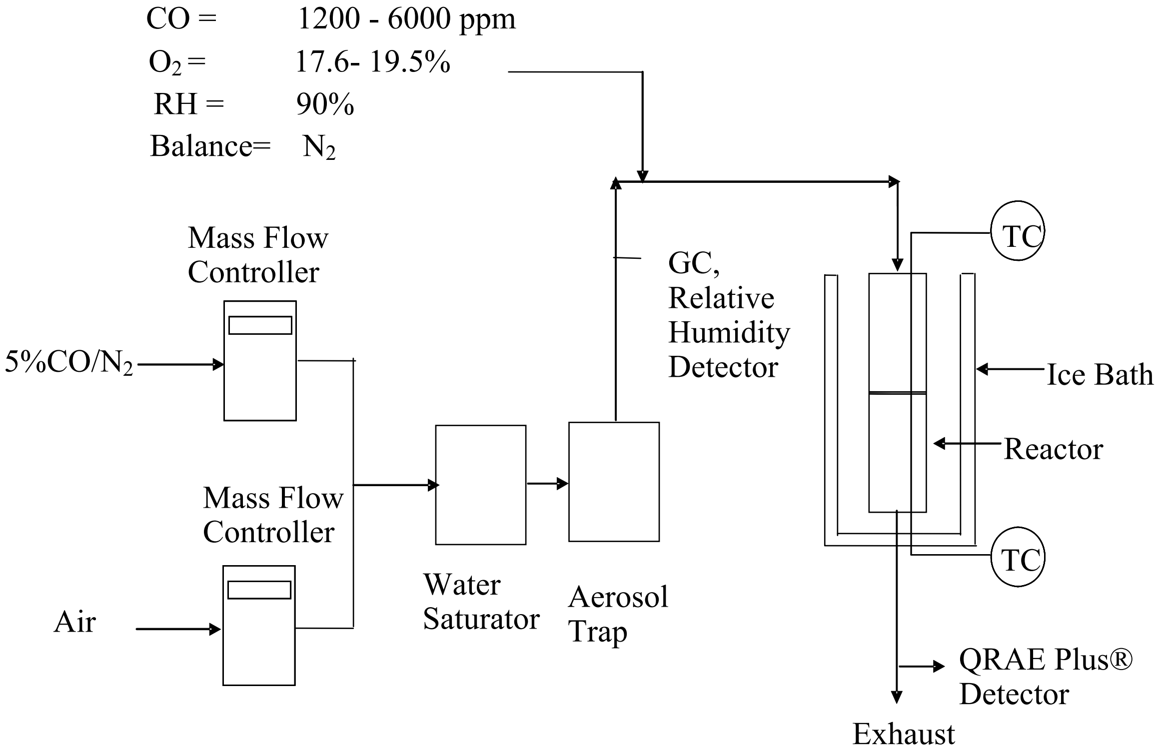

Figure 1: Schematic Diagram of CO Oxidation set-up

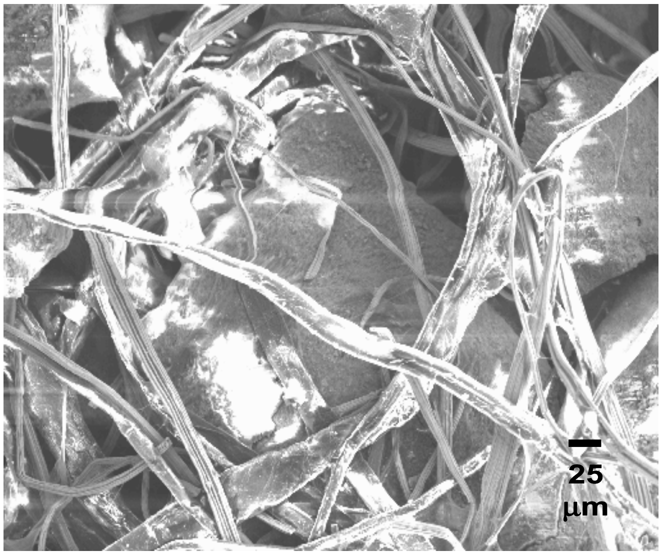

Figure 2: Microfibrous Entrapped Silica support

Results and Discussion

First part of this section discusses the representative results of results obtained from testing the catalyst for EN 403 standards.

As observed from figures 3 and 4 the outlet CO concentration follows a peculiar trend of rising immediately and falling off. This trend can be attributed to adiabatic rise in temperature since CO oxidation is an exothermic reaction. Due to this increased temperature, the self-inhibition of CO reduces thereby increasing the conversion. CO oxidation on Pt catalyst has been known as self-inhibition type of reaction in literature.

As the temperature increases, the conversion increases and outlet concentration of carbon monoxide falls. The gap in measured temperature and adiabatic flame temperature is due to heat loss as effect of improper insulation. The reactor had not been insulated to closely imitate the conditions as faced by the catalyst bed in actual escape mask. One hypothesis that supports this observation could be centered on formation of multiple steady states.

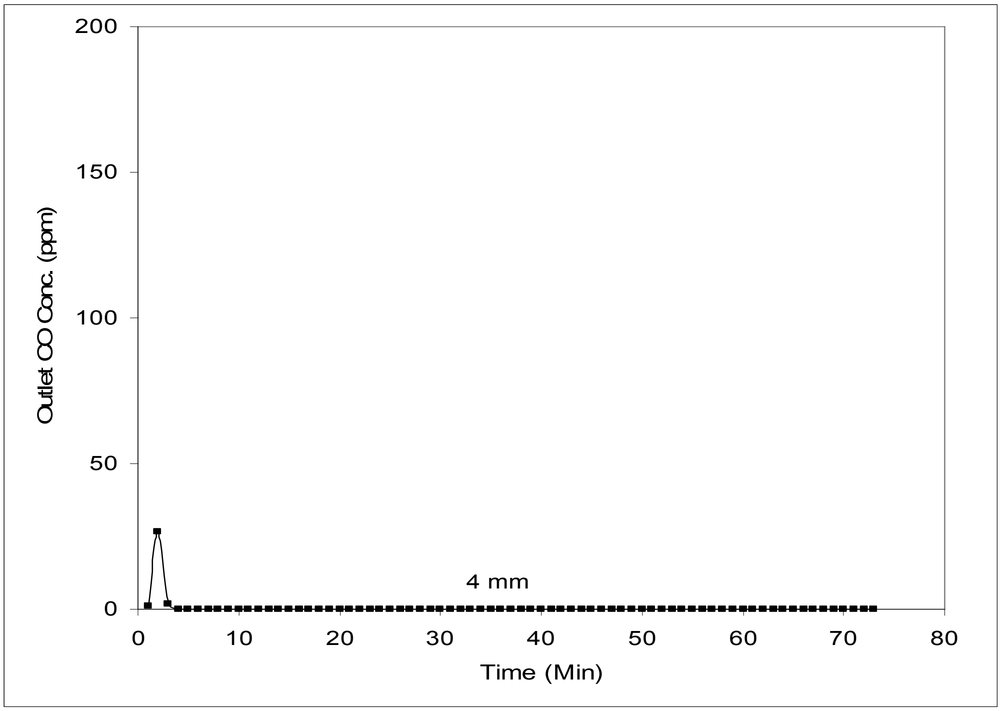

Figure 3: Catalyst Test for EN 403 (Face velocity = 12.5 cm/sec, Temperature = 22 ^{0}C, Bed cross section = 20.26 cm^2, Inlet CO Conc = 2500 ppm)

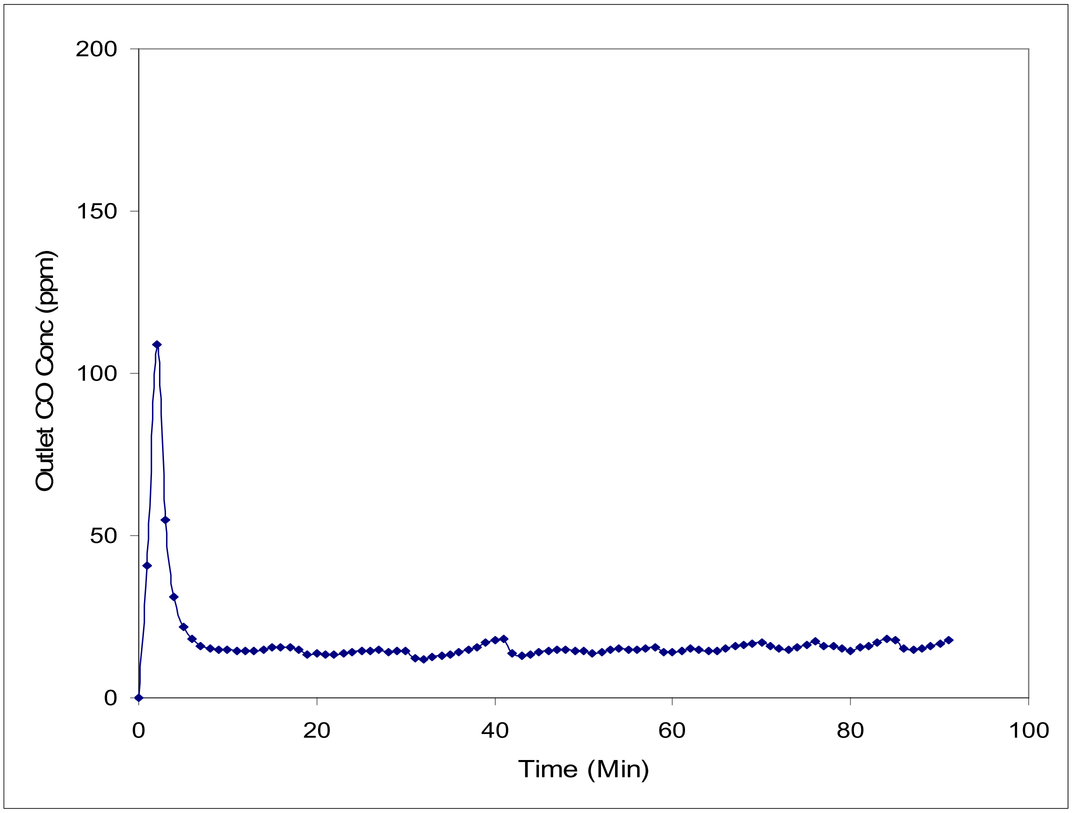

Figure 4: Catalyst Test for EN 403 (Face velocity = 5.88 cm/sec, Temperature = 22 ^{0}C, Inlet CO Conc = 5000 ppm)

Multiplicity in Low Temperature CO Oxidation

As seen in figure 5, the ignition temperature increases monotonically with inlet CO concentration. The graph of extinction temperature vs. CO fraction has a local maximum. The region with two stable states is bounded between the two graphs. Under the extinction branch, only one solution exists which means only one stationary state exists.

Similar results were observed by Harold and Luss [6] who performed oxidation of carbon monoxide on the surface of single pellet of Pt/Al_2O_3. Multiple steady states were observed for all CO concentration in the range of 0.6 – 8% and gas temperatures in the range of 20 -250 ^{0}C. The multiplicity was observed by measuring temperature of the center of pellet as a function of gas temperature and CO mole fraction. At most only two stable stationary states were found for any given set of operating conditions. It could be deduced from studying the bifurcation map that thermokinetic coupling and intraparticle transport limitations were affecting the system.

Numerous researchers attempted in different capacities to model the multiple steady states behavior of CO oxidation reaction.

Harold and Luss [6] attempted to fit the multiplicity behavior of CO oxidation using a bimolecular Langmuir-Hinshelwood rate expression, interparticle and intraparticle transport resistances, and an estimate for the intraparticle activity profile. The kinetic model was found adequate to describe the trends but could not predict quantitative behavior. Herz and Marin [7] attempted to fit the rate data of CO oxidation on platinum surface. The findings indicate that reaction models with no CO adsorption equilibrium assumption fit the rate data more correctly compared to Langmuir-Hinshelwood rate expression that assumes adsorption equilibrium. Harold and Garske [8] proposed various models that can fit experimental rate date at various conditions. It has been demonstrated that the common three step model consisting of reversible CO adsorption, dissociative oxygen adsorption and a Langmuir reaction step can predict qualitatively the reaction behavior under ultra high vacuum conditions. It could predict the shape of the multiplicity region in the catalyst temperature – CO pressure plane. A new method has been proposed in which parameter space has been divided into regions in which different shapes of temperature-CO pressure bifurcation maps would be observed. Five different models have been proposed. Zhdanov and Kasemo [9] proposed that effect of oxide formation on the surface of platinum should be taken into account to accurately describe the shape of bifurcation map in CO oxidation. According to authors, at ultra high vacuum and high CO pressure conditions it may be sufficient to use Langmuir-Hinshelwood model to predict bistability but it would be necessary to take into account oxide formation under oxygen rich environment at atmospheric pressure. Monte Carlo simulations performed could predict the shape of bifurcation map qualitatively under oxygen rich environment. These predictions were found to be in agreement with STM studies of CO oxidation on platinum.

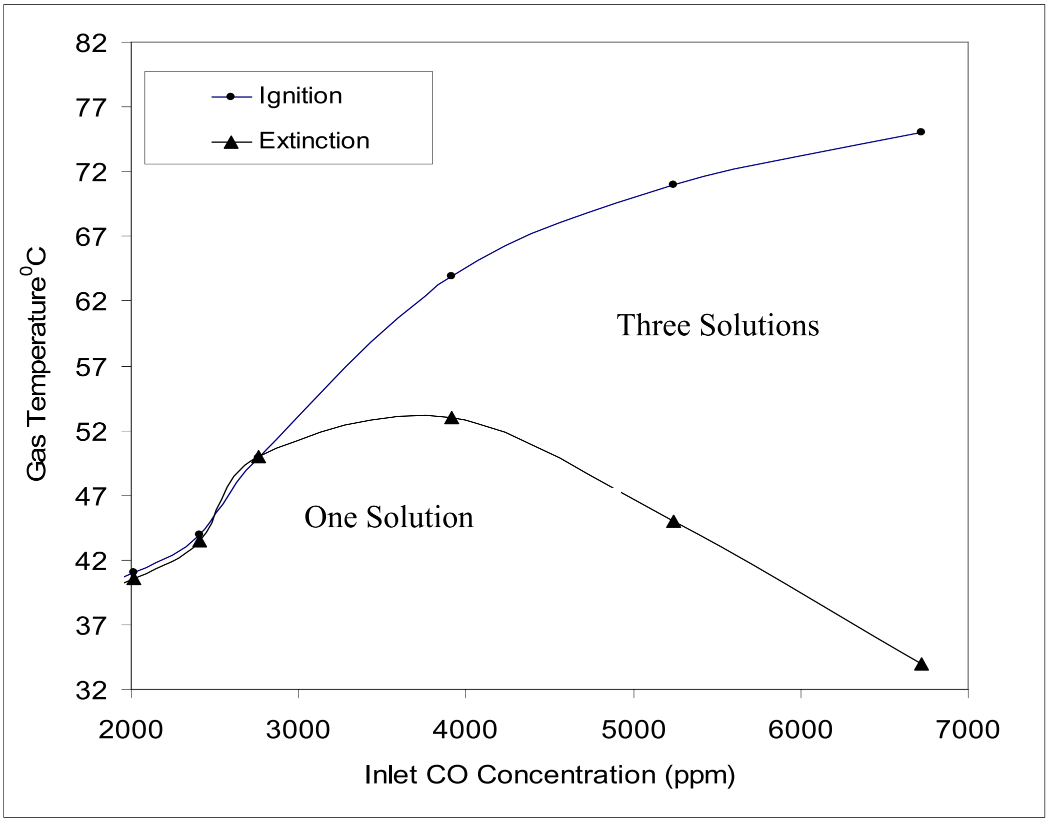

Figure 5: Cross Section of the Bifurcation Set in the Plane of Gas Temperature and CO Feed Volume Fraction (Inlet CO conc = 3600 ppm, Face velocity = 6.8 cm/sec, Relative humidity = 90%)

Hysteresis Effects

This section deals with observations and explanation of hysteresis phenomenon in low temperature CO oxidation reaction.

As seen in figure 6, the inlet CO concentration has been changed from 2500 to 11000 ppm. As inlet CO concentration increase from 2500 to 5500 ppm, the conversion remains constant 100 %. As the inlet concentration increases beyond 6000 ppm, the conversion falls down to 85% and keeps on decreasing with increasing CO concentration. When the CO concentration is decreased from 11000 ppm to 2500 ppm, the conversion-inlet CO concentration follows a different route. The conversion for concentrations between 2500 and 11000 is much lower compared to corresponding conversion on the increasing concentration plot. On the decreasing concentration arm of the graph, CO conversion keeps on decreasing even after decreasing inlet CO concentration down to 6000 ppm. As the concentration falls below 6000 ppm, conversion starts to increase, and attains a 100% level at 2500 ppm, thereby resuming its original position.

This particular phenomenon is a clear indication of occurrence of multiple steady states in low temperature CO oxidation for a promoted precious metal catalyst. Similar results have been observed by many researchers in the past for platinum as catalyst. R Jaree et al [10] report formation of hysteresis and extinction waves in catalytic CO oxidation caused by reactant concentration change. The reaction was studied in packed bed configuration of Pt/Al_2O_3. A model had been proposed to explain this phenomenon. Bykov et al [11] suggest that Langmuir-Hinshelwood mechanism can be used to predict multiplicity of steady states in CO oxidation. Abramova et al [12] take into account the surface non-uniformities of the catalyst to propose a model to explain low temperature CO oxidation at low CO concentrations. This work has been proposed as an extension of ZBG (Ziff, Gulari, Barshad) model. Haaland et al [13] relate the formation of hysteresis loops in CO oxidation to CO island formation. FTIR studies performed to observe the ratio of intensities of the absorption bands due to linear and bridge bonded CO. This ratio was found to be constant thereby suggesting CO island formation. The hysteresis phenomena in both CO reaction probability and CO surface coverage were found to be inversely related. This also suggests blocking of active sites by carbon monoxide on the Pt surface. Salanov et al [14] explained the nature of hysteresis in oxidation of carbon monoxide on platinum. With excess oxygen in the reaction mixture formation of surface oxide of platinum takes place thereby that in turn leads to changing surface properties of platinum and hence the nature of the Hysteresis loop.

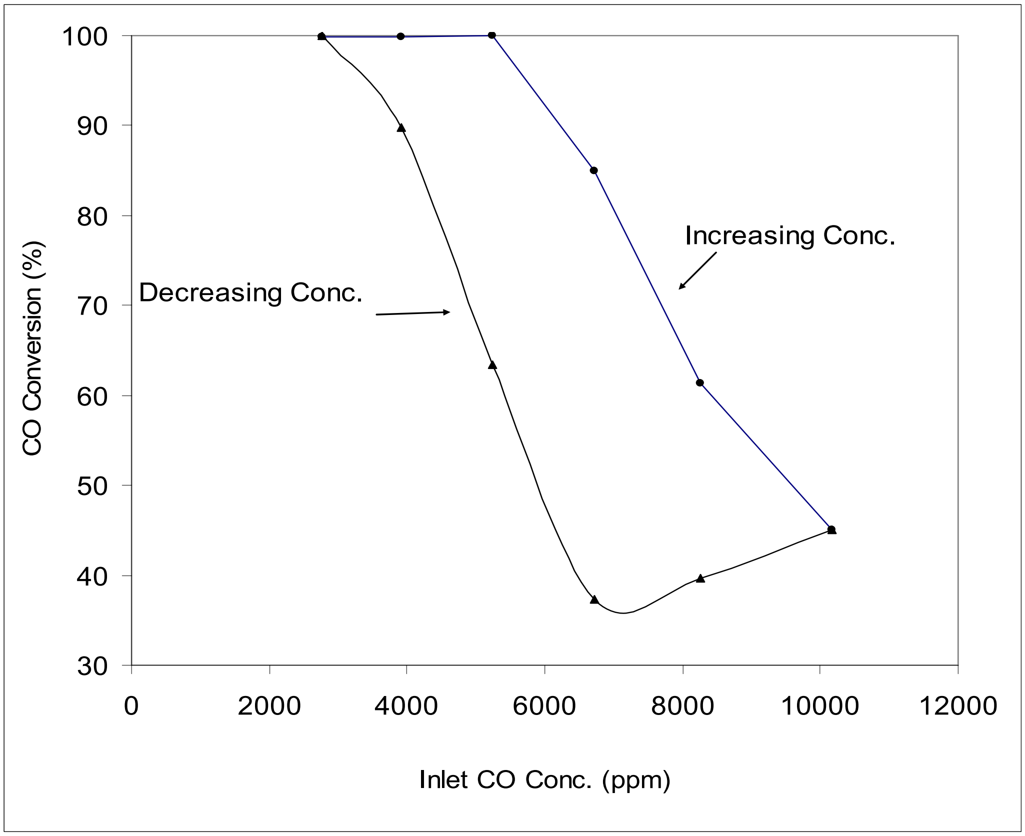

Figure 6: Hysteresis Phenomenon in Low Temperature Oxidation of Carbon Monoxide (Face Velocity = 12.5 cm/sec, Catalyst bed depth = 4 mm, Relative Humidity = 90%)

Steady State Temperature Hysteresis:

Figure 7 shows thermal hysteresis in CO oxidation. As seen from the figure, the steady state temperature rises as a function of inlet CO concentration up-to 6500 ppm value. As the concentration increased beyond 6500 ppm, the temperature starts dropping rapidly and keeps on reducing even if the concentration has been decreased to about 6500 ppm. When concentration has been decreased further to about 5000 ppm, the temperature starts rising and resumes its original value at 2500 ppm inlet concentration. Thus the reaction follows an altogether different path while the concentration decreases.

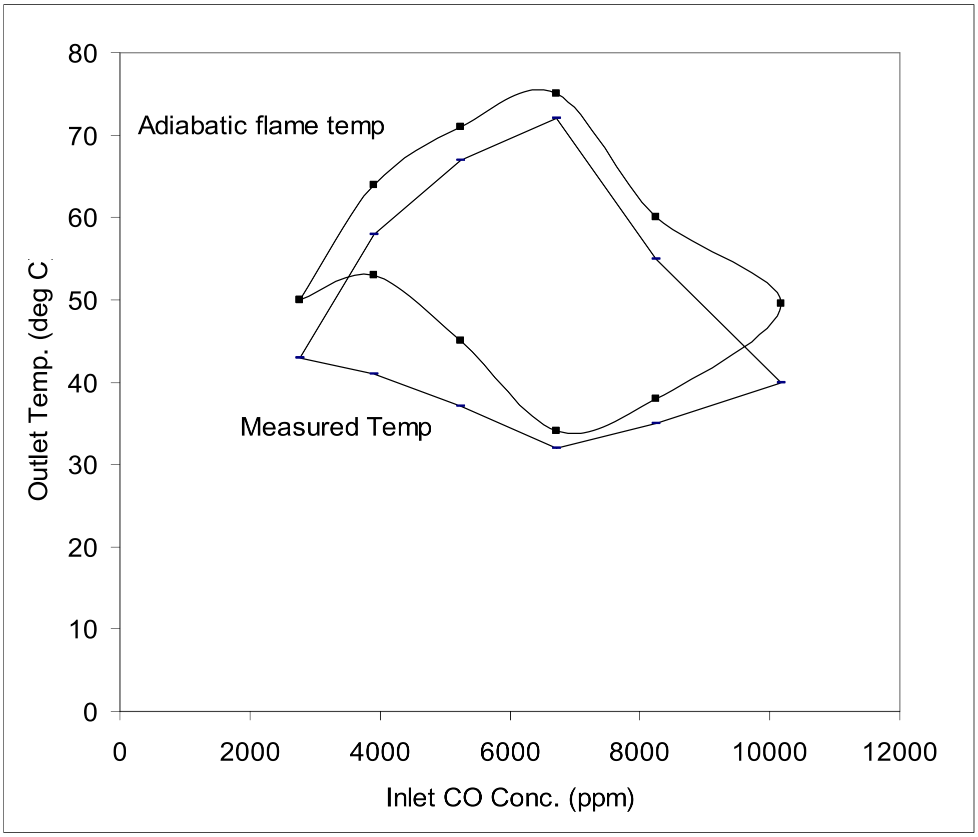

Fig 7: Steady State Temperature Hysteresis (Temperature = 22^{0}C, Face velocity = 12 cm/sec, Relative humidity = 90%)

Conclusion:

CO oxidation catalyst meets the EN 403 standards for a catalyst bed depth of 4 mm. Multiplicity of steady states and hysteresis in CO oxidation could be confirmed.

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