Low Temperature CO Oxidation Using High Contacting Efficiency Microfibrous Entrapped Catalyst: Qualitative Model

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Abstract: The present work deals with Low Temperature CO Oxidation for Fire Escape Mask development. Building and property fires often contain as high as 3600 ppm of carbon monoxide. The goal of this work is to develop a thin layer catalyst (1-5 mm) capable of reducing carbon monoxide from inlet concentrations of 3600 ppm to less than 400 ppm for at least 15 – 60 minutes while meeting other CBRN (chemical, biological, radiological and nuclear) standards recently proposed by NIOSH. The present work deals with developing a suitable microfibrous entrapped catalyst for CO oxidation.

Microfibrous materials are suitable for applications where high contacting efficiency is needed. These materials also have other advantages such as improved thermal management, low pressure drop, and mechanical & structural stability.

In this work, promoted Pt/SiO_2 (150 – 250 μ) has been entrapped into a nickel microfibrous mesh consisting of 4 and 8 μ nickel fibers. This paper discusses effects of temperature, GHSV, inlet CO concentration, and moisture content on the activity of microfibrous supported Pt/SiO_2.

Keywords: Fire Escape Mask; Microfibrous entrapped catalyst; Oxidation; deactivation

Introduction

The prime cause of death in fires is due to carbon monoxide inhalation. It is reported by the American Medical Association that CO is responsible for about 1000 deaths per year and over 10,000 physical injuries. Carbon monoxide can be lethal at concentrations of as little as 400 ppm. The conventional catalysts used for protection against CO inhalation are hopcalites (1). Hopcalites are mixtures of copper and manganese oxides. The issue with these catalysts is that they are sensitive to moisture and deactivate very fast in presence of moisture. Hence these are not suitable for fire escape mask. According to recently published testing guidelines by NIOSH, gases generated in fire can have up-to 95% relative humidity (2). Due to many other important applications along with mask development, of low temperature carbon monoxide oxidation process, it has received considerable attention over a period of time. A number of 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. Catalyst particles are entrapped into 4 and 8 μ sized nickel mesh by means of conventional wet-lay processing technique followed by sintering at high temperature. This mesh can be engineered to change the Voidage by changing fiber diameter, particle diameter, solid loading and fiber loading. Thus pressure drop can be adjusted to suit the application.

Experimental:

Experimental Set-up:

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 8 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 (3). 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.

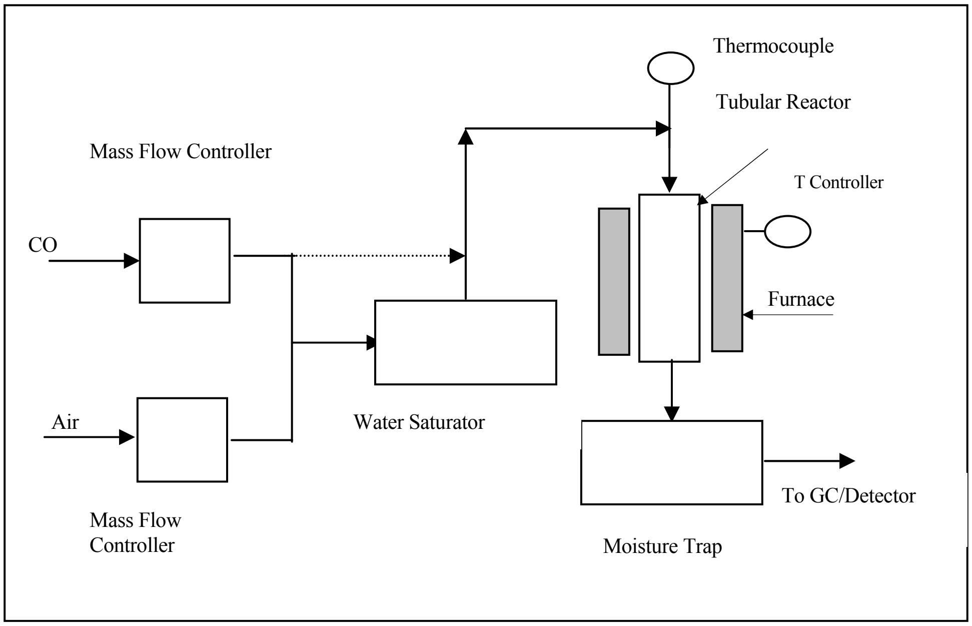

Figure 1: Schematic Diagram of CO Oxidation set-up

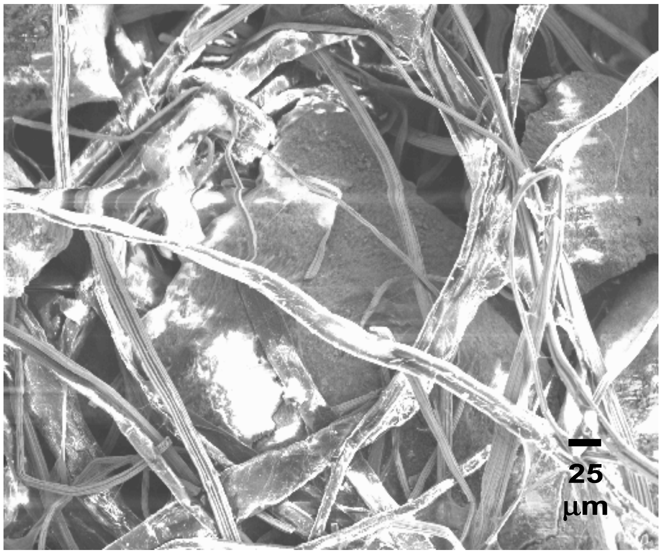

Figure 2: Microfibrous Entrapped Silica support

Results and Discussion

Catalyst Screening:

More than 50 catalysts were tested for suitability. Promoted Pt/SiO_2 was found to be the most active catalyst at room temperature. Figure 3 shows the comparison of activity between promoted and un-promoted Pt/SiO_2. As seen figure promoted catalyst is much more active than un-promoted at room temperature. Pt/SiO2 deactivates very rapidly whereas promoted catalyst shows good activity maintenance. Promoter as an independent catalyst shows very minimal activity.

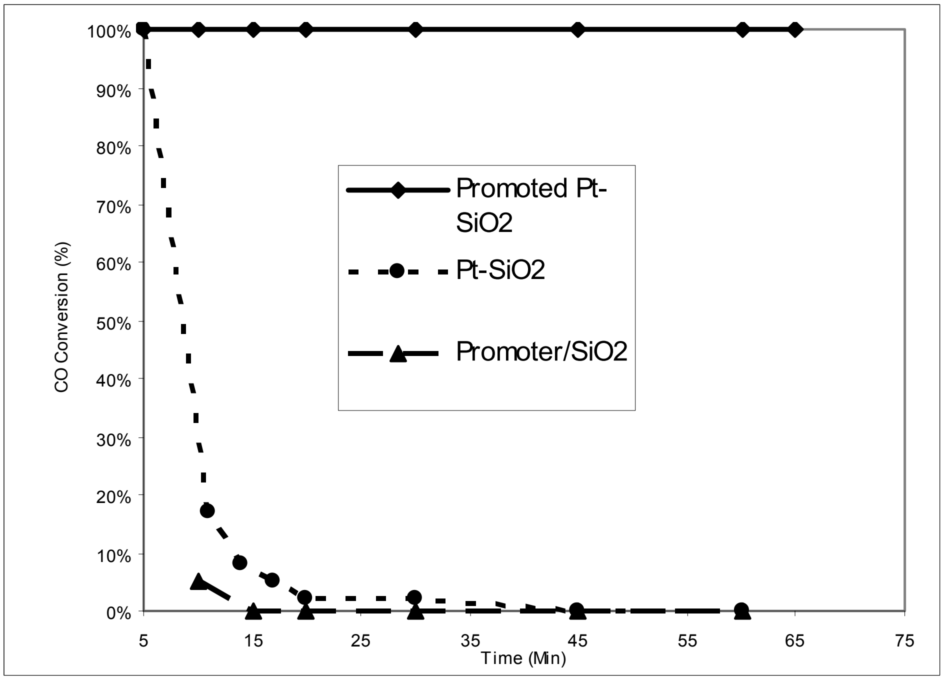

Fig 3: Comparison between promoted and un-promoted catalysts, Inlet CO Conc. = 3600 ppm, Face Velocity = 12 cm/sec

Effect of Moisture Content:

Moisture has been observed to be benign for CO oxidation on promoted Pt/SiO_2 catalyst. Figure 4 shows the comparison between dry and moist CO oxidation conditions. The conversion for feed containing 90% relative humidity is close to 100%. The dry feed deactivated the catalyst at about 17 minutes and deactivation progresses very rapidly.

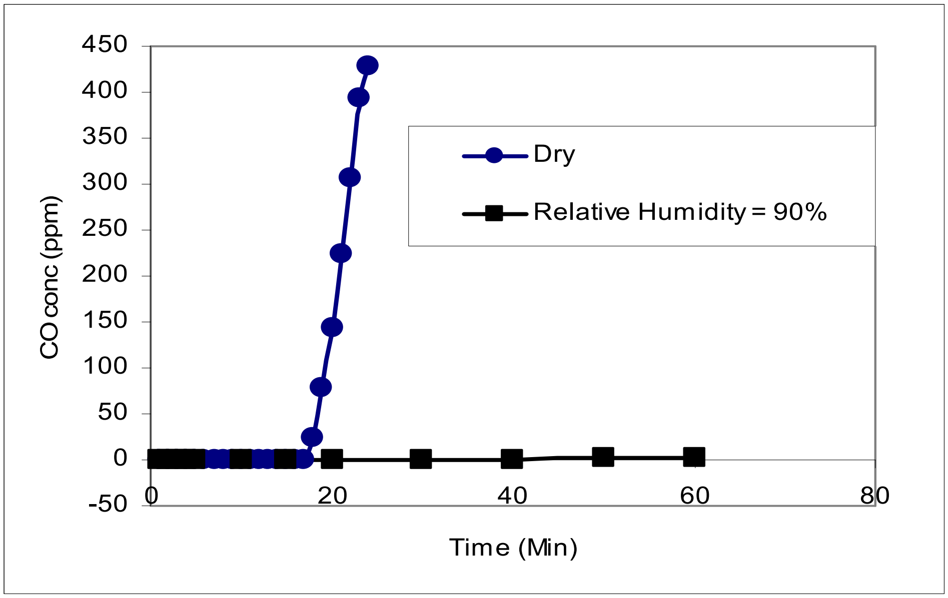

Fig 4: Effect of Moisture on Catalyst Performance, Inlet CO Conc. = 3600 ppm, Face Velocity = 12 cm/sec

Deactivation under dry conditions can be reversed by introducing moisture into the feed. Figure 5 shows the catalyst activity as a function of time in presence of moisture where the feed was switched to dry intermittently to observe the effect. As soon as the feed was switched to dry, the outlet CO concentration starts increasing. At around 350 ppm, outlet concentration, when the feed was switched back to moisture containing gas, the catalyst regains all the activity. The same effect was observed repeatedly.

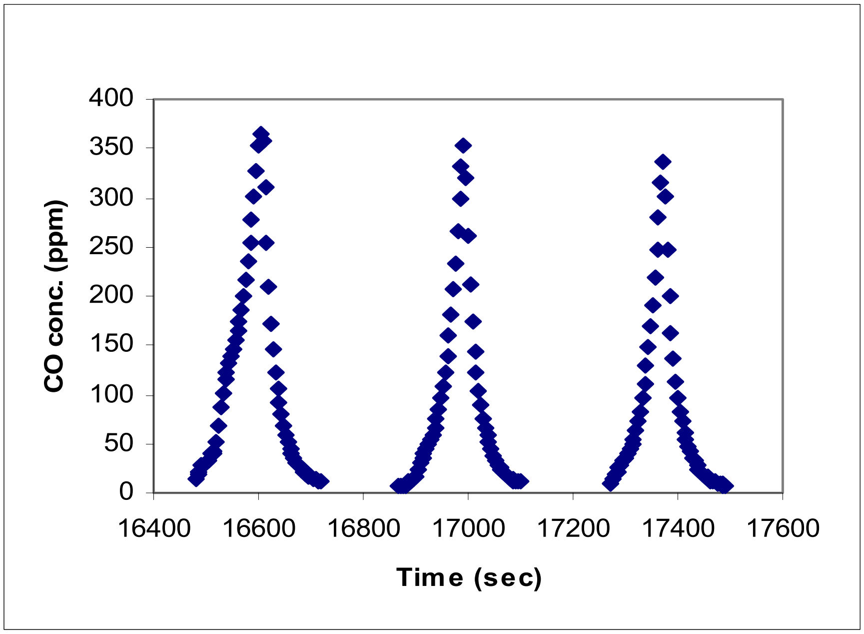

Figure 5: Reversible nature of catalyst deactivation due to moisture. Inlet CO conc. = 2500 ppm, Face Velocity = 8 cm/sec

Effect of Moisture on Un-promoted catalyst:

Figure 6 shows the comparison between CO conversion for dry and moisture containing feeds. As seen in figure, Pt/SiO_2 deactivated more rapidly when moisture is present in the feed.

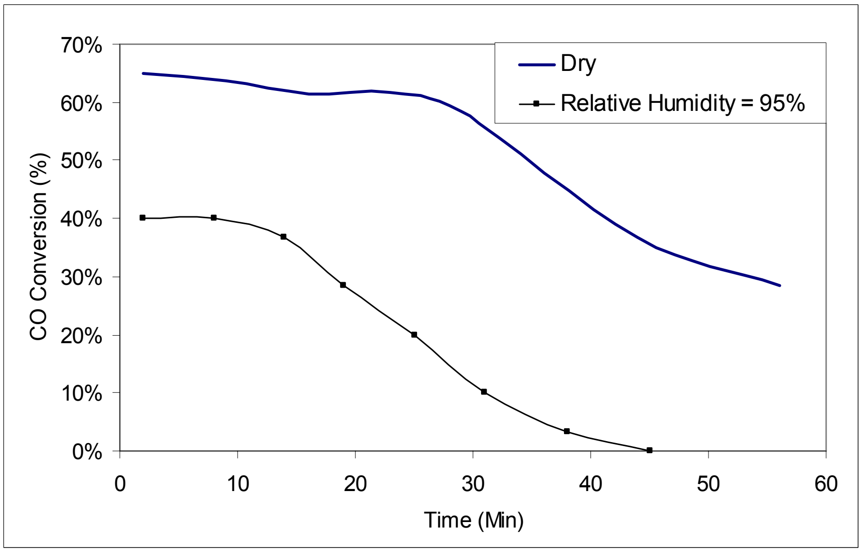

Figure 6: Moisture effect on un-promoted Pt/SiO_2 Inlet CO Conc. = 2500 ppm, Face Velocity = 8 cm/sec

Qualitative Model:

Following observation were made during the course of this study:

1. Promoted catalyst is order of magnitude more active than un-promoted catalyst.

2. Moisture enhances the activity of the promoted Pt/SiO_2 catalyst.
3. Moisture affects the activity of un-promoted catalyst negatively
4. The overall temperature rise when the reactor is operated in adiabatic mode is about 7-8 ^{0}C for both promoted and un-promoted catalyst.

Following are the observation well published in contemporary research literature:

1. Oxygen and carbon monoxide compete for the same sites on Pt surface (4).
2. Carbon monoxide adsorbs on pt surface leading to deactivation of catalyst.
3. CO prefers to form islands on the surface of Pt thereby poisoning an entire part of the surface of the catalyst due to dipole-dipole interaction between two adsorbed CO molecules (5).
4. Carbon monoxide oxidation reaction on noble metal follows Langmuir-Hinshelwood model for kinetics (6).

Based on our observation and published literature, following model has been proposed. Figure 7 shows the surface of the catalyst.

Model assumptions:

1. Manganese exists in the oxide form
2. There are two different types of sites, i. Pt sites, ii. MnO_x sites

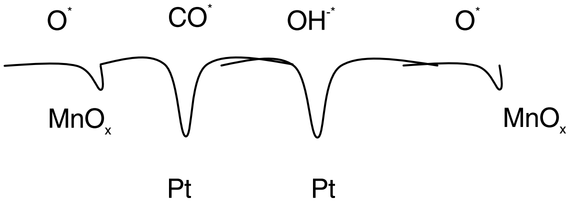

Figure 7: Surface of promoted Pt/SiO_2 catalyst

CO adsorbs onto Pt sites. Oxygen gets adsorbed selectively onto MnO_x sites. Adsorbed oxygen and carbon monoxide react to form carbon dioxide. Water is adsorbed in the hydroxyl group form. Adsorbed water on Pt sites, prevents the formation of CO islands. Since oxygen is supplied by manganese sites, there is no competitive adsorption between carbon monoxide and oxygen. Due to these two reasons, the deactivation in presence of moisture is very slow compared to dry conditions or un-promoted catalyst.

Conclusion:

1. Promoted Pt/SiO_2 has more activity compared to Pt/SiO_2
2. Promoted Pt/SiO_2 has more activity in presence of moisture.
3. CBRN standards of 3600 ppm carbon monoxide to be removed down to 400 ppm for fire escape mask can be met with this microfibrous entrapped catalyst.

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