EFFECT OF CALCINATION STRATEGIES ON ACTIVITY OF Co-Mn CATALYSTS FOR SIMULTANEOUS CONTROL OF CO AND CH$_4$ EMISSIONS FROM CNG FUELLED VEHICLES

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ABSTRACT

 CNG fuelled vehicles are alternative for conventional engines. But these are emitting significant amount of CO and CH$_4$. Therefore, to reduce the emissions, this work aims to develop low cost non-noble metal catalysts for simultaneous oxidation of lean mixture of CO-CH$_4$. Cobalt-Manganese (molar ratio=5:1) catalyst was prepared by co-precipitation followed by calcination under three different strategies. The first strategy was reactive calcination (RC) involving feed of a low concentration of chemically reactive, 4.5% CO-air mixture over the catalyst at low temperature of 160°C in the beginning and gradually increased to 400°C. Under second strategy, the catalyst was also calcined in-situ in flowing air and finally calcined in an electric furnace around 400°C for 4 h under the third strategy. The resulting catalysts were named as Cat-1, Cat-2 and Cat-3 respectively. The catalytic performance was evaluated in a tubular flow reactor under following conditions: Wt. of catalyst=500mg, flow rates of CO and CH$_4$ =1.5 ml/min each and air flow rate=97 ml/min. The Cat-1 showed total oxidation of lean mixture of CO-CH$_4$ at much lower temperature (340°C) in comparison to Cat-2 (380°C) and Cat-3 (400°C) and activity order of the catalysts for CO-CH$_4$ oxidation was as follows: Cat-1 > Cat-2 > Cat-3.

Keywords: Co-Mn catalysts, Reactive calcination, CO-CH$_4$emissions, CNG Vehicle, Pollution control

I INTRODUCTION

Compressed natural gas (CNG) vehicles are considered to be one of the most promising alternatives of conventional vehicles due to soar in petroleum prices and increasing strict emissions limit (Li et al, 2009). CNG fuel contains 92.6% methane (CH$_4$), 5.8% ethane (C$_2$H$_6$), 1.2% CO$_2$ and rest other gases (Cho and He, 2009). Therefore, CNG vehicles have much lower emissions of toxic higher hydrocarbon (HC), nitrogen oxides (NOx) and particulate matter (PM) compared to conventional gasoline and diesel engines (Tang et al, 2009). Unfortunately, the emissions from CNG vehicles have high concentration of CH$_4$ and low concentration of carbon-monoxide (CO). CH$_4$ is a powerful greenhouse gas (GHG), which has approximately 20 times the warming potential of CO$_2$ (Cho and He,

2009). CO and CH_4 being harmful gases also have adverse impact on human health and climate change. A number of methods are employed to control CO-CH_4 emissions, although amongst them, catalytic oxidation using three way catalytic (TWC) converters are recognized as one of the most efficient technique. The important role of automotive catalyst consisting of noble metals (Pt, Pd) are used to completely oxidize these pollutants to non-toxic atmospheric gases like CO_2 and H_2O vapor according to the following chemical reactions:

$$CO + \ 0.5O_2 \longrightarrow CO_2 \qquad\qquad (i)$$

$$CH_4 + 2O_2 \ \longrightarrow CO_2 + 2H_2O \qquad (ii)$$
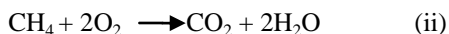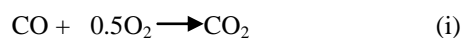
The problem of TWC is that it shows very less activity during cold start condition and the self-poisoning of Pt by CO at low temperatures. Further, the high cost and scarcity of noble metals have long been motivated the search for low cost, highly active and sturdy substitute to control CO and CH_4 emissions (Liu & Stephanopoulos, 1995). Therefore, a variety of transition metals based non -noble metal catalyst such as Mn, Cu, Cr, Fe, Co become appealing due to lower cost and relative plentiful resources (Li et al, 2009). Among all the transition metal oxides, Co_3O_4 is believed to be a good CO-CH_4 combustion candidate (Xianglan et al, 2014). TANG et al. (2009) studied the combustion of CH_4 over Co_3O_4-SnO_2 catalyst and found that Co_3O_4 was the active species, SnO_2 acted as a support or a promoting component in the Co_3O_4-SnO_2 hybrid oxides. Trigueiro et al. (2006) have studied the effect of niobium addition to $Co/\Upsilon Al_2O_3$ and found that both cobalt-containing catalysts (4.5 and 9.3%, by weight, of Co) show a higher catalytic activity when compared to cobalt-containing niobia-alumina catalyst (6.3%, by weight, of Co). On the other hand, platinum and manganese oxide catalysts (Barresi et al, 1992) have been applied in methane combustion. High activity of methane oxidation has also been observed on Mn-doped ZrO_2 by Choudhary et al. (2002). Li et al. (2003) have studied the catalytic combustion of methane activities of Co-Mn mixed oxide catalysts prepared by sol–gel methods. Although the promoting effects of water vapour were discovered on the Co-Mn mixed oxide catalysts, no promoting effects of manganese to the catalytic activity were found.

In the present work, Co/Mn (molar ratio=5:1) mixed catalyst was prepared by co-precipitation method. Both Co and Mn cations can attain variable oxidation states and may be the effective components in mixed-oxide-based catalysts suitable for combustion reactions. The decomposition of catalyst was carried out into three different ways: i) Reactive calcination, ii) Flowing air and iii) Conventionally stagnant air. The effect of different calcination method has been demonstrated. Reactive calcination of the catalyst was performed by reactive gas CO-Air mixture.

II EXPERIMENTAL

2.1. Catalyst preparation

The Co/Mn mixed catalysts (molar ratio=5:1) were prepared following the method described by Li and co-workers, [2009].Co-precipitation of basic carbonates of Co and Mn was carried out by adding drop-wise ammonium bicarbonate solution into the aqueous solution of cobalt nitrate and manganese acetate. The precipitates were aged with stirring at room temperature for 8 h. They were filtered and washed thoroughly with distilled water free of

anions and also with deionized water and with 80 mL ethanol until the pH reached 7.0 followed by drying at room temperature for overnight then at 90°C for 6 h in an electric oven. The calcination of the catalyst precursor was performed under three different strategies at 400 ^{o}C. Firstly, the catalyst was calcined in a specific chemically reactive, 4.5% CO-air mixture termed as reactive calcination (RC) method as described below. The catalyst thus obtained was named as Cat-1. Secondly, it was calcining in flowing air resulting Cat-2. Third strategy was conventional method; calcination was carried out in a stagnant air, producing Cat-3.

2.2. Reactive calcination

The reactive calcination of catalyst was carried out *in situ* in a compact bench scale fixed bed, down flow tubular reactor, details of the reactor is given elsewhere (Prasad and Rattan 2009). A defined amount of the catalyst precursor (equivalent to 500 mg of the calcined Co-Mn catalyst) diluted with α-alumina (S_{BET} = 3.03 m^2 g^{-1}, pore volume = 0.01 cc g^{-1}) to make a total volume of 2 ml at atmospheric pressure was taken. The reactor was placed vertically in a microprocessor temperature controlled split open furnace. The heating rate of the bed was 1 $^{\circ}$C min^{-1} with a temperature control of ±0.2 $^{\circ}$C. Reactive calcination of the precursors was carried out by the introduction of a low concentration of chemically reactive CO–air mixture (4.5% CO) at a total flow rate of 60 ml min^{-1} over the hot precursors. Digital gas flow meters were used to measure the flow rates of CO and air to feed the mixture (dried and CO_2 free) in the required proportion into the reactor. The temperature was monitored with the help of a K-type thermocouple inserted in the thermo-well of the reactor in contact with the precursor bed. The temperature of the bed was increased from room temperature to 160 $^{\circ}$C where CO oxidation started and completed within few minutes with 2°C rise in temperature. After achieving total CO conversion the temperature of the resultant catalyst bed was increased to 400 ^{o}C and maintained for two hour under the same CO-air flowing conditions. For the comparative studies two catalysts were also prepared by usual calcination of the precursor in stagnant air as well as in flowing air at 400°C for 4h.

2.3 Catalytic activity measurement

The activity of the catalysts was measured for simultaneous oxidation of CO and CH_4 in the same reactor as used for reactive calcination of the catalyst. After RC the catalyst bed was cooled to room temperature in the same environment and oxidation of lean mixture of 1.5 % CO and 1.5% CH_4 in air was carried under the following reaction conditions: Catalyst weight 500 mg, and total gas flow rate of 100 ml/min. The reaction temperature ranged from ambient to the value when 100% CH_4 conversion was attainted. Air fed was made free of moisture and CO_2 by passing it through CaO and KOH pellets drying towers. The flow rates of CO, CH_4 and air were monitored with the help of digital gas flow meters. The catalytic experiments were carried out under dynamic conditions of heating at a rate of 1°C/min. The rate of heating was controlled with the help of a micro-processor based temperature controller. The simultaneous oxidations of CO and CH_4 over the catalyst can be represented by equation (iii).

$$CO + CH_4 + 2O_2 \text{ (air)} \rightarrow 2CO_2 + 2H_2O \qquad\qquad \text{(iii)}$$
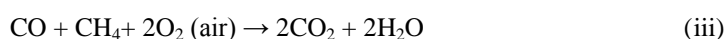
The gaseous reactants and products were analyzed by an on-line gas chromatograph (Nucon series 5765) equipped with porapack q-column, methanizer and FID detector for the concentration of CH_4 components, CO and CO_2. The catalytic activity for the simultaneous oxidation was expressed in term of the conversion of limiting reactants such as; CO, CH_4 and overall CO-CH_4. The fractional conversion of CO at any instant was calculated on the basis of values of the concentration of CO in the feed and product stream by the following equation 1:

$$(X_{CO})_i = [(C_{CO})_{in} - (C_{CO})_{out}] / [C_{CO}]_{in} = [(A_{CO})_{in} - (A_{CO})_{out}] / [A_{CO}]_{in} \qquad (1)$$

Where, concentration of CO is proportional to the area of chromatogram of CO. Similarly, the fractional conversion of CH_4 was calculated using the following equation 2:

$$(X_{CH4})_i = [(A_{CH4})_{in} - (A_{CH4})_{out}]_i / [(A_{CH4})_{in}] \qquad (2)$$

The change in the overall concentration of CO-CH_4 due to simultaneous oxidation at any instant is proportional to the area of chromatogram of CO_2 formed $(A_{CO2})_i$, and overall concentration of CO-CH_4 in the inlet stream is proportional to the area of CO_2 chromatogram $(A_{CO2})_f$ resulting at 100% conversion of CO-CH_4 together, i.e. single peak of CO_2 in GC chromatogram. Thus the overall conversion of CO and CH_4 was calculated as per following equation 4:

$$(X_o)i = [(A_{CO2})_i]/(A_{CO2})_f \qquad (3)$$

III RESULT AND DISCUSSION

The GC chromatogram of a typical reactor inlet and outlet of the simultaneous oxidation of lean mixture of CO-CH_4 experiment is shown in figure 1. Only two chromatogram peaks corresponding to CO and CH_4 were recorded for inlet (Fig 1a) whereas at initiation of oxidation additional small peak of CO_2 appeared in the outlet stream of the reactor (Fig 1b).
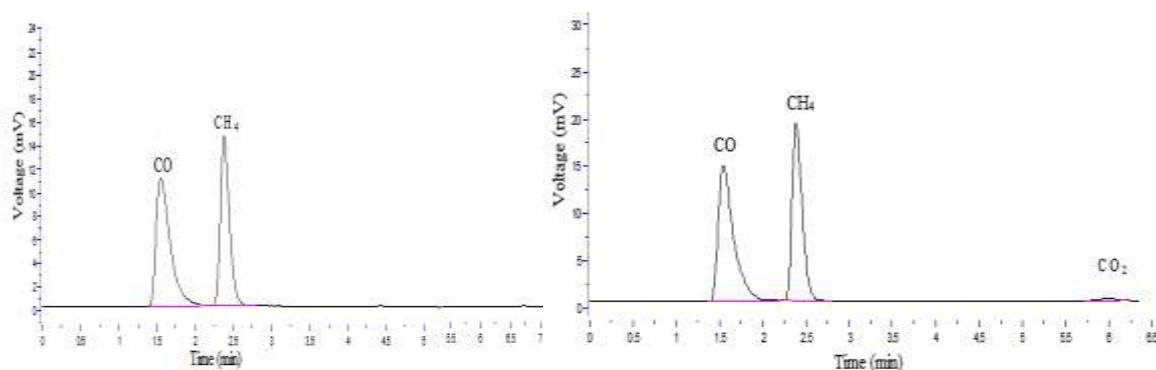

Fig. 1: GC Chromatogram of (a) reactor inlet (b) reactor outlet at initiation of oxidation

The total CO conversion occurred at lower temperature of 150^oC than CH_4 which partially oxidized as shown in fig 2a depicting two peaks of unconverted CH_4 and CO_2. Fig 2b demonstrates complete oxidation of CO and CH_4 to CO_2 illustrating a single peak of CO_2 in the chromatogram.
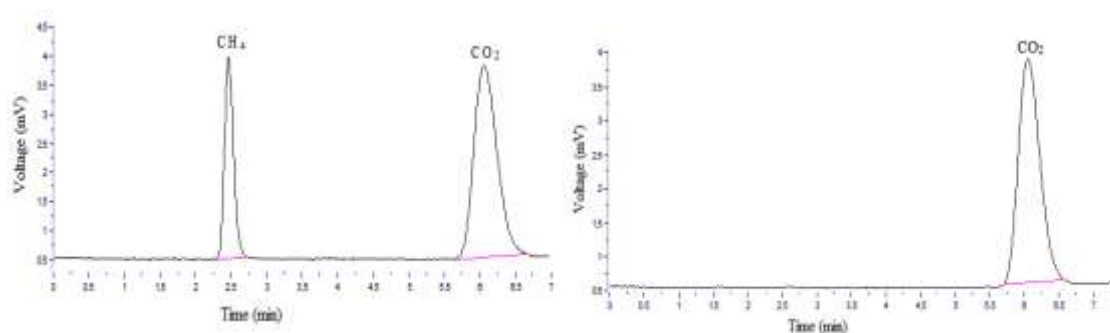
Fig. 2: GC chromatograms of reactor outlet complete oxidation of (c) CO, (d) CO-CH$_4$ to CO$_2$

3.1 Effect of Calcination Temperature

The activity tests of the catalysts were conducted in which CO and CH$_4$ reacted simultaneously with O$_2$. These tests were conducted to evaluate the catalytic activities of Co-Mn catalyst under different calcination conditions as shown in Fig. 3 (a, b). It is very clear from the Fig 3 that all the three catalysts showed conversion of CO-CH$_4$ to CO$_2$ and water at different temperatures depending on their activities upto 400 ^{o}C. From the Figs. it can be seen that CO-CH$_4$ conversion over the prepared catalysts continuously increasing with temperature and then rose to total conversion. Fig. 3 a shows comparison of catalytic conversion efficiencies of Co-Mn mixed oxide catalyst obtained by calcination of the catalyst under various strategies for CO oxidation in simultaneous test. Complete conversion of CO to CO$_2$ took place at 220 ^{o}C and 190 ^{o}C over Cat-2 and Cat-3 respectively while it was at the lowest temperature of 150 ^{o}C over Cat-1.Similarly, from Fig.3 b the temperature of total oxidation of CH$_4$ over Cat-1 was 340°C. While overall conversion of both CO and CH$_4$ were observed at higher temperatures over Cat-2 and Cat-3 as compared to Cat-1 as shown in Fig 3 as well as in table 1. Thus, the Cat-1 showed the highest activity for oxidation of CO as well as CH$_4$.
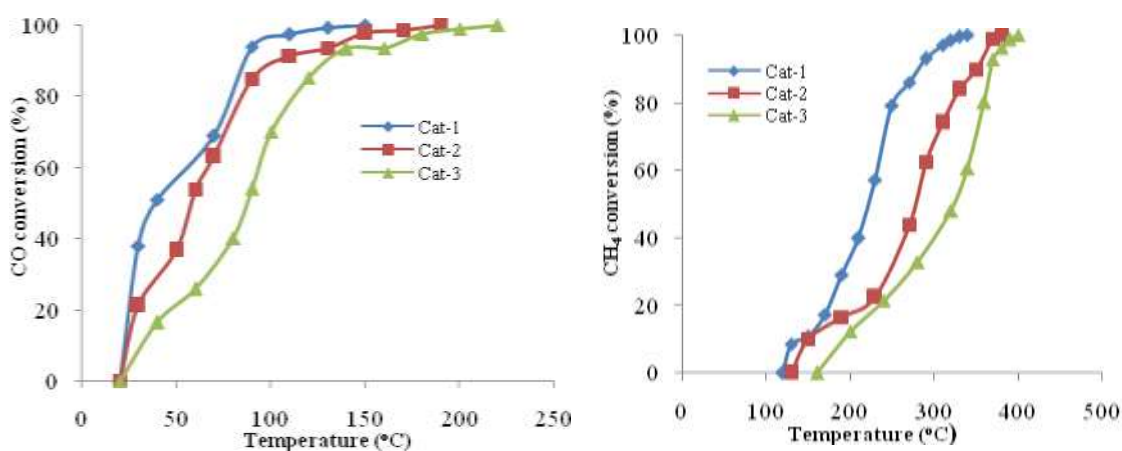

Fig. 3: Conversion of (a) CO Vs temperature (b) CH$_4$ Vs temperature over Cat-1, Cat-2 & Cat-3

Table. 1: Light off characteristics of catalyst for simultaneous oxidation of CO and CH$_4$

Components	Cat-1			Cat-2			Cat-3		
	T_i	T_{50}	T_{100}	T_i	T_{50}	T_{100}	T_i	T_{50}	T_{100}
CO	30	40	150	30	60	190	40	90	220
CH$_4$	130	230	340	150	280	380	180	320	400

IV CONCLUSION

It can be concluded that Co/Mn is an excellent catalyst for simultaneous oxidation of lean mixture of CO-CH$_4$ at low temperature. The method of calcination of the catalyst has great influence on the activity of the resulting catalysts. The relative improvement in the performance of the catalyst for simultaneous oxidation of lean mixture of CO-CH$_4$ is achieved by method of calcination of the catalyst precursor in the following sequence of decreasing order: Reactive calcination > flowing air > stagnant air. Further, the catalytic activity order in the decreasing sequence is as follows: Cat-1>Cat-2>Cat-3. The extraordinary performance in CO-CH$_4$ oxidation of the catalyst is achieved at much lower temperature. Therefore, RC is the best calcination method in comparison to conventional methods for production of Co/Mn mixed for simultaneous complete oxidation of CO-CH$_4$ at low temperature.

V ACKNOWLEDGEMENT

NOMENCLATURE

T_i	Initial combustion temperature
T_{50}	Light off temperature
T_{100}	Complete combustion temperature
X_{CO}	Carbon monoxide conversion
X_{CH4}	Methane conversion

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