Total oxidation of CO by CuMnOx catalyst at a low temperature

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Abstract— The copper manganese oxides catalyst was synthesized by using co-precipitation method with different Cu:Mn ratio for carbon monoxide oxidation. The drying of the precursor at 120^oC temperatures for 12 h in an oven and calcinations at 300^oC in stagnant air, flowing air and in a reactive gas mixture of 4.5% CO in the air known as reactive calcination (RC). The CuMnOx catalyst is prepared into different molar ratio like (Cu:Mn=2:1), (Cu:Mn=1:1) and (Cu:Mn=1:2) for oxidation of CO. The activity of the catalysts was evaluated in a tubular reactor under the following conditions: 100 mg catalyst, 2.5% CO in air, total flow rate 60 mL/min and temperature varying from ambient to a higher value, at which complete oxidation of CO was achieved. The decomposition of mixed copper and manganese nitrate in controlled conditions therefore produced CuMnOx catalyst and it depending on the oxygen concentration and flow conditions of gases during the heat treatment. The prepared catalysts were characterized by XRD, FTIR, SEM-EDX, XPS and BET techniques. The ability to oxidation state and phase composition of CuMnOx catalysts is a key preparation parameter for controlling the CO oxidation.

Index Terms— Carbon monoxide, Catalytic oxidation, Ambient temperature, Hopcalite catalysts, Co-precipitation, Reactive Calcination.

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1 INTRODUCTION

Air pollution has become a major concern in most of the countries in the world. It is responsible for causing respiratory diseases, cancers and serious other illness. In addition of the health effects, air pollution also contributes to high economic losses. The transportation sector i.e. the vehicles (particularly cars, trucks and buses) which run by petrol and diesel are one of the greatest contributors to air pollution. It was expected that motor vehicles emissions contribute to the global emissions, an amount of 21% for carbon dioxide (CO_2), 37% for nitrogen oxides (NOx), 19% for volatile organic compounds, 18% for carbon monoxide (CO) and 14% for black carbon (1).

Carbon monoxide with the chemical formula of CO is a colorless, odorless and tasteless, it is highly toxic and it emitted from vehicle exhaust. It is produced from the partial oxidation of carbon-containing materials. It converted in to the more usual carbon dioxide (CO_2) when there is a reduced availability of oxygen, such as when operating an internal combustion engine in an enclosed space Carbon monoxide (CO) and carbon dioxide (CO_2) from diesel engines are relatively low. The CO emissions are more significant in the spark ignition engines as the fuel/air ratio is often close to stoichiometric at a part of the load and more at full load (2).

A catalytic converter is an automobile emissions control device that converts toxic pollutants in the exhaust gas into less poisonous gas by catalyzing a redox reaction (oxidation or reduction). Catalytic converters are used in internal ignition engines fueled by either gasoline or diesel-including lean burn engines. For the catalyst design, it is essential to explain the catalyst performance parameters into a physical picture of the catalyst structure (3). In the beginning more interest has been focused on catalytic control of CO emissions from automobile exhaust because it is dangerous for the environment. On start-up car exhaust catalysts take a little time to become effective and this primarily due to the time required to heat the catalyst

using the exothermicity of the combustion reactions. If the catalyst could be added that was very efficient for CO oxidations at lower temperatures then this initial warm-up period could be shortened and the cold start problem can be solved (4). In the last 35 years, the catalytic converters have been installed on more than 1000 million vehicles around the world. The choice of the appropriate catalyst is an important step for improving the environment.

The most effective catalysts for CO oxidation at low a temperature in many years are known as hopcalite catalyst (CuMnOx), which is a mixture of copper manganese oxide (5). The catalytic properties of such a system called hopcalite were confirmed by Jones and Taylor in the year 1923; since that time hopcalite has become a well-known oxidation catalyst at room temperature. A literature study reveals that CuMnOx catalyst is extremely active in the amorphous state even at room temperature but it has observed that the CuMnOx catalyst lose his activity after exposition at temperatures above 773K where crystallization of the spinel $CuMn_2O_4$. However, crystalline Cu_2MnO_4 has also been reported by Schwab and Kanungo (6) to be active.

Recently, the low temperature oxidation of carbon monoxide has seen a renaissance in its interest to the catalytic community. Ever since that time, hopcalite catalysts have been employed to oxidize a range of environmentally damaging gasses at low temperatures. A lot of attention has been given to modification of the CuMnOx catalyst in order to remove its faults of moisture for deactivation and low activity. The preparation of the catalyst by other non-conventional methods including synthesis of nano-crystalline copper manganese oxide catalysts by using the supercritical anti-solvent precipitation method (7), copper manganese oxide from sol-gel (8) were reported to give better conversion than commercial hopcalite.

2 EXPERIMENTAL

2.1 Catalyst preparation

The hopcalite catalysts were prepared by co-precipitation method in the molar ratio (Cu:Mn=1:2). Aqueous solutions of 0.25M, $Cu(NO_3)_2.3H_2O$ and 0.50 M, $Mn(NO_3)_2.6H_2O$ were mixed. The co-precipitation was carried out by drop-wise addition of an aqueous solution of Na_2CO_3 (0.25M) in to the above-mixed solution with constant stirring over a magnetic stirrer maintained at pH 8.3. The molar ratio of Cu:Mn in the CuMnOx catalyst is 1:2. The precipitate was recovered by filtration, washing and dried in an electric oven at 120°C for 12hr. The dried precipitate was calcined at 300°C for two hours. After calcinations, we have to get 5.37 gm of CuMnOx catalyst. The same CuMnOx catalyst is also prepared into different molar ratio like (Cu:Mn=1:1) and (Cu:Mn=2:1) for CO oxidation.

2.2 Characterization

2.2.1 X-ray diffraction (XRD)

X-ray diffraction analysis gives information about the phases present in the catalyst and their crystallite size. The X-ray pattern of the catalyst is obtained by using Cu Kα radiation (40 kV, 100 mA) with a Rigaku D/MAX-2400 diffractometer in the range of 2-theta 10° to 80°. The mean crystallite size (d) of the phase of the catalyst is calculated from line enlargement of the most intense reflection.

2.2.2 Fourier transforms infrared spectroscopy (FTIR)

The Fourier transforms infrared spectroscopy (FTIR) analsis provides quantitative and qualitative information for organic and inorganic samples. It identifies the chemical bonds present in a molecule by producing an infrared absorption spectrum. The FTIR analysis was done by Shimadzu 8400 FTIR spectrometer within the range of 400-4000 cm^{-1}.

2.2.3 X-ray photoelectron spectroscopy (XPS) analysis

The XPS is used for determining the binding energy of the elements present in the catalysts. The XPS analysis was done by Amicus spectrometer equipped with A1K$_a$ X-ray radiation. For reference purpose adventitious carbon was used which have a binding energy of 284.6 eV.

2.2.4 N$_2$ adsorption-desorption Isotherm

The N_2 sorption isotherm is used for determining the specific surface area, pore volume and pore size distribution of the catalyst. The area of the hysteresis loop of the adsorption-desorption isotherm provides information about the nature of the pores present in the catalyst. The adsorption-desorption isotherm was recorded by Micromeritics ASAP 2020 analyzer.

2.2.5 Scanning electron microscope (SEM) analysis

Scanning electron microscope (SEM) is a high-resolution electron microscope that produces the image of the sample by scanning it with the help of electron beam. The SEM-EDX was recorded on Zeiss EVO 18 Scanning electron microscope. The EDX is energy dispersive X-ray analyzer it provides information about elemental identification and quantitative composition analysis of the compound present in the catalyst.

2.3 Different calcination conditions

Catalyst precursor was calcined under following three different conditions:

I) Stagnant air calcinations: - In the absence of air calcination at 300°C for 2h in the furnace and catalyst was stored in an air tight glass bottle.

II) Flowing air calcinations: - In the presence of flowing air in the reactor at 300°C for 2h then the catalyst was stored in an air tight glass bottle.

III) Reactive calcination: The calcination of the precursor was performed in situ under a flowing reactive mixture of 4.5% CO-Air at 300°C for 2 hours, just before the activity measurement experiment.

2.4 Performance of the Catalyst for CO oxidation

The catalytic oxidation of CO has performed under the following reaction conditions: 100 mg of the catalyst with feed consisting of a lean mixture of 2.5 vol.% CO in air maintained at a flow rate of 60 mL/min, using a fixed bed tabular flow reactor. The air feed was made free from moisture and CO_2 by passing it through CaO and KOH pellets drying towers. The reaction temperature ranged from ambient to 200°C at a heating rate of 1°C/min.

The rate of heating was controlled with the assist of a micro-processor based temperature controller. The catalytic experiments were carried out under steady state conditions. The flow rates of CO and air were monitored with the help of digital gas flow meters. The gaseous products were analyzed by an on-line gas chromatograph (Nucon Series 5765) equipped with a methaniser, porapack q-column and FID detector for the concentration of CO and CO_2. The catalytic activity was measured for the conversion of CO into CO_2.

3 RESULTS AND DISCUSSION

3.1 Catalyst Characterization

The characterization of CuMnO$_X$ catalyst reveals the morphology, phase identification, material identification, surface area and surface structure.

3.1.1 Morphology of the Catalysts

The textures property of the CuMnOx catalyst was analyzed by scanning electron microscopy (SEM). As seen in the SEM micrograph, the particles presence in CuMnOx (Cu:Mn=1:2) catalyst is highly porous and fine resulted by reactive calcination conditions. The particles of CuMnOx (Cu:Mn=1:2) catalyst less agglomerated, porous and homogeneous as compared to other two catalyst samples. The size of particles in the catalyst (Cu:Mn=2:1) is relatively very large, course, less homogeneous and agglomerated than (Cu:Mn=1:1) and (Cu:Mn=1:2) catalyst. Thus, the different molar ratio of (Cu:Mn) in CuMnOx catalyst considerably affect the porosity, particle size, and morphology of the resulting catalysts.
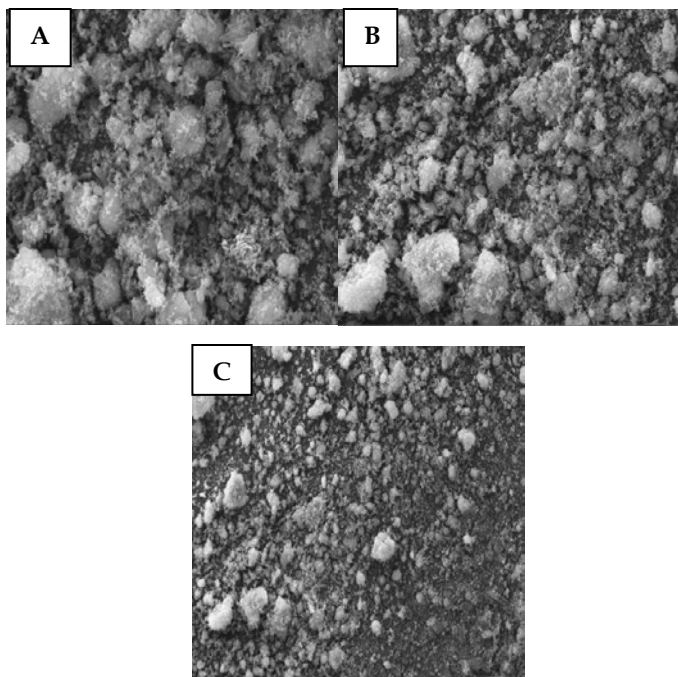
Figure 1. SEM image (10KX) of CuMnO$_X$ catalyst produced in Reactive calcinations A) Cu: Mn=2:1, B) Cu: Mn=1:1, C) Cu: Mn=1:2

3.1.2 Elemental analysis

In the CuMnOx catalyst, the percentages of different elements are presently given by the energy dispersive X-ray (EDX) analysis. It is evident from the results of EDX analysis that all the catalysts were pure due to the presence of Cu, Mn and O peaks only.
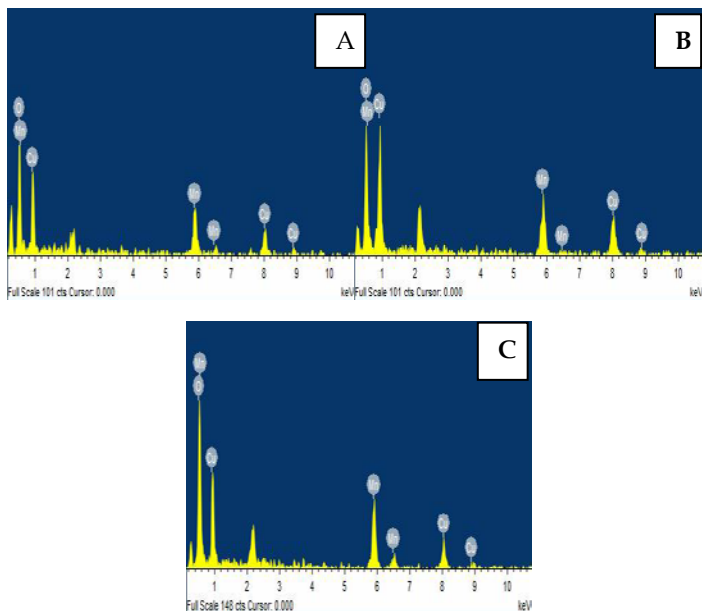

Figure 2. EDX analysis of CuMnO$_X$ catalyst produced in Reactive calcinations A) Cu: Mn=2:1, B) Cu: Mn=1:1, C) Cu: Mn=1:2.

The oxygen content of the CuMnOx (Cu: Mn=1:2) catalyst is least in comparison to other two catalysts (Cu:Mn=2:1) and (Cu:Mn=1:1). This indicates the presence of oxygen deficiency in the CuMnOx (Cu: Mn=1:2) catalyst which makes the high density of active sites.

3.1.3 Phase identification and cell dimensions

The phase identification and cell dimensions of CuMnOx catalyst are generally done by the X-ray powder diffraction (XRD) technique. In the reactive calcination of CuMnOx (Cu:Mn=1:2) catalyst we have to found that it exists in Cu$_{1.2}$Mn$_{4.2}$ phase. The diffraction peak at 2θ of 30.19 corresponds to lattice plane (2 2 0) of face-centered cubic Cu$_{1.2}$Mn$_{4.2}$ (PDF-35-1029 JCPDS file) and crystallite size of the catalyst is 4.45 nm.

In the reactive calcination of CuMnOx (Cu: Mn=1:1) catalyst we have to found that it exists in Cu$_1$Mn$_4$ phase. The diffraction peak at 2θ of 42.70 corresponds to lattice plane (1 2 0) of face-centered cubic Cu$_1$ Mn$_4$ (PDF-30-1042 JCPDS file) and crystallite size of the catalyst is 8.60 nm. In the reactive calcination of CuMnOx (Cu: Mn=2:1) catalyst we have to found that it exists in Cu$_2$Mn$_8$ phase. The diffraction peak at 2θ of 62.19 corresponds to lattice plane (1 1 0) of face-centered cubic Cu$_2$Mn$_8$ (PDF-42-1060 JCPDS file) and crystallite size of the catalyst is 10.90 nm.
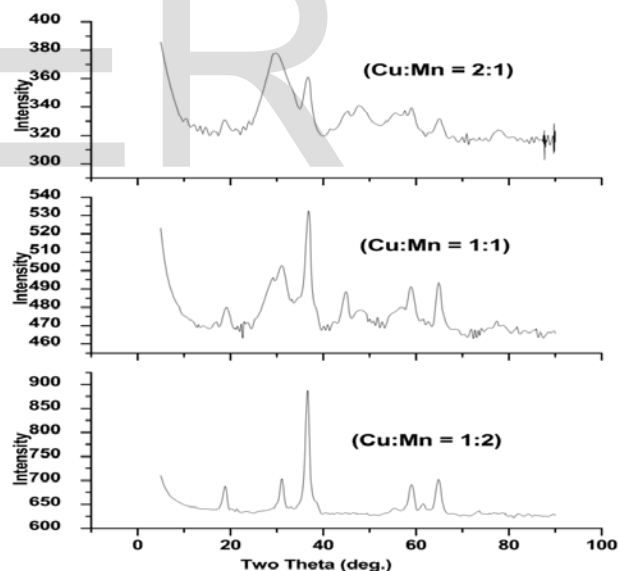

Figure 3. XRD analysis of CuMnO$_X$ A) Cu:Mn=2:1, B) Cu:Mn=1:1, C) Cu:Mn=1:2 catalyst in reactive calcination conditions

In the figure we have to scene that the CuMnOx (Cu:Mn=1:2) catalyst prepared by reactive calcination condition is more effective for CO oxidation at low temperature. We have to also scene that the CuMnOx catalyst the molar ratio of (Cu:Mn = 1:2) is perform better results compared to the other prepared catalyst. Due to the small particle size of the catalyst, they have a more surface area so that they are more effective for CO oxidation.

3.1.4 Identification of the materials presents in a Catalyst

The FTIR analysis of the reactive calcined CuMnOx (Cu: Mn=1:2) catalyst in the transmittance conditions they are four peaks we obtained. The IR band (1635cm^{-1} and 3432cm^{-1}) show the presence of MnO_2, (1300 cm^{-1}) shows -OH group and (532 cm^{-1}) shows CuO group and (2350 cm^{-1}) shows C=O group presence respectively. The MnO_2 vibration mode was observed at 1640 cm^{-1} due to stretching of Mn-O bond.

The IR spectra of CO adsorbed on the reduced catalysts show a low-intensity band for crystallized CuMnOx see in figure which could be attributed to linear CO adsorption on copper. The intensity of the bands decreased with increasing temperature and absorbance was still easily detected on crystallized CuMnOx, even at 633 K. CO disproportionation ($2CO{\rightarrow}C+CO_2$) occurred on the surface of the catalyst and the reaction was activated at high temperatures.

The figure specified that we can have mixed CuO and Cu_2O oxides. This conclusion comes from the fact that the band at 625 cm^{-1} may originate from CuO or Cu_2O and the band at 440 cm^{-1} is observed only for Cu_2O. The addition of oxygen into the CO oxidation process, which degrades the carbon structure. It is worth noting that such an addition of oxygen in the case of layers deposition is sufficient to completely remove the carbon structure.
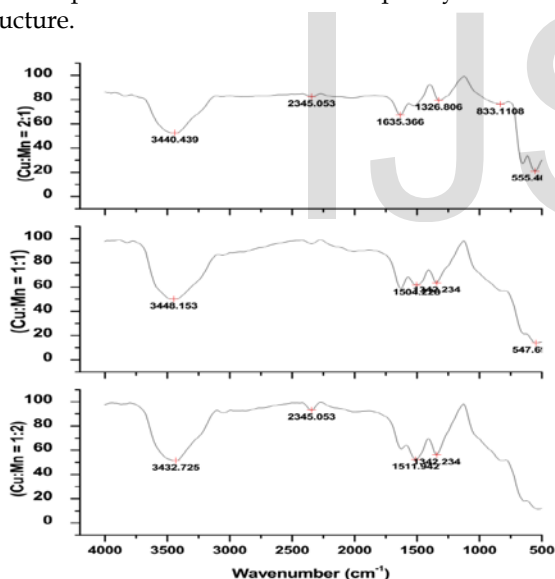

Figure 4. FTIR analysis of CuMnO$_X$ A) Cu:Mn=2:1, B) Cu:Mn=1:1, C) Cu:Mn=1:2 catalyst in reactive calcination conditions.

The weak band at 1300 cm^{-1} indicates the presence of some carbonaceous group in all the catalyst. The spectra of impurities like CO_3^{2-} group at (833.108 cm^{-1} and 1511cm^{-1}) decreases in the following order: (Cu:Mn=2:1) >(Cu:Mn=1:1) > (Cu:Mn=1:2). Thus (Cu:Mn=1:2) is highly pure as compare to (Cu:Mn=1:1) and (Cu:Mn=2:1). Based on the FTIR spectra we state clearly that the types of copper oxides, manganese oxides bands present in a catalyst and types of their oxides phases also present in a catalyst.

3.1.5 Identification and quantification of elements

The oxidation state and binding energy of CuMnOx mixed oxide investigated by X-ray photoelectron spectroscopy (XPS) analysis. It can be proposed that the high binding energy is preferably for the oxidation reaction.
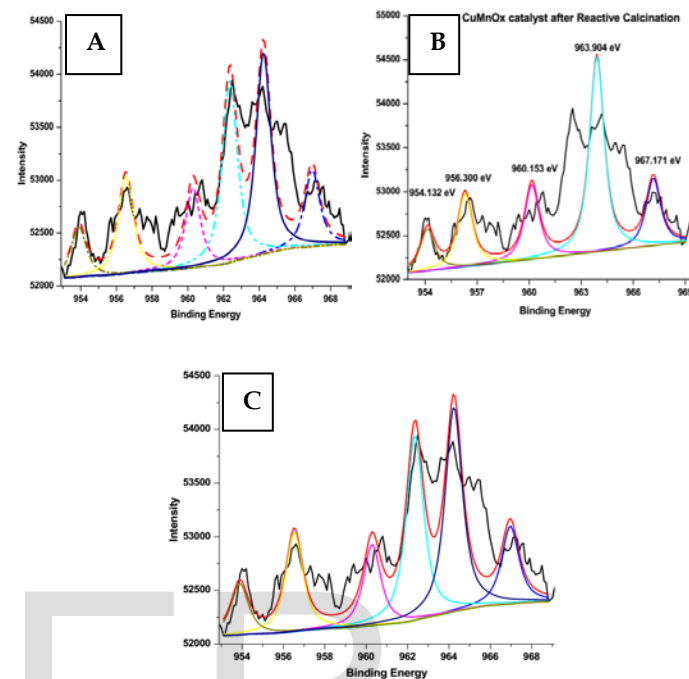

Figure 5. The XPS analysis A) Cu:Mn=2:1, B) Cu:Mn=1:1, C) Cu:Mn=1:2 catalyst in reactive calcination conditions

The highest binding energy peak obtained by CuMnOx (Cu:Mn=2:1, Cu:Mn=1:1, Cu:Mn=1:2) catalyst is 925.05 eV, 963.904 eV and 986.012 eV respectively. The chemical state of C (1s), Cu(2p) and Mn(2p) presence in CuMnOx (Cu:Mn=1:2) catalyst is C-O-C phases, Cu (II) Oxide phases and MnO_2 phase respectively. The presence of lattice oxygen is very low in reactive calcined prepared CuMnOx (Cu:Mn=1:2) catalyst. The content order of $O_a/(O_a + O_l)$ ratio was shown as following: (Cu:Mn=1:2) > (Cu:Mn=1:1) > (Cu:Mn=2:1). It is well known that the high amount of surface chemisorbed oxygen is the most active oxygen preferable for enhancing the catalytic activity for CO oxidation reactions.

3.1.6 Surface area measurement of catalyst

The BET surface area of the CuMnOx (Cu:Mn=2:1, Cu:Mn=1:1, Cu:Mn=1:2) catalyst prepared by the co-precipitation method with a novel route in reactive calcination conditions. The surface area, pore volume and pore size of the various CuMnOx (Cu:Mn) catalyst in RC conditions are discussed below. Clearly, the textural properties of CuMnOx (Cu:Mn=1:8) catalyst are superior to active for CO conversion at low temperature. The average pore volume and pore size of (Cu:Mn=1:8) catalyst is 0.320cm^3/g and 22.7Å which is slightly higher than other two catalysts. The larger more pores in a catalyst means highly interaction of CO molecules with catalyst surfaces and they have to show the better catalytic activity.

Table 1: BET analysis of CuMnO$_X$ (Cu:Mn=2:1, Cu:Mn=1:1, Cu:Mn=1:2) catalyst in reactive calcination conditions

Catalyst	Surface Area (m^2/g)	Pore Volume (cm^3/g)	Ave. Pore Size(Å)
CuMn(2:1)	26.50	0.320	22.70
CuMn(1:1)	31.59	0.430	31.60
CuMn(1:2)	43.402	0.540	40.70

The specific surface area of the three CuMnOx (Cu:Mn=2:1, Cu:Mn=1:1 and Cu:Mn=1:2) catalyst measured by BET method and it match with the SEM and XRD results. The increases in pore volume and pore size of the catalyst is most active for CO oxidation at low temperature, but it is several times deactivated by trace amount of moisture present in the catalyst and so that it is necessary to take the catalyst under the dry condition to remove the moisture content in the catalyst.

4. Catalyst Activity

A CuMnOx catalyst prepared by co-precipitation method and calcination at 300°C for 2hr. The activity of the catalyst for CO oxidation with different composition of Cu and Mn are studied into the laboratory. The precusors are inactive for CO oxidation reactions but all the calcined materials are showed active in CO oxidation reaction. The calcination temperature 300°C is active for CO oxidation reactions because all the precursors presence in a catalyst is crystalline form but increased the reactions temperature the catalyst loose their crystaline phase. The molar ratio of (Cu:Mn) in CuMnOx catalyst is divided into three parts (Cu:Mn=2:1), (Cu:Mn=1:1) and (Cu:Mn=1:2) for activity test conditions.After preparation of the catalyst in different calcination conditions then measured the activity of the catalyst by gas chromatography in to the laboratory.

4.1 Cu$_2$MnO$_x$ (Cu:Mn=2:1)

The copper manganese oxide catalyst was prepared by Co-precipitation method with a range of (Cu:Mn) in a solution varying from 100% Cu to 50% Mn and the activity of the catalyst for CO oxidation was investigated for the materials at following calcination (300°C/2h) conditions. The activity of the Cu$_2$MnOx (Cu:Mn=2:1) catalyst for CO oxidation in different calcinations condition have to done in to the laboratory.
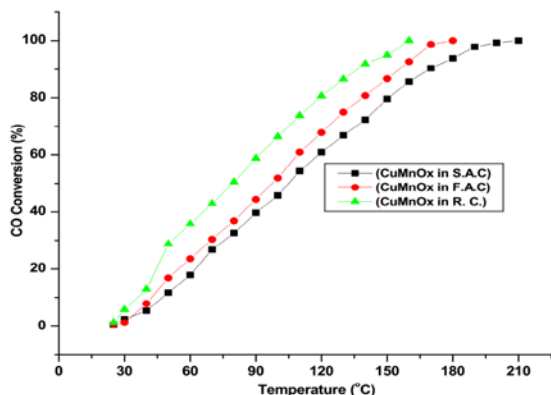
The activity of the catalyst for CO oxidation is increased with increasing of the temperature as shown in figure 6 and table 1. The synergistic effect due to different calcination conditions in the presence of different composition of catalyst. The activity of the catalyst generally depends on the composition of catalysts, preparation conditions and calcinations temperature of the catalysts.

Table 2: Light-off Temperature (L.O.T.) of CuMnOx catalyst with (Cu:Mn=2:1) for CO oxidation in different calcinations conditions.

(Cu:Mn=2:1) catalyst	T$_i$	T$_{50}$	T$_{100}$
Reactive Calcination	25°C	90°C	160°C
Flowing air Calcination	30°C	105°C	180°C
Stagnant air Calcination	30°C	115°C	210°C

The order of activity CuMnOx (Cu:Mn= 2:1) catalyst at different calcination conditions as follows: RC > Flowing air> Stagnant air. The full conversion of CO is highest in reactive calcined prepared CuMnOx catalyst at 160°C temperature and the full conversion of CO in stagnant air and flowing air prepared catalyst is 210°C and 180°C respectively. The order of activity is increased with the increasing of the temperature. With the decreasing of Mn concentration in CuMnOx catalyst, it reduces the activity of the catalyst for CO oxidation.

4.2 CuMn$_2$O$_x$ (Cu:Mn=1:1)

The aqueous solutions of Cu(NO$_3$)$_2$.3H$_2$O and Mn(NO$_3$)$_2$.6H$_2$O were mixed and co-precipitation was carried out by drop-wise addition of an aqueous solution of Na$_2$CO$_3$. The activity of the CuMnOx (Cu:Mn=1:1) catalyst for CO oxidation in different calcinations condition like reactive calcination, flowing air calcination and stagnant air calciantion have to done in to the laboratory. The range of Cu/Mn in CuMnOx (Cu:Mn=1:1) catalyst is 100% Cu to 100% Mn and the resulting materials calcination at (300°C/2h). The activity of the catalyst in RC and FAC is also same from 30°C to 150°C and at 150°C in RC conditions the full conversion of CO was achieved.
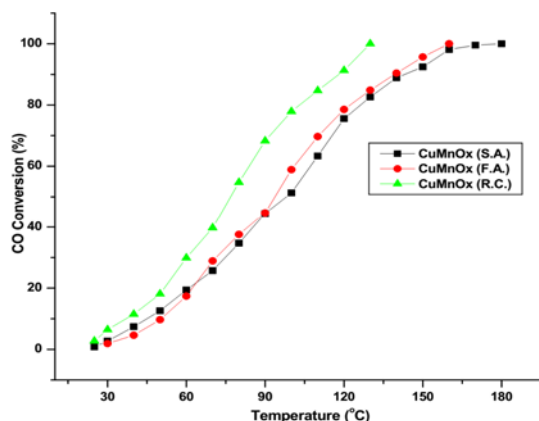

Figure 6. The comparison study of CuMnOx (Cu:Mn=2:1) catalyst for CO oxidation in different calcinations conditions.

Figure 7. The comparison study of CuMnOx (Cu:Mn=1:1) catalyst for CO oxidation in different calcinations conditions.

The order of activity of CuMnOx catalyst in different calcinations conditions as follows: Reactive calcination> Flowing air> Stagnant air. Increases of 1°C of the catalysts bed were observed almost every time due to exothermicity of the reaction near steady state conditions with respect to the ambient temperature. From the table and figure we can get the result that the higher temperature was necessary for CO oxidation reaction over all the three catalysts. In the table 3 shows a comparison of the light-off temperatures of all the catalysts produced by different calcination conditions using CO-air mixture for CO oxidation.

Table 3: Light-off Temperature (L.O.T.) of CuMnOx catalyst (Cu:Mn=1:1) for CO oxidation in different calcinations conditions.

(Cu:Mn=1:1) catalyst	T_i	T_{50}	T_{100}
Reactive Calcination	25°C	70°C	140°C
Flowing air Calcination	30°C	105°C	165°C
Stagnant air Calcination	30°C	110°C	185°C

From the table and figure we have to scene that the reactive calcined prepared CuMnOx catalyst with molar ratio (Cu:Mn = 1:1) is more active for CO oxidation at low temperature as compared to the preparation of catalyst by other methods. The oxidation of CO starts at the room temperature and the full conversion of CO at 140°C temperature by CuMnOx in RC conditions.

4.1 CuMn$_2$O$_x$ (Cu:Mn=1:2)

The catalyst activity tests were carried out to compare the efficiency of the catalyst in different calcination conditions as a function of temperature. The observed temperatures required for total oxidation of CO over the best catalyst formulations CuMn$_2$ in stagnant air, flowing air and reactive calcination were 165°C, 135°C and 110°C respectively.
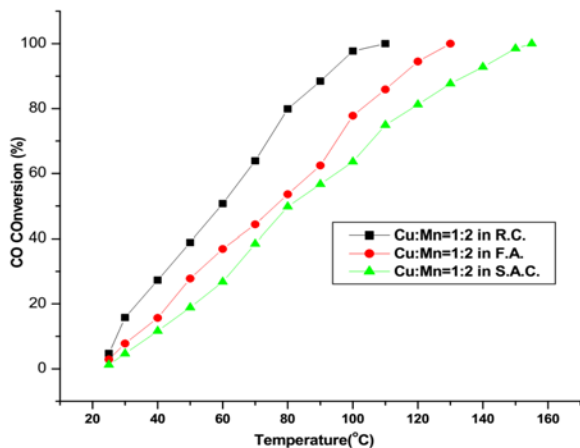

Figure 8. The comparison study of CuMnOx (Cu:Mn=1:2) catalyst for CO oxidation in different calcinations conditions.

The entire catalyst shows an increase in conversion with time on stream and the conversion of CO due to the structural or textural nature of the catalyst. The surface area strongly influenced the activity of the catalyst for CO oxidation and from the characterization results of XRD, SEM and BET we have to finalize that the smallest particle size, crystalline form catalyst is more active for CO oxidation.

Table 4: Light-off Temperature (L.O.T.) of CuMnOx catalyst (Cu:Mn=1:2) for CO oxidation in different calcinations conditions.

(Cu:Mn=1:2) catalyst	T_i	T_{50}	T_{100}
Reactive Calcination	25°C	60°C	110°C
Flowing air Calcination	30°C	70°C	135°C
Stagnant air Calcination	30°C	80°C	165°C

The order of activity of CuMnOx (Cu: Mn= 1:2) catalyst at different calcinations conditions as follows: RC > Flowing air > Stagnant air calcination. The calcined materials are all present in a CuMnOx (Cu:Mn = 1:2) catalyst they are found to be amorphous phase or nano crystalline by SEM and XRD analysis. The improvement in the availability of lattice O^{2-} is considered to be associated with the origin of the increased catalytic activity. It is clear that these catalysts show best performance for the oxidation of CO under ambient conditions.

4.2 The Comparison study of different composition of CuMnOx catalyst like (Cu:Mn=2:1, Cu:Mn=1:1, Cu:Mn =1:2) for CO Oxidation in different calcination conditions

The comparison study of the different composition of CuMnOx catalyst like (Cu:Mn=2:1, Cu:Mn=1:1 and Cu:Mn=1:2) for CO oxidation in different calcination conditions. The conversion of CO increases with the increasing of temperature as shown in figure 9 and table 5. A fresh catalyst is used in all the times at the testing of catalytic activity at each temperature. The CuMnOx catalyst (Cu:Mn = 2:1, Cu:Mn = 1:1) is less active than the (Cu:Mn = 1:2) catalyst.

The activity of the catalyst is generally depends upon the preparation conditions, the molar ratio Cu:Mn, drying temperature and the calcinations temperature of the catalyst. The complete conversion of CO was even at the shorter contact time and the conversion of CO is increased with the increasing of the Mn concentration in the CuMnOx catalyst samples.

From the figure we have to compared the different composition of CuMnOx catalyst in different calcination conditions and the best result is obtained by Cu:Mn catalyst in molar ratio of (Cu:Mn = 1:2) in reactive calcination conditions. A clean surface of catalyst is exposed by a mixture of CO and air so that it becomes quickly covered by with CO since CO requires a single vacant adsorption site while O_2 requires two adjacent sides.
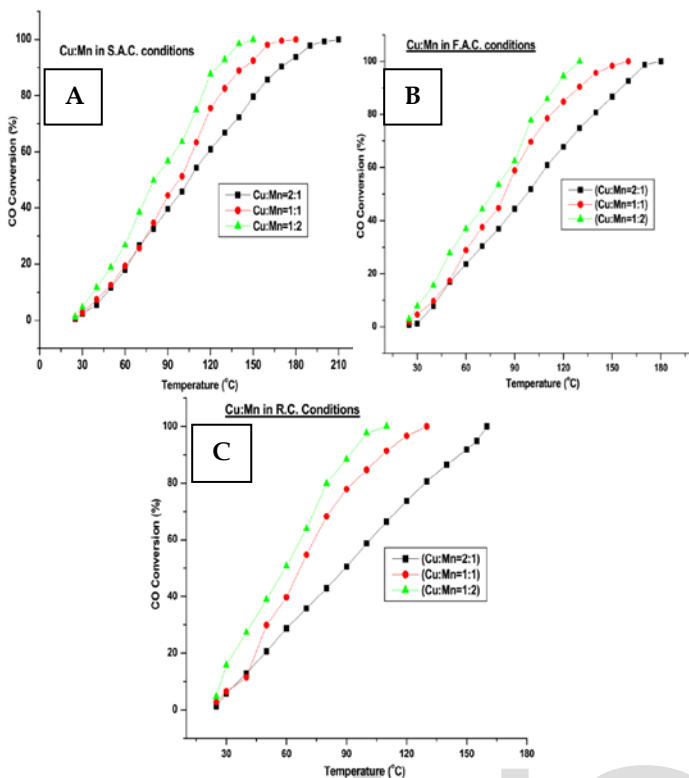
Figure 9. The comparative study of total conversion of CO by different composition of CuMnOx catalyst like (Cu:Mn=2:1, Cu:Mn=1:1 and Cu:Mn=1:2) in **(A)** SAC **(B)** FAC and **(C)** RC.

The higher catalytic activity is increased at the increasing of the temperature and increasing the concentration of oxygen gas presence in a feed air also. The catalytic activity is also faster at the elevated temperatures and CO desorption it significantly allowing for dissociative O_2 adsorptions. From the XPS and FTIR analysis we have to also find out that the binding energy of Mn ions present in 3d electrons in MnO_2 form is higher in the CuMnOx (Cu:Mn = 1:2) catalyst in comparison to the other two catalyst. The compete loss of oxidation capacity of MnO_2 was observed after 3h on stream.

Table 5: The Light-off Temperature (L.O.T.) of different CuMnOx catalyst in different calcination conditions.

Calcination Condition	(Cu:Mn=2:1)			(Cu:Mn=1:1)			(Cu:Mn=1:2)		
	T_i	T_{50}	T_{100}	T_i	T_{50}	T_{100}	T_i	T_{50}	T_{100}
RC	25	90	160	25	70	140	25	60	110
FAC	30	105	180	30	105	165	30	70	135
SAC	30	115	210	30	110	185	30	80	165

In the manganese oxide (MnO_2) the presence of manganese in the form of Mn^{2+}, Mn^{3+} and Mn^{4+} ions and the correlation between the average oxidation state of Mn and reaction rates

The conversion of CO increases with the increasing of temperature as shown in figure 9 and table 5. A fresh catalyst is used in all the times at the testing of catalytic activity at each temperature.It implies that higher average oxidation numbers lead to higher CO oxidation rates.The synergistic effect of copper and manganese in the combination of CuMnOx catalysts can be easily visualized by the results as shown in figure 9. The CuMnOx catalyst (Cu:Mn = 2:1, Cu:Mn = 1:1) is less active than the (Cu:Mn = 1:2) catalyst.

The activity of the catalyst is generally depends upon the preparation conditions, the molar ratio Cu:Mn, drying temperature and the calcinations temperature of the catalyst. All the catalysts having different Cu/Mn ratios and gave higher CO conversion than their individual components of copper and manganese alone. The results are shown in the above table 4 and graph 9 (A), (B) and (C), we have to fulfilled that the following result (Cu:Mn = 1:2) > (Cu:Mn = 1:1) > (Cu:Mn = 2:1) and the order of activity in different calcinations condition is follows: RC > FAC >SAC.

It can be concluded that the optimum molar ratio of Cu/Mn is 1:2 and it exhibited very stable performance over long times on stream. The activity of the catalysts seems to be dominated both by their average oxidation numbers and by the species presence in a catalyst. Although the hopcalite catalyst was discovered around 90 years ago and it also indicates that the catalyst initially oxidized CO before reoxidised in air. The influence of ageing time is known to be important for controlling the activity hopcalite catalyst prepared by co-precipitation method.

5 CONCLUSSIONS

The catalytic oxidation of carbon monoxide at low temperature is an important process for human health protection. The improvement in the CuMnOx catalyst performance prepared by co-precipitation method, with Cu/Mn = ½ and calcined at 300ºC for 2h. The calcination order with respect to the performance of the catalyst for oxidation of CO is as follows: RC> Flowing air > Stagnant air.

The extraordinary performance of the catalyst produced by RC for CO oxidation was associated with the modification in intrinsic textural and morphological characteristics such as surface area, crystallite size, particle size and oxygen deficient defective structure which generate the high density of active sites. So, RC route can be recommended for the synthesis of highly active catalysts.

To reduce the cold start emissions problem from automobile vehicles by using hopcalite catalyst for controlling the urban air pollution. The positive thing is that this catalyst is more active to resist water poisoning compared to the commercial hopcalite catalyst. The precipitant shows the greatest influence on the crystalline phases of the catalyst while the precursor shows a greater effect on the amount of catalytic active sites which are directly related to the CO oxidation activity. The choice of precipitant and the precursor is important in designing the most efficient CO oxidation catalyst.

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