Physico-chemical analysis and study of different parameters of hopcalite catalyst for CO oxidation at ambient temperature

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Abstract: The influence of the experimental parameters like molar ratios of precursor, calcinations temperature, calcinations time, catalytic activity and aging time of binary copper manganese oxides for CO oxidation in dry air at room temperature has been investigated. The catalysts were characterized by means of BET, SEM, and X-ray diffraction. All results were compared with a commercial Hopcalite sample. The effect of doping of promoters in the catalyst such as Silver, Cobalt and Gold has been evaluated and found an apparent result. XRD noticeably indicate that as the crystal nature of hopcalite decreases in the consequence of its activity increases owing to increase of surface area, which was confirmed by BET analysis.

Keywords: CO oxidation, Hopcalite, Co-precipitation, calcinations, BET

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1. Introduction

Carbon monoxide (CO) is a toxic and detrimental gas particularly to human beings and in general, to all life forms that respire[1]. As a result, CO has been termed "the unnoticed poison of the 21st century" [2] and is often called "the silent killer", because it gives no clear warning to its victims that they were at risk. From very beginning to till now it is well known that hopcalite is the most widely used catalyst for CO oxidation. As we know that the emission of carbon monoxide is continuously rising because of increasing number of automobiles, industrial pollution and has been reached on alarming level[3, 4] .CO affects our body and environment very defectively [5, 6]. Many catalysts have come into existence for CO oxidation into carbon dioxide through a very simple reaction. Hopcalite catalyst is preferentially desired for the use of respiratory protection as mask[7]. Optimization of the preparation conditions, and other variables have been increased the concert of hopcalite catalysts [8,9] .Recently, CO oxidation at low ambient temperature has attracted much attention after the sighting by Haruta and co-workers that gold modified hopcalite were highly effective catalysts at low temperatures[10]. Hopcalite is an effective catalyst and deactivated by water but expelling water at moderate temperatures easily restored their catalytic activity[11].

Although the oxidation of CO is conceptually a simple reaction, it has great importance in its claim at ambient conditions. The catalytic complete oxidation of CO at ambient conditions can be an efficient way for solving the environmental problems. Among the various catalysts reported in the literature, Hopcalite (CuMnOx) catalyst has been found most efficient for oxidation of CO at ambient conditions. Therefore, in this investigation a series of CuMnOx catalysts were prepared and characterized by various techniques (BET, TEM, XRD and

cyclocvoltammetry) having different molar ratio and doping of promoters by co-precipitation method for ambient condition oxidation of CO.

2. Materials and Method

2.1 Preparation of Catalysts

The catalysts were prepared having different components and compositions by co-precipitation method [10, 11]. Hopcalite catalysts as well as promoted catalysts were prepared as follows: Aqueous solutions of 0.25M, Cu $(NO_3)_2 \cdot 3H_2O$ (6.04g/100ml) and 0.25M, Mn $(NO_3)_2 \cdot 6H_2O$ (3.59g/50ml) were mixed.   Co-precipitation was carried out by drop-wise addition of an aqueous solution of Na_2CO_3 (0.25M) via a burette in the above mixed solution with constant stirring over a magnetic stirrer maintained at 80^0C to the pH 8.3. The precipitate was recovered by filtration, washing several times with hot distilled water and dried in an electric oven at 120^0C for 16 h. The dried precipitate was calcined at 5 different temperatures ranging from $350\text{-}600^0$ C for two hours. Similarly two more samples with different molar ratio were prepared, such as $CuMnO_x$ [Cu: Mn=1:1] and $CuMn_2O_4$ [Cu:Mn=1:2]. Pure copper oxide and manganese oxides were also prepared by decomposing the respective nitrate precursors at 400 ^oC in a muffle furnace for a comparative study with hopcalite.

2.1.1 Gold promoted hopcalite (Cu-Mn-Au)

An exact aliquot of 8mL gold solution (0.05M $HAuCl_4 \cdot 3H_2O$) was added to the mixed nitrates solution of copper and manganese pre-mixed to give Cu/ Mn=1/2 so that the desired 3%Au content was obtained. During carbonate precipitation the pH of the solution was adjusted to 9 by the drop wise addition of aqueous sodium carbonate (0.25 M). The temperature was maintained at 80^0C with constant stirring during precipitation.

The catalysts Hopcalite $(Cu\text{-}Mn\text{-}O)_x$ were synthesized by co-precipitation (CP) and characterized by different techniques. The experimental parameters like molar ratios of the nitrate precursors, calcinations temperature, and calcinations time were optimized for CO oxidation at ambient temperature. Oxidation of CO was studied in a tubular flow reactor under the following conditions: catalyst wt. = 100 mg, %CO in Air = 2.5, total flow rate of gas = 60 ml/min and ambient temperature. The optimum values of, molar ratio of Cu/Mn was found to be 1:2 and calcinations temperature of the catalyst was 400 ^oC. The doping of promoters in the catalyst such as Silver, Cobalt and Gold improved CO conversion to 49.63%, 53.19% and 61.39% respectively.

2.2 Activity measurement of the catalysts

The catalytic activity for CO oxidation of the catalysts was evaluated in a tubular fixed bed flow reactor. 100 mg catalyst diluted with 4.5 g alumina was placed in the tubular reactor, and the oxidation was carried out at ambient temperature. Alumina does not participate in chemical reaction it is used only for uniform distribution of heat in the reactor. The inlet air was

fed to the reactor at a flow rate of 58.50 ml/min while CO was fed at a flow rate of 1.50 ml/min. The outlet gases were analyzed for CO and CO_2 by an on-line gas chromatograph equipped with a porapack Q-column, a methaniser and a FID detector. Nitrogen was used as a carrier gas and hydrogen as fuel. The temperatures of the oven, injector and detector were maintained at 60, 80 and 80 ^{0}C respectively. CO conversion was calculated using the following formula:

% CO conversion = 100[C_{COin} - C_{COout}]/ C_{COin}

All the prepared catalysts and their calcinations time and calcinations temperature was covered in table 1.

Table 1. Nomenclature of prepared catalysts

S.N.	Nomenclature	Component	Molar Ratio	Calcination Time	Calcination Temperature
1	CuO	-	-	2 hour	400°C
2	MnO$_2$	-	-	2 hour	400°C
3	H Au	Cu-Mn-Au	Cu/Mn = 1/2	2 hour	400°C
4	H Co	Cu-Mn-Co	Cu/Mn = 1/2	2 hour	400°C
5	H Ag	Cu-Mn-Ag	Cu/Mn = 1/2	2 hour	400°C
6	H Ce	Cu-Mn-Ce	Cu/Mn = 1/2	2 hour	400°C

3. Characterization of the catalyst

The BET surface area (S$_{BET}$) of synthesized catalyst powders were determined by MICROMERITICS-ASAP 2020 surface area and porosity analyzer instrument; about 0.3-0.5 grams of sample is weighed and all the samples are degassed at 190^{0}C prior to S$_{BET}$ measurement by using nitrogen gas adsorption. And analyzed by nitrogen adsorbed at -193^{0}C; at a relative pressure (P/P$_o$) = 0.1-0.3. The X-ray diffraction (XRD) patterns of the catalyst samples were obtained on Xpert Pro X-ray diffractometer using Cu/Ni radiation. The accelerating voltage and the applied current were 40 kV and 30 mA, respectively. Transmission electron microscopy (TEM) was performed in a JEOL 2000EX high resolution electron microscope operating at 200 kV. Ultra-high spatial resolution EDS microanalysis was performed in a VG HB601-UX scanning transmission electron microscope (STEM) operating at 100 kV. Cyclic voltammeter were recorded with a three electrode compartment consisting of a platinum disc working electrode, platinum wire counter electrode and Ag/Ag$^+$ reference electrode.

4. Results and Discussions

4.1 Optimization of Cu-Mn molar ratio

The experimental results on CO conversion over various hopcalite catalysts and its components are shown in Figure 1. An increase of temperature of the catalyst bed was observed in the beginning during every experimental run at room temperature due to exothermicity of the oxidation reaction and thus CO conversion was also increasing from initial to a steady value for all the catalysts studied after about 2 hours as can be seen in Figure 1.
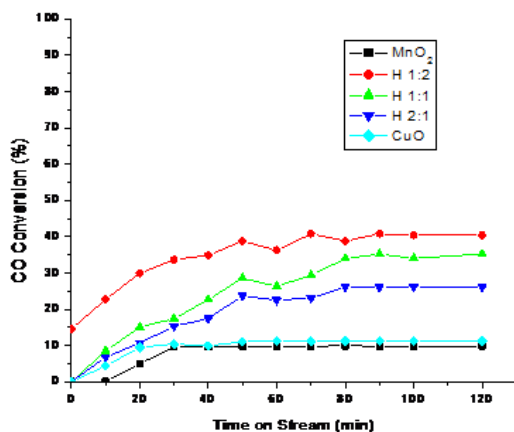

Figure 1. Optmization of Cu/Mn atomic ratio for CO oxidation
(Temp. 36^{0}C, samples calcined at 400^{0}C for 2 h)

Over copper oxide and manganese oxide individually CO conversion resulted 11.3% and 9.8% respectively. Synergistic effect of copper and manganese combination in hopcalite catalysts can be easily visualized by the results shown in Figure 1, as all the catalysts having different Cu/Mn ratios gave higher CO conversion than their individual components copper and manganese alone. It can be seen from the figure that catalyst H 1:2 resulted 40.38% CO conversion which is the highest than H 1:1 and H 2:1 at ambient temperature. Hence it can be concluded that the optimum molar ratio of Cu/Mn is 1:2. For further studies Cu/Mn molar ratio was kept fixed as 1:2. CO conversion order may be given as below:

Cu:Mn = 1:2 > Cu:Mn = 1:1 > Cu:Mn =2:1 > Cu(NO$_3$)$_2$ > Mn(NO$_3$)$_2$

4.2 Optimization of calcinations time

In order to optimize the calcinations time, a fixed temperature of 400 ^{o}C and calcinations time periods of 2h, 6h and 12h (overnight) were selected, the CO conversions achieved over these catalysts were 40%, 27% and 24% respectively. Hence, optimum calcination period of the catalyst is 2 hours is shown in Figure 2.
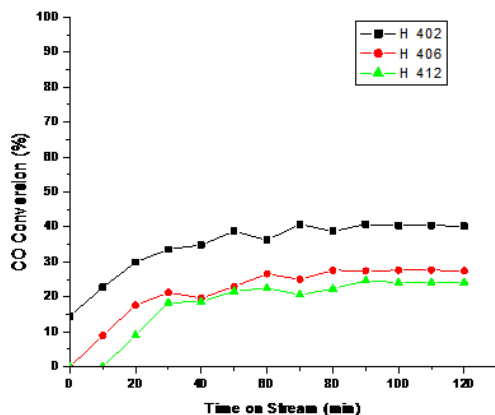
Figure 2. Effect of calcination time on CO Oxidation
(Temperature 36°C, samples calcined at 400°C)

Thus, for further studies calcination time of 2 hours was fixed.

4.3 Effect of calcinations temperature

The calcination temperature always has a marked effect on the catalytic performance. So effort has been made to find the optimum calcination temperature. Thus, catalyst calcined between 350-600°C and studied for CO conversions are shown in Figure 3.
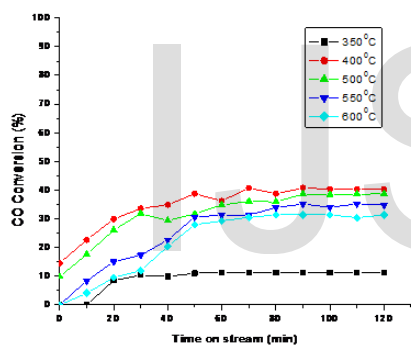

Figure 3. Effect of calcination temperature on catalyst H 2:1 for CO
oxidation (Temperature 36°C, samples calcined for 2 hour)

Figure shows that the catalyst calcined at 350°C gave the lowest CO conversion of 11% which restricts the active phase formation of $CuMn_2O_4$; this is in accordance with the observation of Jones et al (2009). Calcination temperature at 400°C gave a highest CO conversion of 40.38%, because of the amorphous nature and formation of $CuMn_2O_4$ phase as revealed by XRD analysis. A synergetic effect between CuO and amorphous Cu–Mn oxide phases is also confirmed. So now we can say that the optimum calcination temperature lies at about 400°C.

4.4 Effect of promoters doping

Effort has been made to enhance the activity of hopcalite by the addition of low levels of different promoters. Therefore, CO conversion was studied over catalyst samples having 3%, gold, silver, cobalt and ceria separately. For this experiment we have added different-different doping agent as given previously with fixed amount (%) and have compared with pure hopcalite

catalyst separately. And finally as given figure 4. summarizes the performance of all the catalysts with different promoters used for the oxidation of CO. It is very obvious that the order of activity of the catalysts is as follows and final conversion was tabulated in no.2.
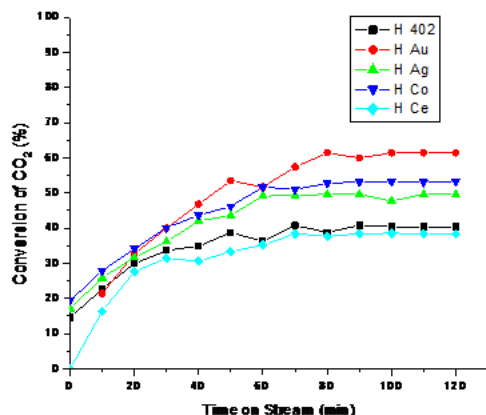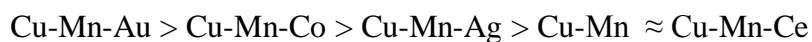
<p style="text-align:center">Cu-Mn-Au > Cu-Mn-Co > Cu-Mn-Ag > Cu-Mn ≈ Cu-Mn-Ce</p>

Figure 4. Performance of all promoters doped (3% wt)
(Temperature 36°C, sample calcined at 400°C for 2 h)

Table 2. Conversion of CO achieved using different promoted catalyst

Catalyst	Final Conversion Achieved
Cu-Mn-Au (H Au)	61.39 %
Cu-Mn-Co (H Co)	53.19 %
Cu-Mn-Ag (H Ag)	49.63 %
Cu-Mn (H 402)	40.38 %
Cu-Mn-Ce (H Ce)	38.39 %

4.5 X-Ray Diffraction studies

Hopcalite Calcined at 400°C gave a significant rise in conversion because of the amorphous nature and formation of $CuMn_2O_4$ phase (38.7419^{o}) as shown in figure 5. At 500°C the activity was a bit lower than catalyst resulted at 400°C. At temperatures 550°C and 600°C the conversion was further decreased as shown in the Figure 5. This may be due to sintering (loss of area) at high temperatures.

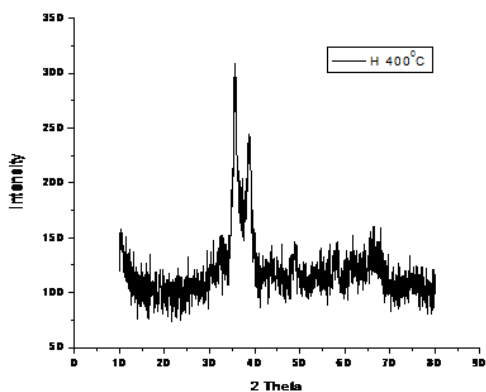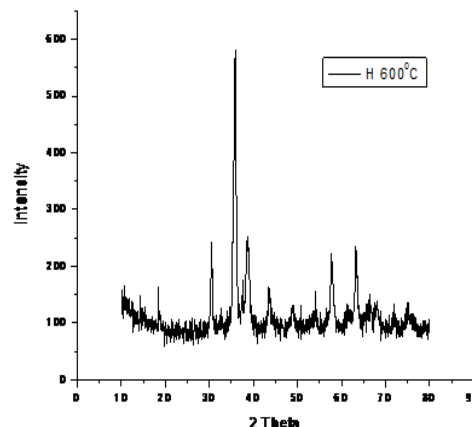Figure 5. XRD analysis of CuMnO$_X$ catalyst calcined at 400°C for 2 hour

Figure 6. XRD analysis of CuMnO$_X$ catalyst calcined at 600°C for 2 hour

At high temperature of 600°C Mn$_2$O$_3$ crystals were observed in XRD at 2 theta values of 30.4752^o, 54.0766^o and 66.2475^o as evidenced in Figure 6. This accounted for the loss of manganese in the active CuMn$_2$O$_4$ phase (38.6617^o) as compared to that of calcined at 400°C. So now we can say that the optimum calcination temperature lies at about 400°C. As the calcinations temperature of catalyst increase their crystalline nature increases as shown in XRD, the peaks obtained in fig. 6 was sharper than the Fig. 5 having calcinations temperature 400°C. We know that the catalyst give good activity in their amorphous state. Low temperature calcined samples are found to be more active than the high temperature calcined ones.

4.6 Cyclovoltammetry

The redox potential is an important parameter as it characterizes the ability of the redox centre to transfer electrons and also to act as a redox catalyst. The effectiveness of CV results from its capability for rapidly observing the redox behaviour over a wide potential range. The electrochemical behaviour of Cu(II) and Mn(II) complexes was investigated using the cyclic voltammetric (CV) technique in DMSO solution containing 0.1M tetra (n-butyl) ammonium perchlorate supporting electrolyte. In Fig. 1, hopcalite shows two anodic peak at the potential Epa = 0.35 V (Cu) and second one at the potential Epa =0.85 V (Mn). These two redox peaks are corresponding to Cu and Mn metal in hopcalite catalyst.
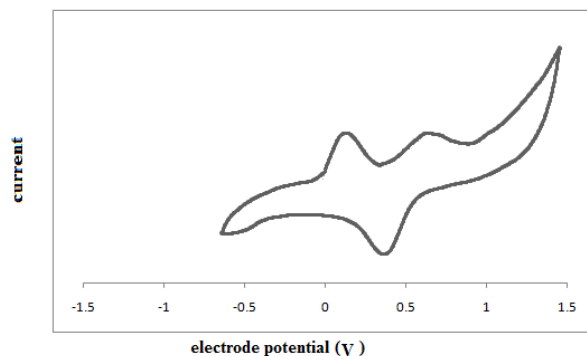
Fig. 7 cyclovoltamogram of hopcalite catalyst

4.7 TEM analyses:

Hopcalite (CuMnO$_x$) catalyst precursor is produced by co-precipitation under controlled conditions of temperature, pH and ageing times. Ageing is a very essential factor which shows considerable effect on the catalytic activity of the resulting material. It has been obviously seen that there occurred morphological changes during aging. The unaged precursor (Fig. 8) was found to be composed agglomerates of irregularly-shaped grains, ca. 35 nm in diameter. In addition, larger diameter (ca. 100 nm) spheres were observed.
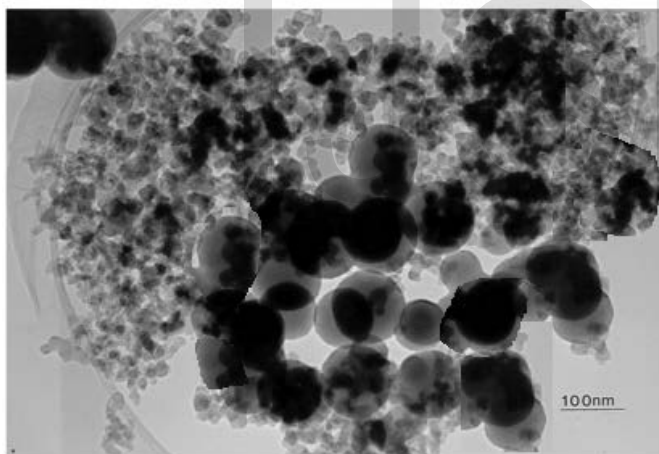

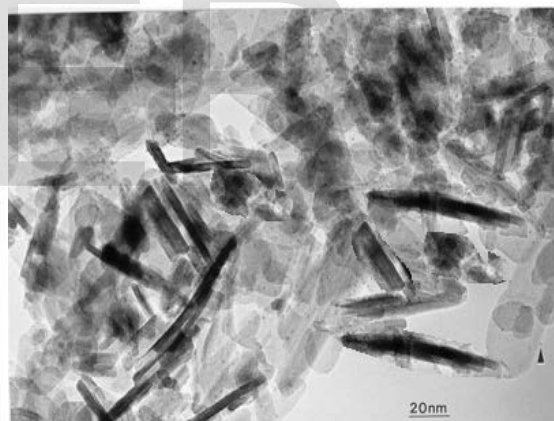Fig.8 TEM of hopcalite derived catalyst without ageing   Fig. 9 TEM of hopcalite derived catalyst after 120 min. of ageing

Ageing for 120 min (Fig. 9) generates a material comprising both needles and platelets with a large range of sizes. Numerous small highly diffracting supported particles, ca. 20 nm in diameter, Further ageing leads to a progressive growth in the size of the needles and platelets. TEM study confirmed its amorphous nature.

5. Conclusion

(a)Ageing of a precipitate is a process which can have a significant effect on the catalytic activity of the resulting material and its morphology.

(b) Hopcalite catalysts prepared with Cu/Mn = 1/2, calcined at 400°C for two hour are most active. Addition of lower levels of promoters can give a significant increase in the activity of hopcalite catalysts. The order of activity of the catalyst was as follows:

Cu-Mn-Au > Cu-Mn-Co > Cu-Mn-Ag > Cu-Mn≈ Cu-Mn-Ce

©The results showed that in the process of preparing the catalysts by CP, different ratios affect obviously their catalytic performance, and catalysts prepared by CP method gave the best result among all.

(d) CV showed that there is electron transfer reactions occurred with chemical reactions.

Acknowledgement

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