

SYNTHESIS AND ACTIVITY EVALUATION OF Ce-Mn-Cu MIXED OXIDE CATALYST FOR SELECTIVE OXIDATION OF CO IN AUTOMOBILE ENGINE EXHAUST: EFFECT OF Ce/Mn LOADING CONTENT ON CATALYTIC ACTIVITY

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ABSTRACT

A series of Mn-doped CeO₂-CuO catalyst (CeO₂-MnO_x-CuO) (Ce/Mn molar ratio of 0.5, 1.0 2.0 and 3.0) were prepared using co-precipitation method for the selective oxidation of CO in automobile engine exhaust. The content of copper was 5.0 wt. % in each sample. Catalysts were installed on the automobile engine exhaust and CO amount was recorded with help of CO sensor, with and without the catalyst. The catalytic converter efficiency was estimated for each catalyst through efficiency formula. It was observed that Ce/Mn catalyst with a molar ratio of 2.0 shows the maximum efficiency (88.35%). Stability of conversion process was analyzed by plotting the CO amount with respect to time. The catalyst with Ce/Mn molar ratio of 2.0 performed the most streamline conversion process with least deviations.

Keywords: base metal oxide catalyst, catalytic converter, CO sensor, CO-precipitation, catalytic activity.

INTRODUCTION

With an increase in the concentration of vehicles on the road, environmental problems have become a huge issue nowadays. Catalytic converters are the best solutions to cover the toxic automobile exhaust pollutants. Due to the broad application in reducing destructive gases from versatile sources, catalytic oxidation of CO has been examined for a few decades [1]. The precious metal catalyst was initially synthesized for CO oxidation, which offers amazing reactant properties at low temperatures. But their huge cost due to the use of precious metals in catalytic technology, limits the commercial use of catalytic converters [2, 3]. History of the catalytic converter has its roots from the first catalytic converter which was implemented by Ford in California in 1974, after series of developmental stages and field tests [4].

Nowadays research is in the pipeline to develop cost-effective catalytic converters for automobiles by using base metals as raw materials. Oxides of Ce have been widely used in oxidation and reduction catalytic reactions because of their excellent oxygen storage/release capacity [5]. It has applications in the oxidation of CO and water-gas shift reaction, low energy reduction of NO, oxidation of NH₃ and methanol dehydrogenation [6, 7]. Improvement in the oxygen storage and release capability of catalyst material lead to the improved performance of the catalyst.[8]. It has been verified that synthesizing the composite like mixture in oxide matrix by adding another base metal increases the chemical and physical catalytic properties of catalyst and enhance its oxygen storage capacity [9]. Doping of Mn in CeO₂ has been reported as an excellent choice to enhance catalytic properties [10, 11]. Researchers reported that addition of Mn and Fe to

the CeO₂-CuO, stabilize the solid solution in the structure and improve the catalytic activity in CO oxidation reactions while Co and Cr impaired the secondary interaction between Cu and Ce and decrease their redox ability [12]. Zhao et al. reported that CuO is most effective in the catalyst when it is lower than 5% by mass. At this composition, Cu species formed the solid solution with Ce-Mn-O that means that they were well dispersed to perform the high efficiency in the catalytic process. At higher percentage of CuO, larger particles were formed. Manganese creates the interaction with ceria, copper and manganese so the valence state and reducibility of material changed. This increases the efficiency of catalyst [7]. Another researcher synthesized the CuO/Ce_{0.6}Zr_{0.4}O₂ with different CuO loading content with impregnation method to analyse the effect of loading content of CuO and found that the best efficiency of catalyst was at 10wt.% of CuO [13].

The structure of the catalyst also plays an important role in the catalytic efficiency. Synthesis of metal foam made by Ni, Cu and Ce oxides catalysts were reported by Peng et al. which consists of macroporous hierarchical structures for the catalytic oxidation of CO. They reported that the highest stability and catalytic activity was recorded for the Ce/Cu molar ratio of 10. This was because of the high surface area of macroporous foam and three-dimensional configuration in the catalyst structure [14]. Another research shows that spinal structure of Co-Mn mixed oxide was synthesized by control decomposition of blended oxalates close to 200 °C, trailed by calcination at 300 °C. They had an amorphous structure with 0.9 molar fraction of cobalt. Their crystallite size grew when cobalt fraction was increased and ultimately spinal structure was formed. The high catalytic activity of this catalyst was depended on both the surface area and cobalt concentration [15].

Besides the composition and structure of catalysts, other parameters like synthesis method, preparation conditions and calcination also affect the catalytic efficiency. Park et al. synthesize CeO₂ catalyst doped with Ni/Cu/Co and then pre-heated them in nitrogen and hydrogen environment before the activity test for the oxidation of CO. They found that preheating of catalysts in such environment decreases catalytic efficiency [16]. Lee et al. have studied the effect of calcination temperature on the catalytic oxidation activity of Ce/TiO₂ catalysts. They found that the Ce/TiO₂ catalyst shows the highest catalytic activity if calcined at 400°C

[17]. Liu et al. studied the effect of calcination on Cu-Co-Ce-O catalyst and reported that the catalyst had structural transformations as the calcination temperature changed and the respective catalyst showed the highest CO oxidation activity at 600°C [18]. Gu et al. studied the effect of synthesis method on the CeO₂-ZrO₂-Fe₂O₃ mixed oxide catalysts for soot combustion in diesel engines. They found that co-precipitation method produces a pure solid solution of Ce-Zr-Fe-O. Other methods like hydrothermal method, sol-gel, citric acid impregnation method and physical mixture method produce free FeO₃ and a solid solution of Ce-Zr-Fe-O and they enhance the catalytic activity by acting synergistically [19].

In the current research, we prepared the base metal catalyst of Ce-Mn-Cu mixed oxide by co-precipitation method for the selective oxidation of CO. Loading content of CuO was fixed at 5.0% by mass as it was already reported for the best efficiency in Ce-Cu-Mn-O catalysts [7, 20]. Effect of Ce/Mn molar ratio on the catalytic activity was investigated. Stability of oxidation process of these catalysts was also studied in this research.

EXPERIMENTAL SECTION

Preparation of Catalysts

Co-precipitation method was used for the synthesis of catalysts. Catalysts were prepared in four different molar ratios. Sulphates of Cu, Ce and Mn of SIGMA-ALDRIGE manufacturer were mixed separately in distilled water to make specific molar solutions of these salts according to Table 1. The amount of copper was fixed to 5.0 wt. % of the total weight of salts in the catalysts. The amount of Ce and Mn were varied at different molar ratios to analyze the effect of their loading content in the catalysts. Complete compositions of catalysts are shown in Table 1.

These solutions were then magnetically stirred for 30 minutes at 1150 rpm as shown in Fig. 1.

Table 1. Composition of Catalysts

Catalyst	Cu	Ce	Mn
Catalyst A	5.0 wt. %	0.5 M	0.5 M
Catalyst B	5.0 wt. %	0.5 M	1 M
Catalyst C	5.0 wt. %	1 M	0.5 M
Catalyst D	5.0 wt. %	1 M	1 M

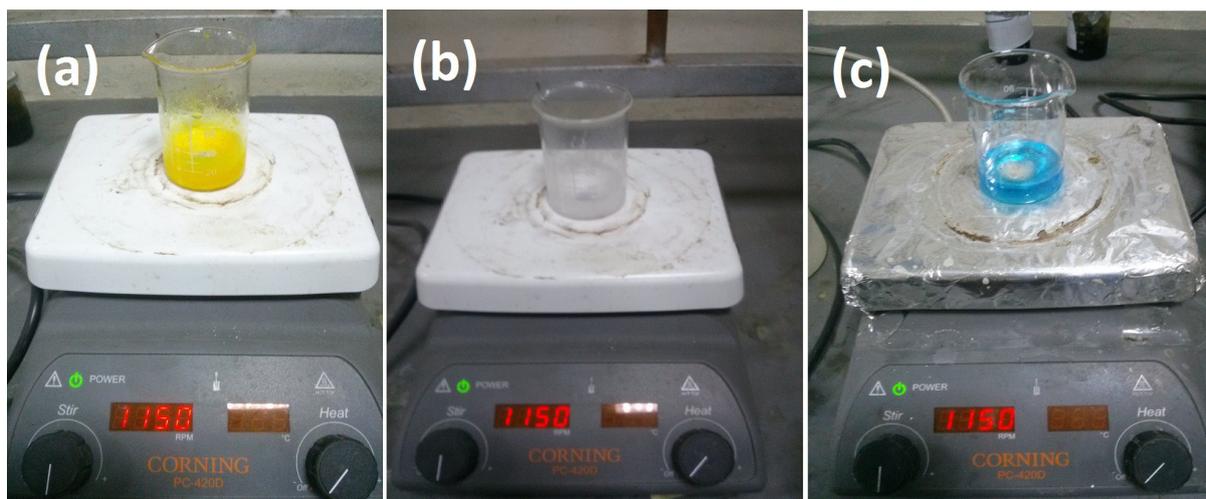


Fig. 1. Shows the stirring of (a) Cerium Sulphate, (b) Manganese Sulphate and (c) Copper Sulphate solutions at 1150 rpm



Fig. 2. Indicates the precipitation in the solutions

Solutions of Cu, Ce and Mn were then mixed in a single container and magnetically stirred for 20 min at 4500 rpm. This step changed the colour of the solutions to dark brown indicating that precipitation had occurred as shown in Figure 2.

Mixed solutions of Cu, Ce and Mn were then left for further precipitation for 12 hr. Precipitates were filtered out with vacuum filter and dried in an oven at 110°C for 12 hr.

Characterization

Characterization was performed by scanning electron microscopy SEM and electron dispersion spectroscopy EDS. To characterize the powder sample, suspensions of the catalyst particles were made in the acetone. Loading ratio of particles in the suspension was 0.5 g per 100 ml of acetone. The suspension was applied on the silicon wafer proceeded with drying at 30°C to study under the scanning electron microscope.

Fabrication of Catalytic Converter

Dried precipitates of nano metal oxide were ground with acetone to make a slurry and then coated on triaxial ceramic gaze substrate with hand layup as shown in Fig. 3. The concentration of catalyst particles in suspension was 0.5 g per 100 ml of acetone. Loading content of suspension on the substrate was 5ml per inch square of the substrate surface area. Catalysts were then dried in an oven at 100°C for 24 hours to remove any moisture content. Catalysts on the ceramic substrate were fixed in closed channels to pass automobile engine exhausts gases from them as shown in Fig. 4.

Performance Evaluation of Catalyst

Testing was performed on the 70 cc petrol motorcycle engine exhaust as shown in Fig. 5. Catalysts were installed in the closed channels and engine exhausts gases were allowed to pass through

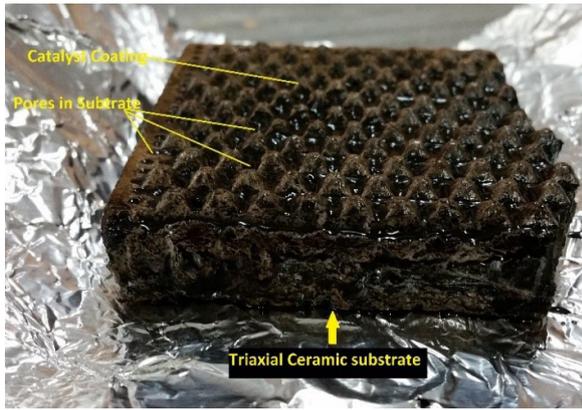


Fig. 3. Catalyst coated on the triaxial porous ceramic substrate

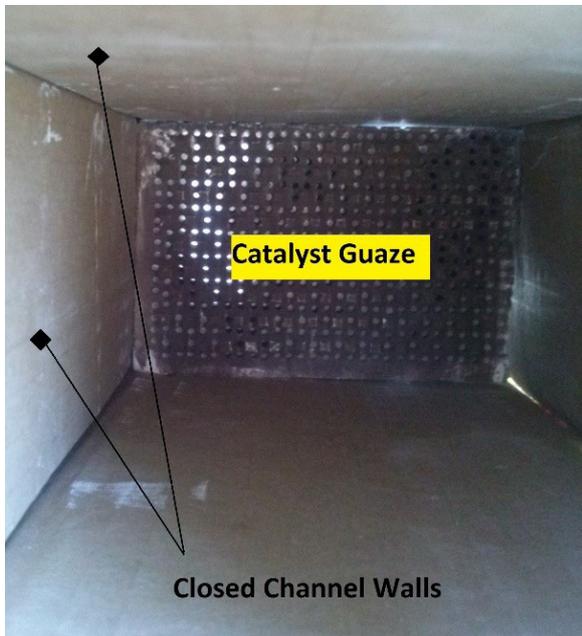


Fig. 4. Inside view of catalytic converter

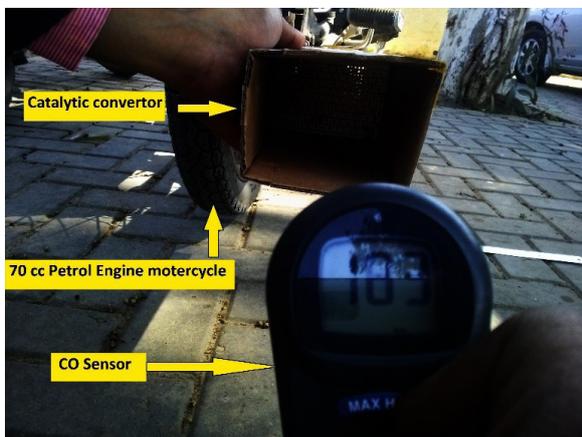


Fig. 5. Testing of catalytic converter

them at the cross-sectional area of $3 \times 2 \text{ in}^2$. CO sensor of model CO-220 of FLUKE manufacturer was used at distance of 2 cm from the exhaust end to measure the amount of CO in ppm, before and after the installation of the catalytic converter.

RESULTS AND DISCUSSIONS

Scanning Electron Microscopy

Scanning electron micrographs (SEM) revealed that the co-precipitation method used in current research for the synthesis of the catalyst, produced particles of 400–500 nm radius as shown in Fig 6 (d).

Electron Dispersion Spectroscopy

Electron dispersion spectroscopy (EDS) results provide the evidence for the presence of elements O, Ce, Mn, Cu and Si. O, Ce, Mn and Cu peaks as shown in Fig. 7 (b), shows the presence of the Ce, Mn and Cu mixed oxide catalyst. Si peak was due to the silicon wafer which was used as a substrate in the EDS analysis.

Conversion Efficiency Monitoring

Catalysts prepared with different compositions were evaluated on the 70 cc petrol engine motorcycle by installing the catalyst inside the engine exhaust. The amount of carbon monoxide was quantitatively analysed with help of carbon monoxide sensor. The amount of CO was measured after every interval of 5 seconds for 25 minutes for each catalyst. The average and standard deviation were calculated for the amount of CO recorded during testing as shown in Table 2 below.

Results show that the catalyst of the mixed oxides of base metals performs the oxidation and their efficiency strongly depends on the molar ratio of the catalyst. The copper content was fixed in all the compositions at 5% by mass. The amount of

Table 2. Amount of CO Recorded for catalysts

Catalyst	CO Amount (ppm)
Without Catalyst	914 ± 41.23
0.5Ce:0.5Mn-5wt%Cu	166.64 ± 25.93
0.5Ce:1Mn-5wt%Cu	396.84 ± 39.92
1Ce:0.5Mn-5wt%Cu	106.44 ± 9.78
1.5Ce:0.5Mn-5wt%Cu	251.28 ± 23.73

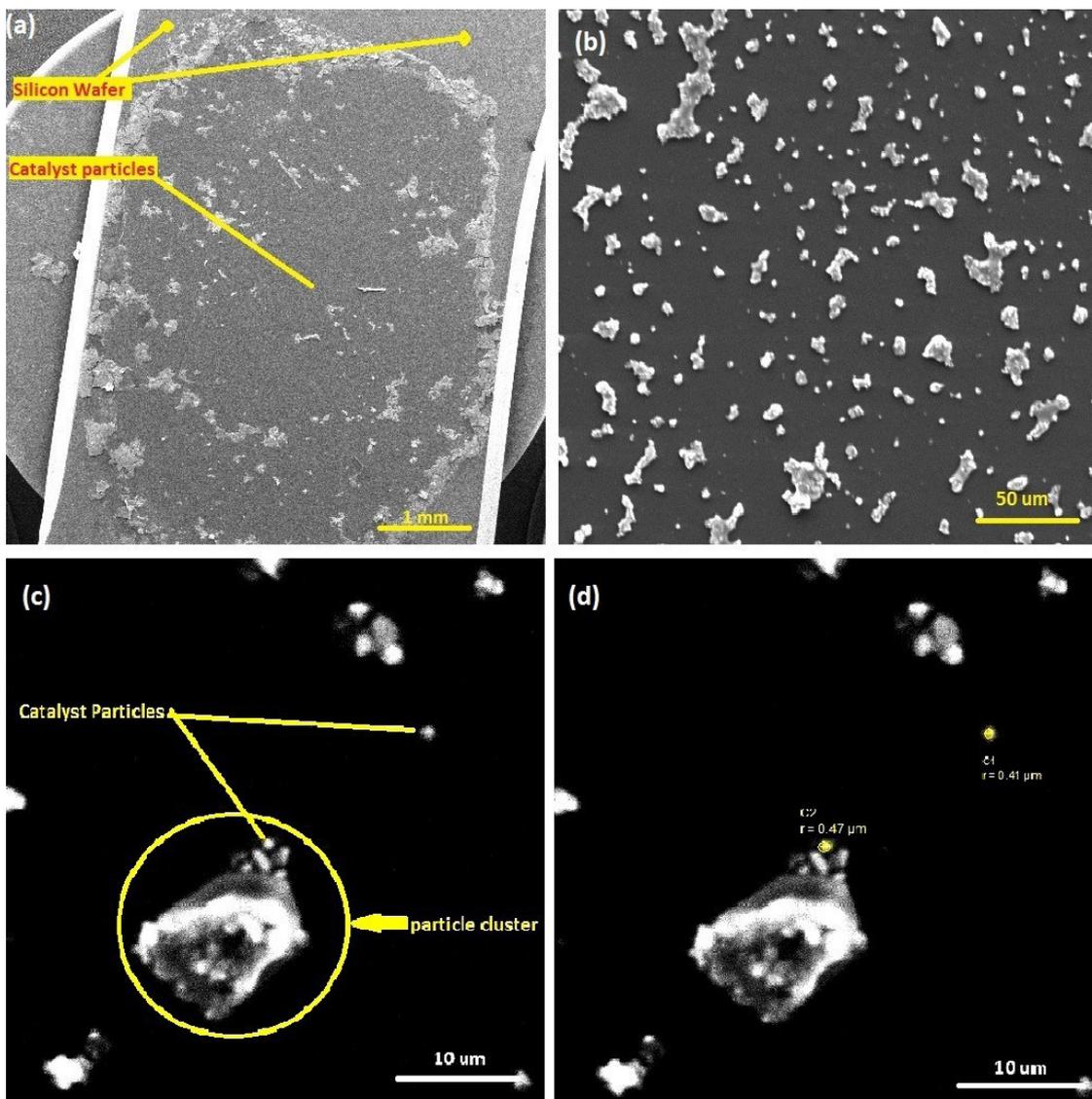


Fig. 6. (a) Overview of the sample. (b) SEM Image of catalyst particles and clusters at 50 μm. (c) SEM image of catalyst particles and clusters at 10 μm. (d) Size of catalyst particles

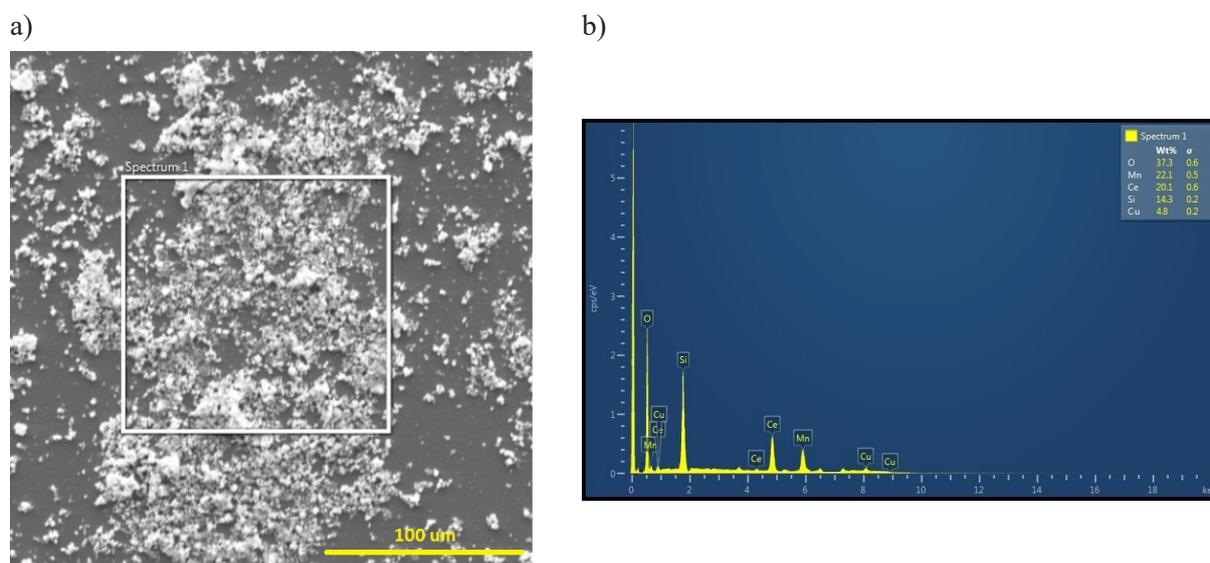


Fig. 7. (a): Catalyst particles during EDS analysis (b): EDS Analysis report of the catalyst

Mn and Ce were varied to study their loading effect on catalytic activity. As the Ce/Mn molar ratio decreases to 0.5, catalytic activity shows the decreasing trend. When Ce/Mn molar ratio increases to 2, it enhances the catalytic oxidation process of CO. Cerium has the main role in this catalyst due to its excellent oxygen storage/release capability. Doping of Mn with Ce-O enhances its activity by stabilizing the solid solution of Ce-Cu-Mn-O [12]. Catalytic activity results of the current research confirm this role of Mn in Ce-Mn-Cu-O catalysts. Further increase in the Ce/Mn molar ratio to 3, decreases the efficiency of catalyst to some extent but it was still more efficient than the Ce/Mn molar ratio of 0.5. This indicates that the maximum efficiency of Ce-Mn-Cu mixed oxide catalyst lies in between the Ce/Mn molar ratio 2 and 3.

Percentage efficiency was calculated with the following efficiency formula [20].

$$\frac{\text{Initial amount of CO} - \text{Final Amount of CO}}{\text{Initial amount of CO}} \times 100$$

Results perspective were made clear by calculating the efficiency and comparing it with Ce/Mn molar ratio as shown in Fig. 9. The minimum efficiency of 56.58% conversion was recorded at the Ce/Mn molar ratio of 0.5. Efficiency increases to 81.76% then 88.35 % at the Ce/Mn molar ratios of 1 and 2 respectively. The efficiency was decreased when the molar ratio of Ce/Mn increased to 3.0, indicating that further increase in molar ratio of Mn, forces it to act as an inhibitor in the respective catalyst.

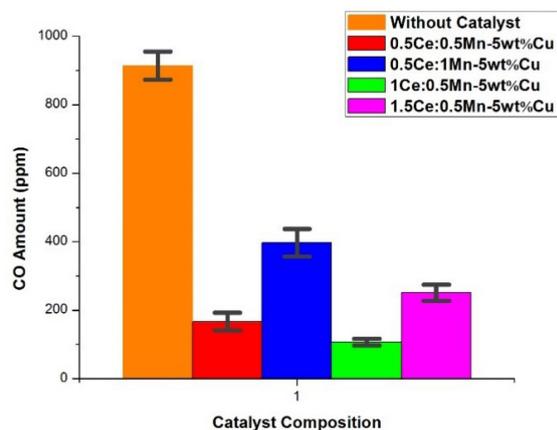


Fig. 8. Amount of CO in ppm recorded for each catalyst

Conversion Process Stability

The amounts of CO in the catalytic conversion process of different catalysts were plotted versus time to analyze the stability of the catalytic activity as shown in Fig. 10.

Ce/Mn catalyst with 2.0 molar ratio performed the most streamline conversions and the Ce/Mn with molar ratio 0.5 showed the unstable conversion process. CO amount in Fig. 10 varies widely with time for the catalyst with 0.5 molar ratio of Ce/Mn and deviated less with respect to time in the catalyst with 2.0 molar ratio of Ce/Mn. CO amount by other catalyst showed approximately the same extent of deviation with respect to time. An assumption can be evolved from the current results that the streamline conversion behaviour also depends on the composition of the catalyst but a further integrated research needs to be conducted to confirm this assumption.

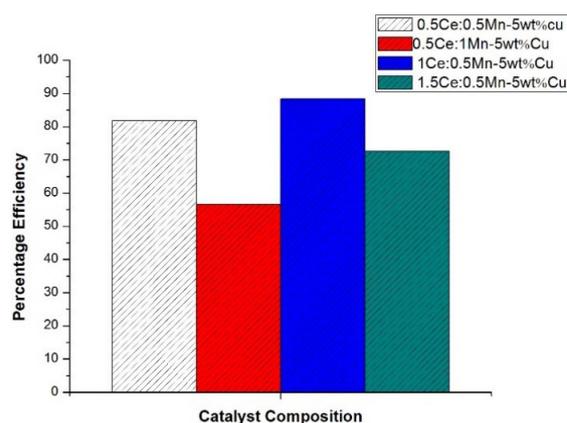


Fig. 9. Activity efficiency comparison of different catalysts

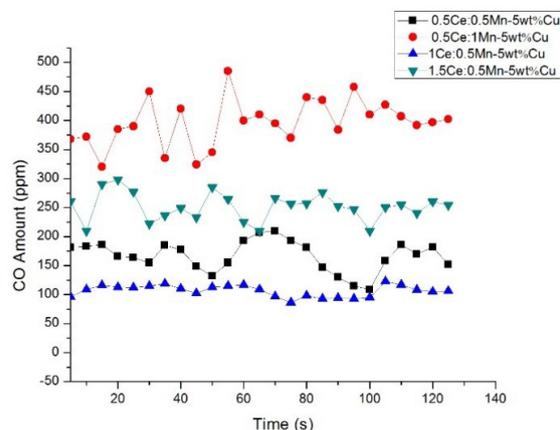


Fig. 10. CO amount for different catalyst with respect to time

CONCLUSION

SEM results reveal the co-precipitation method used in the current research produce the Ce-Mn-Cu mixed oxide catalyst particles of 400–500 nm radius. EDS results confirm the presence of Ce, Mn, Cu and O in the catalyst. Mn doping stabilizes the solid solution in the Ce-Mn-Cu mixed oxide catalyst and increases its efficiency. After reaching the maximum efficiency for Ce/Mn molar ratio of 2.0, Mn starts to act as an inhibitor in the catalyst. The further increase in the molar ratio decreases the efficiency as in Ce/Mn molar ratio of 3.0. It can be assumed that the maximum efficiency of the Ce-Mn-Cu-O strongly depend on the Ce-Mn molar ratio and lies in between the Ce/Mn molar ratio of 2.0 and 3.0. Further research in future would narrow this range for the critical molar ratio of Ce/Mn for the highest efficiency. Ce/Mn (2:1) showed the most streamline and smooth catalytic activity with least deviation of CO amount recorded with respect to time.

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