

## Effect of (Ce, Ag and Au) doping on catalytic activity of $\text{Cu}_1\text{Mn}_8$ catalysts

### 8. General

Addition of low level of promoters into the  $\text{CuMnOx}$  catalyst has proven beneficial in other oxidation catalysts. The improved catalyst performance at the higher doping level is found to associate with the observed increase in surface area. There are many attempts has been made to improve the performance of  $\text{CuMnOx}$  catalyst, in particular by optimizing the preparation conditions and exploring new preparation method [Hutchings *et al.*, 1996]. The addition of gold into the  $\text{CuMnOx}$  catalyst, the rate of CO oxidation is increase, and the rate of deactivation of the catalyst has been reduced [Cole *et al.*, 2010]. When ceria is doped into the transition metal oxides, *in situ* forming ceria oxide could promote oxygen storage and release, enhance oxygen mobility and improved redox property of the catalyst [Zhang *et al.*, 2010].  $\text{CeO}_2$  plays a crucial role in  $\text{Cu-CeO}_2$  catalyst for the total oxidation of CO, exhibiting a particular activity of the various orders of magnitude superior to that of conventional Cu-based catalysts and even comparable to precious metals [Kundakovic and Stephanopoulos 1998; Cao *et al.*, 2008]. A solution of  $\text{AuCl}_4$  is adjusted to the desired pH and gold precipitated onto an indistinct support material by controlled addition of a base [Perrault and Chan 2009]. The inclusion of gold into the nano-rods of rutile, specially prepared in a flowerlike structure, had been reported very high thermal stability (of the gold), most probably due to the substantially reduced gold-gold nano-particle interactions [Khoudiakov *et al.*, 2005].

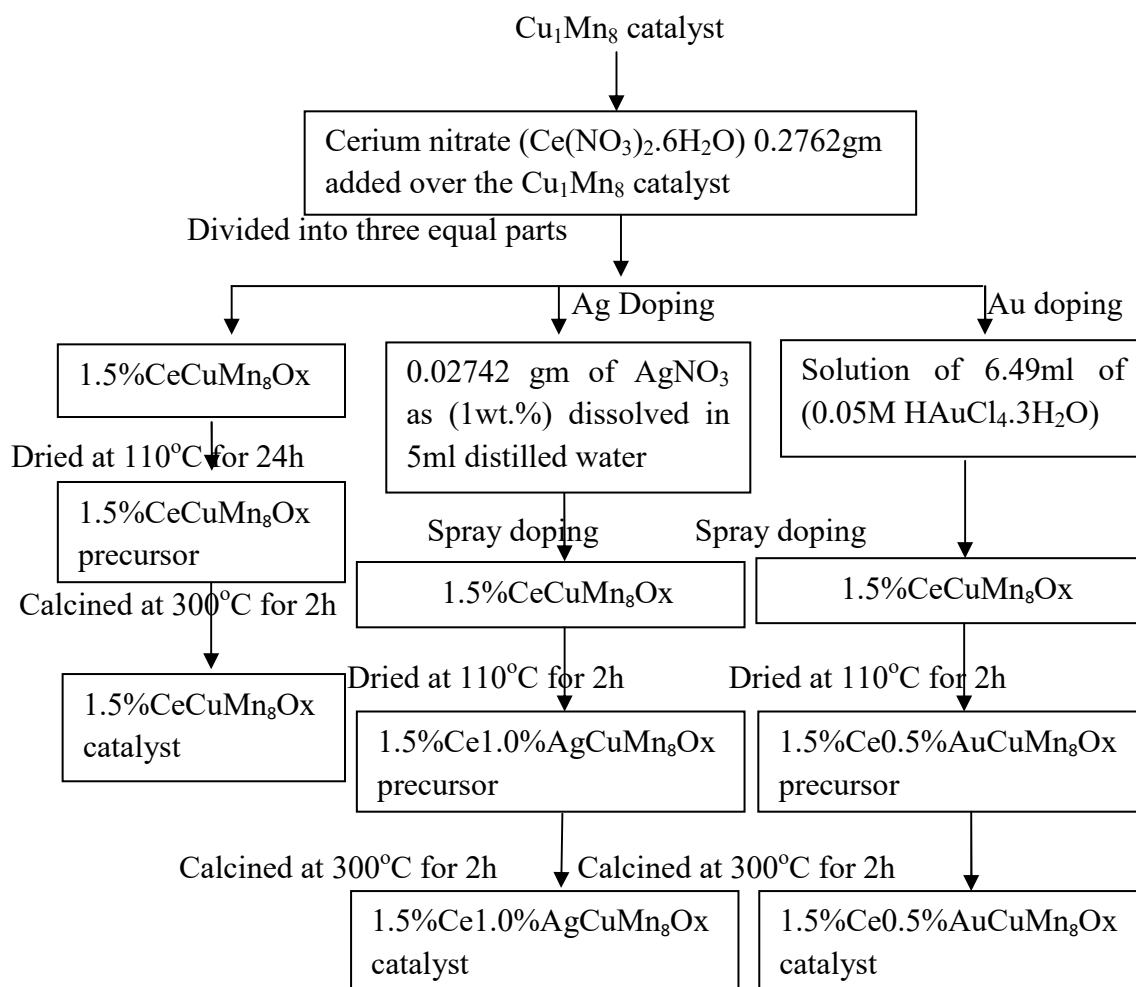
The preparation of catalyst has a crucial role in the performance of resulting catalyst. Addition of Au or Ag into the 1.5% $\text{CeCuMn}_8\text{Ox}$  catalyst has resulted in a marked

improvement in the catalytic performance. The 1.5%CeCuMn<sub>8</sub>O<sub>x</sub> catalyst doped with Au was more active than those that did not contain Au. The results and discussions clearly demonstrate that the precious effect of adding Au to promote CO oxidation activity [Morgan *et al.*, 2010; Solsona *et al.*, 2004]. The main object of this research work to get the effect of noble metal doping into the Cu<sub>1</sub>Mn<sub>8</sub> catalyst can modify the CO adsorption ability of the catalyst. Stagnant air calcination (SAC) of Cu<sub>1</sub>Mn<sub>8</sub> catalyst doped with (Ce, Ag or Au) for the preparation of highly active catalysts for CO oxidation was studied for the first time. This chapter discussed about the addition of noble metal doping into Cu<sub>1</sub>Mn<sub>8</sub> catalyst can modify the CO adsorption ability of the catalyst.

## **8.1 Experimental**

### **8.1.1 Catalyst preparation**

The Cu<sub>1</sub>Mn<sub>8</sub> catalyst was prepared by the co-precipitation method, as discussed earlier in the Chapter 4. Ceria was added in the form of cerium nitrate (Ce(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O) 0.2762gm over the Cu<sub>1</sub>Mn<sub>8</sub> catalyst at the time of precipitation process so that the ceria concentration was made 1.5wt.% by the weight of final catalyst. The precipitate was filtered and washed several times with hot distilled water to eliminate all the anions. After washing dry the precursor at 110°C temperature for 24h into an oven. The preparation of doped Cu<sub>1</sub>Mn<sub>8</sub> catalyst by wet impregnation method was shown in the Figure 8.1. After completing the drying process divided the precursors into two equal's parts according to the weight of catalyst. In the first part, we added 0.02742 gm of AgNO<sub>3</sub> as (1wt.%) in 3.7047 gm of 1.5%CeCuMn<sub>8</sub>O<sub>x</sub> catalyst by wet impregnation method and the second part; we added 6.49ml of (0.05M H<sub>2</sub>AuCl<sub>4</sub>.3H<sub>2</sub>O) in 3.7047 gm of 1.5%CeCuMn<sub>8</sub>O<sub>x</sub> catalyst by wet impregnation method. The nomenclature of the resulting catalysts thus obtained after calcination process was given in table 8.1.



**Figure 8.1:** Preparation of doped  $Cu_1Mn_8$  Catalysts by wet impregnation method

The entire precursor was carried out in a furnace at a stagnant air calcination conditions at  $300^\circ C$  for 2h to produce the catalyst and after calcination it was stored in an airtight glass bottle.

**Table 8.1:** Nomenclature of prepared catalysts

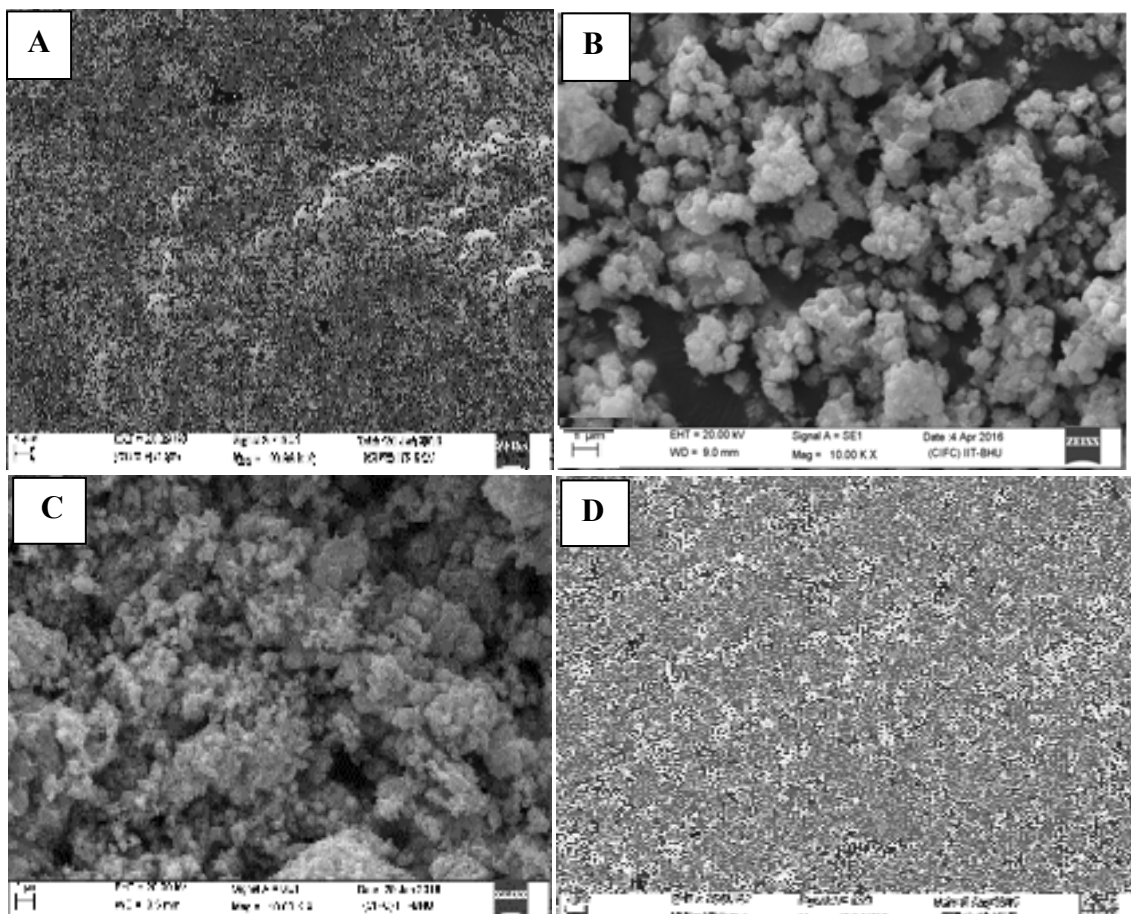
Catalyst Name	Nomenclature
CuMnOx catalyst	$Cu_1Mn_8$
$Cu_1Mn_8$ catalyst cerium doping 1.5wt.% by impregnation method	1.5%CeCuMn <sub>8</sub> Ox
1.5%CeCuMn <sub>8</sub> Ox catalyst silver doping 1wt.% by impregnation method	1.5%Ce1.0%AgCuMn <sub>8</sub> Ox
1.5%CeCuMn <sub>8</sub> Ox catalyst gold doping 0.5wt.% by impregnation method	1.5%Ce0.5%AuCuMn <sub>8</sub> Ox

## **8.2 Catalyst Characterization**

Characterization of the doped and un-doped Cu<sub>1</sub>Mn<sub>8</sub> catalyst reveals their morphology, surface structure, phase identification, material identification and surface area etc. All the catalysts prepared in stagnant air calcination conditions were done by the different techniques and their activity for CO oxidation was discussed below:

### **8.2.1 Morphological analysis**

The SEM image showed that the particle size and morphology of the resulting doped and un-doped Cu<sub>1</sub>Mn<sub>8</sub> catalyst. In SEM micrograph the particles were present in a catalyst was comprised of more coarse, coarse, fine and finest size grains resulted by stagnant air calcination of Cu<sub>1</sub>Mn<sub>8</sub>, 1.5%CeCuMn<sub>8</sub>Ox, 1.5%Ce1.0%AgCuMn<sub>8</sub>Ox, and 1.5%Ce0.5%AuCuMn<sub>8</sub>Ox catalyst, respectively. Figure 8.2 (A), (B), (C) and (D) shows that the SEM image of Cu<sub>1</sub>Mn<sub>8</sub>, 1.5%CeCuMn<sub>8</sub>Ox, 1.5%Ce1.0%AgCuMn<sub>8</sub>Ox and 1.5%Ce0.5%AuCuMn<sub>8</sub>Ox catalyst respectively. The entire catalyst sample was composed of different size of particles. The SEM image of the catalysts derived from calcination of these precursors. In the presence of higher oxidation state phases could be the result of a greater degree of surface interface between the easily oxidisable Mn-phase and the highly reducible Cu-phase. The presence of particles in a 1.5%Ce1.0%AgCuMn<sub>8</sub>Ox and 1.5%Ce0.5%AuCuMn<sub>8</sub>Ox catalyst have a fine size, less agglomerated, and more uniform as compared to the other catalysts. The size of particles present in a Cu<sub>1</sub>Mn<sub>8</sub> catalyst was more coarse, agglomerated and non-uniform in nature.

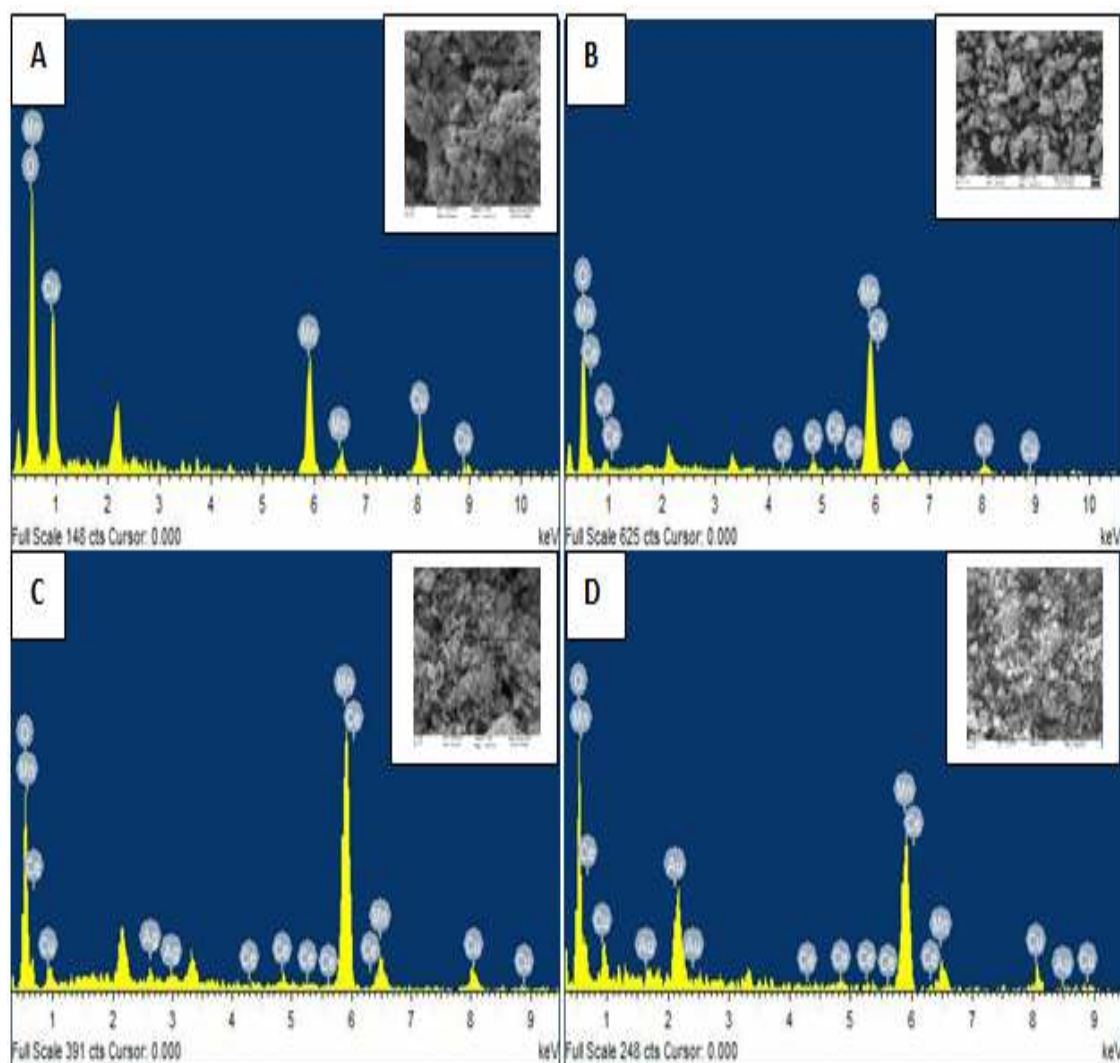


**Figure 8.2:** SEM image of (A)  $\text{Cu}_1\text{Mn}_8$ , (B)  $1.5\%\text{CeCuMn}_8\text{Ox}$ , (C)  $1.5\%\text{Ce}1.0\%\text{AgCuMn}_8\text{Ox}$  and (D)  $1.5\%\text{Ce}0.5\%\text{AuCuMn}_8\text{Ox}$  catalysts

The crystalline  $\text{Cu}_1\text{Mn}_8$  phases have a less activity than the amorphous ones, and the high activity of doped  $\text{Cu}_1\text{Mn}_8$  catalyst for CO oxidation at a low temperature should be attributed to the active amorphous phase. The addition of Au into the  $1.5\%\text{CeCuMn}_8\text{Ox}$  catalyst had a valuable effect on their stability. The stability was related to the presence of  $\text{AuOx}$  into the  $1.5\%\text{CeCuMn}_8\text{Ox}$  catalyst, which also promotes their activity. Activity of the catalyst was increased by the addition of cerium, silver or gold into the  $\text{Cu}_1\text{Mn}_8$  catalyst. Doping of  $\text{Cu}_1\text{Mn}_8$  catalyst by lower amounts of silver or gold was more efficient in improving their catalytic activity for CO oxidation. For the catalysts with and without Au, there was a constant decrease of the surface area when the calcination temperature was increased, and this was apparently due to an increase in particle size due to thermal sintering.

### 8.2.2 Elemental analysis

In the  $Cu_1Mn_8$  catalysts, the percentages of different elements were present analysis by the energy dispersive X-ray (EDX) analysis. The results of energy dispersive X-ray analysis (EDX) has showed that all the catalyst samples were pure due to the presence of their relative elemental peaks only as illustrated in Figure 8.3.



**Figure 8.3:** SEM-EDX image of (A)  $Cu_1Mn_8$ , (B)  $1.5\%CeCuMn_8Ox$ , (C)  $1.5\%Ce1.0\%AgCuMn_8Ox$  and (D)  $1.5\%Ce0.5\%AuCuMn_8Ox$  catalysts

**Table 8.2:** Atomic percentage of a catalyst by EDX analysis

$Cu_1Mn_8$	Cu	Mn	O			Cu/Mn
	10.39	54.46	35.15			0.190
1.5%CeCuMn <sub>8</sub> Ox	Cu	Mn	Ce	O		Cu/Mn
	12.81	55.35	1.24	30.60		0.231
1.5%Ce 1.0%AgCuMn <sub>8</sub> Ox	Cu	Mn	Ce	Ag	O	Cu/Mn
	13.14	57.30	1.14	0.72	27.70	0.229
1.5%Ce0.5%Au CuMn <sub>8</sub> Ox	Cu	Mn	Ce	Au	O	Cu/Mn
	17.22	58.70	1.18	0.45	22.45	0.293

**Table 8.3:** Weight percentage of a catalyst by EDX analysis

$Cu_1Mn_8$	Cu	Mn	O			Cu/Mn
	10.38	55.91	33.71			0.185
1.5%CeCuMn <sub>8</sub> Ox	Cu	Mn	Ce	O		Cu/Mn
	10.60	56.90	1.40	31.10		0.186
1.5%Ce 1.0%AgCuMn <sub>8</sub> Ox	Cu	Mn	Ce	Ag	O	Cu/Mn
	11.35	57.45	1.24	0.90	29.06	0.197
1.5%Ce0.5%Au CuMn <sub>8</sub> Ox	Cu	Mn	Ce	Au	O	Cu/Mn
	11.70	58.90	1.36	0.47	27.57	0.198

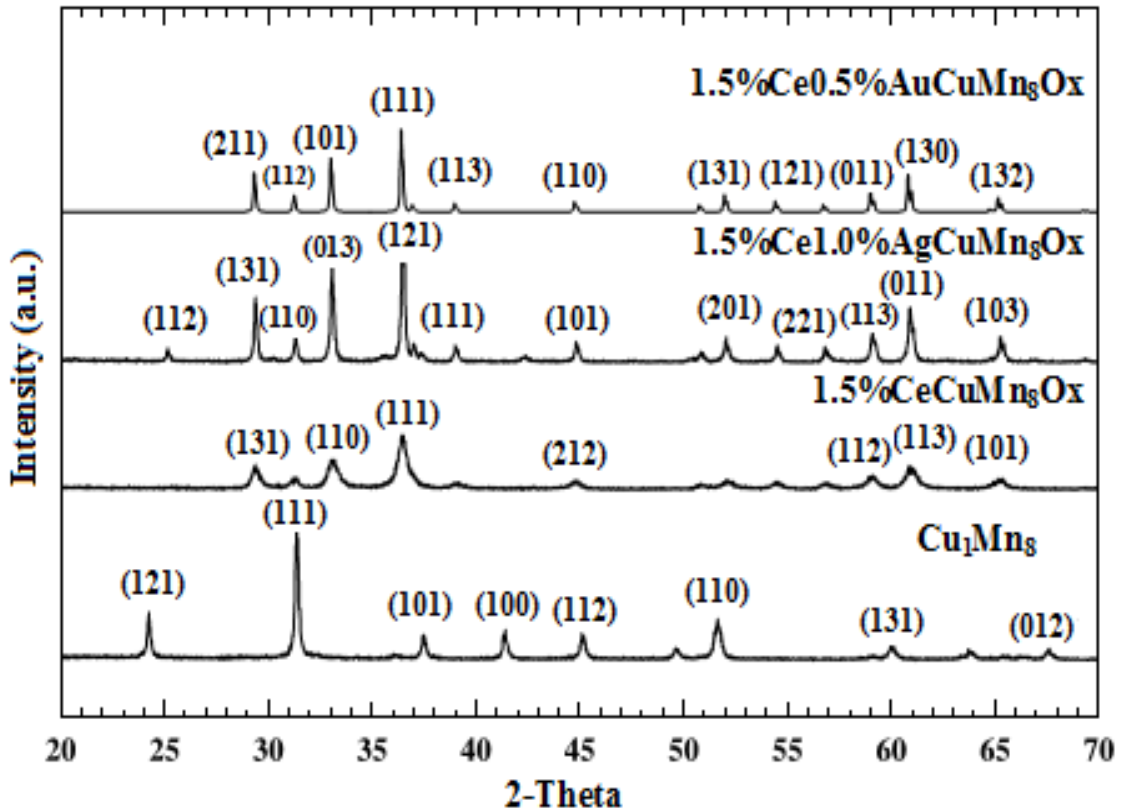
To understand the influence of silver or gold on the activity and stability of the promoted  $Cu_1Mn_8$  catalysts towards CO oxidation, by EDX characterization technique have been carried out. It was clear from the EDX analysis that the atomic percentage of Mn was also higher than Cu in the  $Cu_1Mn_8$  catalyst. The oxygen content of the 1.5%Ce0.5%AuCuMn<sub>8</sub>Ox catalyst was least in comparison to the other catalysts. This

indicates the existence of oxygen deficiency in the 1.5%Ce0.5%AuCuMn<sub>8</sub>Ox catalyst which makes the high density of active sites. The doping materials associated with Cu<sub>1</sub>Mn<sub>8</sub> catalyst to promote the oxygen storage, release and enhanced their oxygen mobility. It was also evident that the addition of silver or gold did not extensively alter the textural properties of the catalysts, but the surface area was increased significantly by the additional of gold. This negligible dispersion indicates that the cell unit of ceria was hardly affecting by the presence of a doping elements. Therefore it was concluded that the dispersed among the ceria crystallites not forming a true solid solution. The catalysts obtained at increasing the heating rates during the calcination step present a slightly decreasing the catalytic activity. It must be noted that a calcination temperature of the catalysts with the presence of gold higher activities and specific activities than the subsequent gold free Cu<sub>1</sub>Mn<sub>8</sub> catalyst.

### **8.2.3 Phase identification and cell dimensions**

XRD analysis of the Cu<sub>1</sub>Mn<sub>8</sub> catalyst doping with Ce, Ag or Au was providing information about the crystallite size and coordinate dimensions presence in the catalysts. Figure 8.4 shows that the XRD analysis of Cu<sub>1</sub>Mn<sub>8</sub>, 1.5%CeCuMn<sub>8</sub>Ox, 1.5%Ce1.0%AgCuMn<sub>8</sub>Ox and 1.5%Ce0.5%AuCuMn<sub>8</sub>Ox catalysts prepared in stagnant air calcination conditions. XRD analysis of the promoted Cu<sub>1</sub>Mn<sub>8</sub> catalyst was used to verify the final phases after heat treatment at calcination conditions. The Cu<sub>1</sub>Mn<sub>8</sub> was come from the interface between the stable re-oxidized CuO and MnO<sub>2</sub> phases and formation take place due to the metal ion concentration of the Cu/Mn oxide phase boundaries to form the spinel structure. In XRD analysis of Cu<sub>1</sub>Mn<sub>8</sub> catalyst, observed that the diffraction peak at 2θ was 32.06 corresponds to its lattice plane (h k l) values was (121), (111), (101), (100), (112), (110), (131) and (012) with JCPDS reference no. (35-0429).





**Figure 8.4:** XRD analysis of the catalysts

The structure was Cubic face-centered  $CuMn_8O_4$  phase with crystallite size of catalyst was 4.70 nm. In 1.5%Ce $CuMn_8Ox$  catalyst diffraction peak at  $2\theta$  was 36.20 corresponds to its lattice plane (131), (110), (111), (212), (112), (113) and (101) with JCPDS reference no. (35-0849). The structure was Body centered  $CuO(Mn)Ce$  phase with crystallite size of catalyst was 2.30 nm. In 1.5%Ce1.0%Ag $CuMn_8Ox$  catalyst diffraction peak at  $2\theta$  was 36.57 corresponds to its lattice plane (112), (131), (110), (013), (121), (111), (101), (201), (221), (113), (011) and (103) with JCPDS reference no. (35-0441). The structure was Tetragonal-body centered  $CuMn(Ce)AgO$  phase with crystallite size of catalyst was 2.06 nm. In 1.5%Ce0.5%Au $CuMn_8Ox$  catalyst diffraction peak at  $2\theta$  was 36.42 corresponds to its lattice plane (211), (112), (101), (111), (113), (110), (131), (121), (011), (130) and (132) with JCPDS reference no. (35-0112). The structure was Cubic face centered  $CuO(MnAu)Ce$  phase with crystallite size of catalyst was 1.65 nm.

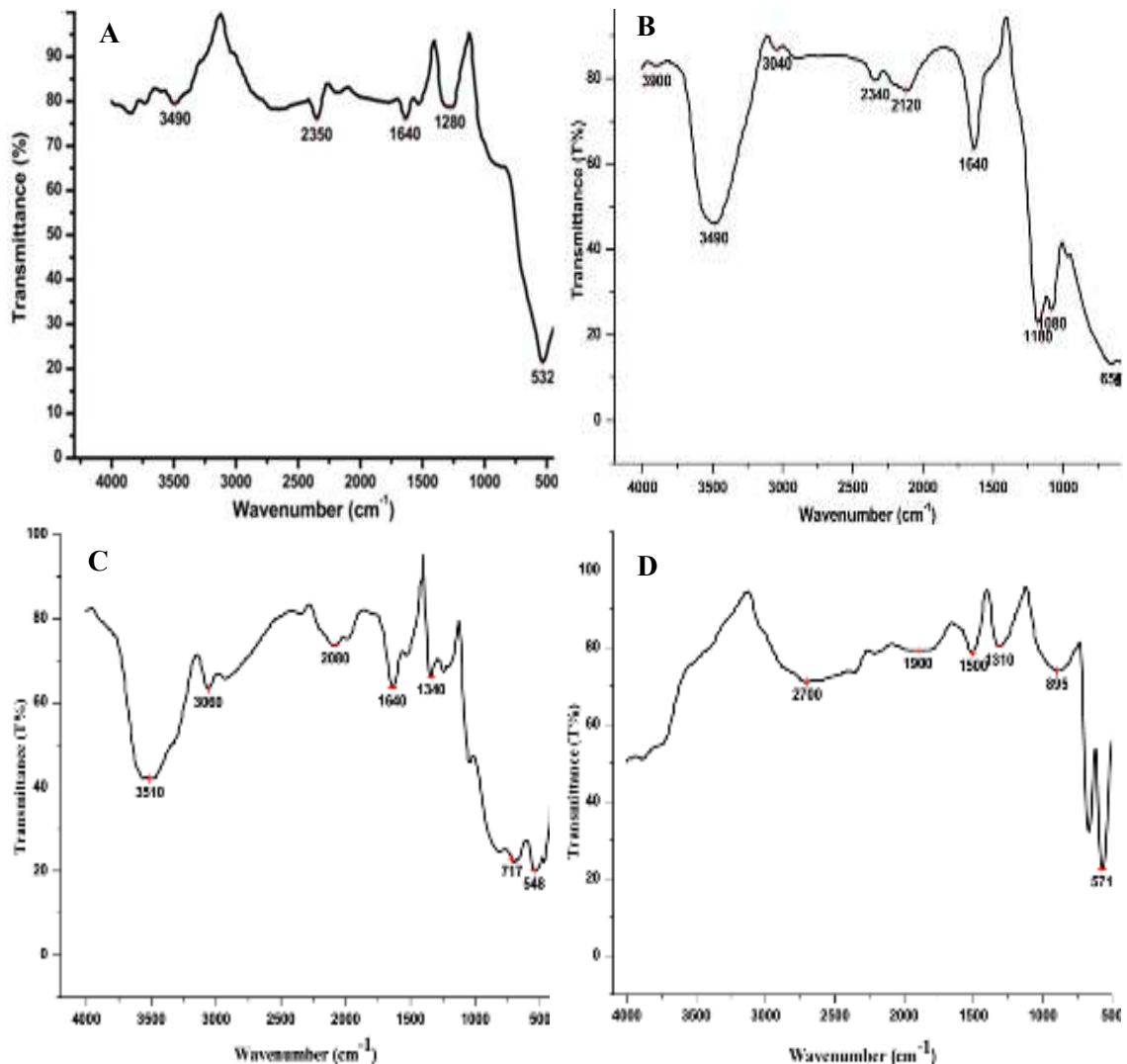
An X-ray diffraction pattern of the 1.5%CeCuMn<sub>8</sub>Ox catalyst has shown that the amorphous and crystalline phases could be clearly identified. The most extreme diffraction peak for metallic Au would be expected at a 2θ value of ca. 36.42 and Au was present in the 1.5%Ce0.5%AuCuMn<sub>8</sub>Ox mainly as Au<sup>0</sup> since the calcination temperature 300°C leads to the reduction of gold. From XRD analysis the crystallite size of particles present in catalysts was as follows: Cu<sub>1</sub>Mn<sub>8</sub> > 1.5%CeCuMn<sub>8</sub>Ox > 1.5%Ce 1.0%AgCuMn<sub>8</sub>Ox > 1.5%Ce0.5%AuCuMn<sub>8</sub>Ox. The highest crystallite sizes of particles were present in Cu<sub>1</sub>Mn<sub>8</sub> catalyst and lowest crystallite sizes of particles were present in 1.5%Ce0.5%AuCuMn<sub>8</sub>Ox catalyst.

After XRD analysis confirmed that the particles present in 1.5%Ce0.5%AuCuMn<sub>8</sub>Ox catalyst were most crystalline form and producing narrow size high-intensity diffraction lines; as compared to other catalysts. The large crystallite size suggests agglomeration due to the in-situ thermal treatment process. XRD peak of 1.5%Ce0.5%AuCuMn<sub>8</sub>Ox catalyst was significantly broader than those of the micrometer-sized sample, indicating that the sample possessed very small size particles. The crystallite size of particles present in catalyst was analysis by the XRD technique was matched with the particle size calculated by the SEM characterization. In further, the experimental results prove that the lower crystallite size of CuMn<sub>8</sub>Ce<sub>FRC</sub> catalyst was highly active for CO oxidation.

#### **8.2.4 Identification of materials**

The metal-oxygen bonds present in the doped Cu<sub>1</sub>Mn<sub>8</sub> catalysts was done by the Fourier transform infrared spectroscopy (FTIR) analysis. The different peaks were shown, various types of chemical group present in the catalyst surfaces at the invested region (4000-400cm<sup>-1</sup>). FTIR analysis was performed to recognize the functional groups of the entire calcined samples. Figure 8.5 (A), (B), (C) and (D) show that the FTIR image of

$\text{Cu}_1\text{Mn}_8$ , 1.5%Ce $\text{CuMn}_8\text{Ox}$ , 1.5%Ce1.0%Ag $\text{CuMn}_8\text{Ox}$  and 1.5%Ce0.5%Au $\text{CuMn}_8\text{Ox}$  catalyst respectively. FTIR analysis of the  $\text{Cu}_1\text{Mn}_8$  catalyst prepared by the stagnant air calcination conditions, there were total five peaks obtained. The transmission spectra at ( $1640\text{cm}^{-1}$ ) has shown the presence of  $\text{Mn}_2\text{O}_3$  group, ( $1280\text{cm}^{-1}$ )  $\text{CO}_3^{2-}$  group, ( $2350\text{cm}^{-1}$ )  $\text{C}=\text{O}$  group, ( $3490\text{cm}^{-1}$ )  $-\text{OH}$  group, and ( $532\text{cm}^{-1}$ )  $\text{CuO}$  group. In the 1.5%Ce $\text{CuMnOx}$  catalyst at the transmittance conditions there were total eight peaks obtained. The IR bands ( $1640\text{cm}^{-1}$ ) has shown the presence of  $\text{Mn}_2\text{O}_3$  group, ( $3490\text{cm}^{-1}$  and  $3900\text{cm}^{-1}$ )  $-\text{OH}$  group, ( $2120\text{cm}^{-1}$  and  $656\text{cm}^{-1}$ )  $\text{CuO}$  group, ( $1180\text{cm}^{-1}$  and  $1080\text{cm}^{-1}$ )  $-\text{COO}$  group and ( $2340\text{cm}^{-1}$ )  $\text{CeO}_2$  group.

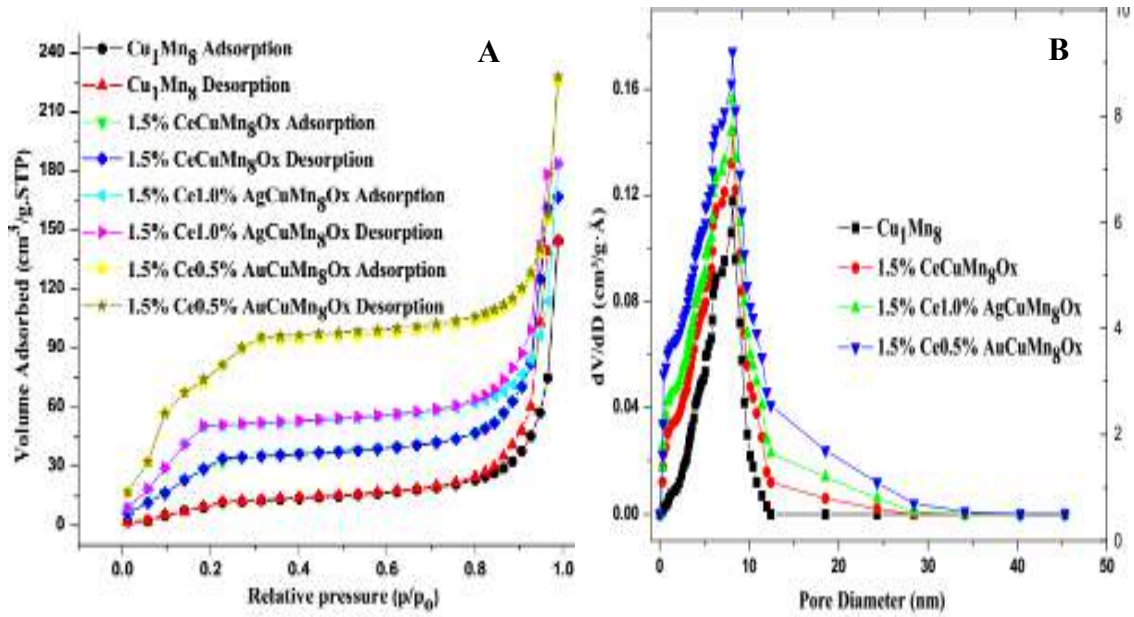


**Figure 8.5:** FTIR analysis of (A)  $\text{Cu}_1\text{Mn}_8$ , (B) 1.5%Ce $\text{CuMn}_8\text{Ox}$ , (C) 1.5%Ce1.0%Ag $\text{CuMn}_8\text{Ox}$  and (D) 1.5%Ce0.5%Au $\text{CuMn}_8\text{Ox}$  catalysts

In the 1.5%Ce1.0%AgCuMn<sub>8</sub>Ox catalyst at the transmittance conditions there were total seven peaks we obtained. The IR band (1640cm<sup>-1</sup>) has shown the presence of Mn<sub>2</sub>O<sub>3</sub> group, (2080cm<sup>-1</sup>) AgOx, (3510cm<sup>-1</sup> and 3060cm<sup>-1</sup>) -OH group, (548cm<sup>-1</sup>) CuO group, and (717cm<sup>-1</sup>)CeO<sub>2</sub> group. In the 1.5%Ce0.5%AuCuMn<sub>8</sub>Ox catalyst at the transmittance conditions there were total five peaks we obtained. The IR band (1900cm<sup>-1</sup>) has shown the presence of Mn<sub>2</sub>O<sub>3</sub> group, (2700cm<sup>-1</sup>)AuO<sub>2</sub> group, (1310cm<sup>-1</sup>) -OH group, (1500cm<sup>-1</sup>) Carbonate species, (571cm<sup>-1</sup>) CuO group, and (895cm<sup>-1</sup>) CeO<sub>2</sub> group. The spectra of impurities like hydroxyl group (-OH) at (3490cm<sup>-1</sup>) decreases in the following order: Cu<sub>1</sub>Mn<sub>8</sub>> 1.5%CeCuMn<sub>8</sub>Ox> 1.5%Ce1.0%AgCuMn<sub>8</sub>Ox> 1.5%Ce0.5%AuCuMn<sub>8</sub>Ox. Thus the 1.5%Ce0.5%AuCuMn<sub>8</sub>Ox catalyst was highly pure as compared to the other catalysts. All the Cu<sub>1</sub>Mn<sub>8</sub> catalysts which originate from the stretching vibrations of the metal-oxygen bond and confirmed the presence of CuO and Mn<sub>2</sub>O<sub>3</sub> phases.

### **8.2.5 Textural properties**

The BET surface area of (CeOx, AgOx or AuOx) promoted Cu<sub>1</sub>Mn<sub>8</sub> catalyst was prepared by the stagnant air calcination conditions as shown in the Figure 8.6. Total pore volume and specific surface area were two major factors which can affect the catalytic activity for CO oxidation. When the activity of the catalyst has been tested, it was found that the 1.5%Ce0.5%AuCuMn<sub>8</sub>Ox catalyst has a higher surface area and pore volume resulted in the maximum CO oxidation. The surface area was a key parameter in determining the catalyst activity for CO oxidation. Activity of the Cu<sub>1</sub>Mn<sub>8</sub> catalyst has highly influenced by the addition of Au or Ag on their surfaces. Textural properties like surface area, pore volume and pore size of 1.5%Ce0.5%AuCuMn<sub>8</sub>Ox catalyst has more efficient for CO oxidation.



**Figure 8.6:** Textural properties of (A) N<sub>2</sub> adsorption-desorption isotherms and (B) Pore size distributions curves.

The larger number of more pores presence in a catalyst surfaces means a larger number of CO molecules capture on their surfaces, and it has to shows the better catalytic activity. The surface area of (1.5%Ce0.5%AuCuMn<sub>8</sub>Ox=129.76m<sup>2</sup>/g) catalyst was much higher than the (1.5%Ce1.0%AgCuMn<sub>8</sub>Ox=115.45m<sup>2</sup>/g, 1.5%CeCuMn<sub>8</sub>Ox = 104.70 m<sup>2</sup>/g and Cu<sub>1</sub>Mn<sub>8</sub> = 85.40 m<sup>2</sup>/g) catalyst as shown in the table and figure.

**Table 8.4:** Textural property of Cu<sub>1</sub>Mn<sub>8</sub> catalysts

Catalyst	Surface Area (m <sup>2</sup> /g)	Pore Volume (cm <sup>3</sup> /g)	Ave. Pore Size (Å)
Cu <sub>1</sub> Mn <sub>8</sub>	85.40	0.310	42.55
1.5%CeCuMn <sub>8</sub> Ox	104.70	0.365	40.70
1.5%Ce1.0%AgCuMn <sub>8</sub> Ox	115.45	0.410	39.35
1.5%Ce0.5%AuCuMn <sub>8</sub> Ox	129.76	0.428	37.65

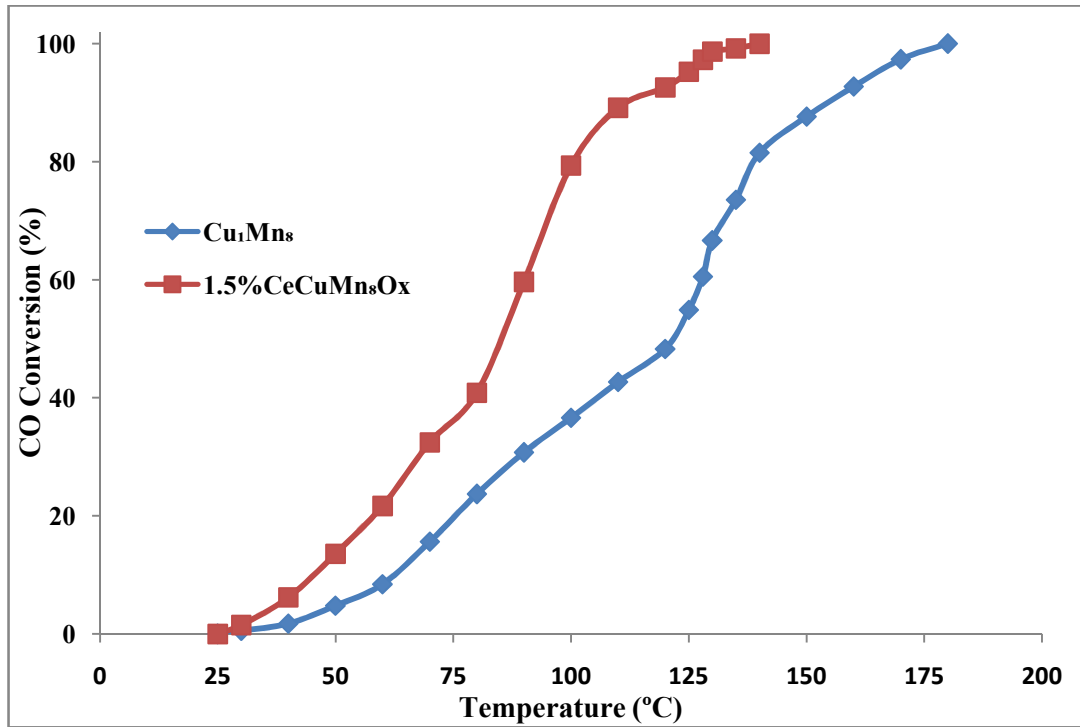
It was also noted that the average pore volume and pore size of 1.5%Ce0.5%AuCuMn<sub>8</sub>Ox catalyst was much superior to the other catalysts. The average pore diameter was also increases with the increasing of calcination temperature because a high-temperature treatment led to particle sintering accompanied with a loss in the active area. In the mesopores, molecules form a liquid-like adsorbed phase having a meniscus of which curvature was associated with the Kelvin equation, providing the pore size distribution calculation. The specific surface area was measured by the BET analysis and it also followed the SEM and XRD results. The 1.5%Ce1.0%AgCuMn<sub>8</sub>Ox and 1.5%Ce0.5%AuCuMn<sub>8</sub>Ox catalyst surface area and pore volume was so high so that it was most active for CO oxidation. The presence of Au in the 1.5%Ce0.5%AuCuMn<sub>8</sub>Ox catalyst increased their stability for long time CO oxidation.

### **8.3 Catalyst performance and activity measurement**

Activity test of the catalyst was carried out to evaluate the effectiveness of different types of doped and un-doped Cu<sub>1</sub>Mn<sub>8</sub> catalysts as a function of temperature. All the catalysts prepared in stagnant air calcination conditions.

#### **8.3.1 Effect of Ceria promoter doping in Cu<sub>1</sub>Mn<sub>8</sub> catalysts**

In the activity test, we have evaluated the performance of Cu<sub>1</sub>Mn<sub>8</sub> and 1.5%CeCuMn<sub>8</sub>Ox catalyst as a function of temperature prepared by stagnant air calcination condition. Improvement in the activity of Cu<sub>1</sub>Mn<sub>8</sub> catalyst, by the addition of ceria was accompanied the increase in the catalyst surface area. The CeO<sub>2</sub> phase presence in a Cu<sub>1</sub>Mn<sub>8</sub> catalyst was accelerating the CO oxidation due to the availability of lattice oxygen. The CO conversion initiated at 40°C over 1.5%CeCuMn<sub>8</sub>Ox catalyst which was less by 15°C over than that of Cu<sub>1</sub>Mn<sub>8</sub> catalyst.



**Figure 8.7:** Activity test of  $\text{Cu}_1\text{Mn}_8$  and 1.5%CeCuMn<sub>8</sub>Ox catalysts

The 50% conversion of CO was achieved at 85°C for 1.5%CeCuMn<sub>8</sub>Ox catalyst which was less by 40°C over than that of  $\text{Cu}_1\text{Mn}_8$  catalyst. The rising of temperature slightly faster CO oxidation was observed on the catalyst. The complete oxidation temperature of CO was 135°C for 1.5%CeCuMn<sub>8</sub>Ox catalyst which was less by 45°C over than that of  $\text{Cu}_1\text{Mn}_8$  catalyst.

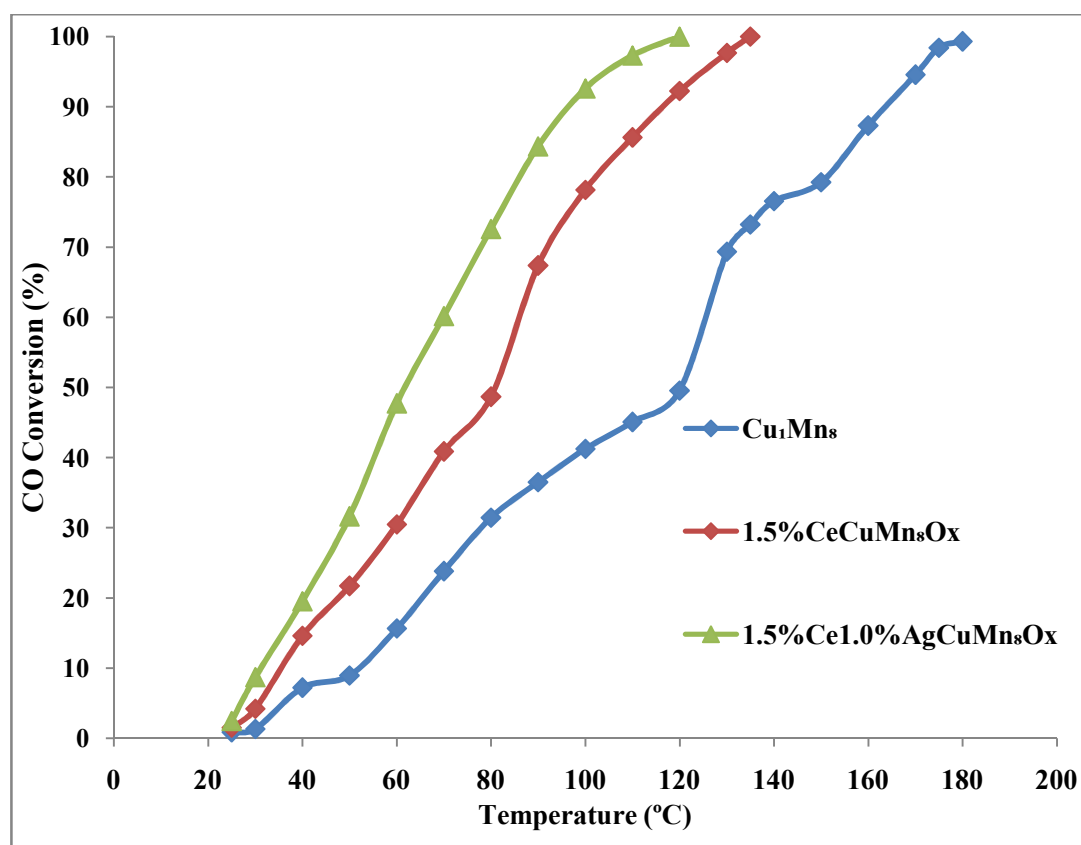
**Table 8.5:** Light off characteristics of ceria doped and un-doped  $\text{Cu}_1\text{Mn}_8$  catalysts

Catalyst	T <sub>10</sub>	T <sub>50</sub>	T <sub>100</sub>
$\text{Cu}_1\text{Mn}_8$	55°C	125°C	180°C
1.5%CeCuMn <sub>8</sub> Ox	40°C	85°C	135°C

From the Table 8.5 and Figure 8.7 we have confirmed that the addition of small amount ceria into the  $\text{Cu}_1\text{Mn}_8$  catalyst has further improving their performance for CO oxidation.

### 8.3.2 Effect of (Ce and Ag) doping in $\text{Cu}_1\text{Mn}_8$ catalysts

The addition of silver into the 1.5%CeCuMn<sub>8</sub>Ox catalyst to improved their performance for CO oxidation. Thus, the  $\text{Cu}_1\text{Mn}_8$  catalyst promoted with AgO and CeO<sub>2</sub> shows a high catalytic activity at a low temperature. The promoters have shown that the greatest effect on the performance of resulting catalyst for CO oxidation. The addition of Ag will introduce the new active sites on the 1.5%CeCuMn<sub>8</sub>Ox catalyst and it also increases the reducibility of the catalyst significantly compared to the un-doped  $\text{Cu}_1\text{Mn}_8$  catalyst. Activity of the surface normalized oxidation rate was similar to the normalized for catalyst mass. Figure 8.8 represents the activity order of  $\text{Cu}_1\text{Mn}_8$ , 1.5%CeCuMn<sub>8</sub>Ox and 1.5%Ce1.0%AgCuMn<sub>8</sub>Ox catalyst for CO oxidation.



**Figure 8.8:** Activity measurement of Ce and Ag doped and un-doped  $\text{Cu}_1\text{Mn}_8$  catalysts

The doped noble metal in  $\text{Cu}_1\text{Mn}_8$  catalysts seems to be quite active for low temperature CO oxidation. An accumulation of Ag was highly dispersing in the various oxides form



of 1.5%CeCuMn<sub>8</sub>Ox catalyst surfaces at the sub-ambient temperature. The oxidation of CO was initiated at 55°C, 40°C and 35°C over than that of Cu<sub>1</sub>Mn<sub>8</sub>, 1.5%CeCuMnOx and 1.5%Ce1.0%AgCuMn<sub>8</sub>Ox catalysts respectively. The 50% conversion of CO was achieved at 70°C for 1.5%Ce1.0%AgCuMn<sub>8</sub>Ox catalyst which was less by 15°C and 55°C over than that of 1.5%CeCuMn<sub>8</sub>Ox and Cu<sub>1</sub>Mn<sub>8</sub> catalyst respectively.

**Table 8.6:** Light off characteristics of Ce and Ag doped and un-doped Cu<sub>1</sub>Mn<sub>8</sub> catalysts

Catalyst	T <sub>10</sub>	T <sub>50</sub>	T <sub>100</sub>
Cu <sub>1</sub> Mn <sub>8</sub>	55°C	125°C	180°C
1.5%CeCuMn <sub>8</sub> Ox	40°C	85°C	135°C
1.5%Ce1.0%AgCuMn <sub>8</sub> Ox	35°C	70°C	120°C

The complete oxidation temperature of CO was 120°C for 1.5%Ce1.0%AgCuMn<sub>8</sub>Ox catalyst which was less than 15°C and 60°C over than that of 1.5%CeCuMn<sub>8</sub>Ox and Cu<sub>1</sub>Mn<sub>8</sub> catalyst respectively. The order of activity of the catalysts matches with their characterization results by XRD, FTIR, SEM-EDX and BET. The interaction of CuO, CeO<sub>2</sub>, Ag<sub>2</sub>O<sub>3</sub> and Mn<sub>2</sub>O<sub>3</sub> with the formation of an exceedingly disordered mixed metal oxide was the cause of higher activity for CO oxidation. The addition of silver promoters into the 1.5%Ce1.0%AgCuMn<sub>8</sub>Ox catalyst, they have an attribute to the larger surface area, amorphous in structure and production of surface adsorbed oxygen it enhances the mobility of lattice oxygen.

### 8.3.3 Effect of (Ce and Au) doping in $\text{Cu}_1\text{Mn}_8$ catalysts

From the activity test, we have observed that the promoting Au into the  $1.5\%\text{CeCuMn}_8\text{O}_x$  catalyst was a great improvement in their catalytic activity. The abundant large pores and specific surface area present in the Au promoted  $1.5\%\text{CeCuMn}_8\text{O}_x$  catalyst has a great potential to further improving their catalytic performance. It was clearly indicated that Au was not only acting as a structural promoter, which consider the high efficiency of highly dispersed Au particles for low-temperature CO oxidation. Figure 8.9 represents the activity order of  $\text{Cu}_1\text{Mn}_8$ ,  $1.5\%\text{CeCuMn}_8\text{O}_x$  and  $1.5\%\text{Ce}1.0\%\text{AuCuMn}_8\text{O}_x$  catalyst for CO oxidation. The  $1.5\%\text{CeCuMn}_8\text{O}_x$  catalyst was highly dispersed in the  $\text{HAuCl}_4$  solution and highly effective for low-temperature CO oxidation.

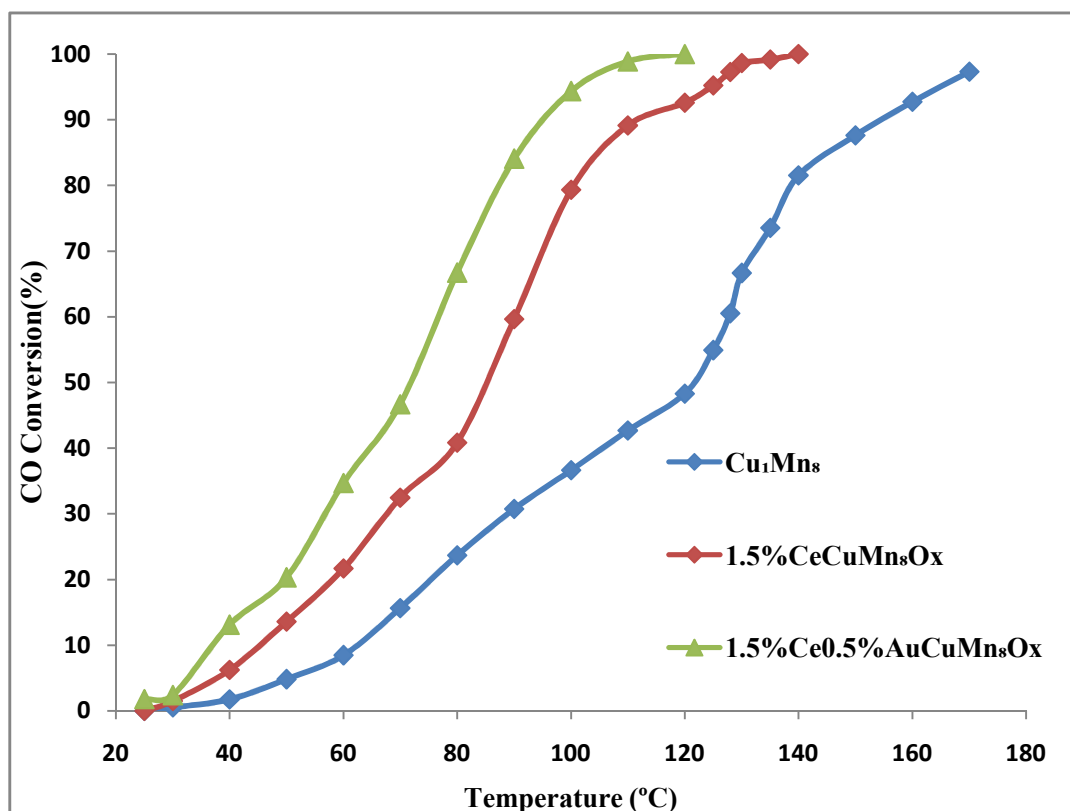


Figure 8.9: Activity measurement of Ce and Au doped and un-doped  $\text{Cu}_1\text{Mn}_8$  catalysts

The oxidation of CO was initiated at 55°C, 40°C and 30°C over the  $Cu_1Mn_8$ , 1.5%Ce $CuMn_8Ox$  and 1.5%Ce0.5%Au $CuMn_8Ox$  catalysts respectively. The 50% conversion of CO was achieved at 65°C over 1.5%Ce0.5%Au $CuMn_8Ox$  catalyst which was less by 20°C and 60°C over than that of 1.5%Ce $CuMn_8Ox$  and  $Cu_1Mn_8$  catalyst respectively.

**Table 8.7:** Light off characteristics of Ce and Au doped and un-doped  $Cu_1Mn_8$  catalysts

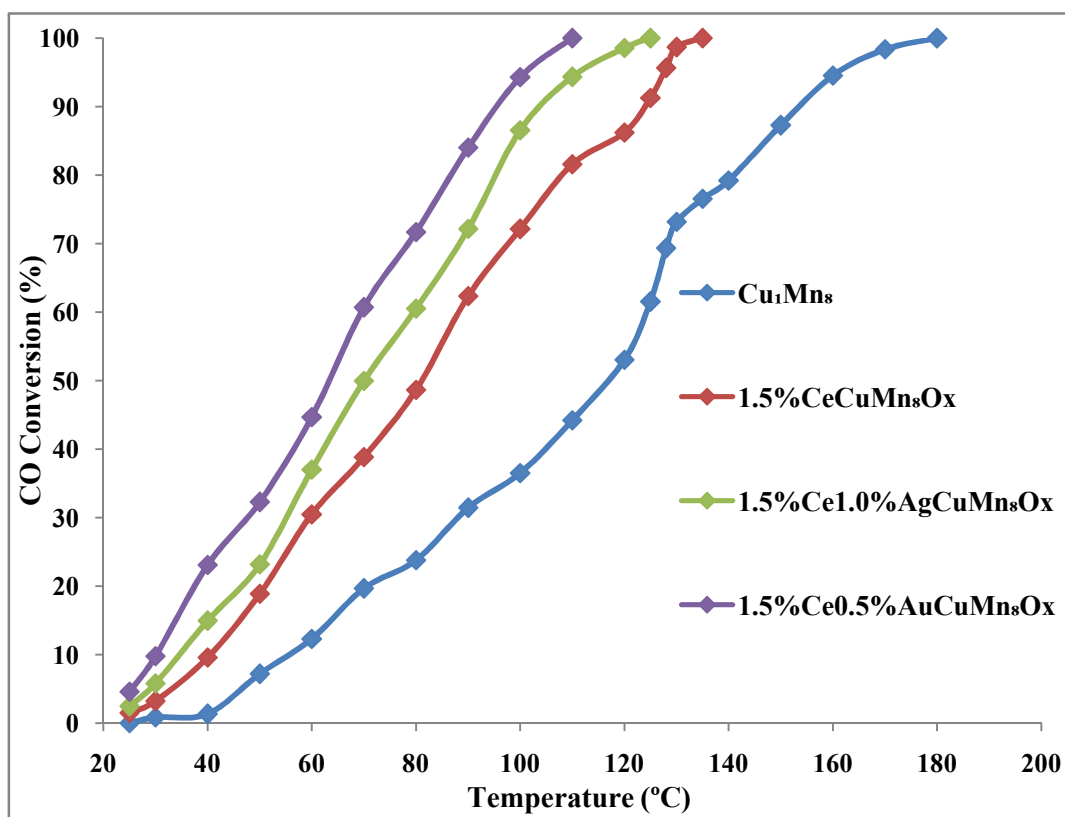
Catalyst	T <sub>10</sub>	T <sub>50</sub>	T <sub>100</sub>
$Cu_1Mn_8$	55°C	125°C	180°C
1.5%Ce $CuMn_8Ox$	40°C	85°C	135°C
1.5%Ce0.5%Au $CuMn_8Ox$	35°C	65°C	110°C

The total oxidation temperature of CO was 110°C for 1.5%Ce0.5%Au $CuMn_8Ox$  catalyst which was less by 25°C and 70°C over than that of 1.5%Ce $CuMn_8Ox$  and  $Cu_1Mn_8$  catalyst respectively. In the 1.5%Ce0.5%Au $CuMn_8Ox$  catalyst, a large number of oxygen atoms adsorbed during the O<sub>2</sub> multi-pulse was smaller than the amount of CO consumed during the first CO multi-pulse series. The CO multi-pulse experiments have detected two distinct types of active oxygen species participating in the CO oxidation. The first type of active oxygen was observed in a similar amount of both the catalysts and associated with the mixed oxide catalyst surface. The second type of active oxygen was found only on the Au-doped 1.5%Ce $CuMn_8Ox$  catalyst; therefore, it was clearly associated with the presence of gold on the surface of catalyst.

#### 8.3.4 Effect of (Ce and Au or Ag) doping in $Cu_1Mn_8$ catalysts

In comparison between the doped and un-doped  $Cu_1Mn_8$  catalysts, we have observed that the 1.5%Ce0.5%Au $CuMn_8Ox$  catalyst has shown the best performance for CO

oxidation. The presence of  $\text{CuO}$ ,  $\text{CeO}_2$ ,  $\text{Mn}_2\text{O}_3$  and  $\text{AuO}$  phases in the  $1.5\%\text{Ce}0.5\%\text{AuCuMn}_8\text{Ox}$  catalyst as evidenced by the XRD and FTIR characterization and may be a possible cause for the higher activity of the catalysts. Figure 8.10 represents the comparison study of un-doped  $\text{Cu}_1\text{Mn}_8$ ,  $1.5\%\text{CeCuMn}_8\text{Ox}$ ,  $1.5\%\text{Ce}1.0\%\text{AgCuMn}_8\text{Ox}$  and  $1.5\%\text{Ce}0.5\%\text{AuCuMn}_8\text{Ox}$  catalyst for CO oxidation. It was proposed that the higher activity of  $1.5\%\text{Ce}0.5\%\text{AuCuMn}_8\text{Ox}$  catalyst recognized to their amorphous structure, surface area and highly dispersed  $\text{CeO}_2$  in the lattice which can promote the generation of surface adsorbed oxygen and improve the mobility of lattice oxygen. After the comparison study, we have observed that the Au doped  $1.5\%\text{CeCuMn}_8\text{Ox}$  catalyst was much active for CO oxidation at a low temperature. Au was acting an oxide support and it was broadly accepted that a CO molecule was chemisorbed on Au atom, while an hydroxyl ion moves from the support to Au(III) ions, creating an anion vacancy.



**Figure 8.10:** Catalytic activity of (Ce and Au or Ag) doped and un-doped  $\text{Cu}_1\text{Mn}_8$  catalysts

In Table 8.8, we have compared the catalytic activity of all the catalysts. The total conversion of CO has occurred at 180°C over  $Cu_1Mn_8$  and 135°C over 1.5%Ce $CuMn_8Ox$  catalyst. The 1.5%Ce0.5%Au $CuMn_8Ox$  catalyst full conversion of CO has occurred at 110°C, which was lowered by 10°C over than that of 1.5%Ce1.0%Ag $CuMn_8Ox$  catalyst.

**Table 8.8:** Light off characteristics of (Ce and Au or Ag) doped and un-doped  $Cu_1Mn_8$  catalysts

Catalyst	T <sub>10</sub>	T <sub>50</sub>	T <sub>100</sub>
1.5%Ce $CuMn_8Ox$	40°C	85°C	135°C
1.5%Ce1.0%Ag $CuMn_8Ox$	35°C	70°C	120°C
1.5%Ce0.5%Au $CuMn_8Ox$	35°C	65°C	110°C

The presence of Ag or Au into the 1.5%Ce $CuMn_8Ox$  catalyst enhances their activity for CO oxidation. The 1.5%Ce1.0%Ag $CuMn_8Ox$  catalyst CO conversion was so high but slightly lower than the 1.5%Ce0.5%Au $CuMn_8Ox$  Catalyst. In the catalytic oxidation process, the CO molecules interact with the oxygen species and resulting vacant oxygen sites were removed by the adsorption of oxygen molecules from the gas phases. The order of activity of the catalysts for CO oxidation was as follows: 1.5%Ce0.5%Au $CuMn_8Ox$  > 1.5%Ce1.0%Ag $CuMn_8Ox$  > 1.5%Ce $CuMn_8Ox$  >  $Cu_1Mn_8$ . CO was regarded as the reductive gas, which partially reduces the surface sites. The heating of precursor in the oxygen-containing atmosphere (calcination process) may increase the amount of highly active oxygen species presence on the catalyst surface. The other species was easily removed by the CO molecules and enhance the rate of this process also observed in the temperature range of 50-120°C.

The catalysts with high surface area shows the high initial activity. The addition of Au or Ag into the 1.5%CeCuMn<sub>8</sub>Ox catalyst their structural property was affected and their oxygen mobility was increased. The CO multi-pulse experiments indicate that the two different types of active oxygen species were found to be concerned in the CO oxidation. One type was observed in a similar amount on both the doped and un-doped Cu<sub>1</sub>Mn<sub>8</sub> catalysts and associated with the mixed oxides, while the second type was only found on the Au-doped catalyst, therefore clearly associated with the presence of gold on the 1.5%CeCuMn<sub>8</sub>Ox catalyst surface. These experimental data clearly demonstrate that the valuable effect of adding Au or Ag on the 1.5%CeCuMn<sub>8</sub>Ox catalyst to improved their performance.

#### **8.4 Concluding Remarks**

The oxidation of CO over the various types of Cu<sub>1</sub>Mn<sub>8</sub> catalysts were significantly influenced by the crystallite size, pore volume, pore size and surface area of the catalyst. Activity of the catalysts was strongly influenced by the presence of Au, Ag and Ce oxides on the Cu<sub>1</sub>Mn<sub>8</sub> catalyst. The additional of smaller amount (1.5wt.%) CeOx into the Cu<sub>1</sub>Mn<sub>8</sub> catalyst to improved their performance for CO oxidation. The presence of active species of Cu<sup>+</sup> makes a strong interaction with ceria to make more oxygen vacancies on the surface of catalyst. Further addition of (1wt.%) AgO<sub>2</sub> or (0.5wt.%) AuO into the 1.5%CeCuMn<sub>8</sub>Ox catalyst also increased their activity for CO oxidation. The new surface sites created upon doping results in improved the catalytic activities for CO oxidation over AuOx or AgOx promoted on 1.5%CeCuMn<sub>8</sub>Ox catalyst. The addition of Au was significantly increases the reducibility of the 1.5%CeCuMn<sub>8</sub>Ox catalyst. It was remarked of high activity at a low temperature that stimulated important current interest in these types of catalysts.