### **Chapter 9**

# Optimization of 3%AgCuMn<sub>8</sub>Ox loading on γ-Al<sub>2</sub>O<sub>3</sub> support

#### 9. General

The success of Cu<sub>1</sub>Mn<sub>8</sub> catalyst has encouraged a big deal of simple work dedicated to useful the role played by each element and the nature of active sites. The novel redox method permitted for the preparation of amorphous Cu<sub>1</sub>Mn<sub>8</sub> catalyst with high surface areas and high activity for CO oxidation at a low temperature [Njagi *et al.*, 2010]. In the CO oxidation process, the oxygen is initially adsorbed on Cu<sub>1</sub>Mn<sub>8</sub> catalyst surface with the energy of activation [Kondrat *et al.*, 2011]. When the temperature is reach sufficient amount so that the adsorption of oxygen reaches enough proportions, therefore the CO passing over the catalyst surfaces either reacts openly with the adsorbed oxygen or else is primary adsorbed and then reacts, after which the CO produced being desorbed [Lee *et al.*, 2016; Solsona *et al.*, 2004]. The support has a strong influence on the activity of resulting catalysts. The main idea of this study to obtain more information about  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> supported 3%AgCuMn<sub>8</sub>Ox catalyst and evaluates the possibility of their practical application in CO oxidation. It is recognized that the phase composition and reduction properties of mixed 3%AgCuMn<sub>8</sub> Ox / $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts depended on the Cu/Mn molar ratio.

The 3%AgCuMn<sub>8</sub>Ox catalyst has shows a good performance for CO oxidation and cheaper than the precious metal catalysts, it could be made more cheaper using gamaalumina ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) support without sacrifice their performance in the reaction [Jones *et al.*, 2006]. The presence of abundant large pores and large surface area in  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support, it has to make a great potential to further improving their performance for CO oxidation. The adding of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support into the 3%AgCuMn<sub>8</sub>Ox catalyst has improved to enhance their dispersion capacity and makes the 3%AgCuMn<sub>8</sub>Ox/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst different from the unsupported 3%AgCuMn<sub>8</sub>Ox catalysts. It indicates that there exists strong interaction between the copper, manganese, silver oxide and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support.

The effect of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> dispersion on the active states and reduction behavior of surface supported 3%AgCuMn<sub>8</sub>Ox catalysts have been investigated by the XRD, FTIR, SEM-EDX and BET analysis. The characterization results confirmed that the Cu<sup>+</sup>, Mn<sup>2+</sup>, Ag and Al mostly existed on the effective surface sites of the 3%AgCuMn<sub>8</sub>Ox/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts. These results indicate that there is a synergistic interface between the copper, manganese, silver and aluminum oxide, which is responsible for the high catalytic activity of CO oxidation. The alumina wash-coated monolith has been widely used in a TWC converter. However, a little attention has been paid on the alumina supported Cu<sub>1</sub>Mn<sub>8</sub> catalyst for CO oxidation [Rattan *et al.*, 2012]. Further, it is recognize that the method of preparation of catalysts determines the dispersion and size distribution of metal crystallites. The spatial division of support effect on the homogeneity of components and the morphology, etc. which in turn strongly affect the catalyst activity [Qin *et al.*, 2010]. The present work was undertaken to search the significance of preparation methods on the morphology and the performance of gama-alumina ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) supported 3%AgCuMn<sub>8</sub>Ox catalyst for CO oxidation.

#### 9.1 Experimental

#### 9.1.1 Catalyst preparation

Gamma alumina ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) support was prepared via hydrothermal synthesis in to two steps (Figure 9.1). Initially, the bohemite is prepared by precipitation of Al(NO<sub>3</sub>)<sub>3</sub>.9H<sub>2</sub>O solution with aqueous 12.5% NH<sub>3</sub> solution at pH 8.5. Later, the precipitates were directly transported to an autoclave at 121°C and 15 psig for 6 hours. After autoclave the precipitate washed free of anions. The washed precipitates (bohemite) AlOOH were thermally decomposed at 600°C calcined for 24 hours to form  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The following reactions (9.1-9.3) occur in the preparation of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>:



Figure 9.1: Steps involved in support synthesis

The prepared  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> supported Cu-Mn system was synthesized by co-precipitation deposition method. The  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> of fraction size (0.6-1.0mm) was used as a support. Different, 10-50% loading of 3%AgCuMn<sub>8</sub>Ox over  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was prepared.



**Figure 9.2**: Preparation of γ-Al<sub>2</sub>O<sub>3</sub> supported 3%AgCuMn<sub>8</sub>Ox catalysts

The required amount of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was suspended in the KMnO<sub>4</sub> solution and coprecipitation deposition was carried out by adding drop wise mixed solutions of copper nitrate and manganese acetate in molar ratio of 1:8 with constant stirring for 2hr. The precipitate was filtered and washed times with hot distilled water to remove all the anions. The solid obtained was dried at 110°C for 24h into an oven. 3%Ag using required amount of silver nitrate solution was sprayed mixed thoroughly in the dried solid followed by calcination by FA method. The nomenclature of the 3%AgCuMn<sub>8</sub>Ox/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts thus obtained after calcination process was given in Table 9.1.

$$Al(NO_3)_3 + 3NH_4OH \rightarrow Al(OH)_3 \downarrow + 3NH_4(NO_3) ------ (9.1)$$

$$Al(OH)_3 \xrightarrow{\text{Autoclaved (121°C)}} AlO(OH) + H_2O ------ (9.2)$$
Bohemite
$$2AlO(OH) \rightarrow \gamma - Al_2O_3 + H_2O ----- (9.3)$$

 Table 9.1: Nomenclature of prepared catalysts

Catalyst Name	Nomenclature
$3\%$ AgCuMn <sub>8</sub> Ox supported $90\%\gamma$ -Al <sub>2</sub> O <sub>3</sub>	$3\%$ AgCuMn <sub>8</sub> Ox/90%\gamma-Al <sub>2</sub> O <sub>3</sub>
3%AgCuMn <sub>8</sub> Ox supported 80%γ-Al <sub>2</sub> O <sub>3</sub>	$3\%$ AgCuMn <sub>8</sub> Ox/80%\gamma-Al <sub>2</sub> O <sub>3</sub>
$3\%$ AgCuMn <sub>8</sub> Ox supported $70\%\gamma$ -Al <sub>2</sub> O <sub>3</sub>	$3\%$ AgCuMn <sub>8</sub> Ox/70%\gamma-Al <sub>2</sub> O <sub>3</sub>
$3\%$ AgCuMn <sub>8</sub> Ox supported $60\%\gamma$ -Al <sub>2</sub> O <sub>3</sub>	$3\%$ AgCuMn <sub>8</sub> Ox/60%\gamma-Al <sub>2</sub> O <sub>3</sub>
$3\%$ AgCuMn <sub>8</sub> Ox supported $50\%\gamma$ -Al <sub>2</sub> O <sub>3</sub>	$3\%$ AgCuMn <sub>8</sub> Ox/50%\gamma-Al <sub>2</sub> O <sub>3</sub>

# 9.2 Catalyst Characterization

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Characterization of the supported and unsupported 3%AgCuMn<sub>8</sub>Ox catalyst reveals the morphology, surface structure, phase identification, material identification and surface area etc. All the catalysts prepared in flowing air calcination (FAC) conditions were done by the different techniques was discussed below.

### 9.2.1 Morphological analysis

The textural property of the supported and unsupported 3%AgCuMn<sub>8</sub>Ox catalyst was analyzed by the scanning electron microscopy (SEM) technique. All the catalysts were prepared under flowing air calcination conditions (Figure 9.3) shows clearly large differences in the microstructure and morphology of the resulting catalysts. As seen in the SEM micrograph the particles presence in a catalyst samples were comprised, of coarse, fine and finest size grains resulted by flowing air calcination of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, 3%AgCuMn<sub>8</sub>Ox/60% $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and 3%AgCuMn<sub>8</sub>Ox catalyst respectively.



Figure 9.3: SEM image of (A)  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, (B) 3%AgCuMn<sub>8</sub>Ox/60% $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and (C) 3%AgCuMn<sub>8</sub>Ox

Particles of 3%AgCuMn<sub>8</sub>Ox catalyst has least agglomerated, more porous, high surface area and uniformly distributed. The smaller size particles present in a 3%AgCuMn<sub>8</sub>Ox catalyst has more efficient for CO dispersed on their surfaces. The surface reform behavior of different size of particles present in a 3%AgCuMn<sub>8</sub>Ox/60% $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and 3%AgCuMn<sub>8</sub>Ox catalyst surfaces during the prolong exposure of CO gas. The size of particles present in  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support was relatively larger, agglomerated and irregular shape as compared to those in 3%AgCuMn<sub>8</sub>Ox/60% $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and 3%AgCuMn<sub>8</sub>Ox catalysts. The fine white and grey crystals clearly indicated that the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support was present in the metallic and oxide form at a higher magnification. The SEM results were also in good agreement with that of the XRD findings. In the 3%AgCuMn<sub>8</sub>Ox/60% $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst, the synergetic effect depends on the catalyst composition and the nature of oxidized compound.

#### 9.2.2 Elemental analysis

In the 3%AgCuMn<sub>8</sub>Ox,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and 3%AgCuMn<sub>8</sub>Ox/60% $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst samples, 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 samples of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, 3%AgCuMn<sub>8</sub>Ox/60% $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and 3%AgCuMn<sub>8</sub>Ox were pure due to the presence of their relative element peaks only as illustrated in Figure 9.4. To understand the influence of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support on the activity and stability of the promoted 3%AgCuMn<sub>8</sub>Ox 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 the Cu, Al, and O in the 3%AgCuMn<sub>8</sub>Ox/60% $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst. The  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support was associated with 3%AgCuMn<sub>8</sub>Ox catalyst promotes the oxygen storage, release and enhanced the oxygen mobility. The oxygen content of the 3%AgCuMn<sub>8</sub>Ox catalyst was least as comparison to the other catalyst

samples. This indicates the presence of oxygen deficiency in the 3%AgCuMn<sub>8</sub>Ox catalyst which makes the high density of active sites so that it was oxidized more CO into CO<sub>2</sub>. The atomic ratio of Cu/Mn in 3%AgCuMn<sub>8</sub>Ox and 3%AgCuMn<sub>8</sub>Ox/60%γ-Al<sub>2</sub>O<sub>3</sub>catalyst was approximately 0.253 and 0.337 respectively, and the weight ratio of Cu/Mn in 3%AgCuMn<sub>8</sub>Ox and 3%AgCuMn<sub>8</sub>Ox/60%γ-Al<sub>2</sub>O<sub>3</sub> catalyst was approximately 0.220 and 0.336 respectively.





Figure 9.4: SEM-EDX image of (A)  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, (B) 3%AgCuMn<sub>8</sub>Ox/60% $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and (C) 3%AgCuMn<sub>8</sub>Ox

The  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support has a high surface area and produced during the calcination process. It also exhibits the high thermal stability and possesses too high cation vacancy which assists the interactions of 3%AgCuMn<sub>8</sub>Ox catalyst. It was an important redox property of 3%AgCuMn<sub>8</sub>Ox catalyst, which highly influenced by their interactions with the support.

# 9.2.3 Phase identification and cell dimensions

X-ray diffraction (XRD) study was carried out to identify the phases and crystallite size present in the catalysts. The XRD peak of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, 3%AgCuMn<sub>8</sub>Ox/60% $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and 3%AgCuMn<sub>8</sub>Ox samples prepared under flowing air calcination conditions as shown in the Figure 9.5. XRD pattern of the 3%AgCuMn<sub>8</sub>Ox catalyst diffraction peak at 20 was 37.20 corresponds to its lattice plane (110) of face-centered cubic. The main phase was found to be CuMn(AgO) form with the crystallite size of the catalyst was 2.423 nm. The  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support structure was found to be cubic in nature, was called a defect cubic spinel structure with vacancies on Al (III) positions with the crystallite size in the range 5.0–10.0nm. Each cell unit contains 32 oxygen and 64/3 Al(III) to fulfill the stoichiometry. Al (III) ions occupy both the octahedral and tetrahedral positions by the relative partial occupancy in each position. XRD pattern of the 3%AgCuMn<sub>8</sub>Ox/ 60% $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst diffraction peak at 2 $\theta$  was 36.50 corresponds to face-centered cubic Cu<sub>1.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support (PDF-24-0735 JCPDS file). The crystallite size of the 3%AgCuMn<sub>8</sub>Ox/60% $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts was 4-6.5 nm. The sharpness of the peaks also indicates that the CuO particles were highly crystalline and broadness of the peaks showed poor crystallization of Mn<sub>2</sub>O<sub>3</sub> with the presence of defects in the crystal structure.



Figure 9.5: XRD analysis of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, 3%AgCuMn<sub>8</sub>Ox and 3%AgCuMn<sub>8</sub>Ox/60% $\gamma$ -Al<sub>2</sub>O<sub>3</sub>

There were no crystalline MnOx phase was observed in 3%AgCuMn<sub>8</sub>Ox/60% $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst, implying that MnOx species may be single layer dispersive on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> surfaces or may be created small clusters with a high amount of dispersion, which

cannot be detected by XRD. The poor crystalline structure of MnOx may favor structural defects formation, in particular, oxygen vacancies giving the best activity for CO oxidation.

## 9.2.4 Identification of the materials presence in a Catalyst

Identification of the metal-oxygen bonds present in the 3%AgCuMn<sub>8</sub>Ox and 3%AgCuMn<sub>8</sub>Ox/60%\gamma-Al<sub>2</sub>O<sub>3</sub> catalyst was made by the Fourier transform infrared spectroscopy (FTIR) analysis. The different peaks were shown, various types of chemical groups present in the 3%AgCuMn<sub>8</sub>Ox and 3%AgCuMn<sub>8</sub>Ox/60%\gamma-Al<sub>2</sub>O<sub>3</sub> catalysts at the invested region (4000–400cm<sup>-1</sup>).



**Figure 9.6**: FTIR analysis of (A) 3%AgCuMn<sub>8</sub>Ox/60%γ-Al<sub>2</sub>O<sub>3</sub> and (B) 3%AgCuMn<sub>8</sub>Ox catalysts

FTIR spectra of the catalyst prepared under flowing air calcination conditions were shown in Figure 9.6. In the 3%AgCuMn<sub>8</sub>Ox/60% $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst (3530cm<sup>-1</sup>) peak represent the presence of –OH group, (2910cm<sup>-1</sup>) CuO group, (1250cm<sup>-1</sup>) CO<sub>3</sub><sup>2-</sup> group, (532cm<sup>-1</sup>) AlO<sub>2</sub> group and (1640cm<sup>-1</sup>) Mn<sub>2</sub>O<sub>3</sub> group. In the flowing air calcination prepared 3%AgCuMn<sub>8</sub>Ox catalysts; which originate from the stretching vibrations of

the metal-oxygen bond and confirms the presence of CuO and  $Mn_2O_3$  phases. The 3%AgCuMn<sub>8</sub>Ox catalyst at the transmittance conditions, there were total five peaks we obtained, the IR band (1630cm<sup>-1</sup>) has shown the presence of  $Mn_2O_3$  group, (3480cm<sup>-1</sup>) - OH group, (540cm<sup>-1</sup>and 2350cm<sup>-1</sup>) CuO group and (1290cm<sup>-1</sup>) AgO<sub>2</sub> group. The spectra of impurities like hydroxyl (-OH) group at (3530cm<sup>-1</sup>) decreases in the following order: 3%AgCuMn<sub>8</sub>Ox/60%\gamma-Al<sub>2</sub>O<sub>3</sub>> 3%AgCuMn<sub>8</sub>Ox. Thus, the 3%AgCuMn<sub>8</sub>Ox catalyst was highly pure as compared to the 3%AgCuMn<sub>8</sub>Ox/60%γ-Al<sub>2</sub>O<sub>3</sub> catalyst.

#### 9.2.5 Surface area measurement

The surface area of supported and un-supported 3%AgCuMn<sub>8</sub>Ox catalyst sample was analysis by the Brunauer Emmett Teller Analysis (BET) technique. The surface area, pore volume and pore size of 3%AgCuMn<sub>8</sub>Ox,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and 3%AgCuMn<sub>8</sub>Ox/60% $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts were presented in the Figure 9.7 and mentioned in the Table 9.2.



**Figure 9.7**: Textural properties of (A) N<sub>2</sub> adsorption-desorption isotherms and (B) Pore size distributions curves

The average pore volume and pore size of the 3%AgCuMn<sub>8</sub>Ox/ $60\%\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst was 0.695cm<sup>3</sup>/g and 60.65Å respectively. All the catalysts were prepared in flowing air calcination conditions. It can be visualized from the Table 9.2 that the pore volume and

pore size of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support was higher than the other catalysts. The slope and height of the steps were clear indications of very well definite mesopores with narrow size pore distribution. Total pore volume and specific surface area which were two major factors which can affects the catalytic activity for CO oxidation. The surface area was a key parameter in determining the catalyst activity for CO oxidation. Average pore diameter of 3%AgCuMn<sub>8</sub>Ox/60% $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst has also increased with the increasing of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support in the 3%AgCuMn<sub>8</sub>Ox catalyst. Clearly, the textural property of 3%AgCuMn<sub>8</sub>Ox catalyst was also highly active for CO oxidation at a low temperature.

Catalyst Name	Surface Area (m²/g)	Pore Volume (cm <sup>3</sup> /g)	Pore Size (Å)	
$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	212.76	0.730	51.70	
3%AgCuMn <sub>8</sub> Ox/ 60%γ-Al <sub>2</sub> O <sub>3</sub>	171.76	0.695	60.65	
3%AgCuMn₀Ox	129.76	0.676	68.45	

Table 9.2: The surface area, pore volume and pore size of the catalysts

Considering the close similarity values of pore volume and pore diameter for both the 3%AgCuMn<sub>8</sub>Ox and 3%AgCuMn<sub>8</sub>Ox/60% $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts, the results can be interpreted as affirmation that the specific surface area of the catalysts was not only the main factor in the CO oxidation on  $\gamma$ -alumina supported 3%AgCuMn<sub>8</sub>Ox catalysts, mainly in the outline of our experiments. The specific surface area was measured by BET analysis and it was also follows the SEM and XRD results. Typical nitrogen adsorption/desorption isotherms of these catalysts with hysteresis loop showing catalysts were mesoporous according to De-Boer classification. The 3%AgCuMn<sub>8</sub>Ox catalyst surface areas of similar magnitude regardless of the preparation atmosphere; however, there was a general increase in surface area as a result of increased  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>

percentages. From this BET characterization we have confirmed that the synthesized, of 3%AgCuMn<sub>8</sub>Ox/60%\gamma-Al<sub>2</sub>O<sub>3</sub> catalyst by the deposition-precipitation method was an appropriate approach for the development of catalysts with enhanced catalytic activity toward CO oxidation.

# 9.3 Catalyst performance and activity measurement

Activity measurement of the catalyst was carried out to evaluate the effectiveness of 3%AgCuMn<sub>8</sub>Ox/60% $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts as a function of temperature. It was evaluated in flowing air calcination conditions. The improved catalytic activity of the catalysts can be ascribed to the unique structural, textural characteristics and the smallest crystallite size.

# 9.3.1 Optimization of metals loading on γ-Al<sub>2</sub>O<sub>3</sub>

The  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support has a strongly influence on the activity of resulting catalyst. Effect of different percentages of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support into the 3%AgCuMn<sub>8</sub>Ox catalysts has also measured for CO oxidation. The  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support was not chemically inactive, and the metal-support interactions can promote or retard the catalytic processes. The coprecipitation involves dissolving both the support and the active phase salts in the same solution, via a pH control. Also, the active phase presence in materials may be precipitated inside the support. For this reason, this method was used for  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support with a metal loading up to 10% or higher. The metals loading on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> were carried out by the deposition-precipitation method to prepare 3%AgCuMn<sub>8</sub>Ox/Z% $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts (Z=0, 10, 20, 30, 40, 50). Figure 9.8 shows that the activity test of various 3%AgCuMn<sub>8</sub>Ox/Z% $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts prepared in flowing air calcination conditions.



Figure 9.8: Effect of metal loading on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support for oxidation of CO The oxidation of CO was initiated below 25°C overall all the catalysts. The complete oxidation temperature of CO was 88°C for 3%AgCuMn<sub>8</sub>Ox catalyst, which was less by 57°C, 44°C, 33°C, 13°C and 27°C over than that of 3%AgCuMn<sub>8</sub>Ox/90% $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, 3%AgCuMn<sub>8</sub>Ox/80% $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, 3%AgCuMn<sub>8</sub>Ox/70% $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, 3%AgCuMn<sub>8</sub>Ox/60% $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and 3%AgCuMn<sub>8</sub>Ox/50% $\gamma$ -Al<sub>2</sub>O<sub>3</sub> respectively. It was evident from the Figure 9.8 that the activity of catalyst increased with increasing of metal loading upto 40% of 3%AgCuMn<sub>8</sub>Ox on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support, with further increase of metal loading the activity was decreased. Thus, the optimum metal loading and support ratio of 3%AgCu Mn<sub>8</sub>Ox/Z% $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst was (3%AgCuMn<sub>8</sub>Ox: $\gamma$ -Al<sub>2</sub>O<sub>3</sub>=40:60). The  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support has strongly influence on the activity of resulting 3%AgCuMn<sub>8</sub>Ox/60% $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst. The large pores size and surface area present in a  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> supported 3%AgCuMn<sub>8</sub>Ox catalyst has a huge potential to improve their performance for CO oxidation.

Catalyst	T <sub>10</sub>	T <sub>50</sub>	T <sub>100</sub>
3%AgCuMn <sub>8</sub> Ox	<25°C	52°C	88°C
$3\%$ AgCuMn <sub>8</sub> Ox/90%\gamma-Al <sub>2</sub> O <sub>3</sub>	30°C	88°C	145°C
$3\%$ AgCuMn <sub>8</sub> Ox/80%\gamma-Al <sub>2</sub> O <sub>3</sub>	<25°C	82°C	132°C
$3\%$ AgCuMn <sub>8</sub> Ox/70%\gamma-Al <sub>2</sub> O <sub>3</sub>	<25°C	64°C	121°C
$3\%$ AgCuMn <sub>8</sub> Ox/60%\gamma-Al <sub>2</sub> O <sub>3</sub>	<25°C	51°C	101°C
$3\%$ AgCuMn <sub>8</sub> Ox/50%\gamma-Al <sub>2</sub> O <sub>3</sub>	<25°C	62°C	115℃

**Table 9.3**: Activity test of supported and unsupported 3%AgCuMn<sub>8</sub>Ox/Z%\gamma-Al<sub>2</sub>O<sub>3</sub> catalysts

The light off characteristics for different percentage of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> supported into 3%AgCuMn<sub>8</sub>Ox catalyst used to evaluate the activity of resulting catalysts was tabulated in Table 9.3. The rising temperature was enlarge the specific surface area and pore volume of the 3%AgCuMn<sub>8</sub>Ox/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst, and their activity for CO oxidation has been increased. These results showed that the nature of both 3%AgCuMn<sub>8</sub>Ox catalyst and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support has a strongly influenced on the catalytic activity of 3%AgCuMn<sub>8</sub>Ox/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst(s) for CO oxidation. In the beginning, the local rise in the temperature of the precursor's crystallites due to very slow exothermic oxidation which ensures very slow decomposition of the precursor then after, slightly faster CO oxidation has been observed. The  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support was thermally very stable and withstands processes required to activate pre-catalysts.

# 9.3.2 Optimum percentage of metal loading on y-Al<sub>2</sub>O<sub>3</sub> support

The effect of metal loading on CO conversion at 101°C is shown in Figure 9.9. It is clear from the Figure 9.9 that the activity order of different catalysts for CO oxidation

was as follows: 3%AgCuMn<sub>8</sub>Ox/60% $\gamma$ -Al<sub>2</sub>O<sub>3</sub>> 3%AgCuMn<sub>8</sub>Ox/50% $\gamma$ -Al<sub>2</sub>O<sub>3</sub>> 3%Ag CuMn<sub>8</sub>Ox/70% $\gamma$ -Al<sub>2</sub>O<sub>3</sub>> 3%AgCuMn<sub>8</sub>Ox/80% $\gamma$ -Al<sub>2</sub>O<sub>3</sub>> 3%AgCuMn<sub>8</sub>Ox/90% $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The higher catalytic activity of 3%AgCuMn<sub>8</sub>Ox/60% $\gamma$ -Al<sub>2</sub>O<sub>3</sub> may open new avenues in searching for CO oxidation at an economical cost. The reason behind the excellent activity of 3%AgCuMn<sub>8</sub>Ox/60% $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst for CO oxidation may be due to the presence of (Cu<sup>+</sup>, Mn<sup>2+</sup> and Ag<sup>+</sup>) metal ions in the 3%AgCuMn<sub>8</sub>Ox catalyst over  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support. Due to the low reactivity with  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support, the 3%AgCuMn<sub>8</sub>Ox catalyst was comparatively very stable over  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> supports.





The nature of 3%AgCuMn<sub>8</sub>Ox catalyst, a key parameter governing the conversion seems to be the geometrical make contact with the 3%AgCuMn<sub>8</sub>Ox catalyst and supporting  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> material, which was preferential by a highly corrugated catalyst surface. This was the reason why the more corrugated 3%AgCuMn<sub>8</sub>Ox/60% $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst ensured the best performance under real operating conditions. The performance

of catalysts was accordance with their characterization. The interactions between the adsorbing molecules and the catalyst can be characterized quantitatively in terms of adsorption/desorption properties.

### 9.3.3 Comparison of 3%AgCuMn<sub>8</sub>Ox and 3%AgCuMn<sub>8</sub>Ox/60%γ-Al<sub>2</sub>O<sub>3</sub> catalyst

The comparative study of 3%AgCuMn<sub>8</sub>Ox and 3%AgCuMn<sub>8</sub>Ox/60%γ-Al<sub>2</sub>O<sub>3</sub> catalysts for total oxidation of CO has been shown in the Figure 9.10. The oxidation of CO has been initiated near around the room temperature ~25°C and the 50% conversion of CO has occurred at 50°C over 3%AgCuMn<sub>8</sub>Ox catalyst which was lowered by 2°C over than that of 3%AgCuMn<sub>8</sub>Ox/60%γ-Al<sub>2</sub>O<sub>3</sub> catalyst. The acceleration of CO oxidation was strongly depends upon the 3%AgCuMn<sub>8</sub>Ox catalyst composition and their effect on γ-Al<sub>2</sub>O<sub>3</sub> support. The complete oxidation of CO has been achieved at 90°C over 3%AgCuMn<sub>8</sub>Ox catalyst, which was less by 11°C over than that of 3%AgCu Mn<sub>8</sub>Ox/60%γ-Al<sub>2</sub>O<sub>3</sub> catalyst. The obtained results confirmed that the highly active 3%AgCuMn<sub>8</sub>Ox and 3%AgCuMn<sub>8</sub>Ox/60%γ-Al<sub>2</sub>O<sub>3</sub> catalysts for CO oxidation was represented in the Table 9.4. Considering the close similarity values of the BET specific surface area, pore volume and average pore diameter for both 3%AgCuMn<sub>8</sub>Ox and 3%AgCuMn<sub>8</sub>Ox/60%γ-Al<sub>2</sub>O<sub>3</sub> catalyst. The characterization work has been shows that the confirmation of specific surface area of the catalysts was the principal factor for the CO oxidation.



Figure 9.10: Comparison of 3%AgCuMn\_8Ox and 3%AgCuMn\_8Ox/60% $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts

The surface area measurements confirmed that the activity behaviors of 3%AgCu  $Mn_8Ox/60\%\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts seems to be due to the most active catalyst, which was derived from 3%AgCuMn\_8Ox +  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst, has the highest specific surface area.

<b>Table 9.4</b> :	Comparison	of 3%AgCuMn <sub>8</sub> Ox	and 3%AgCuMn <sub>8</sub> Ox.	/60% - Al <sub>2</sub> O <sub>3</sub> catalysts
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Catalyst	T <sub>10</sub>	T <sub>50</sub>	T <sub>100</sub>
3%AgCuMn <sub>8</sub> Ox	>25°C	50°C	90°C
$3\%$ AgCuMn <sub>8</sub> Ox/60%\gamma-Al <sub>2</sub> O <sub>3</sub>	25°C	52°C	101°C

In addition to high catalytic activity, the 3%AgCuMn<sub>8</sub>Ox/60% $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts must also comprised significant features like high stability in different conditions, ability to be reuse several times and should have a great forbearance against deactivation. The  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support was not very active, but the presence of 3%AgCuMn<sub>8</sub>Ox can promote the CO oxidation.

# 9.4 Concluding Remarks

Synthesis of supported 3%AgCuMn<sub>8</sub>Ox/Z% $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst by the precipitationdeposition method is an appropriate method for the development of highly active catalysts for CO oxidation. It is recognized that the phase composition and reduction properties of mixed 3%AgCuMn<sub>8</sub>Ox/60% $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts have strongly depended on the catalyst and support ratio. The optimum metals loading on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support is 40%. The optimum catalyst formulation is 3%AgCuMn<sub>8</sub>Ox/60% $\gamma$ -Al<sub>2</sub>O<sub>3</sub> for CO oxidation. The application of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support in 3%AgCuMn<sub>8</sub>Ox improves performance of the catalyst as well as reduces the cost. The performance of 3%AgCuMn<sub>8</sub>Ox/60% $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst has followed the characterization results. The crystalline nature of 3%AgCuMn<sub>8</sub>Ox/60% $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst sample is favor on the structural defects formation, in particular, oxygen vacancies giving the best performance for CO oxidation. The using of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support in 3%AgCuMn<sub>8</sub>Ox catalyst could be made cheaper the 3%AgCuMn<sub>8</sub>Ox/60% $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst without sacrificing their performance for CO oxidation. Therefore, we used  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support in 3%AgCuMn<sub>8</sub>Ox catalyst for improving their performance and reducing their cost.