Chapter 6

Optimization of preparation conditions for catalytic activity of CuMnOx catalysts

6. General

The preparation conditions of the catalyst is highly influence the structural properties like surface area, shape, particle size, pore volume, phases and the strength of interface, which in turn determine the redox property and reactivity of the resulting catalysts [Narasimharao *et al.,* 2015; Qian *et al.,* 2013]. Optimization of the CuMnOx catalyst during the preparation conditions like drying temperature, drying time, calcination temperature, calcination time and the molar ratio of (Cu:Mn) influence the performance of CuMnOx catalysts for CO oxidation [Tang *et al.,* 2009; Hutchings *et al.,* 1998]. In this chapter, we have investigated the effect of wide range of preparation parameters to facilitate the optimal catalyst preparation procedure. A co-precipitation method is used for the preparation of CuMnOx catalyst as discussed in the preparation section 6.1.1. Particle size of the CuMnOx catalyst highly influences the activity of resulting catalyst, with decreasing the particle size; their surface area is increased therefore more CO oxidizes into CO_2 [Clarke *et al.,* 2015]. The drying temperature, calcination temperature and calcination time has a distinct effect on the catalytic activity [Arango-Diaz *et al.,* 2015]. There are many parameters, which can be varied through the catalyst preparation by the co-precipitation method and succeeding the calcination step for controlling the performance of CuMnOx catalyst for CO oxidation [Biemelt *et al.,* 2015].

To date, there are various methods have been applied to the preparation of CuMnOx catalysts; e.g. sol-gel, ultrasonic aerosol pyrolysis, co-precipitation, supercritical anti-solvent precipitation etc. [Kramer *et al.,* 2006]. In these methods, the co-precipitation

method can be produced the highly active sites of the CuMnOx catalyst [Wojciechowska *et al.,* 2007]. Clarke et al. have suggested a novel redox method for room temperature preparation of amorphous CuMnOx catalyst with high surface areas and high catalytic activity for low temperature CO oxidation [Clarke *et al.,* 2015]. In the present work, the prepared CuMnOx precursor was calcined in the flowing air. The catalysts were characterization by several techniques like SEM-EDX, XRD, FTIR, BET and XPS. In this chapter, we have investigated the optimization preparation parameters of CuMnOx catalyst and their performance for CO oxidation.

6.1 Experimental

6.1.1 Catalyst preparation

The CuMnOx catalysts were prepared by the co-precipitation method. All the materials used for the preparation work, were of A.R. grade. A solution of ($Mn(CH_3COO)_2.4H_2O$) was added to ($Cu(NO_3)_2.3H_2O$) and stirred for 1h. The mixed solution was taken in the burette and added drop-wise to a solution of $KMnO_4$ under vigorous stirring conditions for co-precipitation purpose. The resultant precipitate was stirred continuously for 2h. Then filtered and washed several times with hot distilled water. After washing, the precursor was dried in an oven and calcined in flowing air before measuring the catalyst activity. The amount of copper and manganese added was varied in the preparation of Cu_1Mn_y catalysts (y = 0-12). After drying the precursors, the cake was powdered and calcined in a flowing air for measurement of their activity for CO oxidation.

6.2 Catalyst Characterization

Characterization of all the CuMnOx catalysts prepared by calcination in flowing air (FAC) was done by the different techniques and discussed in the following sections.

6.2.1 Morphological analysis

The Scanning Electron Micrographs (SEM) instrument was used for the microstructure analysis of the optimized Cu_1Mn_8 catalyst prepared in flowing air calcination (FAC) conditions. The Cu_1Mn_8 catalyst was composed of different aggregates size of nanoparticles as shown in the Figure 6.1. The SEM micrograph of the various particles present in a Cu_1Mn_8 catalyst was comprised of coarse and excellent sizes in nature. The particles were least agglomerated, highly porous and uniformly distributed.

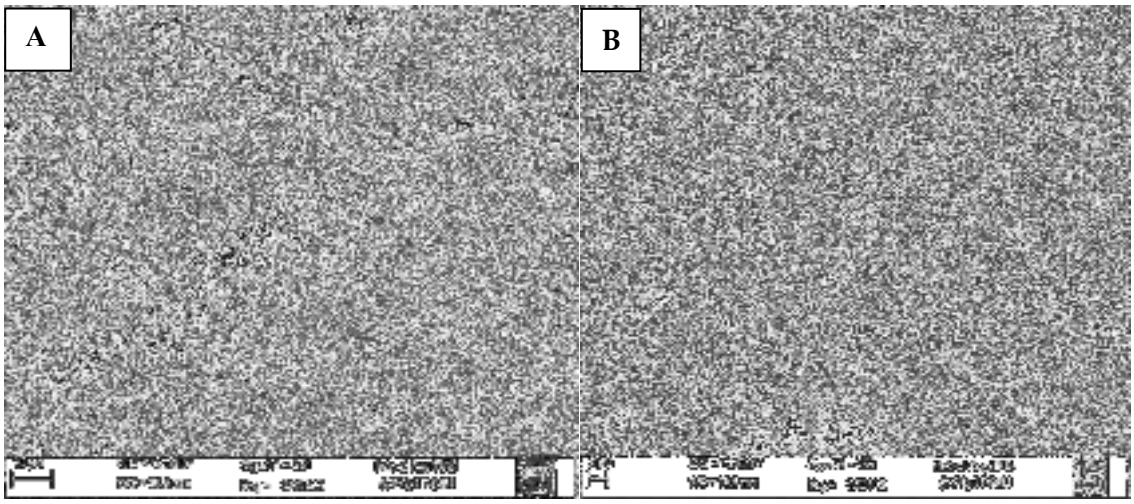

Figure 6.1: SEM image of Cu_1Mn_8 catalyst (A) 2.0KX and (B) 5.0KX magnifications

Due to the lesser particle size of catalyst, more and more CO dispersed on their surfaces. The surface rebuilding behavior of different size of particles presence in a catalyst surfaces throughout the prolonged exposure of CO gas. The drying and calcination temperature oxidized all the impurities present in a catalyst.

6.2.2 Elemental analysis

In the Cu_1Mn_8 catalyst, the percentages of different elements were present analysis by the Scanning electron microscopy (SEM) with energy dispersive X-Ray analysis (SEM-EDX) techniques. It was apparent from the results of SEM-EDX analysis has shown that the Cu_1Mn_8 catalyst was highly pure and there will be no impurity presents in a

catalyst. It was apparent from the Table 6.1 and Figure 6.2 that the weight percentage and atomic percentage of Mn was also higher as comparison of Cu and O.

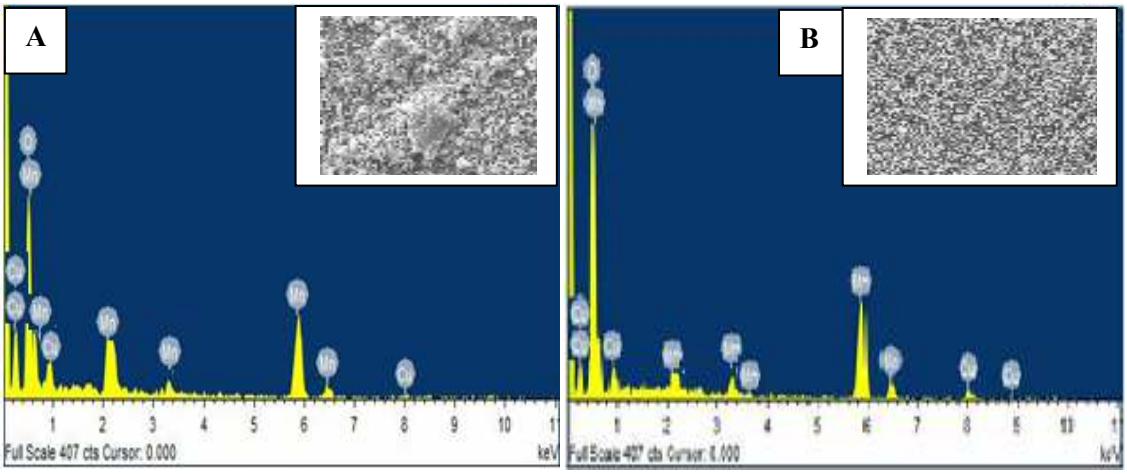

Figure 6.2: SEM-EDX image of Cu_1Mn_8 catalyst (A) 2.0KX and (B) 5.0KX magnifications

The presence of lattice oxygen mobility species in the Cu_1Mn_8 catalyst has enhanced the reaction rate and it might be provided the more surface area of active oxygen species for CO oxidation. The abundant surface oxygen atoms present on the catalyst surfaces can react with the absorbed CO. The atomic percentage of Cu, Mn and O in the Cu_1Mn_8 catalyst was12.61%, 76.38%, and 11.01% respectively and weight percentage of Cu, Mn and O in the Cu_1Mn_8 catalyst was 12.47%, 78.41%, and 9.12% respectively.

Table 6.1: Atomic and weight percentage of Cu_1Mn_8 catalyst

Elemental	Atomic (%)	Weight (%)
O	11.01	9.12
Mn	76.38	78.41
Cu	12.61	12.47
Total	100	100

The atomic ratio and weight ratio of (Cu : Mn) in the Cu_1Mn_8 catalyst was approximate 0.159 and 0.165 respectively. The Cu_1Mn_8 catalyst has similar morphologies which composed of irregular size and shape particles. With the increasing of Mn contents in Cu_1Mn_8 catalyst, the pore size distributions become wider; therefore, more-more CO oxidized into CO_2. The molar ratio of Cu:Mn in the Cu_1Mn_8 catalyst was very similar to the molar ratio of Cu:Mn in the synthesis solutions. The reduction of crystallite size particles present in the Cu_1Mn_8 catalyst can be recognized to the MnO_2 acting as a simple spacer between Cu crystallites and consequently prevent sintering during the heat treatment.

6.2.3 Phase identification and cell dimensions

X-ray Diffraction (XRD) studies of the Cu_1Mn_8 catalyst was carried out to identify the coordinate dimensions and crystallite size present in the catalyst. Cu_1Mn_8 catalyst was prepared in flowing air (FA) calcination conditions and XRD peak of the catalyst was shown in Figure 6.3. The diffraction peak at 2θ of 37.20 corresponds to its lattice plane (221) and (212) of Face-centered cubic $Cu_1Mn_8O_4$ (PDF-65-5570-JCPDS file). The crystallite size of catalyst was 4.23 nm.

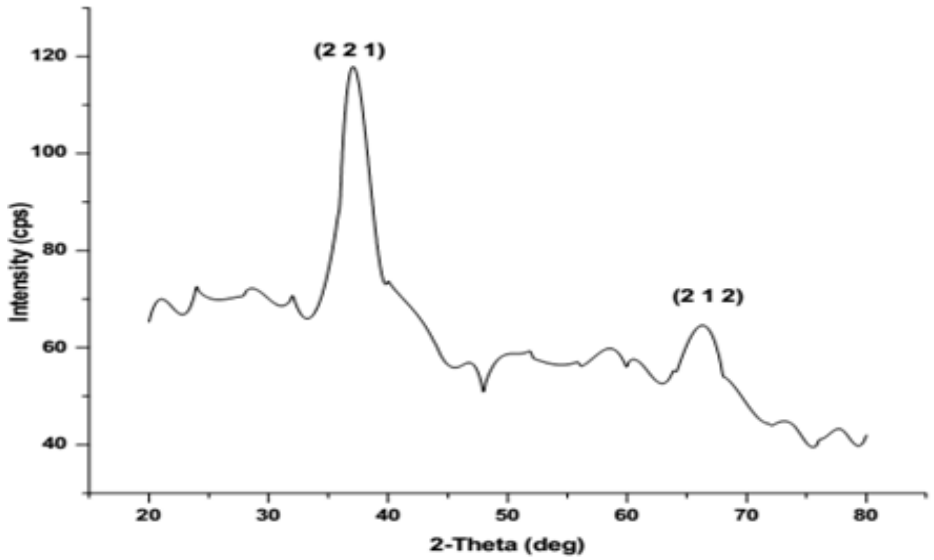

Figure 6.3: XRD analysis of Cu_1Mn_{8FA} catalyst produced by FA calcination

The smaller size particles present in $CuMn_8$ catalyst was more active for CO oxidation at an ambient temperature. The calcination temperature 300°C was found an optimum calcination temperature because raising the temperature beyond 300°C a loss of crystalline phase has occurred in the material and almost amorphous nature was obtained.

6.2.4 Identification of the materials presents in a Cu_1Mn_8 catalyst

The metal-oxygen bonds present in the Cu_1Mn_8 catalyst was identification by the Fourier transform infrared spectroscopy (FTIR) analysis. The different peaks were shows various types of chemical groups present on the catalysts. The FTIR transmission spectra of Cu_1Mn_8 catalyst prepared in flowing air calcination (FAC) condition as shown in the Figure 6.4. There are total five peaks we obtained in the Cu_1Mn_8 catalysts. The main stretching bond of Mn-O, CuO, CO_3^{2-} and C=O group was present in the Cu_1Mn_8 catalyst.

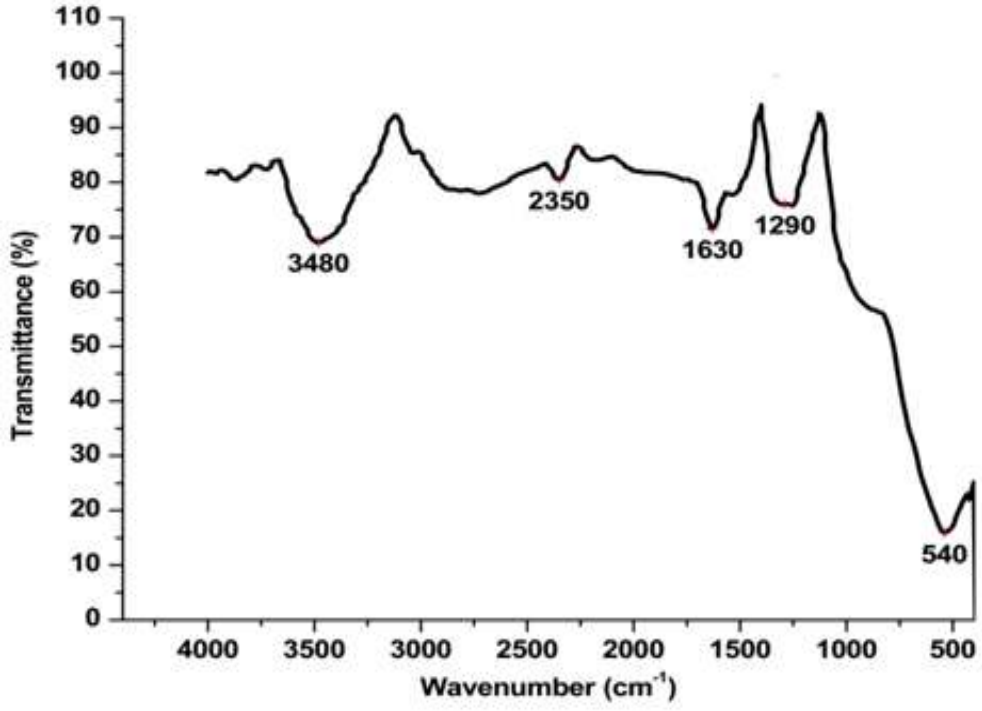

Figure 6.4: FTIR analysis of Cu_1Mn_8 catalyst

The transmission spectra at (1630cm^{-1}) have assigned to MnO_2 group, (1290cm^{-1}) CO_3^{2-} group and (540cm^{-1}) CuO group. The other phases like C=O and hydroxyl group (-OH) were present at (2350cm^{-1}) and (3480cm^{-1}) respectively. In flowing air calcination the Cu_1Mn_8 catalyst has originates from the stretching vibrations of the metal-oxygen bonds and confirmed the presence of CuO and MnO_2 phases. The weak band at (1290cm^{-1}) indicates that the existence of some carbonaceous group in the catalyst sample. The MnOx deposits in a Cu_1Mn_8 catalyst were intimate contact with CuO crystallites and favoring the oxygen transfer between the two metal oxides. This type of CuO-MnO_2 structure interaction led to a formation of the Cu_1Mn_8 phase. The important thing that controls in the propagation of CO oxidation was the thermal diffusion of Cu and Mn cations.

6.2.5 Identification and quantification of elements

The binding energy and oxidation state of Cu_1Mn_8 catalyst was investigated by the X-ray photoelectron spectroscopy (XPS) analysis. The higher binding energy was preferably for CO oxidation. In Figure 6.5 observed that the XPS spectra of Cu_1Mn_8 catalyst prepared in flowing air calcination conditions. The prominent peak of Cu(2p) level in Cu_1Mn_8 catalyst was deconvoluted into six peaks centered. The binding energy of Cu(2p) in Cu_1Mn_8 catalyst was 954.033eV, 956.600eV, 960.844eV, 962.524eV, 964.128 and 967.522eV respectively and the highest intensity peak of Cu(2p) in Cu_1Mn_8 catalyst was obtained at 964.128eV. The binding energy of Mn(2p) in Cu_1Mn_8 catalyst, was 643.52eV and 655.47eV and it will be associated with the presence of Mn^{3+} and Mn^{4+}. The chemical state of Cu, Mn and O present in Cu_1Mn_8 catalyst was Cu(II) oxide, MnO_2 and C-O form respectively.

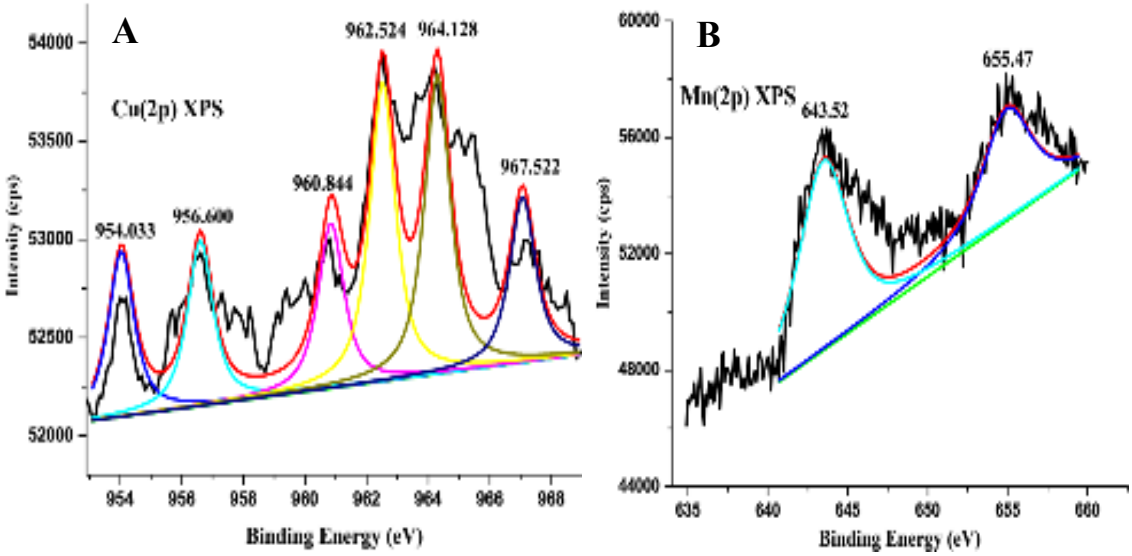

Figure 6.5: XPS analysis of (A) Cu and (B) Mn in Cu_1Mn_8 catalyst

In general, there were two different types of oxygen present in Cu_1Mn_8 catalyst with binding energy of (529.2–530eV) and (531.3–532.2eV). The chemisorbed oxygen recognized as (denoted as Oa, such as O_2^{2-}, O^-, OH^-, CO_3^{2-}, etc.) and lattice oxygen (denoted as O_l such as O^{2-}). In this study the oxygen with the binding energy of 530.8eV could be assigned to the chemisorbed oxygen (Oa). The presence of lattice oxygen was very small in Cu_1Mn_8 catalyst. It was well known that the huge amount of surface chemisorbed oxygen (as the most active oxygen) was preferable for enhancing the catalytic activity for CO oxidation.

Table 6.2: Chemical state and binding energy of Cu_1Mn_8 catalysts

Sample	Elements		
	Cu	Mn	O
Cu_1Mn_8 (FAC)	Cu (II) Oxide 964.128eV	MnO_2 655.47eV	C-O 530.8eV

It was found that $Mn(CH_3COO)_2.4H_2O$ usually decomposed into MnO_2 form and $Cu(NO_3)_2.3H_2O$ usually decomposed into Cu(II) oxide form in flowing air calcination conditions. In Table 6.2, we have seen that the binding energy and chemical state of

Cu_1Mn_8 catalyst prepared in flowing air calcination conditions. These binding energies recommend that the oxide (O^{2-}) species were mostly near the surface of Cu_1Mn_8 catalyst and it was usually accepted that Cu exists in the (II) oxidation state in the binary form. Figure 6.5 indicate that at least some of the Cu^{2+} and Mn^{2+} phase exist near the surface of Cu_1Mn_8 catalyst.

6.2.6 Surface area measurement

The surface area of Cu_1Mn_8 catalyst was analysis by the Brunauer Emmett Teller analysis (BET). The pore volume, surface area and pore size of the Cu_1Mn_8 catalyst prepared in flowing air calcination condition was listed in the Table 6.3. The average pore volume and pore size of Cu_1Mn_8 catalyst was 0.460cm^3/g and 52.30Å respectively.

Table 6.3: The surface area, pore volume and pore size of Cu_1Mn_8 catalyst

Catalyst Name	Surface Area (m^2/g)	Pore Volume (cm^3/g)	Pore Size (Å)
Cu_1Mn_8	101.50	0.460	52.30

The larger number of more pores present on a catalyst surface, means a highly interface of CO molecules with catalyst surfaces, and it causes better catalytic activity for CO oxidation. The further calcination of Cu_1Mn_8 precursor led to significantly decreasing the surface area of resulting catalyst. A correlation between the increasing of Mn concentration and the steady state Cu_1Mn_8 catalyst activity was increased at certain level was revealed. From the characterization work, we can get that the phase composition and reduction properties of Cu_1Mn_8 catalyst was highly depended on the (Cu:Mn) molar ratio.

6.3 Activity test for CuMnOx catalysts

In the activity test, we have analyzed the effectiveness of resulting CuMnOx catalyst prepared in flowing air calcination conditions. The activity was increased with the increasing of temperature from room temperature to certain high temperature for complete oxidation of CO. The optimum preparation conditions were identified with respect to the performance of CuMnOx catalyst for CO oxidation at low temperature. The improved catalytic activity can be ascribed to the unique structural and textural characteristics of the catalysts.

6.3.1 Optimization of Cu:Mn molar ratio in CuMnOx

Activity of the catalyst for CO oxidation over Cu_xMn_y catalyst (x = 0 - 1; y = 0 - 12) showed a maxima with the increasing Mn concentration (Figure 6.6). Thus, the optimum molar ratio of Cu:Mn in the Cu_xMn_y catalyst was 1:8 showing 100% CO conversion at 120^{o}C. The CO oxidation was very much influenced by the Cu:Mn molar ratio. The binary oxides in CuMn- catalyst were more efficient in comparison to individual Cu and Mn oxides.

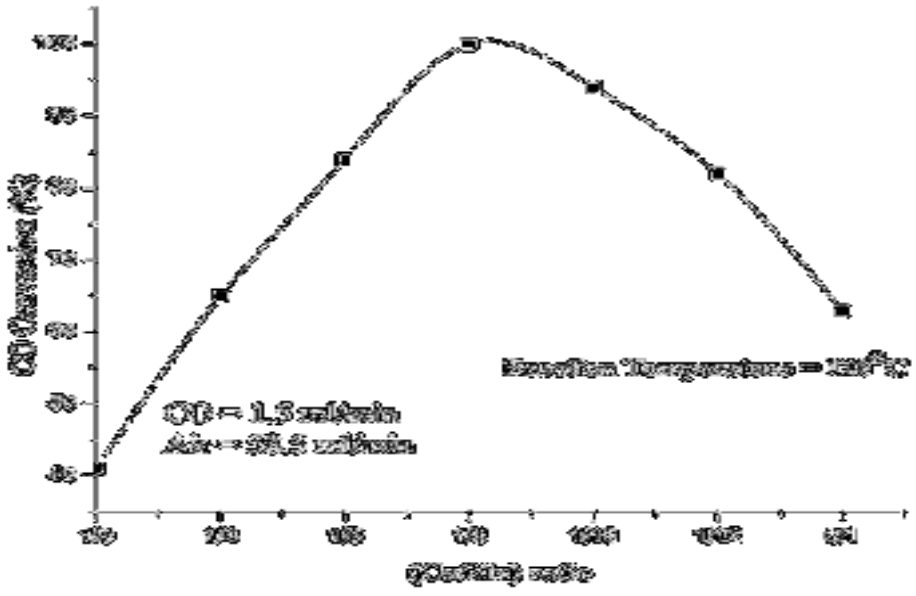

Figure 6.6: Optimization of Cu:Mn Molar ratio in CuMnOx catalyst

For individual Cu-oxide catalyst the conversion of CO was 41.5% while for individual Mn-oxide catalyst conversion was 59%. Individual Cu-oxide and Mn-oxide were prepared by calcination of their nitrate and acetate respectively at 300°C in a stream of flowing air. The binary Cu-Mn oxides have a flexible metal valences ($Cu^{1+/2+}$ and $Mn^{3+/4+}$) which enhance to their specific properties and excellent catalytic activity for CO oxidation.

6.3.2 Optimization of particle size

The size of particles present in Cu_1Mn_8 catalyst was extremely influenced the reaction rate. When the particle size has been decreased; therefore their surface area was increased. The ratio of catalyst surface area and reactant volume was playing a crucial role in controlling the reaction kinetics. The reaction took place on the surface of catalyst; therefore, the increasing of surface area should raise the rate of reaction as well. The particle size provides information about the responsive behavior of the catalysts in an individual process, and the effect of particle size might be attributed to the morphological changes.

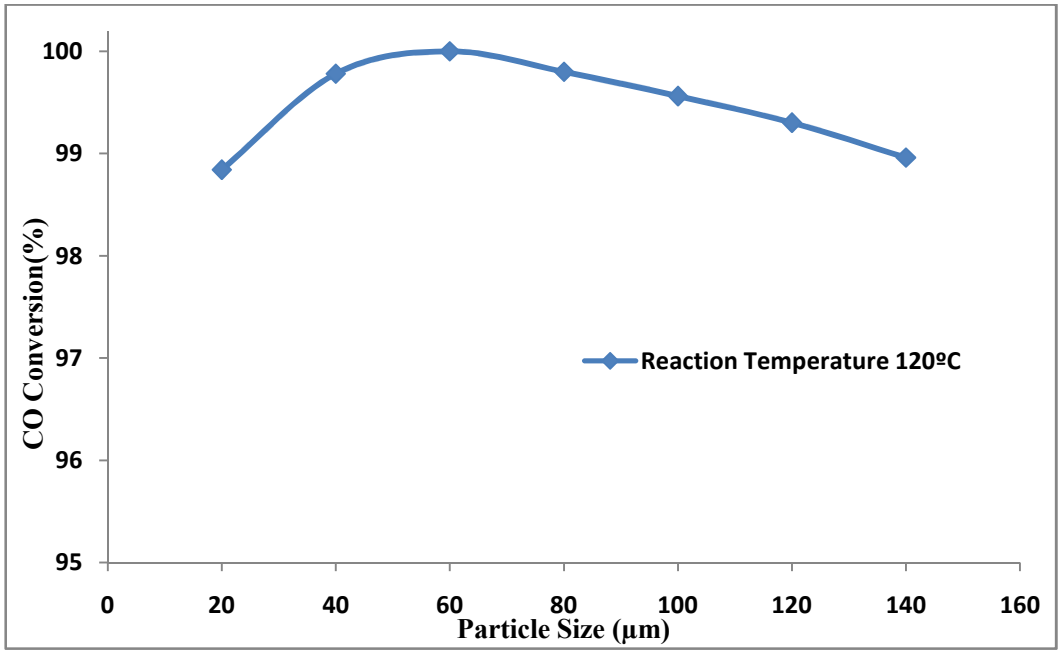

Figure 6.7: Optimization in particle size of Cu_1Mn_8 catalyst

The sieve analysis was separate the various size of particles present in a Cu_1Mn_8 catalyst at the reaction temperature 120°C. The 60-micron(μ) size particles present in Cu_1Mn_8 catalyst was the optimum size for CO oxidation. When the particles present in a Cu_1Mn_8 catalyst was smaller than 10 nanometers, it containing about 10,000 atoms of catalyst and the movements of electrons in the metals were confined, so that their internal energies were increased. The size, shape and morphology of the catalyst particles were confirmed by the SEM, XRD and BET characterization.

6.3.3 Optimization of drying temperature

The drying step has known to be strongly influence on the preparation of final catalyst. During the drying period, the solution may be retained by the porous support, and it may be migrated by capillary flow and diffusion, therefore; the solute redistributed by the de-sorption and re-adsorption. A critical drying temperature produces uniform homogeneous particles of a precursor.

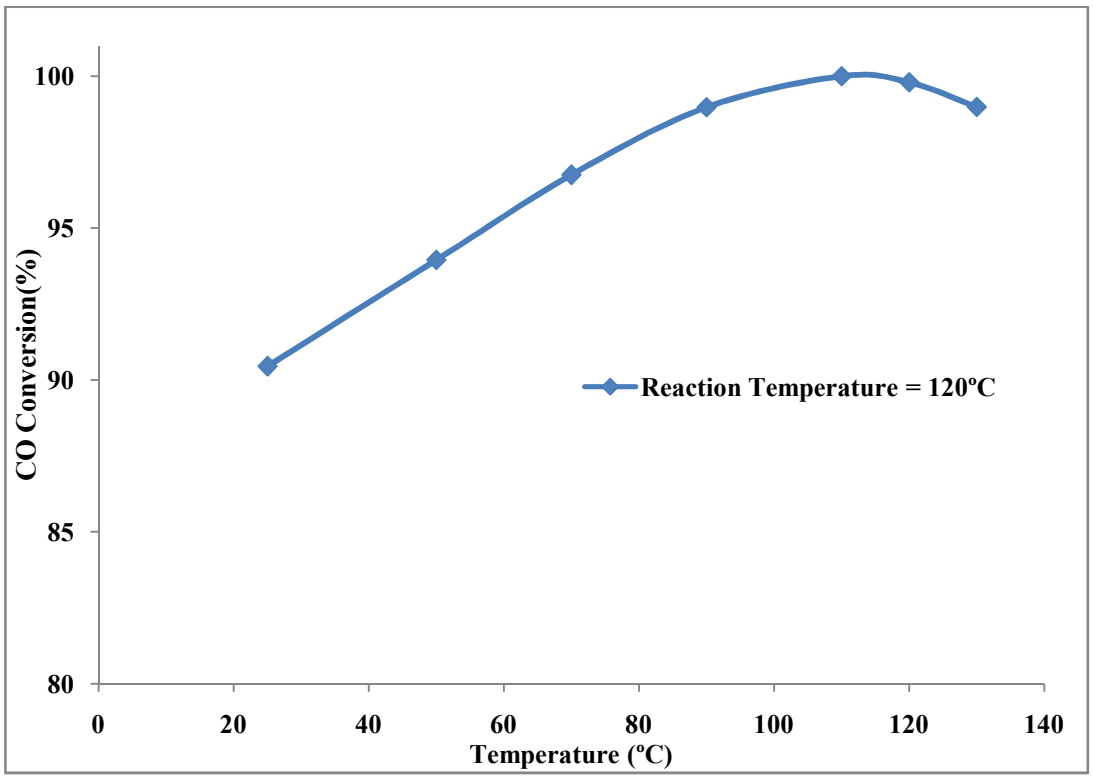

Figure 6.8: Optimization of drying temperature of Cu_1Mn_8 precursor

Activity of the Cu_1Mn_8 catalysts for CO oxidation was carried out to evaluate the effect of drying the wet precipitated precursor at different temperatures (22-120^oC) for 24h followed by calcination in flowing air. The activity of resulting catalyst was increased with the increasing of drying temperature of the precursor up to 110^oC, and further increasing the drying temperature of the precursors their activity was decreased (Figure 6.8). Thus, the optimum drying temperature of the precursor was 110^oC, which produced the catalyst exhibiting the highest activity for 100% CO conversion at 120^oC.

6.3.4 Optimization of calcination temperature

The calcination temperature of the precursor highly influences the performance of resulting Cu_1Mn_8 catalysts. Thus, the precursor of Cu_1Mn_8 catalyst was calcined at different temperatures (200^oC-400^oC) in a flowing air for 2h to find out the optimum calcination temperature.

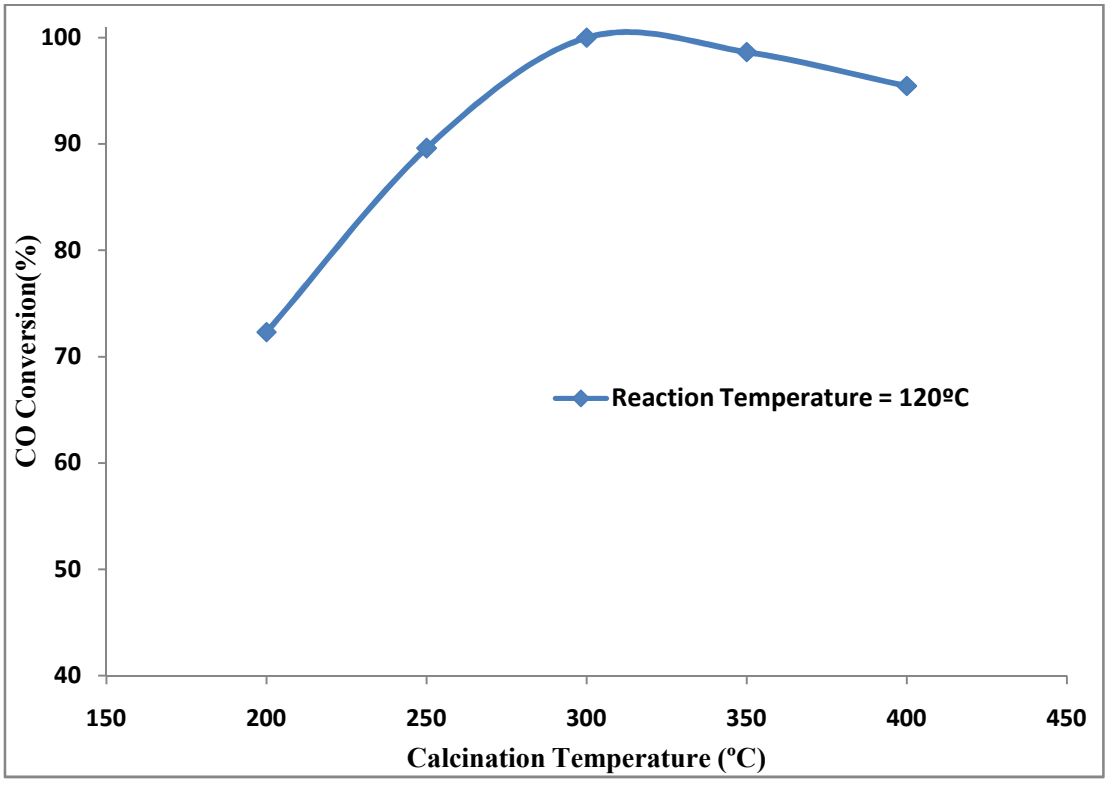

Figure 6.9: Optimization of the calcination temperature of Cu_1Mn_8 precursor

The result of calcination temperature of Cu_1Mn_8 precursor on the produced catalysts for CO oxidation is shown in the Figure 6.9. Plot of CO conversion at 120°C over the catalysts resulted at different calcination temperature of the precursor, shows a maximum for the catalyst produced at 300°C. The catalytic activity decreased for the catalysts produced at higher temperatures than 300°C. Thus, the optimum calcination temperature of the precursor was 300°C.

6.3.5 Optimization of calcination time

Like calcination temperature, the duration of calcination also effect on the activity of resulting catalysts. Thus, to see the effect of calcination time, precursor of Cu_1Mn_8 catalyst was calcined at different times for 30min, 1h, 1h 30min, 2h, 2h 30min and 3h in a flowing air for a 300°C temperature in the reactor.

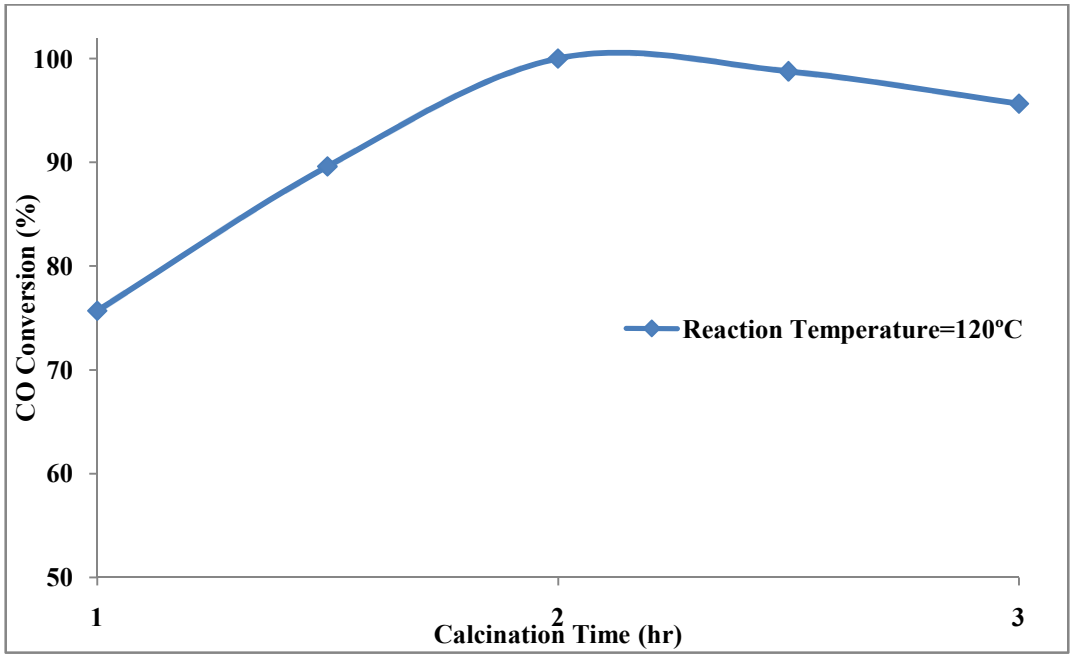

Figure 6.10: Optimization of calcination time of Cu_1Mn_8 precursor

The activity versus calcination time plot shows maxima at 2h under the conditions studied. Thus, the optimum calcination time of Cu_1Mn_8 precursor was 2h. In the flowing air calcination process, the precursor was kept in air at 300°C for 2h; therefore it created the active sites for CO oxidation.

6.3.6 Optimization of weight of catalysts

The conversion of CO was proportional to the weight of catalyst present in a reactor. The weight of catalyst was varying from 50 to 160 mg with a constant value of temperature and the feed composition. In the catalytic reaction, the amount of catalyst was used for the CO oxidation, plays a crucial role since the optimization of them can further improved their performance. The external mass transfer did not limit the conversion rate when the temperature of the catalyst has been increased; therefore the coverage of surfaces by CO oxidation will start to decreases.

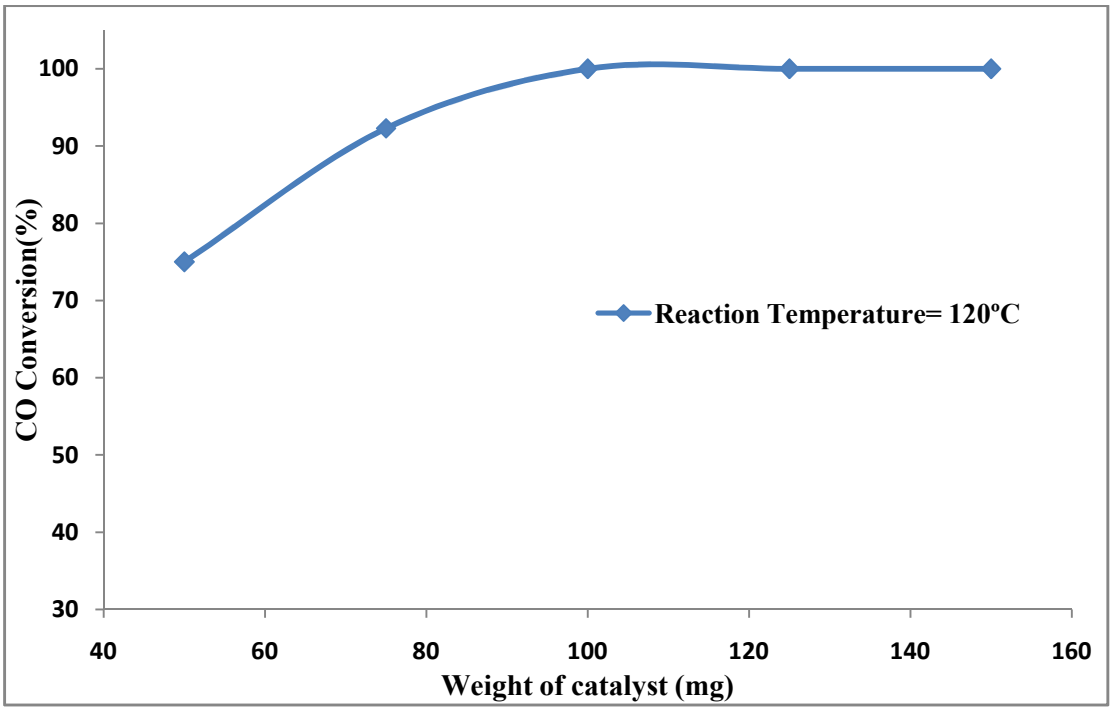

Figure 6.11: Optimization of weight of Cu_1Mn_8 catalyst

The rate of reaction between the adsorbed CO molecules and the oxygen atoms was relatively fast, even at the low temperature. The oxidation states, surface area, crystallinity which strongly influences on the catalytic property and it can be controlled by changing the catalyst composition, metal concentration, additive concentration in the mother liquid, precipitation temperature and calcination temperature, etc. All the reaction was carried out in the steady state conditions. The experiment was

demonstrated at a higher catalyst weight leads to a longer contact time, further, leads to a better catalytic performance. The CO conversion achieved over the different weight of Cu_1Mn_8 catalysts like 50mg, 75mg, 100mg, 125mg and 150mg were 75.55%, 93.95%, 100%, 100% and 100% respectively. After the activity test, we have confirmed that the optimum weight of catalyst was 100mg and further increasing the weight of catalyst their activity was make constant. It can be confirmed that the optimization of the process parameters simultaneously improves the catalytic performance for CO oxidation.

6.3.7 Optimization of CO flow rate

The binding energy of CO was strongly depending upon the concentration of vacancy present in a catalyst surfaces during the steady-state conditions. The enthalpy of CO adsorption representing the strongest donor to the effects of temperature on effective CO oxidation rate constants. In the Figure 6.12, we have observed that the flow rate of CO was varying from 1.0ml/min to 1.75ml/min, and the optimum flow rate of CO for CO oxidation was 1.5ml/min.

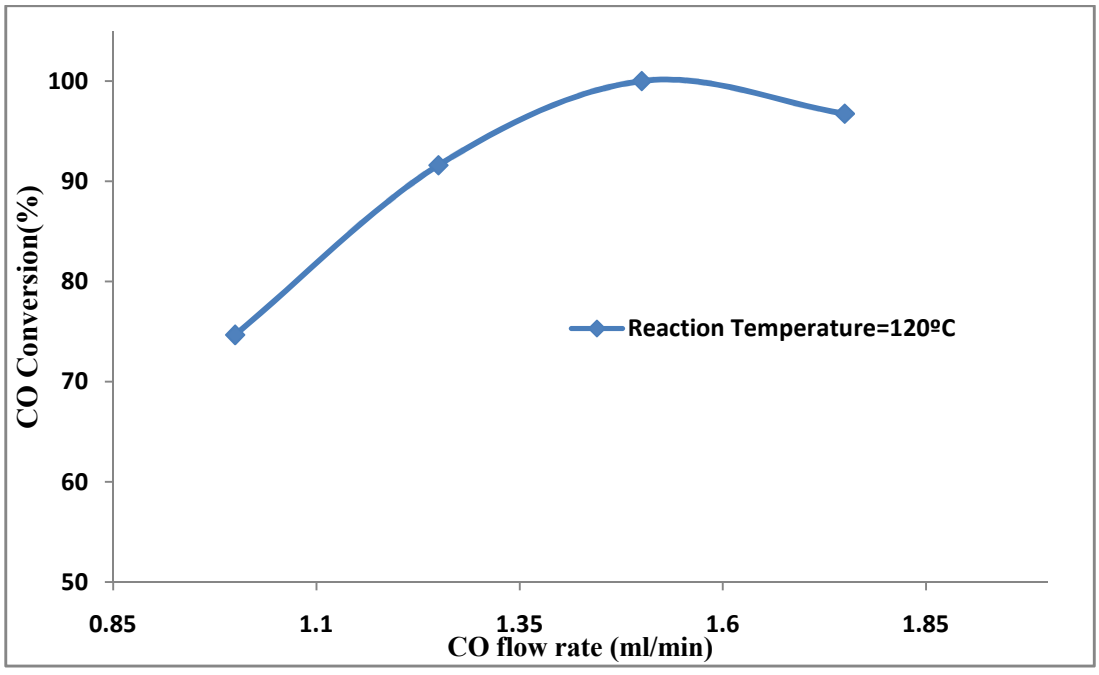

Figure 6.12: Optimization of CO flow rate on Cu_1Mn_8 catalyst

Further increasing the flow rate of CO the activity of the catalyst has been decreased. The different flow rates could be the results if the catalyst particles were packed at various densities, as this leads to various pressure drops over the catalyst bed. At the high temperature, the CO conversion was an increased due to the lattice oxygen consumed with simultaneously CO oxidation. In the process of reactants, adsorption was consider as an exothermic process, while the products desorption was consider as an endothermic process. The increasing oxidation rates were associated with the appearance of a "reactive" CO species which existed in major amounts only during the intermittent operation. The homogeneous nature of Cu_1Mn_8 catalyst was an important factors effect on the high catalytic activity. The CO oxidation rate enhancement was possible, only if the surface was exposed to oxygen for a minimum period without any CO being present in the gas phase. In Table 6.4, we have mentioned that the optimum preparation parameters and experimental conditions of Cu_1Mn_8 catalyst.

Table 6.4: Optimum preparation conditions of Cu_1Mn_8 catalyst

Parameters	**Optimization**
(Cu:Mn) ratio	1:8
Drying temperature	110^oC
Calcination temperature	300^oC
Calcination time	2h
Particle size	60µm
Weight of catalyst	100mg
CO flow rate	1.5ml/min

Many factors which can be varied during the catalyst prepared by the co-precipitation method and the following calcination steps were essential in controlling the activity of Cu_1Mn_8 catalysts for CO oxidation. In this way, we have benchmarked the different parameters on the performance of Cu_1Mn_8 catalyst for CO oxidation.

6.4 Concluding Remarks

It is evident that the activity of a catalyst very much depends on drying temperature, calcination temperature and its duration. The preparation conditions of CuMnOx catalyst for getting excellent catalytic activity are: Cu/Mn molar ratio is 1/8, drying temperature of 110^{o}C, duration of drying 24h, calcination at 300^{o}C for 2h. The optimum operating parameters for CO oxidation was 100mg weight of catalyst at a flow rate of CO (1.5ml/min) with the optimum particle size of 60μ(micron) was used. This study shows that the precipitation and calcination conditions were applied in the preparation procedure are crucial importance. In particular, the catalyst drying and calcination conditions have found to be the most importance and control of these parameters should be incorporated into the design of experimental conditions. The performance of Cu_1Mn_8 catalyst prepared by the flowing air calcination conditions for CO oxidation was associated with the adjustment in intrinsic textural and morphological characteristics such as surface area, crystallite size, particle size, and oxygen deficient faulty composition which creates the high density of active sites.