

The effect of doping on the catalytic activity of CuMnOx catalyst for CO Oxidation

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Abstract: The catalytic oxidation of carbon monoxide (CO) has been more consideration at present times due to its application in many fields. In this study the CuMnOx catalysts in the molar ratio (Cu:Mn=1:8) prepared by the co-precipitation method. After precipitation filtration, washing and drying the sample at 110°C for 16h in an oven and after drying the sample calcined at 300°C temperature in stagnant air, flowing air and reactive calcination (4.5% CO in air). At the time of precipitation, we are doping the CuMnOx catalyst by a little amount of Co, Ce, Fe and Ag promoters. The influence of doping effect on the structural properties of the catalyst and enhance the activity of the catalyst for CO oxidation. The primed CuMnOx doping catalysts were characterized by SEM-EDX, XRD and FTIR techniques. The activity of the catalyst was measured under the following reaction conditions: 100mg of catalyst, 2.5% CO in the air and total flow rate 60 ml/min. The activity order of the catalyst has followed this order: CuMnAg > CuMnCe > CuMnCo > CuMnFe and it is found out that CuMnOx catalyst doping with silver nitrate is shown the best performance for CO oxidation at low temperature.

Keywords: Carbon monoxide, Hopcalite catalyst, Co-precipitation, doping, Reactive calcinations

I. Introduction

Carbon monoxide (CO) is a most poisonous and life threatens gas into the environment, it causes several problems created into the environment. The health effects of CO explored are a headache, fatigue, seizure, coma, fatality, nausea, vomiting and death also. The global background concentrations of CO range between 0.06-0.14 mg/m³ (0.05-0.12 ppm) (1). With the increasing of the population, the number of the vehicle is increased; it causes an insignificant increase in air pollution problem in the world. The emissions from automobiles vehicles are usually the reason for two third of CO produced in the environment. In the comparison of a diesel engine, the gasoline based engine produces more carbon monoxide into the environment (2).

A catalytic converter is a device presence in a vehicle for reducing the toxicity emissions from internal combustion engines. The catalyst presence in a catalytic converter reacts with the CO presence in the exhaust gasses and converted into low poisonous CO₂ gasses and the performance of the catalyst is highly depending upon the types of catalyst presence (3). The hopcalite (CuMnOx) is an effective catalyst for CO oxidation at an ambient temperature, it is prepared from the metal nitrate salts, using the co-precipitation method (4). The CuMnOx is highly active in the amorphous state, but it has lost his activity at the temperature above 500°C, where crystallization of the spinal occurs. The activity of the CuMnOx catalyst is depending upon the structure of the catalyst precursor and the preparation route of the catalyst. The presence of individual phases and their quantitative proportions is depended on the concentration of the reactant solution, pH, temperature and ageing time also (5).

The preparation of the catalyst by novel redox method for room temperature synthesis produced the amorphous CuMnOx catalyst with high surface areas and high catalytic activity for CO oxidation at low temperature. The additional benefit of the catalyst is representing to enhance the resistance of water poisoning (6). To date, they are various methods have been applied to synthesized the CuMnOx catalysts, it including co-precipitation, ultrasonic aerosol pyrolysis, sol-gel, supercritical antisolvent precipitation and reduction methods. Among these methods of CuMnOx catalyst preparation, the usual co-precipitation method can be used to produce highly active sites of the catalyst. The other factors like ageing time and calcination temperatures of the preparation of the catalyst have also influenced the activity of the catalyst (7).

The addition of (3%) cobalt, cerium, iron and silver by deposition precipitation, to a mixed CuMnOx catalyst to improved the performance of the catalyst for CO oxidation. The deposition of dopant on the catalyst to improved the activity of the catalyst and reduced the deactivation of the catalyst (8). In this work the different doped CuMnOx catalyst is tested for CO oxidation at different calcination conditions like stagnant air, flowing air and reactive calcinations of (4.5% CO in air). The hopcalite is the most active reduced catalyst and the liability of the lattice oxygen is one of the important factors that influence the activity. The catalytic activity towards doped CuMnOx catalyst for CO oxidation, it represents the average oxidation number of Mn and the position of nature of the doped cation (9).

II. Experimental

2.1. Catalyst preparation

The CuMnOx catalyst prepared by co-precipitation method, the aqueous solution copper (II) nitrate ($\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$) and manganese acetate ($\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$) were premixed by stirring for 1 hour. After stirring the mixed solution is added to the aqueous KMnO_4 solution under the stirring conditions. The molar ratio of copper/manganese in the CuMnOx catalyst was 1:8.3. After dropped completely the copper manganese solution into the precipitant ageing for 2h, then filtered, washing several times with hot deionized water. After washing drying of the precursor at 110°C temperature for 12h in an oven then calcination of the catalyst in stagnant air, flowing air and reactive calcination (4.5% CO in air) before measuring of the catalyst activity test. The different doping materials like cobalt nitrate, cerium nitrate, silver nitrate and iron nitrate were added individually (3%) in the CuMnOx catalyst at the time of co-precipitation procedure. The nomenclature of the catalysts thus obtained is given in Table 1.

Table 1. The nomenclature of the catalyst samples in this study is as follows.

Catalyst Name	Nomenclature
Co-doped CuMnOx catalyst	CuMnCo
Ce-doped CuMnOx catalyst	CuMnCe
Ag-doped CuMnOx catalyst	CuMnAg
Fe-doped CuMnOx catalyst	CuMnFe

2.2 Characterization

The X-ray diffraction pattern (XRD) is obtained by using Cu $K\alpha$ radiation (40 kV, 100 mA) with a Rigaku D/MAX-2400 diffractometer within the range of 2-theta 10° to 80° . With the help of XRD analysis, we can get the mean diameter (d) of the crystallite. Fourier transforms infrared spectroscopy (FTIR) used for the measurement of different phases presence in the catalyst and the FTIR analysis was done by the Shimadzu 8400 FTIR spectrometer within the range of $400\text{--}4000\text{ cm}^{-1}$. The SEM-EDX was recorded on Zeiss EVO 18 Scanning electron microscope. The SEM produced the image of the catalyst with the help of high-resolution electron beam and EDX provides information about the elemental identification and quantitative composition of the catalyst.

2.3 Different calcination conditions

The CuMnOx precursor was calcined under the three different conditions. In the stagnant air calcination (SAC), the calcination of the precursor was done in a furnace in the absence of air at 300°C for 2 hours to produce the CuMn_2O_4 catalyst. In the flowing air calcination (FAC), the calcination of the precursor was done in presence of flowing air in the reactor at 300°C for 2 hours, just before the activity measurement of the catalyst. In the reactive calcination (RC), the calcination of the precursor was carried out under a flowing reactive mixture of 4.5% CO in air at 300°C for 2 hours. The RC of the precursor is done just before the activity measurement of the catalyst.

2.4 Catalytic Activity Measurement

The activity of the catalyst for CO oxidation has performed under the following reaction conditions: The 100mg of catalyst with the feed gas consisting of 2.5 vol.% CO in the air and the total flow rate was maintained 60ml/min using a fixed bed tabular flow reactor. The air enter into the tabular reactor was made free from moisture and CO_2 by passing it through the drying towers of CaO and KOH pellets. The activity test was carried out in the steady state conditions and the reaction temperature was increased from room temperature to 180°C temperature.

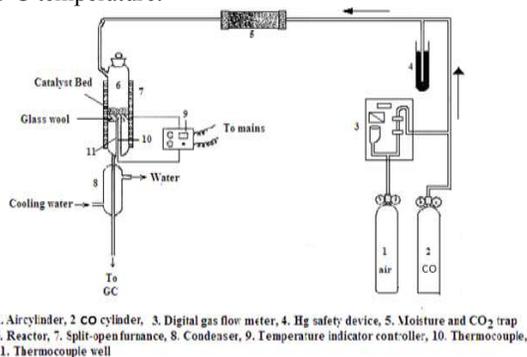


Figure 1. Schematic diagram of Experimental Set up

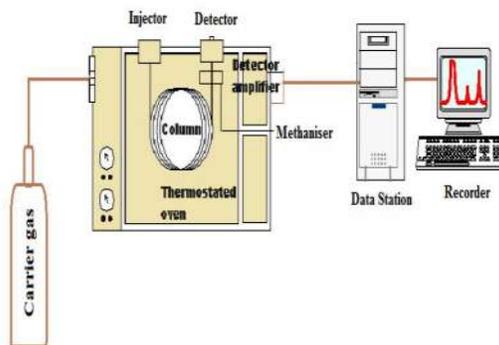


Figure 2. Schematic diagram of Gas Chromatograph

For controlling the heating temperature of the catalyst presence in the reactor was controlled by a micro-processor based temperature controller. To control the flow rates of CO and air through the catalyst in presence of the reactor is done by digital gas flow meters. The feed and product gas stream from the reactor were analyzed by a Nucon Series 5765 online gas chromatogram (GC) equipped with a FID detector, porapack q-column and methaniser for measuring the concentration of CO and CO₂.

III. Results and discussions

The result and discussion of the catalysts characterization by following techniques and the activity of the catalyst for CO oxidation were given below.

3.1 Catalyst characterization

The characterization of CuMnO_x catalyst reveals the material structure, particle size diameter, phase identification and binding energy identification etc.

3.1.1 XRD analysis of the catalysts

The XRD analysis of CuMnO_x catalyst doping with (3%) Co, Ce, Fe, and Ag are individually providing information about the crystalline size and coordinate dimensions presence in the catalysts. The XRD pattern of the catalyst is produced by the reactive calcination conditions display in figure 3.

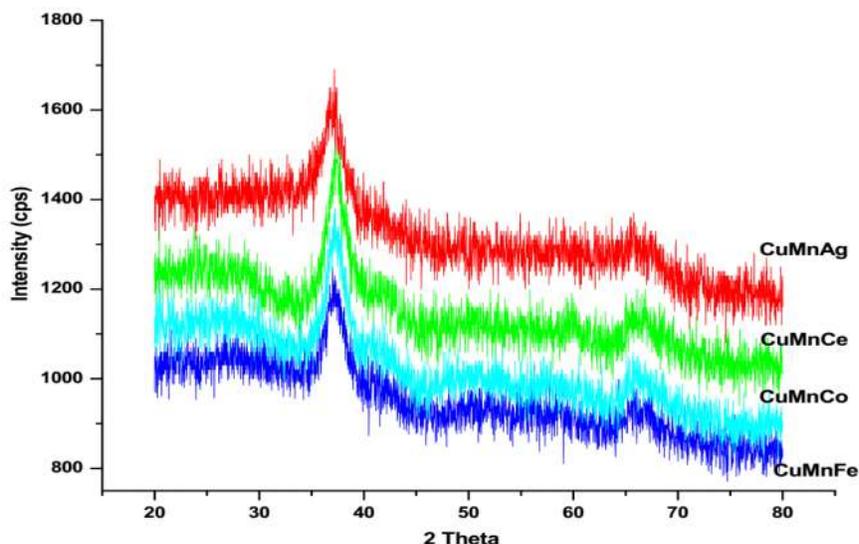


Figure 3. XRD analysis of CuMnO_x catalyst doping with Co, Ce, Fe and Ag nitrate

In the CuMnO_x catalyst doping with 3%Co-Nitrate after RC condition, their diffraction peak at 2θ is 43.50 and corresponds to its lattice plane (2 1 0). The structure is a cubic-centered cubic Cu_{1.5}Mn_{1.5}CoO₄ phase and crystallite size of the catalyst is 3.90 nm. In the CuMnO_x catalyst doping with 3% Ce-Nitrate after RC condition their diffraction peak at 2θ is 28.50 and corresponds to its lattice plane (1 1 2). The structure is body-Centered tetragonal Ce(Mn_{0.2}CuO) phase and crystallite size of the catalyst is 2.90 nm. In the CuMnO_x catalyst doping with 3%, Ag-Nitrate after RC condition their diffraction peak at 2θ is 31.60 and corresponds to its lattice plane (1 1 0). The structure is cubic center CuMn(AgO) phase and crystallite size of the catalyst is 2.40 nm.

In the CuMnO_x catalyst doping with 3% Fe-Nitrate after RC condition their diffraction peak at 2θ is 65.62 and corresponds to its lattice plane (5 3 1). The structure is face-centered, cubic (Cu_{0.5}Mn_{0.5}Fe₂O₄) phase and crystallite size of the catalyst is 3.95 nm. After XRD results we can get confirm that the particle size of CuMnAg catalyst is lower than the other three doped catalysts so that it performs better efficiency for CO oxidation at lower temperatures.

3.1.2 FTIR Characterization

The FTIR transmission spectrum of the catalyst is used to identify the metal oxygen bond present in the catalyst. The FTIR of the catalyst is represented in figure 4, it represents the different types of the chemical group present in the catalyst.

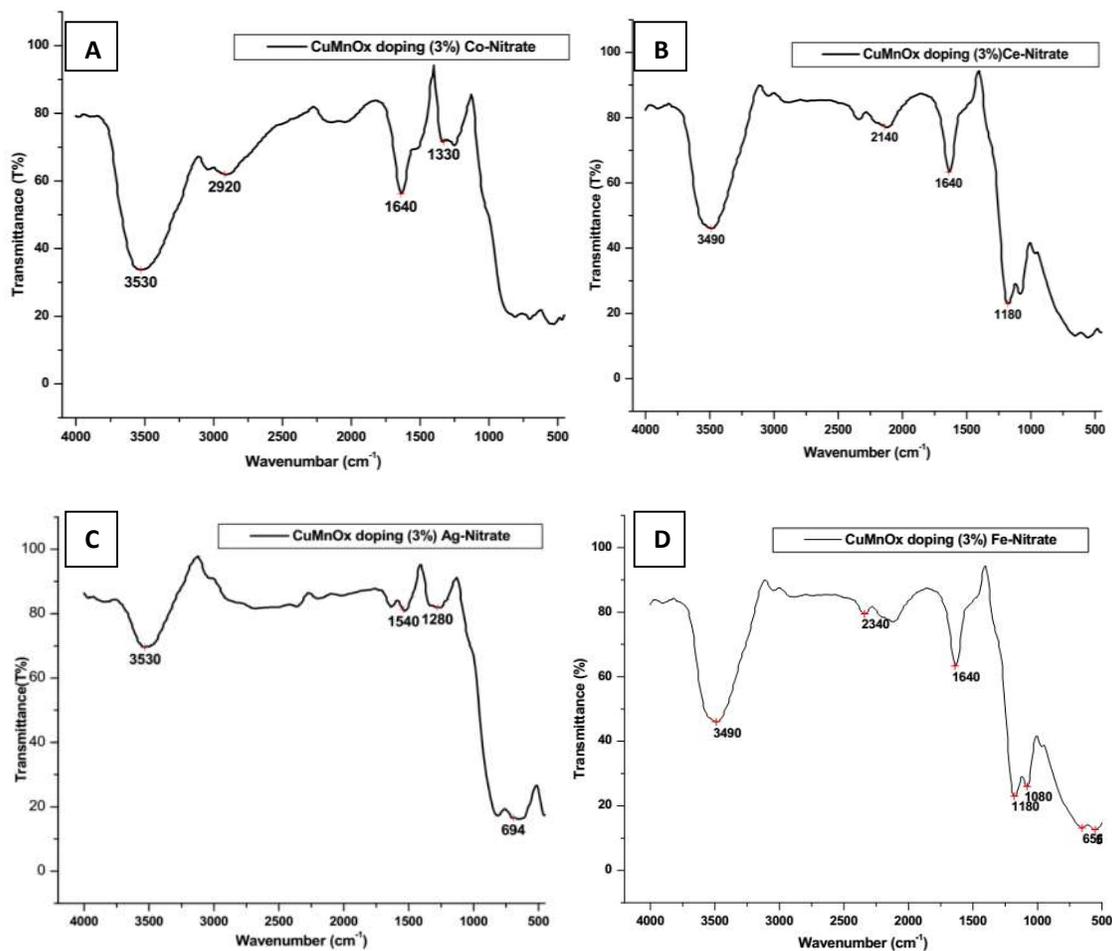


Figure 4. FTIR analysis of A) CuMnCo, B) CuMnCe, C) CuMnAg and D) CuMnFe

The CuMnOx catalyst doping with cobalt, cerium, silver and iron nitrate represent in figure 4, they are prepared by RC method. In the CuMnCo catalyst, the MnO₂ vibration mode was observed at 1640 cm⁻¹ due to stretching of Mn-O bond. The 1330 cm⁻¹ shows the presence of H-OH group, the transmission spectra of 2920 cm⁻¹ shows presence of CuO group and 3530 cm⁻¹ shows the presence of the Co₃O₄ group.

The CuMnCe catalyst in the transmittance conditions they are four peaks we obtained. The brand 1640 cm⁻¹ represents the presence of stretching of Mn-O bond, 3490 cm⁻¹ shows the presence OH group, 2140 cm⁻¹ shows the presence of CuO group and 1180 cm⁻¹ shows the presence of CeO group. In the transmittance conditions of CuMnAg catalyst they are four peaks we obtained, the IR band 1540 cm⁻¹ show the presence of MnO₂ group, the IR band 3530 cm⁻¹ shows the presence of OH group, the IR band 694 cm⁻¹ shows the presence of CuO group and the last IR band 1280 cm⁻¹ represent the presence of AgO group.

In the CuMnFe catalyst, they are seven peaks we obtained, the IR band 3490 cm⁻¹ shows the presence OH group and the IR band (1640 cm⁻¹ and 1180 cm⁻¹) show the presence of Mn-O band. The other bands 2340 cm⁻¹ represent the presence of FeO₂ band, the IR band 658 cm⁻¹ represent the presence of CuO group and the IR band 1080 represent the presence of C-O-C group. The best result we can get from the FTIR analysis is that all the doped catalyst is free from the impurities so that it enhances the activity of the catalyst.

3.1.3 SEM Characterization

The morphology of the catalysts was analyzed by scanning electron microscopy (SEM). It can be the scene that the particle size of the catalyst in crystalline form. The different dopant like Co, Ce, Ag and Fe nitrate is added into the CuMnOx catalyst in RC conditions.

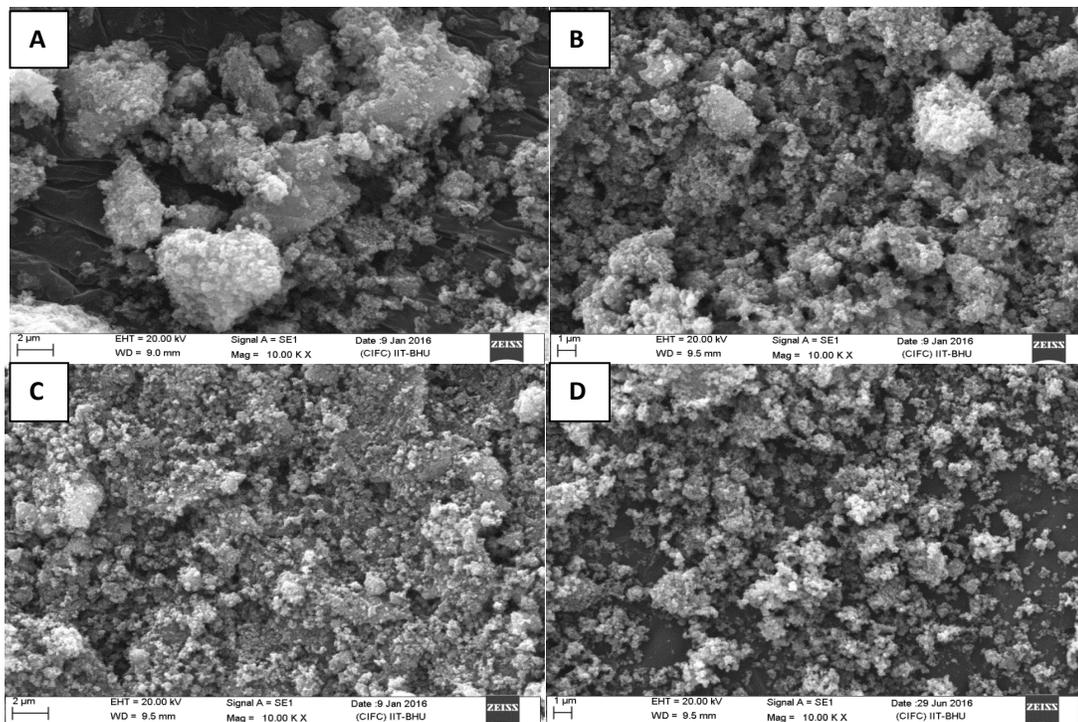


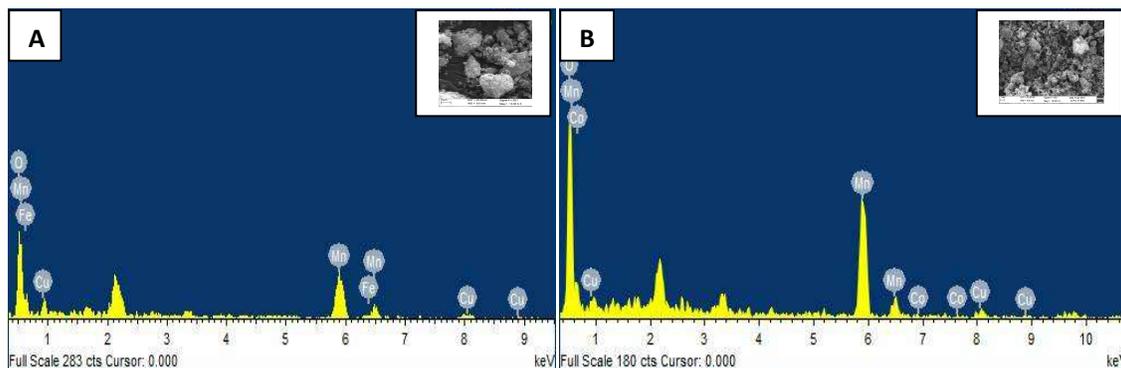
Figure 5. SEM image of A) CuMnCo, B) CuMnFe, C) CuMnCe and D) CuMnAg catalyst

The SEM image clearly shows the large differences in surface morphology by partial substitutions of ions. As seen in the SEM micrograph, the particles were comprised of more coarse, course, fine and finest size grains resulted by RC of CuMnCo, CuMnFe, CuMnCe and CuMnAg respectively. The particles of the CuMnCe and CuMnAg catalyst are less agglomerated, more porous and homogeneous as compared to other two samples. The particle size of the CuMnCo catalyst is relatively very large and agglomerated compared to other three catalysts.

Thus, the different material doped in CuMnOx catalyst followed in the present study considerably affect the porosity, particle size, and morphology of the resulting catalysts. The AgO and CeO₂ prevent the sintering and aggregation of the CuMnOx catalyst and enhance the dispersity of the catalyst. From the figure 5, we can get that the doping materials are evenly distributed in micrometer range on the CuMnOx catalyst surface regardless of the reaction temperature.

3.1.4 Elemental analysis

It is apparent from the results of energy dispersive X-ray analysis (EDX) analysis is that all the samples were pure due to the presence of Cu, Mn, O peaks and their relative doping material peaks are present in the spectra as shown in figure 6. The presence of pure oxides phases of the catalyst which is represented by an analysis of XRD and FTIR characterization.



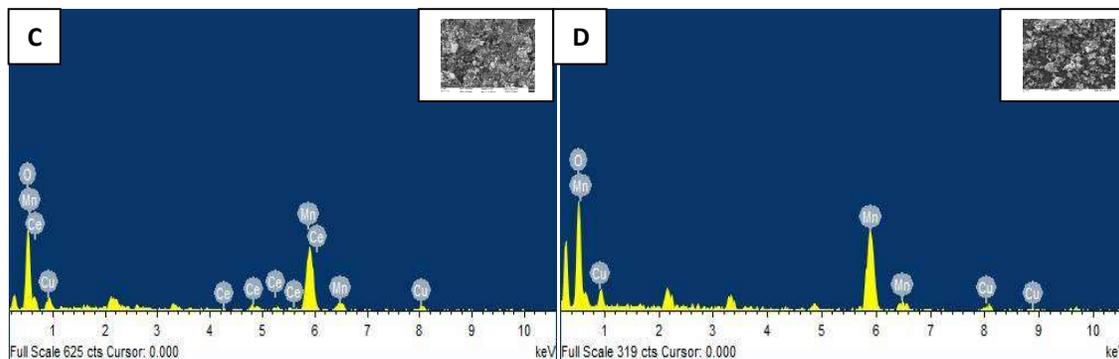


Figure 6. SEM-EDX image of A) CuMnFe, B) CuMnCo, C) CuMnCe and CuMnAg catalyst

From table 2 we can get the relative atomic percentage of Cu, Mn, O and their relative doping material species present in a surface layer of catalyst. It is very clear from the table and figure that the atomic percentage of Mn is higher than Cu in all the four catalysts. The atomic percentage of oxygen in the catalyst prepared by RC is decreased in the following order: CuMnAg > CuMnCe > CuMnFe > CuMnCo.

Table 2. The Atomic percentage of CuMnOx catalyst doping by their respective materials in EDX analysis

CuMnCo	Cu	Mn	O	Co
Atomic percentage	2.70	22.44	73.65	1.20
CuMnCe	Cu	Mn	O	Ce
Atomic percentage	3.48	32.09	63.05	1.39
CuMnAg	Cu	Mn	O	Ag
Atomic percentage	9.82	29.22	58.66	2.30
CuMnFe	Cu	Mn	O	Fe
Atomic percentage	4.69	20.30	72.29	2.71

The atomic percentage of Fe, Ag, Ce and Co in CuMnFe, CuMnAg, CuMnCe and CuMnCo catalyst is 2.71%, 2.30%, 1.39% and 1.20% respectively. The oxygen content of the CuMnAg catalyst is least in comparison to other three prepared catalysts. This indicates the presence of oxygen deficiency in the catalyst of CuMnAg which makes the high density of active sites and the absence of lattice oxygen which creates oxygen vacancy for oxidation reactions. The doping material associated with copper manganese oxides catalyst promote the oxygen storage and release and enhanced the oxygen mobility.

3.2. Catalyst performance and Activity Measurement

The precipitation method highly influences the activity of the CuMnOx catalyst for CO oxidation. The adding of different promoters like (Co, Ce, Ag and Fe) in the CuMnOx catalyst enhanced the activity of the catalyst for CO oxidation at low temperature compared to the undoped CuMnOx catalyst. The activity of the different doped and undoped CuMnOx catalyst was done in different calcinations condition like reactive calcinations (RC), flowing air calcinations (FAC) and stagnant air calcinations (SAC) conditions into the laboratory.

3.2.1. Stagnant air calcination

In the CuMnOx catalyst the molar ratio of Cu:Mn was 1:8.3 and doping with (3%) Co, Ce, Ag and Fe nitrate at the time of precipitation and prepared in the SAC conditions. The oxidation of CO was initiated over undoped and doped CuMnOx catalyst was 25°C temperature and the oxidation of CO is generally depends on the molar ratio copper and manganese. The 50% conversion of CO in undoped CuMnOx catalyst and doped CuMnAg, CuMnCe, CuMnCo, CuMnFe catalyst is 102°C, 60°C, 70°C, 85°C and 120°C respectively and the full oxidation of CO over the undoped CuMnOx catalyst and doped CuMnAg, CuMnCe, CuMnCo, CuMnFe catalyst is 180°C, 110°C, 125°C, 140°C, and 120°C respectively.

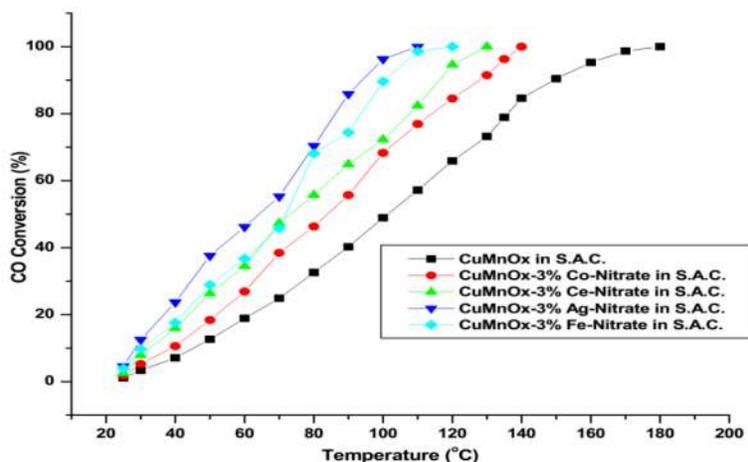


Figure 7. The total oxidation of CO over undoped and doped CuMnOx catalyst in SAC conditions

The light-off characteristics are used to evaluate the activity of the catalysts which is given in table 3. The characteristic temperature T_i , T_{50} , and T_{100} represents the initiation of the oxidation, 50% conversion, and 100% conversion of CO. From table and figure we have to scene that the oxidation of CO was increased with the increasing of the reaction temperature and the reaction is exothermic in nature.

Table 3. The full oxidation of CO over undoped and doped CuMnOx catalyst in SAC conditions

Catalyst	T_i	T_{50}	T_{100}
CuMnOx	25°C	102°C	180°C
CuMnCo	25°C	85°C	140°C
CuMnCe	25°C	70°C	125°C
CuMnAg	25°C	60°C	110°C
CuMnFe	25°C	70°C	120°C

It is very clear from the table and figure, the total oxidation of CO over the undoped and doped CuMnOx catalyst in stagnant air calcination conditions is increased in the following order: CuMnAg > CuMnCe > CuMnFe > CuMnCo > CuMnOx catalyst.

3.2.2. Flowing air calcination

In the flowing air calcination conditions, the calcination of the doped and undoped CuMnOx precursor is done in the presence of air. In the starting conditions, a very slow exothermic reaction for CO oxidation is going on over the catalyst causing rising in local temperature and it reduces the decomposition of the precursor. With the increasing of temperature with the time slightly faster, CO oxidation was observed. It is clear from the table and figure that the oxidation of CO over undoped and doped CuMnOx catalyst was initiated at 30°C and 25°C temperature respectively.

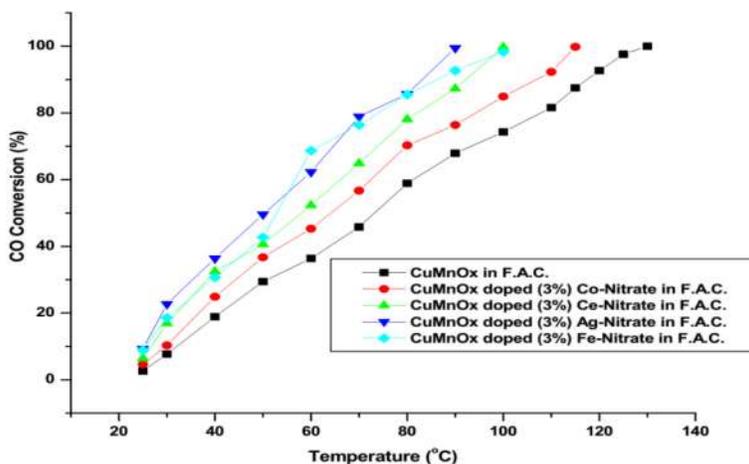


Figure 8. The total oxidation of CO over undoped and doped CuMnOx catalyst in FAC conditions

The 50% conversion of CO in undoped CuMnOx catalyst and doped CuMnAg, CuMnCe, CuMnCo, CuMnFe catalyst is 60°C, 50°C, 55°C, 60°C and 56°C respectively and the full oxidation of CO over the undoped CuMnOx catalyst and doped CuMnAg, CuMnCe, CuMnCo, CuMnFe catalyst is 120°C, 90°C, 100°C, 115°C, and 95°C respectively.

Table 3. The full oxidation of CO over undoped and doped CuMnOx catalyst in FAC conditions

Catalyst	T _i	T ₅₀	T ₁₀₀
CuMnOx	30°C	60°C	120°C
CuMnCo	25°C	60°C	115°C
CuMnCe	25°C	55°C	100°C
CuMnAg	25°C	50°C	90°C
CuMnFe	25°C	56°C	95°C

It is clear from the table and figures the order of activity for different doped and undoped CuMnOx catalyst in FAC conditions is increased in the following order: CuMnAg > CuMnCe > CuMnFe > CuMnCo > CuMnOx catalyst.

3.2.3. Reactive calcination

The reactive calcination of CuMnOx catalyst was carried out in situ in a down-flow fixed scale tubular reactor with a defined amount of CuMnOx precursor diluted with α-alumina to make a total volume 1mL at atmospheric pressure. The full conversion of CO over different doped and undoped CuMnOx catalyst was shown in figure 7. The initiation of the CO oxidation was started at near 25°C in all doped and undoped catalyst and total conversion of CO was increased with the increasing of the temperature.

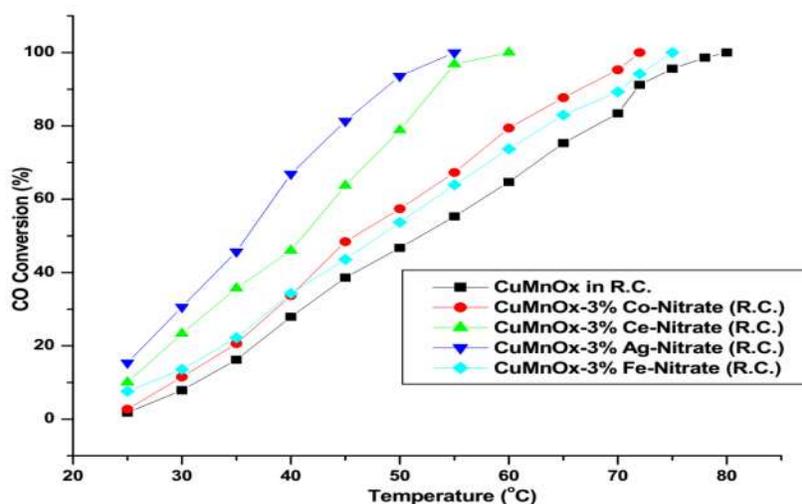


Figure 9. The total oxidation of CO over undoped and doped CuMnOx catalyst in RC conditions

From the figure, it can be concluded that CuMnAg catalyst has a high efficiency for the oxidation of CO at low temperature. The complete oxidation of CO over CuMnAg catalyst is 54°C, which was lowered by 8°C, 18°C, and 21°C than that of CuMnCe, CuMnCo, and CuMnFe catalyst respectively. The total oxidation of CO over undoped CuMnOx catalyst was 80°C temperature respectively. In table 4 shows a comparison of the light-off temperatures of all the catalysts produced by RC using the CO-air mixture for CO oxidation. The improved catalytic activity of doped and undoped CuMnOx catalyst can be ascribed to the unique structural and textural characteristics as the smallest crystalline structure, which is highly dispersed and highest surface area to produce more active sites for catalytic oxidation of CO.

Table 4. The full oxidation of CO over undoped and doped CuMnOx catalyst in RC condition

Catalyst	T _i	T ₅₀	T ₁₀₀
CuMnOx	32°C	55 °C	80 °C
CuMnCo	25°C	45 °C	72 °C
CuMnCe	25°C	40 °C	62 °C
CuMnAg	25°C	35 °C	54 °C
CuMnFe	25°C	50 °C	75 °C

It is clear from the figures and table that the catalyst prepared in reactive calcination conditions was showed the best activity than the catalyst prepared in flowing air and stagnant air calcination conditions. Due to

the reactive calcination of the catalysts increased the open textures pores of the catalyst, it will be a favor for the adsorption of the reactants and desorption of the products and it facilitates the oxidation process. The presence of partially reduced phase in reactive calcined prepared catalyst to provide more oxygen deficient defective structure which creates highest density of active sites to complete oxidization of CO. The order of activity for CO oxidation by various calcination conditions of doped and undoped CuMnOx catalysts were as follows: RC > FAC > SAC.

The CuMnOx catalyst prepared by a co-precipitation method, it possesses of higher catalytic activity and doping low level of Ag, Ce, Co and Fe improved the activity of the catalyst. After the activity test, we can propose that CuMnAg catalyst has a higher activity for CO oxidation compared to other prepared catalyst due to its large surface area, lower in crystalline sized and highly dispersed AgO in CuMnOx catalyst, which can increase the generation of surface adsorbed oxygen to improvement in the catalyst performance. The adding of other promoters like Ce, Co and Fe, improved the performance of the catalyst for CO oxidation and the order of activity for different doped and undoped CuMnOx catalyst as follows: CuMnAg > CuMnCe > CuMnCo > CuMnFe > CuMnOx catalyst.

IV. Conclusions

The CO oxidation over different types of doped and undoped CuMnOx catalyst is considerably influenced by the surface area, pore volume, pore size and crystallite size of the catalyst. From the results and discussions, we can get that the CuMnOx catalysts prepared by co-precipitation method have a higher catalytic activity and the addition of different promoters to improve the performance of the catalyst for CO oxidation. It is proposed that the CuMnOx catalyst doping with silver nitrate (CuMnAg) have a higher catalytic activity compared to other doped catalyst. The order of activity for different doped and undoped CuMnOx catalyst as follows: CuMnAg > CuMnCe > CuMnCo > CuMnFe > CuMnOx catalyst and the order of activity of various calcination conditions was as follows: RC > FAC > SAC. Due to the addition of different promoters into the CuMnOx catalyst, they have an attribute to larger surface area, amorphous in structure and generation of surface adsorbed oxygen it enhance the mobility of lattice oxygen.

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