ORIGINAL ARTICLE

Highly active nano-composite of cobalt–copper–manganese oxides for room temperature CO oxidation

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Abstract

The nano-composite metal oxides are emerging catalytic materials and can be utilized to remediate exhaust pollutants in an energy-efficient way. Thus, Co–Cu–Mn mixed oxide spinel was developed with a glycine combustion route for CO oxidation studies. The composites were characterized by XRD, TEM, N_2-sorption, CO-TPD studies for understanding the structural, particle, and surface nature of the catalysts. The formation of the solid solution was confirmed of Mn in Co–Cu oxides. Furthermore, the high surface area and porosity of Co–Cu–10Mn showed high CO chemisorption and high activity as compared to other Mn composed Co–Cu catalysts. The catalyst composed of 10% of Mn achieved 100% conversion of CO at a low temperature, i.e., 38 °C. The superior catalytic property of Co–Cu–10Mn is attributed to the CuO species from the solid material that has a more excellent synergistic interaction with Co and Mn. These stronger interactions were creating a vacancy site for CO at room temperature. Also, the reaction stability for 6 h was tested without any loss in the catalytic performance.

Keywords CO oxidation · Mix metal oxides · Room temperature conversion · Nanoparticles

Introduction

Since the eighteenth century, the energy demand required for the industrial and automobile processes was achieved through non-renewable resources like natural gas, coal, and petroleum. During the combustion of these carbonaceous fuels, common pollutants such as oxides of nitrogen (NO_x), carbon monoxide (CO), hydrocarbon (HC), and sulfur dioxide (SO_2) are being released into the atmosphere. Carbon monoxide is considered one of the major pollutants released into the atmosphere. The CO being toxic has an adverse effect on human health as it directly binds to the oxyhemoglobin (O_2–Hb) site forming a carboxyhemoglobin (CO–Hb). This results in slow poisoning in humans and other animals, and it is also one of the contributors to greenhouse gases (Badr and Probert 1995). Thus, it is

essential to eliminate the CO formed during the combustion process before it enters the environment. Various research shows the oxidation of CO in variable temperature ranges, but low-temperature CO oxidation has its own industrial and environmental benefits. Currently, the emission control unit utilizes the heterogeneous catalyst composed of precious metals for their higher electron-rich nature that provides a wide redox phenomenon in removing CO (Hirata 2014; Soni et al. 2016). However, the ores of the precious metals are limited, that restricting their utilization and for this reason, various research groups are developing catalyst that is deficient in precious metals (Zou et al. 2008; Fujita et al. 2016; Song et al. 2017; Kerkar and Salker 2020a).

Studies have shown the emerging focus on transition metal-based oxides catalyst to eliminate toxic air pollutants. Commonly, the oxides of copper, manganese, and cobalt have been studied with several combinations by various groups around the globe for efficient conversion of CO to CO_2 due to their high redox properties and low cost (An et al. 2013; Salker and Desai 2016; Bao et al. 2020; Bulavchenko et al. 2020; Rastegarpanah et al. 2020). The recent literature displays the combination of Cu/Mn/Co such as Mn–Cu–Co (Choi et al. 2016), CuMn1/Ce (Lin et al. 2018), Cu_x–Mn composite (Liu et al. 2017), Cu–Mn–X (X = Co, Ce, Zr) (Dey et al. 2017), Cu–Mn loaded ZrO_2–TiO_2 (Gong et al.

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2013), etc. for its efficient CO oxidation activity. Moreover, this represents the combining effect of two or more metals that can synergistically interact to produce a substantial catalytic platform and also can even increase the performance of precious metal or other host metal oxide systems as ascribed from past research (Heemeier et al. 2002; Rani et al. 2018; Kerkar and Salker 2020b). Notably, in every combination of the catalytic system, a key element always provides a specific property to build the overall catalytic performance of the reaction as per the metal present in the combination. While in most of the compositions, it has been noted that Cu has a greater tendency to create synergistic interaction within transition metals for improved surface redox nature. Melodj Dosa et al. prepared nanocatalysts composed of copper and manganese for studying the CO oxidation reaction, wherein the binary and ternary composition resulted in an enhanced catalytic performance (Dosa et al. 2019). Further, they claimed that the presence of Cu species in the solid improves the surface redox behavior, contributing to higher CO conversion yield. Similarly, Yafei Guo et al. investigated the catalytic conversion of CO over Cu/Mn supported carbon nanotube, where they observed enhanced catalytic activity with improved durability towards the reaction (Guo et al. 2016). The effectiveness of Copper species is due to its exchangeable charge from Cu^{+2} to Cu^{+1} during the catalytic reaction, thus capable of developing extendable electronic charge in solid material resulting in higher catalytic activity.

To date, the various mixtures of Co or/and Cu or/and Mn have been discussed above, but the room temperature activity is still a challenging factor that needs to be tacked. In the present work, an attempt was made to prepare the composite oxides of Co, Cu, and Mn by varying the concentration of Mn for efficient conversion of CO to CO_2 at a lower temperature. Considerable success has been achieved by Co–Cu–10Mn catalyst at room temperature CO oxidation and also showed high CO adsorption capacity at room temperature. Meanwhile, the surface desorption studies of CO was performed for investigating trend observed in CO conversion reaction. Further, the characterization with primary tools such as XRD, TEM, N_2-sorption was discussed to understand importance of particle nature and surface area in the catalytic reaction.

Experimental

Preparation of catalyst

Materials

Cobalt nitrate $(Co(NO_3)_2 \cdot 6H_2O)$, copper nitrate $(Cu(NO_3)_2 \cdot 3H_2O)$, and manganese nitrate $(Mn(NO_3)_2 \cdot 4H_2O)$ were brought from Sigma–Aldrich. Glycine was purchased from Thomas Baker. All the chemicals were used without any further treatment.

Preparation via combustion

Composite oxides of cobalt, copper, and manganese were prepared by combustion route using glycine as a fuel. An appropriate amount of cobalt nitrate, copper nitrate, and manganese nitrate was taken by calculating the percent weight ratio of Co:Cu:Mn as 50:50:0, 45:45:10, 40:40:20, and 35:35:30, respectively. Thereafter, the respective metal salts were dissolved in double distilled water along with the calculated amount of glycine. The mixture was then heated at 80 °C with constant stirring, and the concentrated mixture was later kept in an electric oven at 200 °C for 2 h for the combustion process. Finally, the obtained compounds were kept at 500 °C for 4 h to remove the traces of carbon. The prepared composite oxide was introduced as CoO_x–CuO_x, CoO_x–CuO_x–$10MnO_x$, CoO_x–CuO_x–$20MnO_x$, and CoO_x–CuO_x–$30MnO_x$, respectively.

Characterization

The catalysts were studied using the powdered X-ray diffraction technique on the RIGAKU ULTIMA IV diffractometer using Cu Kα source (λ = 1.5418). The particle nature at the nanoscale was examined with HRTEM on Jeol/JEM 2100 instrument operating at 200 kV. The N_2 adsorption studies were carried out on the QUANTACHORME AUTOSORB iQ-MP-C instrument for calculating the specific surface area and pore size distribution. The samples were treated at 200 °C in an inert atmosphere to remove surface adsorbed species. Also, the same instrument was employed for CO–Temperature Programmed Desorption studies to understand the CO reactivity towards the catalyst surface. During CO-TPD studies, 100 mg of catalyst powdered was loaded between quartz wool plugs in a quartz reactor, and the analysis was carried out from room temperature to 400 °C.

Catalytic study

The CO–O_2 reaction was performed on a continuous flow fixed bed glass reactor. The weighed amount of catalyst powder understudy (i.e., 0.9 g) was loaded in between two glass wool plugs. Before the experiment, the catalyst was activated at 200 °C in the N_2 atmosphere before the experiment to remove any adsorbed species. The gases such as N_2 (99.9%), H_2 (99%), and O_2 (99.8%), were brought from a commercial source, and the CO was prepared in the laboratory with the standard preparative route employing formic acid–sulphuric acid reaction (supplementary file). The reaction mixture containing 5% CO and 5% O_2 in 90% N_2 was passed over the catalyst bed with a 5000 ml/min

flow rate during the catalytic CO oxidation. The progress of the entire reaction was monitored on an online gas chromatogram equipped with a TCD detector. A column such as a molecular sieve was used for CO and porapak Q for CO_2 identification. Additionally, the calculation for % CO conversion was carried out by the formula given below:

For the calculation of % CO conversion the following equation has been used:

$$\% \text{ CO conversion} = \left(\frac{\text{CO(out)} - \text{CO(in)}}{\text{CO(in)}} \times 100 \right).$$

Here, CO(in) corresponds to the amount of CO injected in the inlet and CO(out) is the amount of CO at the outlet.

Result and discussion

X-ray diffraction studies

The structural identification of CoO_x–CuO_x, CoO_x–CuO_x–$10MnO_x$, and CoO_x–CuO_x–$30MnO_x$ composite was determined with the powder XRD studies. As depicted from Fig. 1, the composite displays the presence of spinel structure along with CuO that changes as a concentration effect of Mn in CoO_x–CuO_x system. The presence of spinel of cobalt (JCPDS No. 01-078-2177) has been observed in CoO_x–CuO_x composition along with the distinct CuO phase (JCPDS No. 00-048-1548). Eventually, the quantum of CuO species starts diminishing as Mn enters the Co–Cu oxide system that has been clearly seen

Fig. 1 XRD pattern of CoO_x–CuO_x, CoO_x–CuO_x–$10MnO_x$, and CoO_x–CuO_x–$30MnO_x$
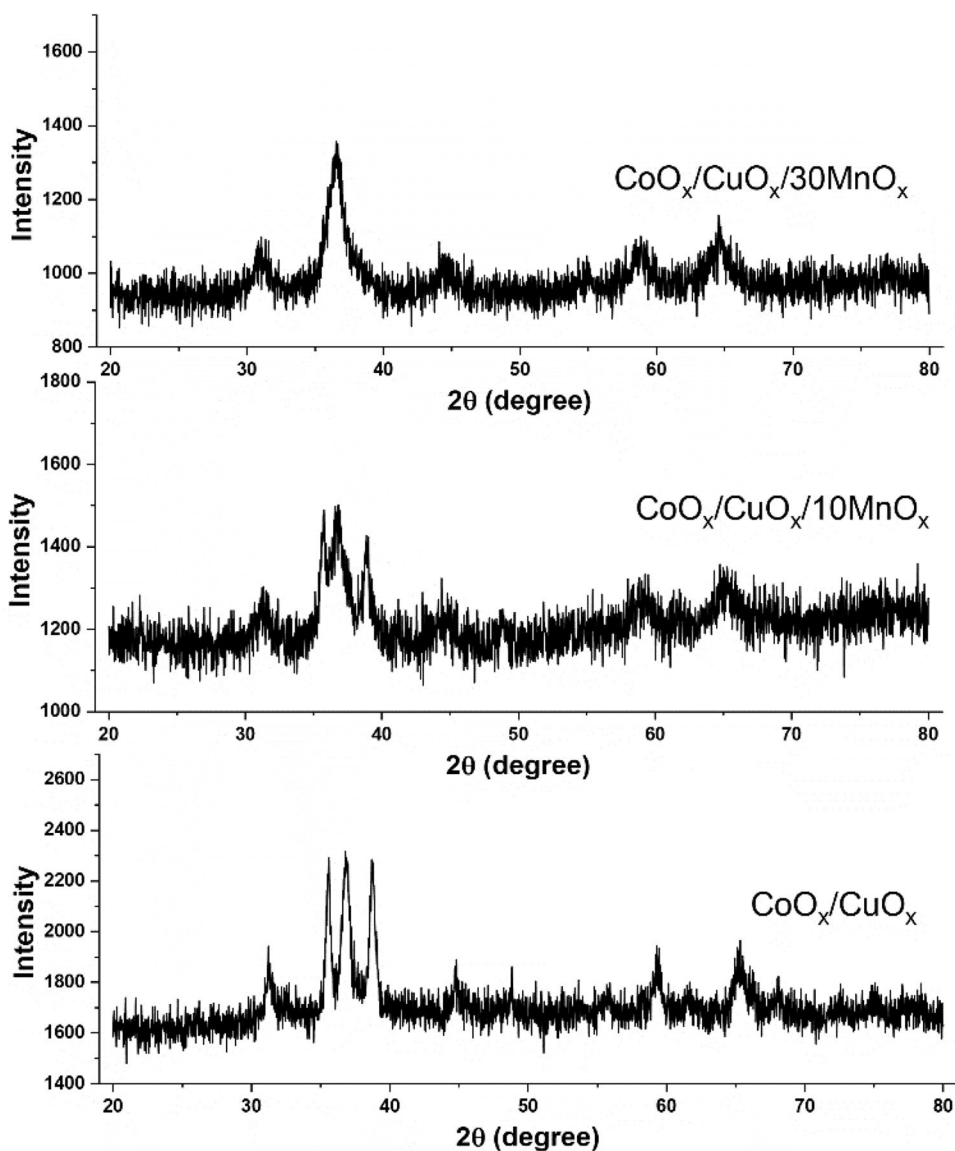
in CoO_x–CuO_x–$30MnO_x$ due to the formation of the solid solution of CoCuMnOx (JCPDS No. 00-047-0324). Thublaor et al. also mention the similar solid solution formation, comparable to the phase observed in Co–Cu–30Mn composite oxide (Thublaor and Chandra-ambhorn 2020). Further, the poor diffraction pattern of the oxides can be concluded from the nano-nature of the material and the larger amount of oxygen vacancies in the oxide material (Liu et al. 2017).

Microscopic study

Figure 2a shows the TEMimage of the CoO_x–CuO_x–$10MnO_x$, which depicts the material in a nanometer region. The image shows the agglomerated particles having a spherical-elongated appearance with a size of below 20 nm. More precisely, the distribution plot (Fig. 2b) showed the various sizes of a particle which mostly falls in 6 to 26 nm range having a higher range of 15 nm. This nano-nature of a particle is essential in the catalytic process as a higher amount of active surfaces gets exposed with a catalyst having a smaller size. Interestingly, these TEM micrographs gave a good agreement between nanostructures with weaker crystallinity of composite material in the diffraction pattern.
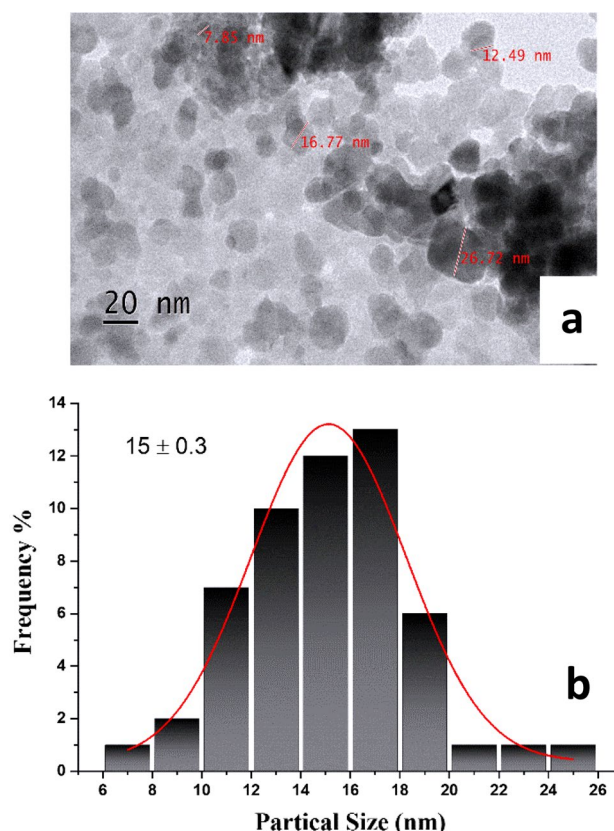

Fig. 2 TEM micrograph and particle size distribution of CoO_x–CuO_x–$10MnO_x$

N₂ adsorption–desorption study

Based on the N₂ adsorption–desorption pattern, the BET surface area, pore size, and pore volume studies were performed and represented in Fig. S1 (supplementary file). According to IUPAC, BET isotherm showed resemblance with type II isotherm having H3 hysteresis loop (Thommes et al. 2015). In BJH pore size distribution, the mesoporous nature of the material was demonstrated to have a pore diameter between 3 and 4.5 nm. The detailed observed values for BET surface area, pore diameter, and pore volume are given in Table 1. The BET surface area studies projected the highest surface area for 10% Mn composed Co–Cu oxide (i.e., 33.7 m²/g) compared to other catalysts in the series. Similarly, the pore diameter demonstrated by Co–Cu–10Mn is 4.31 nm which is the highest in the series. Such porosity in oxide materials is dependent on the type of method employed for the preparation of the oxide material and here, it was due to the evolution of the gases generated during the combustion process (Avgouropoulos and Ioannides 2003).

CO-desorption study

The CO bonding strength by evaluating the CO desorption from the catalyst surface was studied with CO-Temperature programmed desorption (CO-TPD), and the results of the same are presented in Fig. 3. Moreover, this study directly links the CO oxidation activity that generalizes the importance of CO reactivity towards catalysts (Luo et al. 1997). In all the studied samples, CO desorption has been observed in the temperature range of 165–330 °C. In Co–Cu composite oxide, a broad peak of CO desorption is the highest CO desorption at 265 °C. When 10% of Mn was added to CoO_x–CuO_x composite, a shift in CO desorption to lower temperature was detected, clearly seen from the TPD profile of CoO_x–CuO_x–$10MnO_x$. Later, the addition of a higher concentration of Mn (i.e., 20 and 30%) decrease in peak intensity was seen with the increase in Mn concentration, conveying the lesser CO adsorption capacity of CoO_x–CuO_x–$20MnO_x$ and CoO_x–CuO_x–$30MnO_x$

Table 1 BET surface area and porosity study over prepared catalysts

Sr. no	Catalyst	BET surface area m²g⁻¹	BJH pore diameter (nm)	BJH pore volume (cc/g)
1	CoO_x–CuO_x	11.1	3.40	0.026
2	CoO_x–CuO_x–$10MnO_x$	33.7	4.31	0.054
3	CoO_x–CuO_x–$20MnO_x$	24.5	3.53	0.060
4	CoO_x–CuO_x–$30MnO_x$	20.6	3.14	0.048
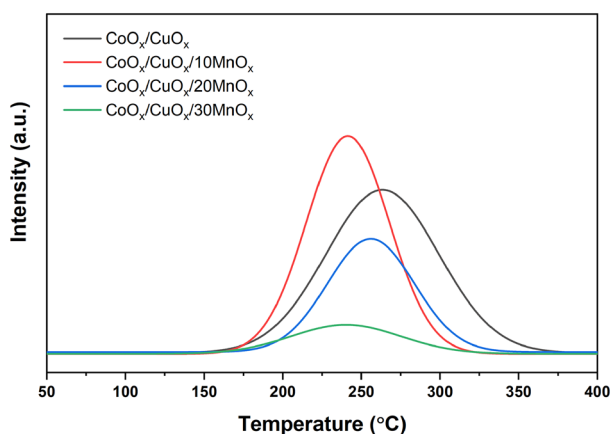
Fig. 3 CO-TPD studies on CoO_x–CuO_x, CoO_x–CuO_x–$10MnO_x$, CoO_x–CuO_x–$20MnO_x$, and CoO_x–CuO_x–$30MnO_x$

Fig. 4 CO–O_2 conversion over CoO_x–CuO_x, CoO_x–CuO_x–$10MnO_x$, CoO_x–CuO_x–$20MnO_x$, and CoO_x–CuO_x–$30MnO_x$ (5% CO and 5% O_2 in N_2 at a flow rate of 5000 ml h^{-1})

composite oxide. The intensity of CO-desorption peaks depends on CO bonding strength with the catalyst surface, which is described as CoO_x–CuO_x–$10MnO_x$ > CoO_x–CuO_x > CoO_x–CuO_x–$20MnO_x$ > CoO_x–CuO_x–$30MnO_x$. According to structural studies (XRD), the CuO phase was detected, which is a critical species in creating more CO adsorption sites in composite oxide by synergistically interacting with the Co and Mn. Further, the decrease in CuO content resulted in poor adsorption of CO over the catalyst surface, justifying the importance of CuO with CO reactivity. While studying CO oxidation studies on the Cu–Mn system, Liu et al. also showed the significant effect of Cu species in generating high surface defects and adsorption behavior in the catalyst (Liu et al. 2017). Eventually, an increase in Cu concentration created a more stable form of Cu–Mn oxide that restricted the redox ability and adsorption of CO on the surface.

Catalytic performance

The oxidation of CO to CO_2 on Co–Cu composite oxides was studied by varying the Mn concentration. All the composite catalysts showed their catalytic behavior towards CO, and the result of the same is presented in Fig. 4. In the prepared composite oxides, Co–Cu composition presented its lowest activity in the series by converting 100% CO to CO_2 at 90 °C. Later the outstanding performance with 10% Mn substitution was observed in the catalytic conversion that was able to convert CO up to 57% at 30 °C, and showing its 100% efficiency at 38 °C. Further, adding 20% and 30% Mn in Co–Cu composite oxide drastically affected the low-temperature CO activity, thereby exhibiting both 100% CO conversion at 60 °C. According to the literature, various types of composite have been reported for CO oxidation but are unable to achieve the room temperature conversion (Qiao
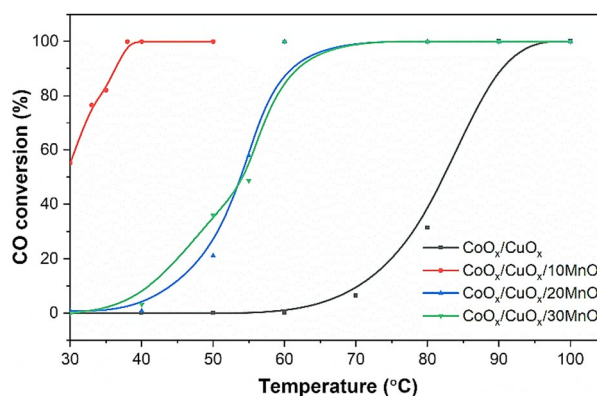
et al. 2011; Dey et al. 2020; Yang et al. 2021). In most previous reports, only a catalytic material composed of precious metals tended to convert CO to CO_2 at room temperature (Luo et al. 2008; Camposeco et al. 2021). While the current study on CoO_x–CuO_x–$10MnO_x$ showed room temperature CO to CO_2 conversion compared to the rest of the catalysts in the series which is exceptionally superior as per the literature survey. The comparative table producing brief literature on CO oxidation over a catalyst composed of Mn–Co or Co–Cu or Co–Cu–Mn is shown in the supplementary file (Tabulated in supplementary Table TS1).

It is well known that the Cu act as a promoter in various catalytic processes such as NO_x reduction (Wang et al. 2015), hydrogen production (Pérez-Hernández et al. 2007), hydrogenolysis of glycerol (Zhang et al. 2021), etc. In the present CO conversion study, the improved catalytic behavior is entirely dependant on CuO content in the composite oxide, which synergistically interacts with Co–Mn and lowers the thermodynamic barrier to enhance the redox property at lower temperatures. While in higher Mn composed oxides the CuO phase was absent and hence resulted in lowering the catalyst property. This variation in CuO was clearly highlighted from the XRD pattern of a composite oxide. Likewise, it has been widely accepted that the presence of the CuO phase in solid material displays a high affinity toward the CO, thus adsorbing more CO on the surface (Hutchings et al. 1996; Martínez-Arias et al. 2000; Zheng et al. 2016). Here, it has been proved with CO-TPD studies by displaying 10% Mn-based composite oxide with a more prominent CO-desorption peak, otherwise decreasing with a higher amount of Mn.

Additionally, the reaction stability was monitored for 6 h at 50 °C in the presence and absence of CO_2 as a preliminary study for its long-term use, which has been presented in Fig. 5. CO_2 being acidic in nature, there is a possibility of CO_2 getting adsorb on the active site of a catalyst and
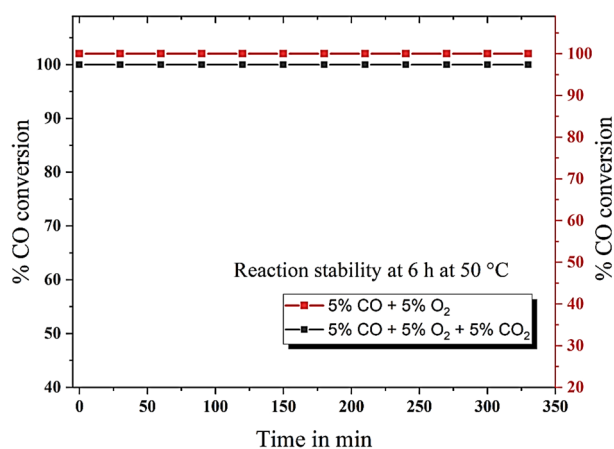
Fig. 5 $CO-O_2$ stability study on Co–Cu–10 Mn catalyst for 6 h

thereby blocking the reaction performance. While the study showed remarkable oxidation without any loss in the activity. Also, the reproducibility of the reaction (Supplementary file Fig. S2) showed an identical conversion pattern for three catalytic cycles, concluding the reproducible behavior of the prepared CoO_x–CuO_x–$10MnO_x$.

Conclusion

In this work, Mn composed Co–Cu composite oxide materials were discussed for efficient CO conversion to CO_2. The glycine combustion was employed to prepare the Co–Cu–Mn nano-composite series. The existence of CuO in the lower concentration of Mn and the formation of a solid solution with a higher Mn concentration was observed with XRD studies. Further through TEM and N_2-sorption studies revealed the nano-nature of the Co–Cu–10Mn composite oxide with high surface area as compared to other oxides from the series. The activity results demonstrated that the nano-composite oxide catalysts followed the order of CoO_x–CuO_x–$10MnO_x$ > CoO_x–CuO_x–$20MnO_x$ > CoO_x–CuO_x–$30MnO_x$ > CoO_x–CuO_x for CO oxidation profile. As displayed from the series of Co–Cu–Mn, only 10% Mn modified Co–Cu composite oxide exhibited an excellent catalytic activity by displaying room temperature CO conversion. Meanwhile, the surface reactivity of CO over the nano-composite oxides studied with CO-TPD exposed the synergistic effect of CuO in Co–Cu–10Mn composite oxide for its remarkable CO adsorption behavior. The highest room temperature conversion is thus attributed to the CuO species, which has a crucial role in converting CO to CO_2. The catalyst reproducibility for CO oxidation was displayed an intact performance of the material. Eventually, the primary reaction stability study for 6 h and the reproducible

result gave a satisfying response without decreasing catalytic performance.

Declarations

Conflict of interest There is no conflict of interest.

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