Bimetallic Co and Mn Supported on Hydroxyapatite Catalyst for Carbon Monoxide Oxidation at Lower Temperature

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Research Article

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Abstract

The series of bimetallic Co and Mn supported on hydroxyapatite catalyst were prepared by successive deposition method and examined for CO oxidation. The CO oxidation activity was compared with monometallic Mn/HAp and Co/HAp. The catalysts are characterized in detail and correlated to the oxidation activity. The XRD, XPS and TPR characterization showed the presence of more facile Co$^{2+}$, Mn$^{3+}$ and adsorbed oxygen due to the interaction between Mn and Co. The 0.4 mol Mn and 0.1 mol Mn deposited on HAp showed formation of maximum active species. The maximum CoO species was observed over bimetallic catalyst compared to the monometallic catalyst. These active lower the activation energy require for CO and oxygen. These species were responsible for the oxidation of CO at lower temperature compared to the remaining catalyst.

Introduction

The CO is most pernicious and toxic gases emitted from industrial and vehicle exhaust. The abatement of CO emission from this exhaust is done by using various noble and non-noble metal supported on Ce, Al, HAp etc. catalysts [More et al. 2018; More et al. 2019; More et al. 2020; Fei et al. 2020; Huawei et al. 2020; Xinjia et al. 2021]. However, the low temperature CO oxidation activity is improved by either modifying the support or active component of the catalyst [More et al. 2019; Zhongqi et al. 2020]. The Mn based catalyst showed formation of carbonate species on the catalyst surface which results in detrimental effect on CO oxidation at lower temperature [Dey et al. 2020]. To improve the low temperature activity of supported Mn catalyst, addition of second metal was preferred over monometallic catalyst. The Mn related bimetallic catalyst are widely studied for complete oxidation of CO [Faure et al. 2015; Liu et al. 2017; More et al. 2019; Bulavchenko et al. 2020; Portillo-Velez et al. 2020]. Furthermore, preferentially exposed (110) plane of Co$_3$O$_4$ nanorods was active for CO oxidation [Jansson et al. 2002; Jiang et al. 2011; Nguyen et al. 2015]. This plane enriched with Co$^{3+}$ species and was responsible for the exceptional catalytic activity for low temperature CO oxidation [Binning et al. 1982; Xie et al. 2009; Iablokov et al. 2015].

Moreover, molecular oxygen was activated into oxygen superoxide ion (O$_2^-$) by surface oxygen vacancies, which actively couples with CO molecule adsorbed on cobalt cations of Co$_3$O$_4$ to form product CO$_2$ [Yu et al. 2009]. The CoO showed weaker metal-oxygen bond among all transition metal oxides. CoO can also be generated through a thermal-driven phase transition [Henrich et al. 1996]. However, CO oxidation using cobalt oxide showed deactivation due to the presence of water/carbonate species on the surface [Mutuberría et al. 1993; Cunningham et al. 1994; Jansson et al. 2001; Thormählen et al. 2001; Grillo et al. 2004]. The deactivation of catalyst could be inhibited by addition of second metal. The Co-Ce- Co and Mn mixed oxide studied for ethanol, butanol and toluene oxidation [Aguilera et al. 2011]. Mn showed preferential oxidation of CO oxidation at 170 ºC due to the rapid removal of carbonate species [Qiang et al. 2010]. However, complete CO oxidation at lower temperature (< 100 ºC) using bimetallic Co and Mn supported on HAp has need to explore in detail with kinetic parameters.
Furthermore, the Mn showed presence of Mn$^{2+}$, Mn$^{3+}$ and Mn$^{4+}$ species having facile redox properties [More et al. 2019]. The bimetallic Mn and Co forms amorphous phase and presence of the higher concentration of active oxygen species [Bulavchenko et al. 2020; Zhang et al. 2018]. Moreover, Hydroxyapatite (HAp) having formula Ca$_{10}$(PO$_4$)$_6$(OH)$_2$ abundance in the nature and is being most studied compound from the apatite class. HAp shows high chemical, thermal stability and weak solubility. It crystallizes in the hexagonal structure in P63/m space group [Henrich et al. 1996; Liu et al. 2012]. HAp is reported for rapid removal of carbonate species from the catalyst surface which was leads to the availability of active sites for CO oxidation [Kunfeng et al. 2013]. In present study, low temperature CO oxidation has been studied with active component modification of Mn/HAp by addition of Co. The CO oxidation activity of Co/Mn/HAp has been studied with detailed characterizations.

**Experimental**

**Catalyst synthesis**

The listed chemicals and reagents were used without further purification for synthesis of bimetallic Mn and Co supported on HAp catalyst. (NH$_4$)$_2$HPO$_4$ (97%), Ca(NO$_3$)$_2$.4H$_2$O (99.5%), NH$_4$OH (25% v/v), Mn(NO$_3$)$_2$.6H$_2$O (99.99%) and Co(NO$_3$)$_2$.6H$_2$O (99.9%). Chemicals were purchased from S D Fine Chemicals.

The hydroxyapatite (HAp) has been synthesized as per reported method [More et al. 2019; More et al. 2020]. The Co$_x$/Mn$_{1-x}$/HAp$_{0.5}$ (x =0.1, 0.2, 0.3, 0.4) catalyst will be prepared by successive impregnation method. In the aqueous slurry of HAp (0.5 mol), requisite moles of the Mn [Mn(NO$_3$)$_2$.6H$_2$O] dissolved in 10 mL distilled water. The mixture was kept under constant stirring for 24 h at 600 rpm. The pH of mixture was maintained at 10 with addition of 25% NH$_4$OH. The mixture was filtered and dried for 12 h at 100 °C and calcined at 400 °C for 4 h. The prepared catalyst was named as Mn$_{0.5}$/HAp. Furthermore, the required moles of Co [Co(NO$_3$)$_2$.6H$_2$O] was added in the 100 mL aqueous slurry of the Mn$_{0.5}$/HAp. pH of the mixture was maintained at 10 with addition of 25% NH$_4$OH with constant stirring. The mixture further filtered and dried for 12 h at 100 °C and calcined at 400 °C for 4 h. Accordingly, the series of catalyst were prepared and labelled as Co$_x$/Mn$_{0.5-x}$/HAp (where, x= 0.1-0.5 mol).

The monometallic 0.5 mol of Mn or Co deposited on HAp using above method and labelled as Mn/HAp or Co/HAp.

**Catalytic activity testing**

The series of bimetallic Co and Mn supported on HAp were examined for low temperature CO oxidation. The catalytic activity was performed under atmospheric pressure by using tubular down flow reactor located in an electrical furnace for gas space hourly velocity (GHSV) of 50,000 mL.g$^{-1}$.h$^{-1}$. 0.5 g catalyst was diluted with 2.0 g silicon carbide. The catalyst was preheated for 1 h at 400 °C with 10% O$_2$ and
helium. The composition of reaction feed was 300 ppm CO, 5% O\textsubscript{2} with He balance. This reaction mixture was passed over the catalyst. The catalytic performances were evaluated in the temperature range of 30-400 °C @ 2 °C.min\textsuperscript{-1}. The micro-GC (Agilent 490) equipped with thermal conductivity detector (TCD) having three columns Porapack Q, MS-5A and CP Sil 5CB. The gaseous feed was analysed by using these columns.

\[
\text{CO conversion} = \frac{[\text{CO}]_{\text{initial}} - [\text{CO}]_{\text{final}}}{[\text{CO}]_{\text{initial}}} \times 100\% \ldots \ldots (1)
\]

Following formulae was used to calculate carbon monoxide conversion from the inlet and outlet CO concentration.

Where, \([\text{CO}]_{\text{initial}}\) and \([\text{CO}]_{\text{final}}\) are initial and final concentration of carbon monoxide respectively. According to following equation rate of carbon monoxide \((r_{\text{CO}})\) was calculated [Mutuberría et al. 1993; More et al. 2019]

\[
\text{Rate}(r) \text{ of reaction (}\frac{\text{CO mol}}{\text{g cat.s}}\) = \frac{\text{Molar gas flow rate (mol/s)} \times \text{CO conversion}}{\text{Weight of the catalyst (grams)}} \ldots \ldots (2)
\]

The apparent activation energy was calculated by using slope of Arrhenius plot \(\ln(r)\) Vs reciprocal of temperature (Fig S\textsubscript{1}).

**Catalyst Characterizations**

The powder X-ray diffraction (PXRD) studies of the catalyst were performed on the Shimadzu XRD 6100 instrument having Ni-filter and Cu K\textalpha\ radiation (\(\lambda =1.54\ \text{Å}, 40\text{kV}, 30\text{mA}\)). The XRD patterns were recorded at scan rate of 4° min\textsuperscript{-1} with 0.02° step size. Smart Sorb 92/93 instrument from Smart Instrument Co. was used to study nitrogen adsorption. The catalyst was preheated at 250 °C in the environment of N\textsubscript{2} purging for 90 minutes followed by N\textsubscript{2} adsorption. The temperature programmed reduction (H\textsubscript{2}-TPR) study is carried out to analyse the surface reducibility of the catalyst. H\textsubscript{2}-TPR study was carried out on Micromeritics AutoChem II equipped with thermal conductivity detector (TCD). In H\textsubscript{2}-TPR analysis, pretreated samples were heated with a gas flow of 5% H\textsubscript{2} in Ar @ 20 mL.min\textsuperscript{-1} with heating rate 5 °C.min\textsuperscript{-1} from ambient temperature to 800 °C. The Kratos Analytical instrument- Model AXIS supra with Monochromatic (AlK\textalpha) 600 X-ray source (1486.6 eV) was used to performed X-ray photoelectron spectroscopy (XPS). The background correction was done by C1s peak at 284.8eV.

**Results And Discussion**

**CO oxidation activity of bimetallic Co\textsubscript{x}/Mn\textsubscript{0.5-x}/HAp catalysts.**
The CO oxidation activity and activation energy of bimetallic Co\textsubscript{x}/Mn\textsubscript{0.5−x}/HAp are shown in Fig. 1 and Table 1. The Co/HAp showed light-off temperature (T\textsubscript{light−off}), 50% CO (T\textsubscript{50}) and 100% CO (T\textsubscript{100}) conversion at 60, 117 and 160 °C respectively. However, bimetallic Co\textsubscript{0.4}/Mn\textsubscript{0.1}/HAp catalyst showed T\textsubscript{light−off}, T\textsubscript{50}, T\textsubscript{100} at 40, 102 and 150 °C respectively. The increasing loading of Co (0.1 to 0.4) in bimetallic Co\textsubscript{x}/Mn\textsubscript{0.5−x}/HAp catalyst showed decrease in T\textsubscript{50}. The Mn/HAp catalyst exhibited CO oxidation at higher temperature compared to all catalyst. However, Mn\textsubscript{5}Co\textsubscript{1}O\textsubscript{x} prepared by coprecipitation showed 100% CO conversion at 250 °C [Bulavchenko et al. 2020]. The Cu supported on Co substituted HAp exhibited T\textsubscript{light−off}, T\textsubscript{50}, T\textsubscript{100} at 73, 130 and 157 °C respectively [More et al. 2019].

In present study, bimetallic Co\textsubscript{x}/Mn\textsubscript{1−x}/HAp showed 100% CO conversion at 170 °C. The Co\textsubscript{0.4}/Mn\textsubscript{0.1}/HAp showed T\textsubscript{50} and T\textsubscript{100} at lower temperature and lowest activation energy (31.3 kJ.mol\textsuperscript{−1}) compared to all catalyst.

| Catalyst          | %CO conversion temperature (°C) | Ea (kJ.mol\textsuperscript{−1}) |
|-------------------|---------------------------------|----------------------------------|
|                   | T\textsubscript{Light−off} | T\textsubscript{50} | T\textsubscript{100} |                           |
| Mn/HAp            | 100                            | 190                  | 250                  | 64.0                     |
| Co/HAp            | 60                             | 117                  | 160                  | 40.5                     |
| Co\textsubscript{0.1}/Mn\textsubscript{0.4}/HAp | 60                             | 125                  | 170                  | 53.1                     |
| Co\textsubscript{0.2}/Mn\textsubscript{0.3}/HAp | 40                             | 121                  | 170                  | 39.3                     |
| Co\textsubscript{0.3}/Mn\textsubscript{0.2}/HAP  | 40                             | 113                  | 160                  | 37.3                     |
| Co\textsubscript{0.4}/Mn\textsubscript{0.1}/HAp | 40                             | 102                  | 150                  | 31.3                     |

The stability test was performed under stationary condition at 400 °C to evaluate the long-term stability and reproducibility of the designed catalyst. The Co/HAp and Co\textsubscript{0.4}/Mn\textsubscript{0.1}/HAp showed 100% CO conversion at 400 °C and stable activity was observed for 1080 min. These results suggest that the active sites are stable at high temperature (Fig. S\textsubscript{2}).

**Characterizations of the bimetallic Co and Mn supported on HAp catalysts.**

**Powder X-ray diffraction and surface area study of Co\textsubscript{x}/Mn\textsubscript{0.5−x}/HAp.**

The XRD patterns of Mn promoted Co/HAp catalysts prepared by successive deposition method are shown in Fig. 1. The PXRD patterns exhibited the diffraction peaks centred at 2θ = 22.7, 25.82, 28.8,
31.98, 33.97, 39.66, 43.88, 46.74, 48.02, 49.54, 53.16, 60.08, 61.78, and 64.06°, which is characteristic of well-defined crystalline phase of hexagonal with space group $P_{63/m}$ of pure HAp (JCPDS 09-0432).

The diffraction peak appearing at $2\theta = 31.86, 37.58, 44.73, 59.31$ and $64.7$ was assigned to the cubic spinel structure of cobalt oxide $\text{Co}_3\text{O}_4$ (JCPDS-9-418). Whereas, $2\theta = 28.95, 32.4, 38.27, 44.43, 49.10, 50.9, 58.21, 60.08$° were due to $\text{Mn}_3\text{O}_4$ phases (JCPDS-24–0734). The standard sample of cobalt oxide and manganese oxide were prepared as per mentioned synthesis procedure which showed CoO (JCPDS-43-1004), $\text{Co}_3\text{O}_4$ (JCPDS-9-418) and $\text{Mn}_3\text{O}_4$ phases (JCPDS-24–0734). The predominant separate phase of CoO peaks was observed at 36.6° [Prieto et al. 2019] in Co/HAp and Co$_x$/Mn$_{0.5-x}$/HAp. The weak intensity of the CoO peak indicates the formation of low crystalline phases. Furthermore, Mn$^{3+}$ is active site for CO oxidation [Lavande et al. 2020]. The MnO$_x$ prepared by same methods shows formation of $\text{Mn}_3\text{O}_4$ species. These results indicate that the addition of Co leads to the formation of $\text{Mn}_3\text{O}_4$ which is the active phase for CO oxidation. In Co/HAp and Co$_{0.4}$/Mn$_{0.1}$/HAp formation of CoO was observed. The Co-O bond weakest bond among transition metal and active for CO oxidation.

The Table 2 shows the surface area of bimetallic Co$_x$/Mn$_{0.5-x}$/HAp catalyst. Mn/HAp and Co/HAp showed comparable surface area. Whereas, surface area decreases with increase in Co concentration. Co$_x$/Mn$_{0.5-x}$/HAp catalyst showed optimum surface area (42.7 m$^2$/g).

| Catalyst          | Surface area (m$^2$/g) |
|-------------------|------------------------|
| HAp               | 28.8                   |
| Mn/HAp            | 56.5                   |
| Co/HAp            | 54.6                   |
| Co$_{0.4}$/Mn$_{0.1}$/HAp | 42.7               |
| Co$_{0.3}$/Mn$_{0.2}$/HAp | 47.5               |
| Co$_{0.2}$/Mn$_{0.3}$/HAp | 47.9               |
| Co$_{0.1}$/Mn$_{0.4}$/HAp | 52.5               |

**Reduction temperature comparisons of Co$_{0.4}$/Mn$_{0.1}$/HAp with Co/HAp and Mn/HAp (H$_2$-TPR)**

The H$_2$-TPR study of Co$_{0.4}$/Mn$_{0.1}$/Hap, Co/HAp and Mn/HAp is shown in Fig. 3. The TPR profile of Mn/HAp includes small shoulder and strong reduction peaks at 325 and 363 °C respectively. These peaks are ascribed to the reduction of Co$^{3+}$ and Mn$^{3+}$ in tetrahedral site of $\text{Mn}_3\text{O}_4$. The hump of peak greater
than 390 °C could be due to the merging of reduction peaks of CoO to Co and Mn$_3$O$_4$ to MnO [Jampaiah et al. 2019; Si et al. 2020; Mojtaba et al. 2021]. The Co$_{0.4}$/Mn$_{0.1}$/HAp catalyst showed shoulder and peaks with hump at 280, 334 and 520°C respectively. These peaks are consonant with the reduction of Mn$^{3+}$, Co$_3$O$_4$, CoO and Mn$_3$O$_4$. The bimetallic Co$_{0.4}$/Mn$_{0.1}$/HAp showed TPR peaks at lower temperature compared to the monometallic Mn/HAp and Co/HAp catalyst. The decrease in reduction temperature indicates that the improvement in redox properties of Mn/HAp after Co addition. The interaction between Co and Mn increases the mobility of oxygen in spinel Co$_3$O$_4$ and could weakened the Co-O bond. The Mn and Co interactions could facilitate the Mn$^{3+}$↔Mn$^{2+}$ and Co$^{3+}$↔Co$^{2+}$ redox cycle, and responsible for the low temperature CO oxidation.

X-ray Photoelectron Spectroscopy (Xps) Study

The XPS spectra of the bimetallic Co$_{0.4}$/Mn$_{0.1}$/HAp, monometallic Co/HAp, and Mn/HAp are shown in Fig. 4. Co$_{0.4}$/Mn$_{0.1}$/HAp exhibits the two deconvoluted peaks for Mn 2p at 641.9, 644.6 and 652.5, 654.9 eV. These peaks are attributed to Mn$^{2+}$ and Mn$^{3+}$ states of Mn$_3$O$_4$ respectively. The XPS peaks at 646.0 eV and 657.2 eV were assigned to satellite peak [Jampaiah et al. 2019]. The Co 2p XPS peaks were observed at 779.8, 781.5 and 795.1, 796.9 eV and corresponds to the Co$^{3+}$ and Co$^{2+}$ species. The Co XPS also consist of two small shake up satellite peaks at 801.68 and 785.1 eV which indicates presence of Co$^{2+}$ species [Wang et al. 2020]. Similarly, the BE peaks correspond to Mn/Hap and Co/HAp enlisted in Table 3. The bimetallic Co$_{0.4}$/Mn$_{0.1}$/HAp exhibited lower binding energy for Mn and Co compared to the monometallic Mn/HAp and Co/HAp. The lower binding energy indicate the weakening of metal-oxygen bond.

The O 1s spectra of the bimetallic Co$_{0.4}$/Mn$_{0.1}$/HAp, monometallic Co/HAp, and Mn/HAp are shown in Fig. 4c. The BE of the lattice (O$_L$), adsorbed (O$_a$), and surface (O$_s$) oxygen observed in the range of 528.9-529.9, 530.5-531.5 and 532.0-532.6 eV respectively [Jampaiah et al. 2019; Waikar et al. 2021]. The concentrations of Mn, Co and O were calculated from peak area and shown in Table 3. The O$_a$ concentration observed higher in bimetallic Co$_{0.4}$/Mn$_{0.1}$/HAp catalyst compared to the monometallic catalyst. However, the O$_a$ concentration increases due to the addition of Co in Mn/HAp. The adsorbed (O$_a$) was active for oxidation of the CO at lower temperature. Furthermore, the Co$_{0.4}$/Mn$_{0.1}$/HAp showed higher concentration of Co$^{2+}$ and Mn$^{3+}$ species on the surface compared to the Mn/HAp and Co/HAp. These results indicate that the increase in the formation of CoO in bimetallic catalyst which could be due to the synergetic interaction between Mn and Co. The bimetallic Co$_{0.4}$/Mn$_{0.1}$/HAp showed higher concentration of Mn$^{3+}$, O$_a$ and Co$^{2+}$ species on surface compared to the monometallic Co/HAp and Mn/HAp. The XPS results are commensurate with XRD.
Table 3
Surface analysis of Mn/HAp, Co/HAp and Co<sub>0.4</sub>/Mn<sub>0.1</sub>/HAp using XPS

| Catalyst                  | Binding energy (eV) | Mn<sup>2+</sup> | Mn<sup>3+</sup> | Mn<sup>4+</sup> | Co<sup>2+</sup> | Co<sup>3+</sup> | O<sub>s</sub> | O<sub>L</sub> | O<sub>a</sub> |
|---------------------------|---------------------|-----------------|-----------------|-----------------|-----------------|-----------------|---------------|---------------|---------------|
| Mn/HAP                    |                     | 642.2           | 644.4           | 646.1           | -               | -               | 532.2         | 530.8         | 529.5         |
| Co/HAp                    |                     | -               | -               | -               | 781.5           | 779.8           | 532.5         | 531.2         | 529.5         |
| Co<sub>0.4</sub>/Mn<sub>0.1</sub>/HAp | 641.9       | 644             | 646             | 780.6           | 778.8           | 532.1           | 530.2         | 528.9         |

| Catalyst                  | Relative area ratio | Mn<sup>2+</sup>/Mn<sup>3+</sup>/Mn<sup>4+</sup> (%) | Co<sup>2+</sup>/(Co<sup>2+</sup>+Co<sup>3+</sup>) | O<sub>s</sub>/O<sub>L</sub>/O<sub>a</sub> (%) |
|---------------------------|---------------------|-----------------------------------------------|-----------------------------------------------|---------------------------------------------|
| Mn/HAP                    |                     | 45.9/33.7/20.5                               | -                                             | 11.96/44.77/43.26                           |
| Co/HAp                    |                     | -                                             | 0.388                                         | 36.26/19.45/44.28                           |
| Co<sub>0.4</sub>/Mn<sub>0.1</sub>/HAp | 23.5/46.2/30.3     | 0.488                                         |                                               | 16.50/28.89/54.59                           |

Correlation Of Characterizations With Activity

The detailed characterization of Mn/HAp, Co/HAp and Co<sub>0.4</sub>/Mn<sub>0.1</sub>/HAp has been performed to elucidate the CO oxidation activity. The XRD results showed formation of amorphous/low crystalline Mn<sub>3</sub>O<sub>4</sub> and CoO species in Co<sub>0.4</sub>/Mn<sub>0.1</sub>/HAp catalyst. The results are in line with XPS result, which showed the satellite peak of CoO phase. The increase in concentration of CoO, Mn<sup>3+</sup> and O<sub>a</sub> was observed in Co<sub>0.4</sub>/Mn<sub>0.1</sub>/HAp compared to the Mn/HAp and Co/HAp. CoO with adsorbed oxygen regulate the adsorption/conversion of CO and recycle the active site [Wang et al. 2021]. More labile oxygen (Oa) observed on catalyst surface after addition of Co in Mn/HAp. The interaction between CoO and Mn<sub>3</sub>O<sub>4</sub> and Mn<sub>3</sub>O<sub>4</sub> in Co<sub>0.4</sub>/Mn<sub>0.1</sub>/HAp responsible for the formation of more labile adsorbed oxygen (Oa) which is active for low temperature CO oxidation. The presence of Mn<sub>3</sub>O<sub>4</sub> and CoO reduces the electron cloud of oxygen and weakens the strength of Co-O bond [Liu et al. 2021]. The hydrocarbon activation takes place through -CH bond adsorption on Mn/HAp [More et al. 2020]. Furthermore, the bimetallic Co<sub>0.4</sub>/Mn<sub>0.1</sub>/HAp showed TPR peaks at lower temperature compared to the monometallic Mn/HAp and Co/HAp. The low temperature reduction indicates the improvement in redox cycle of the Mn and Co of bimetallic catalyst. The redox couples of Co<sup>2+</sup>/Co<sup>3+</sup> and Mn<sup>2+</sup>/Mn<sup>3+</sup> were facilitate the adsorption of CO and oxygen. The bimetallic Co<sub>0.4</sub>/Mn<sub>0.1</sub>/HAp catalyst showed lower activation energy compared to the Co/HAp and
Mn/HAp. The formation of Co$^{2+}$, Co$^{3+}$ and Mn$^{3+}$ active species synergistically decreases activation energy for CO and oxygen which leads to the oxidation of CO at lower temperature.

Conclusion

The bimetallic Mn and Co supported on HAp catalyst were prepared by successive deposition method and investigated for CO oxidation. The bimetallic catalyst showed higher CO oxidation activity at lower temperature compared to the monometallic Mn/HAp and Co/HAp. 0.4 mol Co and 0.1 mol Mn supported on HAp showed presence of higher concentration of active species on catalyst surface and lower activation energy for CO oxidation at lower temperature. The formation of higher adsorbed oxygen species and Co$^{2+}$, Mn$^{3+}$ species observed over catalyst surface. The CoO is weaker bond and therefore form a more labile oxygen. All these species were responsible for oxidation of CO at lower temperature.

Declarations

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Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Availability of data and materials

All data generated or analysed during study are included in this published article and its supplementary information files. The data that support the findings of this generated data were all cited wherever necessary.

Competing interests

The authors declare that they have no competing interests.

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Authors’ contributions

RM: Investigation, formal analysis, writing original draft.

PM: Project administration, writing-review and editing. All authors read and approved the final manuscript.

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**Figures**

**Figure 1**

CO oxidation activity of Co$_x$/Mn$_{0.5-x}$/HAp (x = 0.1, 0.2, 0.3, 0.4). Reaction feed composition: CO 300 ppm, O2 5% and remaining He Balance. GHSV = 50,000 mL.g$^{-1}$.h$^{-1}$
Figure 2

CO oxidation activity of Cox/Mn0.5-x/HAp (x = 0.1, 0.2, 0.3, 0.4). Reaction feed composition: CO 300 ppm, O2 5% and remaining He Balance. GHSV = 50,000 mL.g⁻¹.h⁻¹
Figure 3

Reduction profiles comparison of bimetallic Co0.4/Mn0.1/HAp, monometallic Co/HAp, and Mn/HAp
Figure 4

XPS spectra of Mn/HAp, Co/HAp and Co0.4/Mn0.1/HAp a) Mn 2p b) Co 2p and c) O 1s

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