



Short communication

Promising effect of Ag/Rh paired mesoporous composite-oxide for low temperature NO—CO reaction

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ABSTRACT

A promising effect of the silver and rhodium binary precious metals added composite oxide was investigated for NO-CO redox reaction. The interaction of Ag and Rh enhanced the catalytic property of the overall composite catalyst which brought to 100% conversion of NO and CO at significantly low temperature of 150 °C. Additionally, mesoporous structure composed of such active nano-particles leads in high oxygen mobility and CO reactivity on catalyst surface, showing a good agreement with catalytic performance. Such catalytic enhancement conveys the transfer of electronic cloud from Ag to Rh which is pointing towards good synergy between active Ag—Rh pairs.

1. Introduction

Emission of the gaseous pollutants which have been arising from different combustion processes are causing severe environmental and health related problems. Such pollutants like nitrogen oxide (NO), carbon monoxide (CO), and hydrocarbons (HC) contribute to a significant amount as a consequence of the combustion process from industries, transportations, etc. Therefore, some of the strategies have been attempted for removing the pollutants like NO from the exhaust system by using NH₃, urea etc. and removing the CO with oxygen. But eliminating the NO with CO simultaneously by the redox pathway is perhaps an interesting route to remove them before discharging in the atmosphere, in addition to the present de-NO_x technology. Although different types of catalytic systems and technologies were developed, removing these pollutants simultaneously at a lower temperature is still a remains a challenge. The reason for removing these pollutants at lower temperature is mainly cold start issues, which is common in the regions with cold weather.

Literature provides plenty of ongoing research in concern with developing a stable and highly efficient catalyst using transition metals and also along with precious metals to remove NO and CO [1–5]. Among various types of catalysts, the composite oxide system has received particular attention in the field of heterogeneous catalysis due to the involvement of multiple electronic states. For example, Jiang et al. studied the CeO₂-MoO₃-WO₃/TiO₂ system, which has shown excellent catalytic performance for the NO conversion due to its high redox

property and stronger adsorption property generated by strong interaction among Ce, Mo, W and Ti [6]. Similarly, studies on the composite system also showed that the addition of copper to CeO₂-Fe₂O₃ mix metal oxides produced a more significant impact on NO and CO conversion as that of Cu containing CeO₂ or Fe₂O₃ [7]. The oxides of Co [2,8], Mn [9,10], etc. are also extensively studied in conversion of exhaust gases by adding multiple components to it, which effectively help in producing an active oxide catalyst. Although, transition metals oxides like manganese and cobalt offer excellent catalytic performance but cannot compete with that of precious metals due to their unique electronic property. Due to this reason, precious metals are combined with transition metals that contributes a significant impact in catalyzing exhaust related reactions [11–15]. From the literature, it has been also observed that instead of using single type of precious metal, if used in pairs they can provide more synergistic effect which can enhance the catalytic process [16,17].

The present study aimed to demonstrate the significant effect of Ag—Rh pair for improving the NO-CO redox reaction. Among various precious metal systems, the Rh—Ag pair showed unusual behavior, which has been contributed to a variety of research platforms [18–21]. The Ag—Rh system was applied for NO_x decomposition employing Density functional theory (DFT) by Inderwildi et al. [22]. However, it depicts the active surface formation for NO decomposition after Rh comes in the vicinity with Ag.

In this work, Ag and Rh containing Co—Mn composite oxides series were prepared and studied for its activity towards NO-CO redox

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reaction. Studies like SEM, TEM and BET were carried out to understand the structural and textural aspect of the catalysts. Also, surface studies were done to provide the catalyst activity and reaction studies.

2. Experimental section

The preparation of $\text{CoO}_x\text{-MnO}_x$ and 5% Ag and/or 1% Rh containing composite oxide catalyst were carried out via glycine combustion method using respective metal salt [23]. For the simplicity purpose, the prepared $\text{CoO}_x\text{-MnO}_x$, $\text{CoO}_x\text{-MnO}_x\text{-5%Ag}$, and $\text{CoO}_x\text{-MnO}_x\text{-5%Ag-1%Rh}$ were denoted as MM', MM'-5%Ag, and MM'-5%Ag-1%Rh, respectively. Metal salts used is given in supplementary file. $\text{CoO}_x\text{-MnO}_x$ with a 1: 1 weight ratio of Co: Mn and $\text{CoO}_x\text{-MnO}_x$ containing 5% Ag and/or 1% Rh (weight of Rh and Ag in % mass) was prepared by dissolving a known amount of respective metal salt in double distilled water, and to it an appropriate amount of glycine (Thomas Baker) was added. The mixture was heated with constant stirring for 2 h on hot plate cum stirrer and then kept in an oven at 80 °C for removing excess of water and further heated at 200 °C for 2 h where it gets combusted. The obtained product was then finally heated at 500 °C for 4 h to remove any unburned species. Further the detailed catalysts characterization tool and the NO-CO redox reaction performed have been discussed in the supplementary file (ESI).

3. Result and discussion

The X-ray diffraction pattern of MM' and MM'-5%Ag-1%Rh composite catalysts were recorded to confirm the formation of crystalline phases present in the system. The diffractograms of the same is given in Fig. S1 (Supplementary file) which depicts the presence of Co_3O_4 , MnO_2 and Mn_2O_3 phases. The diffractogram shows low crystalline nature of the composite oxide by giving reflection as broad peaks, indicating the nano nature of the prepared composite catalysts [23].

The SEM and HRTEM micrographs of the MM'-5%Ag-1%Rh was therefore obtained to explore the surface morphology and particle size of the composite oxide. Images of the same are presented in Fig. 1. As depicted in Fig. 1a, the SEM image of $\text{CoO}_x\text{-MnO}_x$ and Rh—Ag containing $\text{CoO}_x\text{-MnO}_x$ displays a spongy porous like morphology. Such types of structure are characteristic of the method employed for the preparation of the catalyst. From literature, it has been observed that similar kinds of SEM data can be obtained when fuel like glycine [24,25] was used during the preparation of metal oxide. The formations of pores in the prepared catalysts are mostly due to the evolution of the gases which develop during the combustion process. In addition, particle sizes and shapes were determined through HRTEM and illustrated in Fig. 1b. At a nanometer range, the HRTEM micrograph of MM'-5%Ag-1%Rh shows spherical shapes having a size less than 40 nm, and by calculating the particle distribution curve (Fig. 1b) it has been confirmed that the highest dispersion of particles are in the range of 20–40 nm. Moreover, this nano-particles existence had reflected as broad peaks in XRD

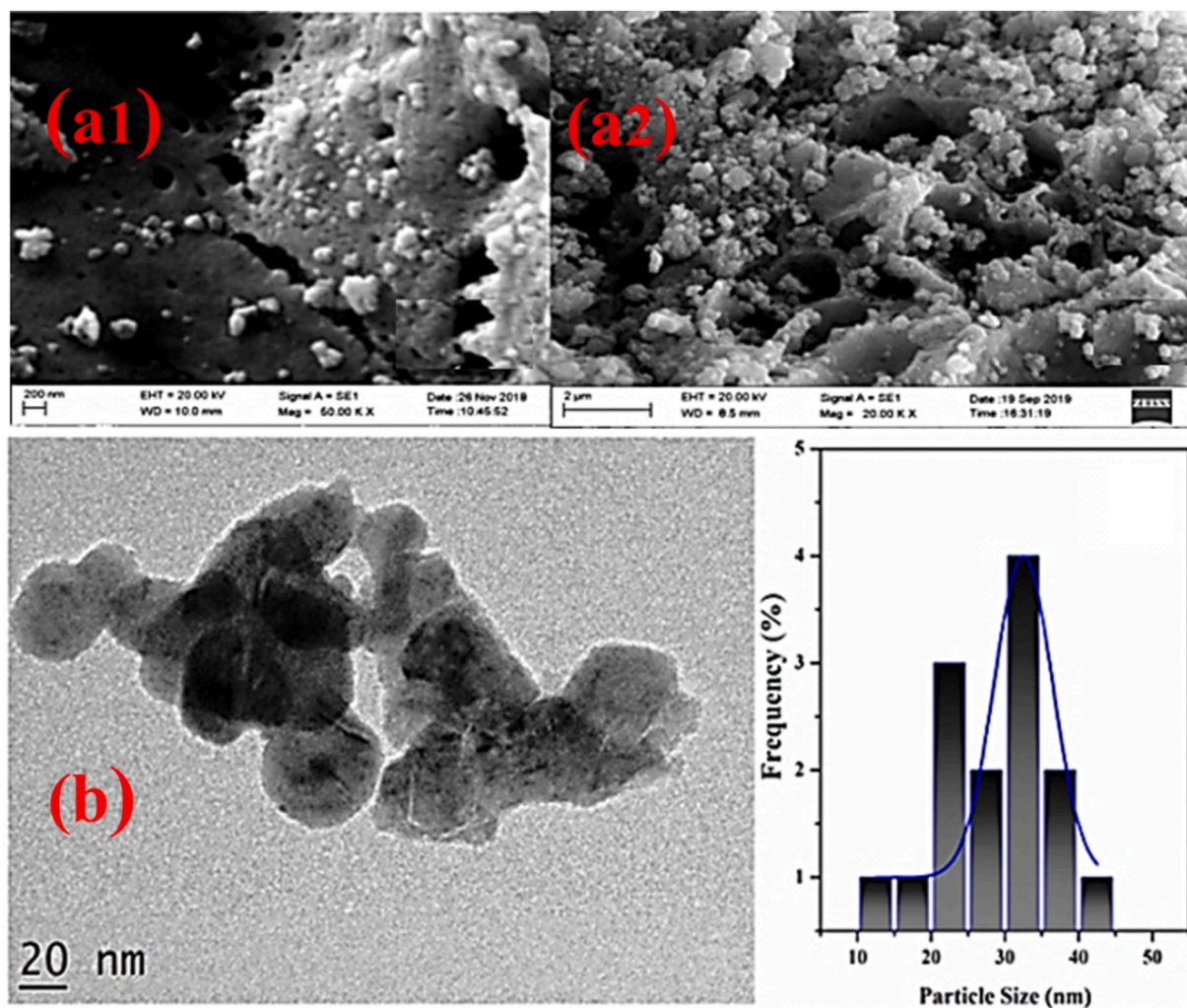


Fig. 1. SEM (a1) MM' & (a2) MM'-5%Ag-1%Rh, (b) HRTEM and particle size distribution of MM'-5%Ag-1%Rh.

studies, as depicted in Fig. S1 (ESI).

Later, BET surface area and pore size distribution were carried out through N_2 adsorption-desorption isotherm over a series of composite oxides and are depicted in Fig. S2 (Supplementary file). Observed isotherms are of typical type IV having a hysteresis loop of H3 type, which is mostly observed for mesoporous or macro-porous structure [26]. These porous structures can be formed during the combustion process as the evolution of gases leads to generating the porous structure of the catalysts. The BET surface area result for MM', MM'-5%Ag, and MM'-5%Ag-1%Rh are $40 \text{ m}^2/\text{g}$, $38 \text{ m}^2/\text{g}$, and $80 \text{ m}^2/\text{g}$, respectively. Thus, showing the incorporation of Rh in the composite system leads to drastically increase in surface area from $38 \text{ m}^2/\text{g}$ to $80 \text{ m}^2/\text{g}$. Further, the pore size and its distribution was evaluated using BJH method for the prepared catalyst (Fig. S2b) which was showing mesoporous pores ranging from 2 nm to 50 nm in size. MM' catalyst showed the pore size of 3.8 nm having a pore volume of 0.078 cc/g whereas an increase in the pore volume was seen after the addition of Ag and Rh in MM' composite oxide system, i.e. 0.108 cc/g (Detailed values are tabulated in supplementary file Table ST1) this may be one of the reasons for high NO-CO conversion as more active surfaces are exposed for the catalytic reaction.

The X-ray photoelectron spectra (XPS) of Co 2p, Mn 2p, Ag 3d, Rh 3d, and O 1s was done to identify their electronic state in the prepared MM'-5%Ag-1%Rh sample. The peaks obtained are de-convoluted using

XPSPEAK software, and the splitted spectra are presented in Fig. 2. The high-resolution Mn 2p spectrum shows Mn 2p_{3/2} and Mn 2p_{1/2}, which can be resolved into four peaks (Fig. 2a). The photoelectron peaks located at 642.07 eV and 653.6 eV were attributed to Mn⁺³, whereas the presence of peaks at 644.87 eV and 656.3 eV shows the existence of Mn⁺⁴ [27,28]. However, the presence of the Mn⁺³/Mn⁺⁴ couple may be the resultant of a preparative route that was chosen for composite synthesis. Fig. 2a depicts the chemical state of cobalt present in the MM'-5%Ag-1%Rh catalytic system. The peaks having a binding energy of 780.03 eV and 781.55 eV from the Co 2p_{3/2} shows the presence of Co^{+2/+3} redox pair in the catalyst system. Further, the presence of shoulder peak at a binding energy of 787.02 eV and 803.30 eV confirms the existence of Co⁺², which are the characteristic shake-up peaks of Co⁺² species [29,30]. In Fig. 2b, the Ag 3d spectrum shows the splitting of Ag 3d_{5/2} and Ag 3d_{3/2}, respectively. The photoemission at a 367.8 eV and 373.8 eV were assigned for the Ag⁺¹ state instead of metallic Ag [31]. Further, the evaluation of the Rh 3d spectrum shows the existence of only Rh⁺³ [32] (309.2 eV for Rh 3d_{5/2} and 313.9 eV for Rh 3d_{3/2}) as ascribed from Fig. 2b. Electronic information of O 1s was also studied and displayed in Fig. S3. The existence of two different kinds of oxygen can be shown by de-convoluting the XPS spectrum. The peak occurred at 529 eV corresponds to the oxygen attached to metal, i.e., lattice oxygen. The peak occurred at higher binding energy (531 eV) can be assigned to the defect

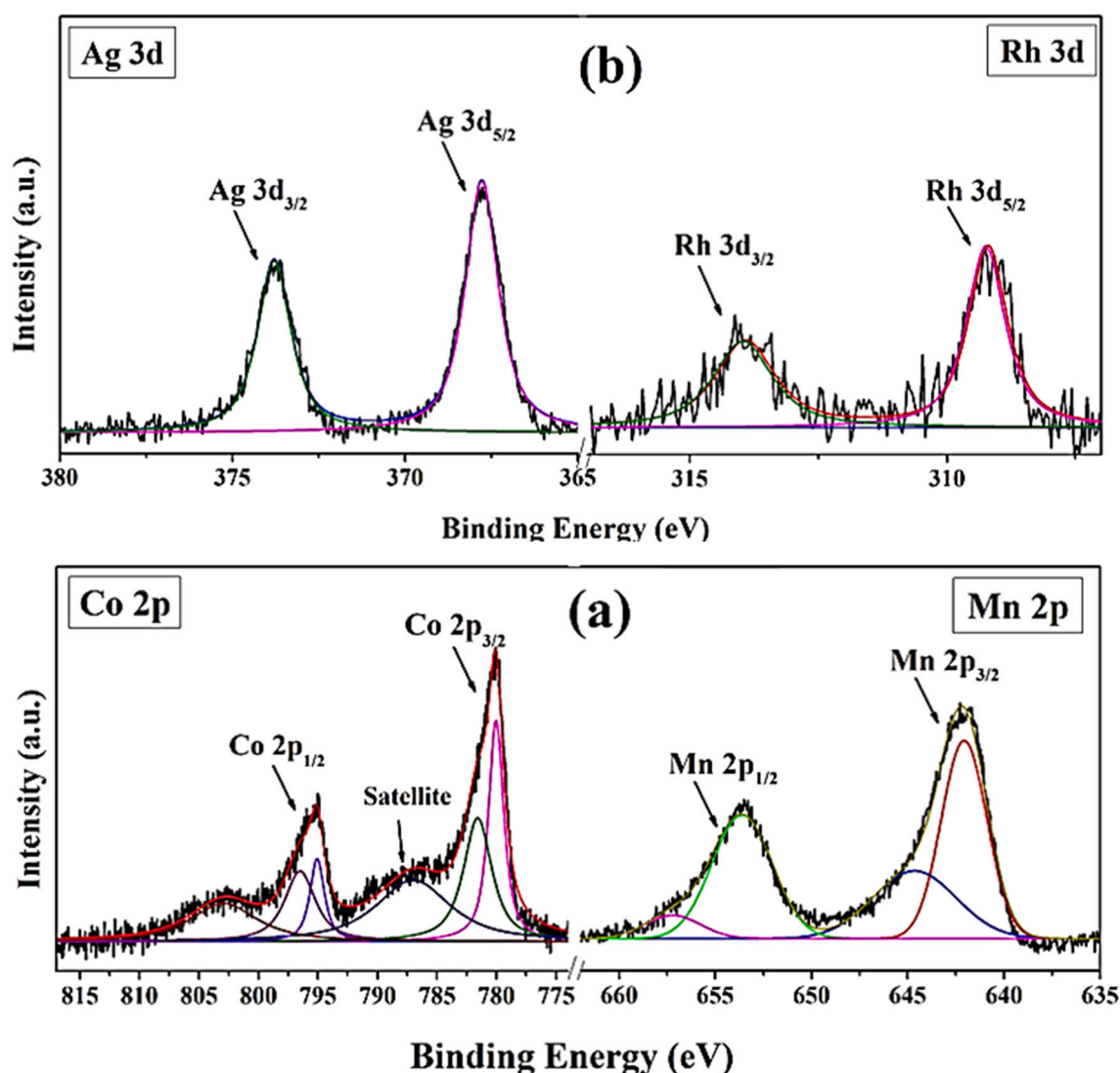


Fig. 2. XPS of Mn 2p, Co 2p (a), Ag 3d and Rh 3d (b) from MM'-5%Ag-1%Rh.

oxygen species (oxygen from defect site) [2,7].

Surface reductions over prepared catalysts were studied using H₂ and the resulted patterns were depicted in Fig. S4. The TPR plot of MM' showed the presence of two peaks at 272 °C and 371 °C conveying the presence of two different stages of reduction processes in the composite. As Ag was introduced in MM' composite system, increased surface reduction was seen, which may be due to the enhancement in synergistic effect by the addition of electron rich Ag. Also, a weak TPR signal detected by consuming surface oxygen at 167 °C, portraying the development of easily reducible sites. Further in MM'-5%Ag-1%Rh composite material the four reduction peaks were detected from which two were appearing below 200 °C (114 °C and 167 °C) and two were above 200 °C (275 °C and 327 °C). Result demonstrates that upon the incorporation of Ag in MM' composite along with Rh could effectively able to increase the amount of surface reduction as compared to the rest of the prepared composite catalyst. The oxygen associated with the precious metal-containing system is easy to consume than a non-precious metal oxide system [33]. This may be the reason for the increase in surface reduction which has been conveyed by the synergetic oscillation of Ag and Rh electronic state in MM' composite.

In order to examine the relationship between the studied catalytic reaction and chemical reactivity of CO with a catalyst surface, the CO desorption studies were performed with the CO-TPD method. Fig. 3 shows the CO-TPD profile of all the prepared catalysts. MM' catalyst shows only strongly adsorbed CO, whereas MM'-5%Ag and MM'-5%Ag-1%Rh showed both weakly chemisorbed CO as well as strongly adsorbed CO species. Two desorption peaks at 97 °C and 236 °C were seen as Ag was introduced in the MM' catalyst system. This weak CO adsorption over the catalyst surface was observed to be increasing as Rh was added to Ag containing MM' composite systems (64 °C and 264 °C). It was observed from the TPD profile that MM'-5%Ag-1%Rh catalyst system contains more amount of weak CO adsorption site, which is considered to be a key factor during the NO-CO redox reaction. Also, this weak desorption pattern observed to be very important and can provide sites for NO to adsorb on it. In catalytic oxidation of CO in oxygen, such a phenomenon of the catalyst surface can be strongly accepted for Mars-Van Krevelen mechanism [34], wherein surface oxygen plays a role in the catalytic process. On the other hand, for NO-CO reaction this mechanism can be partially taking place where the oxygen-deficient sites can be occupied by the oxygen from NO. This suggests the importance of Ag-Rh pair in enhancement of such active species.

To explore the catalyst efficiency after the addition of Ag and Rh in MM', the redox NO-CO reaction over the prepared composite oxide

catalysts were studied and the plot of temperature v/s % NO conversion is given in Fig. 4 (% CO conversion is provided in Fig. S5). From the conversion plot, it can be seen that the insertion of Ag in MM' composite oxide can slightly enhance its activity, whereas adding Rh along with the Ag in MM' composite could achieve 100% conversion at a lower temperature region. This may be one of the evident proving the interaction of Ag-Rh in catalysis process by enhancing the overall electronic structure within the catalytic material. Such advancement in the material leads to synergistic effect which intern develops more active sites for adsorption of reactant as demonstrated from CO-TPD studies. The prepared MM' composite showed only ~25% NO conversion in the temperature region of 50 °C to 250 °C. After the Ag addition (MM'-Ag) this reaction showed up to 70% NO-CO conversion till 250 °C, however, on multiple precious metal incorporation in composite oxide (i.e. MM'-5% Ag-1%Rh) 100% NO-CO conversion was observed at 150 °C which is a quite low temperature as compared to similar catalyst composed of Pd [23]. This is mostly because of the building more enhanced electronic cloud by the presence of silver and rhodium. Such promising effect of binary system was also seen in existing exhaust reactor which composed of Pt-Rh composition due to their higher activity in detoxification studies [16]. In addition, 1% Rh in MM' composite (MM'-Rh) was studied to understand the impact of Rh in catalytic performance, which showed 100% conversion at 190 °C. Here the amount of Rh is not sufficient to bring down the reaction temperature although it showed 100% reaction conversion. By observing result of MM'-Rh it was thus confirmed that the enhancement in the catalyst was not because of Rh alone. In fact this enhancement in catalytic performance in MM'-5%Ag-1%Rh can be interpreted from the synergy interaction produced when Rh is in the vicinity of Ag in the Co-Mn composite oxide system. This synergy can be explained as consequences of the shift in electron cloud from silver to higher electronegative Rh, which is very important for the formation of good synergy. Such a synergistic effect of Ag and Rh was also discussed by J. Pandey et al. in context to catalytic dehydrogenation studies [17]. For prepared composite oxide series as illustrated from conversion plot the order of the activity is as follows MM'-5%Ag-1%Rh > MM'-5%Ag > MM' wherein MM'-5%Ag-1%Rh observed to be a highly active catalyst for NO-CO redox reaction. During the reaction period, it has been found that as reaction proceeds, N₂O tends to form as an intermediate during the NO-CO reaction due to partial NO conversion [7,13]. The formation of N₂O was presented in the chromatogram and depicted in Fig. S6. Also, a recyclability study was performed to confirm the consistency of the catalyst towards the NO-CO reaction. As presented in Fig. S7, MM'-5%Ag-1%Rh showed a similar conversion data for 3

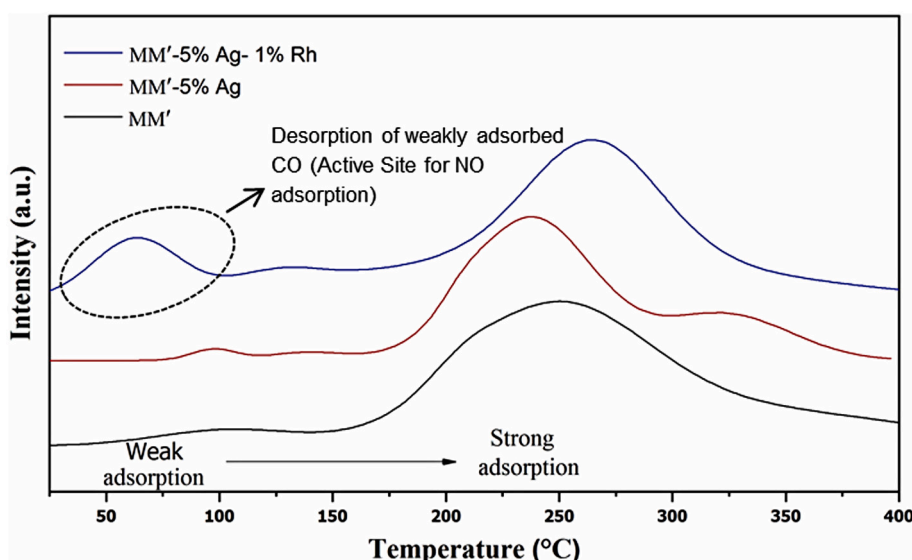


Fig. 3. CO-TPD of MM', MM'- 5%Ag and MM'- 5%Ag – 1%Rh.

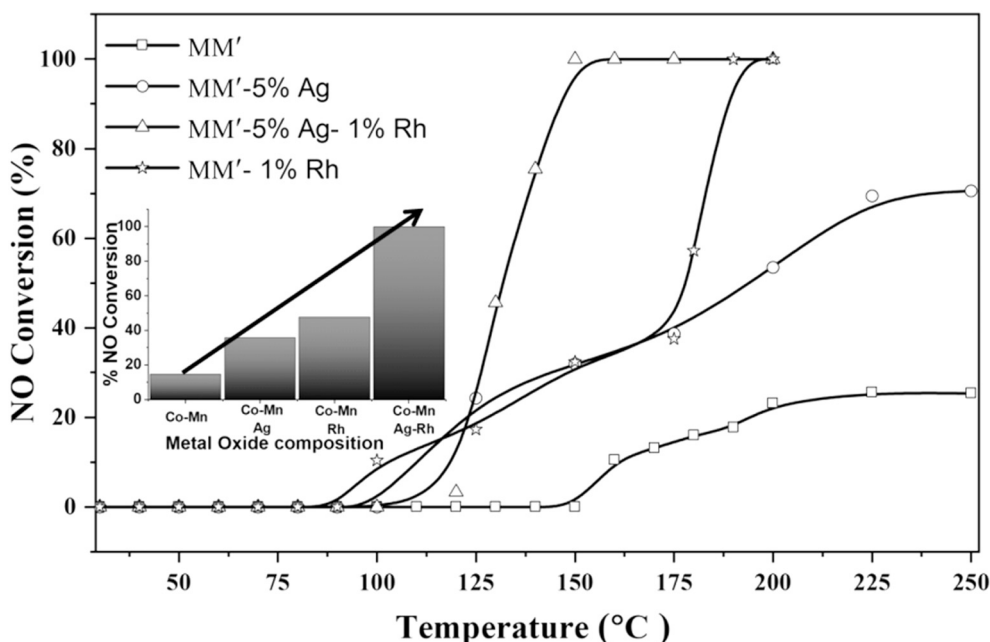


Fig. 4. NO % conversion against catalyst temperature studies from CO-NO redox reaction over a prepared catalyst (5% CO and 5% NO in Ar at flow 5000 ml h⁻¹).

cycle runs.

From Fig. 3 it can be seen that as weak CO chemisorption site increases over the catalytic surface, the enhancement in the catalytic performance had observed. Such Weak CO desorption results in the vacant site for NO. According to S. Roy and others, adsorption of NO on a vacant site is one of the involved steps in NO decomposition over the catalyst surface [35]. This shows the importance of the weak chemisorption site in addition to strong chemisorption sites in NO-CO reaction. Similarly, surface reduction also showed high oxygen mobility in MM'-Ag-Rh when compared with MM', which is another critical criteria for enhancing the simultaneous redox reaction of NO and CO.

4. Conclusion

This work describes the promotional effect of the Ag—Rh pair towards the NO-CO redox reaction. The porous nature of a material formed by agglomerated nano-particles showed an increase in synergy after the insertion of Ag and Rh. Such synergy created by the presence of active species in MM'-5%Ag-1%Rh catalyst resulted in higher oxygen mobility and different CO adsorption sites, which is an essential criterion for the NO-CO redox pathway. As a result, MM'-5%Ag-1%Rh showed a 100% conversion of NO and CO at 150 °C conveying the high efficiency of the catalyst as compared to many other catalysts.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.catcom.2020.106257>.

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