Synthesis and Characterization of Mg doped LaCoO$_3$ Nano-Catalyst for Soot oxidation in Diesel Engines

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Abstract. A series of Mg doped LaCoO$_3$ perovskite nano catalysts were synthesized using sol gel method. The prepared nano catalysts were characterized using the various characterization techniques such as X-Ray, Powder Diffraction, Inductively Coupled Plasma Atomic Spectroscopy, Fourier-Transform Infrared Spectroscopy, Scanning Electron Microscopy, High Resolution Transmission Electron Microscopy, and Brunauer-Emmett Teller. The XRD results showed the purity of the prepared catalyst as no segregated phases were observed and also confirming the crystallinity of the prepared catalyst. The catalytic evaluation shows that upon introduction of Mg into the perovskite structure, the catalytic performances of the catalyst were greatly increased with La$_{0.8}$Mg$_{0.2}$CoO$_3$ giving the lowest $T_{50}$ at 480 $^\circ$C.

Keywords: Catalysis, Catalyst, Perovskite, Sol gel, Magnesium.

1. Introduction

Diesel engines have drawn a great attention in recent times as a result of their high fuel efficacy, cheap maintenance cost and high durability[1]. However, there have been growing concerns about the negative effect that the emissions (mainly soot) that comes out of the exhaust of diesel engines have on both human health and the environment. Several researchers have argued that the modifications of engines can only help in lowering the amount soot produced in the engines to a limited level which does not still satisfy the stringent emissions regulations being put together by various governments of individual countries. These have prompted the need for more advance catalytic after exhaust treatment. One of the most efficient ways to reduce soot from diesel engines is to place a catalyst on the diesel particulate filter located in the engine to help reduce the temperature at which soot is oxidized. Several catalysts have been investigated for use in this regard ranging from mixed metal oxides, spinel, etc. However, the used of perovskite as catalysts have been properly investigated for soot oxidation in DFPs [2, 3]. Perovskites have a general formula of ABO$_3$ where the A site shows a 12 coordination number and the B site presents a 6 coordination number. The doping of perovskite have been reported to improve its catalytic properties[4] . In this research study, Lanthanum based perovskite was doped with magnesium using the sol gel method, characterized and the catalytic activities for soot oxidation was investigated.
2. Materials and Methods

2.1. Materials
All the chemicals used in this research were of analytical grade and were purchased from Sigma-Aldrich India except stated otherwise. The chemicals used includes: La (NO₃)₃·6H₂O, Co (NO₃)₂, Mg (NO₃)₂·6H₂O, Citric acid and HPLC distil water of 99.78%.

2.2 Synthesis of La₁₋ₓMgₓCoO₃ (LMC) Perovskite Catalyst.
La₁₋ₓMgxCoO₃ perovskites Catalysts with x = 0, 0.2, 0.3, 0.4, 0.5 (coded LMC0, LMC1, LMC2, LMC3 and LMC4 respectively) were prepared by the sol gel method as described by [5]. According to this method, 21.65 g of La (NO₃)₃·6H₂O, 6.41 g of Co(NO₃)₂ and 21 g of Citric acid were mixed together in 125 ml of distilled water (LMC0). The resulting solution was gently stirred and heated at 80 °C for 5 hrs to form a purple like gel material. The gel material was dried in the oven at 200 °C for 12 hrs to form the precursor and then calcined at 750 °C for 5 hrs to obtain the final perovskite catalyst. LMC1, LMC2, LMC3 and LMC4 were prepared using the same procedure except that 2.56 g of Mg (NO₃)₂·6H₂O was added in the ratio of 0.2, 0.3, 0.4, 0.5.

2.3. Characterisation
The XRD patterns were recorded at room temperature by using a Rigaku diffractometer, model Geiger flex from 20° to 80°. The FT-IR spectra were collected on a Nicolet-6700 spectrometer. The Scanning Electron Microscopy (SEM) was done on a FE-SEM quanta 200F, FEI 2010 instrument. Transmission electron microscope (TEM) images and energy-dispersive spectroscopy (EDS) results were obtained with a JEOL model 23HYT4UYE Coleman machine. The specific surface area (SSA) of the catalysts was carried out using a Micromeritics Gemini V apparatus. The elemental composition was determined by inductively coupled plasma atomic emission spectroscopy (ICPAES) model DRE, PS-3000UV, LEEMAN LABS, INC, USA.

2.4. Catalytic Performance Studies
The soot oxidation was carried out using the thermo-gravimetric analysis method in a TG–DSC, Q-600 instrument as described by [6]. The prototypical soot that was used in this research work was carbon black which was received from the vehicular emission control laboratory of the CSIR-Indian Institute of Petroleum Dehradun. A soot to catalyst mix of ratio 1:4 weight ratio was thoroughly mixed together in a laboratory mortar so as to ensure homogenous mixture and for tight contact of the catalyst and the soot [7]. A small quantity of the as prepared soot-catalysts mixture was placed in TGA crucible and heated up to 1000°C with a heating rate of 10°C min⁻¹ at a flow rate of 100 ml min⁻¹ air. The performance of the catalyst was obtained by interpolating the T₅₀ conversion temperature against the percentage conversion of soot.
3. Results and Discussion

3.1. Thermogravimetric Analysis (TGA/DTG)

The crystalline phase formation was established with the use of the TGA/DTG analysis from 0 °C- 800 °C and shown in Figure 1. The thermal decomposition of the synthesized representative LMC2 dried at 200 °C. The TGA shows five major decomposition steps in the thermograph. The decomposition steps can be ascertained with the use of the DTG graph. The first decomposition step (D₁) which represent 5% of the compound between 0-120 °C was attributed to adsorbed water molecules while 40% decomposition (D₂) between 120-230 °C was attributed to decomposition of bonded water molecules. As the temperature increases, three decomposition steps were observed. The D₃ decomposition was observed around 230-280 °C which represent about 25% of the compound, can be attributed to the decomposition of the organic compound from the surfactant used. The D₄ decomposition which was related to the bond dissociation and formation of the m=etal salt used occurred between 280-400 °C. The final decomposition (D₅) is assumed to be the crystalline phase formation of the metal oxide within the perovskite. This final decomposition occurred around 550 °C. Based on this decomposition stages, the temperature for calcination of the metal salt was selected above 600 °C. The thermal effect on the metal salt can be represented as proposed below

\[ \text{La (NO}_3\text{)}_2 + C_6\text{H}_5\text{O}_7 \rightarrow \text{LaO (OH)}(\text{S})+H_2\text{O}(g)+\text{NO}_2(g)+\text{CO}_2(g) \]

\[ \text{LaO} (\text{OH})_2(g) \rightarrow \text{LaO(S)}+H_2\text{O}(g), \]

the proposed equation for the dopant is as presented below

\[ \text{Mg(NO}_3\text{)}_2(S) \rightarrow \text{MgO + NO}_2 \]

For the Cobaltite, the proposed decomposition reaction is as follows,

\[ \text{Co(NO}_3\text{)}_2 + C_6\text{H}_5\text{O}_7 \rightarrow \text{CoO(OH)}(\text{S}) + H_2\text{O}(g) + \text{NO}_2(g) + \text{CO}_2(g) \]

\[ \text{CoO(OH)}_2(g) \rightarrow \text{CoO + H}_2\text{O}(g). \]

Therefore, the final perovskite formation mechanism as proposed is presented below,

\[ \text{LaO + MgO + CoO} \rightarrow \text{LaMgCoO}_3 \]

Figure 1. TGA/DTG of LMC2 dried at 200 °C
3.2. X-ray Analysis (XRD)

The crystalline phase formation was established with the use of the XRD analysis. The XRD patterns obtained for La$_{1-x}$Mg$_x$CoO$_3$ (x=0-0.4) are as shown in Figure 4.3.2. The XRD pattern obtained displayed typical peaks related to the rhombohedral perovskite structure (JCPDS-25-1060). The peaks were indexed to obtained crystalline planes 012, 110, 104, 202, 204, and 112. The prominent peaks in LCM0 were found to be characteristics peaks for LaCoO$_3$ according to the literature. However, the doped compounds were found to exhibit the same characteristics peaks. The prominent peaks at 110 and 104 was observed to form a single peak in the XRD patterns of the Mg doped perovskites (LMC1-4). Based on the amount of doped Mg, the intensities were gradually reducing. The lattice parameters were obtained using the Qual X software and are as presented in Table 1. It was observed that the lattice parameters were increasing with increasing Mg concentration.

| Catalyst | a (Å)  | c (Å)  | Surface Area (m$^2$/g) |
|----------|--------|--------|------------------------|
| LMC0     | 5.4270 | 13.0802| 10.54                  |
| LMC1     | 5.4401 | 13.1317| 09.01                  |
| LMC2     | 5.4437 | 13.1421| 08.81                  |
| LMC3     | 5.4450 | 13.1603| 14.77                  |
| LMC4     | 5.4452 | 13.1605| 13.34                  |

Thus the XRD patterns obtained signified the formation of similar crystalline phase to LaCoO$_3$ as reported in literature thus the formation of LaMgCoO$_3$ as designed. Also no detection of any contaminant or isolated phase of oxides such as La$_2$O$_3$, Co$_2$O$_3$, or cobalt oxides at least to the detection limit of the XRD was observed. This shows that a single phase perovskite was formed for all the prepared samples.
Figure 2: XRD patterns of the various synthesized (La$_{1-x}$Mg$_x$CoO$_3$) catalysts and precursor.

Also the diffraction pattern reveals that a well-defined rhombohedral structure was obtained for the un-doped perovskite catalyst (LMC0), with the doublet peak approximately between 2θ=30-33°. Similar observation have also be reported by [8-10]. However, it was observed that when the concentration of the magnesium was increased, the doublet which indicates the rhombohedral structure disappeared evolving into a single peak suggesting a cubic symmetry structure. Literature search also reveals that as a result of the high tolerance of the perovskite structure to distortion, with metallic elements of different sizes and oxidation state, the substitution of La$^{3+}$ which has a higher ionic radius when compared with Mg$^{2+}$ (1.36Å and 0.72Å respectively) into the A site of the LMC0 maintained rhombohedral structure at low magnesium concentration. However on increasing the concentration levels of the magnesium, the symmetry changed to a cubic structure.

Furthermore, it can be said that the incorporation of Mg into the LaCoO$_3$ perovskite structure effects a change in structural and/or stoichiometric which is due to the difference of charge between the substituted lanthanum cation (+3) and the magnesium cation (+2) [11, 12]. This change in structure was seen evidently in the X-ray diffractograms in which there was a slight shift of the diffraction lines towards higher 2θ (Figure 3) as magnesium is being increased as well as a reduction in the intensity of peak suggesting that magnesium has been incorporated into the perovskite structure.
3.3. Elemental Analysis

The elemental composition of the synthesized perovskite catalysts were studied using the ICPAES. The results obtained validated the percentage composition of the elements within the perovskite. The results are as presented in Table 2. From the result obtained LMC0 contains 0 % of Mg as expected while the percentage of Mg reflected in the LMC1-LMC4 (2.64-7.80). The percentage of La, Co and O obtained were found to compare favourably with the theoretical values in parenthesis (obtained from TEM-EDX). This signifies the formation of the perovskite designed.

Table 2: Elemental Analysis of the prepared catalysts.

| Catalyst | % La  | % Mg  | % Co  | % O  | Average particle size (nm) |
|----------|-------|-------|-------|------|---------------------------|
| LMC0     | 66.00 | 0.00  | 11.30 | 22.70| 76.67                     |
|          | (66.50)|       | (11.20)| (22.60)|                           |
| LMC1     | 58.56 | 2.64  | 16.93 | 21.87| 84.40                     |
|          | (57.89)| (2.70)| (16.83)| (22.88)|                           |

Figure 3: Extended Xrd plots of prepared catalyst
Table 1: Composition of LMC catalysts.

| Catalyst | La (%) | Mg (%) | Co (%) | O (%) |
|----------|--------|--------|--------|-------|
| LMC2     | 59.70  | 3.70   | 12.11  | 24.49 |
|          | (58.20)| (3.85) | (12.22)| (24.52)|
| LMC3     | 55.39  | 5.36   | 16.63  | 22.62 |
|          | (55.39)| (5.36) | (16.63)| (22.62)|
| LMC4     | 52.17  | 7.58   | 19.16  | 21.09 |
|          | (52.17)| (7.58) | (19.16)| (21.09)|

The TEM-EDX image is presented in Figure 4 (a, c). The TEM-EDX shows that La, Mg, Co and O are present in the prepared catalyst suggesting that the preparation techniques is appropriate and that the perovskite structure have been formed. The comparison between the theoretical and experimental methods is as shown in the bar chart shown by the side of EDX map as shown in Figure 4 (b and d). From the bar chart it was observed that there was no too much difference between the theoretical and experimental values suggesting the efficiency of the synthesis methods used.

Figure 4: TEM-EDX of selected perovskite catalysts.

Furthermore, the elemental compositions was supported with the use of elemental mapping using different colours. The elemental mapping of the synthesized catalysts are as shown in Figure 5 below. This indicates that all the elements proposed during the design of the perovskite catalysts are present, evenly distributed and also in the designed ratio [9, 10, 13].
3.4. Surface Area Analysis
The results of the surface area analysis of all the prepared catalyst is presented in Table 1. From the result, it was observed that the catalysts exhibited very low surface area and there was no significant change in the surface area even with the doping of the catalyst with magnesium but the surface area obtained from this study is higher than those obtained by similar methods in literature [1, 14, 15]. However, it is well known that the calcination temperature of perovskites have a significant effect on the surface area [8, 10, 16, 17] hence achieving this surface area at this reaction temperature suggest that the temperature used for the preparation is good enough. It was also observed that there is an increase in the surface area of the catalyst when magnesium was being incorporated into the perovskite structure (10-13 m²/g) suggesting that doping of the perovskite has the ability to increase the surface area of the prepared catalyst. There was also no specific trend in the BET of the catalyst which suggests that all the elements have been properly mixed during the preparation process [18-20].

3.5. HRTEM Analysis
The micro- surface analysis was carried out with the use of HRTEM. The HRTEM images obtained for the various prepared perovskite catalysts are as displayed in Figure 4.3.8. The HRTEM images obtained for LMC0 (Figure 6 a, b, c) were compared with selected Mg doped LMC1 (Figure 6 d-f) and LMC2 (Figure 6 g-i). The images for LMC0 shows the crystalline nature of the perovskite catalyst. Figure 6a displays non regular shape crystalline particles which appeared to be coagulated together. Figure 6b shows the higher magnification of the catalyst which indicate the formation of distinct spherical shapes. Figure 6c shows the lattice fringes obtained and the d spacing of 0.23 nm which corresponds to the (101) crystallite orientation as reported in literature. The selected area disperse image inserted in Figure 6c the formation of the regular crystals arranged in patterns. Similar crystalline structures were obtained for LMC1 and LMC2 except for the increase in the d spacing. Their SAED (insert) also displayed well defined circular crystalline pattern to support the formation of Mg doped perovskite as obtained from the XRD studied.
3.6. Catalytic Activity studies

The catalytic activity results were determined from the TGA oxidation of the soot which has been standardized by removing the weight loss that is 300 °C, this is because desorption of the adsorbed water and decomposable oxygen complexes on the surface of the soot takes place below 300 °C as reported in literature by [5, 13, 21, 22]. This method is similar to the one used in the literature by [6, 23, 24]. The standardized conversion plots all through the soot oxidation over the catalysts LMC0, LMC1, LMC2, LMC3 and LMC4 are as shown in Figure 7. However, in order to properly evaluate the catalytic activity of the catalysts on the soot conversion, a raw soot without the catalyst was used as a control sample. The combustion temperature (T_{50} and T_{90}) of the model soot used for this experiment was 598 and 670 °C respectively and when compared with the un-doped catalyst (LMC0) the combustion temperature reduced to approximately 550 and 650 °C respectively. This suggests that LaCoO_{3} (LMC0) has the capability to convert the soot. However, upon the introduction of Mg (dopant) into the parent structure, it was observed that the combustion temperature reduced suggesting that the dopant helped in increasing the catalytic activity of the prepared catalyst. In this research study, LMC1 gave the best catalytic activity for soot combustion out of all the prepared catalysts and the lowest temperature of soot combustion, T_{50} and T_{90} was 487 and 550 respectively.

Figure 6: HRTEM images of selected perovskite catalysts
4. Conclusion
A series of Mg doped on the A site perovskite catalysts were synthesized, characterized and the performance for soot conversion in diesel particulate filter were evaluated. The partial doping of the A site of the perovskite catalysts helps in creating oxygen vacancies which helped in the enhancement of the catalytic properties of the nano catalysts. The XRD of the prepared catalysts showed that the compounds prepared are pure evidenced with good crystalline peaks. LMC1 gave the best results in terms of catalytic performance exhibiting the lowest $T_{50}$ (temperature at which 50 and 90 percent of the soot has been converted) which confirms that the prepared catalysts can be used as an alternative to the present catalyst been used in the diesel automobile industries.

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