Synthesis and characterization of A site doped lanthanum based perovskite catalyst for the oxidation of soot

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Abstract. A sequence of La₁₋ₓCaₓCoO₃ (x=0, 0.2, 0.3, 0.4) perovskites catalysts (coded LAC₀, 1, 2, 3) were prepared by the modified citrate sol–gel method, and their catalytic activities for soot conversion were studied. The characterizations of the prepared catalysts were conducted by Brunauer-Emmett-Teller (BET), Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES), Thermogravimetric/ Differential Thermogravimetric Analysis (TGA/DTG), Scanning Electron Microscopy (SEM), X-ray powder Diffractometer (XRD) and Transmission Electron Microscopy (HRTEM). It was observed that upon the introduction of Ca into the parent perovskite system, the surface area of the prepared catalyst increased. The catalytic performance evaluation of the prepared catalysts showed that upon the doping of Ca into the A-site of LaCoO₃, there was about 30% improvement in the catalytic activity for soot oxidation. The best catalytic performance with soot conversion at Tₜₐ₉ of 484°C was obtained on La₀.8Ca₀.2CoO₃ (LAC₂). The Ca doped LaCoO₃ gave a better catalytic performance when compared with the classical Pt/Al₂O₃. This depicts that the non-noble metal based catalyst is a possible replacement for the noble metal based catalyst.

Keywords: Catalyst, Sol gel method, Soot oxidation, Perovskites, Calcium

1. Introduction
In regulating the discharge of fine particulate matter (PM) emanating from diesel engines, which is generally made up of soot (carbon), a continuously regenerating diesel particulate filter (CRDPF) technology that engages the use of catalytic processes in which soot are physically trapped has been suggested as an efficient after-treatment system [1-3]. Recent reports have argued that the reduction of diesel exhaust pollutants to a minimally accepted level cannot be achieved solely by modifying the engines hence the rigorous efforts being devoted to the development of catalyst for the after treatment processes [2]. For this reason, several catalysts such as the ceria-based materials [4], precious metal [5], alkali-metal oxides [6], spinel oxides [7] have been rigorously studied for soot oxidation combustion. However, of all the above mentioned catalysts, the perovskite oxide which has a general formula of ABO₃ have been of potential interest because of its high stability, economical value and catalytic performance [8-10].

Literature has revealed that doping the perovskite oxide (ABO₃) at the A site has the potential of improving its catalytic activity [11]. The doping of the A site generates oxygen vacancies which increases the lattice oxygen mobility and oxygen desorption necessary for catalytic oxidation processes [12-14]. The oxygen vacancies can play a significant role in soot oxidation activity by allowing more
amount of gaseous oxygen to be absorbed and transferred to the soot surface which enhances the soot oxidation [15, 16].

However, one of the challenges being faced in the development of perovskite catalysts is the maintaining of the structure and at the same time maintaining high surface area due to the calcination temperature been employed in their synthesis. Perovskites catalysts have been prepared and used for NOx conversion by several researchers but to the best of our knowledge, not much has been reported with respect to being used for soot oxidation in detail. Literature has reveal that doping perovskite with Barium has helped in the catalytic oxidation of NOx [15]. This is because barium is beneficial for the absorption of NOx as nitrates. Calcium can also regard as an A site dopant due the similar properties it has with Barium due to their being on the same group in the period table and it abundant availability which makes it cheap. Also calcium has a lower ionic radius which is similar to the rare earth metals in the BO₆ makes it a promising A site dopant for turning the lattice of LaCoO₃. Other reasons for selecting calcium as the dopant includes its low valence state (Ca²⁺) and a relatively weak Ca-O bond strength in compare to rare earth element oxygen bond. This will endow the perovskite material (LaCoO₃) with high oxygen vacancy concentration. Several methods have been used for the preparation of perovskite catalyst such as Pechini gel technique [17], solid state reaction [18], glycine nitrate process, microwave process [2] and the EDTA methods.

In this research study, the nano perovskite La₁₋ₓCaₓCoO₃ catalysts were synthesised by a citrate sol gel method. The catalytic performance of the catalysts for soot oxidation activity were been studied analytically. The prepared nano perovskite catalyst were characterized by thermo-gravimetric analysis (TGA), X-ray diffraction (XRD), BET surface area, High resolution transmission electron microscope (HRTEM), ICPAES and the soot oxidation measurements were carried out using the thermogravimetry method prescribed by Prasad et al. [14]. The results of this research study will provide a potential replacement for the commercially available catalyst for diesel exhaust purification.

2. Materials and Methods

All the chemical used in for this research study was purchased from Sigma Aldrich and were used without further purification. The model soot used was obtained from the vehicle emission laboratory of the Indian Institute of Petroleum Dehradun.

2.1. Methods

La₁₋ₓCaₓCoO₃ perovskites catalysts with x=0, 0.1, 0.2, 0.3, (coded LAC0, LAC1, LAC2 and LAC3 respectively) were prepared by the citrate sol gel method as described above. LAC1 was prepared by mixing 9.74 g of La (NO₃)₃·6H₂O, 0.59 g of Ca (NO₃)₂, 6.41 g of Co (NO₃)₃ and 19 g Citric acid in 125 ml of distilled water. 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. LAC2 and LAC3 were prepared using the same method except for the variation of Ca (NO₃)₂ which is 1.18 g and 1.77 g respectively. The elemental composition was determined by inductively coupled plasma atomic emission spectroscopy (ICPAES) model DRE, PS-3000UV, LEEMAN LABS, INC, USA. The specific surface area of the prepared catalysts was carried out by the BET method from the nitrogen adsorption isotherms obtained at 77 K on the catalyst outgassed at 250°C by means of a Micromeritics Gemini V 2000 apparatus. The XRD patterns of the various prepared catalyst were measured at room temperature using a Rigaku diffractometer, model Geiger flex, ran at 30 kV and 20 mA. The decomposition and crystallization behaviour of the precursor catalyst dried at 200°C was analysed by TG/DTG PERKINS ELMER 2000 model at a heating rate of 5°C min⁻¹ from room temperature to 1000°C in air. The H₂ Temperature-programmed reduction (TPR) was measured on a BEL-CAT chemisorption analyser having a TCD detector. The IR measurements were carried out on a Perkin-Elmer Spectrometer. Scanning Electron Micrographs (SEM) analysis was done using the LEO instrument 435VP model. High Resolution Transmission Electron Micrographs of the catalysts were recorded on JOEL X-650 EM.
2.2. Catalytic activity
The catalytic activity of the catalysts with the soot was carried out using the thermo-gravimetric analysis method by TG-DSC, Q-600 instrument as described by Prasad et al. [14]. The prototypical soot that was used in this research work was obtained 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 [19]. A small quantity of the synthesized soot-catalysts mix was placed in TGA crucible and heated up to 1000°C at a heating rate of 10°C min⁻¹ and a flow rate of 100 mL min⁻¹ air.

3. Results and Discussion.

3.1. Thermogravimetric Analysis (TGA/DTG)
The formation of the crystalline phase of the prepared perovskite catalysts were determined from the TGA/DTG analysis carried out from 0-850°C (a representative LAC2 catalyst dried at 200°C was used) and displayed in Fig. 1. The TGA of the prepared catalyst exhibited a five major decomposition stages. The various stages of the decompositions were established using the DTG graph. From the presented thermographs, the first decomposition (D₁) representing about 5% of the prepared catalysts was found in the region of 0-120°C and can be credited to the absorbed water molecules. The second decomposition (D₂) representing about 40% was observed between 120-230°C and was ascribed to the decomposition of bonded water molecules. With increasing temperature, three major decomposition stages were further observed. The (D₃) decomposition stage observed around 230-280°C representing about 25% of the prepared catalyst was ascribed to the decomposition of the organic moiety used in the preparation procedure. The fourth decomposition stage (D₄) occurred between 280-400°C and can be credited to the bond detachment and formation of metal salt. The final stage of the decomposition (D₅) was observed at around 550°C and it’s assumed to be the crystalline phase formation of the perovskite catalyst. Based on this various decomposition stage, the calcination temperature for the perovskite catalysts was done above 600°C. The thermal effect on the metal salt is proposed in the equation below:

\[
\text{La (NO}_3\text{)}_2 + \text{C}_6\text{H}_5\text{O}_7 \rightarrow \text{LaO (OH)}(\text{S}) + \text{H}_2\text{O}_{(g)} + \text{NO}_2(\text{g}) + \text{CO}_2(\text{g})
\]

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

the proposed equation for the dopant is as presented below:

\[
\text{Ca(NO}_3\text{)}_2(\text{S}) \rightarrow \text{CaO} + \text{NO}_2
\]

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

\[
\text{Co(NO}_3\text{)}_2 + \text{C}_6\text{H}_5\text{O}_7 \rightarrow \text{CoO(OH)}(\text{S}) + \text{H}_2\text{O}_{(g)} + \text{NO}_2(\text{g}) + \text{CO}_2(\text{g})
\]

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

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

\[
\text{LaO} + \text{CaO} + \text{CoO} \rightarrow \text{LaCaCoO}_3
\]
3.2. X-ray Analysis

The crystalline formation of the prepared perovskite catalysts was proven with the xrd analysis. The Fig. 2 below displays the xrd patterns of all the prepared catalysts.

![XRD patterns of the prepared perovskite catalysts and the precursor.](image-url)
The xrd diffractogram of the catalysts showed the characteristics peaks associated with the rhombohedral structure of the perovskite catalysts (JCPDS 25-1060). The various peaks were indexed using the QualX software to get the crystalline planes 104, 202, 024, 241 and 208. Also, the most noticeable peaks in LAC0 are ascribed to the characteristics peaks of LaCoO$_3$ [20]. The various doped catalysts were found to show similar characteristics peaks. Furthermore, it was observed that as the concentration of the dopant (Ca) was increasing, the intensity of the peaks reduced gradually. The lattice parameters of the prepared perovskite catalysts were obtained using the QualX software and presented in table 1. The lattice parameter increases as the amount of dopant increases. In addition, isolated phases such as La$_2$O$_3$, Co$_2$O$_3$ or Cobalt oxides were not detected (at least to the limit of the xrd) suggesting that a single phase perovskite was formed for all the prepared catalyst.

| Catalyst | Surface Area BET (m$^2$/g) | %La   | %Ca   | %Co   | %O   | a (Å) | c (Å)  |
|----------|-----------------------------|-------|-------|-------|------|-------|-------|
| LAC0     | 10.54                       | 49.55 | 0.00  | 12.95 | 37.50| 5.4270| 13.0802|
|          | (49.01)                     |       |       |       |      |       |       |
| LAC1     | 11.98                       | 47.56 | 2.04  | 16.93 | 28.50| 5.4437| 13.1421|
|          | (47.84) (01.82)             |       |       |       |      |       |       |
| LAC2     | 12.81                       | 44.70 | 3.70  | 15.64 | 35.90| 5.4450| 13.1603|
|          | (45.28) (03.80)             |       |       |       |      |       |       |
| LAC3     | 13.26                       | 40.39 | 5.36  | 16.63 | 22.62| 5.4452| 13.1605|
|          | (40.19) (06.94)             |       |       |       |      |       |       |

### 3.3. Elemental Analysis

The elemental analysis of the prepared perovskite catalyst was studied using the ICPAES. The result of the analysis is presented in table 1. The results that was obtained from the analysis revealed the percentage composition of the various elements within the perovskite structure. From the results obtained, it was observed that LAC0 contains 0% of the dopant as expected while the dopants percentages were shown in LAC1-LAC3 (2.04-5.36). Also, the percentages of dopant were observed to be increasing with increase in concentration amount of the dopant as expected. The percentages of La, Co and O were found to compare favourably with the theoretical values in parenthesis (values obtained from the TEM-EDX). The obtained results from the elemental analysis validates the efficacy and efficiency of the preparation procedure used for the catalysts preparation as well as signifies the formation of the perovskite catalyst design [21-23]. Furthermore, the elemental mapping of a representative perovskite catalyst (LAC1) is as displayed in Fig. 3. The result of the mapping shows that there was good distribution of all the elements in the perovskite structure of the catalyst prepared.
3.4. Surface Area Analysis
The results obtained from the surface area analysis of the prepared catalysts are presented in Table 1. The result showed that all the prepared catalysts exhibited low surface area. The surface area was observed to increase from 10.54-13.26 m$^2$/g upon the introduction of the dopant. This suggests that doping the catalysts helps in increasing the surface area. Also, when the surface area of the catalysts prepared in this study was compared to previous work done in literature, it was observed that the surface area in this research was higher. This suggests that the prepared catalysts has the potential to be a better catalyst in term of catalytic activity [24-27]. Literature review suggests that the calcination temperature has a significant effect on the surface area hence achieving this surface area in this work validates the efficiency of the preparation method used [21, 28, 29].

3.5. H$_2$-TPR Analysis
The results of H$_2$-TPR of all the prepared catalysts are as shown in Fig. 4. It was observed that for LAC0, there are three reduction peaks that can be observed at approximately 410°C, 450°C and 585°C respectively. The former two peaks (410 and 450) could be consigned to the reduction of Co$^{3+}$ to Co$^{2+}$, while the peak at 585°C could be apportioned to the reduction of Co$^{2+}$ to Co$^0$ in the un-doped perovskite structure of LAC0 [30]. However, for all the doped perovskite catalysts, it was observed that the reduction peaks shifted towards a lower temperature. The three reduction peaks of LAC1 shifted to 360°C, 415°C and 565°C respectively, and a lesser reduction temperatures were noticed on LAC2 as well as LAC3. This shift to a lower temperature have be credited to the surface segregation of Co as a result of the dopant as suggested by Zhan et al. [20]. Meanwhile, after Ca doping, it was observed that the starting reduction temperature began around 360°C, which was much lower than that of the un-doped sample (410°C). Also, it was observed that for each of the calcium doped catalysts another reduction peak appeared which is approximately above 700°C. However, as the amount of the dopant is being increased, this peak was observed to be more intensified and also shifted to a higher temperature.
3.6. HRTEM Analysis
The HRTEM images of the best catalyst LAC1 is presented in Fig. 5(a). From the HRTEM image it was clear that the shape of the particle is spherical-like and appears to be agglomerated. The SAED image of the catalyst is inserted in Fig. 5(a). The SAED image shows that the prepared catalyst is crystalline in nature which is in consistent with what is observed from the XRD results. The HR-TEM image (Fig. 5b) has a lattice fringe spacing of 0.37 nm and 0.24 nm which corresponds to the crystallite orientation of (110) and (101) [19]. The size of particles was found to be around 60 nm confirming the nano particle nature of the prepared catalysts. The crystallite orientation of (110) has been said to be that of LaCoO$_3$ and (101) has been suggested to be that of Co$_2$O$_3$ [30]. However, the inability of the XRD to confirm the presence of Co$_2$O$_3$ maybe because the amount present is in small quantity. The TEM-EDX as shown in (Fig. 5c) confirms the presence of all the elements (La, Ca, Co and O) used in the preparation of the catalysts. Mostly the presence of calcium shows that the dopant is well doped into the perovskite structure. Additionally, the difference between the experimental and theoretical values shown in (Fig. 5d) shows that the preparation method used is efficient and effective.
3.7. FT-IR Analysis
The FT-IR results of the prepared catalysts are presented in Fig. 6. For the dopant-free catalysts (LAC0), three spectrum bands were observed viz 595 cm\(^{-1}\) (strong), 416 cm\(^{-1}\) (strong) and 665 cm\(^{-1}\) (strong). These bands were in agreement with the vibrational frequencies reported by Zhou et al. [30] corresponding to three normal modes. The doublet bands observed around 595–665 cm\(^{-1}\) corresponds to the \(v_1\) mode and the band observed at 416 cm\(^{-1}\) has been assigned to the \(v_2\) mode. However, upon the introduction of Ca (dopant) into the perovskite catalyst it was observed that the \(v_1\) mode appears to become broader and weaker. Especially for LAC3 which has the highest Ca composition the \(v_1\) mode appears to become one band when compared with LAC0. Also, it was noticed that the intensity of \(v_2\) and \(v_3\) mode decreased when the Ca doping increased. For LAC3 and LAC2, the bands at 875 cm\(^{-1}\) and 1491 cm\(^{-1}\) were detected. These bands have been said to correspond to the out of plane bending and the \(v_3\) mode of the carbonates respectively which could come from the incomplete combustion of Ca and citric acid [30, 31].
3.8. Catalytic Activities of prepared perovskite catalysts.

The results of catalytic activities was determined from the TGA oxidation of the soot which has been standardized by removing the weight loss that is below 300°C, this is because several researchers have revealed that desorption of the adsorbed water and decomposable oxygen complexes on the surface of the soot is what takes place below 300°C [32]. The method adopted here similar to the one used in the literature by Prasad et al. [14]. The standardised conversion plots of the soot conversion over the catalysts LAC0, LAC1, LAC2, and LAC3 are as shown in Fig. 7 and table 2 below. However, in other to properly determine the catalytic activity of the catalysts on the soot conversion, a raw soot without the catalyst was used as a control sample. It was observed that there is a considerable drop in the soot ignition temperature (combustion temperature) of the raw soot and the catalysed soot. The combustion temperature (T_{50} - temperature at which 50% of soot is converted and T_{90} - temperature at which 90% of soot is converted) of the model soot used for this experiment was 598 and 670°C respectively. But when compared with the un-doped catalyst (LAC0) it was observed that the combustion temperature reduced to approximately 550 and 650°C respectively. This suggests that LaCoO₃ (LAC0) has the capability to convert the soot. However, upon the introduction of Ca (dopant) into the parent structure, it was noticed that the combustion temperature reduced suggesting that the dopant helped in increasing the catalytic activity of the prepared catalyst. In this research study, LAC1 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. The various T_{50} and T_{90} of the prepared catalyst is tabulated in the table 2 below. Generally, several reports have suggested that chemosorbed surface oxygen species, O₂¯ and O³ are responsible for the soot catalytic combustion [24]. In addition the doped catalyst exhibited a more

![FT-IR spectral of the prepared catalyst.](image)
catalytic activity than the un-doped suggesting that doping the catalyst can facilitate the release the active oxygen species [33].

![Catalytic activity plots of the synthesized catalysts.](image)

**Figure 7.** Catalytic activity plots of the synthesized catalysts.

| Catalysts | $T_{50}$ | $T_{90}$ |
|-----------|-----------|-----------|
| Raw Soot  | 598       | 670       |
| LAC0      | 550       | 650       |
| LAC1      | 487       | 550       |
| LAC2      | 525       | 580       |
| LAC3      | 501       | 590       |

**Table 2.** Catalytic activity table of the prepared catalysts.

4. Conclusion.
In this research study, a series of A site doped perovskite catalysts were synthesized using the sol gel citrate method and calcination temperature of 750°C. The prepared catalysts were tested for the catalytic performance on soot conversion in diesel engine. All the prepared catalysts exhibited relatively low surface area but the introduction of the dopant helped in increasing the surface area. The catalytic performance of the catalysts was evaluated by considering the soot ignition temperature $T_{50}$ and $T_{90}$ which is the temperature at which 50 and 90 percent of the soot were converted. In this study, the most potent perovskite catalyst was LAC1 in which the soot ignition temperature dropped to 487°C.

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