Research Article

Effect of Preparation Method and Calcination Temperature on LaCoO$_3$ Perovskite Catalyst for Diesel Soot Oxidation

Anupama Mishra and Ram Prasad*

Department of Chemical Engineering and Technology, Indian Institute of Technology (Banaras Hindu University), Varanasi 221005, Uttar Pradesh, India

*Corresponding Author: Email: rprasad.che@iitbhu.ac.in Ph:+919415268192

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Abstract: The present work attempts to scan the effect of preparation methods (co-precipitation, sol-gel and solution combustion synthesis) and calcination temperature (600-800°C) on the efficiency of LaCoO$_3$ catalysts for soot oxidation. All the catalysts were highly selective towards CO$_2$ as no CO was detected in the flue gas. Catalyst produced following co-precipitation method revealed total soot oxidation at the lowest temperature ($T_f = 370^\circ C$) than other two catalysts prepared by sol-gel ($T_f = 420^\circ C$) and solution combustion synthesis ($T_f = 456^\circ C$) methods. Irrespective of the preparation methods, 750°C was the optimum calcination temperature of the precursors resulting LaCoO$_3$ catalysts which exhibited maximum activity for soot oxidation. In addition, the results showed that the specific surface areas of the catalysts decreased with increasing calcination temperature beyond 750 °C and consequently decreasing the activity of the catalyst.

Keywords: Perovskite, LaCoO$_3$, Calcination Temperature, Catalytic Oxidation, Diesel Soot.

1. INTRODUCTION

Diesel engines have a variety of advantages over other engines types, such as higher fuel economy, reliability, durability as well as low maintenance costs [1]. However, a major environmental problem associated with diesel engines is the emission of particulate matter (PM) from the exhaust, which consists mostly of carbonaceous soot and soluble organic fraction (SOF) of hydrocarbons [2]. The health effects of diesel particulate have been a matter of concern for many years, because of both the chemical composition and the particle size spectrum [3]. Most of the soot mass is in 0.1-1.0 μm “accumulation” size fraction, while most of the particles are <10 nm “nano-particle” fraction [4]. Nano-meter pores with diameters ranging 2-4 nm was also detected in the nano size soot particles. Because of their large surface areas and pore volumes, other pollutants in the environment can be adsorbed to soot particles potentially making them more hazardous. Approximately 90 different organic pollutants were detected in the soot, including aromatic compounds and other hydrocarbons. The majorities of the components are mutagens, carcinogens and toxic air pollutants [5]. The small soot particles are respirable and penetrate deep into the lungs [6] where it is able to enter the bloodstream and even reach the brain [7]. They also can accumulate in lungs over time, obstructing oxygen transfer to the blood and causing many health problems. Apart
from health problems soot particles also causes pollution of air, water, and soil, soiling of buildings, reductions in visibility, impact agriculture productivity, global warming and climate change, etc.

Future, emission limits focus on decreasing the allowable emissions of PM for diesel light duty vehicles (LDV) and heavy duty vehicles (HDV) as shown in Table 1 [8]. There is marginal reduction of 10% of PM from Euro-5 corresponding to 2011 regulations to the prescribed Euro-6 (Sept. 2014) regulations for LDV, whereas; reduction of PM emissions is too much (67%) for HDV from Euro-V to Euro-VI. Therefore, with increasingly stringent emission standards, the need for improved emission control systems for PM has become evident.

Table 1. Soot emission limits for light duty diesel vehicle (LDV) and heavy duty vehicle (HDV)

<table>
<thead>
<tr>
<th></th>
<th>LDV (mg/Km)</th>
<th>HDV (mg/kWh)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Euro</td>
<td>5.0</td>
<td>4.5</td>
</tr>
<tr>
<td>5.0</td>
<td>4.5</td>
<td>30</td>
</tr>
</tbody>
</table>

Catalyst coated diesel particulate filter (DPF) is an efficient device to trap and simultaneously burn the soot within the exhaust temperature range (150-450°C) [9]. The soot formula can be approximately given as C₈H [10] which on combustion releases non-toxic gases found in the atmosphere. The complete combustion reaction of the soot can be represented by equation (1).

\[
2C_8H + 16.5O_2 (\text{air}) \rightarrow 16CO_2 + H_2O
\]  

(1)

The catalysts used at present for soot oxidation are based on supported platinum group metals (PGM) [11-13]. The noble metal catalysts are expensive and due to their scarcity to further price increase upon increasing demand. As an alternative to noble metals, recently oxides of transition metal, lanthanide group and alkaline earth metal are widely studied for soot oxidation [14-17]. Neeft et al. [18] arranged few single-component metal oxides for their relative activities in the oxidation of carbonaceous material in following order: La > Mn > Sb > Bi > Ca > Cu > Ag > Ni > Cr > Zr > Ba > Zn. Various types of multi-component catalysts such as perovskite-type oxides [19,20], spinel type oxides [21-23], rare earth metal oxides, hydrotalcite [24-26], mixed transient metal oxides [27-29], etc. are reported in the literature for diesel soot combustion. The thermal stability of perovskite catalysts is very high in comparing to other types of catalysts including noble metals. The stability of the catalyst is highly desirable in comparison to the catalyst having very high initial activity but less stability. So, perovskites seem to be the potential candidates for this application, due to their thermal stability, tailoring capabilities to design the catalyst for soot oxidation and low-cost [30].

Preparation method and calcination temperature have great influence on the performance of the catalysts for most of the reactions. There have been studies reported on CO oxidation and other automotive pollutants [31-33] removal over LaCoO₃ catalysts prepared by specific single method and calcination temperature. However no work has been reported to examine the effects of various preparation methods and calcination temperature on the performance of LaCoO₃ catalysts for diesel soot oxidation. Therefore, the present work is an attempt to scan the effect of preparation methods and calcination temperatures of the precursors on the efficiency of LaCoO₃ catalysts for soot oxidation.
2. EXPERIMENTAL

2.1 Soot Preparation

The soot was prepared by partial combustion of locally available commercial diesel (HP) in lamp with limited supply of air, and collected on the inner walls of an inverted beaker. The soot was collected from the recipient walls and then dried in an electric oven for overnight at 120°C.

2.2 Synthesis of Perovskite type catalysts

LaCoO₃ perovskite catalysts were prepared by three methods i.e. Co-precipitation method (Co-ppt), citric acid sol-gel (SG) method and solution combustion synthesis (SCS). All AR-grade chemicals were used in the preparation of catalysts. First sample was prepared by co-precipitation method described by Klissursski and Uzunova 1990 [34], using nitrate precursors, La (NO₃)₂·6H₂O and Co (NO₃)₂·6H₂O were mixed in the required stoichiometric ratio (i.e. La/Co = 1/1) to make 2.75M aqueous solution. The solution was heated to 65-75°C and then 1.4 M of Na₂CO₃ solution at pH 9 at same temperature was added rapidly with continuous stirring. To ensure a constant pH during the co-precipitation, the sodium carbonate solution had a volume twice as large as that of the nitrate solutions. The precipitate was formed immediately by adding sodium carbonate solution in nitrate solution, which remained stirred for 30 min at the same temperature. After cooling, the precipitate was filtered using vacuum filtration system and washed with hot water repeatedly so as to remove all the nitrate ions. The prepared cake of hydroxyl-carbonate was dried at 105°C for 24h and further calcined separately at 600°C, 750°C and 800°C for 4h. Thus, the three prepared catalyst samples were named as A-600, A-750 and A-800 according to their temperature of calcination.

The precipitation and calcination reactions may be represented by equations, (2) & (3) respectively.

\[
\text{La} (\text{NO}_3)_2 + \text{Co} (\text{NO}_3)_2 + 2\text{Na}_2\text{CO}_3 + \text{H}_2\text{O} + \text{1/2O}_2 \rightarrow \text{LaCo(OH)}_2(\text{CO}_3)_2 + 4\text{NaNO}_3 \quad (2)
\]

\[
\text{LaCo(OH)}_2(\text{CO}_3)_2 \rightarrow \text{LaCoO}_3 + \text{H}_2\text{O} + 2\text{CO}_2 \quad (3)
\]

The second sample of LaCoO₃ was prepared by citric acid sol-gel method [35] in this aqueous solution (0.1M) of La(NO₃)₃·6H₂O and Co(NO₃)₂·6H₂O were mixed with citric acid that was equivalent in gram mole with that of the total cations (La³⁺ and Co²⁺). Resulting red wine colored solution was heated at 80°C under continuous stirring. After 2h of continuous stirring the clear solution gradually transformed into a gel which was translucent and viscous. The wet gel was dried homogeneously overnight in an oven at 120°C in the presence of air. Obtained loose and foamy pink colour solid was heated in two steps. First heating at 450°C for 2h was carried out to decompose the organic and second step of calcination was done at 600°C, 750°C and 800°C for 4h to obtain black porous solid. The prepared catalysts were called as B-600, B-750 and B-800.

The third sample of LaCoO₃ catalyst was prepared by solution combustion method (SCS) [36]. Nitrate precursors of La and Co viz. La (NO₃)₂·6H₂O, Co (NO₃)₂·6H₂O in equi-molar amount were mixed in aqueous solution to make 0.1M solution. The mixture of the nitrates was stirred by a magnetic stirrer and urea as a fuel was added in stoichiometric amounts to the solution. The precursor solution was heated at 80°C, less than boiling temperature of water for 2h to make a concentrated solution. The concentrated solution was placed into an electric furnace at 500 °C to start the fast self-sustaining redox reaction, which gave rise to a perovskite powder. The combustion synthesis involving lanthanum nitrate, cobalt nitrate and urea occurs according to the following overall reaction (4) which gives rise to a perovskite powder and gaseous species:

\[
2\text{La} (\text{NO}_3)_3 + 2\text{Co} (\text{NO}_3)_3 + 8\text{NH}_2\text{CONH}_2 \rightarrow 2\text{LaCoO}_3 + 8\text{CO}_2 + 13\text{N}_2 + 16\text{H}_2\text{O} \quad (4)
\]
The whole reaction can be formally regarded as the combination of two different contributions:

\[
2\text{La (NO}_3\text{)}_3 + 2\text{Co (NO}_3\text{)}_3 \rightarrow 2\text{LaCoO}_3 + 12\text{O}_2 + 5\text{N}_2 \quad (5)
\]

\[
8\text{CO (NH}_2\text{)}_2 + 12\text{O}_2 \rightarrow 8\text{CO}_2 + 16\text{H}_2\text{O} + 8\text{N}_2 \quad (6)
\]

The exothermic reaction (6), namely urea combustion, provides the heat necessary to the completion of decomposition reaction (5), i.e. the endothermic transformation of nitrate into the desired oxide [36]. The resulting powder was further calcined separately at 600°C, 750°C and 800°C for 4h. The prepared catalysts were termed as C-600, C-750 and C-800.

2.3 **Catalytic activity measurements**

The catalytic performances of the prepared catalysts for oxidation of soot were evaluated in a compact fixed bed tubular quartz reactor. The reactor was consisting of two co-axial glass tubes of 20mm and 50mm diameter. A helical coil of quartz tube in between the co-axial tubes served as a pre-heater of the air. There is a hole in the lower part of the outer tube, to take care of breakage due to the expansion or contraction of air in between co-axial tubes as the unit is subjected to the variation of temperature from ambient to the reaction temperature. The pre-heated air enters the catalyst bed, kept in the inner tube as shown in the figure. The product stream from the bottom of the reactor is cooled in a condenser to the ambient temperature and then analysed with the help of an online Gas chromatograph.

The reactor was mounted vertically in a split open furnace. The down flow stream of air was used to avoid the distortion of the bed. The soot-catalyst (catalyst bed diameter 20mm and height 1.27 mm) was placed on a thin layer of glass wool which is supported on perforated quartz disc inside the inner tube. A thermocouple well made of 4mm diameter tube was inserted axially from the bottom all the way to the centre of the disc for temperature measurement and control. The catalytic activity was evaluated by placing 110 mg catalyst-soot mixture in the reactor, and the oxidation was carried out in the temperature range from ambient to total conversion of soot at a constant heating rate of 1°C min\(^{-1}\). Before the reaction, the soot-catalyst mixture, in a 1/10 weight ratio, were milled in an agate mortar for tight contact and with spatula for loose contact.

2.4 **Calculation of the soot conversion**

A graph between chromatogram areas for CO\(_2\) vs. increasing temperature for catalytic soot oxidation was plotted as shown in figure 1 for a typical experimental run. The fractional conversion of soot, \(X\) is defined as:

\[
X = \frac{\text{Mo - M}}{\text{Mo}} \quad (7)
\]

Where, \(\text{Mo}\) is the weight of initial soot taken, which is proportional to total area of the graph bounded between temperature of initiation of soot oxidation(\(T_o\)) and temperature for 100% oxidation of soot (\(T_f\)), can be given as (equation 8)

\[
\text{Mo} \propto \Sigma_{T_o}^{T_f} A_{CO_2} \Delta T \quad (8)
\]

\(M\) is the weight of soot at a typical temperature (\(T_i\)), higher than the temperature (\(T_o\)). The weight loss (\(\text{Mo-M}\)) at temperature \(T_i\), which is proportional to the area bounded by the graph between \(T_o\) and \(T_i\), can be given as (equation 9)

\[
(\text{Mo-M}) \propto \Sigma_{T_o}^{T_i} A_{CO_2} \Delta T \quad (9)
\]

Therefore the value of \(X\) at various extent of reaction can be calculated using the following formula (equation10)

\[
X = \frac{\Sigma_{T_o}^{T_i} A_{CO_2} \Delta T}{\Sigma_{T_o}^{T_f} A_{CO_2} \Delta T} \quad (10)
\]

Thus, the above graph (figure3) can be plotted between conversions vs. temperature as shown in figure7.
2.5 Catalyst characterization

The textural characterisation of the catalysts was carried out by low temperature N₂-sorption method using a Micromeritics ASAP 2020 analyzer. Phase identification of the catalysts were carried out by X-ray diffraction (XRD) patterns on a powder X-ray diffractometer (RigakuUltima IV) using CuKα1 (λ = 1.5405 Å) radiation with a nickel filter operating at 40mA and 40kV. FTIR spectra of the catalysts were recorded in the range of 400-4000 cm⁻¹ on Shimadzu 8400 FTIR spectrometer with KBr pellets at room temperature. XPS of the catalysts was performed on an Amicus spectrometer equipped with Mg Ka X-ray radiation. For typical analysis, the source was operated at a voltage of 15 kV and current of 12 mA. Pressure in the analysis chamber was less than 10⁻⁵ Pa. The binding energy scale was calibrated by setting the main C 1s line of adventitious impurities at 284.7 eV, giving an uncertainty in peak positions of ±0.2 eV.

3. RESULTS AND DISCUSSION

3.1 Textural characterization of the catalysts

The textural properties including BET surface area, total pore volume and average pore diameter of the perovskites studied in the present investigation are summarized in Table 2. It can be seen from the table that the various perovskite have low specific surface area (7-15 m²/g) and Average pore size (13-20 Å), which is in expected range considering the high synthesis temperature in accordance with references [32, 33]. The catalysts formed at 600°C showed the highest surface area irrespective of the preparation methods. Similarly the catalyst obtained at 800 °C displayed the lowest surface area irrespective of the preparation methods. It is very interesting to note that the catalyst (A-750) prepared by co-precipitation and calcined at 750 °C exhibited the highest surface area (11.05 m²/g), the lowest pore volume (0.0061 cm³/g) and comparable Average pore size as compared to catalysts prepared by other methods and calcined at same temperature.

3.2 XRD of LaCoO₃ Catalysts

3.2.1 Effect of preparation method

X-Ray diffractograms of the samples prepared by co-precipitation, sol-gel and SCS methods and calcined at 750 °C, are shown in figure 2, which exhibited the typical X-ray diffraction patterns of the rhombohedral structure of LaCoO₃ perovskite phase (JCPDS No 84-0848) irrespective of the preparation methods. Sharp peaks for the perovskite prepared by sol-gel and SCS methods suggest well developed crystalline phase. Also, no bulk impurity such as Co₃O₄ and La₂O₃ were detectable in the samples prepared by sol-gel and SCS methods. The intensity of the XRD peaks of the sample prepared by co-precipitation method is relatively lower and additional peaks can be seen in the figure 2 than the samples.
prepared by the other two methods. The additional peaks were of La (OH)\textsubscript{3} phase. The unusual presence of La (OH)\textsubscript{3} may be due to the increased basicity of the catalyst surface prepared by co-precipitation method using sodium carbonate solution.

### Table 2. Textural characterization of perovskite catalyst samples

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>BET surface area (m\textsuperscript{2}/g)</th>
<th>Pore volume (cm\textsuperscript{3}/g)</th>
<th>Average pore size (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-600</td>
<td>13.32</td>
<td>0.0043</td>
<td>13.01</td>
</tr>
<tr>
<td>A-750</td>
<td>11.05</td>
<td>0.0061</td>
<td>17.26</td>
</tr>
<tr>
<td>A-800</td>
<td>5.48</td>
<td>0.0054</td>
<td>17.28</td>
</tr>
<tr>
<td>B-600</td>
<td>12.99</td>
<td>0.0040</td>
<td>12.92</td>
</tr>
<tr>
<td>B-750</td>
<td>09.12</td>
<td>0.0074</td>
<td>16.64</td>
</tr>
<tr>
<td>B-800</td>
<td>5.62</td>
<td>0.0025</td>
<td>17.97</td>
</tr>
<tr>
<td>C-600</td>
<td>14.49</td>
<td>0.0063</td>
<td>17.38</td>
</tr>
<tr>
<td>C-750</td>
<td>8.45</td>
<td>0.0040</td>
<td>19.13</td>
</tr>
<tr>
<td>C-800</td>
<td>5.85</td>
<td>0.0069</td>
<td>20.83</td>
</tr>
</tbody>
</table>

**Figure 2.** XRD patterns of LaCoO\textsubscript{3} prepared by (A) Co-ppt,(B) SCS,(C)SG and calcined at 750°C

The crystallite size was estimated using the usual Scherrer equation (11) which is given by

\[ d = \frac{0.89\lambda}{\beta \cos\theta} \]

Where d, \( \lambda \), \( \theta \) and \( \beta \) are the crystallite size, X-ray wavelength (1.518 Å), Bragg diffraction angle and full width of the half maximum (FWHM) of the diffraction peak, respectively. Crystallite size of the samples prepared by various methods is summarized in Table 3. It is clear from the table that on increasing the temperature the crystallite size increased irrespective of the preparation method. Other researchers also reported the similar effect of temperature on crystallite size [36,37]. It is noteworthy that the catalyst (A-
750) prepared by co-precipitation and calcined at 750 °C exhibited the lowest crystallite size (16.06 nm) as compared to catalysts prepared by other methods and calcined at same temperature.

Table 3. Crystallite size of LaCoO₃ samples prepared by various methods

<table>
<thead>
<tr>
<th>Preparation method</th>
<th>CPT</th>
<th>SG(B-750)</th>
<th>SCS(C-750)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst A-600</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Catalyst A-750</td>
<td>11.63</td>
<td>16.06</td>
<td></td>
</tr>
<tr>
<td>Catalyst A-800</td>
<td>21.03</td>
<td></td>
<td>32.13</td>
</tr>
<tr>
<td>Crystallite size</td>
<td></td>
<td>25.61</td>
<td></td>
</tr>
</tbody>
</table>

3.2.2 Effect of calcination temperature on LaCoO₃ prepared by co-precipitation method

The crystalline phases of the LaCoO₃ prepared by co-precipitation method calcined at different temperatures were analyzed by XRD (figure 3). The result shows the formation of LaCoO₃ phase along with impurities like La(OH)₃ (JCPDS No 83-2034). The unusual presence of La(OH)₃ can be explained by hydroxylation of the surface which becomes more pronounced at higher temperatures. The crystallite size (table 3) and intensity of diffraction peaks are, as expected, observed to increase with increasing calcination temperature, because crystallinity are well defined at higher temperatures [36,37].

![Figure 3. XRD analysis of LaCoO₃ calcined at different temperatures, 600°C, 750°C and 800°C](image)

3.3 FTIR of LaCoO₃ perovskite

Figure 4 depicts the infrared absorption spectra of the LaCoO₃ catalyst prepared by co-precipitation method and calcined at 750 °C. The broad absorption bands around 3054 cm⁻¹ and 2345 cm⁻¹ appeared in the IR spectra of the as-prepared LaCoO₃(A-750) corresponded to OH stretching and OH bending of water. The absorption band at 1480 cm⁻¹ was corresponded to nitrate ion. In addition, the band at 1096 cm⁻¹ was corresponded to Co-OH bending which is confirmed with the reported value that MOH bending mode appears below 1200 cm⁻¹ [38]. The absorption band at 583 cm⁻¹ in figure 3 related to Co-O stretching vibration, which was confirmed with the reported value that cobalt-oxygen stretching appears at around 600 cm⁻¹ [39].
3.4 XPS of LaCoO$_3$ perovskite

The characteristic spectra collected for Co 2p and O 1s in LaCoO$_3$ perovskite (A-750) are displayed in figure 5(a) and 5(b) respectively. On the basis of the binding energies of the Co 2p main lines, as shown in figure 5(b), it is difficult to determine the oxidation states of cobalt cations because similar values can be obtained for most of the cobalt oxides and hydroxides (e.g. CoO, Co$_2$O$_3$, Co$_3$O$_4$ and CoOOH). It is reported that the ΔE value of spin-orbit splitting for CoO is 16.0eV, and that of Co$_3$O$_4$ is 15.0eV [40]. For Co$_3$O$_4$ with mixed valence of Co ions, a spin-orbit splitting value of 15.2eV has been reported [41]. Table 4 collects all the binding energy and spin-orbit splitting values of Co for the LaCoO$_3$ perovskite catalyst. The Co 2p XPS spectra of the catalyst consists of two main lines with the spin-orbit splitting (ΔE) falling in the range of Co$_3$O$_4$, implying that the cobalt ions exist in the mixed valence states of +2 and +3. As a result of high-valent Co ion, oxygen vacancies are created which accumulates a large number of adsorption oxygen on the surface.

The O 1s energy spectrum, figure 5(a) consists of two peaks, which correspond to two forms of oxygen, i.e. lattice oxygen O$_{\text{lat}}$ and adsorption oxygen O$_{\text{ads}}$ on the sample surface. The peak at the binding energy of 527.5-530 eV corresponds to the lattice oxygen species (O$^{2-}$, O$^-$), which reflect the redox behaviour of the metal, and the peak at 530-531.5 eV corresponds to the adsorption oxygen species (O$_2^-$, O$_2^{2-}$), that is the active centre for the oxidation.
Table 4. Binding energy and spin-orbit splitting values for Co 2p and O 1s

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Co 2p</th>
<th>O 1s</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-750</td>
<td>779.6</td>
<td>527.9</td>
</tr>
<tr>
<td></td>
<td>794.7</td>
<td>530.4</td>
</tr>
</tbody>
</table>

3.5 SEM of LaCoO₃ perovskite

The SEM images of LaCoO₃ prepared by different methods and calcined at 750 °C, shown in figure 6 revealed that the prepared catalyst samples were highly porous and aggregated. The surface morphology of the catalyst prepared by SCS method is quite different from the other two samples prepared by Co-ppt and sol-gel methods. The surfaces of the catalysts prepared by Co-ppt(A) and sol-gel(C) methods appear to be spongy tendrils while agglomerates of granular particles(B) can be visualized for the sample prepared by SCS method. The particle size of the mixed oxides is small and uniformly distributed.

Figure 6. SEM images of LaCoO₃ prepared by (A) Co-ppt,(B) SCS, (C)SG and calcined at 750°C

3.6 Effect of preparation method on soot oxidation

Method of preparation affects the surface property, morphology, homogeneity, crystallinity and particle size of the catalyst. The combined effect of these factors affects the phenomena of soot oxidation. Figure 7(A) shows the per cent conversion of soot over the LaCoO₃ perovskite prepared by three different methods viz Sol-gel, SCS and Co-precipitation and calcined at 750°C. Soot was air oxidized over the catalyst under tight contact. Table 5 presents the details of the light off temperatures (LOT) of the soot oxidation. From the figure it can be seen that the catalyst produced by co-ppt method resulted complete oxidation of soot at the lowest temperature (T_f = 370°C) than other two catalysts prepared by sol-gel (T_f = 420°C) and SCS (T_f = 456°C). However, this catalyst initiated soot oxidation at higher temperature (T_i = 301°C) than the catalyst prepared by SCS method (T_i = 202°C) but lower than sol-gel method (T_i = 336°C). The SCS method prepared catalyst initiated soot oxidation at the lowest temperature but soot conversion slowly increased with increasing temperature resulted complete oxidation at the highest temperature (T_f = 456°C) than other two catalysts. It is evident from the table 5 that the range of temperature (T_f-T_i) for total soot oxidation was 69, 84 and 254 °C for co-ppt, sol-gel and SCS methods respectively. Thus, the soot oxidation results reported in the figure and in the table show that the co-ppt method of LaCoO₃ catalyst is the best preparation method for soot oxidation. The order of the preparation method according to the activity of the catalyst for soot oxidation was as follows: co-precipitation > sol-gel > SCS.
**Figure 7.** Effect of preparation method on soot oxidation over LaCoO$_3$ calcined at 750°C (A); Effect of calcination temperature on soot oxidation over LaCoO$_3$ prepared by SG (B), SCS (C) and co-ppt (D) methods.

**Table 5.** Characteristic LOT for soot oxidation over LaCoO$_3$ prepared by different methods and calcined at different temperatures.

<table>
<thead>
<tr>
<th>Preparation Method</th>
<th>Calcination temp. (°C)</th>
<th>$T_1$(°C)</th>
<th>$T_{50}$(°C)</th>
<th>$T_f$(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>sol-gel method</td>
<td>600</td>
<td>&gt; 550</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>750</td>
<td>336</td>
<td>389</td>
<td>420</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>379</td>
<td>420</td>
<td>455</td>
</tr>
<tr>
<td>Solution</td>
<td>600</td>
<td>365</td>
<td>&gt; 550</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>750</td>
<td>202</td>
<td>422</td>
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<td></td>
<td>800</td>
<td>229</td>
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<td>Combustion</td>
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<td>452</td>
</tr>
<tr>
<td>Synthesis</td>
<td>750</td>
<td>301</td>
<td>330</td>
<td>370</td>
</tr>
<tr>
<td>Co-precipitation</td>
<td>800</td>
<td>295</td>
<td>342</td>
<td>378</td>
</tr>
</tbody>
</table>
3.7 Effect of calcination temperature of the catalyst on soot oxidation prepared by different methods

Calcination temperature largely affects the crystallite and particle size of the catalyst. In general calcining a perovskite at high temperature increases the crystallinity and the particle size, and at a lower calcination temperature relatively smaller sizes are expected [42]. An increase in the particle size at high temperature is attributed to the accelerating sintering effect of particles. Apart from calcination temperature crystallinity and particle size is also affected by the method of preparation adopted. Here the effects of calcination temperature of the catalysts were studied for the soot oxidation over the LaCoO₃ perovskite. Figure 6(B), (C) and (D) show the percent conversion of soot over LaCoO₃ perovskite prepared by the sol-gel, SCS and Co-ppt methods respectively and calcined at three different temperatures (600, 750 and 800°C). It can be seen from the figure 6(B) that the sol-gel prepared catalyst calcined at 750°C was the most active initiating soot oxidation at 336°C which completed at 420°C. The catalyst calcined at 800°C initiated soot oxidation at higher temperature of 379°C and completed at 455°C. On the other hand catalyst calcined at 600°C did not initiate soot oxidation even at 455°C. Thus, 750°C is the optimum calcination temperature for LaCoO₃ perovskite. The larger particle aggregates formed at 800°C has lower specific surface area and consecutively decreased activity of the catalyst. Other side is that oxygen vacancy order to disorder transition occurs when temperature increases which can decrease the mobility of oxygen species in the bulk [43] and result in the decreasing soot oxidation. Calcining at a lower temperature of 600°C decreased the crystallanity of the perovskite phase which was not favourable for the soot oxidation. Similar observations from figure 6(C) and 6(D) revealed that the optimum calcination temperature was 750°C irrespective of the preparation methods.

Co-precipitation method is known for the formation of crystalline perovskite at lower calcination temperature [44,45]. XRD results (figure2) showed the formation of perovskite phase even at a lower calcination temperature of 600°C for this method. Figure 6(D) shows the percent conversion of soot over LaCoO₃ perovskite calcined at different temperatures. Interesting observation is that the catalyst prepared by co-precipitation method and calcined at 600°C, oxidized soot completely at 452°C. Whereas, the catalysts prepared by sol-gel and SCS, and calcined at 600°C did not give significant results. A higher activity of the catalyst prepared at 600°C indicates the formation of nano-metric crystalline perovskite at lower temperature by co-precipitation method authenticated by the XRD observation (figure 3). Light off temperature characteristics for soot oxidation over LaCoO₃ calcined at different temperature, as shown in Table 5 suggests 750°C as the optimum calcination temperature for the highest soot conversion efficiency.

4. CONCLUSION

Diesel soot emissions have adverse effects on human health, vegetation, environment, monuments, global warming and climate change, and thus government agencies are pressurizing to have strict emission standard. Perovskite catalysts (LaCoO₃) are prepared by Co-ppt, sol-gel and SCS and calcined at different temperatures (600-800°C). The catalysts prepared by co-ppt method show highest surface area and lowest crystallite size than the catalysts obtained by other two methods. The co-ppt method results the best catalyst calcined at 750°C exhibiting total soot oxidation at 370°C within the temperature window of diesel exhaust (150-450°C). The order of the preparation method according to the activity of the catalyst for soot oxidation is as follows: co-ppt > sol-gel > SCS. Irrespective of the preparation methods, 750°C is the optimum calcination temperature, producing the active catalyst for soot oxidation over LaCoO₃ perovskite. Thus, catalyst (A-750) could be recommended for coating of the diesel particular filter.
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The authors declare no conflict of interest

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