

## **CHAPTER 5**

# **EFFECT OF PREPARATION METHODS AND CALCINATION TEMPERATURE OF $\text{LaCoO}_3$ PEROVSKITE CATALYSTS ON THE SOOT OXIDATION**

### **5.1 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 [Banús et al. 2013]. 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 [Abdullah et al. 2008]. 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 [Prasad and Bella 2010]. Most of the soot mass is in 0.1-1.0  $\mu\text{m}$  “accumulation” size fraction, while most of the particles are <10 nm “nano-particle” fraction [McClellan 1989]. Nano-metric 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 [Ramanathan 2007]. The small soot particles are respirable and penetrate deep into the lungs [Meng et al. 2013] where it is able to enter the bloodstream and even reach the brain [Zhu et al. 2007]. 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). Therefore, with increasingly stringent emission standards, the need for improved emission control systems for PM has become evident.

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) [Konstandopoulos and Papaioannou 2008]. The soot formula can be approximately given as C<sub>8</sub>H [Hall-Roberts et al. 2000] which on combustion releases non-toxic gases found in the atmosphere. The complete combustion reaction of the soot can be represented by equation (5.1).



The catalysts used at present for soot oxidation are based on supported platinum group metals (PGM) [Uchisawa et al. 2003a, Uchisawa et al. 2003b]. 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

[Shan et al. 2010, Mishra and Prasad 2014]. 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 [Seiyama 1993].

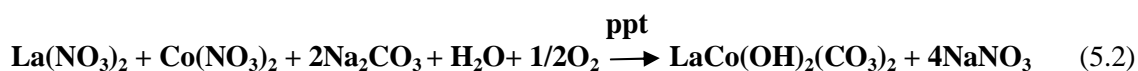
Preparation method and calcination temperature have great influence on the performance of the catalysts for most of the reactions. There have been studies reported on CO oxidation and other automotive pollutants [Seyfi et al. 2009, Russo 2008] removal using  $\text{LaCoO}_3$  catalysts prepared by specific 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  $\text{LaCoO}_3$  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  $\text{LaCoO}_3$  catalysts for soot oxidation.

## **5.2 Experimental**

### **5.2.1 Synthesis of Perovskite Type Catalysts**

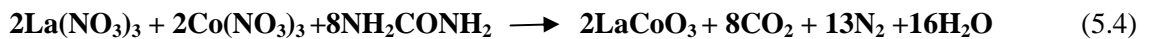
$\text{LaCoO}_3$  perovskite catalysts were prepared by three methods i.e. Co-precipitation method (Co-ppt), citric acid sol-gel (SG) method and solution combustion synthesis (SCS). All AR-grade chemicals were used in the preparation of catalysts. First sample was prepared by co-precipitation method described as by Klissurski and Uzunova [1990], using nitrate precursors ( $\text{La}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ), mixed in the required stoichiometric ratio (i.e.  $\text{La/Co} = 1/1$ ) to make 2.75M aqueous solution. The solution was heated to 65-75°C, then 1.4 M of  $\text{Na}_2\text{CO}_3$  solution at pH 9 and at the 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 maintaining 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, (5.2) and (5.3) respectively.



The second sample of LaCoO<sub>3</sub> was prepared by citric acid sol-gel method [Li et al. 2010] in this method aqueous solution (0.1M) of La(NO<sub>3</sub>)<sub>3</sub>.6H<sub>2</sub>O and Co(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O were mixed with citric acid that was equivalent in gram mole with the total cations (La<sup>3+</sup> and Co<sup>2+</sup>). 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 an electric oven. The 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 LaCoO<sub>3</sub> catalyst was prepared by solution combustion method (SCS) [Pawar and Turkar 2012]. Nitrate precursors of La and Co in equi-molar amount were mixed to make 0.1M aqueous 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, lower 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 (5.4) which gave rise to a perovskite powder and gaseous species:



The whole reaction can be formally regarded as the combination of two different contributions:



The exothermic reaction (5.6), namely urea combustion, provides the heat necessary to the completion of decomposition reaction (5.5), i.e. the endothermic transformation of nitrate into the desired perovskite oxide [Pawar and Turkar 2012]. 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.

### **5.2.2 Catalytic Activity Measurements**

The catalytic performances of the prepared catalysts for oxidation of soot were evaluated in a compact fixed bed tubular quartz reactor as shown in figure 3.9 and discussed in detailed in section 3.6.2.

### **5.2.3 Catalyst Characterization**

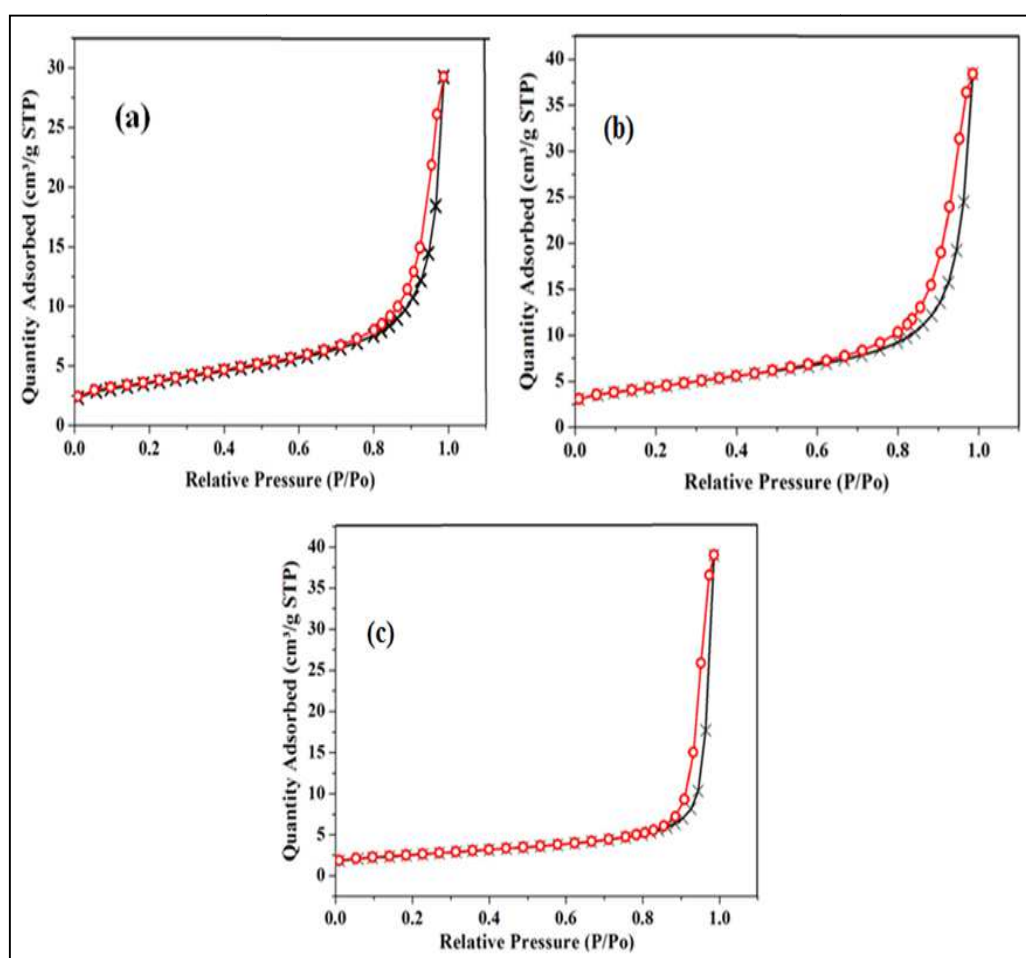
The textural characterisation of the catalysts was carried out by low temperature N<sub>2</sub>-sorption method using a Micromeritics ASAP 2020 analyzer. Phase identification of the catalysts were carried out by X-ray diffraction (XRD) patterns on a powder X-ray diffractometer (Rigaku Ultima IV) using CuK $\alpha$ 1 ( $\lambda = 1.5405 \text{ \AA}$ ) radiation with a nickel filter operating at 40mA and 40kV. FTIR spectra of the catalysts were recorded in the range of 400-4000 cm<sup>-1</sup> on Shimadzu 8400 FTIR spectrometer with KBr pellets at room temperature. XPS of the catalysts was performed on an Amicus spectrometer equipped with Mg K $\alpha$  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<sup>-5</sup> 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  $\pm 0.2$  eV. The surface morphology was studied with FEI Quanta 200 scanning electron microscope (SEM) instrument. An accelerating voltage of 30kV and magnification of 1000 and 20000x were applied.

## **5.3 Results and Discussion**

### **5.3.1 Textural characterization of the Catalysts**

Typical nitrogen physisorption isotherms and pore size distribution curves for the catalyst samples prepared by three different methods and calcined at 750°C, are shown in Figures 5.1 and 5.2 respectively. The nitrogen sorption isotherms exhibit type-IV isotherms with H1 type hysteresis loop. This type of isotherm occurs on porous adsorbent with pores in the range of 1.5-100 nm as can be visualised on pore size distributions curves in figure 5.2. The narrow area of the hysteresis loop present in the sorption isotherms of all the samples is a representative of open textured pores, which offers practically negligible diffusion resistance during reaction. The pore size

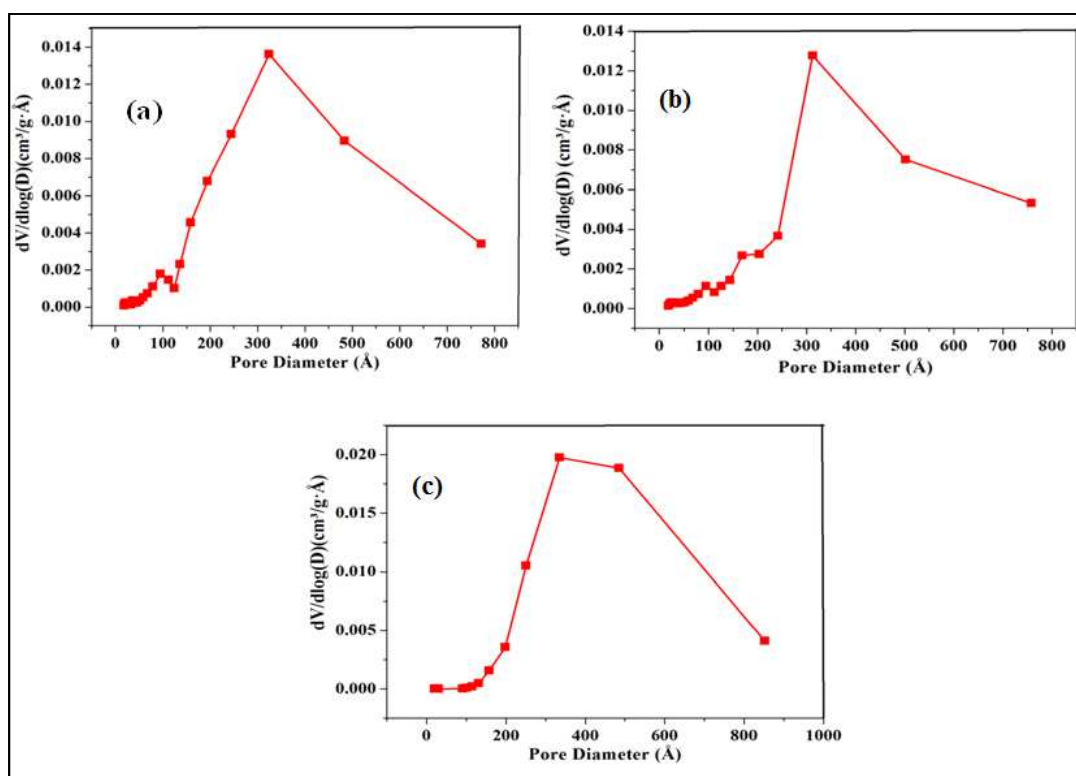
distributions of the catalysts A-750, B-750 and C-750 are shown in Figure 5.2 a, b and c respectively. It can be seen that the pore size distribution curves for A-750 and B-750 are similar in nature than for C-750. In the case of A-750, the most probable pore was found around 340 Å with a distinct second peak at around 95 Å, while in the case of C-750 the first peak appeared around 98 Å with another one around 350 Å. In case of B-750 the most probable pore was found near 340 Å which is wider in comparison to other two catalysts.



**Figure 5.1** N<sub>2</sub> Physisorption isotherms of catalysts (a) A-750 (b) B-750 and (c) C-750, calcined at 750°C

The average pore diameter obtained by BET analysis suggests that catalyst was mesoporous. The initial part of the isotherm is attributed to monolayer adsorption. At

higher pressures the slope shows increased uptake of adsorbate as the pores becomes filled, inflection point typically occurs near the completion of the first monolayer. In the mesoporous materials, due to larger pores, greater number of molecules interacts with each other and displays better catalytic activity. Hysteresis loops occur at moderate relative pressures (around 0.8) and area within the loop is very small suggesting open cylindrical pores of the catalyst.



**Figure 5.2** Pore size distribution curves of catalysts (a) A-750 (b) B-750 and (c) C-750

The textural properties determined by low temperature N<sub>2</sub> physisorption, including BET surface area, total pore volume and average pore diameter of the perovskites studied in the present investigation are summarized in Table 5.1. It can be seen from the table that the various perovskite have low specific surface area (7-15m<sup>2</sup>/g) and Average pore size (13-20 Å), which is in expected range considering the high synthesis temperature. This is in accordance with references [Russo et al. 2008,



Campagnoli et al. 2005]. 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 (11.05m<sup>2</sup>/g), the lowest pore volume (0.0061cm<sup>3</sup>/g) and comparable average pore size as compared to catalysts prepared by other methods and calcined at same temperature.

**Table 5.1** Textural characterization of perovskite catalyst samples

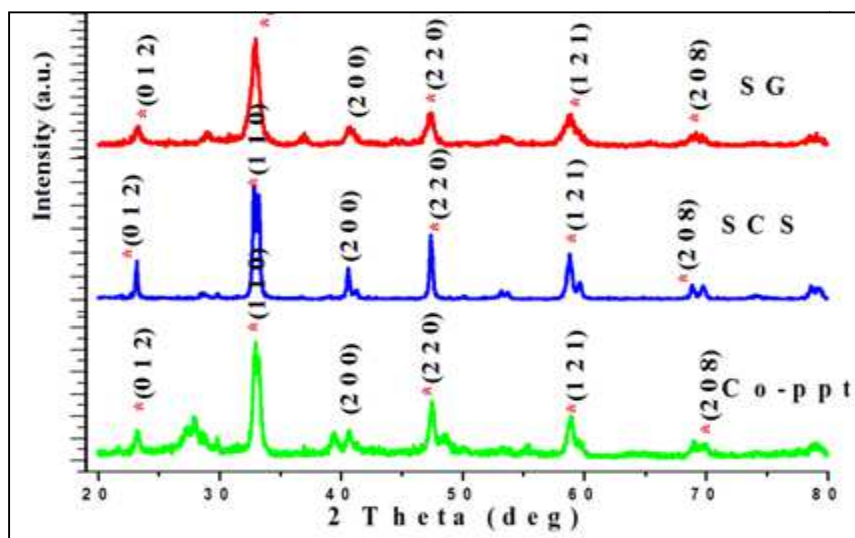
Catalyst	BET surface area (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)	Average pore size (Å)
A-600	13.32	0.0043	13.01
A-750	11.05	0.0061	17.26
A-800	5.48	0.0054	17.28
B-600	12.99	0.0040	12.92
B-750	09.12	0.0074	16.64
B-800	5.62	0.0025	17.97
C-600	14.49	0.0063	17.38
C-750	8.45	0.0040	19.13
C-800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

### 5.3.2 XRD of LaCoO<sub>3</sub> Catalysts

#### 5.3.2.1 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 5.3. The diffractograms exhibited the typical X-ray diffraction patterns of the rhombohedral structure of LaCoO<sub>3</sub> 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 Co<sub>3</sub>O<sub>4</sub> and La<sub>2</sub>O<sub>3</sub> 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 5.3 than the samples prepared by the other two methods. The additional peaks were of  $\text{La}(\text{OH})_3$  phase. The unusual presence of  $\text{La}(\text{OH})_3$  may be due to the increased basicity of the catalyst surface prepared by co-precipitation method using sodium carbonate solution.



**Figure 5. 3** XRD patterns of  $\text{LaCoO}_3$  prepared by (A) Co-ppt, (B) SCS, (C) SG and calcined at  $750^\circ\text{C}$

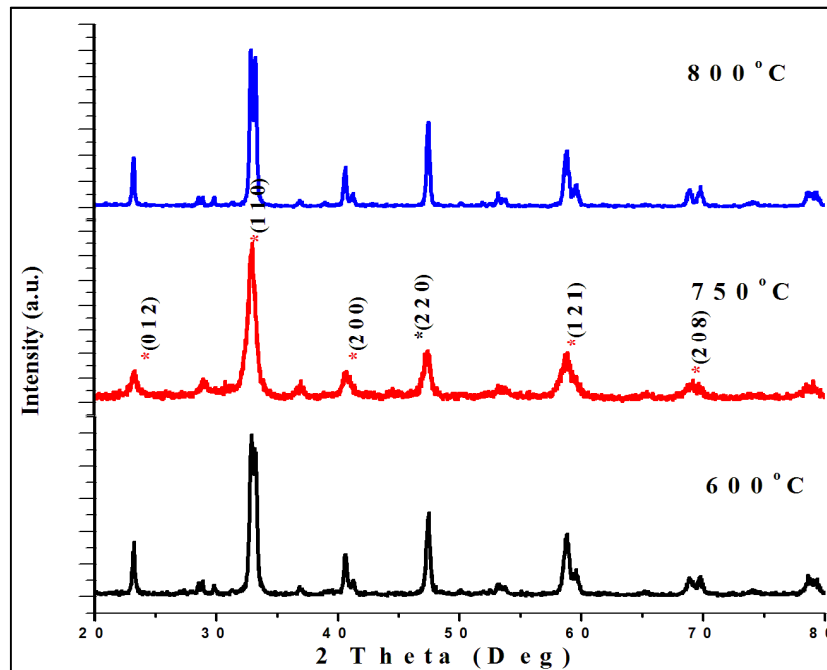
The crystallite size was estimated using the usual Scherrer equation (3.9). Crystallite size of the samples prepared by various methods is summarized in Table 5.2. It is clear from the table that on increasing the temperature the crystallite size increased irrespective of the preparation method. Other researchers also reported the similar effect of temperature on crystallite size [Pawar and Turkar 2012, Papageorgiou 2012]. It is noteworthy that the catalyst (A-750) prepared by co-precipitation and calcined at  $750^\circ\text{C}$  exhibited the lowest crystallite size (16.06 nm) as compared to catalysts prepared by other methods and calcined at the same temperature.

**Table 5.2** Crystallite size of LaCoO<sub>3</sub> samples prepared by various methods

Catalyst	A-600	A-750	A-800	B-750	C-750
Crystallite size (nm)	11.63	16.06	21.03	32.13	25.61

### 5.3.2.2 Effect of Calcination temperature on LaCoO<sub>3</sub>

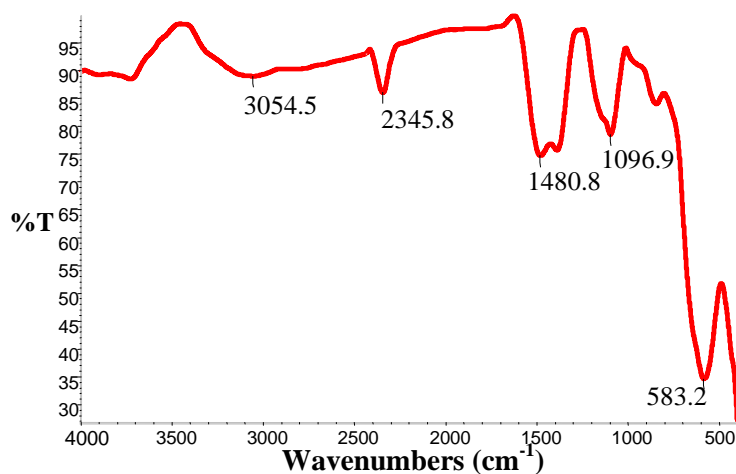
The crystalline phases of the LaCoO<sub>3</sub> prepared by co-precipitation method calcined at different temperatures were analyzed by XRD (figure 5.4). The result shows the formation of LaCoO<sub>3</sub> phase along with impurities like La(OH)<sub>3</sub> (JCPDS No 83-2034). The unusual presence of La(OH)<sub>3</sub> can be explained by hydroxylation of the surface which becomes more pronounced at higher temperatures. The crystallite size (table 5.2) and intensity of diffraction peaks are, as expected, observed to increase with increasing calcination temperature, because crystallinity are well defined at higher temperatures [Pawar and Turkar 2012, Papageorgiou 2012].



**Figure 5.4** XRD analysis of LaCoO<sub>3</sub> (Co-ppt) calcined at different temperatures, 600°C, 750°C and 800°C

### 5.3.3 FTIR of LaCoO<sub>3</sub> (Co-ppt) Perovskite

Figure 5.5 depicts the infrared absorption spectra of the LaCoO<sub>3</sub> catalyst prepared by co-precipitation method and calcined at 750°C. The broad absorption bands around 3054 cm<sup>-1</sup> and 2345 cm<sup>-1</sup> appeared in the IR spectra of the as-prepared LaCoO<sub>3</sub>(A-750) corresponded to OH stretching and OH bending of water. The absorption band at 1480cm<sup>-1</sup> was corresponded to nitrate ion. In addition, the band at 1096 cm<sup>-1</sup> was corresponded to Co-OH bending which is confirmed with the reported value that MOH bending mode appears below 1200 cm<sup>-1</sup> [Nakamoto 1997]. The absorption band at 583 cm<sup>-1</sup> in figure 5.5 related to Co-O stretching vibration, which was confirmed with the reported value that cobalt-oxygen stretching appears at around 600 cm<sup>-1</sup> [Khalil 2003].



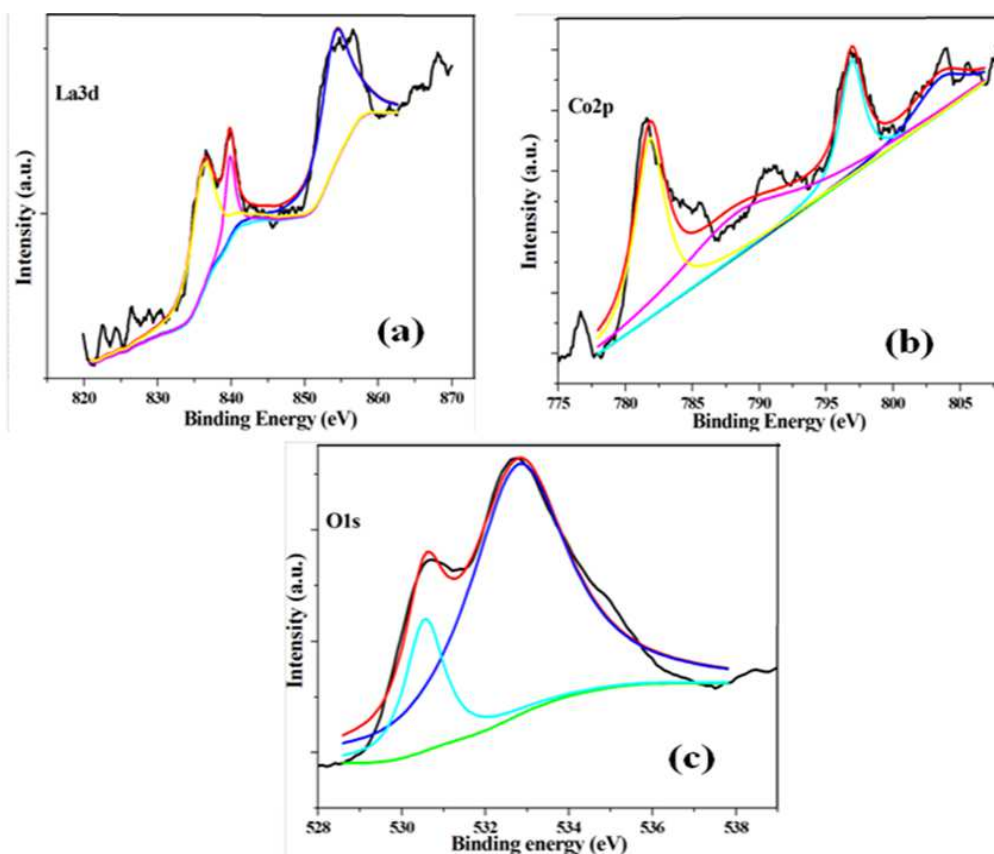
**Figure 5.5** FTIR spectra of the LaCoO<sub>3</sub> (co-ppt) catalyst

### 5.3.4 XPS of LaCoO<sub>3</sub> (Co-ppt) Perovskite

The characteristic spectra collected for La3d, Co2p and O1s in LaCoO<sub>3</sub> perovskite (A-750) are displayed in figure 5.6(a), 5.6(b) and 5.6(c) respectively. On the basis of the binding energies of the Co2p main lines, as shown in figure 5.6(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<sub>2</sub>O<sub>3</sub>, Co<sub>3</sub>O<sub>4</sub> and CoOOH). It is reported that the  $\Delta E$  value of spin-orbit splitting for CoO is 16.0eV, and that of Co<sub>2</sub>O<sub>3</sub> is 15.0eV [Cesar 2000]. For Co<sub>3</sub>O<sub>4</sub> with mixed valence of Co ions, a spin-orbit splitting value of 15.2eV has been reported [Ichimura et al 1980]. Table 5.3 collects all the binding energy and spin-orbit splitting values of Co for the LaCoO<sub>3</sub> perovskite catalyst. The Co 2p XPS spectra of the catalyst consists of two main lines with the spin-orbit splitting ( $\Delta E$ ) falling in the range of Co<sub>3</sub>O<sub>4</sub>, 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 O1s energy spectrum, figure 5.6(c) consists of two peaks, which correspond to two forms of oxygen, i.e. lattice oxygen O<sub>lat</sub> and adsorption oxygen O<sub>ads</sub> on the sample surface. The peak at the binding energy of 527.5-530 eV corresponds to the lattice oxygen species (O<sup>2-</sup>, O<sup>-</sup>), which reflect the redox behaviour of the metal, and the peak at 530-531.5 eV corresponds to the adsorption oxygen species (O<sub>2</sub><sup>-</sup>, O<sub>2</sub><sup>2-</sup>), that is the active centre for the oxidation.



**Figure 5.6** XPS spectra of catalyst A-750

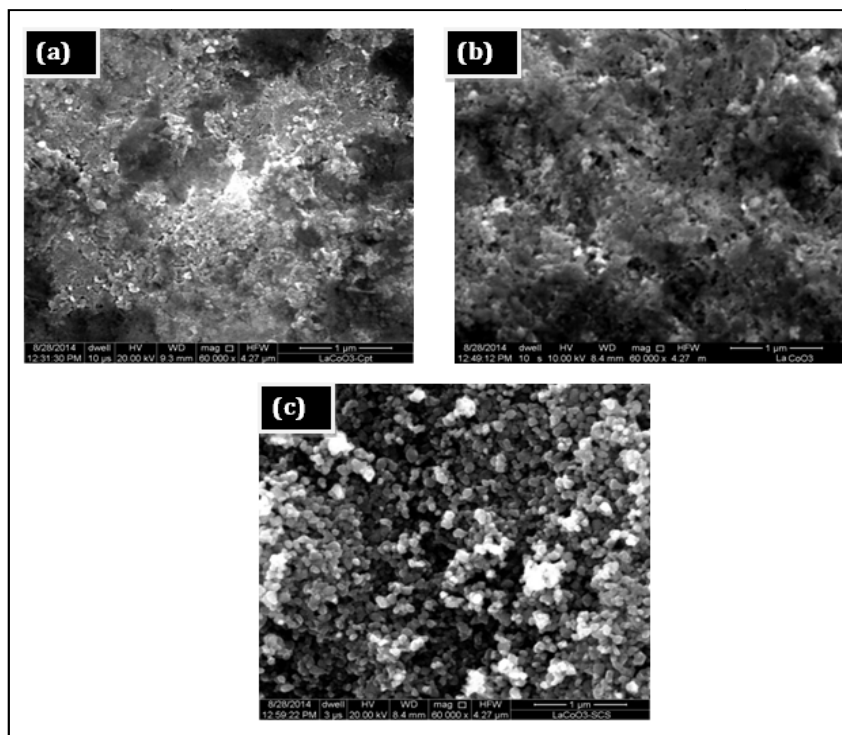
**Table 5.3** Binding energy and spin-orbit splitting values for Co2p and O1s

Catalyst	Co2p			O1s	
	$2p_{3/2}$	$2p_{1/2}$	$\Delta E$	$O_{lat}$	$O_{ad}$
A-750	779.6	794.7	15.1	527.9	530.4

### 5.3.5 SEM of LaCoO<sub>3</sub> Perovskite

The SEM micrographs of LaCoO<sub>3</sub> prepared by different methods and calcined at 750 °C are shown in figure 5.7 which 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 (b) methods appear to be spongy tendrils while agglomerates of granular particles (c) can be

visualized for the sample prepared by SCS method. The particle size of the mixed oxides is small and uniformly distributed for co-ppt and SG methods while for SCS particles are of bigger sizes due to uncontrolled combustion.

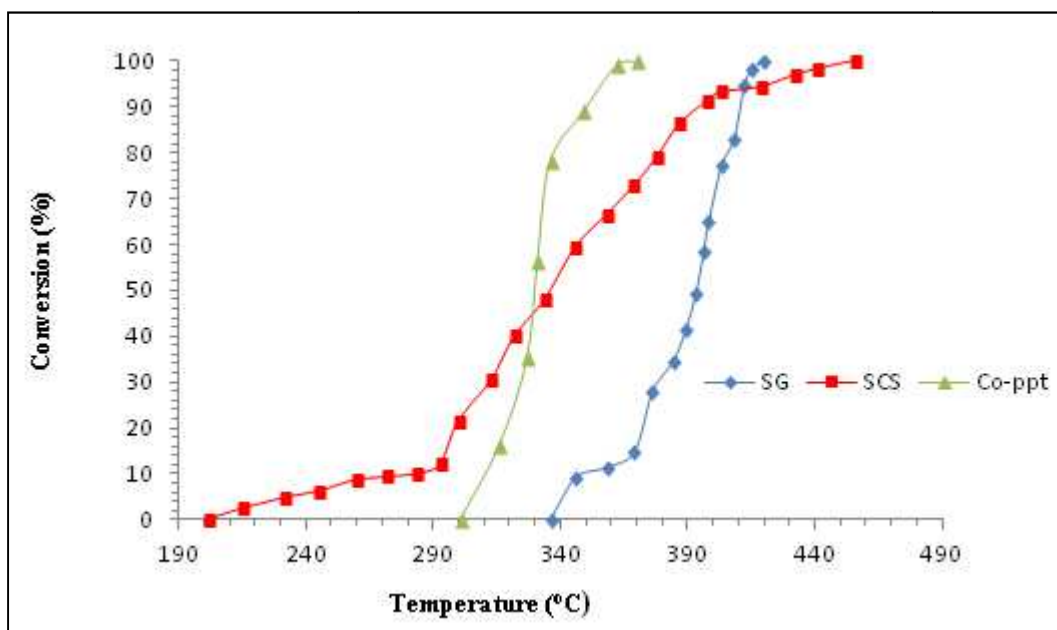


**Figure 5.7** SEM images of  $\text{LaCoO}_3$  prepared by (a) Co-ppt, (b) SG, (c) SCS and calcined at  $750^\circ\text{C}$

### 5.3.6 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 activity of the catalysts for soot oxidation. Figure 5.8 shows the percent conversion of soot over the  $\text{LaCoO}_3$  perovskite prepared by three different methods viz Co-precipitation, Sol-gel and SCS and calcined at  $750^\circ\text{C}$ . The soot was air oxidized over the catalyst under tight contact. Table 5.4 presents the details of the light off characteristics (LOC) of the soot oxidation. From the figure it can be seen that the catalyst produced by co-ppt method resulted completed oxidation of soot at the lowest temperature ( $T_f = 370^\circ\text{C}$ ) than other two catalysts prepared by sol-gel ( $T_f = 420^\circ\text{C}$ ) and

SCS ( $T_f = 456^\circ\text{C}$ ). However, this catalyst initiated soot oxidation at higher temperature ( $T_i = 301^\circ\text{C}$ ) than the catalyst prepared by SCS method ( $T_i = 202^\circ\text{C}$ ) but lower than sol-gel method ( $T_i = 336^\circ\text{C}$ ). The SCS method prepared catalyst initiated soot oxidation at the lowest temperature but soot conversion slowly increased with increasing temperature resulted total oxidation at the highest temperature ( $T_f = 456^\circ\text{C}$ ) than other two catalysts. It is evident from the table 5.4 that the range of temperature ( $T_f - T_i$ ) for total soot oxidation was 69, 84 and  $254^\circ\text{C}$  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  $\text{LaCoO}_3$  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-ppt > SG > SCS.



**Figure 5.8** Effect of preparation method on soot oxidation over  $\text{LaCoO}_3$  calcined at  $750^\circ\text{C}$

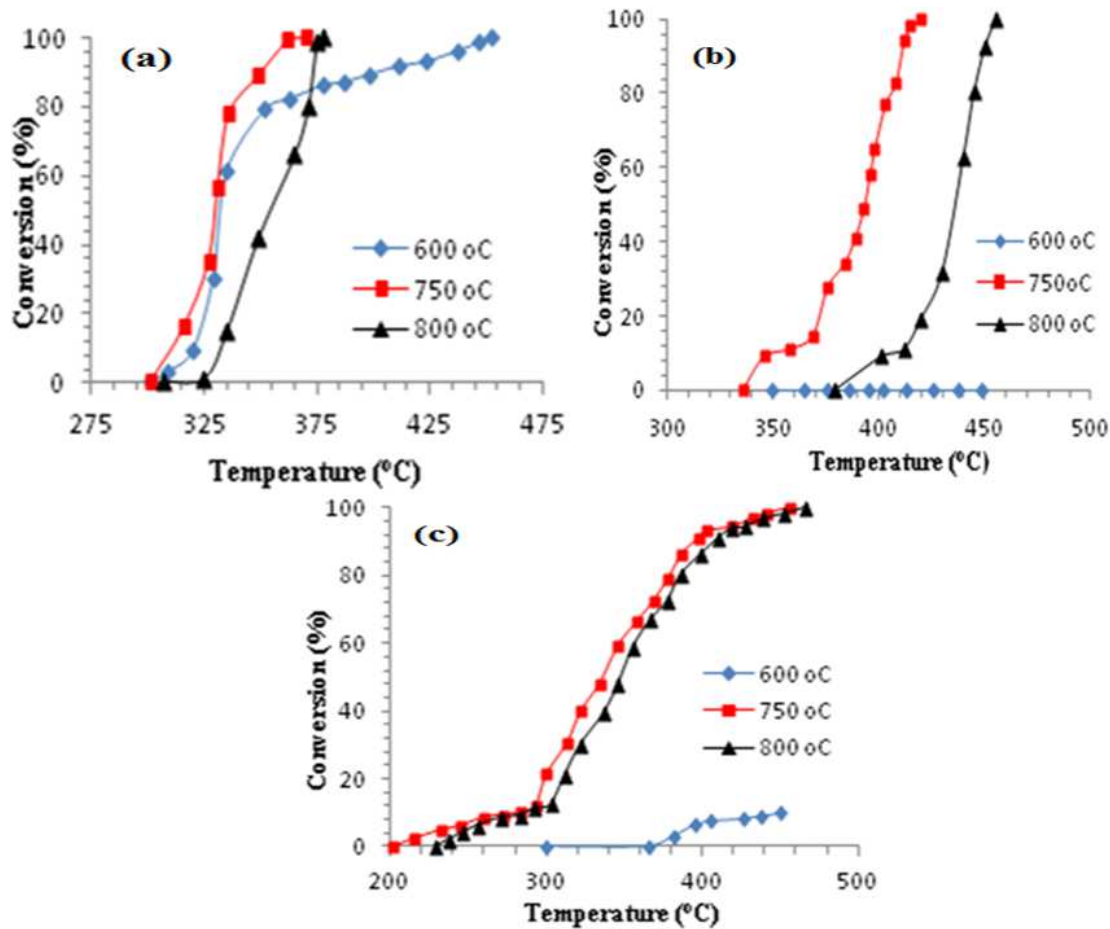


**Table 5.4** Effect of preparation methods and calcinations temperatures for soot oxidation over  $\text{LaCoO}_3$ 

Preparation Method	Calcination temp. ( $^{\circ}\text{C}$ )	$T_i(^{\circ}\text{C})$	$T_{50}(^{\circ}\text{C})$	$T_f(^{\circ}\text{C})$
Sol-gel	600	> 550	-	-
	750	336	389	420
	800	379	420	455
Soln combn syn	600	365	> 550	-
	750	202	422	456
	800	229	435	466
Co-precipitation	600	301	370	452
	750	301	330	370
	800	295	342	378

### 5.3.7 Effect of calcination temperature on the activity of the catalyst for 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 lower calcination temperature relatively smaller sizes are expected [Xiaoping et al. 2008]. An increase in the particle size at high temperature is attributed to the accelerating sintering effect of particles.



**Figure 5.9** Effect of calcination temperature on soot oxidation over LaCoO<sub>3</sub> prepared by (a) Co-ppt (b) SG and (c) SCS method

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 LaCoO<sub>3</sub> perovskite. Figure 5.9 (a), (b) and (c) show the percent conversion of soot over LaCoO<sub>3</sub> perovskite prepared by the Co-ppt, sol-gel and SCS methods respectively and calcined at three different temperatures (600, 750 and 800°C). Co-precipitation method is known for the formation of crystalline perovskite at lower calcination temperature [Angeles et al. 2010, Ha et al. 2010]. XRD results (figure 5.3) showed the formation of perovskite phase even at a lower calcination temperature of 600°C for this method. Figure 5.9(a) shows the percent conversion of soot over LaCoO<sub>3</sub> 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 5.4). It can be seen from the figure 5.9 (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 LaCoO<sub>3</sub> 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 [Yang et al. 1998] and result in the decreasing soot oxidation. Calcining at a lower temperature of 600°C decreased the crystallinity of the perovskite phase which was not favourable for the soot oxidation. Similar observations from figure 5.9(a) and 5.9(c) revealed that the optimum calcination temperature was 750 °C irrespective of the preparation methods. Light off temperature characteristics for soot oxidation over LaCoO<sub>3</sub> calcined at different temperature, as shown in Table 5.4 also suggests 750°C as the optimum calcination temperature for the highest soot conversion efficiency.

### **5.3.8 Thermal Stability of the Catalysts**

Further, experiments were conducted to examine the thermal stability of the catalysts A-750 and B-750 by consecutive soot combustion for five cycles, and the results are

shown in Table 5.5. It is evident from the table that the catalyst B-750 maintained its high catalytic activity for repeated five cycles under the condition of tight contact between catalysts and soot particles. The result indicates that the catalyst prepared by sol gel method (B-750) has good thermal stability than the catalyst prepared by co-ppt method (A-750) which showed the highest activity for soot oxidation. It is well known fact that the high stability with slight less activity catalyst is preferable than the catalyst having very high activity but less stability (section 1.5 catalysts design parameters). So, for further studies sol gel method was chosen for the preparation of catalyst samples.

**Table 5.5** Stability test of catalyst A-750 and B-750 for soot combustion under tight contact

Test Cycle	A-750			B-750		
	T <sub>0</sub> (°C)	T <sub>50</sub> (°C)	T <sub>f</sub> (°C)	T <sub>0</sub> (°C)	T <sub>50</sub> (°C)	T <sub>f</sub> (°C)
1st	301	330	370	336	389	420
2nd	312	346	402	337	390	421
3rd	330	389	446	336	388	421
4th	361	401	476	335	389	419
5th	362	432	502	337	390	420

## 5.4 Conclusions

Perovskite catalysts (LaCoO<sub>3</sub>) are prepared by Co-ppt, sol-gel and SCS and calcined at different temperatures (600, 750, 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 > SG > SCS. Irrespective of the preparation methods, 750°C is the optimum calcination temperature, producing the active catalyst for soot oxidation over LaCoO<sub>3</sub> perovskite. On the basis of comparison made for activity and stability of different catalysts certain conclusions can be drawn. The result

indicates that the catalyst prepared by sol gel method (B-750) has good thermal stability than the catalyst prepared by co-ppt method (A-750) which showed the highest activity for soot oxidation. Since, stability is more important than activity for selection of the catalyst. So, for further studies sol gel method was chosen for the preparation of catalyst samples.