

Low Cost, Ceria Promoted Perovskite Type Catalysts for Diesel Soot Oxidation

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Abstract Perovskite type catalysts with SrCoO_3 and $\text{Sr}_{0.8}\text{Ce}_{0.2}\text{CoO}_3$ compositions have been prepared by co-precipitation and other methods and, their catalytic activity towards diesel particulate matter (PM)/carbon oxidation has been evaluated under the loose contact condition. These catalysts show excellent catalytic activity for PM/carbon oxidation, despite their low surface area and under the loose contact condition. The synergistic effects of Ce incorporation in perovskite and presence of a small amount of potassium appears to be responsible for the high soot oxidation activity of these perovskite type materials. The Ce incorporation seems to be contributing by enhancing the redox property of the catalyst, while it appears unlikely that potassium is contributing by improving the catalyst–soot contact through its volatilization. The catalysts show excellent thermal stability and stable activity under repeated cycles of use.

Keywords Soot oxidation · Perovskite · Diesel emissions · DPF

1 Introduction

Diesel engines are becoming more popular over gasoline engines, due to the better fuel efficiency, low operating cost and high durability. The major pollutants emitted from diesel engines are particulate matter (PM) and NO_x . PM is a potential carcinogen and its effective control is an important target from an environmental point of view. The most promising approach to reduce the particulate matter (PM) from diesel vehicles is after-exhaust treatment i.e. particulate capture using Diesel Particulate Filter (DPF) or other similar devices [1]. However, effective regeneration of DPF is the challenge for its practical feasibility. Catalytic regeneration has already been suggested as the best approach and intensive efforts are being made to develop suitable catalysts. The regeneration catalysts should possess excellent catalytic activity at low temperature with high thermal and chemical stability [2–6]. Perovskite type oxides are good oxidation catalysts and show potential as effective PM oxidation catalyst for the DPF regeneration as well as for the oxidation of Soluble Organic Fraction (SOF). Perovskites are binary oxides with general formula ABO_3 . Availability of a large number of cations, which can fit at both A and B positions, offer perovskite structure a versatile flexibility in their chemical composition. Their structure and properties can also be modified due to the great extent of substitution possible at both A and B sites. The oxygen adsorption and desorption properties of perovskites can play a crucial role for low temperature oxidation of soot/particulate matter. Two types of oxygen viz; α and β desorbs from the perovskite, which is said to be responsible for oxidation reactions at lower and higher temperature respectively. When molecular oxygen adsorbs on the catalytic surface of perovskite, it is accommodated in the O^{2-} vacancies formed by the partial

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substitution of A-site cations by lower valence ions. Such alpha type weakly chemisorbed oxygen, “suprafacial” species are supposed to be responsible for soot oxidation. The catalytically active ‘B’ site cation is mainly responsible for perovskite’s catalytic activity, while its oxidation state and catalytic properties can also be tailored by substitutions at ‘A’ site, signifying the roles of both ‘A’ and ‘B’ site cations. A number of perovskite type and other mixed oxide based catalytic materials have been reported for their activity towards diesel soot emission control [7–10]. Strontium cobaltate, having a wide range of oxygen stoichiometry due to the different oxidation state of cobalt (Co^{2+} , Co^{3+} and Co^{4+}) can exist in several crystalline polymorphs depending on temperature, oxygen partial pressure, and the method of thermal treatment, and is expected to show interesting catalytic properties [11–16]. Promotional effect of alkali metal ions, specially potassium is also frequently reported with several perovskite compositions [17–22]. It is usually claimed that potassium improves the catalyst:soot contact through its volatilization, which is responsible for its promotional effect for catalytic soot oxidation [21].

In this work, we have synthesized SrCoO_3 and $\text{Sr}_{0.8}\text{Ce}_{0.2}\text{CoO}_3$ perovskite type catalysts. Their catalytic activity for carbon/soot oxidation has been studied for their possible application in DPF regeneration. Based on the experimental work reported here, some conclusions are then drawn concerning the role of various constituents of such catalysts, and probable reaction mechanisms.

2 Experimental

Co-precipitation method was used to synthesize SrCoO_3 type perovskite catalysts. Nitrate salts of strontium and cobalt (E-Merck) were mixed together and stirred for 15 min with heating. About 300 mL of 0.5 N KOH solution and 1 M ammonium carbonate were then slowly added to the above metal solutions at a rate of 50 mL/min with a stirring of 100 rpm. The precipitate thus obtained was allowed to settle overnight followed by filtration with thorough washings with de-ionized water. The precipitate cake was kept in an oven at 80 °C for drying and the resultant mass was then calcined at 650 °C for 4 h followed by grinding and further calcination at 950 °C for 8 h.

Co-precipitation method was used also to synthesize $\text{Sr}_{0.8}\text{Ce}_{0.2}\text{CoO}_3$ type perovskite catalysts. Nitrate salts of strontium, cerium and cobalt (E-Merck) were mixed together and followed by precipitation, washing, drying, grinding and heating following the same protocol as used for SrCoO_3 . XRD patterns were recorded on a Rigaku Rint-220HF diffractometer, operated at 40 kV and 50 mA with

a monochromator and using Cu-K α radiation ($\lambda = 0.15418$ nm). Indexing of XRD peaks was done, by using the JCPDS cards for the respective phases. Surface area was measured by nitrogen adsorption using the automatic gas adsorption apparatus BELSORP 28SA (produced by Nippon Bell Co., Japan) and evaluated by BET method. The samples were pre-treated at 300 °C before the nitrogen adsorption experiments. The SEM investigations were carried out by HITACHI S-5000 instrument using 10.0 kV acceleration voltage and 30,000 \times magnification.

Temperature-programmed desorption (TPD) analysis was performed in a thermoquest TPD/R/O 1100 analyzer, equipped with a thermal conductivity (TCD) detector. A fixed bed of catalyst was placed in a quartz tube and sandwiched between two quartz-wool layers; prior to each temperature-programmed oxygen desorption (TPD) run, the catalyst was heated under O_2 flow (40 mL/min) up to 750 °C. After 30 min of isothermal heating at this temperature as a common pre-treatment, the temperature was lowered down to 25 °C under the same flow rate of oxygen, thereby achieving complete saturation. Afterwards, helium was fed to the reactor at 10-mL/min-flow rate and kept flowing for 1 h at room temperature in order to purge out any excess oxygen. The catalyst was then heated up to 1,000 °C at the constant heating rate of 10 °C/min under the same helium flow rate. The total amount of O_2 desorbed during the heating protocol was detected by the TCD detector after proper calibration.

The catalytic evaluation for the combustion/oxidation of carbon black has been studied by thermogravimetry (TG), using a Rigaku-TAS-200 apparatus. Commercially available carbon black was used as model soot (Degussa S.A. Printex-U). For oxidizing carbon black, the mixture of carbon black and catalysts was heated at 5 °C/min from 50–800 °C in air atmospheric. The catalyst:carbon black weight ratio used was 95:5 as well as 66:34 to study the effect of catalyst to carbon ratio. Experiments have been performed in loose contact conditions, i.e., by physically mixing catalyst and carbon black and subsequent homogenization using a spatula. This sample preparation represents more realistic conditions, as the catalyst–carbon contact is relatively poor. The blank experiments were also performed with only catalyst samples to account for any weight loss, due to water desorption. Some of the experiments were also performed using steady state laboratory gas evaluation assembly, which show quite similar results. The catalytic materials were examined for any effect on their structure after using for 24 h continuously. This was done through X-ray diffraction and BET surface area studies on used catalyst samples and also re-evaluating their catalytic activity. To study the affectivity of this catalyst on actual diesel soot, a TG experiment was also performed using the diesel soot collected from the exhaust

pipe of a diesel car. This collection method rather provides the soot with inferior combustivity, as the volatile hydrocarbons are usually not present in the dried soot collected from the tail pipe of a diesel vehicle.

The SrCoO_3 and $\text{Sr}_{0.8}\text{Ce}_{0.2}\text{CoO}_3$ type perovskite catalysts were also studied for their thermal stability. The TG isothermal study has been carried out for 12 h at 900 °C under air atmosphere. The sustainability of the catalytic activity and probable thermal loss of potassium was investigated by using the catalyst for repeated cycles and comparing the catalytic activity of used catalyst with that of fresh one.

3 Results and Discussion

The ICP-AES analysis results of catalysts confirm their targeted chemical composition and stoichiometry. XRD pattern of the sample calcined at 950 °C (Fig. 1) confirms

the formation of crystalline SrCoO_3 phase with perovskite structure and absence of possible impurity phases like SrCO_3 , and Co_3O_4 . The X-ray diffraction analysis and structural investigations thus confirm that SrCoO_3 can be easily synthesized with good purity and crystallinity by using precipitation method. Ce incorporation in perovskite lattice has been attempted by substituting the same at 'A' position. Figure 2 shows the XRD patterns of $\text{Sr}_{0.8}\text{Ce}_{0.2}\text{CoO}_3$ type perovskite catalyst with a prominent peak of CeO_2 , whose intensity increases with increasing Ce content. This infers that only a small amount of Ce could be incorporated in perovskite phase in the present synthesis and that the catalyst formed could be treated as a homogeneous mixture of perovskite and ceria phases, especially at higher ceria contents.

The BET-surface area for SrCoO_3 and $\text{Sr}_{0.8}\text{Ce}_{0.2}\text{CoO}_3$ catalyst are 3.1 and 2.93 m^2/gm respectively, which is in expected range considering the high synthesis temperature. The SEM micrographs (Fig. 3) show that the powders

Fig. 1 X-ray powder diffraction pattern for SrCoO_3 (JCPDS card no. 48-0875)

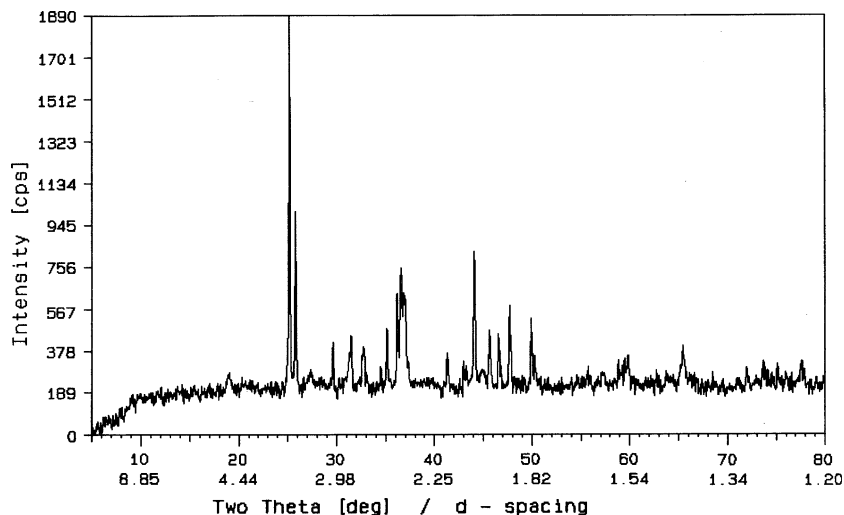


Fig. 2 X-ray powder diffraction pattern for $\text{Sr}_{0.8}\text{Ce}_{0.2}\text{CoO}_3$

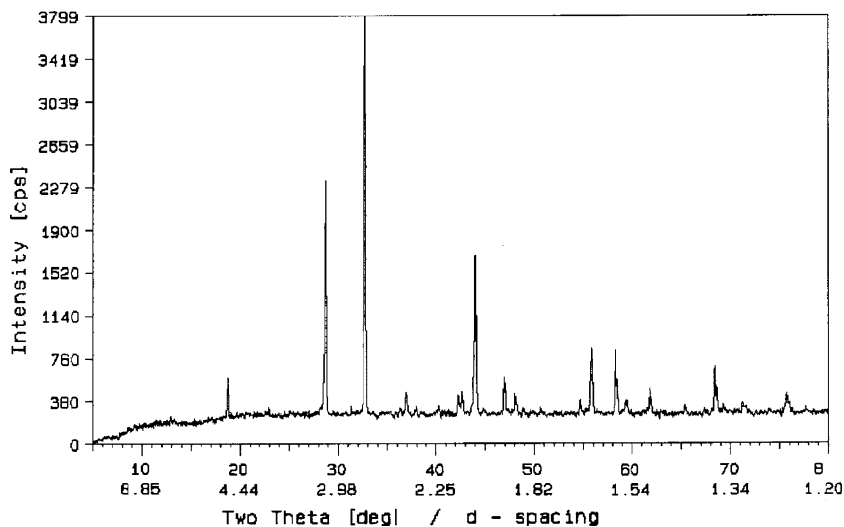
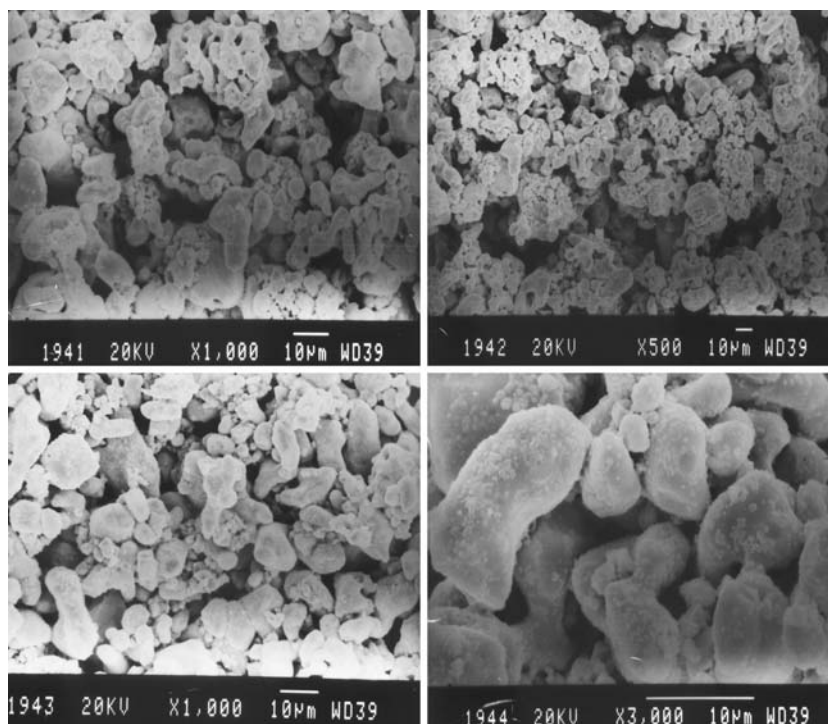


Fig. 3 SEM photograph of $\text{Sr}_{0.8}\text{Ce}_{0.2}\text{CoO}_3$ perovskite catalyst



obtained by co-precipitation method contain at least two different particles, which are big agglomerates and small particles, typical of CeO_2 . SEM studies show the presence of ceria particles in intimate contact with perovskite crystals. The thermal stability (24 h aging) results as well as repeated evaluations of the used catalyst do not show any significant effect on structure, morphology and even catalytic activity. It can be therefore, concluded that the present perovskite type catalytic materials are thermally stable under the oxidative conditions and their thermal stability should be good enough for their possible application in DPF regeneration.

Diesel particulate (soot) is normally composed of carbon core associated with hydrocarbons (SOF), which includes polyaromatic hydrocarbons (PAH) and nitro-PAH, sulphates, water, trace amounts of zinc, phosphorus, calcium, iron, silicon, and chromium [23]. The non-catalytic combustion temperature of soot depends on the contents of adsorbed hydrocarbons, and experimental conditions, but generally exceeds 550 °C. Moreover, the composition of diesel particulate is affected by several engine operation parameters. Thus, it is difficult to collect batches of soot with constant properties and therefore, the model soot is often used. The model soot used in this study is a carbon black from Degussa S.A. (Printex-U) with following physicochemical properties: fraction of adsorbed hydrocarbons (5.2%), ash (<0.1%), C (92.2%), H (0.6%), N (0.2%) and S (0.4%) and shows relatively poor combustibility than natural diesel soot.

Table 1 shows the carbon oxidation evaluation (TG) results in which, the catalyst:carbon black weight ratio used was 95:5. This table gives temperature values T_i (start of the carbon combustion) and T_f (complete combustion of carbon). Catalytic activity of various catalysts was evaluated by comparing these values with and without catalysts under the same experimental conditions. As mentioned before, the experiments were performed under loose contact conditions as described by van Setten et al. [24]. Loose contact offers more realistic conditions as compared to that of tight contact and therefore, has been used in the present study.

There is a considerable difference observed between non-catalyzed reaction of carbon and oxygen as compared to the catalyzed reaction. The non-catalyzed carbon oxidation starts above 400 °C, and maximum activity was observed at about 560 °C with a sharp weight loss due to

Table 1 Carbon oxidation results for using TG technique

Material/catalyst	$T_{\text{(Initial)}}$ (°C)	T_{50} (°C)	$T_{\text{(Final)}}$ (°C)
Carbon (Printex U) bare	400	550	620
SrCoO_3	300	460	520
$\text{Sr}_{0.8}\text{Ce}_{0.2}\text{CoO}_3$	241	420	500

T_i (°C)—Beginning of the carbon combustion

$T_{50\%}$ (°C)—50% combustion of carbon

T_f (°C)—Complete combustion of carbon

Catalyst:carbon ratio used 95:05

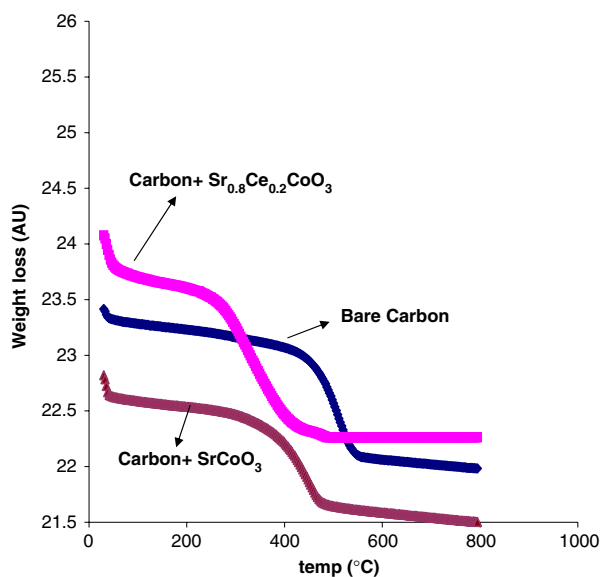


Fig. 4 TG curves showing the weight loss due to carbon oxidation for a mixture of 5% carbon black + 95% catalyst

carbon oxidation to CO_2 . The SrCoO_3 (Fig. 4) catalyst appears to get activated after 250 °C, however, significant oxidation of the carbon is observed beyond 300 °C only. The peak oxidation temperature corresponding to maximum activity is around 460 °C. The exothermic carbon oxidation reaction is expected to propagate the reaction rate after it achieves significant activity. This could be considered as good catalytic activity, in view of the very low surface area of the catalyst used. There was practically no CO generation, which is sometimes present as a product of incomplete combustion. Figure 4 also shows the catalytic activity of $\text{Sr}_{0.8}\text{Ce}_{0.2}\text{CoO}_3$ catalyst, which appears to get activated immediately after 206 °C; and, significant oxidation of the carbon material is started at 241 °C. The T_{50}

was observed around 420 °C. The introduction of Ce in the perovskite seems to improve the catalytic activity significantly. Ce substitution can improve the redox capacity of perovskite while in addition, it may also act as a stabilizer of O^{2-} ions at the catalyst surface [25]. The catalytic activity of the perovskites is found to decrease beyond $\text{Ce} = 0.2$, and it is attributed to the formation of a separate, relatively less active CeO_2 phase. The promotional effect of K present as an impurity cannot be ruled out as the catalysts prepared using other precipitants shows relatively lower catalytic activity. This improved catalytic activity is quite comparable with other catalysts reported by our group and others [26–28]. There was practically no CO generation, showing high CO_2 selectivity of the catalysts. In this way, the Ce incorporated SrCoO_3 shows excellent soot oxidation properties and positive effect of Ce incorporation.

Table 2 shows the carbon oxidation evaluation (TG) results for $\text{Sr}_{0.8}\text{Ce}_{0.2}\text{CoO}_3$ catalyst under the different catalyst:carbon weight ratios. Catalytic activity was compared for the catalyst:carbon black weight ratio of 95:5 and 66:34, under the same experimental conditions. These results show some increase in the T_{initial} with lower catalyst ratio, however, no significant effect was observed with the change in catalyst:carbon ratio. Figures 5 and 6 present the TG results for non-catalyzed and catalyzed diesel soot

Table 2 Carbon oxidation results for $\text{Sr}_{0.8}\text{Ce}_{0.2}\text{CoO}_3$ using different catalyst–carbon ratios

S.No.	Catalyst/Carbon ratio	T_{initial} (°C)	$T_{50\%}$ (°C)	T_{final} (°C)
1	95:5	241	420	500
2	66:33	267	442	510

Fig. 5 Thermo gravimetric analysis (TG) of bare diesel soot

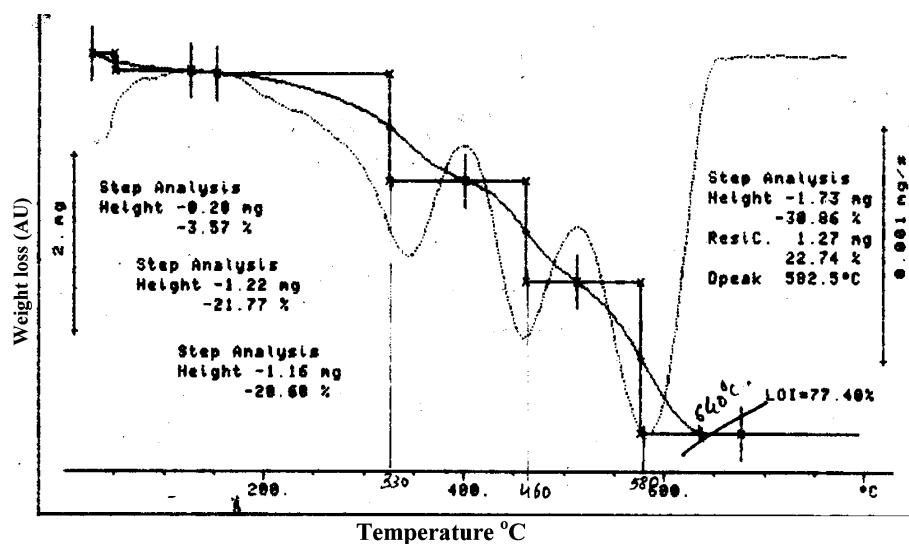
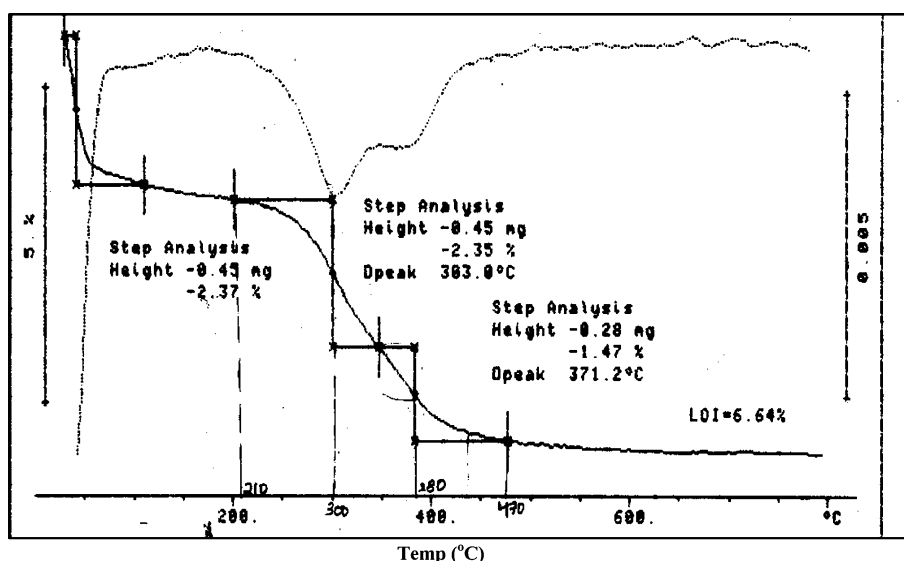


Fig. 6 Thermogravimetric analysis (TG) result of $\text{Sr}_{0.8}\text{Ce}_{0.2}\text{CoO}_3$ + diesel Soot



respectively, using the $\text{Sr}_{0.8}\text{Ce}_{0.2}\text{CoO}_3$ catalyst. In diesel soot oxidation, catalyst plays a synergistic role wherein it catalyses oxidation of hydrocarbons that constituents of soluble organic fraction (SOF) adsorbed on the soot. The reaction being exothermic in nature generates heat that assists the catalytic oxidation of the soot. Therefore the results show excellent catalytic activity even for the same experimental conditions. This validate the activity of present catalyst even for the natural diesel soot.

Figure 7 shows the results for oxygen TPD experiments. The released oxygen species can be divided into two categories depending on temperature [29]. It has been reported that when a perovskite is heated at higher temperature, oxygen vacancies can be formed. $\text{Sr}_{0.8}\text{Ce}_{0.2}\text{CoO}_3$ catalyst evolves following oxygen species: *Alpha Oxygen*: this weakly chemisorbed suprafacial oxygen species is desorbed in a temperature range of 300–600 °C for the present catalyst (Fig. 5) and is related to surface oxygen vacancies.

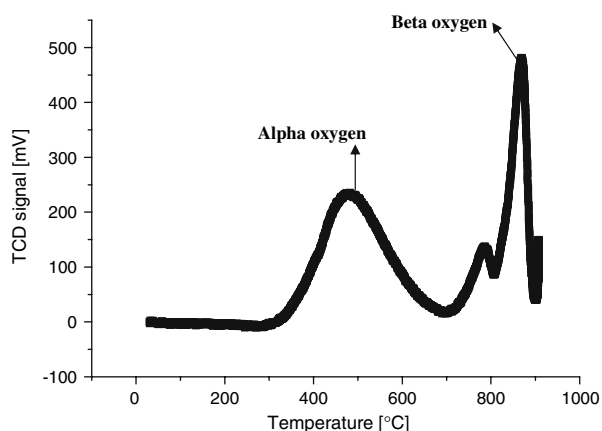


Fig. 7 Temperature programmed desorption (TPD) curve for $\text{Sr}_{0.8}\text{Ce}_{0.2}\text{CoO}_3$ perovskite catalyst

Alpha oxygen can be correlated to the superior activity of this catalyst for diesel soot oxidation. *Beta Oxygen*: It is related to the bulk oxygen of the perovskite, and strongly bound to the perovskite lattice. It desorbs above 700 °C for the present catalyst. This oxygen release is generally not correlated to soot oxidation activity due to its high temperature desorption. The oxidation mechanism of alpha species is generally referred as “suprafacial” because it is connected with the presence of anionic vacancies on the perovskite surface and the mechanism of beta species is referred as “intrafacial” because of its presence as lattice species in layers near to surface. It has been already reported that the non-stoichiometric materials can easily release oxygen and become more active than the stoichiometric [30].

Various mechanisms have been proposed for the catalytic soot oxidation by molecular oxygen. It is difficult to consider the good catalyst–soot interaction under the loose contact conditions, and also due to the fact that both soot and catalysts are in solid phase. We therefore, presume that dissociative adsorption of molecular oxygen on catalyst surface followed by its reaction with the solid soot/carbon can be more acceptable under the practical conditions. The incorporation of higher valence Ce on ‘A’ site can change the oxidation state of Co present at the ‘B’ position, thereby improving the redox properties of catalyst [31–33]. Further, the soot oxidation should involve intermediates and their decomposition can be the rate-determining step. These carbon intermediates are known as “surface oxygen complexes” (SOC’s) [34]. Hong et al. proposed a mechanism based on dissociative adsorption of oxygen for soot-oxygen reaction from their kinetic analysis of the reaction [35]. As per this mechanism by Hong et al., gaseous oxygen is dissociatively adsorbed on the surface of perovskite catalysts, and the resulting atomic O_{ads} species then attack

the reactive free carbon site, C_f to give an oxygen-containing active intermediate, $C^*[O]$. The reaction between $C^*[O]$ intermediate and either O_{ads} (preferably) or gaseous O_2 produces CO_2 through reaction or, reproducing the reaction C_f sites on the soot surface. It is natural that the removal of one carbon atom from the soot surface leaves more, probably two or three reactive surface carbon sites as described under this mechanism.

4 Conclusion

The present study has highlighted the effect of Ce substitution on the catalytic activity of $Sr_{0.8}Ce_{0.2}CoO_3$ type catalyst for particulate matter/carbon oxidation reaction. Small substitution of strontium by cerium, creating a perovskite with improved redox properties, resulted in improved catalytic activity. The promotional effects of ceria incorporation in $SrCoO_3$ and presence of a small amount of potassium appears to be responsible for the high soot oxidation activity of this perovskite type material. The higher activity of the substituted perovskite can therefore be a combined effect of improved redox properties, stability of active oxygen (alpha oxygen) species on catalyst surface as well as promotional effect of potassium impurity. Potassium may be adding to the basicity of the catalyst and it appears unlikely that the promotional effect of potassium is due to its volatility, which can improve the soot–catalyst contact. These low cost, non-noble metal-based catalysts also show excellent thermal stability which also infer the stability of potassium in perovskite structure. We are working on synthesis on nano-perovskites directly on DPF, which offer the excellent catalyst–soot contact, an important parameter for the soot oxidation catalysis and regeneration of DPF. The catalytic activity in absence of NO_x is the most interesting properties of such materials, which offers them an edge over the soot- NO_x catalysts. As the sulfur content of diesel is set to lower in the coming year, the chemical stability of perovskites will also not be a limitation. These catalysts can be synthesized directly on commercially available cordierite or SiC based diesel particulate filters (DPF). Suitability of perovskite type catalysts for flow-through type DPF and their improved stability with low sulfur diesel add to their potential for their application in regeneration of DPF.

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