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Co_3O_4–CeO_2 mixed oxide-based catalytic materials for diesel soot oxidation

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Abstract

Co_3O_4–CeO_2 type mixed oxide catalyst compositions have been prepared by using co-precipitation method and, their catalytic activity towards diesel particulate matter (PM)/carbon oxidation has been evaluated under both loose and tight contact conditions. These catalysts show excellent catalytic activity for PM/carbon oxidation, despite their low surface area. The activation energy observed for non-catalyzed and catalyzed reactions are 163 kJ/mol and 140 kJ/mol, respectively, which also confirm the catalytic activity of catalyst for carbon/soot oxidation. The promotional effects of an optimum amount of cobalt oxide incorporation in ceria and presence of a small amount of potassium appears to be responsible for the excellent soot oxidation activity of this mixed oxide type material. The catalytic materials show good thermal stability, while their low cost will also add to their potential for practical applications.

Keywords: Soot oxidation; Diesel particulate filter; Co_3O_4–CeO_2 type mixed oxide; Catalyst

1. Introduction

Diesel particulate matter (or soot) emitted from diesel engines cause serious problem to human health and environment. Diesel particulate filter (DPF) has so far been the most effective option to control the particulate matter emission, however, low temperature regeneration of DPF is the key limitation for its techno-economic feasibility. Catalytic regeneration is the most desired option to make the DPF technology practically feasible and intensive efforts are being made worldwide towards development of catalytic materials for this application. The catalytic oxidation of diesel particulate may involve activation of carbon atoms within the particulate, exothermic oxidation of hydrocarbons adsorbed on the particulate leading to complete soot oxidation or the catalyst acting as a source of active oxygen, which can be used for the soot oxidation. Many catalysts have been studied for DPF regeneration at the exhaust temperature range of 200–500 °C. Platinum is very widely used catalyst for many catalytic reactions due to its very good oxidation activity but shows moderate activity for the direct soot oxidation, apart from its higher cost [1,2]. Various other catalysts including transition metal oxides based catalysts [3–10] have also been studied and demonstrated for diesel soot oxidation. Rare earth metal oxides based catalytic materials [11–16] have also been widely studied. Many of these catalysts also exhibit the promotional role of alkali or alkaline–earth metal and found that potassium is specially a good soot oxidation promoter for various catalytic systems [17,5]. Some catalysts can oxidize soot particulate by catalyzing the formation of a mobile oxidant; by providing redox sites for the oxidation or by dissociating O_2 and transferring the resulting active O_{ads} to the soot particle in a spillover type mechanism. It has been reported that CeO_2 in combination of other catalysts/metals has the potential to increase the oxidation rate of soot, because of the creation of active oxygen [18]. The promotional activity of CeO_2 has also been attributed to its oxygen storage capacity. In this way, CeO_2 incorporation is likely to improve the redox

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capacity of catalyst, while in addition, it may also act as a stabilizer of O^{2-}, ions at the catalyst surface [19]. In this study, Co_3O_4–CeO_2 based catalytic materials have been prepared and evaluated for their catalytic activity towards the carbon/soot oxidation reaction.

2. Experimental

Co-precipitation method was used to synthesize Co_3O_4–CeO_2 type mixed oxide catalyst compositions. Acetate salts of cerium and cobalt (E-Merck/AR Grade) were used to prepare mixed metal solution in water by mixing together and stirring for 15 min with heating. KOH solution was then slowly added to the above mixed metal solution at a rate of 100 ml/min with stirring of 100 rpm. The precipitate thus obtained was allowed to settle for 6 h followed by filtration and repeated washings with de-ionized water. The precipitate cake was then kept in an oven at 120 °C for drying and the resultant mass was then calcined at 450 °C for 5 h followed by grinding and further calcination at 800 °C for 8 h. The final product thus obtained was ground and homogenized.

2.1. Characterization

XRD patterns were recorded on a Rigaku Rint-220HF diffractometer, operated at 40 kV and 50 mA with a monochromator and using Cu Kα radiation (λ = 0.15418 nm). Indexing of XRD peaks was done, by using the JCPDS database for the respective phases. Surface area was measured by nitrogen adsorption using the automatic gas adsorption apparatus BELSORP 28SA (produced by Nippon Bell Co.) and evaluated by BET method. The samples were pretreated at 300 °C before the nitrogen adsorption experiments. Elemental analysis of the catalytic materials was carried out using Perkin-Elmer ICP-OES 4100 BV instrument to assess the content of cobalt and cerium present. The SEM investigations were carried out by HITACHI S-5000 instrument using 10.0 kV acceleration voltage and 30,000× magnification.

2.2. Catalytic activity test

The catalytic materials were evaluated for their carbon/soot oxidation activity following a batch type temperature programmed reaction (TPR) procedure as well as TG technique. Carbon black and activated carbon were used as carbon sources, respectively. The catalyst and carbon (ca.5 wt%) were mixed thoroughly by grinding in a mortar and pestle. The carbon-catalyst mixture was then palletized, crushed and sieved to 20–100 mesh. Use of carbon black and this mixing procedure gives better reproducibility for catalyst screening. The carbon black has comparatively much inferior combustivity than the actual diesel soot, which contains considerable amount of adsorbed hydrocarbons. The mixture was packed in a fixed bed flow reactor with a programmable heater controller. A gas mixture containing 15% oxygen was flown with the increasing temperature. The outlet gas was analyzed for CO_2 and CO by a TCD based gas chromatograph. The used catalyst samples were further subjected to post-mortem analysis using XRD, chemical analysis, BET-SA characterization tools to investigate any possible impact on their physical and chemical characteristics.

The catalytic evaluation for the combustion/oxidation of activated carbon has been studied by thermogravimetry (TG), using a Rigaku-TAS-200 apparatus. Commercially available activated carbon was used as model soot. For oxidizing activated carbon, the mixture of activated carbon and catalysts was heated at 5 °C/min from 50 to 800 °C in air atmospheric. The catalyst: activated carbon weight ratio used was 95:5. 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.

The activation energy estimations have been done following Ozawa method by proper interpretation of thermogravimetric analysis (TG) data. According to the Ozawa Method, the following relationship links the values of the heating rate with the corresponding values of temperature (T_α) at which a fixed fraction α of carbon is oxidized during each run.

Table 1
XRD peaks of 20 mol% Co_3O_4–CeO_2 synthesized by co-precipitation methods

Pos. (2°θ)	Height (cts)	FWHM (2°θ)	d-Spacing (A)	Rel. int. (%)
14.8919	658.52	0.0669	6.90753	3.51
15.2623	2324.86	0.1840	6.74085	12.39
22.1408	223.54	0.1004	4.66189	1.19
23.6462	159.05	0.1004	4.36893	0.85
30.0059	361.14	0.1004	3.45794	1.93
30.8468	612.47	0.3011	3.36588	3.27
33.2809	18758.37	0.1020	3.12365	100.00
33.3675	10433.92	0.0408	3.12255	55.62
34.6109	206.53	0.1632	3.00709	1.10
36.5183	396.61	0.2040	2.85497	2.11
37.5074	610.89	0.0612	2.78228	3.26
37.7301	553.07	0.0816	2.76645	2.95
38.0777	752.73	0.0612	2.74212	4.01
38.6171	5927.13	0.0816	2.70525	31.60
38.7161	3099.86	0.0408	2.70447	16.53
43.0682	1263.47	0.1224	2.43698	6.74
44.1405	131.61	0.2856	2.38063	0.70
45.1196	165.50	0.2448	2.33158	0.88
45.7018	201.29	0.2040	2.30344	1.07
48.4219	107.18	0.2448	2.18120	0.57
50.5322	244.28	0.2448	2.09573	1.30
52.5558	284.34	0.2040	2.02045	1.52
55.7514	9703.31	0.0816	1.91316	51.73
55.8857	5286.13	0.0816	1.91308	28.18
61.0387	118.68	0.6528	1.76143	0.63
66.4924	7382.39	0.1020	1.63160	39.36
66.6585	3924.60	0.0816	1.63154	20.92
69.8642	1399.49	0.0816	1.56217	7.46
70.0368	727.35	0.0816	1.56220	3.88
77.4994	347.80	0.2040	1.42911	1.85
80.3338	163.31	0.4080	1.38679	0.87
82.7758	1505.22	0.0816	1.35295	8.02
83.0092	623.71	0.1020	1.35276	3.32

$\ln \phi = B - 1.052\{E_\alpha/(RT_\alpha)\}$, where B is a constant lumping α dependant terms E_α is activation energy (kJ mol^{-1}) and R is ideal gas constant (8.314 J/(mol/K)) [20].

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 provides the soot with inferior combustivity, as the volatile hydrocarbons are usually not present in the dried soot.

3. Results and discussion

The detailed characterization and catalytic evaluation studies have been carried out on catalyst with 20 mol% Co_3O_4–CeO_2 and prepared by using the co-precipitation method, as this catalyst showed the best catalytic activity during the screening experiments. Table 1 shows XRD results for 20 mol% Co_3O_4–CeO_2 which, confirm the presence of Co_3O_4 and CeO_2 phases corresponding to JCPDS card numbers 00-042-1467 and 00-034-0394, respectively. Some additional peaks were observed in the XRD pattern (Fig. 1) of this material.

Figs. 2 and 3 show the scanning electron micrograph (SEM) and EDX/chemical mapping of this material, which infers the formation of CeO_2 and Co_3O_4 in very close contact. The ICP-AES analysis results of catalysts also confirm their targeted stoichiometry. The BET-surface area results of these materials are shown in Table 2, which is in expected range considering the high synthesis temperature. The thermal stability and 24 h aging results do not show any significant effect on structure, morphology and even catalytic activity of these materials. It can be therefore, concluded that Co_3O_4–CeO_2 type mixed oxide materials are thermally stable under the oxidative conditions.

Table 2
BET surface area (m^2/g) for various catalytic materials

Catalyst	Synthesis method	BET-SA (m^2/g)
Bare CeO_2	–	85
Bare Co_3O_4	–	3.41
5% Co_3O_4–CeO_2	Co-precipitation	5.6
10% Co_3O_4–CeO_2	Co-precipitation	4.67
20% Co_3O_4–CeO_2	Co-precipitation	4.01
40% Co_3O_4–CeO_2	Co-precipitation	3.2

The non-catalytic combustion temperature of soot depends on 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 (carbon) is often used. Our detailed studies confirmed relatively much inferior combustivity of carbon as compared to the natural diesel soot, which may be due to the absence of hydrocarbons usually adsorbed on diesel soot particles. Table 3 shows the catalyst evaluation (TG) results for bare activated carbon and that with 20% catalyst. This gives temperature values T_i (start of the carbon combustion) and T_f (complete combustion of carbon), while value $\partial T = T_i - T_f$ determines the reaction velocity. Catalytic activity of various catalysts was evaluated by comparing these values with and without catalysts under the same experimental conditions. There is considerable difference observed between non-catalyzed reaction of carbon and oxygen as compared to the catalyzed reaction. The TG results (Table 3) show start of non-catalyzed carbon oxidation above 400 °C, and maximum activity at about 560 °C. The 20 mol% Co_3O_4–CeO_2 type mixed oxide catalyst appears to get

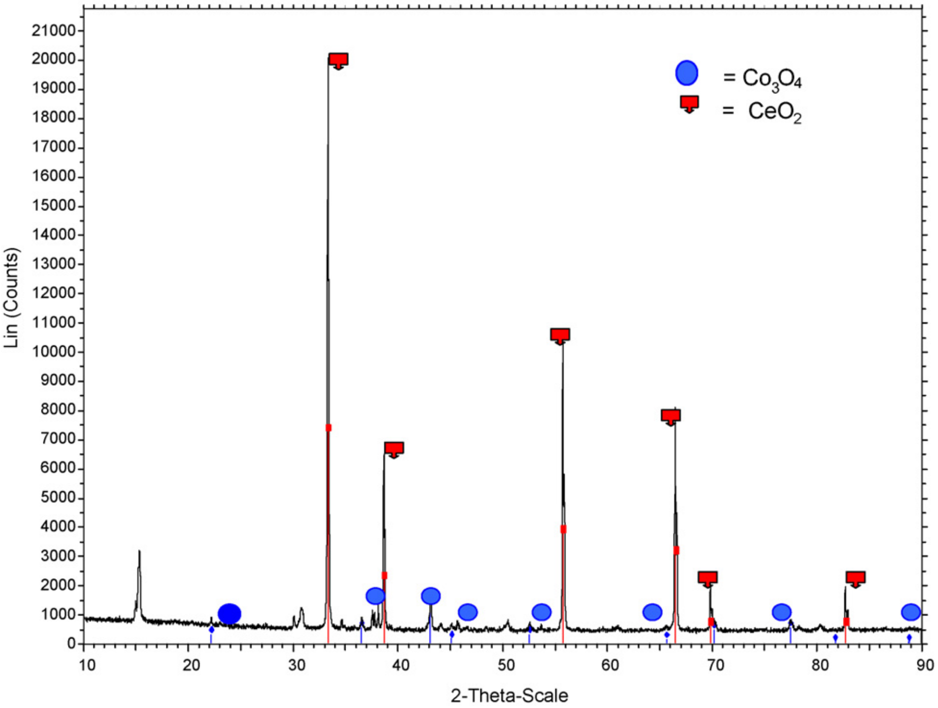
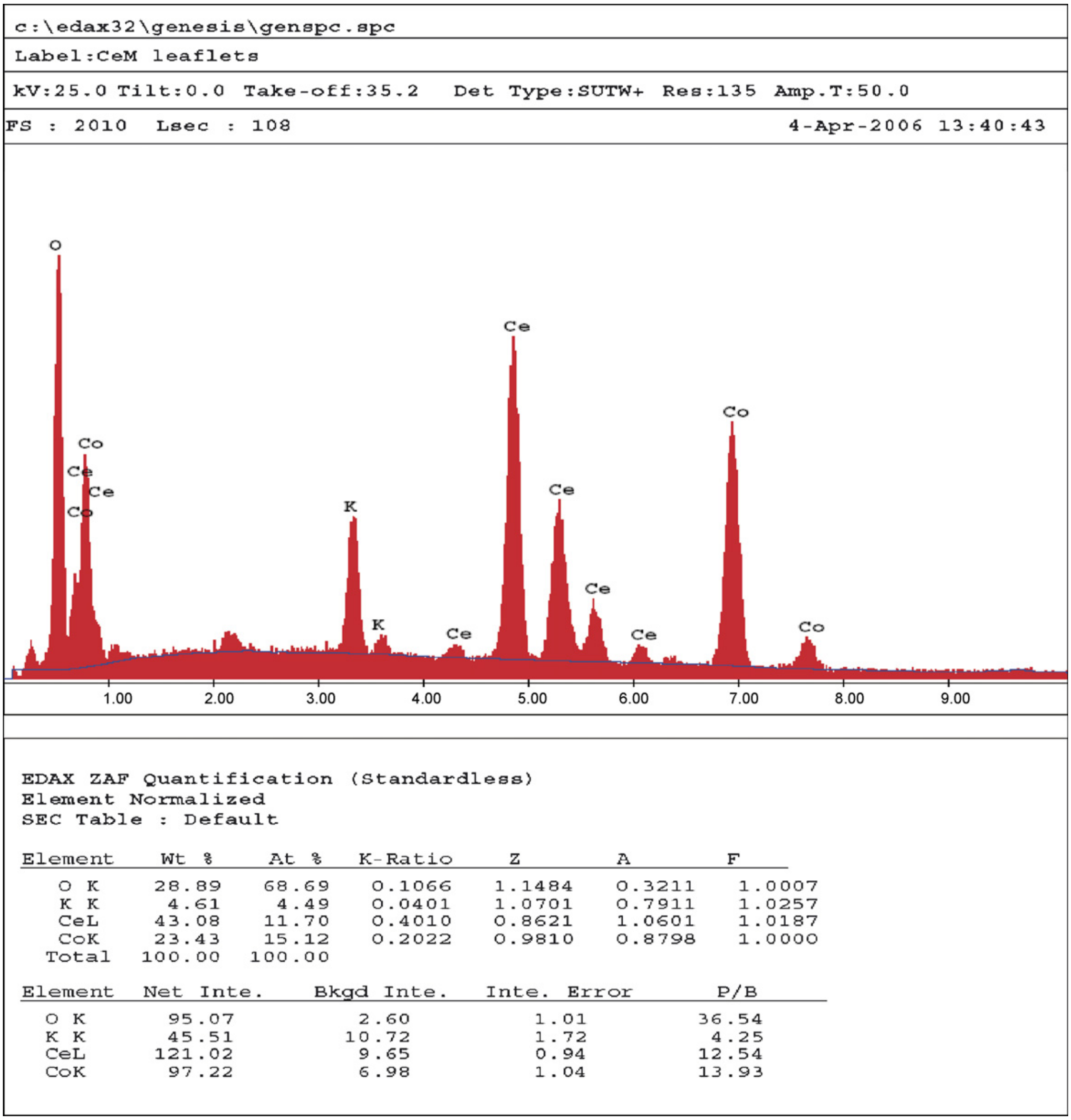


Fig. 1. XRD pattern of 20 mol%Co_3O_4–CeO_2 type mixed oxide material.



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c:\edax32\genesis\genspc.spc
Label:CeM leaflets
kV:25.0 Tilt:0.0 Take-off:35.2   Det Type:SUTW+ Res:135 Amp.T:50.0
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EDAX ZAF Quantification (Standardless)
Element Normalized
SEC Table : Default

Element    Wt %     At %   K-Ratio     Z        A        F
  O K     28.89    68.69   0.1066   1.1484   0.3211   1.0007
  K K      4.61     4.49   0.0401   1.0701   0.7911   1.0257
  CeL     43.08    11.70   0.4010   0.8621   1.0601   1.0187
  CoK     23.43    15.12   0.2022   0.9810   0.8798   1.0000
 Total   100.00   100.00

Element   Net Inte.    Bkgd Inte.    Inte. Error       P/B
 O K        95.07         2.60          1.01          36.54
 K K        45.51        10.72          1.72           4.25
 CeL       121.02         9.65          0.94          12.54
 CoK        97.22         6.98          1.04          13.93
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Fig. 2. EDX of 20 mol%Co_3O_4–CeO_2 type mixed oxide material.

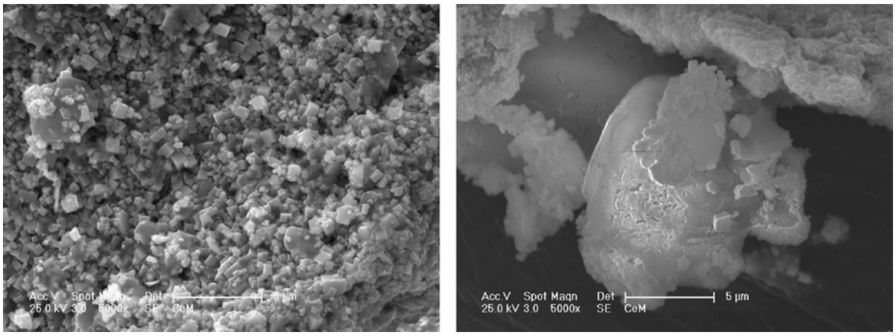

Fig. 3. SEM image of 20 mol%Co_3O_4–CeO_2 type mixed oxide material.

activated immediately after 180 °C; however, significant oxidation of the carbon material is started at 210 °C, while the T_f was observed around 440 °C. Catalytic activity results also show that bare CeO_2 and Co_3O_4 displays negligible catalytic activity in comparison with the catalyst 20 mol% Co_3O_4–CeO_2 which is observed to exhibit best catalytic activity among the various compositions studied.

From the TG results of actual diesel soot shown in Table 4. It is observed that non-catalyzed diesel soot oxidation starts above 200 °C, and complete combustion occurs at about

Table 3
Carbon oxidation results (TG evaluations)

Catalyst composition	Synthesis method	TG results	
		T_i (°C)	T_f (°C)
Bare carbon	–	390	620
Bare Co_3O_4	Calcined at 650 °C	360	590
Bare CeO_2	Calcined at 650 °C	390	620
5% Co_3O_4–CeO_2	Co-precipitation	250	490
10% Co_3O_4–CeO_2	Co-precipitation	250	480
20% Co_3O_4–CeO_2	Co-precipitation	200	440
40% Co_3O_4–CeO_2	Co-precipitation	230	470

T_i (°C), beginning of the carbon combustion; T_f (°C), complete combustion of carbon; Catalyst: carbon ratio used 95:05.

Table 4
Diesel soot oxidation results (TG evaluations)

Material/catalyst	T_i (°C)	T_f (°C)
Bare diesel soot	200	640
20% Co_3O_4–CeO_2 + soot	100	440

T_i (°C), beginning of the soot combustion; T_f (°C), complete combustion of soot; Catalyst: soot ratio used 95:05.

640 °C. The 20 mol% Co_3O_4–CeO_2 mixed oxide catalyst appears to get activated immediately after 150 °C; however, significant oxidation of the soot is started at 190 °C while the T_f was observed around 440 °C. 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. However, the diesel soot used in the present experiment is relatively dried and does not contain significant amount of hydrocarbons. In this way, excellent catalytic activity is observed for soot oxidation for the died soot used.

The carbon oxidation activity results for 20 mol% Co_3O_4–CeO_2 using Temperature Programmed Oxidation (TPO) technique are presented in Fig. 4. The carbon source used for TPO evaluations 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%). The 20 mol% Co_3O_4–CeO_2 catalyst appears to get activated immediately after 300 °C, and considerable oxidation of the carbon material is observed beyond 350 °C. The peak oxidation temperature corresponding to maximum activity is around 470 °C. The exothermic carbon oxidation reaction is expected to propagate the reaction rate after it achieves significant activity. This could be considered as excellent catalytic activity, in view of the very low surface area of the catalyst used. This material shows much better catalytic activity than the bare CeO_2 and bare Co_3O_4. There was practically no CO generation, which is sometimes present as a product of incomplete combustion. The sudden drop in CO_2 generation is because of the consumption of carbon material in the reaction mixture. Therefore, this does not indicate the lowering of activity and rather confirm the complete oxidation of carbon. The activation energy for catalyzed and non-catalyzed reactions have been studied by the Ozawa method [20]. The activation energy experiments were carried out at different heating rates. The activation energy observed for non-catalyzed carbon oxidation is 155–163 kJ/mol and for catalyzed reaction is, 136–142 kJ/mol using activated carbon with 20-mol% Co_3O_4–CeO_2 (co-precipitation method) catalyst (Fig. 5).

The promotional effect of K present as an impurity cannot be ruled out as the catalysts prepared using other precipitants shows relatively less activity. The EDX analysis (Fig. 2) confirms the presence of significant amount of potassium. The catalytic materials show good thermal stability.

Shangguan et al., proposed a mechanism for the catalytic oxidation of carbon, which is valid for many metals and mixed metal oxide type catalysts [21]. In this mechanism, the metal oxide catalysts participate in an oxidation and reduction (redox) cycle, in which the metal is repeatedly oxidized and reduced. The mechanism involves the following steps:

$$M_{\mathrm{reduction}} + \text{gas-O} \rightarrow M_{\mathrm{oxidation}}-O_{\mathrm{ads}}, \quad (1)$$

$$M_{\mathrm{ox}}-O_{\mathrm{ads}} + C_f \rightarrow M_{\mathrm{red}} + \mathrm{SOC}, \quad (2)$$

$$\mathrm{SOC} \rightarrow \mathrm{CO\ or\ CO_2}, \quad (3)$$

where M_{red} and M_{ox}–O represent the reduced and oxidized states of the catalyst, respectively. Gas-O represents the oxidant gas (O_2), C_f denotes a carbon active site (or *free* site) on the carbon surface, and SOC represents a surface carbon–oxygen complex. As per this mechanism, the gaseous oxygen is dissociatively adsorbed on the surface of metal oxide catalyst, 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

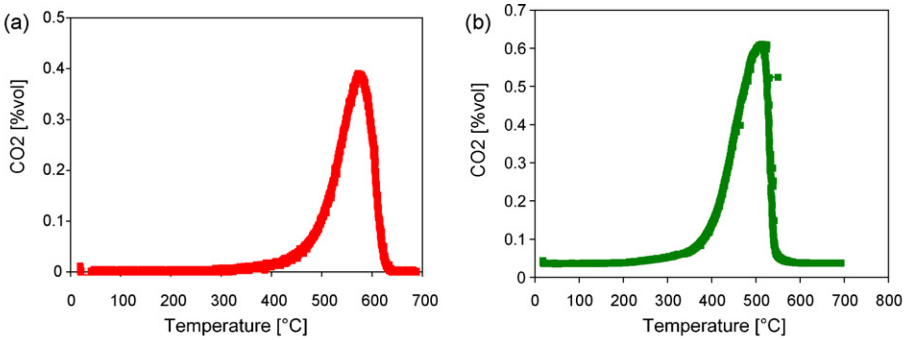

Fig. 4. TPO Results for the carbon oxidation: (a) bare carbon black;(b) carbon black with 20 mol%Co_3O_4–CeO_2 catalyst.

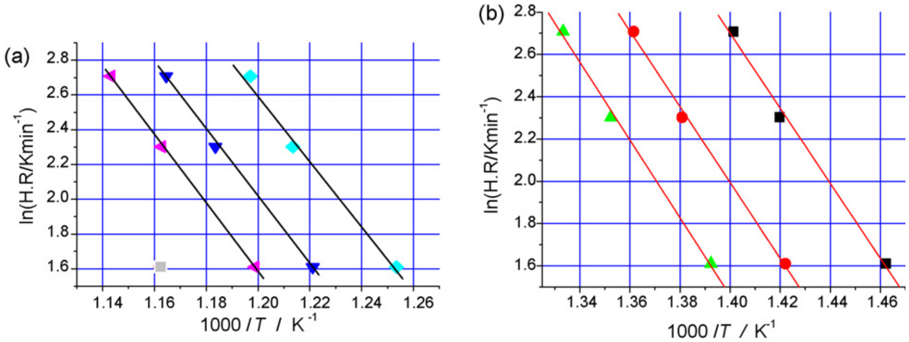

Fig. 5. Activation energy (AE) results for activated carbon oxidation in air: (a) bare activated carbon (without catalyst): 155–163 kJ/mol; (b) with catalyst: 136–142 kJ/mol (activated carbon with 20 mol% Co_3O_4–CeO_2 (co-precipitation catalyst).

either O_{ads} or gaseous O_2 produces CO_2 through reaction or, reproducing the reaction C_f sites on the soot surface. CeO_2 incorporation is likely to improve the redox capacity of catalyst, while in addition, it may also act as a stabilizer of O^{2-}, ions at the catalyst surface. In this way, this mechanism by Shangguan et al. can explain the catalytic activity of present catalyst as well as promotional effect of ceria.

4. Conclusion

The present study has highlighted the effect of ceria incorporation in Co_3O_4 for its catalytic activity towards particulate matter/carbon oxidation reaction. The composite type mixed oxide shows excellent catalytic activity for soot/carbon oxidation, which is much better than the individual components, i.e., Co_3O_4 and CeO_2. Although the ceria incorporation and high temperature synthesis resulted in low surface area, this has improved the redox capacity of material while in addition it may also act as a stabilizer of O^{2-}, ions at the catalyst surface. The incorporation of 20 mol% Co_3O_4 in CeO_2 significantly improves its catalytic activity, which was confirmed by catalytic evaluations using both TG and TPO techniques. Further increase in CeO_2 contents lowers the activity due to formation of isolated, less active ceria phase. The activation energy results also corroborate high catalytic activity of catalysts towards carbon/soot oxidation. The presence of a small amount of potassium appears to be also contributing towards the high soot oxidation activity of this mixed oxide type material. This low cost non-noble metal-based catalyst also shows excellent thermal stability and good potential for its application as a DPF regeneration catalyst.

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