Potential rare-earth modified CeO_2 catalysts for soot oxidation

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The physico-chemical properties of ceria (CeO_2) and rare earth modified ceria (with La, Pr, Sm, Y) catalysts are studied and correlated with the soot oxidation activity with using O_2 and $O_2 + NO$. CeO_2 modified with La and Pr shows superior soot oxidation activity with O_2 compared with the unmodified catalyst. The improved soot oxidation activity of rare earth doped CeO_2 catalysts can be correlated to the increased meso/micro pore volume and the stabilisation of the external surface area. On the other hand, unreducible ions decrease the intrinsic soot oxidation activity of rare earth modified ceria with both O_2 and $NO + O_2$ due to the decreased amount of redox surface sites. The catalyst bulk oxygen storage capacity is not a critical parameter in determining the soot oxidation activity. The modification with Pr shows the best soot oxidation with both O_2 and $O_2 + NO$ compared with all other catalysts.

KEY WORDS: diesel soot; rare earth; ceria; oxidation; catalysis.

1. Introduction

The emission of various pollutants from exhaust gases of the different energy sources leads to serious atmospheric pollution and climate change [1, 2]. Increasingly stringent environmental legislations on the reduction of NO_x and soot from various sources of exhaust gases require the development of new devices/technology that can to a large extent eliminate these pollutants. Compared with exhaust gases from gasoline-powered engines diesel engine exhaust gases are relatively clean with respect to unburned hydrocarbons and carbon monoxide. The large volume diesel engine market and its ever increasing demand in the heavy-duty engine sector, which emits large amounts of soot particulate matter, are of the concern and aftertreatment devices such as particulate traps are necessary [3–7]. Un-catalysed soot (carbon particles) oxidation to CO_2 with a typical diesel engine exhaust gas (having H_2O, NO_x, hydrocarbons (HC), CO and SO_2) occurs generally around 600 °C [3–7]. When the diesel engine is fitted with an un-catalysed trap frequently high temperature regenerations are required, which can be uncontrolled, inefficient, and inconvenient. On the other hand, catalysed soot filter can utilise some of the gaseous components present in the exhaust gas to oxidise soot at much lower temperatures (around 400 °C). A limited decrease in soot oxidation temperature can also be observed when H_2O and SO_2 are present in the exhaust gas. The most important of all the exhaust gas components are O_2 and NO. NO_2 is a more powerful oxidant than O_2 and over the catalyst that can convert NO into NO_2, the

soot oxidation temperature can be significantly decreased. For the efficient utilisation of decreasing amounts of NO produced in modern diesel engines, the NO has to be repeatedly utilised in the soot oxidation cycle. The role of Pt in NO oxidation to NO_2 is well understood, however, the role of support, such as CeO_2, is not obvious. The lattice oxygen or 'active oxygen' of the oxygen storage components (such as CeO_2 used in the aftertreatment catalyst) is able to oxidise soot around 450 °C [3, 8]. However due to poor contact between catalyst and soot such a reaction path way is not efficient.

To overcome the contact problem catalysts, that work on different principles, have been developed [3–8]. The use of the fuel-borne catalysts incorporates a catalyst within the soot particle and increases the number of contact points and, therefore, decreases soot oxidation temperature significantly, from 600 to 350 °C. Similarly, molten salt catalyst can wet the soot surface efficiently and, thereby, increasing the contact between catalyst and soot, and decrease soot oxidation temperature with O_2. However, molten salt catalysts have inherent problems associated with thermal stability. Commercial technologies based on fuel-borne catalysts or NO_2 as an oxidant are presently being used in automobile engines. Though large amount of literature data are available and showing a decrease in catalysed soot oxidation temperature with O_2 alone, so far no commercial technology conclusively showed catalysed soot oxidation activity with O_2. The ambiguous results in different laboratories on (real life) catalysts arising at different reaction conditions are mainly focussed on the preparation of soot-catalyst mixtures and the testing thereof. There is only a very limited amount of data given on the active site(s) of the catalyst. In this article the role of

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surface and bulk catalyst active sites, created by doping with rare-earth cations, in the soot oxidation to CO_2 with O_2 and NO oxidation to NO_2 will be discussed.

CeO_2 is one of the extensively used catalytic components in many after-treatment technologies due to its high activity in redox reactions. CeO_2 is used as a well-known three-way catalyst for CO, HC, and NO_x abatement, as fuel-born catalyst, and in catalysed soot filters in eliminating soot particulates [3–9]. Fuel-born ceria catalyst leads to the uniform formation of CeO_2 nano-particles trapped within soot particle. The redox properties of CeO_2 will generate the active species responsibly for oxidation uniformly through out the soot precursor and will lead to a more efficient oxidation, allowing easier and controllable filter regeneration. CeO_2 is also a major component in many catalysed soot filters or pre-filters. However, not many fundamental studies are reported in the open literature, using CeO_2 or CeO_2 containing materials in soot oxidation. CeO_2 alone as a catalyst or as a support in passive regeneration of particulate filter is probably of little interest due to its low hydrothermal textural stability usually encountered in exhaust gases. At the same time it could lose its redox properties and oxygen storage ability. Modification of CeO_2 with various ions is known to improve the stability towards sintering and also to preserve the oxidation activity of the resulting catalysts. The latter was attributed to changes in the redox properties and creation of oxygen vacancies in CeO_2; both improve the oxygen exchange with the catalyst and oxygen storage capacity. Modification by doping with transition metal and rare-earth oxides will stabilise surface area and will at the same time improve the redox/oxygen storage properties of CeO_2 [8]. However, many of such studies were focussed in three-way catalysis for a gasoline-powered engine. In a few instances it is shown that the dopants in fact could decrease the activity of particular reactions [10]. Recently, it is shown that La^{3+} modified CeO_2 catalysts can improve the soot oxidation activity through the participation of lattice oxygen [8]. Though the surface and bulk catalyst properties are responsible for soot oxidation, they are not thoroughly exploited and conclusively related to the soot oxidation reaction especially over CeO_2. If the properties of the reducible oxide CeO_2 and the active sites responsibly for the soot oxidation are well understood, then the tuning of such materials by modifications will the next step forward in making more active catalysts.

The present study aims at determining the properties of the CeO_2 catalyst responsibly for soot oxidation with O_2. CeO_2 will be modified by doping with different rare-earth ions (La^{3+}, $Pr^{4+/3+}$, Sm^{3+}, and Y^{3+}). Its effect on soot oxidation is studied with using O_2 and $NO+O_2$ and correlated with the surface and the structural-properties of the catalysts. Furthermore, the tentative mechanistic steps in the catalysed soot oxidation are proposed.

2. Experimental

2.1. Catalyst preparation

Catalysts are prepared from Ce^{3+}, La^{3+}, Pr^{3+}, Sm^{3+}, and Y^{3+} nitrate precursors (Aldrich, 99.9%) (Table 1). The required amounts of the nitrate precursor of either single or mixed components (5 g) are dissolved in H_2O (3.3 g). This aqueous solution is dried at 100 °C for 5 h, followed by heating to either 700 or 1000 °C, in static air for 2 h. γ-Al_2O_3, calcined at 1000 °C for 5 h, is used as an inert material for analysing un-catalysed soot oxidation activity. The catalysts are denoted as $CeREO_x\_y$, where 'RE' denotes the 10 wt% doped rare earth oxide and 'y' is the calcination temperature used to prepare the catalysts.

2.2. Characterisation

The BET surface areas and N_2 adsorption isotherms of catalysts are measured by N_2 physisorption at −196 °C in an automatic volumetric system (Autosorb-6, Quantachrome). X-ray diffractogrammes are recorded in a Philips X-ray diffractometer, PW 1840, with Ni-filtered $CuK\alpha$ radiation ($\lambda = 0.15418$ nm). Data is collected between $2\theta = 6$–70° with a step size of 0.02° (total collection time 4 h).

2.3. Soot oxidation in TGA

Thermo gravimetric analysis (TGA) of the soot oxidation of the various samples with O_2 is carried out in a Mettler Toledo, TGA/SDTA851^e instrument. The catalytic activities were measured in both loose (mixed with a spatula) and tight contact (ground in a mortar) mode with catalyst-soot mixtures in 4:1 wt/wt ratio, respectively [6, 7]. Printex-U from Degussa S.A. is used as a model soot whose characterisation is reported elsewhere [8]. A weighed amount of the sample (having less than 1 mg of soot) is placed in a TGA crucible and heated in 100 mL/min air or He to 800 °C with different heating rates. The apparent activation energy of the soot

Table 1
BET surface area of different materials and ^{a}T_{10} and T_{50} temperature

Catalyst	BET surface area, m^2 g^{-1}	Temperature, °C	
		T_{10}	T_{50}
$Al_2O_3\_1000$	–	539	618
CeO_2_1000	2	499	576
$CeLaO_x\_1000$	16	414	459
$CePrO_x\_1000$	11	425	484
$CeSmO_x\_1000$	5	450	520
$CeYO_x\_1000$	2	500	572
CeO_2_700	57	388	450
$CeLaO_x\_700$	48	388	425
$CePrO_x\_700$	44	378	422

^{a}Temperature at 10 and 50% soot conversion, experimental conditions in Figure 3

oxidation is determined by Ozawa [11] method using the following expression:

$$\mathrm{d}\log(\Phi)/\mathrm{d}(1/T_x) = 0.4567 E_a/R \qquad (1)$$

where, Φ is the heating rate used, T_x is the temperature corresponding to $x\%$ soot conversion, E_a is the apparent activation energy in $kJmol^{-1}$. E_a can be estimated from the slope of the least squares straight line fit of the $\log(\Phi)$ versus $1/T_x$ plot. Prior to TGA experiments the set-up is optimised to eliminate possible heat- and mass-transfer effects [12].

2.4. Soot oxidation in fixed bed reactor

The soot oxidation with $NO_x + O_2$ is carried out in a six-flow reactor set-up. A loose contact mixture (mixed with a spatula) of 80 mg of catalyst and 20 mg of soot diluted with 400 mg of SiC is packed between two quartz wool plugs in a tubular quartz reactor (6 mm i.d). The oxidation is carried out with a mixture gas containing 10 vol% O_2, 600 ppm NO and balance Ar. The flow rate through the reactor is maintained at 200 mL/min with a resulting GHSV of ~70,000 L/L/h. The oxidation is carried out by heating the reactor at a rate of 0.6 °C/min. An NDIR analyser is used to monitor CO_2, CO, and NO, respectively.

3. Results

3.1. Characterisation

3.1.1. N_2 adsorption

BET surface areas of various materials prepared are given in Table 1. The surface area of CeO_2 is found to be 57 to 2 $m^2 g^{-1}$, when calcined at 700 and 1000 °C, respectively. The rare-earth ions selected in this study are known to form solid solution and, as a consequence, also stabilise the CeO_2 crystallites towards sintering, resulting in a less severe surface area decline [13]. However, the surface area decreased for $CeREO_x\_700$ catalysts, compared with CeO_2_700. CeO_2_700 shows a narrow pore size distribution around 10 nm (Figure 1). The rare-earth ion modifications lead to bimodal pore size distribution. The pore size also shifted to from 10 to around 15 nm (meso pore range) and above 50 nm (meso/macro pore range). The effect of rare earth ion dopant on the increase of the surface area is only evident for the catalysts prepared by 1000 °C calcination. For $CeREO_x\_1000$ catalysts the surface area is mainly arising from meso-macro pore range, and considered as external surface area.

3.1.2. XRD

Doping with different rare-earth cat-ions decreased the intensity of the peaks and shifted them to different 2θ values (not shown) and only a single phase corresponding to the cubic fluorite type structure is observed
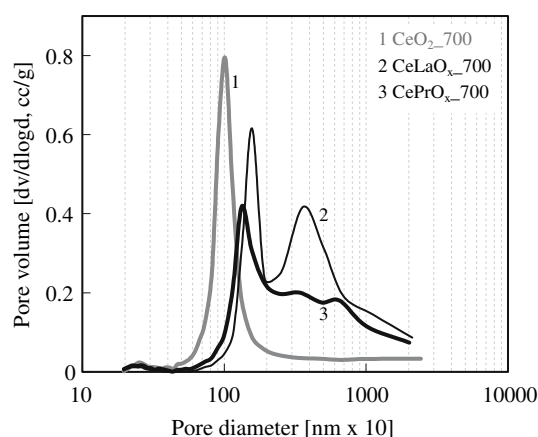

Figure 1. BJH analysis of N_2 adsorption isotherms over selected catalysts as indicated.

in all $CeREO_x\_1000$ catalysts. In the case of La^{3+} and Sm^{3+} modified catalysts, 2θ shifted to lower values, suggesting the incorporation of the relatively larger ions into CeO_2 cubic structure forming the solid solution [13]. Similar observations are made for catalysts prepared by 700 °C calcinations.

3.2. Activity tests

3.2.1. Soot oxidation with O_2

Figure 2 shows soot conversion during oxidation in O_2, for catalyst-soot mixtures in loose contact mode. The TGA data is normalised by removing the weight loss (below 300 °C) due to H_2O and adsorbed hydrocarbons/very reactive surface oxygen complexes of soot. The onset temperature T_{10}, temperature at 10% soot conversion, is above 530 °C for all the catalysts studied. Using Al_2O_3, soot oxidation (referred to as un-catalysed soot oxidation) is complete between 500 and 670 °C with T_{50} temperature at 50% soot conversion at 605 °C. The presence of ceria-based catalysts decreased T_{50} by about 5–15 °C. However,
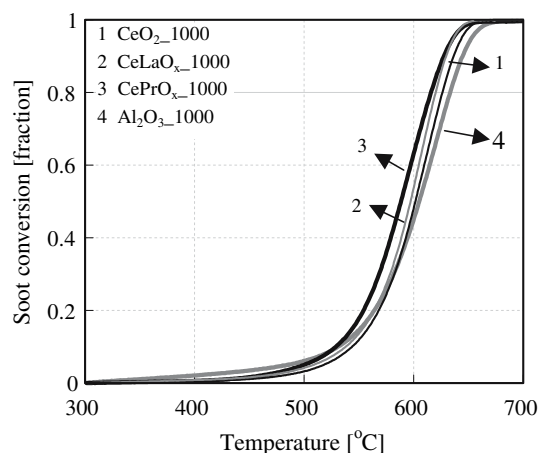

Figure 2. Soot oxidation with O_2 over selected catalysts as indicated. Reaction conditions: TGA, catalyst:soot- 4:1 wt/wt, contact = loose, heating rate = 10 °C/min, air flow = 100 mL/min.

the onset temperature of soot oxidation is not influenced. The influence of the catalysts in the loose contact mode is very limited, which is in agreement with previous studies [3–8]. Among the materials examined in loose contact mode, $CePrO_x\_1000$ is found to have better activity. The soot oxidation activity followed the trend $CePrO_x\_1000 > CeLaO_x\_1000 \sim CeO_2\_1000 > Al_2O_3\_1000$.

Using O_2 as the oxidising agent under the loose contact conditions the catalyst ranking is ambiguous due to uncertainties of catalyst soot mixing. The meaningful influence of the rare-earth ion doping on the intrinsic activity of CeO_2 can, therefore, only be studied in the tight contact mode, mixing with a mortar. Figure 3 shows the TGA results of catalysts, prepared by 1000 °C calcination, in tight contact with soot. With $Al_2O_3\_1000$, no appreciable change of onset temperature T_{10} (451 °C) or T_{50} (618 °C) is observed in the soot oxidation compared with the loose contact mode. Al_2O_3 has no redox or oxygen storage catalytic sites. In the tight contact mode, the CeO_2_1000 and $CeREO_x\_1000$ catalysts showed a considerable decrease in the soot oxidation temperatures at all conversion levels (T_{10} and T_{50} shifted to lower temperatures by about 40–150 °C). Among the catalysts $CeLaO_x\_1000$ showed superior performance followed by $CePrO_x\_1000$, in which for both modified catalysts the T_{10} and T_{50} temperatures decreased by more than 100 °C. The soot conversion with catalyst in the tight contact mode followed below trend. $CeLaO_x\_1000 > CePrO_x\_1000 \sim CeSmO_x\_1000 > CeYO_x\_1000 > CeO_2\_1000 > Al_2O_3\_1000$. For the catalysts prepared by 700 °C calcination (Figure 4) the soot conversion followed the order $CePrO_x\_700 \sim CeLaO_x\_700 > CeO_2\_700$. These "700" catalysts are more active than catalysts prepared by 1000 °C calcination.

The BET surface areas of the various catalysts studied and the T_{10} and the T_{50} temperatures of soot oxidation are given in Table 1. No correlation is observed

Figure 4. Soot oxidation with O_2 over catalysts as indicated. Reaction conditions: TGA, catalyst:soot-4:1 wt/wt, contact = tight, heating rate = 15 °C/min, air flow = 100 mL/min.

between the BET surface area and the soot oxidation in loose contact mode or in tight contact mode for the catalysts prepared by 700 °C calcination. In contrast, for the catalysts prepared by 1000 °C calcination, in tight contact with soot, a clear correlation of the decrease in the soot oxidation temperature with the increase in the surface area is seen. It is not possible to correlate the total surface area with soot conversion in tight contact mode if the catalyst has micro pores since soot particles will not fit in micro pores, even under tight contact conditions [14]. The N_2 adsorption isotherm suggests that the surface area of all catalysts, prepared by 1000 °C calcination, can be correlated to the external surface area, which is accessible for spreading the soot, especially in the tight contact mode. The $CeREO_x\_700$ catalysts have a higher external surface area compared with CeO_2_700 and all the other catalysts. The higher external surface area explains the superior performance of the $CeREO_x\_700$ in spite of having a relatively lower BET surface area compared to CeO_2_700.

To evaluate the effect of rare earth doped CeO_2 and the possible changes in redox properties on soot oxidation activity, it is necessary to compare catalysts having similar external surface area under the tight contact conditions. Figure 5 shows the soot conversion over CeO_2_1000 and $CePrO_x\_1000$. The soot conversion over $CeLaO_x\_1000$ is also shown for comparison. The soot conversion temperature decreases over the surface area normalised CeO_2_1000 catalyst compared with that of $CePrO_x\_1000$ or even $CeLaO_x\_1000$ having a higher surface area. This observation shows that the intrinsic redox behaviour of the unmodified CeO_2 is more effective in the oxidation of soot. One could expect this since for a surface area normalised CeO_2 more redox sites are available in respect to those of $CeLaO_x\_1000$ catalyst, where surface segregation of un-reducible La^{3+} is expected. This segregation will not lead to a direct participation in soot oxidation. From Figure 5 one can
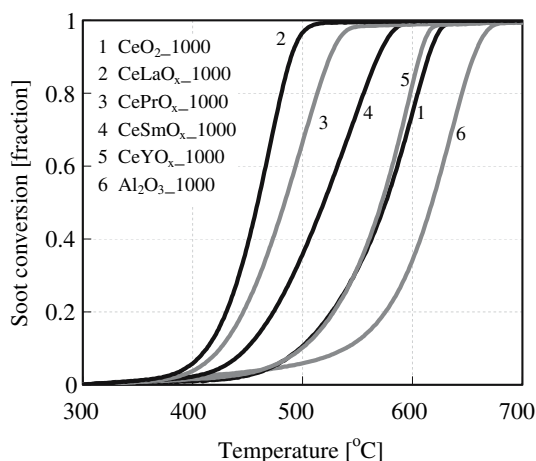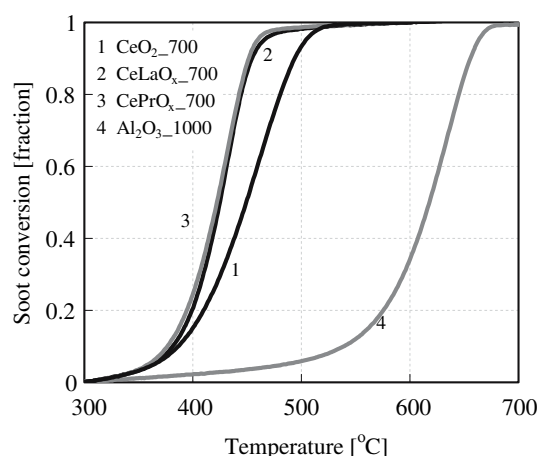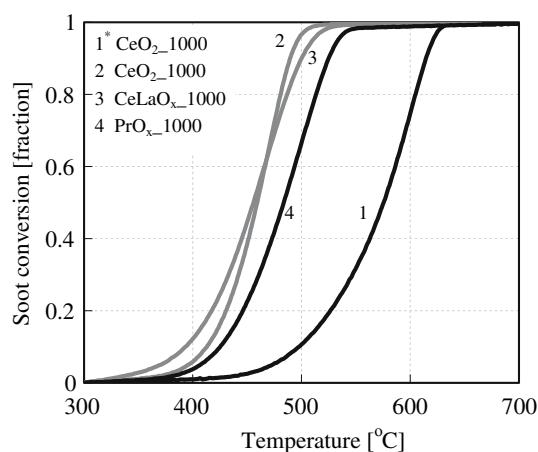

Figure 3. Soot oxidation with O_2. Reaction conditions: TGA, catalyst:soot-4:1 wt/wt, contact = tight, heating rate = 15 °C/min, air flow = 100 mL/min.

Figure 5. Comparison of soot oxidation over surface area normalised CeO_2 with other catalysts. CeO_2* represents surface area of CeO_2 normalised to that of $CePrO_x$. Reaction conditions-TGA, catalyst:soot-4:1 wt/wt, contact = tight, heating rate = 15 °C/min, air flow = 100 mL/min.

suggest that in the catalysts studied the possible modification by the rare-earth cat ions in surface redox properties is not as important as that of the changes in the external surface area.

In Figure 6 the ratio of the external surface area of the catalyst to that of the initial soot surface area is plotted against the temperature (T_x) at different conversion levels (x). The soot conversion below 475 °C can be considered entirely related to a catalysed oxidation (as the onset of un-catalysed soot oxidation is above 530 °C). Above 475 °C, the resulting soot conversion is due to the contribution from both catalysed and uncatalysed soot oxidation. Form Figure 6 it can be derived that, if the majority of the soot has to be converted by catalysed oxidation, the normalised catalyst external surface area to the initial soot surface area ratio should be above 0.4. It can also be concluded that La^{3+}
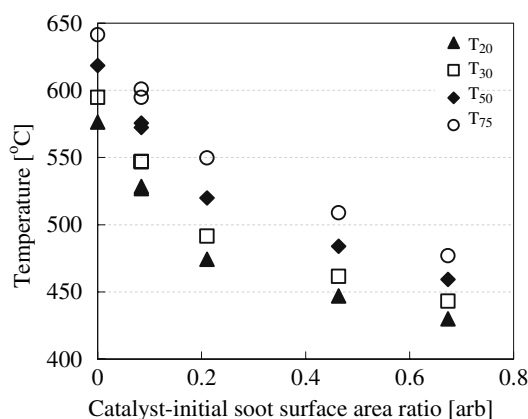
and $Pr^{3+/4+}$ modified CeO_2 catalysts are more efficient in catalysing the soot oxidation (around 75% catalysed soot conversion at 475 °C).

3.2.2. Activation energy

By applying different heating rates during soot oxidation in TGA, Ozawa plots are constructed at various soot conversion levels (an example for CeO_2 is shown in Figure 7). The plots of the logarithmic heating rates used versus the inverse temperatures at various soot conversion levels showed a good linear fit. Such experiments are carried out for all the catalysts. In Table 2 the soot oxidation activation energies (E_a) estimated from the slopes of linear fits are given. The activation energy for the un-catalysed reaction is around 150 kJmol^{-1}. Presence of a catalyst, even under tight contact mode, does not influence this activation energy significantly. The small changes observed in the activation energy are due to the experimental nature of the TGA technique used (oxygen diffusion and heat transfer influence). The unchanged activation energy indicates that only the rate of reaction is increased in the presence of the catalyst, but the soot oxidation reaction mechanism does not change.

3.2.3. Bulk oxygen for soot oxidation

Figure 8 shows the weight loss due to soot oxidation in He with catalyst-soot mixtures in tight contact mode. The weight loss is arising from the soot oxidation due to the participation of surface and bulk lattice oxygen. The soot oxidation activity of the PrO_x_1000 catalyst is included in Figure 8, as it can contribute a significant amount of bulk oxygen for soot oxidation compared
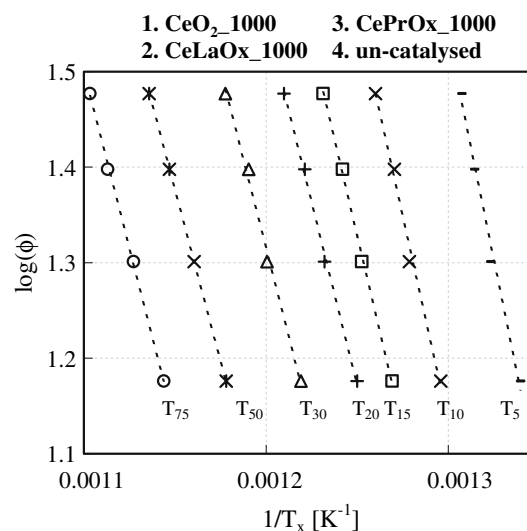

Figure 6. Effect of surface area ratio of catalyst to initial soot, on T_x, temperature at 'x%' soot conversion. Reaction conditions-TGA, catalyst:soot-4:1 wt/wt, contact = tight, heating rate = 15 °C/min, air flow = 100 mL/min.

Figure 7. Ozawa plots over CeO_2 at different soot conversion levels. Φ-different heating rates applied during soot oxidation, and T_x (temperature at 'x%' conversion). Reaction conditions-TGA, catalyst:soot-4:1 wt/wt, contact = tight, Φ = 15, 20, 25 and 30 °C/min, air flow = 100 mL/min.

Table 2
Apparent activation energy (E_a) calculated by Ozawa plot at different soot conversions

| Catalyst	Apparent activation Energy [kJmol^{-1}] at 'x%' conversion						
	5	10	15	20	30	50	75
Al_2O_3	–	159 ± 5	153 ± 1	183 ± 35	177 ± 34	143 ± 2	142 ± 3
CeO_2	168 ± 12	156 ± 10	146 ± 4	139 ± 5	135 ± 7	129 ± 1	133 ± 2
$CeLaO_x$	132 ± 10	139 ± 4	133 ± 4	135 ± 3	133 ± 3	123 ± 2	127 ± 4
$CePrO_x$	155 ± 7	144 ± 7	145 ± 5	140 ± 8	138 ± 10	130 ± 9	133 ± 10
$CeSmO_x$	148 ± 12	153 ± 9	144 ± 11	146 ± 10	145 ± 6	153 ± 12	148 ± 43
$CeYO_x$	134 ± 28	143 ± 20	141 ± 19	139 ± 17	139 ± 16	143 ± 10	140 ± 6

For reaction conditions see figure 6
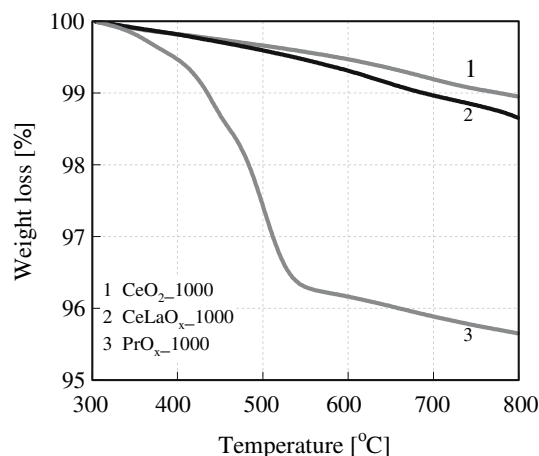
Figure 8. Soot oxidation over the catalysts as indicated in He. Reaction conditions-TGA, catalyst:soot-4:1 wt/wt, contact = tight, heating rate = 10 °C/min, He flow = 100 mL/min.

with other catalysts. No appreciable weight loss is observed over the CeO_2_1000 or the $CeLaO_x$_1000 catalysts. This indicates that the bulk reduction properties of the catalysts, which only show above 700 °C in H_2-TPR is not important in determining the soot oxidation properties [8]. The PrO_x_1000 catalyst shows more than two orders of magnitude soot oxidation in He due to the participation of bulk O_2. This catalyst was, however, found to be a poor soot oxidation catalyst (not shown) compared with rare-earth ion-doped catalysts. The above results rule out the involvement of the catalyst bulk reduction properties in the soot oxidation.

The activation energies of the soot oxidation in O_2 and in He over PrO_x_1000 in tight contact with soot are given in Table 3. The activation energy of around 150 kJmol^{-1}, during oxygen assisted soot oxidation. This is in agreement with generally reported values in literature. When the soot oxidation is carried out in He, where one can assume the lattice oxygen, mainly bulk oxygen for PrO_x_1000, are participating in the oxidation, the apparent activation energy is found to be around 240 kJmol^{-1}. This high activation energy indicates that the participation of bulk oxygen in the soot conversion is rather limited or absent at all.

Table 3
Apparent activation energy of soot oxidation over PrO_x with oxygen and in He

Catalyst	Apparent activation Energy [kJmol^{-1}] at $T_{5\%}$
PrO_x–O_2	145 ± 38
PrO_x–He	234 ± 9

For reaction conditions see Figure 5 for soot oxidation with O_2, and Figure 8 for soot oxidation in He

3.2.4. Soot oxidation with NO_2

Figure 9 shows the soot oxidation activity with $NO + O_2$ under loose contact conditions. The NO molecule can access all the catalytic sites and NO_2 production, therefore, should depend on the surface area of the catalysts. Though $CeLaO_x$_1000 has higher surface area compared with CeO_2_1000, the extent of soot oxidation activity is not that different. On the other hand, the Pr modified catalyst showed the superior performance in soot oxidation. The above observations indicate that the modification with a more easy to be reduced cation can provide a more oxygen rich surface leading to the improved formation of NO_2 and, therefore, leads to superior soot oxidation.
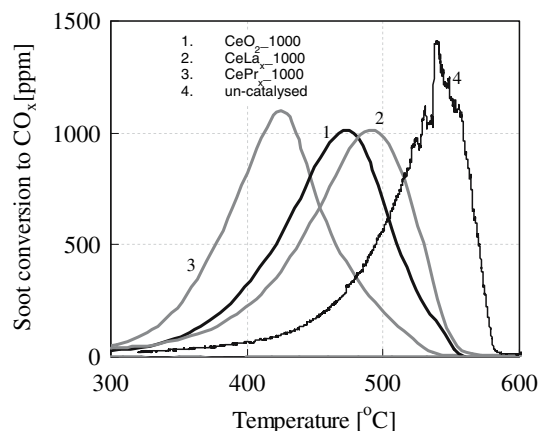

Figure 9. Soot oxidation with $NO + O_2$. Reaction conditions: fixed bed, catalyst:soot-4:1 wt/wt, contact = loose, heating rate = 0.6 °C/min, 600 ppm $NO + 10$ vol% O_2 flow = 200 mL/min.

4. Discussion

The effect of rare-earth ion-doping on CeO_2, which is thought to influence the catalytic properties in many instances in a positive way, is investigated here in more detail. The surface areas obtained are more related to the real world operation (Table 1) considering the fact that high temperatures usually encountered during soot oxidation in exhaust gases. The soot oxidation over the various catalysts has been studied using O_2 in loose and tight contact conditions. Loose contact did not show a significant decrease in the soot oxidation temperature irrespective of the selected catalyst or the surface area of the catalyst, consistent with reported literature. When the soot particle is not in a close contact with the catalyst surface, the catalyst lattice oxygen cannot be transferred to the soot surface [8]. Therefore, it is adopted to test the catalysts using a tight contact condition. The soot conversion temperature strongly decreased over the rare-earth modified CeO_2 catalysts (see Figure 3 and Figure 4). The possible reasons for the increase in activity of rare-earth doped CeO_2 catalysts in the soot oxidation with O_2 are probed by the different catalyst characterisation techniques. One of the parameters, that can explain the differences in catalysed soot oxidation temperature with O_2, is the catalyst surface area. Comparison of the BET surface areas of all catalysts to that calculated from crystallite size measured from XRD (not shown) in the respective catalysts, suggest that most of it can be related to the external surface of crystallites. CeO_2_700 had higher BET surface area ($58 \ m^2 \ g^{-1}$) compared with that of $CeREO_x\_700$ catalysts ($< 48 \ m^2 \ g^{-1}$). Though the pore volume is relatively higher for CeO_2_700, it is not accessible for the spreading soot (around 30 nm particles) even in the tight contact mode. Doping with La^{3+} or $Pr^{3+/4+}$ led to an increase in this intra particle void volume (to around 15 nm) and especially led to an important increase in macro-pore volume (>50 nm, see Figure 1 indicating the more open structure of $CeReO_x\_700$ particles). This open structure leads to the increased accessibility of $CeREO_x$ redox sites to soot and, therefore, increases the soot oxidation rate (see Figure 4).

The sintering of CeO_2 seems to be more important in the high catalyst preparation temperature (1000 °C) and

dopants in general decrease the sintering process and, therefore, preserve the crystallite size. This is also reflected in the increased BET surface area of these catalysts (Table 1). Most of the surface areas in the catalysts, prepared by 1000 °C calcination, can be linked to the macro pores or external surface area, which are accessible for the spreading soot. Under the catalyst preparation and the soot oxidation conditions used the smaller crystallite sizes not only increase the external surface area, but also lead to good mixing of the catalyst and soot and as a consequence to a decrease in the oxidation temperature. However, these experiments do not reveal the intrinsic activity of modified catalytic sites.

Figure 10 depicts how the soot particles could be present over the catalysts having a different external surface area under the ideal tight contact conditions. Simple calculations reveal that a monolayer of soot particles under the experimental conditions used can be easily spread over the catalyst having $8 \ m^2 \ g^{-1}$ surface area. Because of the high surface area of the $CeLaO_x\_1000$ catalyst it can be assumed that a monolayer of primary soot particles could be present, though this may not be easy to accomplish even under the tight contact conditions used. Considering the low surface area of CeO_2_1000, the soot particles can only be spread in multilayers due to the lower surface area. Though the surface of CeO_2_1000 is intrinsically more active due to the restricted accessibility of the catalyst active sites to gas-phase oxygen and to the soot layers, this will lead to lower soot conversions, as observed. The intrinsic activity of the redox catalysts, therefore, cannot be obtained by simple tight contact experiments using a fixed weight of the catalyst. For analysing the effect of rare-earth ion-doping on the soot oxidation, which changes the CeO_2 surface/bulk redox properties, the external catalyst surface area has to be normalised (see Figure 5) for studying such soot oxidation. When the surface area was normalised the intrinsic activity of CeO_2_1000 was found to be higher than that of the rare-earth ion-doped CeO_2 catalysts.

The soot oxidation activity may also depend on the nature and extent of incorporation of dopant into the CeO_2 structure, which influences the surface properties of the catalyst to different extents. The XRD measurements show that La^{3+} forms solid solution efficiently compared with all the other ions used and, therefore, the
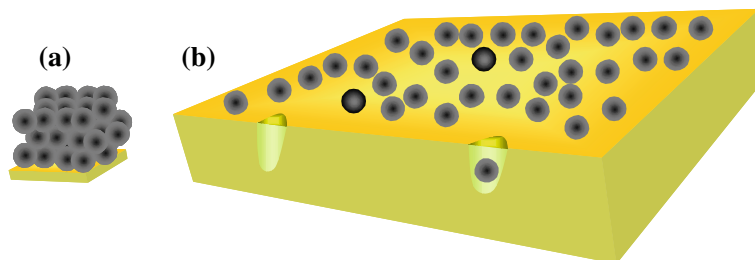

Figure 10. Depiction of primary soot particle in tight contact with (**a**) CeO_2_1000 and (**b**) $CeLaO_x\_1000$ catalysts under ideal spreading.

catalyst CeLaO$_x$_1000 is also relatively more active. With a Pr$^{3+/4+}$ though it is not possible to fully ascertain the extent of solid solution formation with CeO$_2$. Looking, however, at the improvement with regards to the surface area ($\sim$11 m^2 g^{-1}), we can assume that it forms solid solutions efficiently. The CePrO$_x$_1000 activity is less than that observed for CeLaO$_x$_1000. However, in spite of its lower surface area of CePrO$_x$_700 (44 m^2 g^{-1}) showed slightly better soot conversion compared with CeLaO$_x$_700 (48 m^2 g^{-1}). Most of the praseodymium ions are expected to be present in 4+-oxidation state in CePrO$_x$ catalyst, which leads to a surface enriched with oxygen responsibly for the soot oxidation. However, the presence of the non-reducible ions such as La^{3+}, leads to a surface enrichment with oxygen vacancies, especially when it is segregated to the surface, which could decrease the overall oxidation function of the catalyst.

The improvements in the activity of the various reactions observed in the rare-earth ion-doped CeO$_2$ based catalysts are mainly correlated to the changes in catalyst redox properties. However, there is no indication of such correlation in the soot oxidation activity. This is further supported by soot oxidation carried out in He (Table 3 and Figure 8). Higher amounts of soot is oxidised over PrO$_x$_1000 under He. The bulk reduction of CeLaO$_x$_1000 and CeO$_2$_1000 can be expected to take place at higher temperature and, therefore, this did not result in a significant soot oxidation under He. However, in the presence of oxygen the CePrO$_x$_1000 and CeLaO$_x$_1000 catalysts are more active compared with PrO$_x$_1000 (not shown). This suggests that the involvement of only surface reducible layers in soot oxidation is taken place. Furthermore, the high activation energy for the soot oxidation involving bulk oxygen (around 250 KJmol^{-1}) suggests that the bulk oxygen diffusion to the surface is much slower and only the surface lattice oxygen is important in determining soot oxidation under oxidising conditions.

The estimation of the activation energies in the tight contact mode using catalysts will be reasonably better than that calculated using the loose contact mode. Because of the good contact between the catalyst and the soot, the heat dissipation will be more efficient and its effect will not influence the activation energy calculations. The apparent activation energy (E_a) is found to be around 150 KJmol^{-1} (Table 2) over the various catalysts studied under the different contact conditions. The E_a values are also found to be similar at the different soot conversion levels, though the nature of soot could have changed with the conversion. The unchanged E_a values under various conditions in the present study indicate that the catalyst only increases the rate of the reaction, through the well-known redox-cycle, Ce^{4+}↔Ce^{3+}.

The soot oxidation activity with NO+O$_2$ (Figure 9) indicated that the oxygen enriched catalyst surface, which is present in CeO$_2$ or in CePrO$_x$, is responsible for the higher soot oxidation activity. More detailed catalyst characterisation and soot oxidation activity NO+O$_2$ will be presented elsewhere.

5. Conclusions

In general the rare-earth ion-modified CeO$_2$ catalysts lead to an improved soot oxidation activity using O$_2$ due to stabilisation of surface area. CePrO$_x$ shows superior activity with both O$_2$ and NO+O$_2$. To take full advantage of the catalyst in the soot oxidation with O$_2$ in the real systems, the external surface area of the reducible catalyst should be increased as it is shown there is a strong correlation in decreasing soot oxidation temperature. To take the full advantage of NO present in the exhaust gas, the increases in both total and reducible surface area are necessary. Furthermore, similar catalysed soot oxidation activation energies (150 KJmol^{-1}) with O$_2$ indicated that the catalyst is only facilitating the oxygen transfer to the soot surface and is not changing the reaction mechanism. The bulk oxygen storage capacity is not a very important parameter in determining the soot oxidation over the studied catalysts. Based on the above studies better catalysts can be designed for an improved soot oxidation.

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