

Diesel soot combustion activity of ceria promoted with alkali metals

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Abstract

Catalytic oxidation technique for reducing particulate emissions from diesel engines is based on the use of a catalyst in order to decrease the combustion temperature of soot down to the same range of temperature of exhaust gases. The main objective of this work was to investigate the promotional effect of alkali metals in the soot combustion activity of ceria-based catalysts. Our study pointed out that the order of activity in soot oxidation depends on the nature ($\text{Cs} > \text{Rb} \approx \text{K} > \text{Na}$) and the amount of the metal. Another key factor resulted to be the choice of the precursors (chlorides are almost inactive). The activity is correlated to the presence of carbonate species, carbon–oxygen complexes (C–O–M, with M alkali metals) being the active sites; these species react with carbon of soot producing CO_2 and a reduced form “C–M” that is reoxidized by molecular oxygen to reform C–O–M. A major drawback resulted to be the loss of metal and consequent deactivation after prolonged aging at 1023 K, especially under water-containing atmosphere.

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1. Introduction

The popularity of the diesel engine vehicles is due to their higher fuel efficiency and their longer durability with respect to gasoline ones. The relatively high oxygen concentration (air/fuel ratio is higher than 20) leads to a low-temperature combustion and a lower emissions of CO and hydrocarbons. The main problem in diesel exhaust is the higher level of particle and NO_x emissions that cannot be converted by using a traditional oxidation/three way catalyst. Indeed, the time of residence of particles in the channel of monolith is too short for a complete oxidation, while the difficulties in the reduction of NO_x are a drawback of the high oxygen content in the exhaust gas.

In the last years, the attention on negative effects of diesel particulate matter on health has grown because human body has no protective measures against PM10; moreover recent studies indicate particulate matter as a potential human carcinogen agent. Because of the more strict laws on emission, various emission–reduction technologies have been developed: among them, filtering followed by catalytic oxidation is one of the more promising [1]. Catalytic oxidation technique is based on

the use of a catalyst in order to decrease the temperature of combustion of soot in the same range of temperature of exhaust gases. This approach is affected by several drawbacks: catalytic filter regeneration is very complex because of the very variable conditions of reaction, and the process is quite slow because of the poor soot–catalyst contact. In fact, the solid particles are immobile when deposited and due to their size they cannot penetrate into catalyst’s pores. Another important operative constraint is represented by the wide range of temperature expected for the exhausted gases (from 473 to 873 K), depending upon engine load. Consequently a useful catalyst has to operate efficiently at low temperatures but has also to be thermally stable.

Several catalyst formulation for soot oxidation has been studied in the last years, and the most promising are catalysts based on Cu/K/M/(Cl) [2–4], where M is V, Mo or Nb, or systems based on Co/K/MgO or CeO_2 [5–7]. Ceria alone or in combination with other oxides is also active in oxidation of carbon particles [8–14] and it is believed that the mechanism of action is based on redox activity of the material. That is the effectiveness of the catalyst can be related to its ability to deliver oxygen from the lattice to the gas phase (or better to the soot reactant) in a wide temperature range [15].

The presence of alkali metals (AM) has been shown to bring substantial benefit to several catalyst formulations for soot

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oxidation [3–6,16,17]; they are suggested to increase the catalyst/soot contact by increasing surface mobility and to favor the oxidation of soot by consuming the carbon to form carbonate species during soot combustion.

Potassium and alkali metals in general are also very active in carbon gasification [18–25]. In addition, the use of ceria and potassium additives contributes to the formulation of active dehydrogenation catalysts; in particular the use of potassium helps in the elimination of carbon deposits that are detrimental for the activity of the catalyst [26].

These data suggested us to investigate, in this paper, potassium and other alkali metal additives as promoters in cerium oxide systems for soot oxidation. The effect of different metals, precursors and loading is evaluated and a likely mechanism of action is put forward based on our evidence and on literature review results. The effect of prolonged hydrothermal aging is also considered in the evaluation of these formulations.

2. Experimental procedures

2.1. Catalyst preparation

AM doped catalysts (M = Na, K, Rb and Cs) were prepared by incipient wetness impregnation of the support (CeO₂, Grace Davison) with an aqueous solution of the appropriate metal salts (MOH, M₂CO₃ and MCl). AM loading was in the range of 3–13.5 wt.%. The catalysts will be indicated as CeXM where X indicates the amount of alkali metal (wt.%) and M the metal. After deposition the catalysts were dried at 373 K overnight and calcined in air at 773 K for 3 h (fresh samples) and at 1023 K for 12 h (aged samples). Additional tests were carried out on potassium deposited on TiO₂ (P25 Degussa) and ZrO₂ (Grace Davison).

2.2. Catalyst characterization

All samples were characterized by X-ray powder diffraction (XRD), porosimetry (BET) and temperature programmed reduction (TPR).

XRD patterns were recorded on a Philips X'Pert diffractometer operated at 40 kV and 40 mA using nickel-filtered Cu K α radiation. The spectra were collected using a step size of 0.02° and a counting time of 40 s per angular abscissa in the range of 20–145°. The Philips X'Pert HighScore software was used for phase identification. The mean crystalline size was estimated from the full width at the half maximum (FWHM) of the X-ray diffraction peak using the Scherrer equation [27] with a correction for instrument line broadening. Rietveld refinement [28] of XRD pattern was performed by means of GSAS-EXPGUI program [29,30].

Redox activity was measured by TPR experiments: samples (50–60 mg) are heated at a constant rate (10 K/min) in a U-shaped quartz reactor, from r.t. to 1273 K in a flowing hydrogen/argon mixture (30 ml/min, 5.22% H₂ in Ar): the hydrogen consumption was monitored using a thermal conductivity detector. In order to obtain a quantitative

evaluation of H₂ consumed, the apparatus was calibrated with the reduction of CuO to Cu. Analysis of products was carried out with an on line quadrupole mass spectrometer (Balzers).

Surface areas were measured with a Carlo Erba Sorptomatic 1990 instrument using the BET method.

2.3. Catalytic activity

The catalytic activity for the combustion of soot [31–34] was determined from peak-top temperature (T_m) during temperature programmed oxidation (TPO) of catalyst–soot mixtures. Each catalyst was accurately mixed with soot (Printex-U soot by Degussa AG) in a mortar for 10 min in order to achieve a tight contact [35]. A catalyst/soot weight ratio of 20:1 was adopted. The kind of contact between catalyst and soot is extremely important [1,36]: the tight contact conditions are poorly representative of the real working conditions experienced by the catalyst deposited in a catalytic trap, but they allow a rapid screening of catalysts under reproducible experimental conditions.

During the TPO measurements 25 mg of mixture were heated at a constant rate (10 K/min) in a quartz reactor, while the gas flow (N₂ with 6% of O₂) was kept fixed at 400 ml/min. The catalyst temperature was checked by a chromel–alumel thermocouple, located on the catalyst bed. The outlet flow was monitored by a gas IR and paramagnetic analyzers (Magnos 106 and Uras14, ABB), recording the percentages of O₂, CO and CO₂ at the outlet of the reactor.

A series of tests were carried out for catalyst/soot mixtures, in order to verify the reproducibility of results; the peak temperatures show differences always less than 5 K.

3. Results and discussion

3.1. The effect of the nature and the amount of alkali metals

All CeO₂-based samples prepared in this study, either fresh or after aging, were characterized by surface area and XRD measurements and their characteristics are summarized in Table 1. XRD features show only peaks attributable to cerium oxide and the cell parameters obtained by Rietveld refinement suggest that alkali metals do not modify ceria lattice parameter (Table 1). Surface area values indicate that deposition of alkali metals remarkably reduces available surface, reduction being dependent on the type of metal and on its quantity. Aging under air causes also a significant sintering evaluated from surface area loss and increase of particle size.

Soot combustion studies were carried out under TPO conditions in a micro flow reactor. The peak temperature for uncatalyzed soot oxidation is 858 K, and this result is close to the values reported by other authors [37]. Catalytic activity results on CeO₂ with different amount of K, deposited as KOH are shown in Figs. 1 and 2. Bare cerium oxide is an active support: it does oxidize soot at 663 K but, after aging, it experiences a remarkable loss of activity (T_{max} at ca. 700 K) correlated to a remarkable loss in specific surface area. The best results (with a

Table 1
Characteristics of samples used in this study

Sample	SA (m ² /g)		Particle size ^a (Å)		Cell parameters ^b (Å)	
	Fresh	Aged	Fresh	Aged	Fresh	Aged
CeO ₂	57	22	70	112	5.4111(1)	5.4108(1)
Ce3K	32	12	144	580	5.4114(3)	5.4108(1)
Ce6.5K	22	13	224	580	5.4110(2)	5.4108(1)
Ce10K	20	14	209	475	5.4112(1)	5.4105(1)
Ce13.5K	15	8	309	505	5.4112(1)	5.4103(1)
Ce10Na	2	<1	374	753	5.4110(1)	5.4113(1)
Ce10Rb	14	6	122	424	5.4109(1)	5.4106(1)
Ce10Cs	18	4	128	402	5.4107(1)	5.4105(1)

^a Calculated by Scherrer equation.

^b By Rietveld refinement.

T_{\max} of 643 K) are achieved using CeO₂ promoted with 10 wt.% of potassium; remarkably, after calcination, this temperature does not change significantly. Results of TPO experiments point out that there is a minimum amount of promoter (ca. 6 wt.%) needed to induce a beneficial effect in soot oxidation and a maximum amount that provides the best performance (10 wt.% shows the best performance; a bigger amount of promoter decreases the activity). In addition the presence of potassium stabilizes also the activity of CeO₂ after calcination, but this is not correlated to a stabilization of the ceria surface area, as the deposition of alkali metals reduces the available surface. This effect is very important because a useful catalyst has to operate efficiently at low temperature, but has to preserve activity also at high temperature. For every composition, exception made for 3 wt.%, we can observe this stabilizing effect, being T_{\max} for fresh and aged samples very similar.

In order to verify if during aging the rearrangement of potassium and interaction with the support could explain the stabilization effect, we have calcined CeO₂ at 1023 K for 12 h

before addition of potassium. TPO results are shown in Fig. 3. The activities of the catalysts obtained with the two different methods are similar thus ruling out a responsibility of potassium and ceria interaction in the activity promotion.

The behaviour of the other AM (Na, Rb, Cs) is shown in Fig. 4. A typical curve with a minimum in the oxidation temperature between 6.5 and 10 wt.% of promoter is observed. Moreover, decreasing along the group, the catalytic activity increases with cesium hydroxide being the most efficient catalyst in soot oxidation.

In order to evaluate the role of the precursor we compared also the results by using different precursors in the deposition. In the case of potassium, KOH, KCl and K₂CO₃ have been added (10 wt.% of potassium on CeO₂) and the results are shown in Fig. 5. Similar results have been obtained in samples promoted with KOH and K₂CO₃, while the addition of KCl results in an increase of ca. 100 K in the oxidation temperature.

Fig. 6 shows the temperature programmed reduction profiles of ceria and ceria doped with increasing amount of potassium. The reduction feature of pure ceria is well known [38,39] and it shows the characteristic bimodal profile with two peaks at low (ca. 770 K) and high (ca. 1100 K) temperature attributable respectively to reduction of small crystallites and/or surface ceria and to reduction bulk and large ceria crystallites. Addition

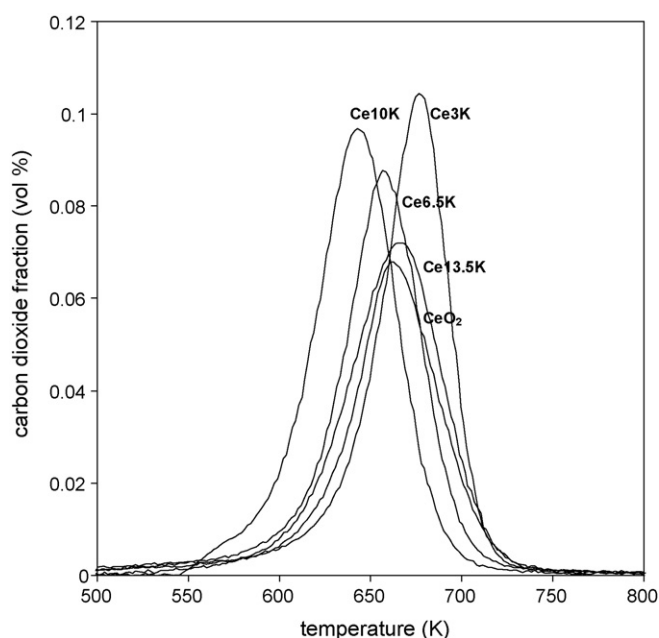


Fig. 1. TPO profiles of CeO₂ doped with different amount of K (3–13.5 wt.%) as KOH.

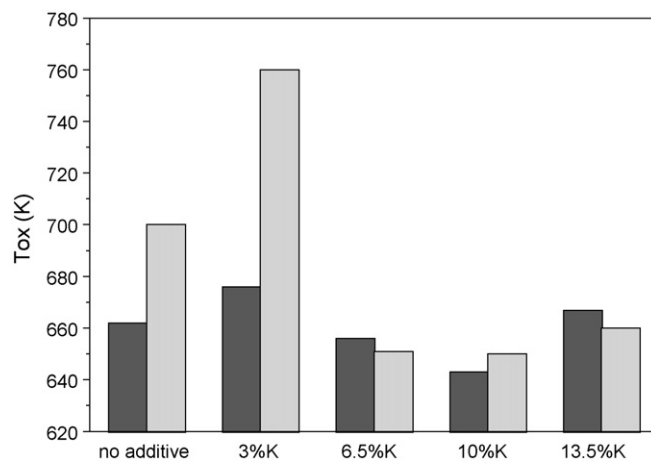


Fig. 2. TPO results of CeO₂ doped with different amount of K (3–13.5 wt.%) as KOH, fresh (dark) and calcined (light) samples.

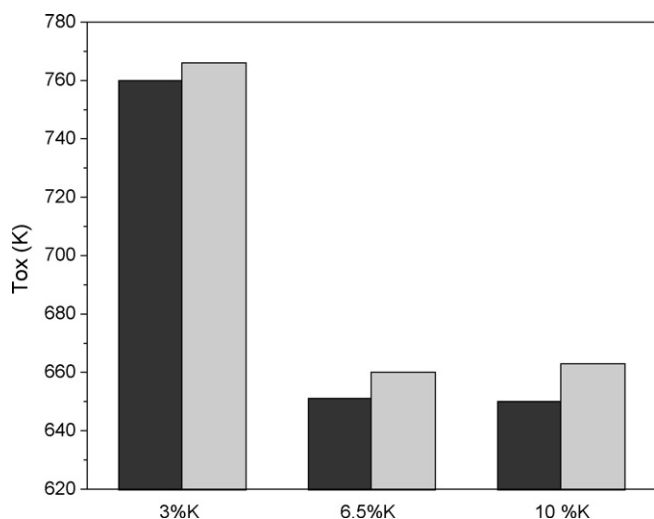


Fig. 3. TPO results of aged Ce(3–13.5)K samples prepared by adding KOH on fresh (dark) and aged (light) CeO₂.

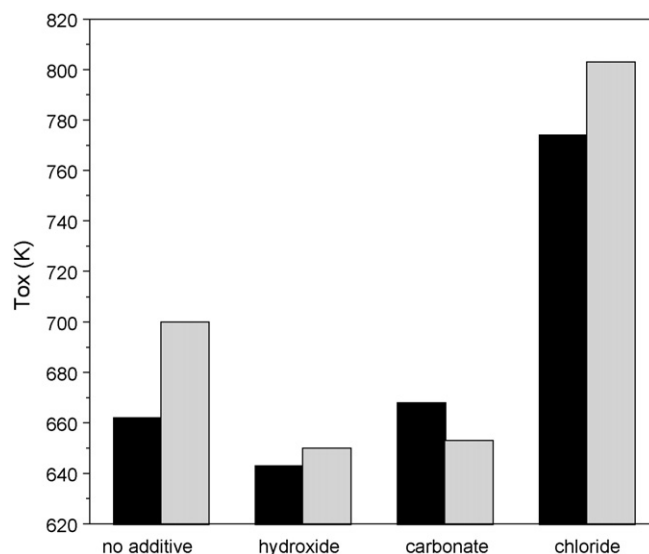


Fig. 5. Comparison of catalytic activity among different precursor of potassium added on CeO₂, fresh (dark) and calcined (light) samples.

of potassium slightly modifies the shape and position of the low temperature peak and it strongly increases the hydrogen consumption that characterizes the second peak. Quantitative analysis of the reduction profiles is reported in Table 2, which shows that the amount of oxygen extracted (equivalent to hydrogen removal) increases with the addition of potassium up to a loading of 10 wt.%; then a plateau is reached and for higher amount of potassium the oxygen extracted is almost constant. Analysis of the reaction products from reduction shows that in the presence of potassium the majority of oxygen extracted is in the form of CO, while modest quantities of CO are formed in the absence of potassium. Interestingly, doping using KCl as precursor does not result in CO formation. Negligible formation

of CO in the TPR of pure ceria has been sometimes observed and it can be due to reduction of residual carbonates operated by hydrogen in the range of temperature 700–900 K [40]. In our case the presence of potassium strongly enhances formation of surface carbonates, which in H₂-TPR are reduced to CO and H₂O. As an example, Fig. 7 shows the CO and H₂O profiles in the TPR of pure ceria and ceria doped with potassium from KOH compared with similar TPR profiles of a typical “non reducible” support like ZrO₂. In both cases (K-promoted CeO₂ and ZrO₂) a large amount of CO is formed in the range of temperature 650–900 K, independent of the reduction characteristics of the support (see Table 3). Therefore the presence of potassium does not modify the reduction characteristics of

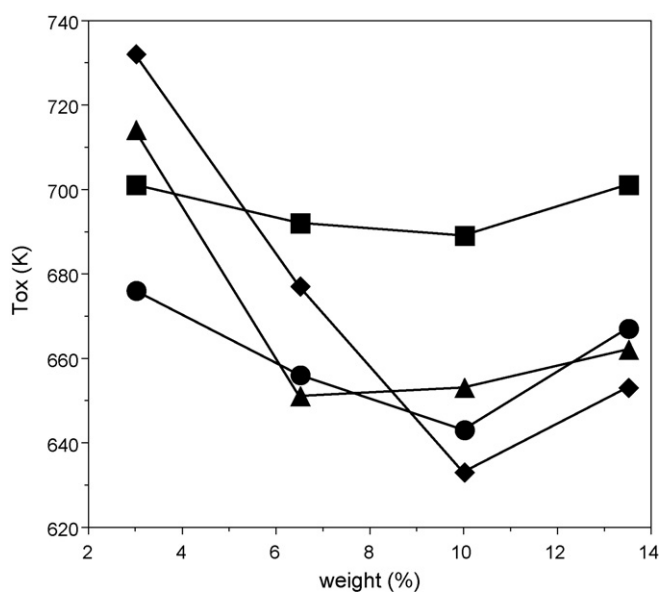


Fig. 4. TPO results for CeO₂ doped with different amount (3–13.5 wt) of M (Na, K, Rb, Cs) as MOH. TPO results of aged Ce(3–13.5)K samples prepared by adding KOH on fresh (dark) and aged (light) CeO₂.

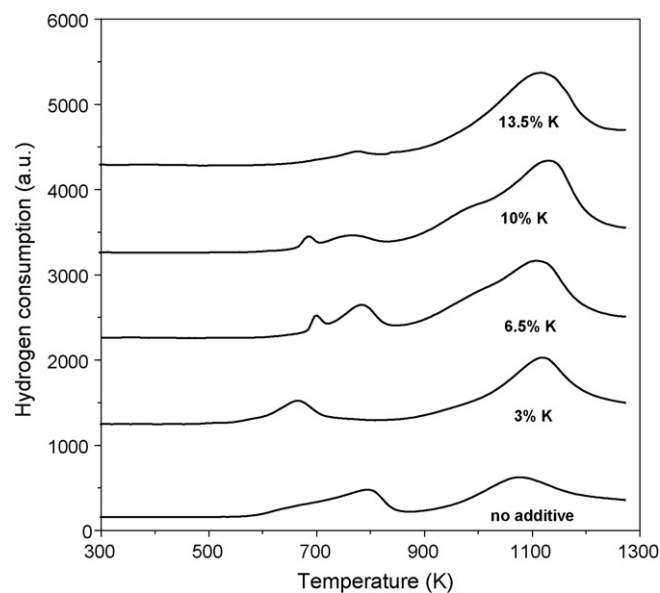


Fig. 6. Experimental TPR profile of pure CeO₂ and CeO₂ doped with different amount (3–13.5 wt.%) of K as KOH.

Table 2
Oxygen extracted in TPR experiments for pure cerium and CeO₂ doped with K as KOH (fresh samples)

Sample	O ₂ extracted × 10 ⁴ (mol/g sample)
CeO ₂	6.40
Ce3K	7.13
Ce6.5K	9.58
Ce10K	10.46
Ce13.5K	10.16

Table 3
CO formation in H₂-TPR of bare and doped CeO₂ and ZrO₂ for TPR profiles see Fig. 6

Sample	CO (μmol/g)
CeO ₂	71
CeK	1534
ZrO ₂	17
ZrK	2073

ceria but it strongly enhances formation of surface carbonates. A similar reduction behaviour is observed by doping ceria with the other alkali metals (see Fig. 8). Quantitative analysis (Fig. 9) shows the oxygen amount extracted in TPR experiments per mol of alkali metal for all the investigated samples. This value increases upon descending the AM group: the contribution of sodium is the smallest one; cesium

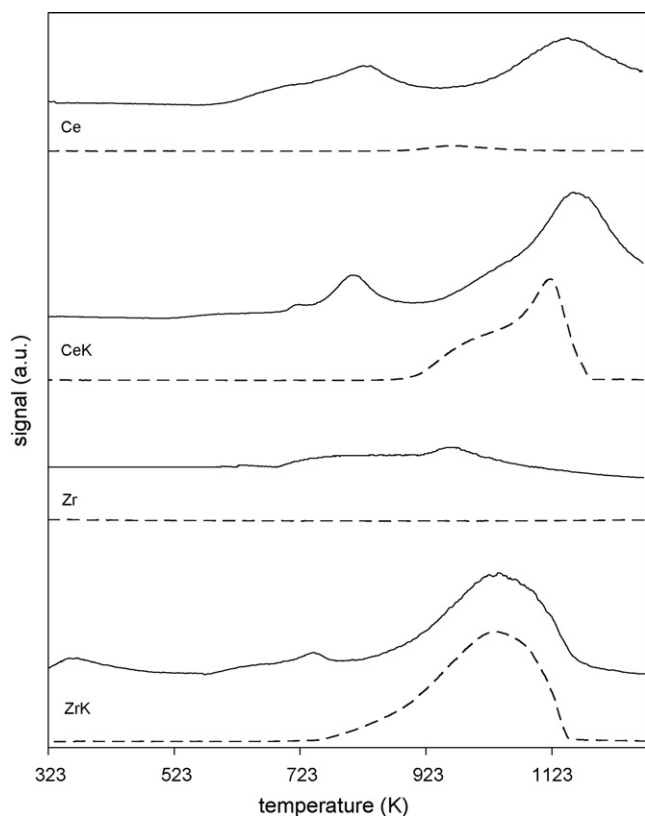


Fig. 7. CO (broken line) and H₂O (solid line) profiles in the TPR of undoped and K-doped CeO₂ and ZrO₂.

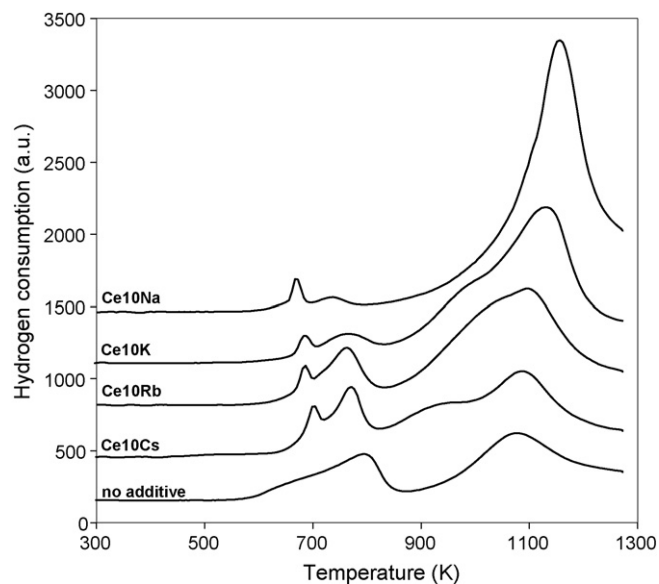


Fig. 8. Experimental TPR profile of pure CeO₂ and CeO₂ doped with alkali metals as MOH (10 wt.%).

conversely, produces the higher amount. As we have pointed out previously, the amount of oxygen (apart from the contribution of oxygen from ceria, which is similar in all samples) is correlated to the reduction of carbonate species; it is shown that by doping with heavier alkali metals the amount of carbonate adsorbed on support increases.

The overall behaviour of ceria promoted with alkali metals which shows a maximum of activity as a function of loading, can now be explained by considering two opposite factors. For this purpose let us consider Fig. 10 which shows the activity of K-promoted cerias (fresh samples), the oxygen extracted in TPR experiments and the surface area against the loading of potassium. We have previously pointed out that the soot oxidation temperature shows a minimum at around 10 wt.% of potassium. Remarkably, the amount of oxygen extracted increases progressively when the amount of potassium increases until 10% of K, where a plateau is reached. On the

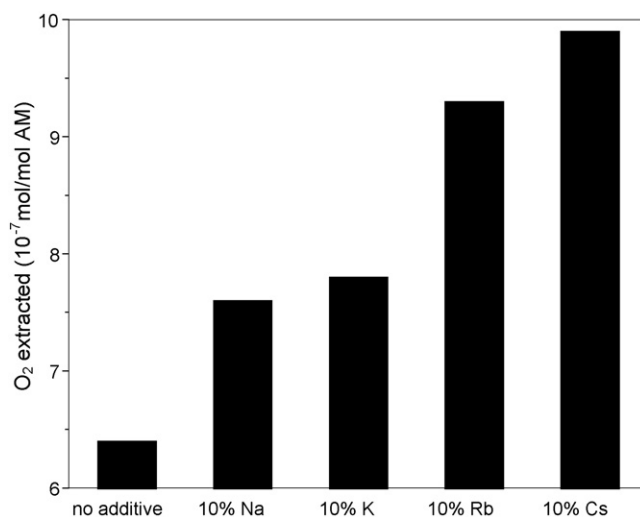


Fig. 9. O₂ extracted per mol of alkali metals calculated from TPR experiments.

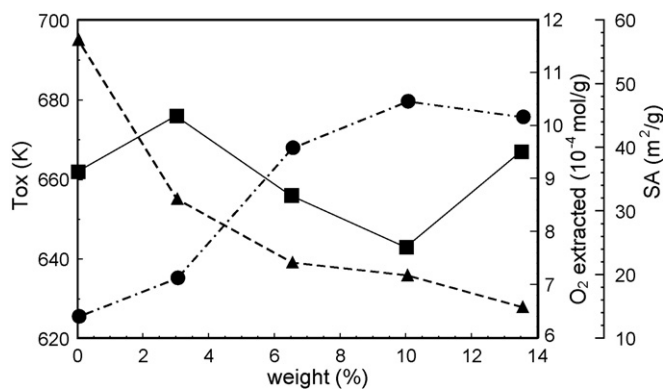


Fig. 10. Comparison among activity (left, ■, —) surface area (right, ▲, ---) and O₂ extracted (right, ●, - - -) versus the amount of potassium in CeO₂ promoted with K as KOH (fresh samples).

contrary, surface area decreases when the amount of potassium increases. Hence, the combination of these two opposite factors can explain the overall activity behaviour with a minimum in T_{\max} versus the amount of K.

3.2. The role of alkali metals: mechanism of reaction

Despite several reports in literature on catalysts containing potassium [37,41–43] for soot oxidation, the role of this element is still unclear and no evidence were found in the literature for doping with other alkali metals. On the other hand several mechanistic studies were carried out in order to understand the role of potassium and the other alkali metals in gasification of carbonaceous materials reaction [44–47]. In these cases it was pointed out the important role of both surface and bulk properties. It is generally accepted that oxygen-containing species play a key role in the catalytic activity of alkali metal compounds during carbon gasification.

Based on these results, we can put forward two different mechanisms to explain the increased activity operated by AM. In the first one, AM are supposed to act with a redox mechanism correlated to the redox cycle of cerium oxide. The catalytic role of potassium can be attributed to its effective participation in an oxidation–reduction cycle between K_xO_y and K_xO_{y+1} [48,49]. The redox cycle of potassium can be correlated to that of cerium oxide: K_xO_y is oxidised by O₂ to give K_xO_{y+1} ; then there is an oxygen transfer from K_xO_{y+1} to reduced ceria to restore CeO₂ which can subsequently oxidize soot particles.

In the second hypothesis, the activity of AM is correlated to the presence of carbonate species. The activity can be interpreted in terms of oxygen exchange mechanism in which the carbon–oxygen complexes (C–O–AM) are the active site [50,51]: these species react with carbon of soot producing CO₂ and a reduced form “C–AM” that is reoxidized by molecular oxygen to reform C–O–AM.

Although the catalytic results on K-promoted cerium oxide might suggest that alkali metals act with a redox mechanism correlated to the redox cycle of CeO₂, additional tests conducted on “redox-inactive” supports like TiO₂ and ZrO₂ (where promotion by potassium is still observed, see Fig. 11),

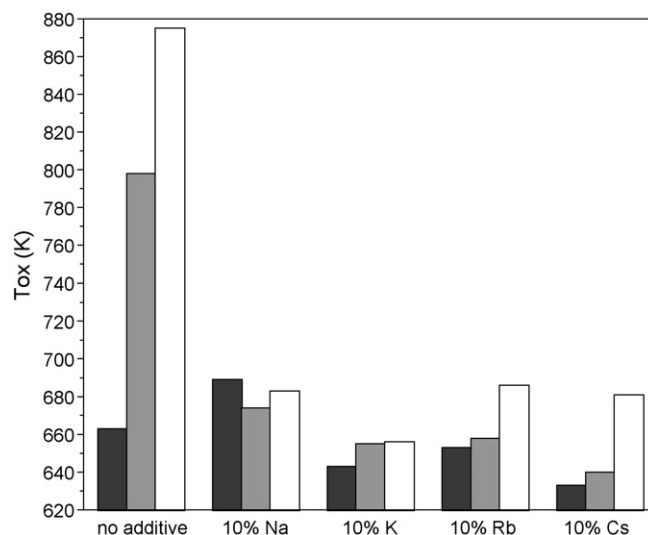
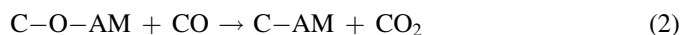


Fig. 11. TPO results of CeO₂ (black), ZrO₂ (grey) and TiO₂ (white) doped with M (Na, K, Rb and Cs) added as MOH. For zirconia- and titania-based catalysts surface area measurements indicate that the available surface decreases from 79 to 19 m²/g, observed in undoped zirconia and titania, to 23–34 m²/g and to 6–10 m²/g for the doped systems, respectively.

and analysis of CO profiles from TPR curves, indicate a likely contribution of carbonates in the reaction.

The activity can be interpreted in terms of oxygen exchange mechanism in which the carbon–oxygen complexes (C–O–AM) are the active site, i.e. the AM promote the oxidation of carbon site located near the catalyst. The effect of alkali metals is to favor the chemisorption of molecular oxygen with the formation of carbon surface complexes that eventually reacts with soot. Consequently, the catalyst is an oxygen carrier that acts transferring the oxygen from the gas phase to the carbon surface.

We can summarize the mechanism of reaction of alkali metals in the following sequence:



where AM is the alkali metal (Na, K, Rb and Cs), C–AM represents the reduced form of carbon–oxygen complexes and C–O–AM is the oxidized form. The oxidized form reacts with carbon of soot to liberate CO (Eq. (1)); some amount of it is desorbed from the system, the other reacts with the oxidized specie to produce the reduced form and CO₂ (Eq. (2)). The reduced species C–AM react then with molecular oxygen (Eq. (3)) to give C–O–AM and the overall reaction ($\text{C} + \text{O}_2 \rightarrow \text{CO}_2$) is a net consumption of carbon by gaseous oxygen. The role of alkali metals is that of promoting the dissociative chemisorption of oxygen.

Several studies on carbon gasification promoted by alkali metals pointed out the formation of carbon–oxygen complexes (C–O–AM) [50,51]. Moulijn and co-workers [52] and Yuh et al. [53,54] studied the interaction between carbonaceous surface

and alkali metals with DRIFTS and FTIR, respectively; IR spectra show bands typical of surface oxygen-complexes. Moreover, in excellent agreement with our results, Yuh found that the activity of KOH and K_2CO_3 is very similar and that KCl is not active. In particular, Yuh found that all samples, except for those prepared from KCl, presented two characteristic C–O–AM IR bands at 1050 and 1400 cm^{-1} , thus correlating the activity to surface oxygen complexes. This would explain also the absence of relevant CO formation we observed in the TPR of K–CeO₂ derived from chlorides. A possible explanation of this behaviour is the formation of stable salts in the presence of chlorides ions, as pointed out by Moulijn and Kapteijn [55], due to the strong interaction of the latter with alkali metals. Potassium cation can interact with carbon and with Cl^- ; if the anion is strong, as in the case of chlorides, K^+ interaction with carbon is not favoured [56] and the net effect is the formation of a smaller amount of carbonate species which are the active sites of the reaction.

As far as the order of reactivity is concerned (Cs > Rb ≈ K > Na), this could be related to the redox cycle efficiency, i.e. oxygen transfer from catalyst to carbon and release of carbon–oxygen complexes from carbon surface. The lower electronegativity of Cs compared to the other would imply that dissociative chemisorption of O₂ occurs more readily on Cs and that a stronger electrostatic attraction with the surface oxygen would decrease the possibility of agglomeration, thus resulting in better dispersion [49].

3.3. The effect of hydrothermal aging

Different aging conditions were also applied to check for stability under more severe conditions, closer to the “real” applications. All samples were subjected to aging for 50 h

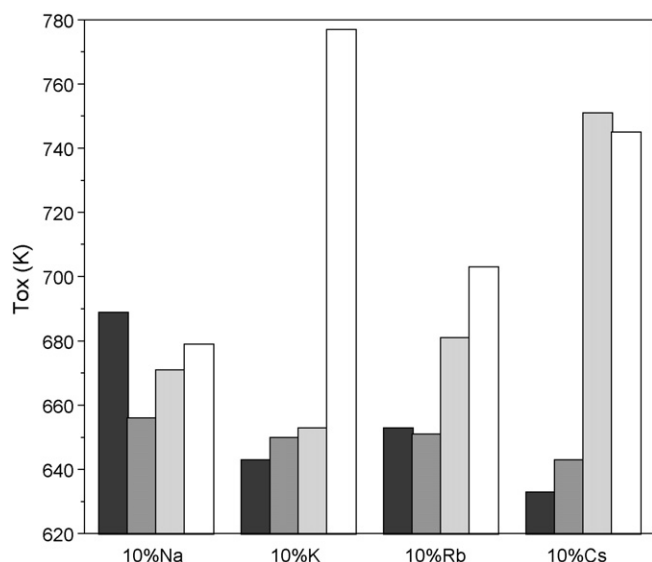


Fig. 12. TPO results of alkali metals added on CeO₂ after different thermal treatment: fresh (black), calcined 12 h under air at 1023 K (dark grey), calcined 50 h under air at 1023 K (light grey) and calcined 50 h at 1023 K under air/water flow (white).

Table 4

AM loss after calcination and under air, H₂O/air atmospheres at 1023 K for 50 h

Composition	wt.%
Ce10Na fresh	7.53
Ce10Na air aging	6.5
Ce10Na H ₂ O/air aging	1.1
Ce10K fresh	6.83
Ce10K air aging	4.22
Ce10K H ₂ O/air aging	0.46
Ce10Rb fresh	9.43
Ce10Rb air aging	2.18
Ce10Rb H ₂ O/air aging	4.05
Ce10Cs fresh	8.80
Ce10Cs air aging	0.35
Ce10Cs H ₂ O/air aging	0.70

under air and water (10%)/air mixtures at 1023 K. This aging procedure included also cooling down at room temperature twice during the treatment. In order to obtain these mixtures a saturator was added before the inlet of the furnace.

On the aged samples we carried out TPO experiments to check the activity (Fig. 12) and elemental analysis (Table 4) in order to evaluate changes in the alkali metals content. It is shown that severe aging dramatically influences the activity of the catalysts; in particular the presence of water at high temperature causes an almost complete loss of metal (with the exception of Rb) with severe deactivation (especially for K and Cs). Overall the best results in terms of thermal resistance are achieved with Na systems where the fresh sample is the less active among the series of alkali metals, but it resists better to hydrothermal treatments. Formation of volatile compounds, enhanced in the presence of water, seems to be the reason for the loss of active phase with consequent deactivation [55,57].

4. Conclusion

In summary we have shown that alkali metals promote the activity of ceria for soot oxidation. The promotion seems to be rather independent on interaction between ceria and the metal through a redox cycle, instead it might be correlated to surface carbonate complexes which are formed after deposition of alkali metals. This explains why “redox inactive” supports like TiO₂ and ZrO₂ still benefit from AM deposition.

Activity is dependent on the nature and the amount of the metal. Chloride precursors resulted in poor final catalysts while hydroxide and carbonates are more efficient precursors. Mild aging conditions does not influence the promotion activity of the catalysts, while aging under more severe conditions in the presence of water causes a significant loss of activity, thus excluding a potential use of these promoters under “real” conditions.

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