

Catalytic systems based on Ce, Zr, K for soot oxidation

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Systems based on Ce-Zr are used in catalytic converters for their oxygen storage ability. Recently, their application for soot abatement is under investigation. In this paper, preliminary results of the performance of Ce-Zr systems with the addition of K are reported by varying potassium content and calcination temperature. The powder catalysts were prepared by a variant of the citrates route developed at University of L'Aquila. Characterization of the catalysts after calcination was performed by different techniques: profile fitting of the XRD data, estimation of surface composition by XPS, evaluation of catalytic performance by temperature programmed oxidation tests of the soot-catalyst mixture and of redox properties by carbothermic reduction and subsequent oxidation in a high resolution thermobalance. The characterization by XRD showed that the system maintains the crystallographic structure Fm-3m and that the potassium is segregated on the grain boundaries. The catalytic activity results showed that the systems are particularly active even after 10 hours of calcination at 900°C in fluidized bed. This temperature is high enough to get reasonably stable systems for practical applications. Moreover, the soot oxidation rate has a maximum at 368°C in the sample with the best performance, therefore in the range of temperatures of diesel engine exhaust gases. The XPS data showed the presence of Ce, Zr, K and also of significant amount of Cl. Other formulations were prepared by adding small amounts of the different potassium halides.

1. Introduction

Ceria – zirconia systems are widely utilized in the catalytic converters of the last generation. Indeed these systems display an usual oxygen storage capacity: i.e. they are able to release oxygen in reducing conditions while in oxidizing conditions are able to reincorporate it back. This peculiar property is due to the structure of the Ce-Zr solid solutions which keeps almost fixed the position of cerium cations inside the crystal lattice during the redox cycles. Therefore a relevant amount of studies have been performed by the catalytic converters manufactures in order to get the necessary know-how, but also in the patent and open literature (Trovarelli, 2002).

On the contrary it is less known that this systems when doped with potassium may display an interesting activity in the soot abatement. Catalysts for the soot oxidation are usually based on noble metals such as platinum. Apart from the costs of the noble metals, the utilization of platinum significantly increases the oxidation of NO to NO₂,

which is particularly environmentally undesired (this property is called PM10-NO_x trade off). Therefore the research and the development of new catalytic systems based on non-noble metal elements may be of practical interest and environmentally relevant. In this paper we report the results obtained on Ce – Zr – K systems which are found to be active in the soot abatement at temperature lower than 400°C, therefore in the range of temperatures of diesel engine exhaust gases.

2. Experimental

Catalysts were prepared according to the variant of the citrate method developed at L'Aquila University (Villa, 2007). Five steps are foreseen by this particular manufacture procedure: i) preparation of aqueous solutions containing the desired cations, citric acid and ammonium hydroxide. No nitrates should be utilized in this step. Therefore zirconium propoxide, cerium and potassium acetate were used for this purpose. They were added to an aqueous solution of citric acid and after dissolution were put together in a single beaker and neutralized with ammonia; ii) concentration in a rotavapor was carried out in about 3 hrs in order to reach a final temperature of 90°C and a pressure of 20 mbar; iii) final drying to remove the residual amount of water and ammonia was performed by a slow heating under vacuum up to 230°C. A meringue of solid consistency is obtained which is ground and sieved in order to obtain a powder finer than 100 mesh; iv) decomposition of the organic substance (citric acid) was performed in a fluidized bed at temperature around 330 – 390 °C, utilizing a gas flow of 1.5% O₂ in N₂ stream; v) final calcination performed in a fluidized bed reaching finally a temperature (T_c) of 500 or 700 or 900°C for 10 hrs. A few samples were also calcined at lower temperature (400°C) as described in Table1. Various catalysts (K_xZr_{0.25}Ce_{0.71}O₂) were also prepared with different amount of potassium x=0.04-0.44 (1-10wt% nominal content).

X-ray diffraction (XRD) patterns were obtained with Cu K α radiation (Philips, model 3710). The dimensions of the coherently diffracting domains (crystallite size) were determined from the full width at half – maximum (FWHM) of the XRD peaks using the Scherrer equation. The various phases were identified by the search – match method (JCPDS data base), the phase compositions and cell parameters being determined with great accuracy by full profile fitting refinement (Rietveld method), using the Hill & Howard procedure, the WYRIET program, and the structural data necessary from ICDD (Young, 1993; Hill et al., 1987; Shannon et al., 1969).

Specific surface area (SSA) data were obtained by the B.E.T method with a Micromeritics instrument (ASAP 2000).

Catalytic activity tests towards soot oxidation were carried out on mixtures of soot and catalyst prepared by carefully grinding the two components in an agate mortar in order to assure an intimate contact. The initial soot/catalyst mass ratio was 0.1. The soot utilized was collected at the exhaust of a gas oil burner fed with commercial gas-oil (H/C molar ratio: 1.75, sulphur content: 0.05wt%). The soot samples (obtained at $\alpha=18$) present particle dimensions in the range 33-58nm with an average size of 48 nm and a specific surface area of 112 m²/g, as previously reported (Palma et al., 2007).

The temperature programmed catalytic activity tests were performed in a high resolution thermobalance (TA Instruments Q500) in the temperature range 25-700°C, with a heating rate of 10 °C/min and an air flow rate of 60 cm³/min (STP).

In the same apparatus temperature programmed reductions with soot as reductant and re-oxidations with air were carried out. The experimental procedure consists of: i) helium flow temperature-programmed reduction of a soot-catalyst mixture, in which the

soot is used as a reducing agent (carbothermic reduction); ii) air flow temperature-programmed oxidation of the previously reduced mixture.

3. Results

Figure 1 shows the XRD spectrum for the sample with nominal content of potassium 4% after calcination at 900°C for 10 hrs in fluidized bed. XRD refinement shows that the sample is fully monophasic with Fm3m structure.

Also all the other samples measured have similar spectra and are strictly monophasic.

Table 1 gives the structural parameters obtained from XRD refinement for the sample with different nominal potassium content after calcination at different temperatures.

A brief examination of Table 1 shows that cell parameters display significant variations but are not correlated to potassium content, nor to the calcination temperature. The crystal sizes obviously increase with the calcination temperature (samples with K content 4%). Cell volumes are smaller than pure cerianite (158.45 \AA^3), which is clearly due to the smaller steric requirement of zirconium (Zr^{4+} ionic radius 0.86 \AA) compared to cerium (Ce^{4+} ionic radius 0.94 \AA). The localization of potassium is still to be found, because no crystal phases containing K were found in the XRD spectra. K has a much larger ionic radius (1.52 \AA) and therefore it would certainly increase the cell dimension if fitted inside the crystal Fm3m structure. In the pure cerianite the mean Ce – O distance is 2.33 \AA while in K_2O (Fm3m) is 2.79 \AA , therefore with an increase of 0.46 \AA which is high enough to determine an increase of the cell volume. On the other hand the profile fitting with or without K gave the equivalent results indicating a certain indifference of the structure refinement to the stoichiometric variation. This is rather surprising considering the differences in the electron numbers (K 19, Zr 40, Ce 58 for neutral atoms). Therefore as the fitting of the K inside the lattice must be rejected, a localization at the grain boundary, as can be easily checked by performing an XPS spectrum.

Results of specific surface area measurement are also shown in Table 1. Generally, the effect of increasing calcination temperature results in a drop of surface area in agreement with the increase of crystallite size obtained by XRD.

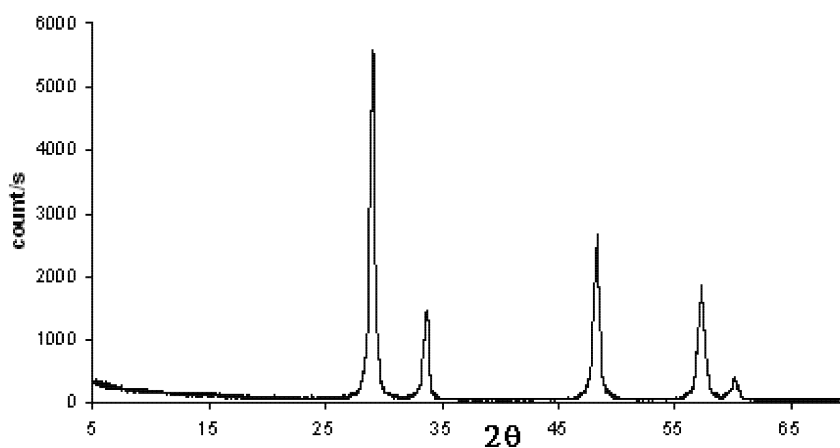


Figure 1. XRD spectrum for the sample with nominal content of potassium 4% calcined at 900°C

Table 1. Structural and textural characteristics of samples used in this study

K nominal content (%)	Tc (°C)	Crystallite Size (Å)	a (Å)	V (Å ³)	SSA (m ² /g)
1	500	105	5.3394(2)	152.22	29.4
1	700	115	5.3362(2)	151.95	11.1
1	900	225	5.3349(1)	151.84	11.0
4	400	62	5.3443(4)	152.64	33.4
4	500	63	5.3384(4)	152.14	25.5
4	700	105	5.3322(2)	151.61	17.1
4	900	200	5.3329(1)	151.67	12.3
7	500	110	5.3444(2)	152.65	11.6
7	700	165	5.3473(2)	152.90	20.8
7	900	210	5.3475(1)	152.91	8.6
10	500	60	5.3326(3)	151.64	10.4
10	700	195	5.3465(2)	152.83	5.8
10	900	240	5.3319(1)	151.58	8.1

Figure 3 reports the XPS obtained for the sample calcined at 900°C with nominal potassium content 7%. The nominal surface composition of 9% is only slightly higher than 7%. Therefore if potassium is not fitted inside the structure, it may be lost in the gas phase during calcination as it frequently occurs for potassium doped samples. However, the same figure shows a significant and unexpected presence of chlorine (4%). Since chlorine was not deliberately added as a reagent it must necessarily be present as an impurity of the reagents utilized: indeed both citric acid and zirconium propoxide contain chlorine (6 and 14 ppm respectively).

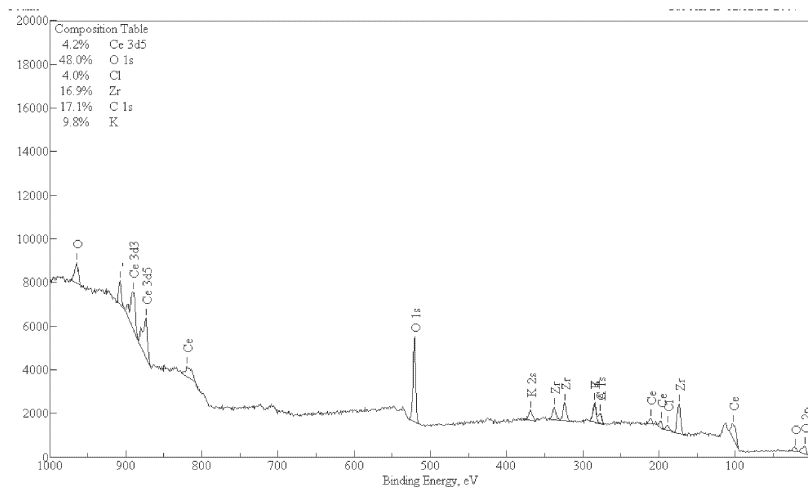


Figure 3. XPS of the sample with 7% nominal content of potassium calcined at 900°C

Table 2. The effect of different additions on catalytic activity.

Type of addition	T _m °C
+ KCl	390
+ KF	394
17.5 mg Cl as HCl _{aq}	368
35 mg Cl as HCl _{aq}	371

Therefore, in order to check whether the presence of halides at the surface of the catalyst is relevant in soot combustion we impregnated with an aqueous solution containing potassium halides the sample at 7% nominal potassium content calcined at 900°C and for other samples we added deliberately hydrochloric acid to the overall solution before concentration and drying. In both cases the samples had a final calcination at 900°C in fluidized bed for 10 hrs.

Table 2 shows the value of temperature of maximum oxidation rate (T_m) after the above mentioned additions. The variation found are not relevant but it is noteworthy that the best performance (T_m =368°C) was obtained after addition of HCl_{aq}, for comparison the catalyst without addition (K=7%, T_c=900°C) has a peak of maximum oxidation rate at 378°C.

The catalytic activity towards soot oxidation of different catalysts was compared in terms of temperature of maximum oxidation rate of soot (T_m) evaluated by tests in thermobalance. Results of activity tests are reported in Figure 4 where T_m is plotted as function of potassium nominal content at different calcination temperatures (T_c).

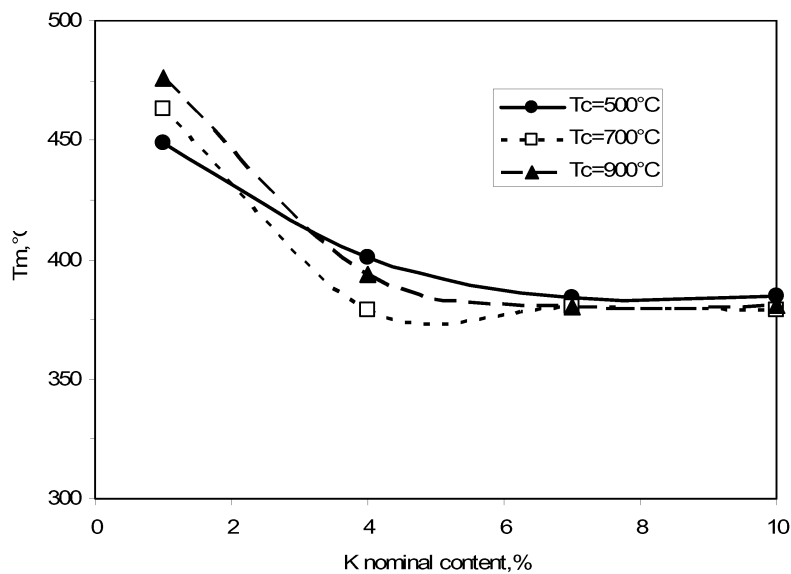


Figure 4. Trend of temperature of maximum oxidation rate of soot (T_m) vs potassium nominal content at different calcination temperatures (T_c).

All the catalysts examined are active in promoting soot combustion in the range of temperature from about 300 to 475°C, reducing T_m of about 140°C (for the less active) up to 240°C (for the most active) with respect to uncatalysed soot oxidation ($T_m=620^\circ\text{C}$). From Figure 4 it appears that increasing the K content in the catalyst results in an increased catalytic activity up to a 7% potassium content, further increase of potassium content does not effect catalytic activity. For the last value of K the catalytic activity is no more affected by the calcination temperature as it occurs for catalysts at lower potassium content (1-4%).

With respect to the mechanism involved in oxidation of soot, several authors (Ciambelli et al., 2003; Pisarello et al., 2002) pointed out the importance of redox properties of the catalyst, and the use of supports based on cerium oxide is shown to confer interesting properties to soot combustion catalysts (Lamonier et al., 2001, Setiabudi et al, 2004; Aneggi et al. 2006, Atribak et al., 2008). Therefore we have carried out cycles of reduction by soot and re-oxidation of different catalysts prepared in order to investigate the role of redox properties on the combustion of soot.

Results of carbothermic reduction of catalyst at 4% of K nominal content and at different calcination temperatures are reported in Figure 5. Catalysts calcined at lower temperatures, 400 (not reported) and 500°C, show a well defined reduction peak at 400°C and subsequent reduction at temperatures higher than 450°C (peak at $T>700^\circ\text{C}$). In contrast catalysts calcined at higher temperatures (700, 900°C) do not present the first reduction peak. This behaviour is justified by the presence of small ceria-zirconia nanocrystallites (see Table1) in the uppermost layers responsible for the occurrence of the first peak at lower calcination temperatures, which at increasing calcination temperature increase in their size and progressively modify to bulk ceria-zirconia responsible of reduction at higher temperatures (Aneggi et al. 2006, Atribak et al., 2008).

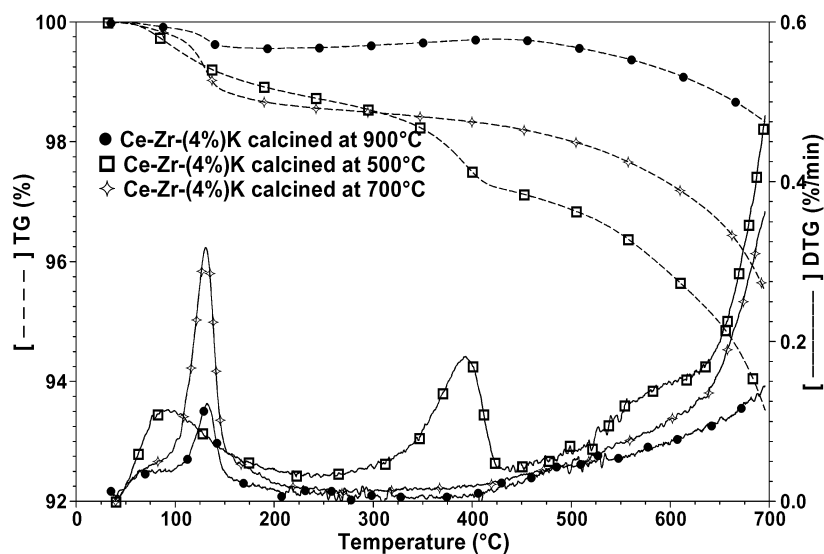


Figure 5. Carbothermic reduction of catalyst at 4% nominal content and different calcination temperatures.

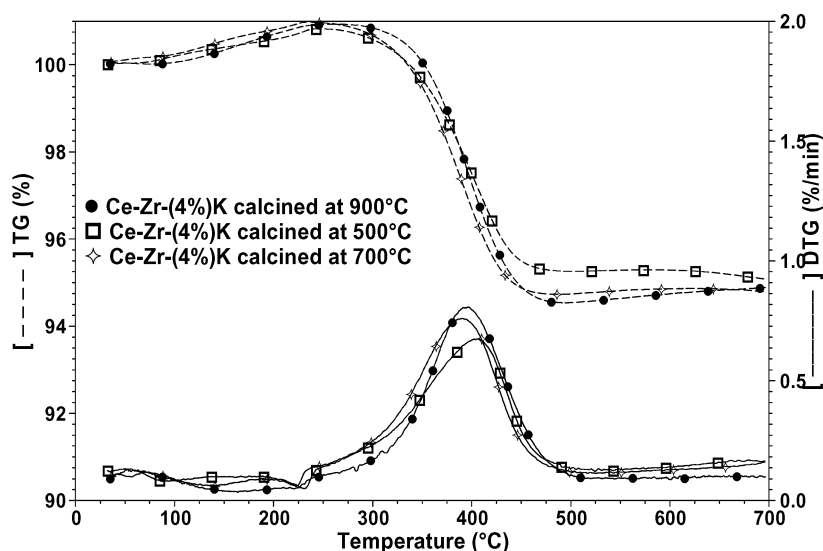


Figure 6. Re-oxidation (after reduction) of soot mixtures with catalystt 4% nominal content and different calcination temperatures.

Moreover, a more pronounced weight loss (in the range 200-700°C) due to carbothermic reduction is observed at lower calcination temperatures (5.2% at $T_c=500^\circ\text{C}$) with respect to those at higher calcination temperatures (3.1% at $T_c=700^\circ\text{C}$, 1.2% at $T_c=900^\circ\text{C}$). On the other hand these results (in terms of extent of reduction) cannot be justified by a variation of specific surface area which was observed to varying between $25.5\text{ m}^2/\text{g}$ at 500°C to $17.1\text{ m}^2/\text{g}$ at 700°C , to $12.3\text{ m}^2/\text{g}$ at 900°C .

Therefore, although the catalysts at lower calcination temperatures determine a decrease in the onset temperature of reduction and an increase in the amount of catalyst that can be reduced, they show a higher temperature of maximum soot oxidation rate (T_m). Hence, these properties seems not have a primary role on the catalytic activity towards soot oxidation.

Results of re-oxidation tests on catalyst at 4% of K nominal content and at different calcination temperature are reported in Figure 6. It is relevant to note that the temperature ranges within which the catalysts re-oxidise (Figure 6) are similar and practically coincident with those at which soot oxidation occurs during normal catalytic activity tests. This suggests that the catalytic activity is related to the rate of catalyst re-oxidation.

Conclusions

The soot combustion behaviour of Ce-Zr systems doped with potassium has been investigated. Results of catalytic activity tests show that the addition up to 7% nominal content of potassium on the catalyst surface promotes the soot oxidation at lower temperature. The catalytic activity of the catalysts seems related to their ability to give oxygen available for soot oxidation.

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References

- Aneggi E., M. Boaro, C. de Leitenburg, G. Dolcetti, A. Trovatielli, 2006 *Catal. Today* 112, 94.
- Atribak I., A. Bueno-Lopez, A. Garcia-Garcia, 2008, *Catal. Comm.* 9, 250.
- Ciambelli P., V. Palma, P. Russo, S. Vaccaro, 2003, *J. Mol. Catal. A:Chemical* 204-205, 673.
- Hill R.J., C.J. Howard, 1987, *J. Appl. Cryst.* 20, 467.
- Lamonier J.F., N. Sergent, J. Matta, A. Aboukar's, 2001, *J. Therm. Anal. Calorimetry* 66, 645.
- Palma V., P. Russo, G. Matarazzo, P. Ciambelli, 2007, *Appl. Catal. B: Environ* 70, 254.
- Pisarello M.L., V. Milt, M.A. Peralta, C.A. Querini, E.E. Miro', 2002, *Catal. Today* 75, 465.
- Setiabudi A., J. Chen, G. Mul, M. Makkee, J.A. Moulijn, 2004, *Appl. Catal. B: Environ* 51, 9.
- Shannon R.D., C.T. Prewit, 1969, *Acta Crystallogr. B* 25, 295.
- Trovarelli A., 2002, *Catalysis by ceria and related materials*, Catalytic science series vol II, Imperial college Press
- Villa P.L , 2007, US patent nr 7,166,267
- Young R.A., 1993, *International Union of Crystallography*, Oxford University Press.