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Promotional effect of rare earths and transition metals in the combustion of diesel soot over CeO_2 and CeO_2–ZrO_2

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Abstract

The soot combustion behavior and the textural and structural characteristics of CeO_2 and a series of ceria-modified materials have been studied. It is shown that ceria doped with transition metals (Zr and Fe) and rare earth elements (La, Pr, Sm, Tb) results in more active catalysts with enhanced textural properties. ZrO_2 enhances the thermal stability and the oxygen storage capacity of pure ceria, resulting in better performance in soot oxidation. Remarkably, cerium–zirconium solid solution doped with rare earth does not achieve lower temperature of combustion, providing performances comparable to CeO_2 and CeO_2–ZrO_2. Cerium doped with Fe_2O_3 presents the better results as far as fresh samples are taken into account, but suffers from a net loss of activity after calcination. TGA experiments under N_2 atmosphere have confirmed the key role of oxygen storage capacity in soot oxidation.

Keywords: Ceria; Ceria–zirconia; Fe_2O_3; Soot oxidation; Diesel; Oxygen storage; Combustion

1. Introduction

Among the several techniques that have been developed for reducing particulate emissions from diesel engines, filtering followed by catalytic oxidation is one of the more promising. The basic idea of catalytic approach consists in the use of a catalyst to achieve the onset of regeneration at a temperature comparable to that of exhaust gases. Unfortunately, this method is affected by several drawbacks [1]: (i) catalytic filter regeneration is made difficult by the very variable conditions of reaction; (ii) the process is quite slow because of the poor soot–catalyst contact; actually, the solid particles are immobile when deposited and due to their large size can not penetrate into catalyst's micropores or mesopores; (iii) the temperature in the exhaust gases may vary in a wide range (indicatively from 473 to 873 K), depending upon engine load. Consequently, a useful catalyst has to operate efficiently at low temperatures and also to be thermally stable.

Several catalyst formulations for soot oxidation have been studied in the last years, and the most promising are those based on Cu/K/M/(Cl) (where M is either V, Mo or Nb) [2–4], that have been investigated in detail due to their high activity at low temperature.

Regarding the intimate mechanism involved in the oxidation of carbon, several authors pointed out the importance of redox properties of the catalyst. 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 solid carbon reactant) in a wide temperature range [1]. Recently, it has been reported that the use of supports based on cerium oxide confers interesting properties to soot combustion catalysts due to high availability of surface oxygen and high surface reducibility [5–9]. The success of oxygen storage systems based on ceria is due to their ability to change oxidation state during operation (i.e. CeO_2 to CeO_{2-x}) maintaining structural integrity, thus allowing oxygen uptake and release to occur easily. State of the art material for oxygen storage in TWC is constituted by ceria and ceria–zirconia mixed oxides doped with small amounts of rare earth elements, added to enhance the redox features of ceria [10]. Homogeneity of solid solutions, structural features and composition are key parameters in successful redox catalyst design. Since it is being reported in the literature that a strong relationship exist between oxygen storage/redox capacity and

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soot combustion activity [11], it is of interest to investigate here if the knowledge that has been accumulated on redox systems for TWC can help in developing more active soot combustion catalysts.

In this study a series of ceria-based catalysts modified with rare earth (Sm, Pr, Tb, La) and transition metal elements (Zr, Fe) have been prepared and characterized from a structural and textural point of view. The effect of doping in the activity of soot combustion is also described by putting particular attention in correlating soot oxidation activity with oxygen storage and structural properties of the materials.

2. Experimental procedures

2.1. Catalyst preparation and characterization

Three classes of materials were prepared and characterized: ceria–zirconia solid solutions, ceria–zirconia doped with rare earth elements (La, Pr, Sm, Tb) and ceria and ceria–zirconia doped with Fe. They were prepared by coprecipitation starting from nitrates. Precipitates were dried at 393 K and calcined at 773 K for 2 h (fresh samples). Aged samples were prepared following calcination in air at 1023 K for 12 h. Chemical composition of all samples investigated is reported in Table 1.

Textural characteristics of all fresh and aged samples were measured according to the B.E.T. method by nitrogen adsorption at 77 K, using a Sorptomatic 1900 instrument (Carlo Erba).

Structural features of the catalysts were characterized by X-ray diffraction (XRD). XRD patterns were recorded on a Philips X'Pert diffractometer operated at 40 kV and 40 mA using nickel-filtered Cu Kα radiation. Spectra were collected using a step size of 0.02° and a counting time of 40 s per angular abscissa in the range 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 [12] with a correction for instrument line broadening. Rietveld refinement [13] of XRD pattern was performed by means of GSAS-EXPGUI program [14,15]. The accuracy of these values was estimated by checking their agreement against the values of the lattice constant, assumed to comply with the Vegard's law [16].

2.2. Catalytic activity

The catalytic activity for the combustion of soot was quantified by the peak-top temperature (T_m) during temperature programmed oxidation (TPO) of catalyst–soot mixtures [1,17–20]. Each catalyst was accurately mixed with soot in a mortar for 10 min in order to achieve a tight contact [21]. The kind of contact between catalyst and soot is extremely important [1,22]: 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 screen of catalysts in reproducible experimental conditions.

A soot/catalyst weight ratio of 1:20 was adopted. 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 (N_2 with 6% of O_2) was kept fixed at 400 ml/min. The catalyst temperature was checked by a chromel-alumel thermocouple, located on the catalyst bed. The outlet composition was measured by IR and paramagnetic gas analyzers (Magnos 106 and Uras14, ABB), by recording the percentages of CO, CO_2 and O_2 at the output 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 lower than 5 K.

Soot oxidation activity was also tested by running TGA experiments (Q500, TA Instruments) either in the presence or in the absence of oxygen (N_2 atmosphere). In order to achieve the stoichiometric ratio between the amount of soot and the oxygen that the catalyst can donate, we used a soot/catalyst weight ratio of 1:115. The total flow of N_2 in the furnace was 100 ml/min. Samples were pre-treated for 1 h at 423 K to eliminate water absorbed, then they were heated at a constant rate (10 K/min) up to 1073 K; the weight loss of the sample, after subtraction of the blank, can be considered as an indication of activity of soot oxidation by oxygen from the catalyst.

Table 1
Characteristics of samples used in this study

Sample	Composition	B.E.T. surface area (m^2/g)		Crystallite size (nm)[a]		T_m (K)	
		Fresh	Aged	Fresh	Aged	Fresh	Aged
CZ100	CeO_2	57	22	7	11.2	662	700
CZ75	$Ce_{0.75}Zr_{0.25}O_2$	73	44	6.3	10	660	673
CZ44	$Ce_{0.44}Zr_{0.56}O_2$	96	54	4.7	13	675	674
CZ28	$Ce_{0.28}Zr_{0.72}O_2$	100	58	6.2	13	695	711
CZ0	ZrO_2	79	44	11.8	15.9	798	810
CF95	$Ce_{0.95}Fe_{0.05}O_{1.975}$	92	10	5.4	44.4	639	749
CF85	$Ce_{0.85}Fe_{0.15}O_{1.925}$	77	22	7.5	31.1	662	722
CZF95	$Ce_{0.47}Zr_{0.48}Fe_{0.05}O_{1.975}$	106	25	3.9	8.8	672	715
CZF85	$Ce_{0.45}Zr_{0.40}Fe_{0.15}O_{1.925}$	132	22	3.5	8.9	684	716
CZLa	$Ce_{0.48}Zr_{0.50}La_{0.02}O_{1.99}$	93	54	4.0	5.6	687	685
CZPr	$Ce_{0.48}Zr_{0.50}Pr_{0.02}O_{1.99}$	99	55	4.1	6.1	683	678
CZSm	$Ce_{0.48}Zr_{0.50}Sm_{0.02}O_{1.99}$	92	50	4.3	6.4	684	679
CZTb	$Ce_{0.48}Zr_{0.50}Tb_{0.02}O_{1.99}$	96	50	4.2	6.3	687	691

[a] Calculated with Scherrer formula from X-ray diffraction patterns.