



Synergic effect of Cu/Ce_{0.5}Pr_{0.5}O_{2-δ} and Ce_{0.5}Pr_{0.5}O_{2-δ} in soot combustion



Verónica Rico-Pérez^a, Eleonora Aneggi^{a,*}, Agustín Bueno-López^b, Alessandro Trovarelli^a

^a Università di Udine, Dipartimento Politecnico di Ingegneria e Architettura, via del Cottonificio 108, 33100 Udine Italy

^b University of Alicante, Department of Inorganic Chemistry, Carretera de San Vicente del Raspeig, 03690, Spain

ARTICLE INFO

Article history:

Received 17 December 2015

Received in revised form 11 February 2016

Accepted 24 February 2016

Available online 26 February 2016

Keywords:

Soot oxidation

Ceria

Praseodymium oxide

NO oxidation

CeO₂

ABSTRACT

A series of 5%Cu/Ce_{0.5}Pr_{0.5}O_{2-δ} and Ce_{0.5}Pr_{0.5}O_{2-δ} mixed oxides have been prepared and combined in different ratios. The resulting catalysts have been characterized by N₂ adsorption, XRD, Raman spectroscopy and H₂-TPR and tested for soot combustion by means of temperature-programmed experiments. The optimum catalyst for soot combustion in NO_x/O₂/N₂ atmosphere is the mixture containing 40% Cu/Ce_{0.5}Pr_{0.5}O_{2-δ} and 60% Ce_{0.5}Pr_{0.5}O_{2-δ}. This mixture is more active than a reference catalyst containing the same amount of copper distributed in the whole Ce-Pr mixed oxide support. The benefit of mixing Ce_{0.5}Pr_{0.5}O_{2-δ} particles with and without copper in a single catalyst formulation is that the participation of the two soot combustion mechanisms based on active oxygen and NO₂, respectively, is optimized. The particles with copper mainly promote the catalytic oxidation of NO to NO₂ (the NO_x-assisted mechanism) while those without copper are more effective in promoting the active oxygen mechanism. If copper is loaded homogeneously in all the Ce_{0.5}Pr_{0.5}O_{2-δ} particles, the positive effect of copper improving NO₂ production is offset by the lower efficiency of the active oxygen mechanism, due to a lack of active oxygen on the Ce_{0.5}Pr_{0.5}O_{2-δ} support.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Health and environmental problems are the reasons for the important concern about the removal of soot particles emitted from diesel engine [1,2]. Filtering in a DPF (Diesel Particulate Filter) followed by combustion is one of the most promising technologies for soot abatement. Since the onset temperature for soot combustion is too high for spontaneous regeneration of the filters, it is necessary to ignite soot periodically by raising the temperature with or without diesel fuel addition [3,4] and catalysts are required to promote filter regeneration.

Several different catalysts have been studied for soot combustion [5], and formulations containing ceria-based materials are among the most promising; however, thermal stability of bare ceria is rather poor and ceria undergoes rapid sintering at high temperatures, which adversely affect its catalytic properties [6–8]. Therefore, modification of ceria is necessary in order to improve the stability towards sintering and the oxidation activity of the resulting catalysts. An approach to boost the catalytic activity is the preparation of materials with appropriate morphologies that can

provide a large number of soot-catalyst contact points and that can expose more reactive planes enhancing the oxygen release capacity [9–11]. Improved thermal stability and changes in the physico-chemical properties of ceria are also obtained by introducing other metal ions into the ceria structure, which may change the redox properties and may favour the creation of the oxygen vacancies improving the oxygen mobility through the catalyst [12–17]. The most promising doped-ceria active phases seem to be those containing Pr, Zr or La as main dopant [18–26], where the optimum loading depends on the dopant size and on the resulting redox properties [27].

The catalytic combustion of soot promoted by ceria-based catalysts takes place through two different reaction mechanisms, which are usually referred to as the active oxygen mechanism and the NO_x-assisted mechanism [27]. In the active oxygen mechanism, ceria exchanges its oxygen with gas-phase O₂ creating highly reactive oxygen species (the so-called “active oxygen”), and active oxygen oxidizes soot very efficiently. Some authors have related these active oxygen species with the formation of superoxides and peroxides on the ceria surface [28,29]. They could form via oxygen adsorption on the reduced surface of ceria in the vicinity of soot and then they react with carbon forming CO₂. On the soot/ceria interface, soot can reduce ceria initiating the “active oxygen” route that can promote the oxidation by a spillover mechanism. The main

* Corresponding author.

E-mail address: eleonora.aneggi@uniud.it (E. Aneggi).

Table 1
Composition of catalyst formulations investigated.

Sample name	Catalyst composition (wt.%)	
	(5%)Cu/Ce _{0.5} Pr _{0.5} O _{2-δ}	Ce _{0.5} Pr _{0.5} O _{2-δ}
CePr	0	100
20CuCePr + 80CePr	20	80
40CuCePr + 60CePr	40	60
60CuCePr + 40CePr	60	40
80CuCePr + 20CePr	80	20
CuCePr	100	0
(2%)CuCePr	(2%)Cu/Ce _{0.5} Pr _{0.5} O _{2-δ}	0

limitation of this reaction pathway is the short lifetime of the active oxygen species, which must be able to reach the soot particles. In a real DPF, the solid–solid contact between soot and catalyst particles is limited to few contact points and this hinders the transfer of active oxygen from ceria to soot. The other pathway, the so-called NO_x-assisted mechanism, involves the catalytic oxidation of NO to NO₂, which is more oxidizing than NO and O₂ and successfully initiates soot combustion [1,27,30–35]. This is the basis of the so-called continuously regenerating trap (CRT) developed by Johnson Matthey [36], where a Pt catalyst accelerates NO oxidation. It has been reported that the NO oxidation capacity of ceria-based oxides can be improved by impregnation of transition metals, like copper, and this would be interesting to develop noble metal-free soot combustion catalysts [37,38]. Comparing the two ceria-catalysed soot combustion mechanisms, the main advantage of the NO_x-assisted mechanism is that NO₂ is stable and does not have lifetime restrictions to move from the catalyst to soot particles. However, the intrinsic reactivity of active oxygen is believed to be much higher than that of NO₂ [39].

In this study we investigate in detail soot oxidation activity over a series of Cu loaded Ce_{0.5}Pr_{0.5}O_{2-δ} catalysts with different amount of copper. The catalysts have been prepared by mixing Cu/Ce_{0.5}Pr_{0.5}O_{2-δ} with Ce_{0.5}Pr_{0.5}O_{2-δ} in appropriate amount in order to obtain increasing Cu content. Considering previous investigations [23], the Ce_{0.5}Pr_{0.5}O_{2-δ} mixed oxide has been selected for this study as optimized ceria-based soot combustion catalyst, and copper has been selected as transition metal to improve the NO oxidation capacity. The aim of the study is to demonstrate that the design of soot combustion ceria-based catalysts can be improved in formulations that contain a combination of ceria particles with and without copper in order to optimize the simultaneous and synergic contribution of the two oxidation mechanisms (active oxygen and NO_x assisted) to the overall combustion reaction.

2. Experimental

2.1. Catalyst preparation

Ce_{0.5}Pr_{0.5}O_{2-δ} was prepared by mixing in an agate mortar the proper amounts of cerium nitrate (Treibacher Industrie) and praseodymium nitrate (Sigma-Aldrich) followed by calcination at 500 °C for 3 h. 5 wt.% Cu was deposited over Ce_{0.5}Pr_{0.5}O_{2-δ} by incipient wetness impregnation of Ce_{0.5}Pr_{0.5}O_{2-δ} with the appropriated amount of Cu(NO₃)₂·2.5H₂O (98%, Sigma-Aldrich). Finally, it was dried overnight at 100 °C and calcined at 500 °C for 3 h.

The investigated catalysts were obtained by mixing proper amounts of Ce_{0.5}Pr_{0.5}O_{2-δ} and 5%Cu/Ce_{0.5}Pr_{0.5}O_{2-δ} with a spatula in different weight ratios. The resulting mixtures will be referred to as xCuCePr + yCePr, where x and y indicate the weight percentage of 5%Cu/Ce_{0.5}Pr_{0.5}O_{2-δ} and Ce_{0.5}Pr_{0.5}O_{2-δ} in the mixture, respectively (see Table 1).

For comparison, an additional catalyst with 2% of copper (2%Cu/Ce_{0.5}Pr_{0.5}O_{2-δ}) was prepared by incipient wetness

Table 2
Main characteristics of catalysts investigated.

Sample	Cu ^a (wt.%)	BET surface area (m ² /g)	Lattice parameter (Å) ^b	Particle size (nm)
CePr	0	24	5.4147(3)	12
20CuCePr + 80CePr	1	27	5.4143(3)	12
40CuCePr + 60CePr	2	26	5.4127(3)	12
60CuCePr + 40CePr	3	26	5.4126(3)	12
80CuCePr + 20CePr	4	30	5.4117(1)	12
CuCePr	5	26	5.4116(3)	12
(2%)CuCePr	2	26	5.4141(3)	12

^a nominal copper loading.

^b Lattice parameter calculated with Rietveld refinement for a cubic structure.

impregnation of Ce_{0.5}Pr_{0.5}O_{2-δ} with the copper precursor following the previously described impregnation and calcination procedures. This reference catalyst will be referred to as (2%)CuCePr. The characteristics of all catalysts are summarized in Table 2.

2.2. Catalysts characterization

Textural properties of all catalysts were studied by nitrogen adsorption at –196 °C, using a Tristar 3000 gas adsorption analyser (Micromeritics). 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. Diffractograms were collected using a step size of 0.02° and a counting time of 40 s per angular abscissa in the range 20–80°. The Philips X'Pert HighScore software was used for phase identification. The mean crystallite size was estimated from the full width at the half maximum (FWHM) of the X-ray diffraction peak using the Scherrer equation [40] with a correction for instrument line broadening. Rietveld refinement [41] of XRD pattern was performed by means of GSAS-EXPGUI program [42,43].

Raman spectra were recorded in a Jobin Yvon Horiba Raman dispersive spectrometer with a variable-power He-Ne laser source (632.8 nm) and 1 mW laser power, using a confocal microscope. The laser approached the sample using an Olympus 10× lens. The spectra were acquired after 2 scan of 120 s each one.

The reducibility of the catalysts was studied by temperature-programmed reduction (TPR) experiments; catalysts (50 mg) were heated at a constant rate (10 °C/min) in a U-shaped quartz reactor from room temperature to 500 °C under a flowing hydrogen/nitrogen mixture (35 ml/min, 4.5% H₂ in N₂). The hydrogen consumption was monitored using a thermal conductivity detector (TCD). Quantification of H₂ consumption was carried out by calibrating the signal with the introduction of known amounts of hydrogen.

2.3. Catalytic activity

Samples for catalytic measurements were prepared by mixing accurately each catalyst with soot (Printex-U by Degussa AG) in tight and loose contact mode. The former was achieved by mixing a soot/catalyst (1/20 wt ratio) in an agate mortar for 10 min, while loose contact samples were obtained by mixing soot/catalyst (1/4 wt ratio) for 2 min with a spatula. Soot oxidation for samples mixed under tight contact conditions was tested by running TGA experiments (Q500, TA Instruments) under O₂/N₂. The soot-catalyst sample (ca. 10 mg) was placed in a small flat Pt crucible licked by an air flow (60 ml/min) tangent to the sample, and heated at a constant rate (10 °C/min) up to 800 °C. Before the catalytic tests the samples were subjected to a 1 h pre-treatment at 150 °C under inert atmosphere in order to eliminate the adsorbed water. As a

Download English Version:

<https://daneshyari.com/en/article/45501>

Download Persian Version:

<https://daneshyari.com/article/45501>

[Daneshyari.com](https://daneshyari.com)