Applied Catalysis B: Environmental 146 (2014) 1–11

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

journal homepage: www.elsevier.com/locate/apcatb

Diesel soot combustion ceria catalysts☆

A. Bueno-López*

Inorganic Chemistry Department, University of Alicante, Ap. 99 E03080, Alicante, Spain

ARTICLE INFO

Article history:
Received 13 September 2012
Received in revised form 11 February 2013
Accepted 18 February 2013
Available online 26 February 2013

Keywords:
DPF regeneration
Soot
Ceria
Doped-ceria
Diesel engine contamination

ABSTRACT

Different aspects of the ceria-catalyzed Diesel soot combustion reactions have been critically discussed, such as the high catalytic activity of ceria for Diesel soot combustion in comparison to some other potential catalysts, the potential ceria-catalyzed Diesel soot combustion mechanisms (the so-called NO_2-assisted mechanism and the active oxygen mechanism) and the effect of ceria doping with suitable cations like those of Pr, La or Zr. Ceria must be doped in order to enhance thermal stability, but ceria doping also changes different physicochemical and catalytic properties of ceria. Zr-doping, for instance, has a double role on ceria as soot combustion catalyst: enhances ceria oxidation capacity of the adsorbed NO_x species (positive effect) but stabilizes NO_2 on surface (negative effect). The surface properties of a ceria catalyst are usually more important than those of bulk: high surface area/small crystal size usually has a positive effect on the catalyst performance and, in mixed oxides, the surface composition also plays a role. The optimal dopant loading depends on the foreign cation being, for instance, around 5–10%, 20–30% and 50 mol% for La^{3+}, Zr^{4+}, and $Pr^{3+/4+}$, respectively.

1. The problem

Soot particles are formed as undesired by-products in combustion process, being one of the main pollutants emitted by Diesel engines together with NO_x, CO and unburned hydrocarbons [1]. Typical gas exhaust composition of a Diesel car, which is summarized in Table 1, is 30–80 ppm hydrocarbons, 200–1500 ppm CO, 300–1650 ppm NO (~0 ppm NO_2), 5–18% O_2, >2% H_2O and >2% CO_2.

Soot particles consist of a carbon nucleus with some inorganic material and adsorbed hydrocarbons, SO_x, and water [2]. Fig. 1 shows TEM images of a real soot sample. The single particles of few nanometers present an amorphous core surrounded by a graphitic shell, and such single particles agglomerate in larger entities with size typically in the range 0.1–10 μm [3].

Several adverse effects on health have been attributed to soot. A fraction of these particles (the so-called PM-10, with size smaller than 10 μm) can penetrate the respiratory tract and are deposited on lungs increasing cancer risk, asthma and bronchitis. The adsorbed hydrocarbons are mutagenic substances and SO_x in contact with water form strong acid compounds.

Diesel particle traps with different designs can be used for soot removal from gas streams, wall-flow monoliths being the most popular [3,4]. Fig. 2 shows a commercial SiC Diesel Particulate Filter (DPF). The structure of this type of filters is similar to that of honeycomb monoliths, but with 50% of the channels plugged in one side of the piece and the remaining channels plugged in the opposite side. The gas stream is allowed to enter into the filter only through the open channels of the exposed side, and goes through the porous walls while soot particles get stuck on the walls. Finally it leaves the filter by a neighboring channel. The preferred materials to manufacture DPF filters are cordierite ($2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$) and SiC, because they are able to support the demanding thermal conditions of the regeneration steps. There have been reported temperature gradients of 100 °C/cm along both radial and longitudinal directions of DPFs [5]. Important differences in physical properties between cordierite and SiC are their melting temperatures (~1400 and ~2700 °C, respectively) and their expansion coefficients (2.0×10^{-6} and 4.3×10^{-6} from 25 to 800 °C, for cordierite and SiC respectively). Due to these differences SiC is able to support the high temperatures reached during filters regeneration better than cordierite but is more prone to suffer damages due to thermal shock. Large SiC filters, as those used in Diesel cars, are made of several pieces glue together in order to improve the thermal shock resistance (see Fig. 2) while cordierite filters can be made in single pieces.

Once soot is collected on a filter different regeneration strategies can be applied. The thermal combustion of Diesel soot usually

---

☆ This review article summarizes the contents of the keynote lecture with the same title presented at the 7th edition of the International Conference on Environmental Catalysis hold in Lyon (France) in September 2012.

* Tel.: +34 600948665; fax: +34 965903454.
E-mail address: agus@ua.es

0926-3373/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apcatb.2013.02.033

Table 1
Typical Diesel exhaust features measured with a 1600 cc HDI Diesel engine running on commercial Diesel fuel at different rates and with different loadings.

Temperature	<550 °C
[Hydrocarbons]	30–80 ppm
[CO]	200–1500 ppm
[NO]	300–1650 ppm
[NO_2]	~0 ppm
[O_2]	5–18%
[H_2O]	>2%
[CO_2]	>2%

needs temperatures above 450 °C, and catalysts play a key role to lower the ignition temperature [6]. The commercially available technologies for filters regeneration are [7]:

- The PSA system: A Ce-fuel additive leads to the formation of CeO_2 particles well embedded into the soot structure, which lower the ignition temperature of soot. Once a high pressure drop is detected by a sensor, fuel is injected and its combustion produces an increase of the exhaust gas temperature that promotes soot ignition. Ceria catalyzes soot combustion and diminishes the amount of fuel required for trap regeneration. Recently, iron-based catalysts are being also used.
- The Continuously-Regenerating-Trap (CRT) system (by Johnson Matthey) consists of a wall-flow trap with an upstream flow-through Diesel oxidation catalyst (with Pt) that converts NO to NO_2, which is much more oxidizing than NO and O_2 (and also oxidizes CO and hydrocarbons) and that rapidly reacts with soot.

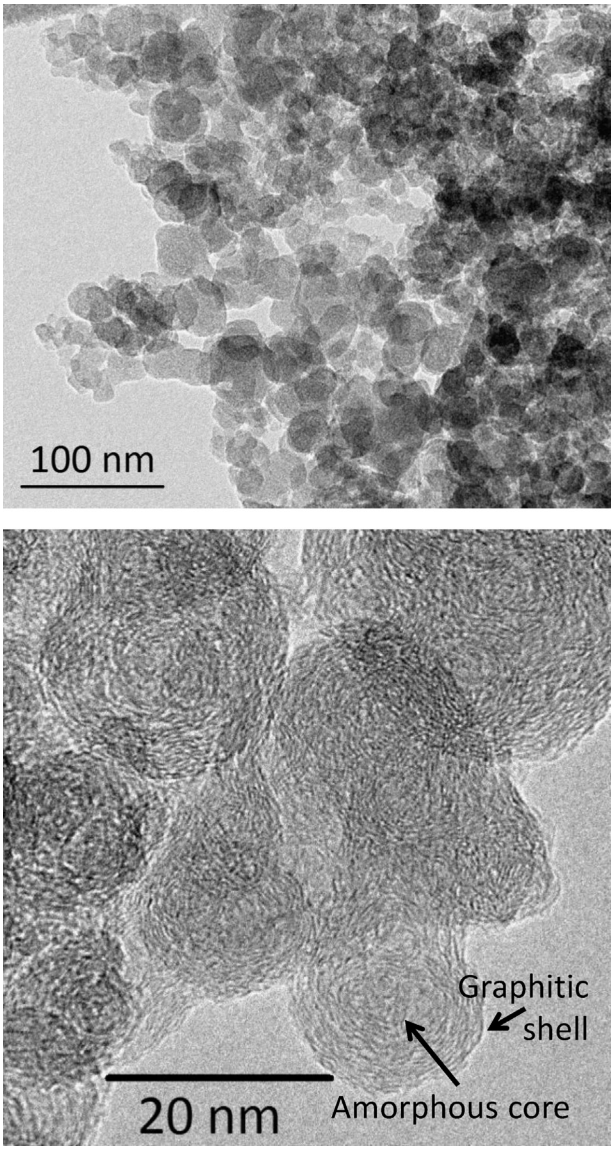

Fig. 1. TEM pictures of a real Diesel soot sample.

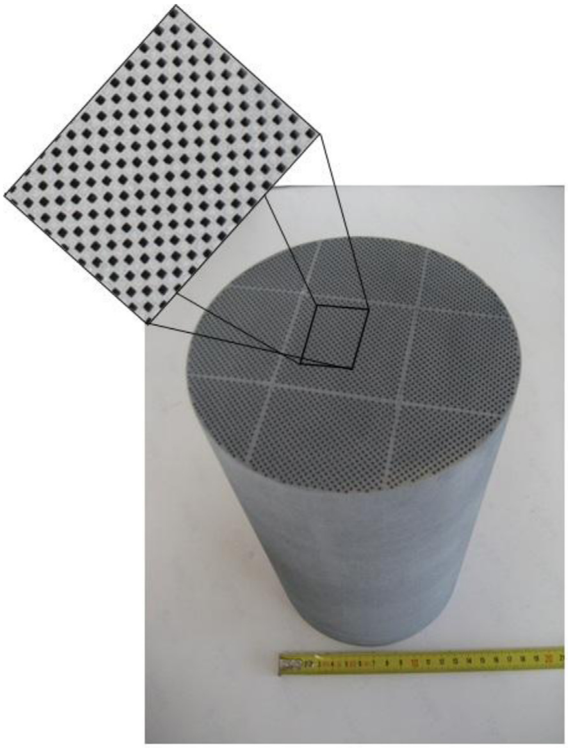

Fig. 2. Picture of a commercial SiC Diesel Particulate Filter (DPF).

Both systems work properly, but there are still some aspects to be improved. The main drawbacks of the PSA system is the fuel penalty, which is estimated in about 4%, the CeO_2 deposits on the filter that require periodic cleaning or trap over-sizing, and the high investment costs (additives, additive-storage tank, dosing pump, pressure and temperature sensors, control electronics, etc.). The main drawback of the CRT system is the low sulphur tolerance, and substitution of noble metals by cheaper active phases would be desirable. In addition, in both cases the problem of NO_x emissions remains unsolved.

Some other filters regeneration strategies are being investigated, such as modifications of the CRT systems that incorporate active phases in the filter instead of or in addition to that in the previous oxidation catalyst or the Toyota Motors DPNR (Diesel Particulate NO_x Reduction) system. A number of catalytic active phases are under study in order to develop noble metals-free regeneration strategies and ceria-based materials are among the promising active phases.

2. Why ceria catalysts for soot combustion?

The capacity to store and release oxygen is one of the particular properties of ceria that makes this material exceptionally effective in several catalytic applications [8]. Ceria presents this property due to the ability of cerium to switch between the Ce^{4+} and Ce^{3+} oxidation states and to incorporate more or less oxygen into the crystal structure depending on various parameters, such as the gas