



Continuously regenerating Diesel Particulate Filters based on ionically conducting ceramics



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ABSTRACT

This study reports a mechanistic study of the soot oxidation on Yttria-Stabilized Zirconia (YSZ), a non-reducible oxide with intrinsic bulk oxygen mobility. Temperature-Programmed Oxidation (TPO) and isotope exchange experiments demonstrate the key role of bulk oxygen species in the oxidation process. When “intimate” soot/YSZ contact is achieved after in situ carbon deposition via propylene cracking, lattice oxygen ions are the predominant species involved in the oxidation reaction. Based on isotopic TPO experiments performed with different oxygen partial pressures in “tight” contact mode and oxygen exchange measurements, it is proposed that the ignition of the soot oxidation on YSZ can be described as a fuel-cell-type electrochemical mechanism at the nanometric scale. The efficiency of this electrochemical process seems to depend both on the YSZ/soot contact and on the oxygen partial pressure. In addition, YSZ porous membranes were fabricated in order to simulate porous walls of YSZ-based DPFs. These membranes are effective for soot filtering and soot oxidation with oxygen starts at temperatures over 430 °C, in real soot/catalyst contact.

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1. Introduction

CO₂ emissions of Diesel vehicles, and more importantly those of Hybrid Diesel Cars (HDC), are significantly reduced as well as their dependence on fossil fuel. However, European standards for Diesel cars restrict the Particulate Matter (PM) emissions by combining a limit number (6.0×10^{11} particulates/km) with a limit mass (5 mg/km) as well as durability of after-treatment system. Since 2011, all new Diesel cars, sold in EU, are equipped with a Diesel Particulate Filter (DPF) to drastically remove soot particulates. DPFs present high filtering efficiency (>99%) but must be periodically regenerated due to soot particles accumulation [1,2]. Active regeneration is a process triggered by fuel post-injection, which is used for increasing the exhaust temperature up to the soot ignition, via exothermic oxidations of unburnt hydrocarbons in the Diesel Oxidation Catalyst (DOC) placed up-stream the DPF. To limit the fuel overconsumption provoked by post-injections, catalysts are used to promote the soot oxidation process, either added in the combus-

tion chamber as liquid additives (Ce, Fe, etc.) [2–7] or deposited in the DPF channels. The former solution, called Fuel Born Catalyst (FBC), allows tight solid/solid interactions which strongly improve the soot oxidation catalytic process at 500 °C [8]. Nevertheless, the FBC process requires investment costs due to the presence of the additives, the tank as well as the dosing pump. In addition, accumulation of ashes can occur in the DPF. Another approach is the continuously regenerating trap (CRT) which uses NO₂ to oxidize the carbonaceous particles. This gas can oxidize soot in a more efficient way and at lower temperatures (usually from 250 °C) than oxygen [9]. Unfortunately, this technology presents the drawback to increase the NO₂/NO_x ratio [10]. In addition, the next EURO 6 standards will require the utilization of a NO_x catalytic after-treatment device [11]. The latter will be preferentially placed between the DOC and the DPF since it is more efficient with a high NO₂/NO_x ratio [12,13]. Therefore, it is uncertain if the required NO_x-to-soot ratio for successful regeneration will be achieved in future engines, making crucial the development of O₂-CRT.

Various families of catalysts have been reported in the literature to be effective for soot oxidation by oxygen. Perovskites [14–16], spinel-types [17,18], and ceria-based oxides [19,20] are the most extensively investigated. The mechanism of soot oxidation with oxygen has been clearly established in the literature that lattice

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oxygen ions of the catalyst are active for soot oxidation, as well as their dependence on the number of active redox sites [19–25]. In addition, soot oxidation predominantly takes place at the particulate/catalyst interface, underlying the crucial importance of the soot/catalyst contact [26–29]. Ceria-based materials exhibit a Mars and Van-Krevelen mechanism [21,23]. The reducibility of ceria (Ce^{4+} into Ce^{3+}) and its high oxygen storage capacity can generate mobile bulk species effective for soot oxidation. Substitution of ceria with various cations can improve their redox properties. For instance, it was shown that a partial substitution of Ce^{4+} by La^{3+} can enhance the catalytic performances for soot oxidation by increasing the reducibility and then the quantity of active lattice oxygen species [21]. Comparing zirconium versus lanthanum substitution in a ceria solid solution, Katta et al. [30] have concluded that La-doped ceria is more active for soot combustion due to the extrinsic oxygen vacancies induced by La^{3+} substitution which improve the oxygen mobility. Aneggi et al. [31] have confirmed that soot particles are oxidized by surface active oxygens donated by different compositions of ceria–zirconia solid solutions. The vacancies induced by the oxidation are refilled by gaseous oxygen and/or subsurface bulk oxygen. Therefore, the activity is linked with the specific surface area (quantity of Ce^{4+} cations on the surface) as well as with the bulk oxygen mobility characterized by the oxygen storage capacity. A dual mechanism seems to occur on ceria-based catalyst coupling a surface redox process (surface oxygen exchange) and a reverse-spillover of bulk oxygen species.

Our technological target is the development of an O_2 -assisted CRT, suitable with EURO 6 standards, which will not require either a fuel overconsumption or a noble metal. The idea is to elaborate a DPF using a catalytic material in order to provide sufficient contact points with the soot particles. Yttria-Stabilized Zirconia (YSZ), an O^{2-} ionically conducting ceramic, was selected as the main component of this O^{2-} -assisted CRT because (i) YSZ presents high chemical and thermal stability as demonstrated in sensors (Lambda sensors) and solid oxide fuel cells technologies, up to 1000 °C in both reducing and oxidizing atmospheres, (ii) YSZ powders can be easily sintered and transformed into monolithic devices. Therefore, our objective is to develop a YSZ-based O_2 -assisted CRT. On the contrary with all oxide catalysts reported in literature for soot combustion [14–25,27,31], YSZ does not present any redox properties in Diesel exhaust conditions (oxygen excess). Indeed, neither Zr^{4+} , nor Y^{3+} can change their oxidation states. However, YSZ is known to be an intrinsic O^{2-} conductor due to the presence oxygen vacancies inside its crystallographic structure. The first part of this study demonstrates the catalytic performances of YSZ powder (using different contacts soot/catalyst) for soot combustion. The catalytic mechanism which initiates soot oxidation on this non-reducible oxide has been studied by Temperature-Programmed Oxidation (TPO) with labeled O_2 . In the second part, porous YSZ membranes were developed to simulate the porous walls of YSZ-based DPFs. Their filtering and catalytic properties were investigated in quasi real conditions.

2. Materials and methods

2.1. Soot particles production

PM was produced by using a mini Combustion Aerosol Standard (mini-CAST, Jing Ltd., Switzerland) which was used as soot generator. Soot particle size distribution was measured using a SMPS (Model 3080, TSI Inc., St. Paul, MN, USA) with a differential mobility analyzer (DMA) (TSI, Model 3081) column and condensation particle counter (CPC) (TSI, Model 3772). It was operated with a sheath flow of 4 L min^{-1} and an aerosol flow of 0.3 L min^{-1} . The particle diameter scanning was from 12.4 to 562 nm, and each scan

required 3 min. The mini-CAST soot generator produces soot particles with physical and chemical properties similar to those of diesel engines. It allows controlling size and chemical composition in a wide range. The generator uses a laminar diffusion flame and consists of an inner burner gas flow and an outer sheath air flow. Oxygen is transported by diffusion from the sheath flow, oxidizing the fuel gas. The flame is “cut open” at halfway to its tip, using N_2 (Linde Gaz, 99.9995%) for quenching the reaction and stabilizing the formed soot particles. Propane (Air Liquide, 99.9995%) was used as fuel, and filtered compressed air was used as sheath gas flow. The mini-CAST was operated at a propane flow of 0.06 L min^{-1} and an air sheath flow of 1.55 L min^{-1} . The N_2 flow for quenching the flame was 7.5 L min^{-1} . After soot particle formation, an air dilution flow of 6.2 L min^{-1} was fixed inside the mini-CAST to obtain a total flow of 15 L min^{-1} at the outlet. Soot generated from the mini-CAST under these conditions presented a size particle distribution centered at around 80 nm with a maximal concentration at 4×10^8 particles/ cm^3 . Although the quantity was higher, the size distribution was similar to that given by diesel engines [32,33]. Besides, Ferge et al. [34] reported a similar EC (Elemental Carbon)/TC (Total Carbon) ratio (~ 0.95) for PM emitted from a diesel engine and from a mini-CAST under similar conditions to those used in the present work. SEM and TEM images of soot obtained from this mini-CAST in the mentioned working conditions show a similar morphology and microstructure with diesel engine soot [35]. Thus, soot generated by the mini-CAST is a good proxy for diesel PM. The reactivity of this CAST soot was compared with that of the Printex U model soot (purchased from Degussa), which was widely used in previous studies [19–21,26,36,37].

2.2. YSZ physical and chemical characterizations

Yttria-Stabilized Zirconia (YSZ) powder, containing 8 mol% of yttria from TOSOH, (ZrO_2)_{0.92}(Y_2O_3)_{0.08}, was used as purchased. The BET surface area and the pore volume (BJH method) were measured employing nitrogen physisorption at -196 °C using a Micromeritics Tristar. The morphology of the YSZ powder was observed by SEM (Hitachi S800 FEG) applying an acceleration voltage of 15 kV. The samples were deposited on a carbon self-adhesive tape that was then stuck on an aluminum holder and coated by a gold film using cathodic pulverization. In addition, the distribution in size of the YSZ grains was measured by using the laser granulometry technique. XRD patterns were performed on a powder X-ray diffractometer (aD8A25 Bruker) using $\text{Cu K}\alpha$ ($\lambda = 0.15406$ nm) radiation and a graphite back-monochromator. Patterns were recorded for 2° values comprised between 10° and 80° by a 0.02° step, with step duration of 94.5 s. The possible presence of chemical impurities (Cl, Na, S, Al, Ti, Si) was analyzed by using a ICP-OES Horiba Jobin Yvon Activa apparatus. The YSZ powder was previously dissolved by an acidic attack.

High-resolution transmission electron microscopy (TEM) was achieved with a JEOL 2010 LaB6 microscope. The acceleration voltage was 200 kV with LaB6 emission current and the point resolution was 0.19 nm. The samples were previously dispersed in isopropanol using ultrasonic bath. One drop at the surface of this suspension was sampling and then deposited on holey carbon coated 200 mesh, Cu, PK/100 grid.

The surface $\text{Zr}^{4+}/\text{Y}^{3+}$ ratio was determined by X-ray photoelectron spectrometry (XPS, Kratos Ultra DLD spectrometer) using a $\text{Al K}\alpha$ ($h\nu = 1486.6$ eV) X-ray source. XPS analyses were performed in hybrid mode (magnetic and electrostatic detections) with scanning energy in the analyzer of 20 eV for each element. The binding energies were calibrated using C1s peak of contaminant carbon (BE = 284.6 eV). The Zr atomic percent was determined from the

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