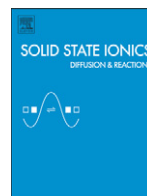




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## Isothermal catalytic oxidation of diesel soot on Yttria-stabilized Zirconia

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### ABSTRACT

Long-term isothermal experiments of soot combustion were performed on Yttria-stabilized Zirconia, an oxygen ionic conductor, at 370, 390 and 410 °C. At these temperatures, isotopic experiment confirms that mobile YSZ bulk oxygens oxidize soot at the soot/YSZ interface. In parallel, the surface oxygen exchange process replenishes YSZ oxygen atoms. After long-term isothermal experiments, HR-TEM observations reveal that the remaining soot particles form a continuous thin film on some YSZ grains, which inhibits the oxygen potential gradient, then stopping the oxidation process. All these experiments are in good agreement with the proposed fuel-cell type mechanism of soot on YSZ.

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### 1. Introduction

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]. EURO 6 standards will require the utilization of a NOx catalytic after-treatment device [2], preferentially placed between the Diesel Oxidation Catalyst (DOC) and the DPF [2,3]. Therefore, NO<sub>2</sub> can no more be utilized as an oxidant for soot combustion. This makes crucial the development of effective catalysts for soot combustion with oxygen, combining activity at low temperatures and an excellent stability at high temperatures for complying the necessary durability. Oxide catalysts are intensively investigated to perform soot oxidation with oxygen, such as perovskites [4–6], spinel-types [7,8], and ceria-based oxides [9,10]. Lattice oxygen ions of these oxide catalysts are involved in the soot oxidation process [9,11–16]. The most effective family seems to be the ceria-based materials and more specifically the Ce–Pr mixed oxide [10], even if many studies have been performed in the presence of NO which can be oxidized into NO<sub>2</sub> onto ceria. The reducibility of ceria (Ce<sup>4+</sup> into Ce<sup>3+</sup>) and its high oxygen storage capacity can generate mobile bulk species effective for soot oxidation. A dual mechanism seems to occur on

ceria-based catalyst coupling surface oxygen exchange and a reverse-spillover of bulk oxygen species. A key point in the soot oxidation process is the soot/catalyst contact since the reaction takes place or, at least, is initiated at the particulate/catalyst interface [17–20].

We have recently reported that purely Yttria-stabilized Zirconia (YSZ), an O<sup>2-</sup> ionically conducting ceramic without any redox property, is a promising catalyst to continuously oxidize soot with oxygen in Diesel exhaust conditions [21]. Isotopic Temperature-Programmed Oxidation (TPO) experiments using labeled oxygen <sup>18</sup>O<sub>2</sub> demonstrate the key-role of bulk oxygen species in the oxidation process. Considering an “intimate” soot/YSZ contact surface, obtained after in-situ carbon deposition via propylene cracking, lattice oxygen ions are the predominant species involved in the oxidation reaction. From isotopic TPO experiments performed with various oxygen partial pressures in “tight” contact mode and oxygen exchange measurements, we assumed that the ignition of the soot oxidation on YSZ involves 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. Electrochemical oxidation of the soot could occur at the soot/YSZ interface while oxygen electrochemical reaction takes place at the triple phase boundary (tpb) soot/gas/YSZ. Soot particulates could act both as a reactant and a current collector.

To obtain further insights into this mechanism, this study reports long-term isothermal soot oxidation on YSZ catalyst, performed at 370 °C, 390 °C and 410 °C. At 390 °C, the same experiment was also performed by switching from normal to isotopically labeled oxygen. Extracted kinetic data as well as HR-TEM characterizations of the soot-

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catalyst mixture are discussed in relation with the proposed fuel-cell type electrochemical mechanism.

## 2. Experimental

### 2.1. Preparation of the soot/YSZ mixture

Soot was obtained from a mini Combustion Aerosol Standard (miniCAST, Jing Ltd. Switzerland) soot generator as described in [23]. The soot particles were produced with a mini-CAST burner from a propane/air flame. Therefore, they are not containing inorganic matter such as metals. On the other hand, these mini-CAST soots show an EC (Elemental Carbon)/TC (Total Carbon) ratio of ~0.95, closed to that reported in the literature for real Diesel soots [22]. Ytria-stabilized Zirconia (YSZ) powder, containing 8 mol% of yttria from TOSO, ( $\text{ZrO}_2$ )<sub>0.92</sub>( $\text{Y}_2\text{O}_3$ )<sub>0.08</sub>, was used as purchased. Collected soot and YSZ powder were mixed with a weight ratio of 1:4 and crushed for 20 min in a mortar in order to improve the soot/YSZ agglomerate contact, conventionally denoted as tight contact mode.

### 2.2. Catalysts activity

Isothermal Oxidation Experiments (IOE) were performed with the catalyst/soot mixtures prepared as described in Section 2.1. Samples (25 mg: 5 mg soot/20 mg YSZ) were placed in a fixed-bed tubular quartz reactor (internal diameter = 8 mm) and heated in helium up to a selected temperature (370 °C, 390 °C or 410 °C) with a heating ramp of 10 °C/min. When the temperature stabilized (~30 min) in the set point, the gas was switched to an O<sub>2</sub>/He mixture containing 5% O<sub>2</sub> with an overall flow of 8 L h<sup>-1</sup>, corresponding to a GHSV of around 160 000 h<sup>-1</sup>. The soot combustion rate was monitored as a function of time. Combustion products, CO and CO<sub>2</sub>, were on-line analyzed using a micro-gas chromatograph (SRA 3000) and an infrared analyzer (HORIBA 3000). The CO production was negligible at 370 °C and 390 °C and around 10–15% in comparison with CO<sub>2</sub> production at 410 °C.

IOE were carried out until the CO<sub>2</sub> production rate becomes negligible, i.e. for 24 h at 370 °C, 20 h at 390 °C and 6 h at 410 °C. Then, samples were cooled-down to room temperature in helium. After IOEs, Temperature Programmed Oxidation (TPO) tests were performed with 5% O<sub>2</sub> in He (8 L h<sup>-1</sup>) and a heating ramp of 10 °C/min from room temperature up to 750 °C. CO and CO<sub>2</sub> products were analyzed as a function of the temperature, using the same techniques described for IOE experiments.

An IOE measurement was performed at 390 °C for 5.5 h in the presence of labeled oxygen, i.e. 5% <sup>18</sup>O<sub>2</sub> in He, with an overall flow of 1.8 L h<sup>-1</sup>. Reactant mixtures were monitored with mass flow controllers (Bronkhorst El Flow select with an accuracy better than 1%) from a cylinder of <sup>18</sup>O<sub>2</sub> (Euriso-top, 97.95% <sup>18</sup>O, 1.54% <sup>16</sup>O and 0.51% <sup>17</sup>O, 99.999% purity) and a second one of He (Linde Gas, 99.995% purity). The different isotopic combustion products were analyzed in the gas stream by a mass spectrometer (HIDEN ANALYTICAL HPR20). Signals at m/z 28, 30, 44, 46, 48 amu corresponding to C<sup>16</sup>O, C<sup>18</sup>O, C<sup>16</sup>O<sub>2</sub>, C<sup>16</sup>O<sup>18</sup>O and C<sup>18</sup>O<sub>2</sub> respectively, were recorded during IOEs and TPOs.

### 2.3. Catalyst characterizations

The surface area BET and the pore volume (BJH method) were measured by employing nitrogen physisorption at -196 °C using a Micromeritics Tristar. They confirm the mesoporous behavior of the YSZ powder with low surface specific area (14 m<sup>2</sup> g<sup>-1</sup>) and pore volume (0.06 cm<sup>3</sup> g<sup>-1</sup>). Pores present a double distribution in size with a predominant centered at around 2.5 nm and a second one at 35 nm. Therefore, Diesel soot particulates which present a diameter between 30 and 300 nm [24] cannot penetrate into the porosity of the YSZ grains. SEM images (Hitachi S800 FEG), applying an acceleration voltage of

15 kV, reveal large spherical agglomerates with diameters in the range 20–160 μm and a median diameter (d50) of around 68 μm.

High-resolution transmission electron microscopy (HR-TEM) was achieved with a JEOL 2010 LaB6 microscope in order to characterize the soot/YSZ before and after IOE experiments. The acceleration voltage was 200 kV with LaB6 emission current and the point resolution was 0.19 nm. A dispersion of the catalyst crushed in ethanol was deposited on standard holey carbon-covered copper TEM grids. EDX analysis was carried out by using an ISIS Oxford Instrument.

## 3. Results

### 3.1. HRTEM investigations of the soot/YSZ mixtures

TEM images were captured to characterize the quality of the contact between soot and the YSZ powder. Fig. 1a displays that the preparation of the sample (the samples were previously dispersed in isopropanol using ultrasonic bath) for TEM observations can dislocate the YSZ powder to obtain smaller grains of few hundred nanometers. Nevertheless, without this specific preparation, YSZ agglomerates are too thick to be observed with TEM. Therefore, even if the TEM observations are not fully representative of the real soot/YSZ mixture, they give insights of the interface soot/YSZ. The majority of the soot particulates are not in contact with YSZ grains. Primary soot particulates are spherules which have a diameter of around 20 nm, as already observed for collected Diesel soot [25]. These primary particles exhibit a well-known shell-core structure where long-range layers are concentrically arranged along the outermost periphery [26]. Short Amorphous layers are located in

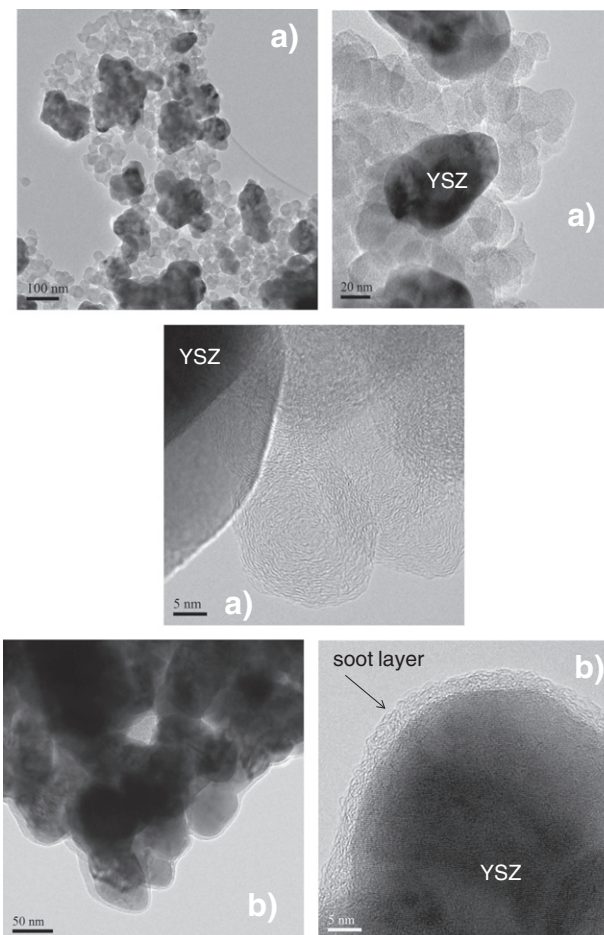


Fig. 1. HRTEM pictures of the soot/YSZ mixture (a) before IOE experiments at 390 °C and (b) after.

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