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

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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.

## 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 TOSOH,  $(\text{ZrO}_2)_{0.92}(\text{Y}_2\text{O}_3)_{0.08}$ , 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  $\text{O}_2/\text{He}$  mixture containing 5%  $\text{O}_2$  with an overall flow of 8 L  $\text{h}^{-1}$ , corresponding to a GHSV of around 160 000  $\text{h}^{-1}$ . The soot combustion rate was monitored as a function of time. Combustion products, CO and  $\text{CO}_2$ , 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  $\text{CO}_2$  production at 410 °C.

IOE were carried out until the  $\text{CO}_2$  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%  $\text{O}_2$  in He (8 L  $\text{h}^{-1}$ ) and a heating ramp of 10 °C/min from room temperature up to 750 °C. CO and  $\text{CO}_2$  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%  $^{18}\text{O}_2$  in He, with an overall flow of 1.8 L  $\text{h}^{-1}$ . Reactant mixtures were monitored with mass flow controllers (Bronkhorst El Flow select with an accuracy better than 1%) from a cylinder of  $^{18}\text{O}_2$  (Euriso-top, 97.95%  $^{18}\text{O}$ , 1.54%  $^{16}\text{O}$  and 0.51%  $^{17}\text{O}$ , 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  $\text{C}^{16}\text{O}$ ,  $\text{C}^{18}\text{O}$ ,  $\text{C}^{16}\text{O}_2$ ,  $\text{C}^{16}\text{O}^{18}\text{O}$  and  $\text{C}^{18}\text{O}_2$  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  $\text{m}^2 \text{g}^{-1}$ ) and pore volume (0.06  $\text{cm}^3 \text{g}^{-1}$ ). 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  $\mu\text{m}$  and a median diameter ( $d_{50}$ ) of around 68  $\mu\text{m}$ .

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

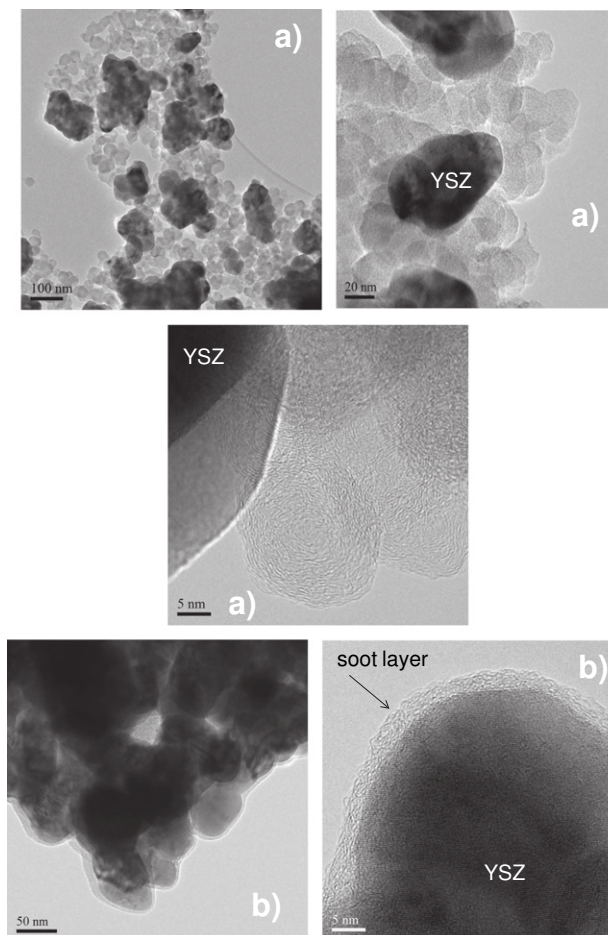


Fig. 1. HRTEM pictures of the soot/YSZ mixture (a) before IOE experiments at 390 °C and (b) after.

the vicinity of the core. These primary particles are agglomerated in the form of grapes. Fig. 1b shows the remaining soot after a long-term IOE at 390 °C. Spherules have disappeared and have been replaced by thin films of few nanometers which perfectly cover some YSZ grains. These thin films of soot also have a different organization than the initial particles. This indicates that the soot grapes are gradually consumed at the contact points and slowly spread over the YSZ grains.

### 3.2. Isothermal oxidation experiments

A typical IOE is reported in Fig. 2 which displays the variation of the rate production of CO<sub>2</sub> with time at 390 °C. Slight production of CO was only observed at 410 °C with selectivity to CO<sub>2</sub> always larger than 90%. A small production peak of CO<sub>2</sub> is observed during the first minutes after the introduction of oxygen. The area of this first peak, denoted as S<sub>1</sub>, is extremely small in the range 2–4 μmol and does not significantly vary with the temperature (Table 1). This first peak probably corresponds to the combustion of the soluble organic fraction of the soot particles, which is much more reactive than the carbon core. Then, CO<sub>2</sub> production rate increases and reaches a plateau which corresponds to the maximal values. As the temperature of IOE increases, the time to reach the plateau and its duration decrease. This steady state was reached after 110, 42 and 20 min for 370, 390 and 410 °C, respectively. We have estimated the quantity of soot consumed before reaching the plateau from the CO<sub>2</sub> production rate, denoted as S<sub>2</sub> area in Fig. 2. The consumed soot proportion relative to the initial quantity seems to be almost constant and represents around 15–20%. One can assume that this level corresponds to the soot particles that are initially in contact with the surface of the YSZ agglomerates. Therefore, the catalytic performances measured during the plateau are not limited by the YSZ/soot contact points. These maximal catalytic rate values were used for extracting the apparent activation energy which was found to be 140 kJ mol<sup>-1</sup>. This value is in good agreement with the data reported in the literature for ceria-based catalysts in tight contact mode [10]. The increase in the catalytic rate before reaching the plateau is probably linked to the exothermicity of the reaction which locally heats the catalyst. As far as the number of soot/YSZ contact points starts to decrease, the catalytic rate gradually decays with time and finally vanishes to zero (Fig. 2). At this point, 99.8 wt.% of the soot was burned. However, even after 24 h at 370 °C, 20 h at 390 °C and 6 h at 410 °C, the samples collected after the end of IOEs are gray (in contrast with the white color of the YSZ powder), showing that the soot particles were not fully oxidized, as experimentally observed by HR-TEM (Fig. 1b). Fig. 3 displays TPO measurement on the soot/YSZ mixture after IOE at 370 °C for 24 h which is compared with similar TPO tests performed on a “fresh” soot/YSZ mixture and the bare soot. The remaining soot after IOE (only 0.2 wt.% of initial soot loading) generates two CO<sub>2</sub> production peaks, the first one centered at

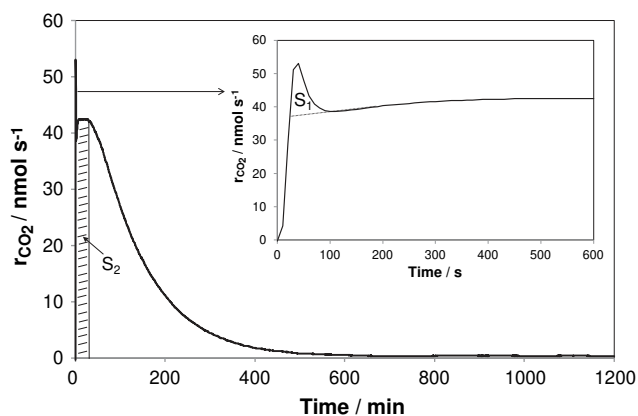


Fig. 2. Variation of the CO<sub>2</sub> production rate as a function of time at 390 °C. The onset part represents a zoom of the first 10 min.

**Table 1**  
Catalytic parameters during IOE on the YSZ/soot mixture.

T <sub>IOE</sub> /°C	r <sub>CO2-max</sub> /		S <sub>1</sub> /μmol	S <sub>2</sub> /μmol	Stotal/μmol	S <sub>2</sub> /Stotal/%
	nmol s <sup>-1</sup> g <sup>-1</sup>	nmol s <sup>-1</sup>				
370	73	5.2	2	108	567 (6.8 mg)*	19
390	212.5	15.5	4.2	61.6	416 (5 mg)	15
410	338.5	24.1	3.2	86.1	397 (5.3 mg)	21.7

\* This value corresponds to the initial soot loading, calculated from the overall production of CO and CO<sub>2</sub>.

515 °C and the second one centered at around 615 °C. The second CO<sub>2</sub> production is linked to the soot not in contact with YSZ but takes place at a significantly lower temperature than the one observed with the bare soot. This is another confirmation of soot structure modification after a long-term IOE, as already observed by HR-TEM. The first peak corresponds to the CO<sub>2</sub> production observed on the “fresh” YSZ/soot mixture. Therefore, soot particles were in contact with YSZ grains but, surprisingly, cannot be oxidized during long-term IOE between 370 and 410 °C.

### 3.3. Isotopic isothermal oxidation experiment

Isotopic-IOE was performed at 390 °C with 5% <sup>18</sup>O<sub>2</sub> in helium. Fig. 4 shows CO<sub>2</sub>, 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> production rates as a function of time as well as the <sup>18</sup>O/<sup>16</sup>O ratio in the CO<sub>2</sub> production. Before and during the plateau, the main product is C<sup>16</sup>O<sub>2</sub>. This confirms that the soot oxidation occurs with the YSZ bulk oxygen species. The production of C<sup>16</sup>O<sup>18</sup>O linearly increases and then reaches a maximum and decays when the C<sup>18</sup>O<sub>2</sub> production begins. This indicates that the surface oxygen exchange process between gaseous and YSZ oxygens is effective. As far as one oxygen atom reacts with soot, one is incorporated inside the YSZ. After 3 h, the <sup>18</sup>O/<sup>16</sup>O ratio in the CO<sub>2</sub> production is 1, meaning that 50% of YSZ oxygen atoms (22 mg of catalyst) were exchanged by gaseous oxygens. To oxidize 5 mg of soot, i.e. around 400 μmol of C, 800 μmol of oxygen atoms are required to produce CO<sub>2</sub>. However, YSZ powder only contains 314 μmol O. Then, the overall quantity of YSZ oxygen atoms has to be exchanged 2.5 times. Therefore, after 5 h, YSZ mainly contains <sup>18</sup>O species. This explains why the main products, after 5 h, are predominantly composed of <sup>18</sup>O, i.e. C<sup>16</sup>O<sup>18</sup>O and C<sup>18</sup>O<sub>2</sub>. Referring to our previous study [21], the soot oxidation process on YSZ can only occur when oxygen is present in the gas phase. In addition, the surface oxygen exchange can only take place when YSZ is interfaced with soot. Therefore, one can assume that the driving force is the oxygen chemical potential gradients between YSZ oxygen vacancies interfaced with soot and those exposed to the stream at tpb. After a long-term IOE, HR-TEM observations indicate that the remaining soot particles

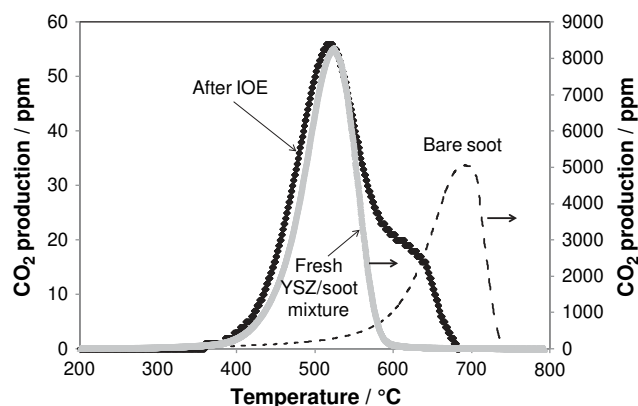
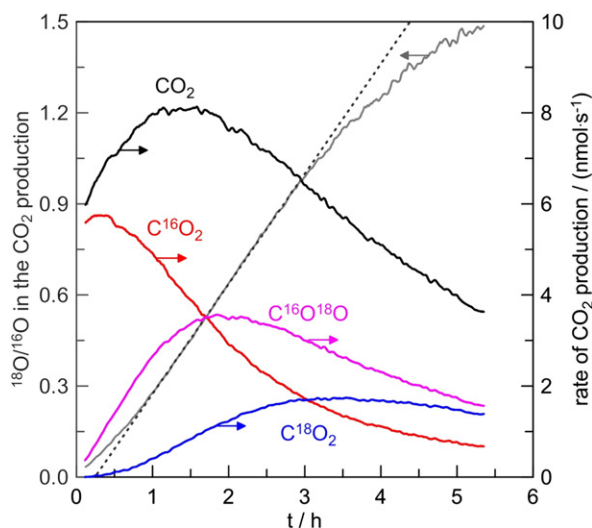


Fig. 3. CO<sub>2</sub> production versus temperature on the soot/YSZ mixture after IOE at 370 °C for 24 h, on a fresh soot/YSZ mixture and on the bare soot. Reactant mixture: 5%O<sub>2</sub>/He. Overall flow: 8 L h<sup>-1</sup>, heating ramp = 10 °C min<sup>-1</sup>.



**Fig. 4.** Isotopic CO<sub>2</sub> production rates as well as the <sup>18</sup>O/<sup>16</sup>O ratio in the CO<sub>2</sub> production as a function of time during IOE at 390 °C. Reactant mixture: 5% <sup>18</sup>O<sub>2</sub>/He.

form a continuous thin film on the surface of some YSZ grains (Fig. 1b). If this film is porous, oxygen can diffuse at the soot/YSZ interface and remove the oxygen chemical potential gradient. On the other hand, if the film is dense, there is no more gas/YSZ interface. For both cases, it stops the oxidation process by removing the oxygen chemical potential gradient. This can explain the remaining soot after long-term IOEs.

#### 4. Conclusions

Long-term isothermal experiments of soot combustion were performed on Ytria-stabilized Zirconia at 370 °C, 390 °C and 410 °C. Isotopic experiment confirms that bulk YSZ oxygens are the active species to oxidize soot at the soot/YSZ interface. In addition, the mechanism involves effective surface oxygen exchange to replenish YSZ oxygen atoms which have oxidized soot. After a long-term isothermal experiment, HR-TEM observations reveal that the remaining soot particles (only 0.2 wt.% of the initial quantity) 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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