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High-throughput approach to the catalytic combustion of diesel soot

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ABSTRACT

A methodology for the evaluation of diesel soot oxidation catalysts by high-throughput (HT) screening was developed. The optimal experimental conditions (soot amount, catalyst/soot ratio, type of contact, composition and flow rate of gas reactants) ensuring a reliable and reproducible detection of light-off temperatures in a 16 parallel channels reactor were set up. The temperature profile measured in the catalyst/soot bed under TPO conditions when the exothermic combustion of soot takes place was shown to provide an accurate measurement of the ignition. Its reproducibility and relevance were checked. The results obtained with a reference noble metal free catalyst ($La_{0.8}Cr_{0.8}Li_{0.2}O_3$ perovskite) agree very well with literature data. Qualitative mechanistic features could be derived from these experiments, stressing the likely limiting step of oxygen transfer from catalyst surface to soot particulates to ignite the soot combustion. Ceria material was shown to be more appropriate than perovskite one. From an HT screening of a large diverse library (over 100 mixed oxides catalysts) under optimized conditions, about 10 new formulations were found to perform better than selected noble metal free reference materials.

1. Introduction

Despite their recent development on passenger cars, diesel particulate filters (DPF) are still facing major issues like: high regeneration temperature, pore plugging with irreversible pressure drop, mechanical and chemical instability due to the severe regeneration cycles, etc. The development of a new generation of catalytic filters requires the discovery of catalysts to be deposited within the filter, able to ensure soot combustion at lower temperatures, avoiding the use of additives in diesel formulation [1,2]. These catalysts have to be active without pre-reduction under hydrogen (on-board requirement), resistant under hydrothermal conditions and in the presence of SO_2, but also be able to undergo high temperatures and thermal shock during regeneration sequences. Their texture and structure also have to favour a contact as intimate as possible with soot particles, since the combustion involves oxygen activation on catalytic centers, followed up by transfer of activated oxygen towards the soot particles to initiate the oxidation of the surface oxygenated complexes (SOC) [3–5]. Finally, the development of efficient catalytic materials also aims at reducing the filter volume and weight, within the general context of process intensification for car and truck exhaust after-treatment.

Combinatorial methods and high-throughput experimentation (HTE) are now frequently used to rapidly investigate broad domains of catalyst compositions [6]. It requires parallel screening techniques to evaluate the performance of each formula, generally conversion, selectivity or yield in targeted products [7]. For the present case of diesel soot combustion, the efficiency of a new catalyst formula can simply be evaluated by a temperature controlled combustion between an oxygen containing gas and a packed bed of soot particulates, mixed in a tight or loose contact with the powdered catalyst: the lower the temperature of light-off, the faster the combustion of all the packed soot proceeds, the better the tested catalyst formula can be considered. For the case of HTE parallel screening, an accurate control of the process parameters is obviously required to compare the screened formulations under fair conditions.

Few works are reported in the literature to evaluate catalytic soot combustion under screening conditions. Reichenbach et al. [8] used automated thermo-gravimetric analysis to evaluate the performances of alkali metal doped oxides for the combustion of synthetic soot. Olong et al. [9] applied infrared thermography for primary screening libraries with up to 206 catalyst–soot mixtures. However, the testing conditions can be considered as relatively far removed from real soot combustion in a DPF: (i) screening at fixed

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temperature, generally below the light-off temperature, (ii) soot/catalyst contact not precisely controlled and (iii) static reaction conditions instead of dynamic combustion.

In order to improve the data quality in a HT approach of soot combustion (reproducibility, realistic conditions), we used in this study a 16 parallel reactor bench to screen soot/catalysts mixtures, packed in tight or loose contact, heated under controlled combustion conditions (temperature-programmed oxidation or TPO). The continuous monitoring of the catalytic bed temperature allowed an accurate detection of the exothermic peak associated to soot combustion. Additionally, the screening experiments were compared to TPO experiments in a conventional fixed-bed reactor, to ascertain the accuracy of the measured light-off temperature in the parallel reactors. In order to demonstrate the ability of the HT screening to clearly assess the light-off performance for soot–catalysts mixtures, the operating conditions were systematically varied (temperature ramp, gas composition and flow rates, soot/catalyst ratio, etc.), keeping the composition of the catalyst unchanged. Characterization of the physico-chemical state of the tested soot/catalyst mixtures was also carried out (particle size distribution, Raman micro cartography to investigate soot/catalyst contact) to identify possible relationships with light-off performances.

Only noble metal free mixed oxides were considered in this study, since it was decided ab initio to explore categories of materials cheaper than the usually noble metal containing commercial systems. For this reason, the two reference materials were selected free of noble metals: cerium oxide which is widely used in automotive exhaust treatment, and perovskite which represents a class of mixed oxide materials known for their efficiency in soot catalytic combustion [10].

2. Experimental

2.1. Catalysts and soots

Ceria used in this work was a commercial sample (CeO_2 HSA) supplied by Rhodia. The selected perovskite $La_{0.8}Cr_{0.8}Li_{0.2}O_3$ was synthesized either using the conventional "citrates" method or the "combustion" method [10] reported as a suitable technique to prepare small-sized catalyst particles. For the latter, an aqueous solution of metal precursors (nitrates), in stoichiometric ratio, was mixed with urea, an excess of about 250% being kept for the fuel to oxidizers ratio. This solution was stirred for 15 min, and then transferred into a ceramic vessel. The synthesis was performed in an oven, the ceramic vessel filled with the precursor solutions being directly introduced at 600 °C. The reaction between the oxygen originated from nitrates decomposition with urea is highly exothermic, the thermal peak exceeding 1000 °C [10]. The self-sustaining reaction takes place within 10 s [11]. For comparison, the same perovskite formulation was synthesized by a conventional "citrates" method.

The soot sample was collected in the exhaust stream of a 2.2 L Renault diesel engine after an oxidation catalyst. Soots are collected after several NEDC (New European Driving Cycle) cycles (in order to collect 30 g of soot). The collecting system is placed after a diesel oxidation catalyst in order to limit the quantity of hydrocarbons stored on the soots.

2.2. Characterization

X-ray diffractograms of powder samples were performed on a Siemens D500 diffractometer, using a Cu Kα radiation ($\lambda = 0.154184$ nm). The diffractograms were recorded in a range from 3° to 80° theta, using a 0.02 pass. The identification of crystallised phases was realised using the ICDD-JCPDS database and the DiffracPlusEva software.

The particle size distribution of powder samples was measured using a Microtrac S3500 Particle Size Analyzer. The Microtrac® S3500 employs a tri-laser technology to allow even in the submicron range, that the measurements are made without typical sample-to-sample variation evident in many other systems. A spherical shape of the particles was assumed. The percentage of particles having a certain size was measured from the total solid volume.

Specific surface areas were measured on an ASAP 2010 equipment, from N_2 adsorption isotherms by applying the BET equation. The samples were previously desorbed under 10^{-2} bar at 300 °C for 1 h.

Raman spectra of the samples were recorded with a LabRam HR Raman spectrometer (Horiba-Jobin Yvon) equipped with a confocal microscope. The 514.53 nm exciting line of a 2018 RM Ar+–Kr+ laser (Spectra Physics) was focused using a ×50 long working distance objective. The spectra collected using an 1800 grooves mm^{-1} grating were accurate within 2 cm^{-1}. The spectral evolution with the laser power was previously examined to determine the most suitable power. Thus, a power on the samples of 2 mW was usually chosen. However, spectra at room temperature in air were recorded at a power of only 150 μW under a microscope, to avoid dehydration.

2.3. Catalytic tests

Catalytic tests were performed either in a 16 parallel reactors bench (commercialised as SWITCH 16) or in a classical fixed bed single-reactor bench. In the case of SWITCH 16, the 6 mm internal diameter reactors are made of Inconel and are connected to the stream lines by VCR fittings. The 16 reactors can be heated to 650 °C with a ramp raging from 1 to 5 °C/min. They are fed with the same stream composition and velocity. Each reactor is equipped with a thermocouple K allowing to measure continuously the bed temperature with an accuracy of 0.5%. A complete description of the system can be found elsewhere [7]. Reaction products of one selected reactor can be monitored by mass spectrometry using an Inficon CPM instrument [7].

In a standard experiment of temperature-programmed oxidation, the 16 stainless steel reactors were loaded with 40 mg of soot or mixtures of 40 mg soot with 400 mg of catalyst. In most cases, the soot was manually mixed with the catalyst in an agate mortar (tight contact). Some samples were prepared in loose contact, either as a mixture done with a spatula, or by using two separate layers for soot and catalyst. Standard oxidation experiments were performed from 25 to 600 °C with a heating rate of 5 °C/min, under a 40 mL/min gas flow (50% O_2 in He). Several experiments were carried out in order to study the influence of gas composition, soot/catalyst ratio, type of contact between soot and catalyst, space velocity, on the catalytic performance in term of ignition temperature. The temperature corresponding to the combustion light-off was recorded with a thermocouple introduced within the catalyst bed. The gaseous products stream could also be analyzed online by a mass spectrometer.

3. Results and discussion

3.1. Materials characterization

3.1.1. Soot

The X-ray diffractogram of the soot is shown in Fig. 1. The diffraction pattern of the diesel soot sample exhibits two distinct features: (i) an amorphous structure, characterised by very broad

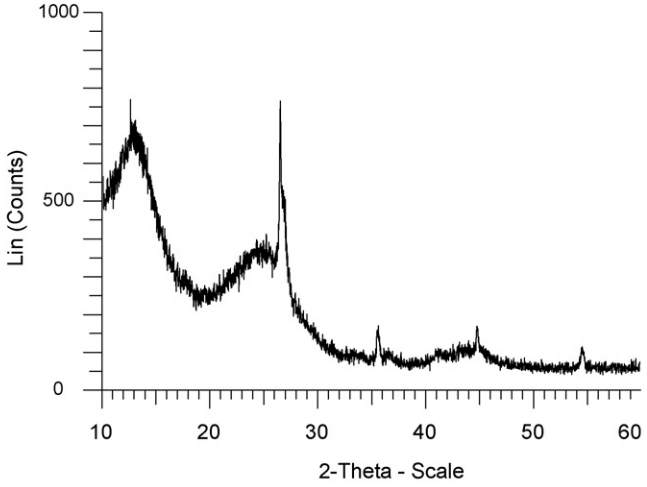

Fig. 1. XRD diffraction pattern of diesel soot.

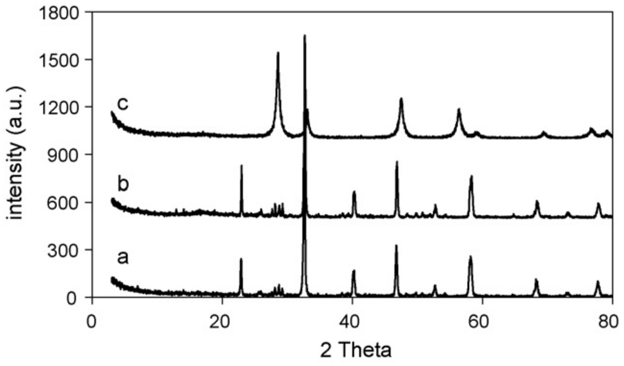

Fig. 2. XRD diffraction pattern: (a) $La_{0.8}Cr_{0.8}Li_{0.2}O_3$ "combustion"; (b) $La_{0.8}Cr_{0.8}Li_{0.2}O_3$ "citrates"; (c) CeO_2.

diffraction lines, very similar to the diffractogram of Printex XE2 or Printex 90 already reported in literature [12], and (ii) thin and intense reflections at 26.8° (0 0 2 layer), 44.5° (1 0 1) and 54.9° (1 0 2), which reveal the presence of a crystalline graphite structure. This characteristic of the real diesel soot could be related to the presence of a diesel oxidation catalyst before the filter.

3.1.2. Catalysts

The X-ray diffractograms of the synthesized $La_{0.8}Cr_{0.8}Li_{0.2}O_3$ perovskite and the commercial CeO_2 HSA are shown in Fig. 2.

The diffraction lines of $La_{0.8}Cr_{0.8}Li_{0.2}O_3$ samples confirmed the presence of a crystalline lanthanum chromite perovskite phase, identified when comparing with the ICDD-JCPDS database. The diffraction peaks could be indexed to (1 0 0), (1 1 0), (1 1 1), (2 0 0), (2 1 1) and (2 2 0) corresponding to the cubic structure of perovskites. The diffractograms of the two perovskites, prepared by urea combustion and citrates methods, are very similar, the slightly higher peak intensities in the case of "combustion" synthesis route revealing a better crystallinity. As no significant secondary phases were detected, the Li appears successfully introduced in the perovskite structure.

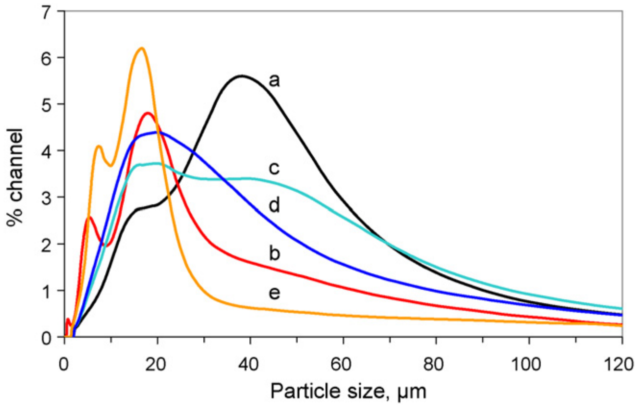

Fig. 3. Particle size distribution: (a) soot; (b) CeO_2; soot/CeO_2 mixtures (c) loose contact; (d) tight contact; (e) "highly tight" contact.

The XRD analysis confirms a fluorite structure in the case of CeO_2 HSA sample. The diffraction lines of the calcined (600 °C) sample are more intense than those of the fresh sample, due to sintering. The specific surface areas of the catalysts used in this study are presented in Table 1.

The "combustion" synthesis route provides a higher surface area, since this method favours the formation of small-sized catalyst particles [10]. The sintering of ceria after calcination is confirmed by the loss of surface area.

3.2. Characterization of soot–catalyst mixtures

The particle size distributions of diesel soot and of HSA ceria, as well as different mixtures of them, are shown in Fig. 3. In the case of the diesel soot sample, the particles are agglomerated in aggregates with a broad size range, with an average size of ≈40 μm. The average particle size of ceria is ≈20 μm.

Different types of contact between soot and ceria were used in this study. The soot and ceria were mixed: (i) by shaking the two powders directly in the reactor ("highly loose contact"); (ii) by thoroughly mixing soot and catalyst with a spatula ("loose contact"); (iii) by grinding ceria and soot in an agate mortar ("tight contact"); (iv) by ball milling of ceria and soot ("highly tight contact"). As can be seen in Fig. 3, the tighter the contact, the narrower the particle size distribution, with an average particle size decreasing from ≈40 μm (loose contact) down to less than 20 μm by using ball milling (highly tight contact). Ball milling was applied at different rotation rates, and the value of 150 rot/min was found the optimal. Increasing further the rotation rate leads a very broad particle size distribution, with an irreversible appearance of large aggregates. This behaviour is probably related to structural changes induced by the highly energetic ball milling at high spinning rates.

The RAMAN spectra of diesel soot and ceria are shown in Fig. 4 and the soot/ceria mixtures in Fig. 5.

In the case of ceria, the strong absorption band at 460 cm^{-1} is characteristic of the first-order Raman-active mode of the cubic fluorite structure [13]. The band at 1030 cm^{-1} is likely to correspond to residual nitrates, expected from nitrate decomposition in fresh ceria. As matter of fact, NO_x desorption (essentially as NO) is observed during thermo-desorption of fresh ceria, with a maximum at 510 °C. Note however, that for the screening

Table 1
Specific surface areas of the catalysts used

Catalyst	$La_{0.8}Cr_{0.8}Li_{0.2}O_3$ "combustion"	$La_{0.8}Cr_{0.8}Li_{0.2}O_3$ "citrates"	CeO_2 fresh	CeO_2 calcined at 600 °C	CeO_2 calcined at 800 °C
SSA (m^2/g)	9	1.6	325	217	54

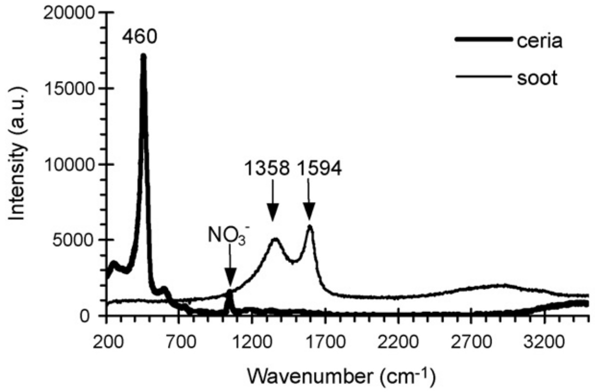

Fig. 4. Raman spectra of fresh CeO_2 HSA and of diesel soot.

procedure, all catalysts were calcined at 600 °C which excludes any significant role of NO_x during the combustion process.

The soot Raman spectrum presents two strong and broad overlapping bands at ≈1360 and 1595 cm^{-1}. They are assigned to the first-order D and G bands analogous to those of a disordered graphite structure [12].

The homogeneity of the contact of soot with ceria was studied by RAMAN microprobe analysis. The area analyzed is of ca. 1 μm diameter. As shown in Fig. 5, in the case of a "loose" contact some zones display only the characteristics bands of soot, whereas in other analyzed areas the bands of both ceria and soot are observed. This shows that, on the micrometer scale, parts of the soot are not in contact with ceria. In the case of "tight" contact, whatever the zone analyzed, the bands of ceria and soot are always found together, although their relative intensities may vary.

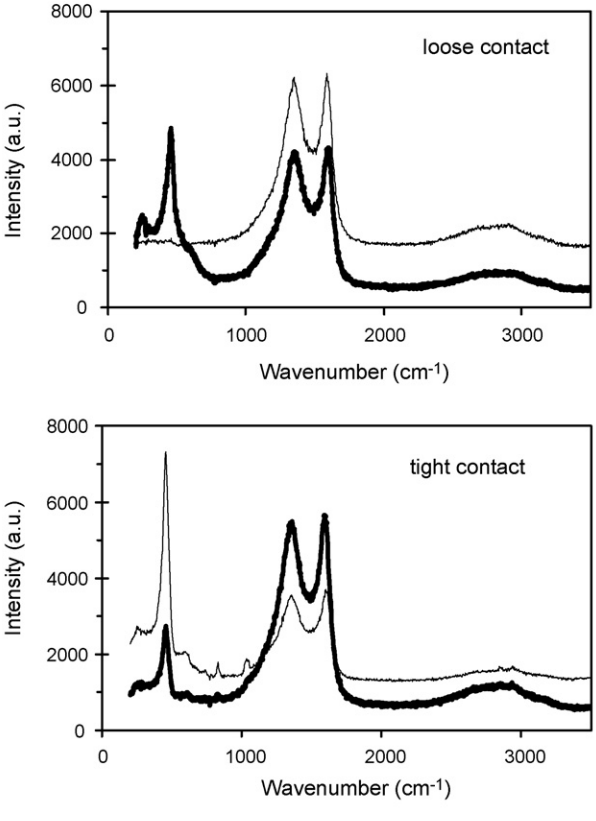

Fig. 5. Raman micro-cartography of ceria/soot mixtures.

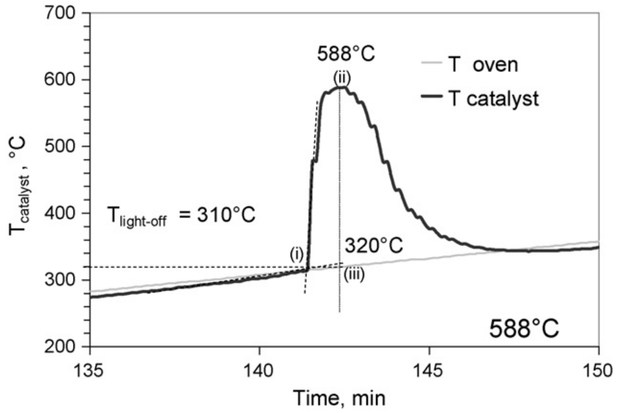

Fig. 6. Light-off identification in diesel soot combustion: 40 mg soot/400 mg fresh CeO_2 in tight contact under 40 mL/min 50% O_2/Ar.

3.3. Optimization of reaction conditions for light-off measurements

3.3.1. Light-off temperature as ranking criterion

The key step in the soot combustion process consists in the ignition of soot. This ignition takes place at the surface of the soot in contact with a catalyst particle, probably via a transfer of oxygenated species from ceria to the soot that constitutes a key kinetic step of the soot ignition process [14,15]. Ignition occurs when two conditions are achieved: (i) transfer of enough oxygen to the soot leading to a combustion at the surface; (ii) oxidation rate is fast enough to induce a strong increase of the local temperature. Once initiated, the catalytic light-off phenomenon propagates throughout the whole mass of soot allowing the thermal soot combustion. Indeed, the apparent combustion temperature might depend on the thermal characteristics of the reactor as well, an adiabatic reactor favouring lower light-off temperature.

Fig. 6 shows the temperature profile of the catalyst/soot system during a combustion experiment. The oxidation of soot particles takes place within a short time interval (2–3 min), and is characterised by a strong exothermic effect. The efficiency of such a process can be expressed in terms of light-off temperature, which is usually defined as the temperature at which a significant oxidation of the soot (generally 50%) is obtained. In the present case of high-throughput screening, we defined the light-off temperature as the intersection between the tangent to the temperature ramp profile, when it starts to deviate from linearity, with the tangent to the temperature peak corresponding to the exothermic reaction (i), i.e. 310 °C in Fig. 6. The maximum temperature (ii) corresponding to the exothermic peak (588 °C) was not considered as a significant parameter, since it depends on the amount of soot. On the contrary, the reactor temperature (iii) corresponding to the maximum of the exothermic peak (320 °C) was found independent on the soot amount, and therefore can be considered as a ranking criterion as well.

3.3.2. Optimal HTE operating conditions

In order to realise a high-throughput screening of catalysts in diesel soot combustion, a crucial point is to develop a suitable method for a reliable light-off measurement, in terms of accuracy and reproducibility.

Firstly, the operation of SWITCH16 was verified in blank experiments, without any soot or catalyst. Using different temperature ramps from 2 to 7.5 °C/min, each of the 16 reactors temperature profiles was verified. A linear response was obtained for all these tests, a heating rate of 5 °C/min being however considered as optimum.

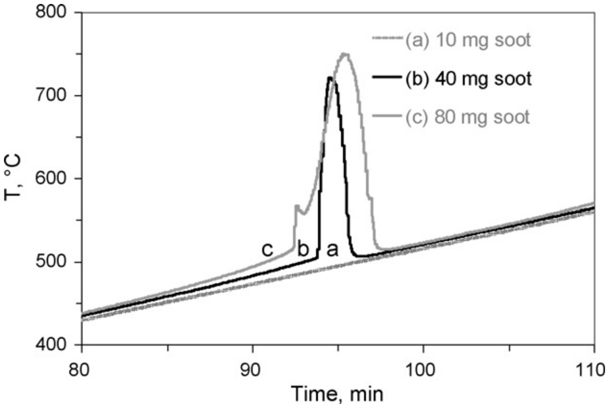

Fig. 7. Exothermic peak during the combustion of various soot amounts (no catalyst used).

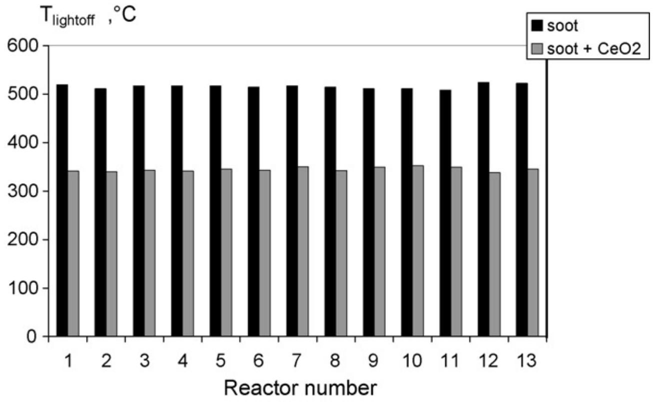

Fig. 9. Light-off for soot combustion as a function of the reactor used in the parallel reactor [40 mg soot] or [40 mg soot/400 mg fresh CeO_2] in tight contact under 40 mL/min 50% O_2/Ar (reactors 14–16 were kept empty in that case).

The next step was to assess experimental conditions ensuring an accurate identification of the light-off when a soot/catalyst system was used. Ceria was used as reference catalysts in these experiments. Different parameters were varied, i.e. the soot amount, the catalyst/soot ratio, the type of contact and the composition of gas reactant. More than 200 combustion tests have been performed in order to establish the optimal reaction parameters and to check the accuracy and the reproducibility of the protocol used for light-off identification.

The intensity of exothermic effect produced by the soot combustion depends firstly on the amount of soot used, as shown in Fig. 7. By using 10 mg of soot, the exothermic peak was not visible, whereas with 80 mg of soot the temperature peak is very broad and not symmetric (shoulder at low temperature). 40 mg soot was found an optimum amount.

The effect of various ceria/soot ratios (from 1:1 to 100:1) was investigated. Increasing the ceria/soot ratio led to a decrease of the light-off temperature. However, when the amount of soot was below the optimal value, a high catalyst/soot ratio was not sufficient for good light-off monitoring, the temperature peak being too dispersed. The optimal value for the catalyst/soot ratio was found to be 10:1.

3.4. Light-off reproducibility in parallel reactors

Keeping in mind that the output data during rapid screening consists essentially in light-off temperature, it was important to check that the temperature peak indeed corresponds to the combustion of soot. Analysis of the gaseous products stream performed by on-line mass spectrometry (MS) shows that the CO_2 signal corresponds perfectly to the temperature profile measured by the thermocouple placed in the ceria/soot bed, within the same time scale (Fig. 8). Quantitative analysis by MS and integration of the CO_2 and CO profiles provided a correct carbon balance (close to 100% accounting for the fraction of inorganic compounds in the collected soot) when compared to the carbon introduced as soot.

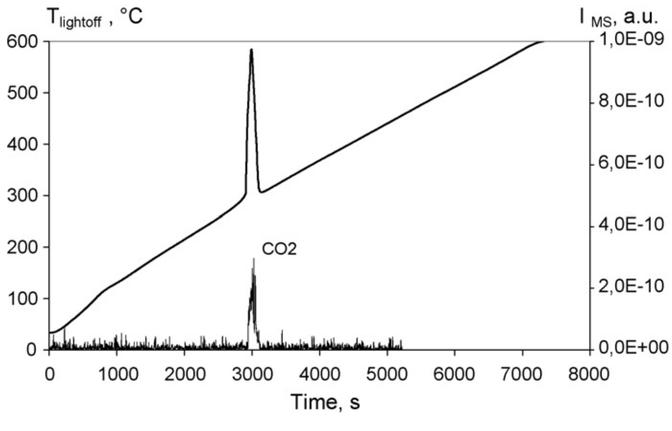

Fig. 8. Comparison of light-off identification by the temperature profile and by on-line analysis of the gaseous products stream; 40 mg soot/400 mg fresh CeO_2 in tight contact under 40 mL/min 50% O_2/Ar.

The reproducibility of light-off temperature measurements in the 16 parallel reactors was also verified. The reactors were filled with the same sample (soot or soot/catalyst mixture) and fed it with the same reactant (40 mL/min of 50% O_2 in Ar). The results in Fig. 9 showed that the light-off temperatures for the soot alone has an average of 515 °C with a standard deviation of 4.5 while it is 344 °C (±3 °C) for the soot/CeO_2 mixture. Therefore at low ignition temperature, the 95% confidence interval is estimated at ±3 °C. In order to validate the reproducibility of the light-off, the soot alone and different soot/catalyst mixtures were also tested in a classical reactor using temperature-programmed oxidation (TPO analysis). The light-off temperatures recorded by TPO were the same as those obtained in the parallel reactor.

Taking into account that the thermal conductivities of He and Ar are very different, 156.7 and 17.9 mW m^{-1} K^{-1}, respectively, the influence of the inert gas used as diluent for oxygen was studied. The light-off temperature of the soot and the mixture ceria/soot with the reactant 50% O_2 diluted with Ar or He was found the same. Thus, the light-off temperature was found to be independent of the nature of the inert diluent used, under the prevailing testing conditions.

3.5. Comparison with conventional catalysts in standard reactors

The reproducibility of HTE results with respect to results reported in the literature for similar catalyst/soot samples in conventional reactor was checked in the case of the perovskite $La_{0.8}Li_{0.2}CrO_3$ synthesized either by the "combustion" or the "citrate" method. A light-off for soot combustion at 325 °C (Fig. 10) was found similar to that mentioned in the literature for a similar catalyst under close operating conditions [10].

As also seen in Fig. 10, the light-off temperature of $La_{0.8}Li_{0.2}CrO_3$ perovskites prepared either by "combustion" or "citrates" method are very close, 320 and 340 °C, respectively. Since both materials present similar structures but quite different BET surfaces (Table 1), this points out that the catalyst specific surface area is not a sensitive factor for controlling the light-off temperature.

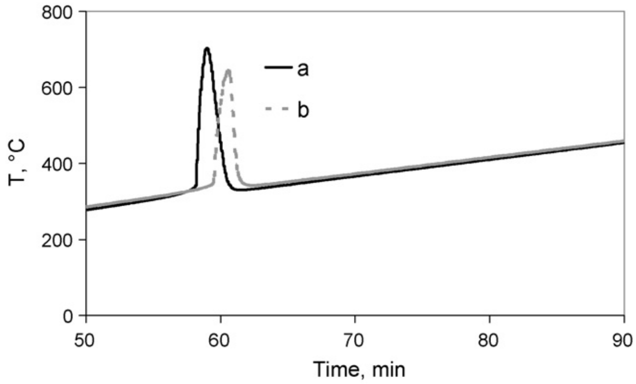

Fig. 10. Light-off for soot combustion on $La_{0.8}Li_{0.2}CrO_3$ perovskite "combustion" (a) and "citrates" (b): 40 mg soot/400 mg catalyst in tight contact under 40 mL/min 50% O_2/Ar.

Table 2
Light-off temperatures as a function of calcination temperature

Catalyst	CeO_2 fresh	CeO_2 calcined at 600 °C	CeO_2 calcined at 800 °C
$T_{lightoff}$ (°C)	310	340	330

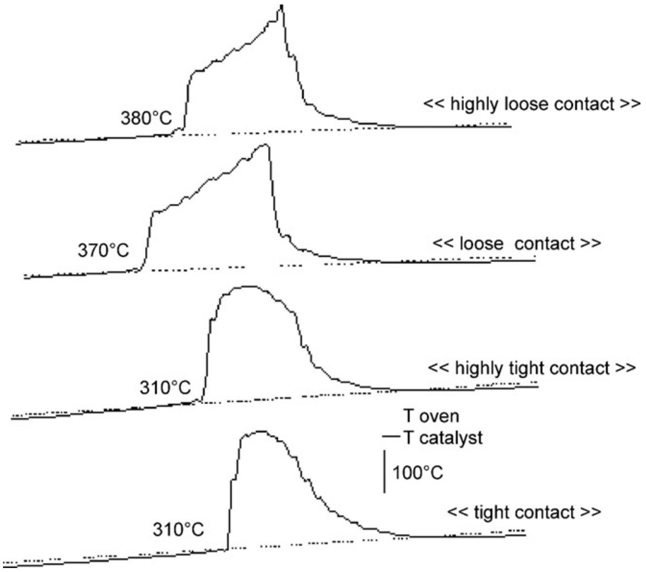

Fig. 11. Light-off for soot combustion as a function of contact type between the catalyst and the soot: 40 mg soot/400 mg CeO_2 under 40 mL/min 50% O_2/Ar.

3.6. Influence of catalysts and operating parameters on light-off temperature

3.6.1. Catalyst surface area

The calcination of ceria at different temperatures leads to different degree of sintering, as revealed by surface area measurements (Table 1). However, as already pointed out for perovskite materials, the decrease of the specific surface has only a minor impact on the light-off temperature, as shown in Table 2. This might indicate that the light-off process is not controlled by the oxygen activation on the catalyst surface.

3.6.2. Oxygen concentration and space velocity

As seen in Table 3, only a relatively moderate variation of the light-off temperature, of ca. 25 °C, is observed when the space velocity is increased by 10 times or the oxygen concentration is increased from 10 to 50%. This tends to indicate that the light-off limiting steps are little dependent of oxygen pressure and contact time, which would fit with the hypothesis that the oxygen transfer from the catalyst to the soot particulates controls essentially the light-off process. Note however, that even if the soot oxidation reaction has been ignited on the catalyst, a high gas space velocity using He as a very high heat capacity inert gas, may generate a 'cooling' effect affecting the temperature that is required for thermal combustion of soot. The slight increase of light-off temperature with increasing space velocity could be possibly related to this "cooling" effect. All these assessments are being checked through a micro-kinetic analysis under progress.

The presence of H_2O (10% steam) in the reactant gas phase improves the catalytic performance, the light-off temperature being reduced by ca. 20 °C. In line with the previous discussion, this phenomenon might be attributed to the effect of steam on oxygen mobility, generally improved after ceria surface hydroxylation [16]. Other effects like catalyst/soot interface wetting allowing a better oxygen transfer could also be considered.

Table 3
Light-off temperature for diesel soot combustion in the presence of CeO_2 HSA for a "tight" contact (40 mg soot, 400 mg ceria)

Total flow rate (mL/min)	40	40	100	200	400
% O_2	10	50	50	10	10
$T_{lightoff}$ (°C)	335	310	330	340	360

3.6.3. Catalyst/soot contact

The most significant impact on light-off temperature originates from the degree of contact between the catalyst particles and the soot. The soot combustion starts at ≈60 °C higher temperature when the "loose" is used instead of "tight" contact (Fig. 11). However, no significant impact on light-off is observed when the "tight" contact is improved (by ball milling) or when different methods are used to obtain the "loose" contact. A quite different temperature profile is observed for "loose" and "tight" contact. When a "tight" contact is used, the temperature increases very rapidly after soot ignition and reaches a maximum in a few seconds, as does the CO_2 signal. In the case of "loose" contact, the temperature increases and reaches the light-off temperature for the thermal combustion of the soot, which then takes place more progressively. The maximum temperature is in that case reached at the end of combustion process, as does the CO_2 production.

Again, such observation can be qualitatively explained on the basis of the determining step of oxygen transfer. In the case of loose contact, the interfacial sites between catalyst and soot are scarce. Consequently, though the light-off may proceed with a rather abrupt profile (enough surface oxygen provided by the ceria for ignition), the flux of oxygen remains limited for the thermal combustion of the soot all over the process which explains the linear profile until the soot is burned out. In the case of tight contact, the number of interfacial sites is much higher as shown from Raman investigation, which allows a flux of oxygen large enough to ensure a combustion run-away throughout the whole bed of particulates.

When a configuration based on two separate layers of soot and catalyst is used (i.e. practically without interfacial sites), no catalytic effect is observed, independently of the position of catalyst, below or on top of the soot bed. The light-off observed in this case is close to that of the natural soot combustion (>500 °C). Even if at the soot/catalyst interface some soot ignition takes place, the effect is not energetic enough to induce the whole combustion of the soot bed.

Table 4
Light-off temperature for diesel soot combustion in the presence of catalyst under different reaction conditions

Catalyst/conditions	"Tight contact"		"Loose contact"	
	40 mL/min 50% O_2	200 mL/min 10% O_2	40 mL/min 50% O_2	200 mL/min 10% O_2
CeO2 HSA	310	340	370	410
$La_{0.8}Cr_{0.8}Li_{0.2}O_3$	340	365	500	500

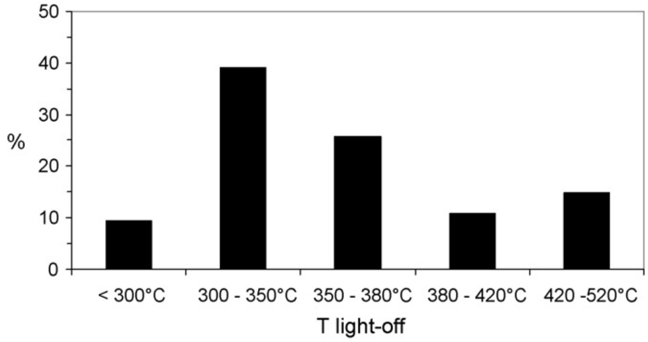

Fig. 12. High-throughput approach in soot combustion: % of catalysts tested classified in function of their light-off temperature.

3.6.4. *Catalyst nature vs. reaction conditions*

The reactions conditions were found to affect differently the light-off temperature according to the nature of the catalyst used. Table 4 presents the light-off temperature for various reaction conditions, changing contact time, partial pressure of oxygen and soot/catalyst contact. As can be seen in the case of ceria and $La_{0.8}Cr_{0.8}Li_{0.2}O_3$ perovskite, the light-off temperature increases by ≈100 and 160 °C, respectively, when going from mild (first column) to severe and realistic conditions (forth column). In line with the above discussion, this phenomenon can be related to a larger capacity of ceria to provide surface active oxygen species necessary to induce the soot combustion, as well as to its capacity to regenerate these oxygen species.

From the above observation, the following recommendation for an HTE screening procedure can be derived: in order to ensure light-off identification for widely diverse samples, it is preferable to choose testing conditions favouring a large range of light-off temperatures. This corresponds to mild testing conditions with a tight catalyst/soot contact, a high contact time and a high concentration of oxygen.

3.6.5. *Screening statistics*

Based on the development of this high-throughput procedure adapted to diesel soot combustion, a catalyst screening was carried out. More than 100 diverse noble metal free formulations of mixed oxides were tested under mild conditions (tight contact, catalyst/soot = 10, 50% O_2, 40 mL/min).

As seen in Fig. 12, it is verified first that the chosen "mild" testing conditions permit an unambiguous ranking of the performances over a large range of light-off temperatures. Second, it was found that about 10% of the solids tested exhibited a light-off temperature significantly below 300 °C, i.e. more active than the reference HSA ceria and perovskite catalysts, as targeted initially. Though these formulas under patenting procedure cannot be disclosed at present, it can be stressed that they could hardly have been foreseen from existing knowledge, underlining the efficiency of the HTE methodology in that peculiar domain.

4. Conclusion

This study aimed to validate a high-throughput procedure for ranking diverse catalysts able to initiate soot combustion at low temperature. A detailed investigation of the impact of the main operating parameters on light-off temperature was carried out by varying contact time, partial pressure of oxygen, degree of contact between catalysts and soot particulates, catalyst/soot ratio. A set of optimum conditions for HT screening in parallel reactor was thus determined, ensuring a large span of light-off temperature for a convenient ranking of catalysts library. Tentative mechanistic features were deduced from these experiments, stressing the key role of oxygen transfer from the catalyst to the soot particulate for determining the light-off temperature, while parameters such as catalysts surface area, soot loading were shown to be little sensitive. Finally, the efficiency of the methodology was demonstrated by discovering new noble metal free formulas better performing that commercial ceria and $La_{0.8}Li_{0.2}CrO_3$ perovskite reference materials.

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