

Article

Enhanced Soot Oxidation Performance of CeO₂-Promoted La₂O₂SO₄ Catalytic Oxygen Storage Materials for Gasoline Particulate Filters

Luciana Lisi ^{*}, Elisabetta Maria Cepollaro , Michele Emanuele Fortunato  and Stefano Cimino 

Istituto di Scienze e Tecnologie per l'Energia e la Mobilità Sostenibili (STEMS)—CNR, Via Marconi 4, 80125 Napoli, Italy; elisabettamaria.cepollaro@stems.cnr.it (E.M.C.); micheleemanuele.fortunato@stems.cnr.it (M.E.F.); stefano.cimino@cnr.it (S.C.)

* Correspondence: luciana.lisi@cnr.it

Abstract

This study investigates the synergistic promotional effects of CeO₂ and La₂O₂SO₄ as composite catalytic oxygen storage systems for soot oxidation in Gasoline Particulate Filters (GPFs) across a broad operating temperature range. Two 5 wt % CeO₂-promoted Lanthanum oxysulfate compounds were prepared by mechanical mixing of pure phases or by supporting CeO₂ via incipient wetness impregnation with a cerium nitrate precursor. The soot oxidation activity was evaluated using Thermogravimetric Analysis coupled with Mass Spectrometry (TG-MS) under both anaerobic and lean-O₂ (1% vol.) environments, with the performance benchmarked against pure La- or Pr-oxysulfates and CeO₂ reference materials. Comprehensive characterization via XRD, SEM, N₂-physisorption, and H₂-TPR revealed that the observed synergistic effects transcend the simple additive properties of the individual components.

Keywords: lanthanum oxysulfate; oxygen storage capacity; GPF; soot; catalytic combustion; exhaust aftertreatment

1. Introduction

The automotive sector is shifting toward Gasoline Direct Injection (GDI) engines—replacing Port Fuel Injection (PFI)—as a strategy to mitigate transport-related CO₂ emissions. GDI technology provides enhanced thermal efficiency and precise injection control, leading to reduced fuel consumption and lower CO₂ output. Despite these benefits, the proximity of the injection point to the combustion chamber can decrease mixture homogeneity. This leads to the formation of fuel-rich regions that promote increased production of unburned hydrocarbons and soot, consequently requiring the mandatory installation of a Gasoline Particulate Filter (GPF) [1–3].

Despite the fact that GDI exhaust gas temperatures (ranging from 400 to 700 °C) are typically higher than those in a Diesel Particulate Filter (DPF), catalytic materials in Gasoline Particulate Filters (GPFs) face a significant challenge. This is primarily due to the very low O₂ concentration—a result of stoichiometric combustion—and the absence of NO₂, which is removed by the upstream three-way catalyst (TWC) [4]. Therefore, catalytic coatings for GPFs must rely on materials with a high oxygen storage capacity (OSC), such as ceria and perovskites. These materials, thanks to their easy oxygen mobility, are capable of releasing their lattice oxygen even under low or zero O₂ partial pressure and then



Academic Editors: Wenpo Shan, Yuechang Wei and Jing Xiong

Received: 20 February 2026

Revised: 20 March 2026

Accepted: 15 April 2026

Published: 1 May 2026

Copyright: © 2026 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the [Creative Commons Attribution \(CC BY\)](https://creativecommons.org/licenses/by/4.0/) license.

recovering their original oxidation state during the transient phases when a higher amount of O₂ is present in the exhaust gas (fuel cut mode) [5–9].

The activity of CeO₂ is based on the Ce⁴⁺ to Ce³⁺ redox cycle; however, the high temperatures of exhaust gases can be responsible for the irreversible transformation into Ce₂O₃ and, consequently, the irreversible decrease in its OSC [2,10,11]. Doping CeO₂ with foreign elements, such as Mn, Fe, Cu, Zr, Pr, Sm, and U, can promote the formation of different kinds of defects in its lattice that enhance oxygen mobility and/or increase the thermal stability [5,6,10–16]. Silver nanoparticles were also proposed as CeO₂ promoters [17] due to their role as oxygen collectors of active oxygen species generated on surface oxygen vacancies of ceria that spill over to react with soot, thus facilitating its oxidation under oxygen-deficient conditions. The importance of this oxygen delivery route was also highlighted by Wang et al. [18] for their Ag-promoted Fe₂O₃@CeO₂ catalysts. CeO₂ could act as the gateway of oxygen release/storage for Fe₂O₃. Consequently, Fe₂O₃ particles grafted with CeO₂ showed a high oxygen utilization.

Rare earth oxysulfates (Re₂O₂SO₄) have been investigated for their high OSC, good thermal stability, and cyclability [19–25]. The high OSC of these compounds stems from the redox chemistry of S, which can undergo a complete reduction from S⁶⁺ (in the oxysulfate) to S^{2−} (in the oxysulfide) [11–19]. This corresponds to a significant capacity of 4 moles of O per mole of catalyst, vastly exceeding the theoretical 0.5 moles available from CeO₂ or 1 mole for transition metals such as copper in perovskite catalysts [9]. The ability to reversibly operate these redox cycles while preserving the crystal structure is attributed to the structural similarity between the oxidized (Re₂O₂²⁺ and SO₄^{2−} layers) and reduced (Re₂O₂²⁺ and S^{2−} layers) compounds [19–21]. Among a series of Lanthanides (La, Pr, Nd, and Sm), Pr-oxysulfate exhibited redox cycles at the lowest temperature due to a significant promotional effect exerted by the peculiar presence of both Pr⁴⁺/Pr³⁺ species on the surface. Similar effects are reported for Eu-oxysulfate due to Eu³⁺/Eu²⁺ surface multivalence state [25], whereas cerium, although having the redox couple Ce⁴⁺/Ce³⁺, does not form stable oxysulfates [21]. However, Praseodymium and Europium are critical raw materials with higher pricing compared to La and Ce [21].

In a previous work [26], we investigated for the first time the ability of transition metal (Cu, Co)-promoted lanthanum oxysulfates (LaOS) for the oxidation of soot under GPF conditions, in the absence of O₂, showing a complete reduction into the corresponding oxysulfide occurring without any sign of its undesired (irreversible) decomposition. When the metal-promoted LaOS materials were exposed to a very low O₂ partial pressure, the oxysulfide was quickly re-oxidized, restoring the original oxysulfate. In contrast, pure CeO₂ was not able to activate the Ce⁴⁺/Ce³⁺ reaction under the same severe anaerobic conditions, but it showed better catalytic soot oxidation activity at lower temperatures in the presence of O₂. Moreover, Zhang et al. [27] revealed a synergistic improvement in the oxygen storage capacity (OSC) of CeO₂ when supported on LaOS at various loadings. When tested in the anaerobic CO oxidation, these composite materials exhibited both larger OSC and higher reaction rates than the single oxides across a wide temperature range (400–700 °C). By following the reaction between CO and CeO₂/¹⁸O-labelled LaOS composites, they demonstrated that CO reacted primarily with lattice oxygen from CeO₂, and the resulting oxygen vacancies were then efficiently refilled by oxygen atoms supplied from LaOS via the solid–solid interface. Thus, CeO₂ worked as an oxygen gateway, and LaOS served as an oxygen reservoir. The same authors also investigated the preparation of Ce-substituted La-oxysulfates [28] and assigned the high rates of oxygen release and storage to the redox property of Ce³⁺/Ce⁴⁺ and the possible structural distortion of SO₄ units in the oxysulfate lattice. Consistently, Shen and Naito [29] also found a favourable effect of 5% Ce substitution on the redox cycle of sulfur of LaOS.

In this study, we developed a composite catalyst pairing CeO₂ and LaOS to bridge the performance gaps across the diverse temperature and oxygen regimes of GPF operation. While CeO₂ can provide high activity at low temperatures in oxygen-rich environments, LaOS excels at high temperatures and can operate under anaerobic conditions. We explored the synergistic interaction between these components using 5% CeO₂-promoted LaOS prepared by two distinct methods. Specifically, we report the first investigation of carbon soot oxidation under both anaerobic and lean-O₂ environments mimicking gasoline exhaust, benchmarking the performance of these catalytic oxygen storage materials against pure La- and Pr-oxysulfates as well as CeO₂ references.

2. Results and Discussion

2.1. Characterization of Materials

Table 1 summarizes the main characterization results for the as-prepared Lanthanum and Praseodymium oxysulfates (LaOS and PrOS, respectively) alongside the commercial CeO₂ nanopowder and two composite CeO₂ + LaOS materials (5Ce + LaOS_M: mechanical mixture; 5Ce/LaOS_I: impregnated catalyst). The maximum theoretical OSC (wt %) is calculated considering the complete reduction from S⁶⁺ (in the oxysulfate) to S^{2−} (in the oxysulfide) and from Ce⁴⁺ to Ce³⁺ (in the ceria).

Table 1. Summary of the characterization results for the nominally pure LaOS, PrOS and commercial CeO₂, and the two composites CeO₂ + LaOS: BET specific surface area, crystal phases and system, average crystallite size, unit cell volume and maximum theoretical oxygen storage capacity.

	BET s.a. m ² g ^{−1}	Crystal Phases	Phase Content wt %	Crystallite Size ^a nm	Unit Cell Vol Å ³	OSC _{max} wt %
LaOS	2.7	La ₂ O ₂ SO ₄ (Monoclinic)	100	81 ± 3	493.8	15.8
PrOS	5.0	Pr ₂ O ₂ SO ₄ (Monoclinic)	98.9 ± 0.1	77 ± 4	472.3	15.6
		Pr ₆ O ₁₁ (Monoclinic)	1.1 ± 0.1	37 ± 6	994.0	
CeO ₂	38	CeO ₂ (Cubic)	100	35 ± 3	158.8	4.6
5Ce + LaOS_M	6.1	La ₂ O ₂ SO ₄ (Monoclinic)	95.0 ± 0.1	82 ± 5	493.7	15.2 ^b
		CeO ₂ (Cubic)	5.0 ± 0.1	33 ± 2	158.9	
5Ce/LaOS_I	7.0	La ₂ O ₂ SO ₄ (Monoclinic)	93.7 ± 0.2	76 ± 4	493.8	15.2 ^b
		Ce _{0.8} La _{0.2} O _{1.9} (Cubic)	6.3 ± 0.2	9 ± 1	167.8	

^a average of the values calculated from the most intense diffraction peaks for each phase. ^b calculated as the linear combination of the corresponding figures for pure LaOS + CeO₂.

XRD analysis (Figure 1) confirmed that the high-temperature treatment (1000 °C) of corresponding sulfate salts under an inert atmosphere led to the formation of monoclinic La- and Pr-oxysulfate phases (PDF No. 04-016-0017 and 04-016-0018). Trace amounts (ca 1 wt %) of the monoclinic Pr₆O₁₁ phase (PDF No. 04-007-2299) were additionally detected in the case of PrOS. The La- and Pr-oxysulfate phases exhibited characteristic unit cell volumes of 493.8 Å³ and 472.1 Å³, in line with the characteristic contraction of ionic radii alongside the lanthanide series [21]. Their average crystallite size estimated by the Scherrer equation, applied to the five most intense diffraction peaks, was equal to 81 ± 3 nm and 77 ± 4 nm for LaOS and PrOS, respectively. As regards the composite materials, 5Ce + LaOS_M retained the unit cell volume and the average crystallite size of the parent LaOS and the commercial cubic CeO₂ (PDF No. 04-016-4610), whose actual content was confirmed at 5.0 ± 0.1 wt %.

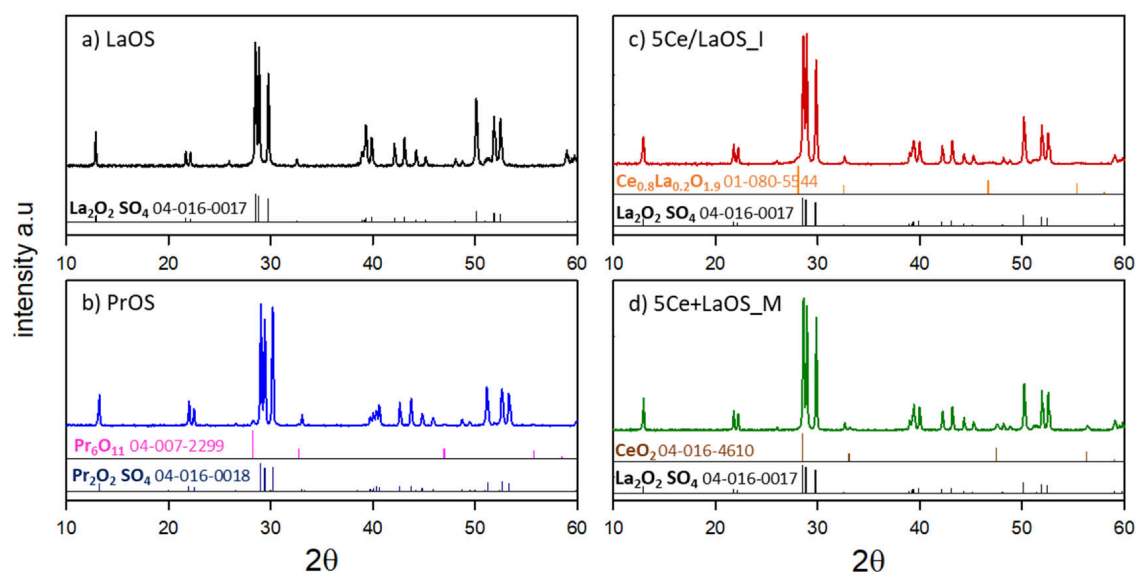


Figure 1. XRD patterns for nominally pure La- and Pr-oxysulfates (a,b), and composite 5Ce/LaOS_I (c) and 5Ce + LaOS_M (d) materials with a 5 wt % CeO₂ content. Reference ICDD peak bars are reported at the bottom of each panel for phase identification.

At variance, the 5Ce/LaOS_I material prepared by impregnation showed a characteristic enlargement of the unit cell volume of the cubic ceria phase from ca 159 up to 167.8 Å³, which was due to the migration of some La into the lattice and formation of the mixed Ce_{0.8}La_{0.2}O_{1.9} phase (PDF No. 01-080-5544) [30,31]. Its content was estimated equal to 6.3 ± 0.2 wt % (corresponding to the nominal 5 wt % loading of CeO₂), and it was characterized by relatively smaller crystallites (9 ± 1 nm).

The BET surface areas of LaOS and PrOS (2.7 and 5 m² g^{−1}, respectively; Table 1) were slightly larger than the corresponding parent sulfates due to the evolution of SO₂ and O₂ during the high-temperature pre-treatment [20,24] but indicate the absence of any substantial micro/meso-porosity and the formation of polycrystalline aggregates, previously confirmed by TEM [26]. CeO₂-promoted LaOS samples displayed similar BET surface areas (6–7 m²/g) regardless of the preparation method; in the case of the physical mixture, the value slightly exceeds the expected figure obtained as a linear combination of the two contributions from the parent materials, probably due to the mechanical activation of the powders disrupting some polycrystalline domains.

2.2. H₂-Temperature Programmed Reduction

In Figure 2, the TPR profiles of 5Ce + LaOS_M and 5Ce/LaOS_I are compared with those of pure LaOS, PrOS and CeO₂. In line with previous results, the commercial CeO₂ sample showed two small and separate reduction events starting respectively at ca 300 °C (peaking at 495 °C, inset of Figure 2) and 650 °C (with a maximum at 890 °C, tailing under isothermal conditions at 900 °C), which are normally assigned to the reduction in surface and bulk ceria [32–34]: the amount of H₂ consumed indicates that ca 50% of the Ce⁴⁺ was reduced to Ce⁺³ at the end of the TPR in agreement with Caputo et al. [32]. On the other hand, the H₂-TPR profiles of pure PrOS and LaOS samples showed onset temperatures at ca 650 and 670 °C, respectively, with a first (partially unresolved) reduction peak at ca 760 °C, more pronounced for PrOS, eventually followed by a continuous increase up to 900 °C, where the reduction process continued under isothermal conditions. It should be mentioned that the maximum temperature was limited to 900 °C to avoid the possible partial decomposition of the oxysulfate phase under H₂ leading to the release of SO₂ (undetectable in the TPR apparatus) [24]. Nevertheless, the total amount of H₂ consumed

at the end of the TPR test accounted (within the experimental uncertainty) for the complete transformation of each of the oxysulfate phases into their corresponding oxysulfides. The faster reduction rate in the temperature range up to 880 °C was previously assigned to the promoting effect of the presence of Pr^{4+} species on the surface of the oxysulfate that are more easily reduced to Pr^{3+} , in turn favouring the reduction of S from +6 to −2 in the oxysulfide [21,22]. This is consistent with the trace amounts of Pr_6O_{11} detected in the PrOS sample.

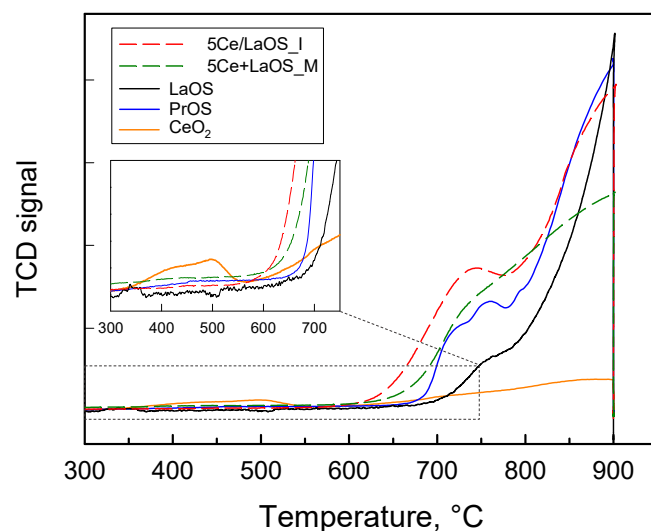


Figure 2. H_2 -TPR profiles for pure (LaOS, PrOS, CeO_2) and composite (5Ce + LaOS_M, 5Ce/LaOS_I) oxygen storage materials.

Notably, despite the 5Ce + LaOS_M sample being a mechanical mixture of the two CeO_2 and LaOS solids, its redox behaviour differed substantially from the combination of the TPR profiles of the parent samples. The reduction process by H_2 started at as low as 600 °C (inset of Figure 2) and displayed a higher rate over LaOS (as well as PrOS), up to ca 850 °C. As for the pure LaOS sample, the overall amount of H_2 consumed at the end of the isothermal step at 900 °C corresponded to the complete transformation into the La-oxysulfide. It should be noted that the large H_2 consumption measured up to 850 °C with the composite sample cannot be simply associated with the reduction in the ceria content, since it far exceeds the corresponding theoretical required amount. This clearly indicates that CeO_2 is rather acting as a promoter or catalyst by activating H_2 and by drawing oxygen from the lattice of the LaOS to replenish the oxygen vacancies [24]. Interestingly, the promotional effect of CeO_2 on the transformation of the La-oxysulfate into its corresponding oxysulfide was also evident when the two solids had a limited interfacial contact area, as expected in the case of a mechanical mixture. However, the 5Ce/LaOS_I sample guaranteed further improvements of the redox performance as shown by the clear left-shift of its reduction profile in Figure 2. In particular, the onset temperature for reduction was as low as 570 °C, and the H_2 consumption rate was always faster than for LaOS as well as PrOS samples for temperatures up to 850 °C. It can be argued that this result was due to the larger contact surface area between the two phases when CeO_2 was dispersed on the LaOS via impregnation, as well as to an enhanced oxygen mobility caused by the partial substitution of La [30,31] that was detected in the ceria lattice (Table 1). Similarly, some limited substitution of cerium into the lanthanum oxysulfate lattice following the reducing treatment [28] cannot be completely ruled out. Analogous promoting effects were previously reported with Me/LaOS composites doped with small amounts (1 wt %) of transition metals (oxides), increasing in the order $\text{Co} > \text{Mn} > \text{Cu}$ [22].

2.3. Soot Oxidation Under Anaerobic Conditions

Figure 3 presents the results of TG experiments of soot combustion performed under anaerobic conditions (inert flow) for the pure materials and the two composite samples. Pure LaOS, PrOS, CeO₂ and carbon soot were all stable when heated under inert flow conditions up to 835 °C and did not spontaneously release any molecular oxygen [23,26]. However, each of the pure OS materials was capable to oxidize carbon soot when mixed with it by employing lattice oxygen to form CO_x. Among all tested materials, the commercial CeO₂ nanopowder exhibited the lowest activity [26]: the onset temperature for soot oxidation (estimated from the derivative TG profile, Figure 3b) was around 750 °C, and the maximum weight loss rate occurred only at the test's upper thermal limit (835 °C). Consequently, isothermal kinetics were sluggish, yielding a final weight loss of only −4.7%, which falls below the complete utilization of the theoretical oxygen storage capacity (Table 1), considering the conversion to CO₂ (−5.7%) or to CO (−7.2%). In fact, MS traces indicated the release of both CO₂ and CO at comparable extents in the evolved gases (Figure 3c,d).

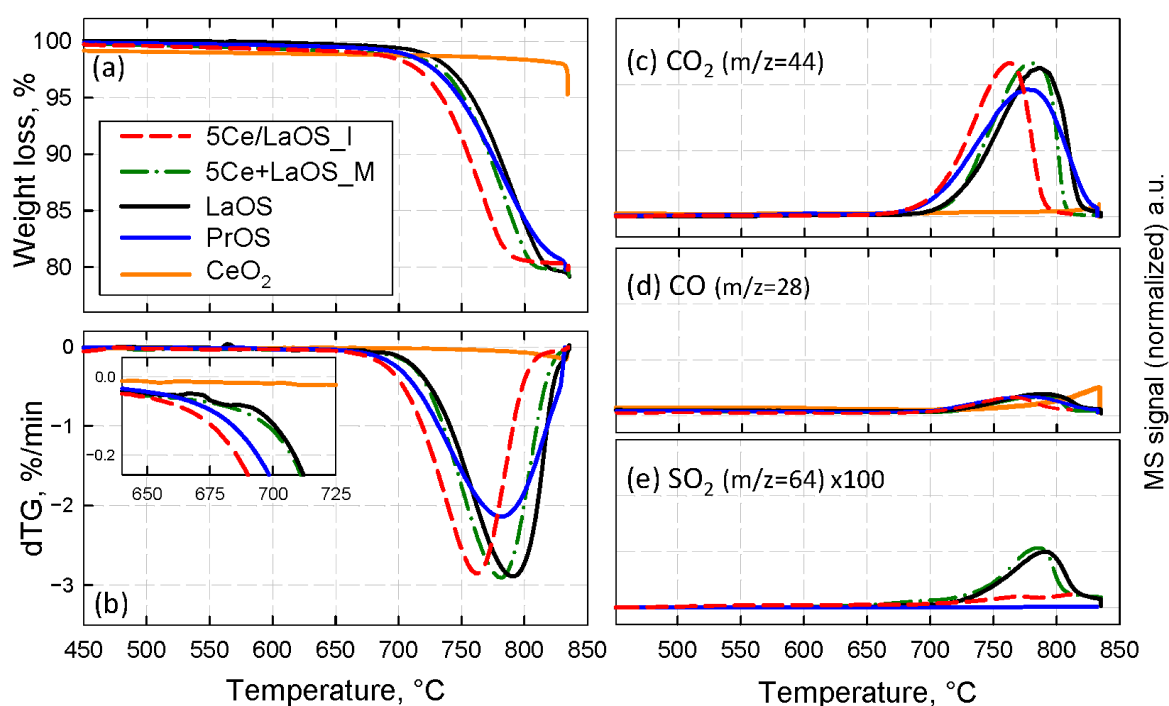
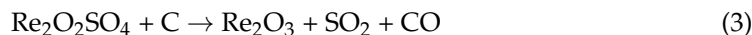
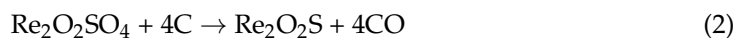


Figure 3. TG-MS experiments under anaerobic conditions (Ar flow) for 1:9 mixtures of carbon soot in tight contact with pure (LaOS, PrOS, CeO₂) and composite (5Ce + LaOS_M, 5Ce/LaOS_I) oxygen storage materials: weight losses (a) and corresponding derivative profiles (b); MS signals for CO₂ (c), CO (d) and SO₂ (e) in the evolved gas.

PrOS and LaOS displayed distinctly better oxidation performance than CeO₂ when mixed with soot, showing an onset temperature for weight loss respectively at 660 and 675 °C, in line with the onset of the reduction of the oxysulfate phases during the corresponding H₂-TPR. Thereafter, weight loss proceeded, showing dTG peaks centred at 780 and 790 °C. This is remarkable when considering that the maximum reduction rate during the H₂-TPR was not achieved below 900 °C and points to the very strong reducing potential of solid carbon even if its contact area with the oxysulfate phase was relatively limited (mechanical mixture). Both samples eventually reached a stable weight at the end of the experiment: their final weight losses (20.0% and 21.0%, respectively, for PrOS and LaOS) largely correspond to the values calculated (19.3% and 19.5%) for the deep oxidation

of a soot fraction to form CO₂ via reaction (1), utilizing all of the oxygen storage capacity deriving from the complete transformation of the oxysulfate into its oxysulfide.



Accordingly, the MS traces for CO₂ emission (Figure 3c) closely resembled the corresponding dTG peaks. Also, the temporal traces at $m/z = 28$ (Figure 3d) followed identical patterns: considering the contribution at $m/z = 28$ deriving from CO₂ mass fragmentation (11.4% of the signal at $m/z = 44$), it can be argued that CO formation via reaction (2) was negligible, providing almost complete selectivity to CO₂. Moreover, the SO₂ trace for PrOS was flat across the entire temperature range up to 835 °C (Figure 3e), indicating that the undesired irreversible decomposition of the oxysulfate by reaction (3) did not occur. In the case of LaOS, some trace amounts of SO₂ were detected, peaking at the same temperature of CO₂. Despite a fully quantitative assessment not being performed, the concentration of SO₂ was estimated to be lower than that of CO₂ by a factor of around 500 (considering MS sensitivity factors of 2.1 and 1.4, respectively), implying that the La₂O₂SO₄ was converted with very high selectivity (99.8%) via reaction (1). It should be highlighted that the slightly larger weight loss and the associated SO₂ emissions, already reported by our group during similar experiments with La-oxysulfate + soot [26] mixtures, were most probably affected by some undetected impurities of Lanthanum sulfate, which is more easily decomposed during heating with soot under anaerobic conditions.

Visual inspection of the powders recovered after the TG experiments (cooled to room temperature under inert flow) confirmed the presence of some residual soot, consistent with its initial amount exceeding the maximum available oxygen content of the materials (and the formation of CO₂). The corresponding XRD patterns (Figure 4) indicate the complete transformation of LaOS and PrOS into their hexagonal La- or Pr-oxysulfides (PDF No. 04-016-0019 and 04-016-0020, respectively): the latter was also accompanied by a small amount (0.9 wt %, Table 2) of Pr₂O₃ (hexagonal, PDF No 00-006-0410) deriving from the reduction of Pr⁴⁺ to Pr³⁺ in the oxide phase detected in the original sample.

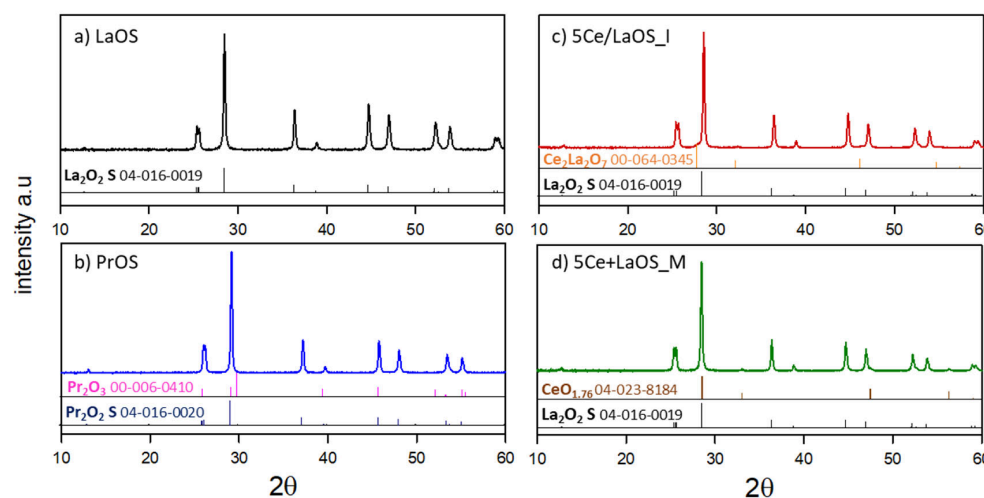


Figure 4. XRD patterns for LaOS (a), PrOS (b) and composite 5Ce/LaOS_I (c) and 5Ce + LaOS_M (d) materials recovered in their reduced form at the end of the anaerobic oxidation of soot in the TG-MS up to 835 °C under flowing Ar. Reference ICDD peak bars are reported at the bottom of each panel for phase identification.

Table 2. Summary of the results from XRD analysis of the pure and composite OSC materials recovered in their reduced form after the anaerobic oxidation of soot in the TG-MS up to 835 °C under flowing Ar.

	Crystal Phases	Phase Content wt %	Crystallite Size ^a nm	Unit Cell Vol Å ³
LaOS	La ₂ O ₂ S (Hexagonal)	100	43 ± 3	98.9
PrOS	Pr ₂ O ₂ S (Hexagonal)	99.1 ± 0.3	45 ± 3	93.4
	Pr ₂ O ₃ (Hexagonal)	0.9 ± 0.3	-	58.2
Ce + LaOS_M	La ₂ O ₂ S (Hexagonal)	95.3 ± 0.2	44 ± 3	98.7
	CeO _{1.76} (Cubic)	4.7 ± 0.2	29 ± 3	158.4
Ce/LaOS_I	La ₂ O ₂ S (Hexagonal)	94.7 ± 0.5	44 ± 3	98.8
	Ce ₂ La ₂ O ₇ (Cubic)	5.3 ± 0.5	15 ± 1	167.9

^a average of values calculated from the most intense diffraction peaks for each phase.

The addition of just 5 wt % of CeO₂ to the LaOS phase proved effective to favour the deep oxidation of soot under anaerobic conditions as shown by the corresponding weight loss curves that were shifted toward lower temperatures for both composite materials. The promoting effect of ceria was limited to only 10 °C in the case of 5Ce + LaOS_M (mechanical mix), reaching a peak in the dTG curve at 780 °C. On the other hand, the 5Ce/LaOS_I impregnated material attained the maximum rate of reaction at as low as 760 °C, and the onset temperature for soot oxidation was also anticipated by ca 30 °C with respect to the parent LaOS (Figure 3b), thus outperforming the PrOS sample, too. The temporal profiles for the evolved CO₂ followed the same (anticipated) trends, and once again the CO emission was negligible, confirming the very high selectivity towards the total oxidation of soot (Figure 3c,d). In addition, the SO₂ trace was almost flat for the 5Ce/LaOS_I composite material over the whole temperature range, reflecting the removal of sulfate impurities due to the preparation method. The higher effectiveness of adding Ceria by impregnation is consistent with the smaller average dimension and better dispersion of its crystallites on the LaOS phase. Moreover, it most probably also benefits from the doping effect of La [30,31] in the Ce_{0.8}La_{0.2}O_{1.9} and Ce₂La₂O₇ mixed phases that were detected by XRD analysis in the fresh and reduced samples, respectively, which displayed similar volumes (168 Å³) of their cubic unit cell (Table 2). At variance, the commercial ceria mixed with LaOS turned into a partially reduced CeO_{1.76} phase at the end of the experiment, without any sign of significant La-substitution, and thus preserved its original smaller cubic unit cell (158 Å³) as well as the larger average dimension of its crystallites (Table 2).

2.4. Soot Oxidation Under Lean-O₂ Conditions

Soot oxidation experiments in TG-MS were also repeated under a flow of 1% O₂/Ar, and the results are presented in Figure 5a,b in terms of weight profiles as a function of temperature/time together with the corresponding derivative curves. Moreover, panels in Figure 5c,d report the transient concentration profiles of O₂ and CO₂ in the evolved gas relevant to the two extreme cases of the pure CeO₂ nanopowder and the 5Ce/LaOS_I composite material. CO (as well as SO₂) emissions were negligible for all tested materials under oxidizing conditions.

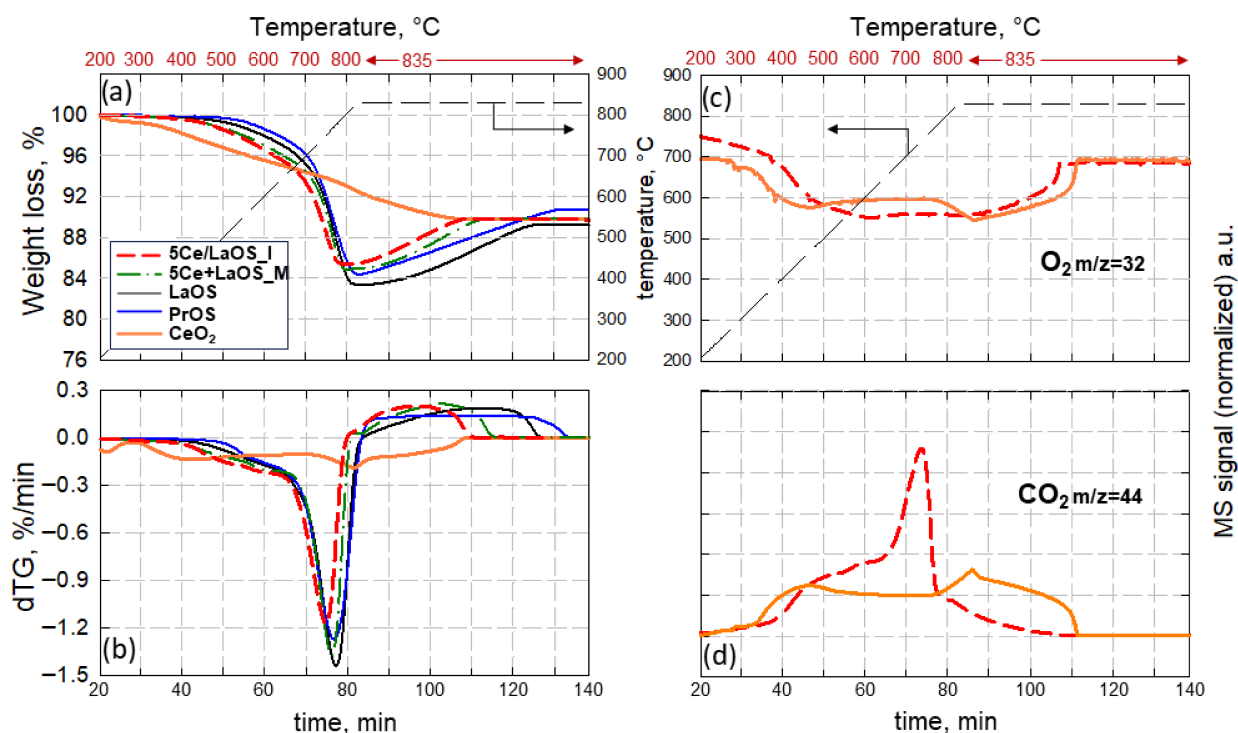


Figure 5. TG-MS experiments under 1% vol. O₂ flow conditions for 1:9 mixtures of carbon soot in tight contact with pure (LaOS, PrOS, CeO₂) and composite (5Ce + LaOS_M, 5Ce/LaOS_I) oxygen storage materials: weight losses (a) and corresponding derivative profiles (b); MS signals for O₂ (c) and CO₂ (d) in the evolved gas for CeO₂ and 5Ce/LaOS_I.

In line with previous reports [26], the TG trace for the CeO₂ catalyst mixed with soot decreased monotonically down to the expected value corresponding to the complete burn-out of the carbon content (10%). The corresponding CO₂ emission profile shows that soot oxidation started from as low as 300 °C and reached a maximum rate around 420 °C, then continued almost unchanged up to ca 760 °C. The O₂ consumption in the gas mixture strictly mirrored the CO₂ formation trend: this confirms that ceria acted as a catalyst by oxidizing carbon soot via the oxygen available on its surface, resulting in oxygen vacancies which, in the presence of O₂ in the gas phase, can be continuously replenished, closing the redox cycle. As such, Figure 6 presents the Arrhenius plot for the soot oxidation rate per gram of ceria (R_{CeO_2}), which is proportional to the dTG value at each temperature. The corresponding apparent activation energy, estimated from the slope of the line in the low-temperature (and low conversion) range, is equal to 86.6 kJ/mol, which agrees with typical values reported for the oxidation of soot on CeO₂ [35]. However, the rate of reaction rapidly approached a roughly constant value for temperatures beyond 400 °C, which indicates that the process proceeded under purely external mass transfer control: this is due to the relatively slow transport of O₂ from the TG flow chamber into the crucible freeboard and its subsequent diffusion through the crucible to the surface of the catalyst particles [26]. Interestingly, under those conditions, the concentration of O₂ on the surface of the catalyst was actually zero, and the rate of reaction increased only when some additional oxygen from the CeO₂ lattice became available, i.e., above 750 °C, consistent with the activation temperature measured during the anaerobic oxidation tests. Accordingly, this second oxidation event reached a small peak at 835 °C to continue during the isothermal stage until all the soot was consumed, while the lattice oxygen of CeO₂ was simultaneously restored.

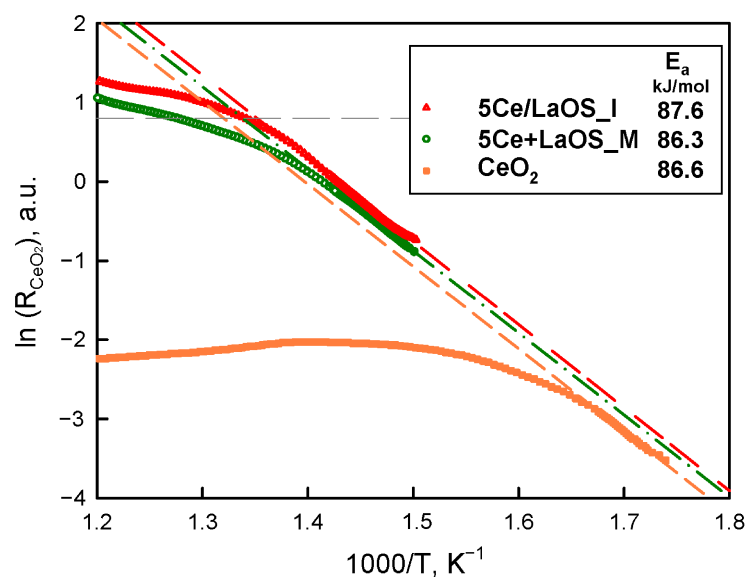


Figure 6. Arrhenius plots for the soot oxidation rate per unit mass of ceria over composite 5Ce + LaOS_M, 5Ce/LaOS_I materials in comparison with pure CeO₂, with indication of the corresponding apparent activation energies calculated from the low conversion data.

All other materials containing an oxysulfate phase displayed a markedly different TG profile, characterized by an onset of soot oxidation shifted to higher temperatures with respect to pure CeO₂ and a much faster maximum weight loss rate (Figure 5b) that was achieved between 750 and 775 °C. Oxidation activity increased in the order 5Ce/LaOS_I > 5Ce + LaOS_M ≥ PrOS > LaOS, i.e., following the same trend observed during the anaerobic tests. The corresponding deep minima in the weight profiles were systematically lower than expected for the removal of the entirety of the soot content, suggesting that the (partial) transformation of the oxysulfate phase into its corresponding oxysulphide was occurring. Thereafter, when most of the soot was consumed/oxidized, the samples started to regain weight until they eventually recovered the level corresponding to the re-formation of the oxysulfate phase. Accordingly, the CO₂ emission trace (shown for the case of 5Ce/LaOS_I, Figure 5d) mirrored the dTG profile up to the temperature corresponding to the maximum oxidation rate and then rapidly dropped due to the complete consumption of the solid carbon. On the other hand, the O₂ trace mirrored the CO₂ profile only from low to moderate temperatures up to 500 °C, where it stabilized at the same level observed with pure CeO₂. Once more, this is consistent with the instauration of an external mass transfer-limited regime. However, in this case, the CO₂ formation rate did not level-off but increased further along with the temperature due to the increasing availability of oxygen from the lattice of the oxysulfate phase, which was initially transferred to the catalytically active ceria phase [27]. Given the analogy with the anaerobic oxidation tests, for temperatures beyond ca 670 °C, the remaining soot also started to oxidize directly at the contact points with the oxysulfate phase and not only through the CeO₂ catalytic gateways.

Due to the negligible soot combustion with pure LaOS below 500 °C, it can be argued that in the case of the composite CeO₂ + LaOS materials, the low-temperature oxidation was exclusively catalyzed by the active sites of ceria. As such, Figure 6 reports the catalytic reaction rates on the composites after normalization for the unit mass of CeO₂. It can be observed that the soot oxidation rate over each composite material increased along with temperature with the same apparent activation energy (87 ± 0.7 kJ/mol) that was measured for the case of pure CeO₂ nanoparticles, suggesting an identical mechanism of activation. However, the specific rate per gram of ceria was higher (from 22 to 38%) over the composites, thus indicating that a larger number of active sites were present

than over pure CeO_2 , and they were most probably located at the interface with the LaOS. Notably, the 5Ce/LaOS_I sample displayed the fastest specific rate (ca 12–15% higher than 5Ce + LaOS_M counterpart). This generally agrees with a larger contact area between phases that can be obtained via the impregnation procedure rather than by mechanical mixing. Nevertheless, the possible promoting effect deriving from the formation of novel oxygen vacancies, due to the observed partial substitution of La into the ceria lattice, cannot be completely ruled out. In contrast to the case of pure CeO_2 , Figure 6 confirms that the specific soot oxidation rate over both the composite materials continued to increase along with temperature (though much more slowly) also beyond 500 °C (i.e., when the molecular O_2 was already consumed), eventually exceeding the limit for the external mass transport regime (recalculated considering the actual content of ceria). This can be rationalized with the utilization of lattice oxygen from the LaOS reservoir diffusing towards the active sites located at the interface with ceria, consistently with results of Zhang et al. [27] for CO oxidation. Under such an O_2 -depleted regime at intermediate temperatures, the activity between 5Ce/LaOS_I and 5Ce + LaOS_M appeared more pronounced. However, a precise kinetic evaluation from dTG data was precluded by the relatively high soot conversion levels and the concurrent phase transformation of LaOS into its oxysulfide.

Interestingly, once the combustion of soot was completed, the maximum rate of catalyst reoxidation (i.e., weight gain) also appeared to have an upper limit (Figure 5b) that was relatively unaffected by either the type of oxysulfide (La or Pr) or the presence of 5% CeO_2 mixed with or impregnated on LaOS. Accordingly, the O_2 consumption rate remained constant during the reoxidation phase (as shown in Figure 5c, for 5Ce/LaOS_I), clearly indicating that the intrinsic kinetics were fast and the reoxidation process was O_2 -diffusion limited.

XRD analysis of the samples after the soot oxidation tests under 1% vol. O_2 confirmed the complete recovery of the initial La- and Pr-oxysulfate and ceria phases, with unchanged crystal structures and parameters, indicating easy and reversible transformations occurring during the redox cycles.

SEM images of the two composite materials recovered after the soot oxidation experiments under either 1% vol. O_2 or anaerobic flow conditions at high temperature (i.e., containing fully oxidized La-oxysulfate and fully reduced La-oxysulfide species, respectively) are presented in Figure 7. The re-oxidized oxygen storage materials (Figure 7a,c) retained their characteristic macroporous structure made of grains with a wide size distribution up to 1–2 μm deriving from the agglomeration of primary crystalline LaOS particles, whose pristine dimensions were previously found in the range 30–190 nm by TEM [26]. Despite ceria-based nanoparticles not being clearly distinguished from the main LaOS phase due to poor contrast variation, the 5Ce/LaOS_I showed numerous smaller nanoparticles adhering on top of the larger LaOS grains, confirming a better interaction and larger contact area between phases with respect to the mechanical mixture counterpart, consistent with XRD and reactivity results. Moreover, the complete transformation into the La-oxysulfide phase at the end of the anaerobic oxidation tests did not significantly alter the morphology of the samples, also considering the residual presence of some small nanoparticles of unburned carbon soot.

Current experiments demonstrate that the La-oxysulfate–oxysulfide transformation is structurally reversible during soot combustion experiments with Ce + LaOS composites. However, their suitability for GPFs depends on long-term stability across thousands of redox cycles—a requirement yet to be validated. Previous studies on similar materials (Pt- CeO_2 /LaOS [27]) showed stable redox cycling at 600 °C alternating 1.4% vol. H_2 with 0.7% vol. O_2 feed streams. Similarly, a Co-doped LaOS [24] was reported to be stable during redox cycles of chemical looping combustion of methane at 800 °C. Notably, it

was also reported that the long-term cyclic stability of the $\text{Re}_2\text{O}_2\text{SO}_4/\text{Re}_2\text{O}_2\text{S}$ systems was strongly enhanced in the presence of even small contents of S-bearing compounds, such as those commonly found in the fuel stream [36].

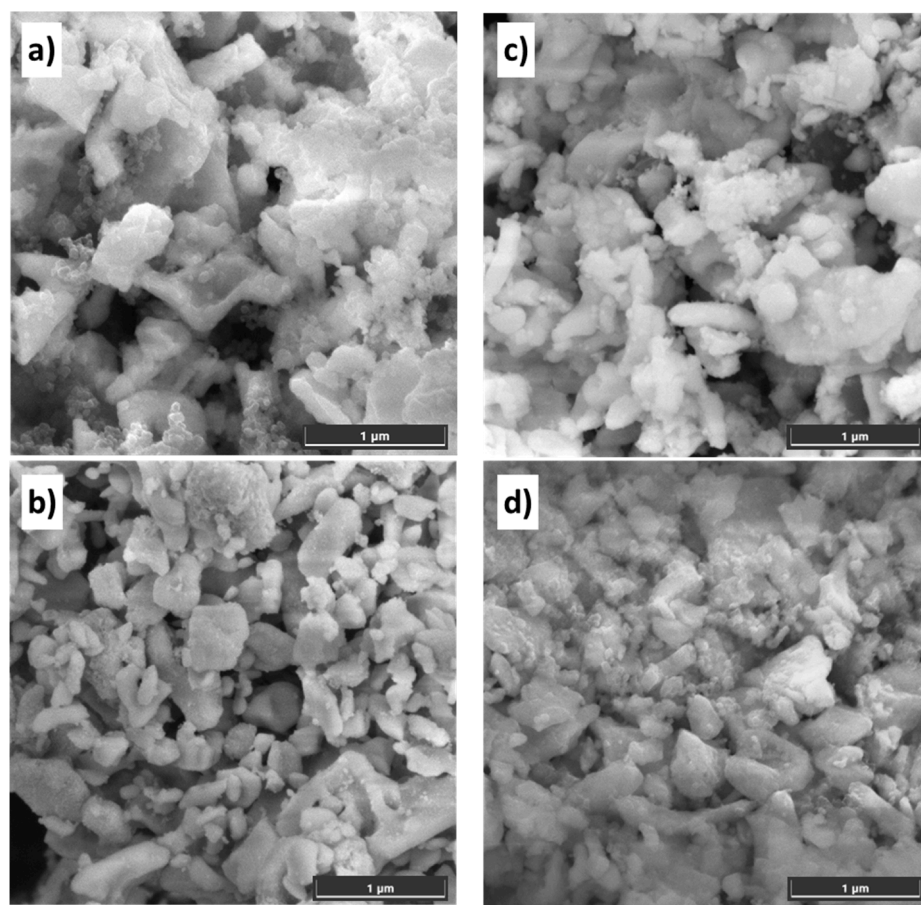


Figure 7. SEM images of 5Ce/LaOS_I (a,b) and 5Ce+LaOS_M (c,d) composite oxygen storage materials recovered at the end of soot oxidation tests under either 1% O_2 (a,c) or anaerobic (b,d) flow conditions at max temperature of 835 °C.

3. Materials and Methods

Lanthanum oxysulfate (LaOS) and Praseodymium oxysulfate (PrOS) were obtained by the thermal decomposition of their corresponding sulfates ($\text{La}_2(\text{SO}_4)_3$ Sigma-Aldrich (St. Louis, MO, USA) purity 99.99%; $\text{Pr}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ Fischer Scientific Italia (Segrate, Italy), purity 99.9%) by heating them at 10 °C min^{-1} up to 1000 °C and holding for 2 h under inert flow. Commercial CeO_2 nano-powder was supplied by Aldrich ($\leq 25\text{ nm}$, Aldrich Product No. 544841-25G, St. Louis, MO, USA).

A mechanical mixture of CeO_2 (5 wt %) and LaOS was prepared by intensively grinding the LaOS and CeO_2 powders with a pestle in an agate mortar (5Ce + LaOS_M). A further composite sample with identical nominal composition was prepared by impregnation of LaOS with a Ce nitrate water solution followed by drying at 120 °C and calcination at 850 °C for 2 h in 1% O_2/Ar (5Ce/LaOS_I).

XRD patterns of fresh samples and after high-temperature soot oxidation experiments were collected using a Philips X'Pert PRO apparatus (Malvern Panalytical, Malvern, UK) with $\text{CuK}\alpha$ radiation (anti-scatter slit width 7.5 mm) in a 2θ range 5–80°, which was scanned using a step size of 0.013° and a scan speed of $0.156^\circ \text{ s}^{-1}$. Background correction, fitting, peak attribution, and calculation of lattice parameters (WPPF) were performed using SmartLab Studio II software v4.5.162.0 and PDF-5+ 2025 database (ICDD). Average

dimensions of crystallites were estimated by the Scherrer equation applied to the most intense peaks of each phase. Phase quantification was performed by the Rietveld method.

The morphology of fresh and used samples was investigated with a FE-SEM TESCAN CLARA (S8154) (Tescan, Brno, Czech Republic) scanning electron microscope (SEM).

N₂ adsorption–desorption measurements at 77 K were performed in a Quantachrome Autosorb 1-C (Anton Paar GmbH, Graz, Austria) after degassing the samples at 150 °C for 3 h under a high dynamic vacuum. The specific surface area was evaluated by the BET method.

Temperature Programmed Reduction (TPR) analysis was carried out with a Micromeritics AutoChem 2020 (Norcross, GA, USA) equipped with a TC detector. Powder samples (150 mg) were pre-treated in situ under air flow at 500 °C for 1 h; after cooling to room temperature, the flow was switched to 2% vol. H₂/Ar mixture (50 cm³ min^{−1}) and the temperature was ramped at 10 °C min^{−1} up to 900 °C for 1 h.

Soot oxidation experiments were carried out in a Setaram Labsys Evo TGA-DTA-DSC 1600 (Caluire-et-Cuire, France) flow microbalance either under inert (Ar) or 1% O₂/Ar flow (50 cm³ min^{−1}) by heating up at a rate of 10 °C min^{−1} from 130 °C to 835 °C, then holding for 60 min at the maximum temperature. Commercial Degussa Printex-U (Evonik Degussa, Essen, Germany) was employed as a model for GDI soot in this study since they share similar morphologies and oxidation behaviour [6]: ca 6–8 mg of it was mixed with the catalyst powder in a 1:9 weight ratio in tight contact (intensively milled together in an agate mortar for 10 min) and loaded in an alumina crucible. Reference experiments were also carried out on pure CeO₂, LaOS and PrOS. A Pfeiffer ThermoStar G Mass Spectrometer (Aßlar, Germany) equipped with a Secondary Electron Detector (MS-SEM), was employed to continuously analyze the gases evolved during reaction by recording the temporal profiles at $m/z = 18$ (H₂O), 28 (CO), 32 (O₂), 44 (CO₂), and 64 (SO₂).

4. Conclusions and Outlook

A synergistic promotional effect was found by doping La₂O₂SO₄ with a small amount (5 wt %) of CeO₂ to obtain advanced catalytic oxygen storage systems for soot oxidation in Gasoline Particulate Filters (GPFs). The composite materials, prepared by either mechanical activation or impregnation, showed a higher oxygen mobility during H₂-TPR, which consistently translated into enhanced deep oxidation activity for carbon soot under anaerobic conditions with respect to the reference pure La- or Pr-oxysulfates. Despite CeO₂ on its own displaying very poor activity below 800 °C in the absence of molecular O₂, when in contact with LaOS, it helped extract the oxygen stored in the oxysulfate lattice starting from 630 °C to sustain the selective combustion of soot to CO₂. At the same time, the La-oxysulfate progressively transformed into its oxysulfide phase, guaranteeing the full deployment of a remarkable 15.2 wt % oxygen storage capacity. Under lean-O₂ conditions, the CeO₂ active surface promoted the catalytic combustion of soot from as low as 300 °C, but a significant acceleration was observed above 450 °C when an additional oxygen flux from the LaOS increased the reaction rate above the threshold level otherwise set by the external mass transport limitations for O₂. Furthermore, beyond 630 °C, the LaOS phase itself started to contribute directly to the deep oxidation of the carbon soot particles in close contact with it.

Following complete soot combustion, the La₂O₂S fraction was readily regenerated to La₂O₂SO₄ in the presence of molecular O₂, even at low partial pressures. This reoxidation process exhibited rapid intrinsic kinetics at temperatures relevant to GPF applications, fully restoring the original textural and morphological properties of the oxygen storage materials. Acting as a gateway for oxygen extracted from the La₂O₂SO₄ bulk, ceria demonstrated a more pronounced promotional effect when a larger interfacial contact area was provided

and upon partial substitution with La, as observed with the impregnated composite compared to the mechanically mixed counterpart. These results suggest that the combination of two different catalysts, one (a doped Ceria) covering the low-temperature and aerobic conditions and the other one (LaOS) covering the mid–high-temperature and anaerobic conditions, can be effective, and the potential occurrence of an interaction between the two phases does not represent a drawback. Eventually, the CeO₂ and LaOS contents in the composites can be tailored to meet specific low-temperature catalytic activity and oxygen storage capacity requirements of real GPFs.

The catalytic oxidation performance of the composites may be further enhanced by increasing both the exposed surface area of the La₂O₂SO₄ phase and the ceria–oxysulfate interface. Alternative preparation strategies for the synthesis of LaOS using (carbon) templates and/or a precipitating agent, as well as refining the mechanical activation step, could further advance this objective. More sophisticated core–shell nanoarchitectures can be envisaged, containing a LaOS core surrounded by a porous CeO₂ shell.

While current results confirm the structural reversibility of the lanthanum oxysulfate–oxysulfide transformation during soot combustion, long-term stability over thousands of redox cycles remains to be proven for GPF applications. Under harsh operating conditions the oxygen storage capacity and the catalytic properties of the CeO₂+LaOS composites may be compromised by phase segregation at the complex interface or by the progressive loss of minimal sulfur-bearing compounds. Specifically, assessing the stability of performance requires ad hoc experimental designs where the catalyst is applied as a thin washcoat layer on a typical wall flow filter and solid carbon soot is periodically or continuously deposited on it to serve as the reducing agent.

Author Contributions: Conceptualization, L.L. and S.C.; methodology, L.L.; validation, S.C.; investigation, E.M.C. and M.E.F.; data curation, E.M.C. and M.E.F.; writing—original draft preparation, L.L. and S.C.; writing—review and editing, L.L. and S.C.; supervision, L.L.; funding acquisition, L.L. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Ministero Università e Ricerca—Italy (PRIN2022—JRT7WZ). E. M. Cepollaro acknowledges the European Union—Next Generation EU under the National Recovery and Resilience Plan (NRRP), Mission 04 Component 2 Investment 3.1, Project Code: IR0000027-CUP:B33C22000710006-iENTRANCE@ENL: Infrastructure for Energy TRAnSition aNd Circular Economy @ EuroNanoLab.

Data Availability Statement: Data are contained within the article.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Singh, E.; Kim, N.; Vuilleumier, D.; Skeen, S.; Cenker, E.; Sjöberg, M.; Pickett, L. Particulate Matter Emissions in Gasoline Direct-Injection Spark-Ignition Engines: Sources, Fuel Dependency, and Quantities. *Fuel* **2023**, *338*, 127198. [CrossRef]
2. Johnson, T.; Joshi, A. Review of Vehicle Engine Efficiency and Emissions. *SAE Int. J. Engines* **2018**, *11*, 1307–1330. [CrossRef]
3. Richter, J.M.; Klingmann, R.; Spiess, S.; Wong, K.-F. Application of Catalyzed Gasoline Particulate Filters to GDI Vehicles. *SAE Int. J. Engines* **2012**, *5*, 1361. [CrossRef]
4. Giechaskiel, B.; Melas, A.; Valverde, V.; Otura, M.; Martini, G. Challenging Conditions for Gasoline Particulate Filters (GPFs). *Catalysts* **2022**, *12*, 70. [CrossRef]
5. Sartoretti, E.; Martini, F.; Piumetti, M.; Bensaid, S.; Russo, N.; Fino, D. Nanostructured Equimolar Ceria-Praseodymia for Total Oxidations in Low-O₂ Conditions. *Catalysts* **2020**, *10*, 165. [CrossRef]
6. Martínez-Munuera, J.C.; Zoccoli, M.; Gimenez-Mañogil, J.; García-García, A. Lattice oxygen activity in ceria-praseodymia mixed oxides for soot oxidation in catalysed Gasoline Particle Filters. *Appl. Catal. B Environ.* **2019**, *245*, 706–720. [CrossRef]
7. Moreno-Marcos, C.; Torregrosa-Rivero, V.; Albaladejo-Fuentes, V.; Sánchez-Adsuar, M.S.; Illán-Gómez, M.J. BaFe_{1-x}Cu_xO₃ Perovskites as Soot Oxidation Catalysts for Gasoline Particulate Filters (GPF): A Preliminary Study. *Top. Catal.* **2019**, *62*, 413–418. [CrossRef]

8. Torregrosa-Rivero, V.; Moreno-Marcos, C.; Albaladejo-Fuentes, V.; Sánchez-Adsuar, M.S.; Illán-Gómez, M.J. BaFe_{1-x}Cu_xO₃ Perovskites as Active Phase for Diesel (DPF) and Gasoline Particle Filters (GPF). *Nanomaterials* **2019**, *9*, 1551. [CrossRef] [PubMed]
9. Martinovic, F.; Galletti, C.; Bensaid, S.; Pirone, R.; Deorsola, F.A. Soot oxidation in low-O₂ and O₂-free environments by lanthanum-based perovskites: Structural changes and the effect of Ag doping. *Catal. Sci. Technol.* **2022**, *12*, 5453–5464. [CrossRef]
10. Li, P.; Chen, X.; Li, Y.; Schwank, J.W. A review on oxygen storage capacity of CeO₂-based materials: Influence factors, measurement techniques, and applications in reactions related to catalytic automotive emissions control. *Catal. Today* **2019**, *327*, 90–115. [CrossRef]
11. Polychronopoulou, K.; Zedan, A.F.; AlKetbi, M.; Stephen, S.; Ather, M.; Katsiotis, M.S.; Arvanitidis, J.; Christofilos, D.; Isakovic, A.F.; Al Hassan, S. Tailoring the efficiency of an active catalyst for CO abatement through oxidation reaction: The case study of samarium-doped ceria. *J. Environ. Chem. Eng.* **2018**, *6*, 266–280. [CrossRef]
12. Piumetti, M.; Bensaid, S.; Andana, T.; Dosa, M.; Novara, C.; Giorgis, F.; Russo, N.; Fino, D. Nanostructured Ceria-Based Materials: Effect of the Hydrothermal Synthesis Conditions on the Structural Properties and Catalytic Activity. *Catalysts* **2017**, *7*, 174. [CrossRef]
13. Zhu, H.; Chen, Y.; Wang, Z.; Liu, W.; Wang, L. Catalytic oxidation of CO over mesoporous copper-doped ceria catalysts via a facile CTAB-assisted synthesis. *RCS Adv.* **2018**, *8*, 14888–14897. [CrossRef] [PubMed]
14. Sahoo, T.R.; Armandi, M.; Arletti, R.; Piumetti, M.; Bensaid, S.; Manzoli, M.; Panda, S.R.; Bonelli, B. Pure and Fe-doped CeO₂ nanoparticles obtained by microwave assisted combustion synthesis: Physico-chemical properties ruling their catalytic activity towards CO oxidation and soot combustion. *Appl. Catal. B Environ.* **2017**, *211*, 31–45. [CrossRef]
15. Han, C.; Yoko, A.; Taufik, A.; Ohara, S.; Nishibori, M.; Ninomiya, K.; Kiuchi, H.; Harada, Y.; Adschiri, T. High Oxygen Storage Capacity of Ultrasmall Mn-Doped CeO₂ Nanoparticles via Enhanced Local Distortion and Mn(II) Lattice Substitution. *Chem. Mater.* **2025**, *37*, 1205–1214. [CrossRef]
16. Shelly, L.; Schweke, D.; Danon, A.; Rosen, B.A.; Hayun, S. Exploring the Redox Properties of Ce_{1-x}U_xO_{2±δ} (x ≤ 0.5) Oxides for Energy Applications. *Inorg. Chem.* **2023**, *62*, 11456–11465. [CrossRef]
17. Wu, S.; Yang, Y.; Lu, C.; Yuan, Y.S.; Qian, G. Soot Oxidation over CeO₂ or Ag/CeO₂: Influences of Bulk Oxygen Vacancies and Surface Oxygen Vacancies on Activity and Stability of the Catalyst. *Eur. J. Inorg. Chem.* **2018**, *2018*, 2944–2951. [CrossRef]
18. Wang, H.; Jin, B.; Wang, H.; Ma, N.; Liu, W.; Weng, D.; Wu, X.; Liu, S. Study of Ag promoted Fe₂O₃@CeO₂ as superior soot oxidation catalysts: The role of Fe₂O₃ crystal plane and tandem oxygen delivery. *Appl. Catal. B Environ.* **2018**, *237*, 251–262. [CrossRef]
19. Machida, M.; Kawamura, K.; Ito, K. Novel oxygen storage mechanism based on redox of sulfur in lanthanum oxysulfate/oxysulfide. *Chem. Commun.* **2004**, *21*, 662–663. [CrossRef]
20. Machida, M.; Kawamura, K.; Ito, K.; Ikeue, K. Large-Capacity Oxygen Storage by Lanthanide Oxysulfate/Oxysulfide Systems. *Chem. Mater.* **2005**, *17*, 1487–1492. [CrossRef]
21. Machida, M.; Kawano, T.; Eto, M.; Zhang, D.; Ikeue, K. Ln Dependence of the Large-Capacity Oxygen Storage/Release Property of Ln Oxysulfate/Oxysulfide Systems. *Chem. Mater.* **2007**, *19*, 954–960. [CrossRef]
22. Valsamakis, I.; Flytzani-Stephanopoulos, M. Sulfur-tolerant lanthanide oxysulfide catalysts for the high-temperature water gas shift reaction. *Appl. Catal. B Environ.* **2011**, *106*, 255–263. [CrossRef]
23. Lisi, L.; Mancino, G.; Cimino, S. Chemical looping oxygen transfer properties of Cu-doped lanthanum oxysulphate. *Int. J. Hydrogen Energy* **2015**, *40*, 2047–2054. [CrossRef]
24. Cimino, S.; Mancino, G.; Lisi, L. Performance and Stability of Metal (Co, Mn, Cu)-Promoted La₂O₂SO₄ Oxygen Carrier for Chemical Looping Combustion of Methane. *Catalysts* **2019**, *9*, 147. [CrossRef]
25. Joshi, P.U.; Deshpande, U.P.; Bhobe, P.A. Emerging Potential of Eu₂O₂SO₄ in Reversible Oxygen Storage: A Comparative Study with Pr₂O₂SO₄. *J. Phys. Chem. C* **2026**, *130*, 3400–3409. [CrossRef]
26. Cepollaro, E.M.; Cimino, S.; Infante, M.R.; Lisi, L. Metal-Promoted La₂O₂SO₄ for High-Temperature Soot Oxidation in Catalyzed Gasoline Particulate Filters. *Ind. Eng. Chem. Res.* **2024**, *63*, 19466–19475. [CrossRef]
27. Zhang, D.; Kawada, T.; Yoshioka, F.; Machida, M. Oxygen Gateway Effect of CeO₂/La₂O₂SO₄ Composite Oxygen Storage Materials. *ACS Omega* **2016**, *1*, 789–798. [CrossRef]
28. Zhang, D.; Yoshioka, F.; Ikeue, K.; Machida, M. Synthesis and Oxygen Release/Storage Properties of Ce-Substituted La-Oxysulfates, (La_{1-x}Ce_x)₂O₂SO₄. *Chem. Mater.* **2008**, *20*, 6697–6703. [CrossRef]
29. Shen, W.; Naito, S. Easy precipitation method for preparation of cerium added La₂O₂SO₄ used for oxygen storage. *Adv. Mater. Res.* **2014**, *886*, 196–199. [CrossRef]
30. Zhang, B.; Li, D.; Wang, X. Catalytic performance of La–Ce–O mixed oxide for combustion of methane. *Catal. Today* **2010**, *158*, 348–353. [CrossRef]
31. Bhavsar, S.; Isenberg, N.; More, A.; Veser, G. Lanthana-doped ceria as active support for oxygen carriers in chemical looping combustion. *Appl. Energy* **2016**, *168*, 236–247. [CrossRef]

32. Caputo, T.; Lisi, L.; Pirone, R.; Russo, G. On the role of redox properties of CuO/CeO₂ catalysts in the preferential oxidation of CO in H₂-rich gases. *Appl. Catal. A Gen.* **2008**, *348*, 42–53. [[CrossRef](#)]
33. Boaro, M.; Vicario, M.; de Leitenburg, C.; Dolcetti, G.; Trovarelli, A. The use of temperature-programmed and dynamic/transient methods in catalysis: Characterization of ceria-based, model three-way catalysts. *Catal. Today* **2003**, *77*, 407–417. [[CrossRef](#)]
34. Zimmer, P.; Tschöpe, A.; Birringer, R. Temperature-Programmed Reaction Spectroscopy of Ceria- and Cu/Ceria-Supported Oxide Catalyst. *J. Catal.* **2002**, *205*, 339–345. [[CrossRef](#)]
35. Jian, S.; Yang, Y.; Ren, W.; Xing, L.; Zhao, D.; Tian, Y.; Ding, T.; Li, X. Kinetic analysis of morphologies and crystal planes of nanostructured CeO₂ catalysts on soot oxidation. *Chem. Eng. Sci.* **2020**, *226*, 115891. [[CrossRef](#)]
36. Ikeue, K.; Eto, M.; Zhang, D.J.; Kawano, T.; Machida, M. Large-capacity oxygen storage of Pd-loaded Pr₂O₂SO₄ applied to anaerobic catalytic CO oxidation. *J. Catal.* **2007**, *248*, 46–52. [[CrossRef](#)]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.