

Promoted lanthanum oxysulfates as regenerable catalysts for soot oxidation in GPFs

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Significance and Relevance

The temperatures of exhaust emissions from gasoline engines are higher than from diesel engines but the very low level of O_2 represents a critical issue for soot combustion.

Metal promoted lanthanum oxysulfate was proposed for the first time as possible catalyst to cover the high temperature range of soot oxidation in Gasoline Particulate Filters (GPF). This catalyst can reversibly use its lattice oxygen, completely turning into oxysulfide, to effectively oxidize soot to CO_2 also under inert flow and restoring the original oxysulfate structure even under very low O_2 levels, typical of emissions from a gasoline fueled engine.

Preferred and 2nd choice for the topic: Automotive and stationary emission control Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

Gasoline Direct Injection (GDI) engines although more efficient than Port Fuel Injection (PFI) ones, produce a large amount of soot in the fuel-rich areas thus requiring the use of Gasoline Particulate Filter (GPF). Although the exhaust temperatures of a GDI (from 400 to 700 °C) are potentially high enough for homogeneous soot oxidation on the GPF, the very low level of O₂, due to the stoichiometric fuel combustion, represents a critical issue along with the almost complete absence of NO₂ removed in the upstream Three Way Catalyst (TWC)¹. Moreover, in hybrid electric vehicles, despite their good fuel economy, the alternate switch between battery and internal combustion engine can cause soot emissions even higher than from vehicles without any electrification.

Lanthanum oxysulfate has a high Oxygen Storage Capacity (OSC) coupled to a very good thermal stability and cyclability that can potentially represent key-features for a catalyst which should operate under these severe conditions².

Promoted $La_2O_2SO_4$ has been investigated for the first time as potential high-temperature soot oxidation catalysts to be used in catalyzed GPFs.

Materials and Methods

Lanthanum oxysulfate was obtained by thermal decomposition of $La_2(SO_4)_3$ by heating it at 1000 °C for 2 h under He flow. Portions of $La_2O_2SO_4$ were impregnated with copper, cobalt or cerium by impregnation of the corresponding nitrate salts.

Soot oxidation experiments were carried out in a thermobalance coupled to a mass spectrometer (TG-MS) either under inert (Ar) or under 1% O_2 /Ar flow. Materials were characterized before and after the soot combustion by ICP-MS, XRD, TEM and porosimetric analysis.

Results and Discussion

The TG-MS results showed that, despite the solid state of soot, its reaction with $La_2O_2SO_4$ deeply affected the onset temperature of the reduction to La_2O_2S under inert atmosphere. Specifically, the oxidation of carbon soot promoted the extraction and consumption of the lattice oxygen species from $La_2O_2SO_4$, which otherwise does not spontaneously release O_2 . Nevertheless, for the unpromoted oxysulfate the undesired irreversible decomposition into lanthanum oxide, associated with the emission of SO₂, occurred.

This is effectively inhibited by the small addition of cobalt, copper or cerium to the catalyst, which not only effectively promoted the lattice oxygen mobility of the material, favouring the selective combustion of soot in the absence of O_2 starting from 630 °C, but totally inhibited the decomposition



with emission of SO₂, as shown in Fig.1. CeO₂, typically used in DPFs under excess oxygen, did not activate soot oxidation under inert atmosphere. Under 1% O₂, soot combustion was catalyzed by the active surface oxygen starting from temperatures as low as 400 °C, but at T \geq 630 °C the high OSC of the promoted lanthanum oxysulfate greatly boosted soot oxidation. When all carbon soot was burnt, the lanthanum oxysulfide phase produced by the reaction was completely reoxidized to the original La₂O₂SO₄ phase by the O₂ in the gas even at so low partial pressures, thus restoring the original catalyst.



Figure 1 TG-MS analysis under inert flow for 1:10 mixtures of soot with metal (Cu, Co) promoted $La_2O_2SO_4$ compared to reference CeO₂: weight losses and corresponding derivative profiles and MS signals for CO₂ (m/z = 44) and CO trace (m/z = 28).

References

- 1. B. Giechaskiel, A. Melas, V. Valverde, M. Otura, G. Martini, Catalysts 2022 12, 70
- 2. S. Cimino, G. Mancino, L. Lisi, Catalysts 2019, 9, 147

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