Silver-modified perovskites as soot oxidation catalysts for Gasoline Particulate Filters

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Introduction

European standards for Diesel cars restrict the particulate matter emissions by combining a limit number (PN: 6.0×10^{11} particulates/km) with a limit mass (PM: 4.5 mg/km) as well as durability of after-treatment system. From 2014, PN and PM limits are also introduced for the approval of gasoline-fuelled vehicles. While conventional Port Fuel Injection (PFI) gasoline vehicles can easily comply with these limits, their Direct Injection (GDI) counterparts are found to emit systematically above this threshold by up to 1.5 orders of magnitude [1,2]. The Euro 6b legislations will tolerate a PN limit at 6.0×10^{12} particulates/km for these GDI vehicles but this standard will be strengthened from 2017 (Euro 6c) to reach the level of Diesel cars. It is therefore expected that GDI vehicles may require the installation of Gasoline Particulate Filters (GPF). At the same time, the penetration of GDI vehicles is expected to rapidly grow in the near future in both the European and the US markets. This is due to their improved fuel efficiency compared to the conventional PFIs as well as their ability to be implemented in hydride cars. Therefore, it is of strong interest to develop catalysts for the regeneration of GPF. Comparing to Diesel ones, GDI exhausts contain much lower amounts of oxygen. The scientific issue consists in the development of catalysts effective for soot oxidation at low oxygen levels. For cost and sustainability reasons, it is also necessary to avoid the utilization of noble metals. This study examines the use of Ag-modified manganites and ferrites as soot oxidation catalysts for GPF.

Materials and Methods

Two series of perosvkites, $La_{0.5}Sr_{1-x}Ag_xMnO_3$ and $La_{0.5}Sr_{1-x}Ag_xFeO_3$ (with x=0.05, 0.1, 0.15, 0.2 and 0.25), were prepared by a complex route from the thermal decomposition of the chelated nitrate precursors, following by calcinations at 800°C for 4h under air flow. The obtained samples were named as xM or xF, according to the silver percentage introduced during the preparation and the chemical nature of the perovskites (M for manganites and F for ferrites). The chemical composition of the samples was measured by inductively coupled plasma-emission spectroscopy. BET specific surface area was estimated by nitrogen adsorption at liquid nitrogen temperature in a Micromeritics ASAP 2000 apparatus. The X-ray diffraction pattern of the materials was recorded at room temperature using X-ray power diffractometer Bruker D5005 with CuKα radiation. The microstructure and surface morphology were characterized by scanning electron microscopy (FEI ESEM-XL30). Surface properties of all samples were analysed by using O_2-TPD and TPR. A model soot (Printex-U) and the respective catalyst powder (soot:catalyst weight ratio of 1:4) were mixed and crushed for 15 minutes in a mortar in order to improve the soot/catalyst agglomerate contact (tight contact). Although loose contact condition more approaches to real condition, tight contact condition is helpful to reflect the intrinsic characteristics of the catalysts. TPO analyses were carried out in the presence of 1% of O_2 in helium (100 mL/min) with a heating ramp of 10°C/min from room temperature to 750 °C.

Results and Discussion

The morphology of Ag-modified ferrite observed by SEM is mostly characterized by the formation of dense foil-shape particles, while manganese-perovskite series exposes a macroporous and less agglomerate morphology. The ICP analysis confirms the presence of targeted chemical compositions and the amount of Ag. However, XRD spectra reveal the presence of metallic silver which is partially incorporated into the perovskite structure. In the case of 25M, small reflections attributed to the presence of $Ag_{1.8}Mn_8O_{16}$ were detected. O_2-TPD experiments have shown that the Mn-perovskites are positively affected by the presence of Ag due to the improvement of their redox properties (Mn^{4+}/Mn^{3+}), probably linked with the formation of $Ag_{1.8}Mn_8O_{16}$. On the other hand, highly agglomerated surface metallic silver on the Fe-perovskites partially blocks its capacity to adsorb oxygen on the surface oxygen vacancies. TPR analysis confirms the strong improvement of the reducibility of both series in the presence of Ag.

Figures 1 gives values of T20 (Temperature at 20% of soot conversion) and the overall quantity of O_2 desorbed during TPD as a function of the Ag loading into the Mn-perovskites. The T20 value of the un-catalyzed soot was found to be 670 ºC. The addition of silver to the catalysts formulation clearly improves the catalytic performances of Mn-perovskite but not those of ferrites. Values of T20 of Mn-perosvkites linearly decrease with the Ag content as well as with its ability to release oxygen.

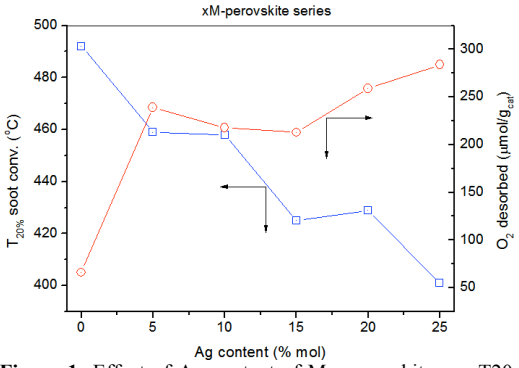

Figure 1: Effect of Ag content of Mn-perovskites on T20 of soot oxidation and O_2 desorption during TPD.

Significance

Modified Ag-manganites can provide a better stabilization and dispersion of the deposited silver species in comparison to the ferrite ones. These stabilized surface Ag oxides strongly improve the reducibility and the ability to release oxygen, and then the catalytic performances for soot oxidation of manganites, close to gasoline conditions.

References

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