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La/Sr-based perovskites as soot oxidation catalysts for Gasoline Particulate Filters

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ABSTRACT

$La_{0.6}Sr_{0.4}BO_3$ type-perovskites (with B = Fe, Mn or Ti) were synthesized by a complex route from the thermal decomposition of the chelated nitrate precursors, as soot oxidation catalysts under low oxygen partial pressures. The nature of the B-site cation modifies the morphology, the structural symmetry, the charge compensation mechanism and the redox properties. The generation of oxygen vacancies is predominant in LSF while an increase in the oxidation state of B cations occurs in LSM and LST, respectively. A direct link was established between the reducibility of the perovskites and their ability to oxidize soot. Fe and Mn-based perovskites exhibit similar catalytic behaviors, superior to LST, which are attributed to the presence of oxygen vacancies in LSF and Mn^{4+} cations in LSM. This latter redox property is particularly suitable to oxidize soot at low oxygen partial pressures, as encountered in gasoline direct injection engine exhausts.

1. Introduction

The penetration of Gasoline Direct Injection (GDI) vehicles is expected to rapidly grow in the near future in the European and US markets. This is due to their improved fuel efficiency compared to the conventional Port Fuel Injection (PFI) engines as well as their ability to be implemented in hybrid cars. GDI engines would potentially help the manufacturers to meet the target set in both EU and USA on the fleet-average carbon dioxide (CO_2) emissions of future vehicles. To further decrease the contribution of the transport sector (around 12% at present), the Particulate Matter (PM) emissions of automotive engines are now regulated in terms of mass and number [1]. The Euro 6a legislations will tolerate a PN limit at 6.0×10^{12} particulates/km for 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). Therefore, it is of strong interest to develop catalysts for the regeneration of GPF. Comparing to Diesel exhausts, GDI ones contain much lower amounts of oxygen. The GPF will be located downstream the Three-Way Converter (TWC) which is using the major part of oxygen in the exhaust to oxidize unburnt hydrocarbons and carbon monoxide. Therefore, 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 perovskites as soot oxidation catalysts for GPF. This family of oxides is known for its deep oxidation catalytic activity, hydrothermal stability and favorable cost [2,3]. Perovskites present a general formula of the form ABO_3 where the larger size A-cation shows a 12-coordination number, while the B-cation coordinates with 6 neighboring atoms. Substitution of A and/or B atoms with metals possessing different oxidation states may enhance the catalytic activity due to the formation of structural defects such as anionic or cationic vacancies and/or change in the oxidation state of the transition metal to maintain the electro-neutrality of the compound [4]. Perovskites were already widely investigated for Diesel soot oxidation [3–11]. The catalytic activity is mainly related to the following properties of these materials: surface and bulk mobility of the catalysts oxygen species, capacity to complete redox cycles at high temperatures and thermo-stability of the surfaces [3–6]. Furthermore, the reactivity of perovskites for soot combustion has been related with the abundance of suprafacial oxygen (α-oxygen) weakly chemisorbed on the surface and able to enrich (with oxygenated species) the surface of soot particles via a spillover mechanism [4,7,8].

This study reports the preparation and characterizations of $La_{0.6}Sr_{0.4}BO_3$ type-perovskites (with B = Fe, Mn or Ti), as promising

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materials to catalyze the soot combustion reaction under relatively low oxygen partial pressures close to GDI conditions.

2. Experimental

2.1. Preparation of perovskite-catalysts powders

Powders of lanthanum-strontium manganite, $La_{0.6}Sr_{0.4}MnO_3$ (LSM), and lanthanum-strontium ferrite, $La_{0.6}Sr_{0.4}FeO_3$ (LSF), were prepared by a complex route from the thermal decomposition of the chelated nitrate precursors [12,13]. The following reagents were used: $La(NO_3)_3{\cdot}6H_2O$ (Fluka®, ≥99.0%), $Sr(NO_3)_2$ (Sigma–Aldrich®, ≥99.0%), $Mn(NO_3)_2{\cdot}4H_2O$ (Sigma–Aldrich®, ≥97.0%), $Fe(NO_3)_3{\cdot}9H_2O$ (Sigma–Aldrich®, ≥99.99%) and maleic acid (Alfa Aesar®, 99%). The nitrate precursors were dissolved in a 10% w/w aqueous solution of maleic acid. Lanthanum nitrate was firstly introduced in the solution, then strontium nitrate and finally manganese or iron nitrate. The molar ratio of La/Sr/Mn or Fe/maleic acid was the following 0.6/0.4/1/8.6. After the dissolution of the salts, the pH of the mixture was raised to 8 by adding ammonium hydroxide solution (Sigma–Aldrich®, 25% NH_3). Most of the water was then evaporated on a heating plate. The mixture was put overnight in an oven at 110 °C and produced a powder precursor. This latter was heated at 350 °C (2 °C/min) for 2 h to remove the organic compounds and finally calcined at 800 °C (4 °C/min) for 4 h, under air flow. Lanthanum-strontium titanate, $La_{0.6}Sr_{0.4}TiO_3$ (LST), was synthesized by the Pechini-type polymerized complex route, based on polyesterification between citric acid and ethylene glycol [14]. Titanium tetraisopropoxide ($Ti\{OCH(CH_3)_2\}_4$), used as precursor (Sigma–Aldrich®, ≥97.0%), was dissolved in ethylene glycol (Sigma–Aldrich®, ≥99%) and subsequently, anhydrous citric acid (Alfa Aesar®, ≥99.5%) was added to this solution. After achieving complete dissolution, $La(NO_3)_3{\cdot}6H_2O$ and $Sr(NO_3)_2$ were added and the mixture was stirred for 1 h at 60 °C until it became transparent. N_2 gas was constantly burbled into the system to avoid the early hydrolysis of the Ti precursor. The molar ratio of La/Sr/Ti/citric acid/ethylene glycol was the following 0.6/0.4/1/10/40. The colorless clear solution was heated with stirring on a hot plate to promote polarization and remove excess solvents. After cooling down, a dense resin-aspect material was obtained. This latter was calcined as described before for LSM and LSF materials.

2.2. Characterizations

The chemical composition of the samples was measured by inductively coupled plasma-emission spectroscopy, ICP-OES (Varian). BET specific surface area was estimated by nitrogen adsorption at liquid nitrogen temperature in a Micromeritics ASAP 2000 apparatus. The samples were degassed for 2 h at 300 °C under vacuum. The X-ray diffraction pattern of the materials was recorded at room temperature using a X-ray powder diffractometer Bruker D8 ADVANCE A25 equipped with a Ni filter and a fast detector LYNX-EYE containing 192 channels for a detector opening of 2.94°. The Cu Kα radiation (λ = 154178 nm) was used in a wide range of Bragg angles 2θ (10–80°) with a step of 0.02047° and recording time for each step of 0.5 s.

The microstructure and surface morphology were characterized by scanning electron microscopy (FEI ESEM-XL30).

Reaction products during Temperature-Programmed Desorption of oxygen (O_2-TPD) experiments were analyzed by using a HPR-20 QIC HIDEN ANALYTICAL mass spectrometer, operated in selected ion mode with a SEM detector. 100 mg of catalyst sample were loaded in a fixed-bed tubular quartz reactor. After a pre-treatment at 500 °C for 1 h in presence of He (1.8 L/h), the sample was exposed to pure oxygen (1.8 L/h) for 30 min, and then cooled down to room temperature (RT). Then, the flow was switched to He (1.8 L/h) and the reactor was purged for an additional 1 h in order to stabilize the mass spectrometer signals. The temperature was then increased from RT to 800 °C using a linear temperature program at 10 °C/min and held for 30 min.

Temperature programmed reduction (TPR) analyses with hydrogen were carried out on samples (100 mg) in the same reactor used for O_2-TPD experiments. TPR was performed with a flow of 1.8 L/h of 1 vol.% H_2 in He increasing the temperature from room temperature to 800 °C at a heating rate of 10 °C min^{-1}. The reduction profiles were obtained following mass $m/e = 2$ corresponding to H_2 with the same mass spectrometer than for O_2-TPD experiments. X-ray photoelectron spectroscopy (XPS) spectra were recorded on a Thermo ESCALAB 250 electron spectrometer with a monochromatized Al K_α X-ray source (1486.6 eV) and a passing energy of 20 eV. C1s (binding energy 284.8 eV) of adventitious carbon was used as the reference. XPS spectra were deconvoluted using XPSPEAK 41 program by the curve fitting after the Shirley-type background subtraction.

2.3. Soot oxidation tests

Catalytic performances of the synthesized perovskites were performed by using Temperature-Programmed oxidation (TPO) tests on powder mixtures. Model soot (Printex-U) and the respective catalyst powder (soot:catalyst weight ratio of 1:4) were mixed and crushed for 15 min in a mortar to improve the soot particles/catalyst agglomerates contact (tight contact). TPO analyses were carried out in the presence of 1% of O_2 in helium (6 L/h) with a heating ramp of 10 °C/min from room temperature to 750 °C, on a fixed-bed tubular quartz reactor (internal diameter = 8 mm). The reaction products (CO and CO_2) were continuously recorded by IR on-line analyzer EMERSON NGA2000. To convert the CO_2 and CO concentrations into soot conversion data, the total amount of CO_2 and CO evolved was considered to correspond to 100% conversion of soot. Carbon and oxygen mass balances were found to be within 2%, meaning that the difference between the introduced mass of soot and the overall quantity of produced CO and CO_2 did not exceed 2%. TPO experiments were carried out three times and results were reproducible with 2% accuracy in “tight” contact mode.

3. Results and discussion

3.1. Structural, morphological and textural properties

Fig. 1a shows the diffraction patterns of the synthesized materials. All the XRD patterns of LSM, LSF and LST powders calcined at 800 °C for 4 h mainly contain the targeted perovskite phase. Nevertheless, one can distinguish some structural distortions depending on the nature of the B cation. To facilitate the analysis of such differences, the XRD patterns in the 2θ range from 30 to 42° were enlarged (Fig. 1b). As can be observed, the position of the characteristic reflections is closer for LSF and LST and slightly different for LSM. LSM seems to exhibit a rhombohedral symmetry while LSF should present an orthorhombic structure and LST rather a cubic structure (small diffraction lines present in LSF are not present in LST). From a general point of view, perovskite-type materials show deviations from its ideal cubic structure (space group Pm3m-O_h) at room temperature, presenting two different phases with orthorhombic and rhombohedral symmetries [15]. Such structural distortions are related to the size of the A and B-site cations, its charge, relative concentration and chemical nature. To evaluate the expected effect of B-site cation size in the stability of the perovskite