Key factors in Sr-doped LaBO₃ (B = Co or Mn) perovskites for NO oxidation in efficient diesel exhaust purification

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ABSTRACT

Perovskites have attracted attention in recent years as an economic alternative to noble metals in oxidation processes. Synthesis conditions of $LaCoO_3$ and $LaMnO_3$ perovskites have been studied varying citrate to nitrate molar ratio in the starting solution, pH and calcination protocol, with the aim of obtaining high purity perovskites, absence of impurities, and with enhanced textural properties. Once synthesis conditions were established, strontium was incorporated in the perovskite lattice as a textural and structural promoter, by substituting lanthanum with different doping levels, i.e. $La_{0.9}Sr_{0.1}BO_3$, $La_{0.8}Sr_{0.2}BO_3$, $La_{0.7}Sr_{0.3}BO_3$, $La_{0.6}Sr_{0.4}BO_3$ and $La_{0.5}Sr_{0.5}BO_3$ with B = Co or Mn. The prepared solids were characterized in terms of crystalline phase identification (XRD), specific surface area (N₂ adsorption–desorption at −196 °C), reducibility and oxidation state of transition metal ions (H₂-TPR), quantification of adsorbed oxygen species (O₂-TPD) and surface elemental composition (XPS). Charge imbalance associated to strontium (Sr^{2+}) incorporation in the perovskite lattice in substitution of lanthanum (La^{3+}) was preferentially balanced by Mn^{4+} promotion in $La_{1−x}Sr_xMnO_3$ perovskites, whereas formation of oxygen vacancies seems to be the mechanism for charge compensation in $La_{1−x}Sr_xCoO_3$ perovskites, where Co ions remained as Co^{3+} ions. Strontium doped perovskites further improved NO conversion compared to the non-substituted formulations. The best NO oxidation performance was obtained with $La_{0.7}Sr_{0.3}CoO_3$ and $La_{0.9}Sr_{0.1}MnO_3$ samples, achieving maximum NO conversion of 83 and 65% at 300 and 325 °C, respectively. Higher oxidation capacity of $La_{0.7}Sr_{0.3}CoO_3$ sample was associated to the higher oxygen mobility and exchange capacity between oxygen in the lattice and gas phase oxygen. It is worth noting that prepared perovskites presented far higher NO oxidation capacity than platinum-based NSR model catalysts, confirming perovskites as an economic alternative to catalyze NO oxidation reactions in automotive catalysis.

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1. Introduction

Diesel engines present higher fuel efficiency than stoichiometric gasoline engines and thereby emit less CO_2 to the atmosphere. In contrast, the clean-up of diesel exhaust gases is even more challenging than gasoline engines exhaust gases, due to the nature of the emission, including soot, and also due to the net oxidizing environment that limits NO_x reduction [1]. In order to meet stringent emission standards, diesel engines implemented catalytic processes such as Diesel Oxidation Catalyst (DOC) [2] or Diesel Particulate Filter (DPF) [3]. In the DOC, unburned hydrocarbons as well as carbon monoxide are completely oxidized to CO_2 and H_2O while NO is converted into NO_2. Afterwards, soot is trapped in DPF and continuously regenerated by oxidation with NO_2 produced in the DOC. However, this strategy fails in meeting EURO VI standards regarding NO_x emissions, and consequently additional catalytic strategies are mandatory to be implemented, such as NO_x Storage and Reduction (NSR) [4] or Selective Catalytic Reduction (SCR) [5]. In the NSR technology, NO-to-NO_2 oxidation is considered a primary step to promote NO_x storage via nitrites or nitrates [6,7] formed over an alkali or alkali-earth material, because NO_2 adsorption occurs much faster than NO [4]. In the SCR technology NO-to-NO_2 oxidation is also of critical importance [8] being well known that the fast SCR reaction activates when $NO/NO_2 = 1/1$ (molar ratio), achieving high NO_x conversion even at lower temperature. Thus, the significance of NO-to-NO_2 oxidation reaction in automotive exhaust purification is relevant and merits further research on novel catalyst formulations.

Noble metal based catalysts have been commonly employed in order to promote NO oxidation in automotive catalysis. How-

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ever, the use of noble metal (especially Pt) results in high cost and poor thermal stability under highly oxidative conditions [9]. In that sense, perovskites have attracted attention in recent years as potential, low-cost alternative to noble metal in oxidation processes [10]. In the perovskite lattice (with the general formula ABO_3), the B cation coordinates with oxygen in octahedral structure, and A cation locates in the center of the dodecahedral structure. Perovskites activity for oxidation reactions seems to be related with some specific structural properties, such as change of oxidation state of B cation, active oxygen mobility and ion vacancy defect [11]. During oxidation reactions, lattice oxygen is thought to be catalytically active and its consumption and regeneration is relative to cycling the oxidation state of neighboring transition metal ions ($B^{3+} \leftrightarrow B^{4+}$) and/or ($B^{2+} \leftrightarrow B^{3+}$) [12]. In that sense, it has been reported that the catalytic activity of perovskites is far influenced by the type of B cation and its oxidation state cycling feasibility [13].

LaMnO$_3$ and LaCoO$_3$ perovskites have been proposed as active perovskites for NO oxidation reactions [11,14]. In particular, LaMnO$_3$ perovskite is somewhat unusual in that Mn^{3+}/Mn^{4+} mixed oxidation state is usually observed even for nominal stoichiometry LaMnO$_{3+\delta}$ (with Mn^{4+} content of 2δ per formula unit), opposite to most other perovskites. However, it has been proposed that electroneutrality of the lattice is accomplished by generating cation vacancies, instead of oxygen over-stoichiometry, as perovskite lattice cannot accommodate interstitial oxygen ions [15,16]. On the other hand, stoichiometric LaCoO$_3$ perovskite usually presents some oxygen deficiency in the lattice, represented by LaCoO$_{3-\delta}$, and the charge balance is accomplished by the presence of some cobalt as Co^{2+}. This Mn^{3+}/Mn^{4+} and Co^{2+}/Co^{3+} reversible oxidation state is thought to be a key factor for oxidation reactions [17–20].

The oxidation state of B cation can be modulated by varying preparation steps during the perovskite synthesis, such as calcination temperature [21], non-stoichiometry of cations A or B [12,14] or substituting La^{3+} by lower oxidation state cations, such as Ca^{2+}, Ba^{2+} or Sr^{2+}, or even higher oxidation state cation such as Ce^{4+}. Strontium-doped LaMnO$_3$ and LaCoO$_3$ perovskites have been used for a wide range of applications [10,22–24]. The introduction of lower oxidation state Sr^{2+} in substitution of La^{3+} in LaMnO$_3$ and LaCoO$_3$ lattice generates a net charge imbalance that may be compensated by alteration of the oxidation state of a fraction of transition metal, e.g. Mn^{4+} or Co^{4+}. Alternatively, the oxidation state of transition metal could be maintained unaltered (Mn^{3+} or Co^{3+}), but instead oxygen vacancies could be generated in the lattice to attain the charge balance. Even a mixed situation showing altered oxidation state of transition metal along with oxygen vacancies in the lattice could be expected.

Oxide-based catalysts have typically shown much lower activity than Pt-based catalysts under the kinetics-controlled temperature regime. However, Kim et al. [25] prepared La$_{0.9}$Sr$_{0.1}$CoO$_3$ and La$_{0.9}$Sr$_{0.1}$MnO$_3$ perovskites and reported NO oxidation activity similar to or higher than those of Pt-based catalysts under realistic automotive conditions. Li et al. [26] prepared a series of La$_{1-x}$Sr$_x$CoO$_3$ ($x = 0.1, 0.2, 0.3, 0.4$ and 0.5), and they found, after the NO$_x$ storage tests, the La$_{0.7}$Sr$_{0.3}$CoO$_3$ perovskite had the best NO-to-NO$_2$ performance and the largest NO$_x$ storage capacity (NSC) at 300 °C. These authors also suggested possible NO$_x$ storage routes on La$_{1-x}$Sr$_x$CoO$_3$. To our knowledge, a similar study of strontium-doped Mn-based perovskites has not been reported and results compared with those of Co-based perovskites.

More recently, Dong et al. [22] prepared a series of La$_{0.7}$Sr$_{0.3}$MnO$_3$ perovskite-type catalysts by the sol-gel method using citric acid as the complexant. They concluded that variation of synthesis conditions, namely the calefactive velocity, the calcination temperature and the pH of the precursor solutions, greatly affect the morphology of the perovskite catalyst and, consequently,

the NO-to-NO$_2$ activity and NO$_x$ storage capacity of La$_{0.7}$Sr$_{0.3}$MnO$_3$ perovskite-type catalysts.

In this work, we look deeply into the identification of the main changes in physico-chemical properties induced by the modification of different parameters (i.e. synthesis conditions or lanthanum partial substitution by strontium). Consequently, relevant information on the key factors for the NO-to-NO$_2$ oxidation is extracted, along with the main differences derived from the chemical nature of B cation (Co or Mn) in the perovskite-based catalyst. This information would allow designing noble-metal-free catalysts competitive to substitute conventional Pt-containing NSR catalysts. We prepare, characterize and test NO oxidation activity of stoichiometric LaMnO$_3$ and LaCoO$_3$ as well as strontium doped La$_{1-x}$Sr$_x$MnO$_3$ and La$_{1-x}$Sr$_x$CoO$_3$ perovskites ($x = 0.1, 0.2, 0.3, 0.4$ and 0.5). Firstly, the study focuses on the optimizing of the synthesis conditions during the sol-gel process to improve the oxidation capacity, including citrate to nitrate ratio, pH of the gel and calcination protocol to get pure perovskites with no phase segregation and enhanced textural properties; then special attention is focused on the correlation of NO-to-NO$_2$ activity with the physico-chemical properties of the prepared strontium-doped perovskite-based catalysts.

2. Experimental

2.1. Perovskite catalyst preparation

All perovskites were prepared the by citric acid sol–gel method [27]. Appropriate amounts of La(NO$_3$)$_3$·6H$_2$O (*Fluka*), Co(NO$_3$)$_2$·6H$_2$O (*Sigma Aldrich*), Mn(NO$_3$)$_2$·4H$_2$O (*Merck*) were dissolved in distilled water under vigorous stirring. Then citric acid (C$_6$H$_8$O$_7$·H$_2$O, CA) was added as a complexing agent and organic loading for the combustion process with a citrate to nitrate (CA/N) molar ratios of 0.7, 1.1 or 1.5. The pH value was adjusted to 3, 4.5, 6, 7, 8 or 9 by ammonia (25% as NH$_3$, *Panreac*). After solvent evaporation at 80 °C, the gel was further dried at 120 °C overnight and then calcined in 5% O$_2$/He (60 mL min^{-1}) or static air at desired temperature (600 °C, 700 °C, 800 °C or 900 °C) for 4 h. Table 1 resumes the nomenclature and synthesis conditions of all catalyst. The general nomenclature set for each sample was as follows: LaCoO$_3$ (LCO) or LaMnO$_3$ (LMO) with the specific synthesis conditions in brackets (citrate to nitrate molar ratio/pH/calcination temperature), as for example LCO (1.1/7/700). In order to determine if the synthesis method was repetitive this sample was prepared twice (with + in Table 1).

In order to synthesize strontium doped La$_{1-x}$Sr$_x$CoO$_3$ and La$_{1-x}$Sr$_x$MnO$_3$ perovskites, adequate amount of Sr(NO$_3$)$_2$ (*Sigma Aldrich*) was added to the initial solution following the same procedure as stated before. The following samples with increasing La substitution degree by Sr were synthetized: La$_{0.9}$Sr$_{0.1}$BO$_3$, La$_{0.8}$Sr$_{0.2}$BO$_3$, La$_{0.7}$Sr$_{0.3}$BO$_3$, La$_{0.6}$Sr$_{0.4}$BO$_3$, La$_{0.5}$Sr$_{0.5}$BO$_3$, with B = Mn or Co.

A Pt-based catalyst (1.5% Pt–15% BaO/Al$_2$O$_3$) was prepared as a reference by consecutive wetness impregnation. Firstly, a specific load of platinum (1.5%) was incorporated to the alumina support by dissolving the adequate amount of tretaammineplatinum (II) nitrate [Pt(NH$_3$)(NO$_3$)$_2$] on distillate water. Then, the same process was repeated for barium incorporation (15%) using the adequate amount of barium acetate [Ba(CH$_3$COO)$_2$] as precursor. After each impregnation, the catalyst was calcined at 500 °C for 4 h.

2.2. Catalyst characterization

X-ray diffraction (XRD) patterns were obtained on a Philips PW1710 diffractometer. The samples were finely ground and were