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Effect of A-site deficiency in LaMn$_{0.9}$Co$_{0.1}$O$_3$ perovskites on their catalytic performance for soot combustion

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ABSTRACT

The influence of lanthanum stoichiometry in Ag-doped (La$_{1-x}$Ag$_x$Mn$_{0.9}$Co$_{0.1}$O$_3$) and A-site deficient (La$_{1-x}$Mn$_{0.9}$Co$_{0.1}$O$_{3-\delta}$) perovskites with x equal to 10, 20 and 30 at.% has been investigated in catalysts for soot combustion. The catalysts were prepared by the amorphous citrate method and characterized by XRD, nitrogen adsorption, XPS, O$_2$-TPD and TPR. The formation of a rhombohedral excess-oxygen perovskite for Ag-doped and a cubic perovskite structure for an A-site deficient series is confirmed. The efficient catalytic performance of the larger Ag-doped perovskite structure is attributed to the rhombohedral crystalline structure, Ag$_2$O segregated phases and the redox pair Mn^{4+}/Mn^{3+}. A poor catalytic activity for soot combustion was observed with A-site deficient perovskites, despite the increase in the redox pair Mn^{4+}/Mn^{3+}, which is attributed to the cubic crystalline structure.

1. Introduction

Metal oxides with a perovskite-type structure (ABO$_3$) have been among the most studied oxides of the past 30 years in oxidation reactions due to their lower cost compared to their noble metal counterparts [1]. Moreover, these versatile structures with high structural stability exhibit the possibility of accommodating different metals in their A- and B-sites. The substitution of the trivalent A-site metal ion with a bivalent or tetravalent metal cation (A′) may be accompanied by a modification of the oxidation state of the B-site metal cation or by the formation of structural defects, leading to non-stoichiometry [2,3]. Non-stoichiometric compounds mean mixed-valence compounds with non-integral electron/atom ratios [4,5]. In the case of perovskite-type oxides, non-stoichiometry can arise from cation deficiency (in A- or B-site), oxygen deficiency or oxygen excess [6,7]. Because the BO$_3$ array in the perovskite structure forms a stable network, the large A cations at twelve-coordinated sites can be either partly or wholly missing, forming A-site deficient perovskites; meanwhile, B-site vacancies are energetically disfavored because of the large formal charge and small size of B-site cation vacancies. Moreover, in perovskite-type oxides, oxygen vacancies are more common than cation vacancies in both ABO$_3$ and BO$_3$ frameworks. The application of perovskites to heterogeneous catalysis can be traced back to 1960 [8], starting with the oxidation of hydrocarbons and carbon monoxide [9,10]. Great achievements in academics and heterogeneous catalytic application studies have been highlighted in a recent review [11] focused on A- and B-site substitution. Large increases in the catalytic activity of LaFeO$_3$ [12] and LaMnO$_3$ [13] can be achieved by A-site deficient perovskites with a low substitution of a monovalent Ag$^+$ by a trivalent A^{3+} cation. Song [14] reported that Ag-substituted manganites displayed a much better performance in VOC combustion than their non-substituted counterparts, with the highest activity being recorded for 30% Ag substitution. Similarly, Kaddouri [15] noted that 20% substitution of La^{3+} by Ag$^+$ in a non-stoichiometric LaMnO$_{3.15}$ structure exhibited the highest catalytic performance. In an earlier work reported by Pecchi [16], it was demonstrated that the cubic structure of LaMnO$_3$ changed to rhombohedral LaMnO$_{3.15}$ upon Co substitution by Mn, with a subsequent increase in catalytic performance for complete combustion reactions. A similar behavior was reported recently by Wang for a LaMn$_{0.9}$Fe$_{0.1}$O$_3$ perovskite [17]. The oxygen mobility and the redox properties of the transition metals, crucial parameters that modulate the activity of perovskites in oxidation reactions, can be modified by doping with a different oxidation state A-cation. For La$_{1-x}$Sr$_x$MnO$_3$, a close relation has been reported of the reducibility of the perovskite and the amount of labile oxygen with the rate of propane oxidation [18]. To increase the redox properties and

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oxygen availability, two series of defective A-site perovskite-type oxides were synthesized by substituting the A-site (La^{3+} by Ag^{+}) and by varying the stoichiometry of the A-site. The proposed defect will highlight the role of oxygen mobility, compensated by changes in the charge of the cations or the creation of cation or oxygen vacancies. This work aims to improve the performance of $LaMn_{0.9}Co_{0.1}O_3$ perovskites for soot combustion through the preparation of non-stoichiometric lanthanum perovskites by: (i) substituting La^{3+} ions with Ag^{+}, including a monovalent Ag^{+} in the lattice in place of a trivalent La^{3+}; and (ii) decreasing the stoichiometry of La^{3+} ions with A-site deficient formation.

2. Materials and methods

2.1. Preparation

Different A-sites, namely, (i) non-substituted $LaMn_{0.9}Co_{0.1}O_3$; (ii) Ag-doped ($La_{1-x}Ag_xMn_{0.9}Co_{0.1}O_3$); and (iii) deficient ($La_{1-x}Mn_{0.9}Co_{0.1}O_{3-\delta}$) perovskites ($x = 0.1, 0.2, 0.3$) were prepared using stoichiometric amounts of aqueous solutions of the nitrates of the corresponding metals added to an aqueous solution of citric acid with a 10% excess over the number of cations. The resulting solution was stirred for 15 min at room temperature and slowly evaporated at 70 °C under vacuum in a rotary evaporator, until formation of a gel was achieved. The gel was dried in an oven, in which the temperature was slowly increased to 250 °C and maintained overnight to yield a solid amorphous citrate precursor. The resulting powder was crushed, sieved to obtain the required particle size ($<200\,\mu m$) and calcined at 700 °C in air for 10 h.

2.2. Characterization

The specific areas were calculated from nitrogen adsorption isotherms, recorded at the liquid nitrogen temperature on a Micromeritics apparatus Model ASAP 2010. X-ray powder diffraction (XRD) patterns were obtained using nickel-filtered $CuK\alpha_1$ radiation ($\lambda = 1.5418$ Å) with a Rigaku diffractometer. Surface analysis was performed on a VG Escalab 200R electron spectrometer provided with an Mg Kα X-ray source and a hemispherical electron analyzer. Prior to analysis, the samples were degassed at 300 °C for 1 h inside the pre-treatment chamber of the spectrometer. TPR and oxygen TPD experiments were performed in a TPR/TPD 2900 Micromeritics system with a thermal conductivity detector. The reduction profiles were recorded using a 5% H_2/Ar flow at 40 mL min^{-1} at a heating rate of 10 °C min^{-1} from ambient temperature to 700 °C. For the TPD experiments, the samples were preheated in an O_2 flow for 1 h at 700 °C, cooled to room temperature in the same atmosphere and in a helium flow, then heated at 10 °C min^{-1} and the oxygen desorption monitored using a TCD. The oxidation state of manganese was determined by dissolving the samples in a known excess of an ammonium ferrous sulfate standard dissolution and titrating the excess Fe(II) with potassium permanganate. The titration was performed twice for each sample with the reproducibility of results always within 2% [19].

2.3. Catalytic activity

The catalytic activity for soot combustion was evaluated using carbon black (CB) as a model of soot. The catalyst and CB mixture, with a 4:1 ratio, was prepared by mixing 4 mg of CB and 16 mg of catalyst in tight contact. The catalytic oxidation of soot was conducted in a thermogravimetric apparatus (Netzch 409 PC) with 7.5 mg of the mixture heated in 180 mL min^{-1} of 12%O_2/He at 10 °C min^{-1} up to 800 °C. The temperature at which combustion occurred at the maximum rate, denoted as T_m, was taken as the measure of the catalytic activity. The Stationary Point Method [20] was used to calculate the apparent activation energy. Typically,

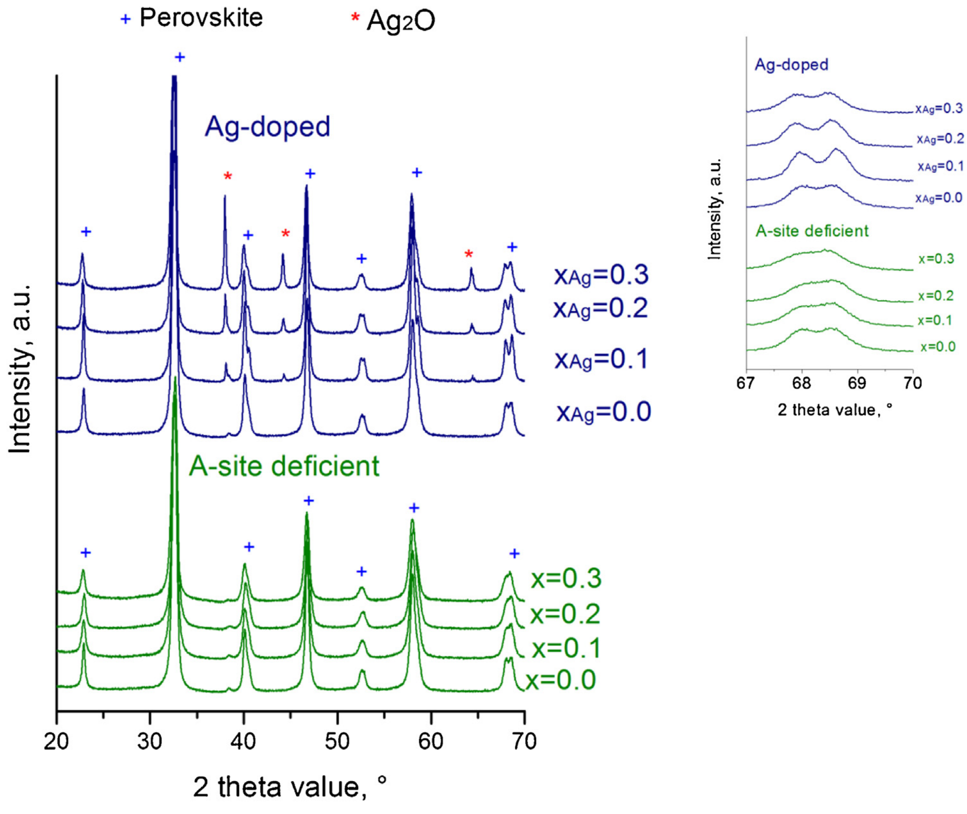

Fig. 1. XRD of A-site deficient and Ag-doped perovskites.