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Structural and chemical reactivity modifications of a cobalt perovskite induced by Sr-substitution. An *in situ* XAS study

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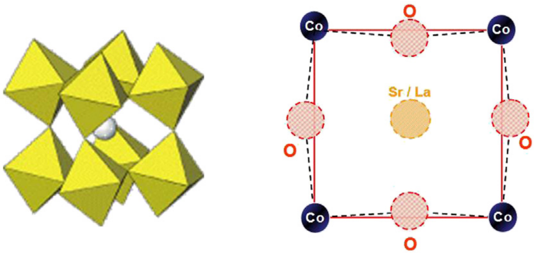
HIGHLIGHTS

- A Sr-substituted lanthanum cobalt perovskite has been prepared by spray pyrolysis.
- It has been established that Co(III) cations are present in both perovskites.
- $LaCoO_3$ is a less reducible phase than the substituted $La_{0.5}Sr_{0.5}CoO_{3-\delta}$.
- After reoxidation of reduced $La_{0.5}Sr_{0.5}CoO_{3-\delta}$, a 100% Co(III) spinel is obtained.

GRAPHICAL ABSTRACT



Strontium modifies the structure and reactivity of $LaCoO_3$ perovskite

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ABSTRACT

$LaCoO_3$ and $La_{0.5}Sr_{0.5}CoO_{3-\delta}$ perovskites have been studied by *in situ* Co K-edge XAS. Although the partial substitution of La(III) by Sr(II) species induces an important increase in the catalytic oxidation activity and modifies the electronic state of the perovskite, no changes could be detected in the oxidation state of cobalt atoms. So, maintaining the electroneutrality of the perovskite requires the generation of oxygen vacancies in the network. The presence of these vacancies explains that the substituted perovskite is now much more reducible than the original $LaCoO_3$ perovskite. As detected by *in situ* XAS, after a consecutive reduction and oxidation treatment, the original crystalline structure of the $LaCoO_3$ perovskite is maintained, although in a more disordered state, which is not the case for the Sr doped perovskite. So, the $La_{0.5}Sr_{0.5}CoO_{3-\delta}$ perovskite submitted to the same hydrogen reduction treatment produces metallic cobalt, while as determined by *in situ* XAS spectroscopy the subsequent oxidation treatment yields a Co(III) oxide phase with spinel structure. Surprisingly, no Co(II) species are detected in this new spinel phase.

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1. Introduction

Oxides with perovskite structure (ABO_3) are of interest because of their electric, magnetic and, especially, its outstanding properties as oxidation catalysts [1–7]. In particular, a previous work from our group [8] showed as these perovskite present a high oxidation activity, especially when Sr cations are incorporated in the structure. Additionally, many papers have been published about Sr doped cobaltites, and some authors have found that the spin configuration of the $LaCoO_3$ changes by introducing Sr(II) atoms [9–11]. But there is no agreement about the origin of these new physical and chemical characteristics: formation of Co(IV) ions or oxygen vacancies [12,13]. In a previous work [14], we have shown as the Sr(II) cations modify the spin state because of differences in

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sizes and generation of oxygen vacancies. In some cases, especially for catalytic applications, these solids need to be transformed by hydrogen reduction at high temperature. The reduction treatment of these ABO_3 phases performed under controlled reduction conditions can produce a well-dispersed transition metal B on a matrix comprising the A_2O_3 oxide phase as a support (Co/La_2O_3 in our case). So, knowing how the presence of Sr on the original perovskite phase modified the effect of the reduction treatment, changing the temperature of the process but also the state of the reduced transition metal dispersed on the support is a main goal for the application of these materials. With this purpose, herein, we have investigated by means of *in situ* X-ray absorption spectroscopy (XAS) at the Co K-edge, the reduction process of these two perovskites, $La_{0.5}Sr_{0.5}CoO_{3-\delta}$ and $LaCoO_3$, paying special attention to any changes induced in the structure and chemical reactivity of the Strontium-substituted cobalt perovskite after high temperature reduction and oxidation treatment.

2. Experimental

2.1. Preparation of solids

The two cobaltites, $La_{0.5}Sr_{0.5}CoO_{3-\delta}$ and $LaCoO_3$ were synthesized by a spray pyrolysis methodology described elsewhere [15,16]. Previously, 0.1 M solution containing $La(NO_3)_3 \cdot 6H_2O$ (99.99%, Aldrich), $Co(NO_3)_2 \cdot 6H_2O$ (>98%, Fluka), and $Sr(NO_3)_2$ (>99%, Fluka) were prepared and used as precursors. After nebulization, the precursors were introduced into two consecutive online furnaces, at 250 and 600 °C, respectively. At the end, amorphous powders of the solids were collected. After an annealing treatment at 600 °C for 4 h, these amorphous powders supplied $LaCoO_3$ and $La_{0.5}Sr_{0.5}CoO_{3-\delta}$ crystalline perovskites with rhombohedral structures [16].

2.2. Characterization techniques

XRD patterns of the samples were recorded using a Siemens D-500 diffractometer, working in a Bragg–Brentano configuration, with a Cu anode, and applying a voltage of 36 kV and a current of 26 mA. A step size of 0.02° and an accumulation time of 10 s per step were used for the scans.

The Temperature Programmed Reduction (TPR) experiments were made using a 5% H_2/Ar gas mixture (50 ml/min total flow) up to 750 °C with a heating rate of 10 K/min. As previously described, the experimental conditions were chosen to assure that no peaks coalescence occurs [17]. H_2 consumption was registered by means of a thermal conductivity detector (TCD) pre-calibrated using CuO. Also, a mass spectrometer in line with the TCD, previously calibrated with reference mixtures, was used to detect variations of hydrogen concentration and possible sub-products formation.

The X-ray absorption spectra (XAS spectra) were recorded at the BM25 beam line (SPLINE) of the ESRF synchrotron (Grenoble, France). The spectra were acquired at the Co K-edge in transmission mode using a suitably modified commercial infrared cell (Specac), and self-supported wafers of the perovskite samples prepared using the optimum weight to maximize the signal-to-noise ratio in the ionization chambers ($\log I_0/I_1 \approx 1$). Both, the EXAFS and XANES regions of the XAS spectra were collected after the corresponding treatments. For the thermal treatments a set of mass flow controllers were used for dosing the gases to the cell, with a total flow of 100 ml/min. In all cases, the gas mixtures used for the hydrogen reduction and reoxidation treatments (H_2, 500 °C, 30′; O_2, 500 °C, 30′) were the same to those described in the TPR experiments. A standard Co foil was introduced for energy calibration after the second ionization chamber (I_1) and measured simultaneously. Typically, the XAS spectra of Co *K*-edge were recorded from 7500 to 8700 eV, with a variable step energy value, with a minimum 0.5 eV step across the XANES region. After mathematical extraction from the XAS spectra, the EXAFS oscillations were Fourier transformed in the range 2.0–12.0 $Å^{-1}$. Reference spectra for CoO, Co_3O_4 and metallic Co were recorded using standard reference samples.

3. Results and discussion

3.1. Structural and chemical characterization of cobaltites

The two perovskite samples, $LaCoO_3$ and $La_{0.5}Sr_{0.5}CoO_{3-\delta}$, prepared by spray pyrolysis and calcined at 600 °C present rhombohedrical structures (R-3c), as determined by XRD [15]. Also, as shown in a previous publication [14], after calcination the XANES spectra (Fig. 1a) and the Fourier Transform (F.T.) of the EXAFS region (Fig. 1b) of the Co K-edge XAS spectra are typical for perovskite structure [6,11,12]. Moreover, the XANES spectra are clearly different from the two cobalt oxide references, Co_3O_4 and CoO, also included in Fig. 1. The higher energy of the edges of both cobalt perovskites indicates a higher oxidation state of cobalt than in the references, which must correspond to Co(III) species. As this energy is the same for both perovskite samples, and the oxidation state of cobalt in the $LaCoO_3$ solid can be unambiguously assigned to Co(III) species, this similarity in the edge energy can be taken as an evidence for the absence of Co(IV) species in the Sr-substituted sample. Although some authors claim the existence of Co(IV) ions in this kind of substituted perovskites [18], this fact allows us to conclude that oxygen vacancies must be distributed in the structure in order to compensate the different cationic charge between La(III) and Sr(II). So, considering that no Co(IV) species are present in the Sr-substituted solid, differences in charge between Sr (2+) and La (3+) must be reflected in a number of oxygen vacancies corresponding to a stoichiometric δ value of 0.25, that is $La_{0.5}Sr_{0.5}CoO_{2.75}$.

As mentioned above, the F.T. magnitude of the EXAFS spectra (Fig. 1b), is similar to those reported previously for perovskite structures [11]. Differences in intensity for the overlapping peaks in the 3–4 Å range, higher for the $LaCoO_3$, can be explained considering the structural disorder caused by the presence of oxygen vacancies in the Sr-containing sample and/or by interferences between the EXAFS oscillation components coming from Sr and La in the second coordination shell [14].

3.2. Reactivity changes induced by Sr

As mentioned before, the insertion of Sr(II) atoms in the “A” position of ABO_3 perovskites was primarily intended to increase the catalytic reactivity of the original $LaCoO_3$ cobaltite by inducing changes in the cobalt oxidation state and/or the formation of oxygen vacancies, as a result of the presence of Sr(II) species substituting the La(III) atoms. In a previous paper [8], we have showed as the $LaCoO_3$ perovskite presents an important activity for the thermal oxidation of carbon, producing a decrease in its temperature of combustion of ca. 150 °C and a significant increase in the selectivity toward CO_2. When Sr cations are incorporated, a further 30 °C decrease in the combustion temperature is observed. Also, the selectivity to CO_2 increases from 89 to 94%. So, it is clear that incorporation of Sr(II) cations modified the catalytic performance of the cobalt perovskite. Differences in reactivity have also become evident in the TPR profiles included in Fig. 2. After calcination at 500 °C, the profile of the Sr-containing sample presents two main peaks centered at 355 and 450 °C, respectively. The reduction process is completed at 500 °C, when the perovskite structure collapse as the cobalt is completely reduced, as deduced from the TPR profile. This fact has been verified by XRD (not

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