Structure, Morphology and Redox Properties of $La_{1-X}Sr_xCoO_3$ Perovskites

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In order to produce more efficient catalysts, it is necessary to understand the relationship between the solid structure and the catalytic properties of solids. ABO_3 perovskite type oxides are one of the most flexible frameworks in solid state chemistry; both A and B ions can be replaced or removed without destroying its fundamental arrangement. This allows manipulation of the electronic structure through doping with other cations or by adding/removing anions. A and B selection allows the modification of properties such as the oxidation state of the transition metal (redox properties), oxygen stoichiometry, bond energy and oxygen mobility in the red, distance between active sites and the collective properties of the solid [1,2]

In the present work a series of $La_{1-x}Sr_xCoO_3$ mixed oxides were studied to asses the effect on the structure, morphology and redox properties of the perovskite by substitution of La^{3+} by Sr^{2+}.

The $La_{1-x}Sr_xCoO_3$ (x = 0 - 0.4 and 1) series was synthesized by the auto combustion method [3] and characterized by XRD, BET surface area, TPR/TPO and SEM-EDX analyses. The TPR/TPO analysis was performed to $La_{1-x}Sr_xCoO_3$ ($x \leq 0.2$) using H_2 and O_2 pulses. SEM analyses were performed on the powder oxides covered with C and Au for elemental and morphologic analyses respectively.

XRD analyses show only the peaks corresponding to the perovskite structure, corroborating the fact that the auto-combustion method is appropriate for the synthesis of these solids. EDX analyses showed a chemical composition very close to the theoretical one, with surface areas in the order of 3-18 m^2/g, with the higher surface area shown by $La_{0.6}Sr_{0.4}CoO_3$ solid which decreases when the calcination temperature increases due to sintering of the perovskite phase (table 1).

The increase of the degree of substitution (x) of $La_{1-x}Sr_xCoO_3$ slightly increases the surface area and the reduction of the solid (table 1), due to formation of oxygen vacancies produced when La^{3+} is substituted by Sr^{2+}, increasing the mobility of oxygen species from the bulk to the surface of the solid where it reacts with the reducing gas [4]. SEM analyses indicated that the macro porosity of the solids decreases with Sr content (figure 1), probably due to the fact that Sr softens the auto-combustion gel during the synthesis. The in situ XRD patterns measured during the reduction of $LaCoO_3$ indicate that metallic Co is formed through intermediate species; also some oxygen species mobility is evidenced before destruction of the perovskite phase. The redox processes occurring on these solids are reversible

at 900ºC, since after the redox cycle the initial perovskite phase is recovered. The increase on the Sr content does not seem to affect the crystallinity of the solid in the range studied (x = 0-0.4 and 1); however, it slightly influence the macro porosity and reduction of the solids, properties that will be related to the catalytic behaviour of the solids in further work.

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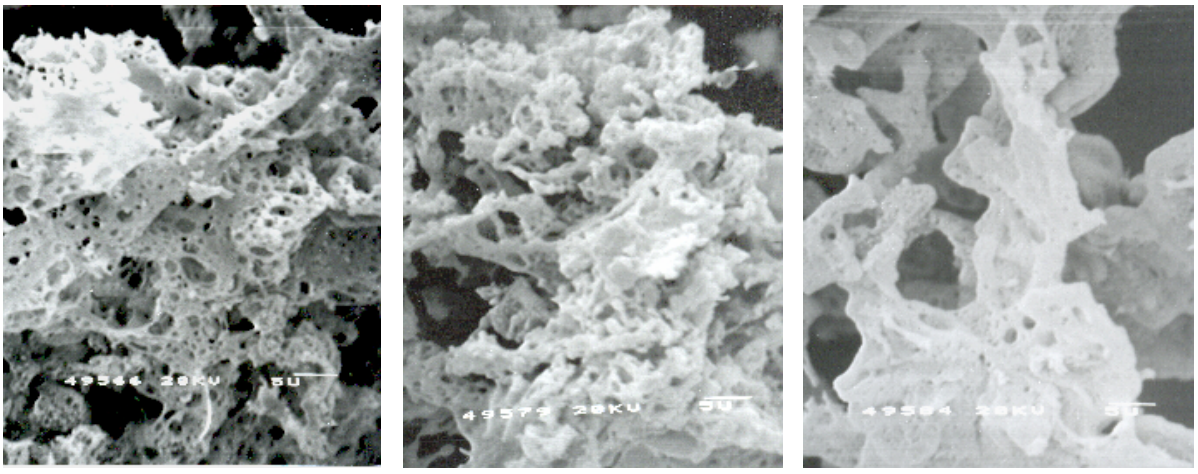
Table 1. Characterization of the synthesised perovskites

SÓLID	Tcal (°C)	A.S (m^2/g)	EDX Metal/Ni	XRD Initial Phase	Red – Oxd (%)	XRD After Redox treatment
$LaCoO_3$	700	5	La/Co = 0.99	$LaCoO_3$	82 - 60	$LaCoO_3$
$La_{0.9}Sr_{0.1}CoO_3$	700	8	La/Co = 0.89 Sr/Co = 0.06	$La_{0.9}Sr_{0.1}CoO_3$	84 - 71	$La_{0.9}Sr_{0.1}CoO_3$
$La_{0.85}Sr_{0.15}CoO_3$	800	8	La/Co = 0.84 Sr/Co = 0.10	$La_{0.9}Sr_{0.1}CoO_3$	88 - 59	$La_{0.9}Sr_{0.1}CoO_3$
$La_{0.8}Sr_{0.2}CoO_3$	700	12	La/Co = 0.76 Sr/Co = 0.13	$La_{0.8}Sr_{0.2}CoO_{3-x}$	84 - 55	$LaCoO_3$, $La_{0.8}Sr_{0.2}CoO_{3-x}$
	800	10			83 - 57	
	900	5			85 - 64	
$La_{0.7}Sr_{0.3}CoO_3$	800	14	La/Co = 0.68 Sr/Co = 0.21	$La_{0.6}Sr_{0.4}CoO_3$	-	-
$La_{0.6}Sr_{0.4}CoO_3$	800	18	La/Co = 0.63 Sr/Co = 0.22	$La_{0.6}Sr_{0.4}CoO_3$	-	-



x = 0 **x = 0.4** **x = 1**

Fig. 1. Effect of the substitution (x) on the morphology of the perovskite phase.