

## Soot oxidation on Ag substituted $\text{LaMn}_{0.9}\text{Co}_{0.1}\text{O}_{3.5}$ perovskites

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### Introduction

Perovskites-type oxides, represented by the general formula  $\text{ABO}_3$  has been widely used in numerous applications due to their unique crystal structure, nonstoichiometric oxygen, acid-base property and redox properties. The number of potentially interesting perovskites in the oxidation reactions is very great, owing to the number of A and B cations that can enter into this structure. The partial substitution of the cation B by B' of similar oxidation state and ionic radius has been widely studied to improve perovskite stability or enhance its redox efficiency [1]. It is well known that the nature and the amount of the metal to be substituted in position A may also stabilize an unusual oxidation state of the cation in position B and/or produces oxygen vacancies. It is proposed to improve the activity or enhance the redox efficiency of  $\text{LaMn}_{0.90}\text{Co}_{0.1}\text{O}_3$  perovskite with low silver substitution substituting a trivalent cation, such as  $\text{La}^{3+}$  by a monovalent cation, such as  $\text{Ag}^+$  to be used calcined and reduced as catalysts on the catalytic combustion of soot.

### Materials and Methods

The  $\text{La}_{1-x}\text{Ag}_x\text{Mn}_{0.9}\text{Co}_{0.1}\text{O}_3$  ( $x_{\text{Ag}} = 0.0, 0.1, 0.2, 0.3$ ) perovskites were prepared by the citrate method, calcined at 700 °C and characterized by nitrogen adsorption, XRD, SEM, TPR,  $\text{O}_2$ -TPD and XPS. The catalytic activity of the calcined and reduced perovskites was studied using carbon black, CB, as a model of soot. The catalyst and carbon black mixture for the assessment of the catalytic activity was prepared mixing 4 mg of CB and 16 mg of catalyst in tight contact. The catalytic oxidation of soot was carried out in a thermogravimetric apparatus (Netzsch 409 PC) with 7.5 mg of the mixture heated in 180  $\text{mL min}^{-1}$  flow of 12% $\text{O}_2$ /He at 10°C  $\text{min}^{-1}$  up to 800°C.

### Results and Discussion

The catalytic activity was estimated from the temperature corresponding to the maximum of DTG curve,  $T_m$ , shown in Table 1. Higher values for  $T_m$  mean lower catalytic activity. The  $T_m$  for the uncatalyzed CB combustion is 650°C, so all tested samples exhibit a significant catalytic activity; increasing with Ag content [2]. The BET specific areas do not show significant differences with Ag content, while a large decrease, ~ 40 to 50%, upon the reductive treatment almost independent of the Ag content can be detected, Table 1. The XRD patterns of the calcined perovskites reveal that the rhombohedral-hexagonal structure is obtained for the  $\text{LaMn}_{0.9}\text{Co}_{0.1}\text{O}_3$  and low Ag substituted ( $x_{\text{Ag}} = 0.1$  and 0.2) samples, however a certain drop of crystallinity is observed for  $x_{\text{Ag}}=0.3$ . After the reductive treatment, the silver-substituted perovskites show three diffraction lines of increasing intensity upon Ag substitution at  $2\theta$  values of 37.96°, 44.14° and 64.30°. The close proximity of the strongest diffraction lines of  $\text{Ag}^0$  (JCPDS 04-0783) and  $\text{Ag}_2\text{O}$  (JCPDS 12-793) made very difficult, if not

impossible, to unequivocally identify the oxidation state of the bulk silver. The  $\text{Ag}_2\text{O}$  mean crystal size evaluated by using the Debye Scherrer equation at  $2\theta=37.96^\circ$  is shown in Table 1. The TPR profiles indicates a first reduction ascribed to the reduction of the network with the formation of oxygen-deficient perovskite and a shoulder corresponding to the reduction of segregated  $\text{Mn}^{4+}$  oxide. A second reduction stage, starting at 650°C, corresponds to the formation of  $\text{Co}^0$  and  $\text{MnO}$  phases and the consequently destruction of the perovskite structure. The peak's shift towards lower temperatures indicates a growth in crystal size.

Table 1 Surface area, crystal size and temperature at the maximum rate combustion,  $T_m$ , for  $\text{La}_{1-x}\text{Ag}_x\text{Mn}_{0.9}\text{Co}_{0.1}\text{O}_3$  perovskites.

	$S_{\text{BET}}, \text{m}^2\text{g}^{-1}$		$d_{\text{hkl}} \text{Ag}_2\text{O}, \text{nm}$		$T_m, ^\circ\text{C}$	
	calcined	reduced	calcined	reduced	calcined	reduced
$\text{LaMn}_{0.9}\text{Co}_{0.1}\text{O}_3$	29	15	0.0	0.0	458	459
$\text{La}_{0.9}\text{Ag}_{0.1}\text{Mn}_{0.9}\text{Co}_{0.1}\text{O}_3$	27	17	26	43	430	459
$\text{La}_{0.8}\text{Ag}_{0.2}\text{Mn}_{0.9}\text{Co}_{0.1}\text{O}_3$	30	16	29	42	394	422
$\text{La}_{0.7}\text{Ag}_{0.3}\text{Mn}_{0.9}\text{Co}_{0.1}\text{O}_3$	30	18	29	45	371	419

Three different surface oxygen species were detected by XPS for the Ag-substituted perovskites: (i), surface lattice oxygen species ( $\text{O}_{\text{lat}}^{2-}$ ) at 529.8 eV; (ii), weakly adsorbed oxygen species ( $\text{O}_{\text{ads}}^-$ ) such as hydroxyl and/or carbonate groups at 531.0–531.4 eV; and (iii), loosely adsorbed superoxide species ( $\text{O}_{2\text{ads}}^-$ ) species at 532.4–532.6 eV. The appearance of  $\text{O}_2^-$  super oxides species at binding energies higher than 532 eV, is a consequence of the lower oxidation state of the  $\text{Ag}^+$  inserted into the network

### Significance

The high increase in the catalytic activity at higher Ag substitution suggest that the activity of these materials for soot combustion is improved by two factors: i) the increasing of surface oxygen species content, closely related to higher material capacity for oxygen transfer from catalyst to carbonaceous surface and ii) the formation of  $\text{Ag}_2\text{O}$  crystals for the higher-Ag-content perovskites. The high thermal resistance of the perovskite-type structure upon a reductive process decreases the catalytic activity for soot combustion due to both a sintering  $\text{Ag}_2\text{O}$  process and a decrease in the surface area entailing a decrease of the oxygen exchange and the number of contact points between catalyst and soot.

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### References

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