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Oxygen mobility in $LaCoO_3$ perovskites

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Abstract

This work reports a study of oxygen mobility in a variety of $LaCo_{1-x}Fe_xO_3$ perovskites. The methods used to evaluate oxygen reactivity were temperature programmed oxygen desorption and oxygen isotopic exchange. Three kinds of oxygen are distinguished, depending on their reactivities. First, surface oxygens were found to be the most active forms of oxygen. In oxygen desorption experiments, they are responsible for two desorption peaks, designated as α_1- and α_2-oxygens in this work. Grain boundary oxygen is distinguished from bulk oxygen, and is proposed to be responsible for β-oxygen desorption observed at high temperature (>750 °C). These two kinds of oxygen, surface and grain boundary oxygen, are however quickly exchanged with the gaseous oxygen during the isotopic exchange reaction. The third kind, and less reactive, oxygen species is proposed to be the bulk oxygen. The mobility of this oxygen in the bulk of $LaCoO_3$ is measured by the initial rate of isotopic exchange. Its mobility is related to the activation of the bulk Co^{3+}, and migration of some anionic vacancies.

Keywords: Perovskite; Oxygen mobility; Oxygen isotopic exchange; Temperature programmed oxygen desorption

1. Introduction

Perovskites are mixed oxides of general formula ABC_3 with A and B cations in dodecahedral and octahedral environments, respectively. Since the beginning of the 70's, some oxidic perovskites (ABO_3) have been known to be efficient catalysts for gas phase oxidation reactions [1]. Among the possible compositions, cobalt and manganese based perovskites were found to be highly active [2–4]. Nevertheless, the perovskites generally display low specific surface areas [4], depending on the synthesis conditions of the solids. A raise in activity is generally observed with the increase in specific surface area, as discussed by Gunaserakan et al. [5] who tested $La_{0.8}Sr_{0.2}MnO_3$ (prepared by the Pechini method) calcined at different temperatures in the CH_4 oxidation reaction. Voorhoeve [6] first distinguished two different oxidation mechanisms, depending on the molecule to oxidize, designated as suprafacial (CO) and intrafacial (CH_4) mechanisms. The distinction between the two processes was made on the basis of the type of oxygen involved in the oxidation reaction. For the suprafacial reactions, the reaction between the oxygen dissociatively adsorbed on the surface and the molecule to oxidize is proposed as the rate limiting step. Contrarily, the intrafacial reactions occur when lattice oxygen becomes involved in the reaction. Then, the removal of a lattice oxygen, or the process of reoxidation of the transition metal (and the incorporation of the dissociated oxygen into the bulk), becomes rate determining.

In this work, two methods were used to measure the oxygen mobility in $LaCoO_3$ perovskites synthesized by different routes: temperature programmed oxygen desorption (TPD–O_2) and oxygen isotopic exchange (OIE) in order to propose a view of the oxygen mobility in $LaCoO_3$ perovskites.

2. Experimental

2.1. Sample synthesis

In this work, results obtained in different studies are summarized in order to propose a view of the oxygen mobility in nanocrystalline $LaCoO_3$. Then, $LaCoO_3$ was synthesized by different procedures. The SS sample was synthesized by solid state reaction of the oxide precursors at high temperature (1000 °C) [7]. The COP sample was prepared by simultaneous precipitation of the nitrate precursors [7]. After drying, the solid

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was calcined at 700 °C. The CIT sample was synthesized by complexation of the nitrate salts by citric acid [7], followed by calcination of the dried precursor at 600 °C. Different samples were crystallized by grinding of the single oxide precursors. Among these samples, Co1, Co2 and RG were ground under different conditions in order to obtain specific surface areas over a large range. For sample Co1 synthesis, La_2O_3 and Co_3O_4 as precursors were ground in one-step, resulting in a low specific surface area [8]. Co2 [8] and RG [7] were ground in two-steps. After a first step for perovskite crystallization, an additive (with a mass ratio additive/perovskite equal to 1) was added to the perovskite, and the mixture (additive + perovskite) was ground for a second step for about 20 h. NaCl (Co2) or ZnO (RG) were used as additives for this second grinding step. At the end of this grinding step, the additive was dissolved, and the perovskite obtained was calcined under air (ramp = 2 h, 4 h at 550 °C). Finally, the COPRG sample was synthesized by grinding of an amorphous coprecipitate (obtained following the procedure described for the COP synthesis). The so obtained precipitate was dried and calcined at 500 °C, and then ground in two steps, as for RG.

2.2. *Characterization*

X-ray diffraction patterns were obtained using a SIEMENS D5000 diffractometer with CuKα radiation, for 2θ between 15 and 75°. Specific surface areas were determined by the BET method from the N_2 adsorption isotherms recorded at −196 °C using an OMNISORP 100 instrument. Prior to these measurements, the samples were evacuated at 200 °C for 4 h. Sample compositions were measured by ICP using a P40 apparatus from Perkin-Elmer.

Oxygen thermodesorption (TPD–O_2) were performed on a RMX100 multi catalyst testing system (Advanced Scientific Desing Inc.) equipped with a quadrupolar mass spectrometer and a TCD for analysis. Conditions of test were: 10 NmL/min He, T from 25 to 900 °C with a ramp of 5 °C/min. Before the desorption experiments, the samples were calcined at their respective calcination temperature under 20% O_2 in He (20 mL/min).

Oxygen exchange experiments were carried out in a recycle U-shaped microreactor coupled to a quadrupolar mass spectrometer. A pressure of 50 mbar of $^{18}O_2$ was set in the reactor at the temperature of test, and evolutions of $^{18}O_2$, $^{16}O_2$ and $^{18}O^{16}O$ concentrations recorded on the MS. Before test, samples were calcined at their calcination temperatures under O_2.

More detailed information about the experimental procedures and apparatus can be found in the above cited references [7–10].

3. Results and discussion

3.1. *Physical properties*

All the synthesis procedures result in the perovskite phase crystallization (JCPDS card 09–0358) (Table 1). Weak reflexions attributed to Co_3O_4 (JCPDS card 42–1467) were also observed for SS, Co1 and COPRG. As observed from Table 1, synthesis conditions, and especially calcination temperatures were found to strongly affect the specific surface area of the solids. Crystal growth and agglomeration processes can explain the observed decrease in specific surface area as the calcination temperature is raised. Then, the higher the calcination temperature, the higher the crystal domain size (D_1 in Table 1), and the lower the specific surface area (S_{BET} in Table 1). It is however observed that a fraction of the surface area is generally lost by contact between the elementary crystals. This is characterized by the S_{th}/S_{BET} ratio (see Table 1), which varies over a large range (from 27.8 for SS to 2.2 for COPRG), and is explained by the occurrence of grain boundaries between crystals. Then, the higher the calcination temperature, the higher the crystal domain size, and also the higher the S_{th}/S_{BET} ratio.

3.2. *Oxygen mobility in $LaCoO_3$*

3.2.1. *Temperature programmed oxygen desorption*

The TPD experiments revealed the desorption of three kinds of oxygen which were designated as α_1, α_2 and β as mentioned above [7]. The global amount of oxygen desorbed as α_1- and

Table 1
Physical properties of the samples

Sample	SS	COP	CIT	RG	Co1	Co2	COPRG
Ref.	[7]	[7]	[7]	[8]	[8]	[8]	[7]
Calcin. temp. (°C)	1000	700	600	550	550	550	550
Formula[a]	$LaCo_{0.97}O_3$	$LaCo_{0.98}O_3$	$LaCo_{0.96}O_3$	$LaCo_{0.80}Fe_{0.20}O_3$	$La_{0.94}Co_{0.97}Fe_{0.03}O_3$	$La_{0.93}Co_{0.90}Fe_{0.10}O_3$	$LaCo_{0.93}Fe_{0.03}O_3$
Crystalline phases[b]	P, weak Co	P	P	P	P, weak Co	P	P, weak Co
D_1 (nm)[c]	73.9	32.2	26.9	16.3	16.4	16.4	16.5
S_{BET} ($m^2 g^{-1}$)[d]	0.4	3.5	6.6	17.1	4.2	10.9	18.7
S_{th}/S_{BET}-[e]	27.8	7.3	4.6	2.9	11.9	4.6	2.2

(f) Calcined at 200 °C, (g) respectively calcined at 200–300–500 °C.

[a] Measured by ICP.

[b] Phase recognition by comparison with JCPDS files (P, perovskite; C, Co_3O_4).

[c] Crystal domain size evaluated by mean of the Scherrer equation after Warren's correction for instrumental broadening.

[d] Calculated by the BET method from N_2 adsorption isotherms.

[e] Ratio between the theoretical surface area and the BET surface area. Theoretical surface area evaluated supposing cubic particle shape of size D_1 and crystal density of 7.29.