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Synthesis, characterization and catalytic properties of $La_{2-x}Sr_xNiO_{4-\delta}$

M. Beltrán [1], J.M. Domínguez [2], A. Montoya [2], G. Tavizón [1], L. Vicente [1] and T. Viveros [3]

[1] *Facultad de Química, División de Estudios de Posgrado, 04510 México, D.F., Mexico*
[2] *Instituto Mexicano del Petróleo, ICA, Apdo. Postal 14-805, 07730 México, D.F., Mexico*
[3] *Universidad Autónoma Metropolitana, Ingeniería Química, Apdo. Postal 55-534, 09340 México, D.F., Mexico*

Various compositions x in the catalyst system $La_{2-x}Sr_xNiO_{4-\delta}$ have been prepared by conventional techniques and characterized by X-ray powder diffraction, electron microscopy and BET surface measurements. The catalytic properties of these catalysts have been tested in the propylene oxidation reaction. The catalytic activity can be correlated with the oxygen content and with the strontium substitution.

Keywords: X-ray powder diffraction; electron microscopy; BET surface measurements; chemical properties of perovskite oxides; perovskite oxide catalysts

1. Introduction

K_2NiF_4-type mixed oxides consist of alternating layers of ABO_3 perovskite and AO rock salt. In this structure it is possible to change the different metallic site ions or substitute them by other ions and hence obtain a series of compounds where the effects of substitutions on the different chemical and physical properties can be seen.

Perovskite oxides are known to be important catalysts in practical processes such as oxidation [1–3] and hydrogenation [4,5]. In contrast with simple perovskites, the catalytic action of K_2NiF_4-type oxides has been less studied and, in analogy with perovskites as $LnBO_3$ (Ln: rare earth, B first transition metal row) [6], catalysts with that structure are suitable materials for research of reactivity of surface oxygen and catalytic activity. Nitadori and Misono [7] have studied the catalytic properties of $La_{2-x}Sr_xCoO_4$ for propane oxidation and, recently [8], they studied the valence control and reduction by CO of the system

$La_{2-x}Sr_xNiO_{4-\delta}$. It has to be noted that this system has received [9,10] atention because its analogy with the superconductor $La_{2-x}Sr_xCuO_{4-\delta}$.

In this work we prepared a series of Sr-substituted catalysts. The characterization comprised the determination of cell parameters, surface areas, valence of the Ni ion and oxygen deficiency. With respect to the catalytic activity of these compounds, the effect of Sr-substitutions on the propylene oxidation reaction was tested.

2. Experimental

Preparation. The $La_{2-x}Sr_xNiO_{4-\delta}$ series in the range $0 \leqslant x \leqslant 1.4$ were prepared from mixtures of metal nitrate solutions of known assay (precursors were: La_2O_3, NiO, $SrCO_3$). The resulting solution was evaporated to dryness and then the residual solid was calcined in an alumina crucible at 900°C for 16 h. Finally, the samples were ground into powders, pelleted and sintered at 1350°C in air for 48 h.

Characterization. Powder X-ray diffraction data were obtained by using a Siemens Crystalloflex 810 automatic powder diffractometer over the range $4° \leqslant 2\theta \leqslant 70°$, at room temperature, using CuK_α radiation. Surface area were measured by the BET technique using N_2 adsorption (Quanta Sorb apparatus) at 75 K. Average Ni valence was determined by dissolution of the samples in dilute hydrochloric acid and potassium iodide, followed by iodometric titration with sodium thiosulfate.

Scanning electron microscopy (SEM) and electron dispersion analysis (EDS) for morphology and chemical composition, respectively, were performed on a Jeol-100 CX microscope operating at 20 keV.

Catalytic tests. The oxidation of propylene was carried out in an atmospheric system using a differential fixed bed glass reactor. A sample of approximately 0.1 g was loaded and activated under an air stream at 400°C for 4 h. A gaseous stream of propylene and oxygen at a fixed molar ratio was fed into the reactor at

Table 1
Unit cell parameters body-centered tetragonal

x	a (Å)	c (Å)	c/a	V (Å^3)
0	3.859	12.659	3.280	188.571
0.2	3.848	12.658	3.289	187.476
0.4	3.817	12.717	3.300	185.371
0.6	3.811	12.602	3.306	183.067
0.8	3.810	12.534	3.289	181.995
1.0	3.821	12.433	3.2540	181.545
1.2	3.821	12.400	3.2451	181.051

Table 2
Surface areas and composition of catalysts

x	Surface area ($m^2\ g^{-1}$)	Composition
0	1.34	$La_2Ni^{2+}_{0.58}Ni^{3+}_{0.42}O_{4.21}$
0.2	0.88	$La_{1.8}Sr_{0.2}Ni^{2+}_{0.67}Ni^{3+}_{0.33}O_{4.06}$
0.4	0.56	$La_{1.6}Sr_{0.4}Ni^{2+}_{0.44}Ni^{3+}_{0.56}O_{4.08}$
0.6	0.42	$La_{1.4}Sr_{0.6}Ni^{2+}_{0.41}Ni^{3+}_{0.59}O_{4.00}$
0.8	0.53	$La_{1.2}Sr_{0.8}Ni^{2+}_{0.40}Ni^{3+}_{0.60}O_{3.91}$
1.0	0.21	$La_{1.0}Sr_{1.0}Ni^{2+}_{0.29}Ni^{3+}_{0.71}O_{3.86}$
1.2	0.31	$La_{0.8}Sr_{1.2}Ni^{2+}_{0.12}Ni^{3+}_{0.88}O_{3.84}$
1.4	1.07	$La_{0.6}Sr_{1.4}Ni^{2+}_{0.11}Ni^{3+}_{0.89}O_{3.75}$

Table 3
Nominal stoichiometry and as measured by EDS

Element line (wt%)			
La L	Ni K	Sr K	
84.28	15.72	0.0	experimental
82.55	17.44	0.0	nominal
74.62	16.36	9.02	experimental
74.63	17.99	5.372	nominal
67.07	18.06	14.87	experimental
70.33	18.57	11.09	nominal

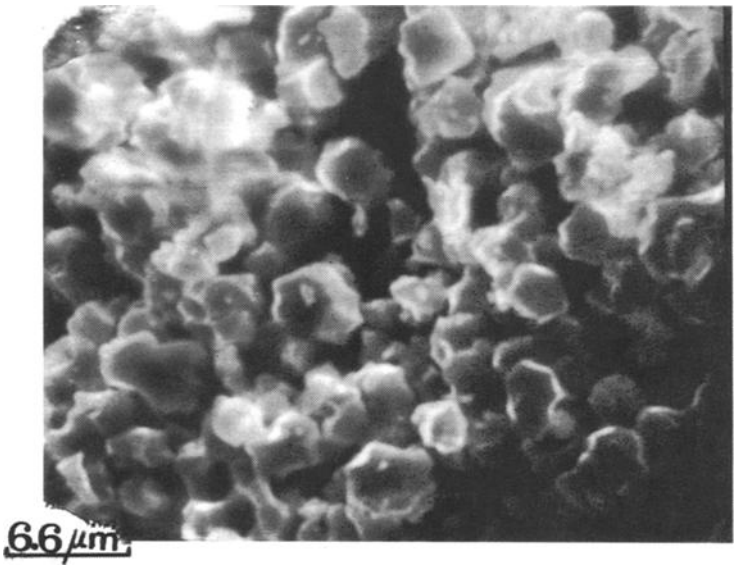

Fig. 1. Scanning electron micrograph of $La_{1.0}Sr_{1.0}NiO_{3.86}$.

a 180 ml/min total flow. The products were analysed by gas chromatography using a Hewlett-Packard chromatograph.

3. Results

3.1. CATALYSTS AND THEIR PHYSICAL PROPERTIES

The samples in the range $0 \leqslant x \leqslant 0.5$ were black, beyond that value they showed a dark brown color. All were single phase with I4/mmm space group

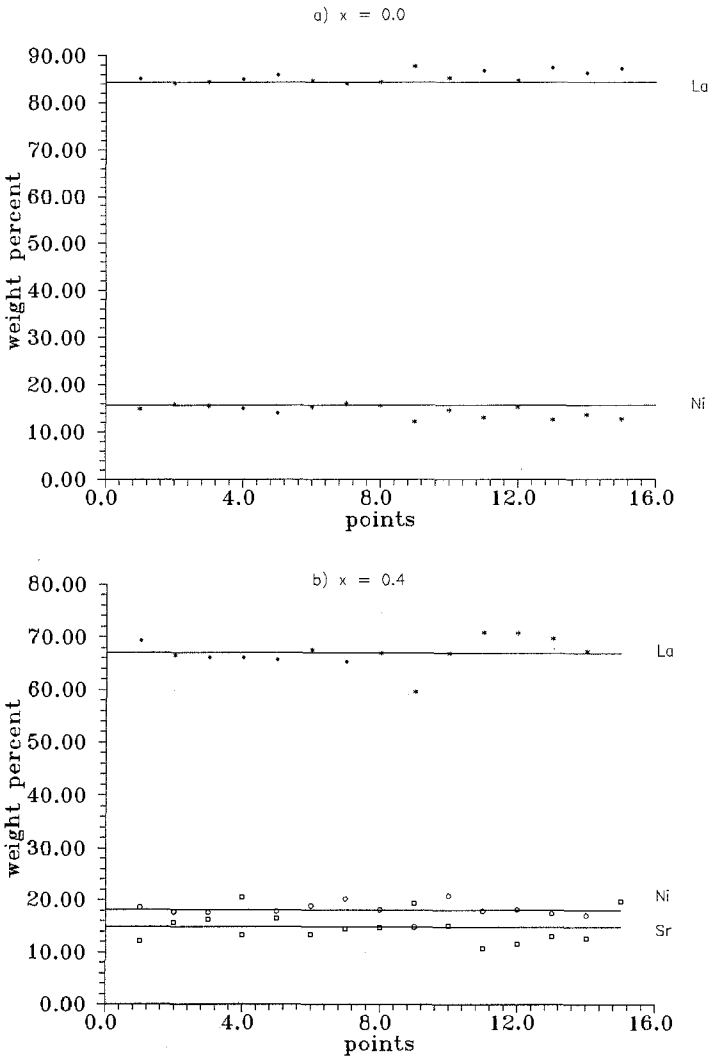

Fig. 2. Compositional fluctuations (point analysis). (a) $La_2NiO_{4.21}$, (b) $La_{1.6}Sr_{0.4}NiO_{4.08}$.

symmetry. The crystallographic data are summarized in table 1. Surface areas of the samples and bulk compositions of the metal ions measured by iodometric titration are shown in table 2. The surface areas of the samples were all less than 2 $m^2\ g^{-1}$ because of the high calcination temperature. The average oxidation number of the nickel ion increases monotonically with the increase in x, ranging from 2.40 ($x = 0$) to 2.98 ($x = 1.4$). The nonstoichiometry in oxygen varied from an oxygen-excess composition for $x = 0$–0.4 to an oxygen-deficiency for $x = 0.8$–1.4.

Scanning electron micrographs were taken at room temperature. Fig. 1 shows that the particles are about 1 to 3 μm, the smaller particles having an hexagonal-like shape. To check the stoichiometry of the sintered material, we per-

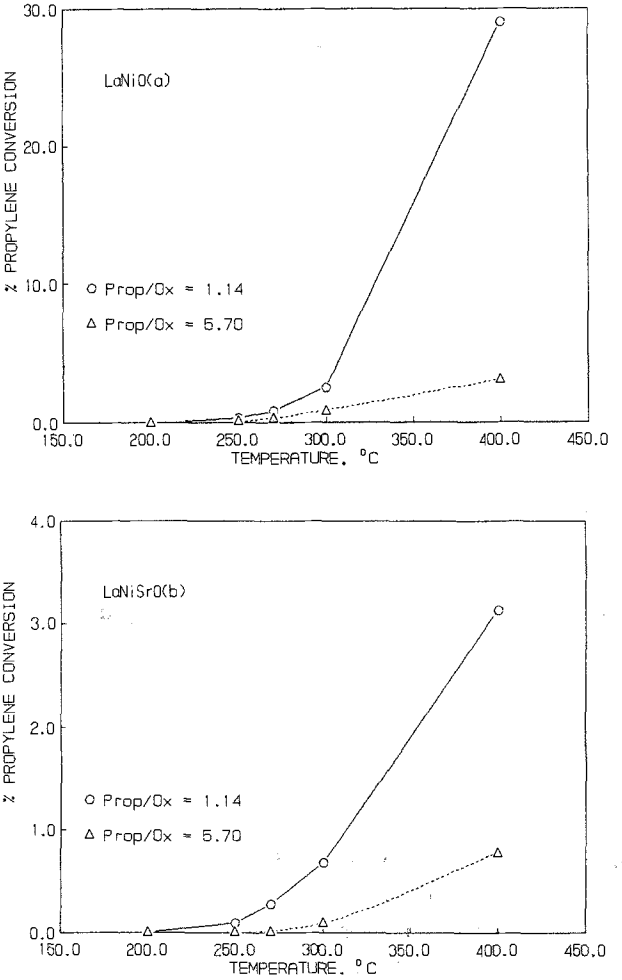

Fig. 3. The catalytic activity for propylene oxidation over $La_{2-x}Sr_xNiO_{4-\delta}$. (a) $x = 0.0$, (b) $x = 0.6$, (c) $x = 1.2$.

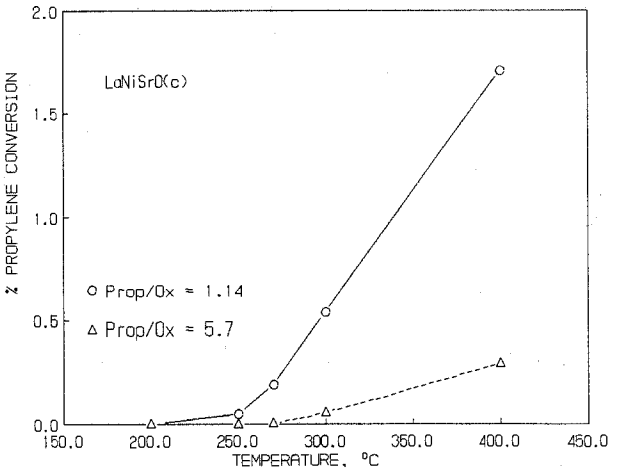

Fig. 3. (continued).

formed quantitative electron dispersive analysis (EDS) on a crystal by crystal basis (200 Å diameter point analysis). Figs. 2a and 2b show the compositional fluctuations when Sr is added to the catalysts. In the absence of Sr, Ni and La are distributed homogeneously; but adding Sr makes composition fluctuations become important.

3.2. CATALYTIC ACTIVITY FOR THE COMPLETE OXIDATION OF PROPYLENE

The activity for the propylene oxidation is shown in fig. 3 for two different values of the propylene/oxygen mol ratio ($r = 1.14$ and 5.70). The only reaction products were CO_2 and H_2O. As it is shown, for $x = 0.0$ and $x = 0.6$ the conversion is very low and increases slightly with temperature, reaching an ignition temperature under oxidizing conditions ($r = 1.14$), but not under reducing atmospheres ($r = 5.70$). For $x = 1.2$ there is no ignition temperature in the temperature range of the experiments (200–470°C).

4. Discussion

The variation in oxidation numbers of Ni (from 2.40 for $x = 0$ to 2.98 for $x = 1.4$) is consistent with the results of Nitadori et al. [8] and Goparakrishnan et al. [11] with a change in the stoichiometry when x moves from an oxygen excess to an oxygen deficiency. In the series the substitution of La^{3+} by Sr^{2+} removes electrons from the metal–oxygen octahedron and increases the oxidation of Ni. As x is increased the structure is distorted and the volume of the cell (V)

decreases. This effect has been related to a Jahn–Teller distortion [10], and it must reflect important changes in electronic configurations [12].

Due to the high calcination temperature (1350°C for 48 h) surface areas have a very low value (0.2–1.3 $m^2\ g^{-1}$). Reducing the time of calcination and the temperature increases the areas (1.5–2.5 $m^2\ g^{-1}$) but the samples are not very stable (they become a very fine dust after 48 h). This could be improved for example by coprecipitation or sol–gel methods.

The preparation method allows to obtain regular crystallites (hexagonal-like shape) as shown by the micrographs. The EDS analysis showed that in absence of Sr the distribution of La and Ni in the crystallites is quite homogeneous, but adding Sr makes the homogeneity of La and Ni in the bulk decrease with respect to the nominal composition. In several cases the rim borders of crystallites are richer in Sr, and so it seems that Sr segregates towards the periphery, or perhaps there is interdiffusion between the elements. This point deserves further study.

The oxidizing power of the catalyst was higher in absence of Sr, and for a more oxidizing atmosphere. In fact, for reducing atmospheres the catalysts did not show an ignition temperature. This temperature was about 308°C for $x = 0$ and 410°C for $x = 0.6$; i.e. it shifts to higher values as x is increased. The catalytic activity also decreased as La ions were substituted by Sr.

The catalytic activity can be correlated to the oxygen content. At low La substitution ($x = 0.0$, 0.2) there is an excess of oxygen whereas for higher values ($x = 1.4$) there is a deficiency. The activity follows the same trend, as x is increased the activity decreases. This suggests that the oxidation takes place using the labile oxygen in the lattice, which is then reincorporated from the gaseous oxygen [6]. These results do not agree with those of Nitadori and Misono [7] who found a volcano-type behaviour for the activity with a maximum at $x = 1.0$ for the system $La_{2-x}Sr_xCoO_4$. Perhaps this might be due to the higher activity of Ni in comparison to Co as was shown for ABO_3-type perovskites [13]. Experiments are under way to elucidate this fact for several intermediate compositions.

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