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Lanthanum based high surface area perovskite-type oxide and application in CO and propane combustion.

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Abstract: The perovskite-type oxides using transition metals present a promising potential as catalysts in total oxidation reaction. The present work investigates the effect of synthesis by oxidant co-precipitation on the catalytic activity of perovskite-type oxides LaBO_3 (B= Co, Ni, Mn) in total oxidation of propane and CO. The perovskite-type oxides were characterized by means of X-ray diffraction, nitrogen adsorption (BET method), thermo gravimetric and differential thermal analysis (ATG-DTA) and X-ray photoelectron spectroscopy (XPS). Through a method involving the oxidant co-precipitation it's possible to obtain catalysts with different BET surface areas, of 33-44 m^2/g , according the salts of metal used. The characterization results proved that catalysts have a perovskite phase as well as lanthanum oxide, except LaMnO_3 , that presents a cationic vacancies and generation for known oxygen excess. The results of catalytic test showed that all oxides have a specific catalytic activity for total oxidation of CO and propane even though the temperatures for total conversion change for each transition metal and substance to be oxidized.

Keywords: perovskites; oxidation; propane.

Introduction

The removal of CO, unburned hydrocarbons (HC), and NO from automotive exhaust requires catalytic devices in which these pollutants are eliminated. Catalytic combustion offers one of the most efficient means for controlling atmospheric pollution (1). Although noble metals, such as palladium, platinum, and Rhodium are well known with higher activity (per site than metal-oxide catalysts, they present several disadvantages, such as higher volatility, high cost, and poor availability. Compared with noble metals, base metal catalysts present a lower but still sufficient activity as oxidation catalysts, and have

the advantages of lower costs and the potential market in energy generation systems in domestic and small scale industrial applications. For this reason perovskite type compounds have received wide attention, which have been incorporated into the design of the novel combustors (2,3).

A perovskite-type oxide has an ABO_3 type crystal structure wherein cations with a large ionic radius have twelve coordination to oxygen atoms and occupy A-sites, and occupy B sites. A and O form a cubic closest packing, and B is contained in the octahedral voids in the packing. If the ionic radii are r_A , r_B and r_O , to form a perovskite crystal structure, the tolerance factor (t) = $(r_A + r_O) / (r_B + r_O)$ must lie within the range $0.8 <$



$t < 1.0$, and $r_A > 0.090$ nm, $r_B > 0.051$ nm. A great many elements can form ideal or modified perovskites depending on the tolerance factor. The ideal perovskites structure appears only in a few cases for tolerance factors very close to 1 and at right temperatures. In other conditions different distortions of the perovskites structure will appear. Deviations from the ideal structure with orthorhombic, rhombohedral, tetragonal, monoclinic and triclinic symmetry are known, although the latter three are scarce and poorly characterized [4]. Nonstoichiometry in perovskites can arise from cation deficiency (in the A or B site), anion deficiency or anion excess. Much attention has particularly been paid to lanthanum – transition metal based perovskites oxides, which were introduced into catalysis some 30 years ago (5,6), but they are available for perovskites in which the metal in position A and/or B has been partly substituted with another metal, thus establishing a large group of active oxides described by the general formula $A_{1-x}A'_x B_{1-y}B'_y O_{3\pm d}$, where d stands for excess oxygen resulting from non-stoichiometry of these species [7].

Lanthanum-based perovskites containing transition metal in B-site, ($LaBO_3$, B = Co, Fe, Ni or Mn), show catalytic activity close to the noble metal, presenting low cost and high thermal stability [8]. The perovskites type oxides are of interest for catalytic oxidation and reduction reactions associated with automotive exhaust emission control [9]. They have been tested in oxidation of CO and hydrocarbons, NO_x reduction and hydrogenation and hydrogenolysis reactions [7].

In this work, the effect of oxidant - coprecipitation synthesis on the catalytic activity of perovskite-type oxides $LaBO_3$ (B = Co, Ni, Mn) is investigated, using as a model the total oxidation of propane and CO.

Experimental

A number of methods have been used in the synthesis of perovskites; the choice of a particular one depends mostly on the expected use for these oxides. The $LaCoO_3$, $LaMnO_3$ and $LaNiO_3$ perovskites oxides were prepared by oxidant – coprecipitation. The catalysts were pre-

pared using 20 mmol of aqueous solution (100 mL) of metal's salts ($Co(NO_3)_2 \cdot 6H_2O$ to $LaCoO_3$, $MnCl_2 \cdot 4H_2O$ to $LaMnO_3$ and $Ni(NO_3)_2 \cdot 6H_2O$ to $LaNiO_3$) mixed with 100 mL of aqueous solution of lanthanum nitrate (20 mmol). The mixture was added drop wise to a rapidly stirred (nitrogen stream) solution of sodium hydroxide (7.2g 0.18 mol) in sodium hypochlorite (3.5 M, 30ml). Use of inert atmosphere minimizes carbonate contamination in the final product. The resultant gel was washed repeatedly with deionized water (3x200 ml), then washed with acetone (3x 50ml) and dried under vacuum.

The powder was dried at 60 °C for 12h, after that it was calcinated at 600°C for 2 hours.

The catalysts were characterized by X-ray powder diffraction (XRD) on a 65- Rich Seifert & Co diffractometer by using $CuK\alpha$ radiation for determination of the final structure. Patterns were recorded between a 2θ of 20° and 65° with step size of 0.05° with 30kV and 40mA.

The specific surface areas were obtained by nitrogen adsorption at 77 K, evaluated using the BET equation on an automatic Quantachrome Aparatus, Autosorb – 1 C, in the 0, 05-0,095 relative pressure range. The powders were degassed at 300°C for 1h before the measurements.

The thermal decomposition with the temperature of the powder before heating at 60°C for 12h and passed by a sieve of 200 mesh was performed in N₂ by using a TGA-DTA of Shimadzu and TA Instruments, under N₂ flow (50 mL min⁻¹), and 10 °C min⁻¹ from room temperature to 600°C.

The X-ray photoelectron spectra (XPS) were obtained with a VGESCALAB MKII, employing Mg K α radiation (1253.6 eV) under a high vacuum of 3×10^{-8} Torr. The binding energies were calibrated by using a C1s peak (284.6 eV) as a background.

Temperature programmed reduction (TPR) experiments were performed in a system with a thermal conductivity detector. The reducing gas was a mixture of 3% H₂/N₂ (1.8 l/h) and heating 10°C/min was employed.

The catalysts were tested in combustion of propane and CO. The catalytic measurements were realized in a fixed-bed reactor, working in atmospheric pressure. For characterization of the catalytic activity, it was used 10mg of powder.

Before the reaction, the powder is pretreated for 1.5h at 400°C with synthetic air: O₂ (20±0.5)% and N₂ (80±0.5)%, 1.8 l/h. The feed gas composition was CO (0.97%), C₃H₈ (0.507%), O₂ (2.02%) and N₂ (balance), 1.8 l/h, on-line continuous analysis of reactants and products was performed using a gas chromatograph CG 9001 Finnigan, provided with a thermal conductivity detector. For CO and CO₂ analyses were utilized an independent ND-IR detector.

Results and discussion

The method employed was oxidant-coprecipitation, developed by Barnard et al [10] to LaCoO₃ catalyst synthesis.

The catalyst preparation in basic conditions, due to the presence the sodium hydroxide and sodium hypochlorite as oxidant agent, yields probably LaBOH (B= Co, Mn, Ni). This was reported by Vydasagar et al [11] as the hydroxide gel to be dehydrated.

The advantage in this method is that the dehydration of the gel occurs at low temperatures (60°C), due to the initial dehydration in the presence of acetone.

Controlled dehydration of hydroxide-gel, using water and a miscible solvent, presents positive results in obtain solids with high specific surface areas. The displacement of water by acetone allows a reduction of superficial tension and leads a smallest capillary force; producing weak agglomeration and keeping opened the particle structure. The result is a lowest collapse during calcination [12].

The perovskites type oxide LaCoO₃, LaMnO₃ e LaNiO₃ presented specific surface area of the 44, 38 and 33m²/g, respectively.

Figure 1a, 1b and 1c display the TGA and DTA curves of respective catalysts. It can be observed that the samples present endothermic peaks at low temperatures, corresponding to the fissorssorved water elimination.

The strong mass loss region from 300 and 500°C was attributed to the decarbonization and dehydration, process accompanying the perovskite structure formation. DTA curves of these samples exhibit essentially only endothermic

peak the range, centered at 318 and 440 °C for LaCoO₃, 340 and 420 °C for LaMnO₃, 318 and 470 °C for LaNiO₃. This different behavior probably due to the different decomposition mechanism of hydroxide gels. In LaNiO₃ catalyst, the carbonate quantity is bigger, when compared to another catalyst, due to the catalyst has been stayed more time during the filtration process (72 h), once fine grain was formed, diffculting the filtration process.

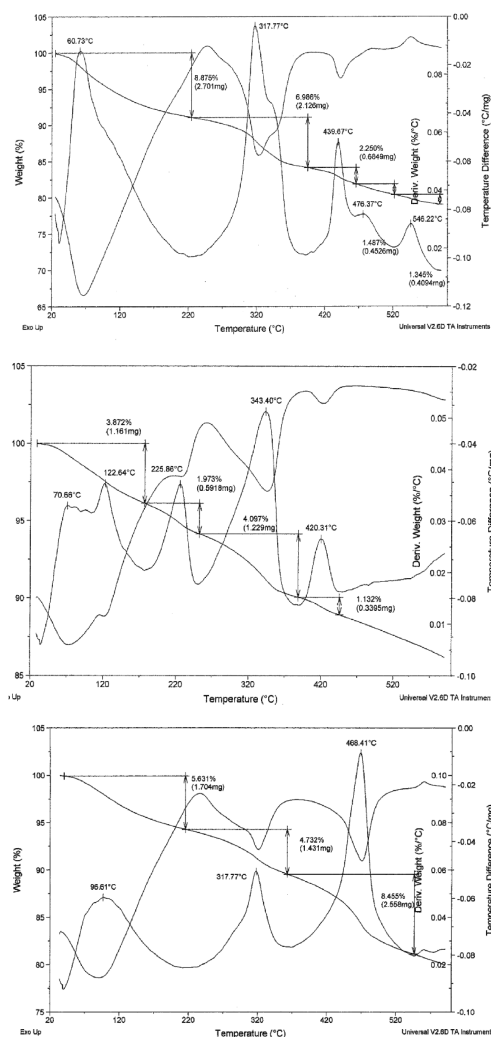


Figure 1. TGA and DTA analysis for (a) LaCoO₃ (b) LaMnO₃ (c) LaNiO₃ catalysts

The oxides at low temperatures present typical structure of perovskite (Figure 2), what can be confirmed comparing with standard archives JCPDS and literature [13-15]. The catalyst LaNiO_3 and LaCoO_3 presented rhombohedral structure and the LaMnO_3 presented orthorhombic structure. In the catalysts LaCoO_3 and LaNiO_3 there's a peak represented by (*), referring to lanthanum oxide (La_2O_3), indicating a cationic excess. In the LaNiO_3 exists a peak (•), which confirms the presence of NiO , and was reported by others authors [16]. The catalyst LaMnO_3 doesn't present a La_2O_3 peak; it is possible that this oxide presents cationic vacancies coming with an excess of negative species of oxygen. This fact can originate a spontaneous transition of 15-30% of Mn^{3+} to Mn^{4+} to reestablish the electroneutrality of system [17].

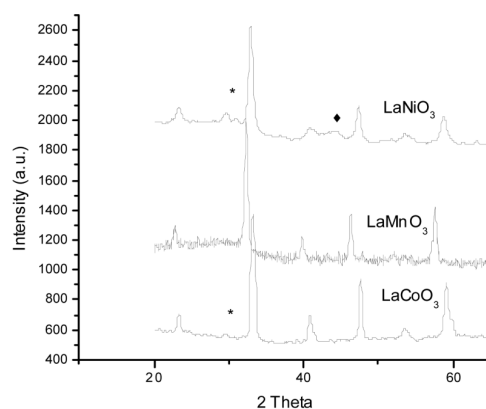


Figure 2. XRD spectra for the LaCoO_3 , LaMnO_3 and LaNiO_3 catalysts.

The surface characterization was realized for XPS analysis using C1s as reference. Table 1 contains binding energies values: O 1s, La 3d, Co 2p, Mn 2p and Ni 2p. Several works demonstrate that the majority of cations are present in trivalent form [18,19].

The analysis date for LaCoO_3 and references to the La $3d_{5/2}$ are registered in 835.3 eV and 838.8 eV. These values are similar to that presented in the literature [20] for the pure lanthanum oxide (La_2O_3) in 834.4 eV and 837.8 eV. These

Table 1. XPS results to perovskite type-oxides.

Level	LaCoO_3 (eV)	LaNiO_3 (eV)	LaMnO_3 (eV)
O(1s)	529.8	529.78	536.5
	532.4	531.79	
La(3d)	835.3	835.54	841.1
	838.8	854.14	845.0
B(2p)	779.9	851.45	649.1
	795.5	854.14	660.1
O/La	5.23	4.02	5.73
La/B	1.80	1.56	0.79
O/(La + B)	3.38	2.45	2.53

data indicate that lanthanum is probably present in trivalent form.

The sign in 779.9 and 795.5 eV corresponds to the Co $2p_{3/2}$ and Co $2p_{1/2}$ respectively, which is typical when Co^{3+} is present. On the other hand, the absence of peaks in 785 – 788 eV proves the inexistence of Co^{2+} , and then the theory about the existence of cations in trivalent form.

The XPS spectra of LaCoO_3 , present two O 1s photolines that correspond to two different oxygen species. The lower binding energy, 529.8 eV, can be associated with lattice, while the higher energy, 532.5 eV, can be associated with the species of adsorbed oxygen, although this latter fraction should also contain adsorbed oxygen. The amount of oxygen absorbed-adsorbed can be represented by the species O and OH^- [16].

In the literature [20], the binding energy corresponding to the oxygen species appear in 528.3 and 531.9 eV. For the species OH^- , these values are 529.7 and 532.2 eV, respectively. The similarity between OH^- binding energies results in that the values presented in this work indicate a higher possibility of this species to exist.

In the catalyst LaMnO_3 the absence of peak in high energy value indicates the presence only of the lattice oxygen. Alterations in the crystalline structure and also in the electronic structure can be responsible by displacement of the peak for higher energy values.

The Mn 2p spectra presents three signals which corresponds to Mn^{3+} (647.40 eV), Mn^{4+} (658.7 eV) and the presence of a peak, indicating the absence of Mn^{2+} .

The information obtained by XPS is important to compare the stoichiometry of compounds (Table 1). The atomic relation La/Co on surface is 1.8. This suggests a lanthanum excess or Co-deficiency on LaCoO_3 surface. Some authors have observed the presence of lanthanum excess in the perovskite structure ($\text{La/Co} > 1$). Tejuca et al. [19] reported the relation La/Co is 1.2 in the catalyst LaCoO_3 , obtained by acetate synthesis. The more pronounced case was observed by O'Connell et al. [20], which prepared the catalyst LaCoO_3 through precipitation of nitrate solutions of salts, with tetraethylammonium hydroxide. In this case the relation La/Co was 4.26, showing the lanthanum excess on surface. This excess on surface catalyst is attributed to two phases formation; the first corresponding to the pure perovskite and the second for La/perovskite. In the first, the cationic vacancies are compensated by high valences of oxygen and cobalt. In the second, the cationic vacancies are compensated by anionic vacancies, being more interesting for catalysis.

It has been reported by others authors that the LaCoO_3 is considered as a stoichiometric system. On the other hand, this system was showed as non-stoichiometric, as reported by Spinicci et al [21]. In the non-stoichiometric system, generally there is a deficiency of net lanthanum, which can be compensated, by increasing the metal valence or by oxygen or by creation of anionic vacancies.

In this work, it can be observed that the lanthanum ions quantity is almost twice of cobalt ions. It is possible to suppose the formation of stoichiometric LaCoO_3 with other lanthanum-based compounds, like lanthanum oxide, proved by X-ray diffraction.

In LaMnO_3 catalyst, the relation La/Mn is 0.79, suggesting the non-stoichiometric lanthanum manganite phase with lanthanum deficiency. To keep the charge equilibrium, the conversion can be considered: $\text{Mn}^{3+} \rightarrow \text{Mn}^{4+}$. This transition comes with vacancies formation and presence of oxygen excess. Taguchi et al. [22]

found the relation La/Mn changing from 1.5 to 2, depending on method used to obtain LaMnO_3 . However, part of lanthanum isn't incorporated in perovskite, but presented as oxide, and part of this oxide is carbonated.

The peaks of lanthanum and nickel are located in the same energy range (835-855 eV). There is a overlapping for $\text{La}3d_{3/2}$ and $\text{Ni}2p_{3/2}$. The peak near 870 eV is characteristic for Ni^{2+} in NiO , that was reported by Guo et al [23].

The atomic relation La/Ni on surface is near 1.6, which suggests the excess of lanthanum or deficiency of nickel on oxide surface of LaNiO_3 . In this case, the lanthanum excess is the more probable factor, due to X-ray diffraction, that shows both the nickel oxide and the perovskite phases.

Due to this quantity of positive ions in the structure, there is an oxygen ion excess, and part of this oxygen is absorbed in the structure.

The relation between oxygen and total metallic ion $[\text{O}/(\text{La} + \text{B})]$ in the catalyst LaCoO_3 is near to 3.4, according to the result obtained by O'Connell et al [20]. In the catalyst LaMnO_3 this relation is near 2.5, both higher than that would be expected if the stoichiometry exists. This proved the materials can present oxygen excess in case of LaCoO_3 ; for LaMnO_3 there are cationic vacancies. By the way, there is a catalyst LaCoO_3 with cobalt deficiency and LaMnO_3 with manganese deficiency. However, the majority of non-stoichiometric oxygen in LaCoO_3 catalyst, when compared to LaMnO_3 , can indicate the major cationic vacancies in first case. In the LaMnO_3 , vacancies are minimized by transition of $\text{Mn}^{3+} \rightarrow \text{Mn}^{4+}$. This relation for LaNiO_3 is 2.5, which confirms the oxygen excess.

To obtain information about reducibility of studied catalyst and to identify the reduction temperature, it was realized a temperature-programmed reduction. The profile is showed on figure 3.

In the figure 3a, which refers to LaCoO_3 , according to Guo et al. [23], it is observed the catalyst reduction in two steps: in the first, the Co^{3+} to Co^{2+} reduction; in the second, Co^{2+} to Co^0 .

In the case of LaMnO_3 catalyst, figure 3b, it is observed a peak due to the d-oxygen, non-stoichiometric reduction and, consequently, reduction of Mn^{3+} , as reported by Tejuca et al. [24].

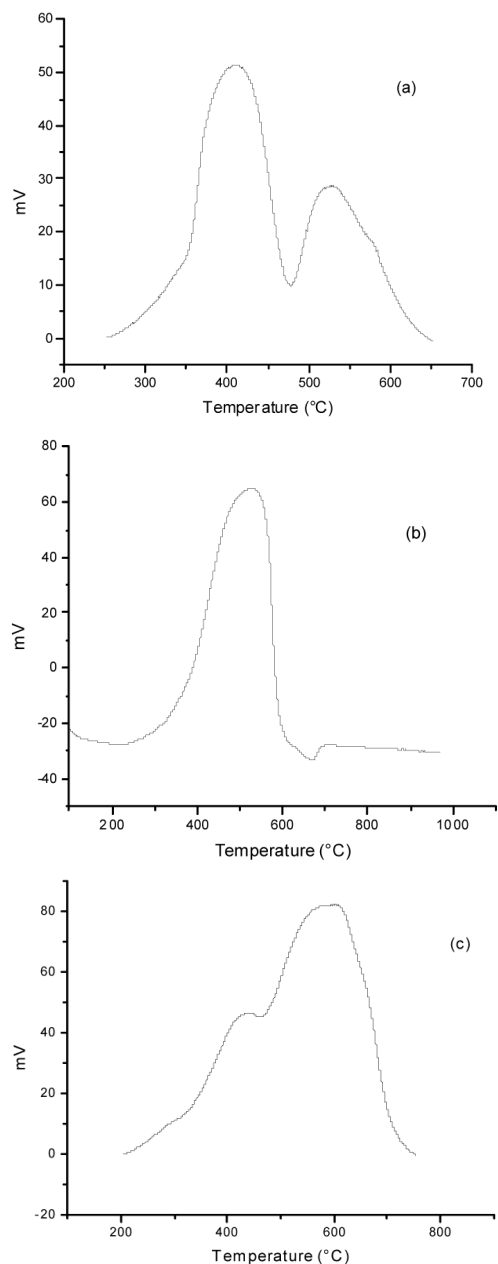
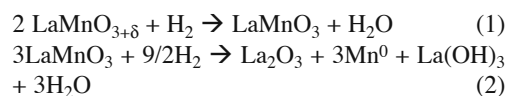
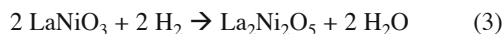


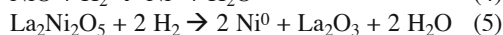
Figure 3. TPR – a) LaCoO₃, b) LaMnO₃, c) LaNiO₃



In figure 3c, which refers to LaNiO₃, it is observed a small shoulder near 451 °C, corresponding to La₂Ni₂O₅ formation, which results of Ni³⁺ to Ni²⁺ reduction, and the second peak (600 °C), to Ni²⁺ to Ni⁰ reduction. This transformation, reported by Lima & Assaf [11], is according reaction bellow:

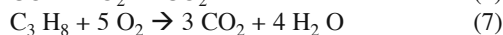
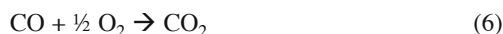


and



This shoulder indicates both the NiO presence and the perovskite phase. Through an X-ray diffraction it was possible to identify the NiO phase. Furthermore, the first peak corresponds simultaneously to the Ni³⁺ to Ni²⁺ reduction in the perovskite structure, and Ni²⁺ to Ni⁰ reduction of the nickel oxide contained in the sample. The second one corresponds to the Ni²⁺ to Ni⁰ reduction of La₂Ni₂O₅ according to equation 5.

The conversion results were determined according to the reactions:



The CO oxidation (Figure 4) occurs at lower temperatures, when compared to propane. According values to CO conversion it was observed that the more efficient catalyst for this reaction was LaCoO₃, that started the conversion at 130°C and presented a maximum under 200°C, while LaMnO₃ presented this maximum near 300°C. LaNiO₃ started the conversion near 300°C that is a high temperature when compared to the others catalysts. The good conversion is mentioned to the LaCoO₃ by Shu & Kaliaguine [13].

The results to propane oxidation are presented in figure 5. It shows that conversion grows up according to the temperature for all catalysts. The perovskites LaCoO₃ and LaMnO₃ presented the better conversion than LaNiO₃.

There are many discussions about perovskites activity. The more commons are: Oxidation states of transition metal ion, the amount of non-stoichiometric oxygen, the deviation of the lattice, it is observed in literature

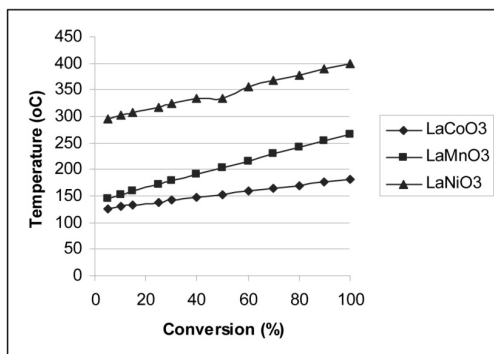


Figure 4. Conversion of perovskite type oxide for CO oxidation.

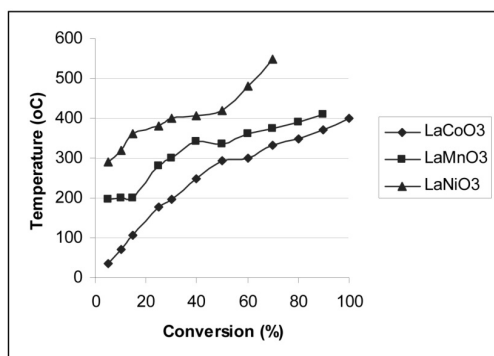


Figure 5. Conversion of perovskite type oxide for propane oxidation.

that the non-stoichiometric oxygen can be a considerable factor for interpretation of catalytic activity in a perovskite series of transition metals [19]. Therefore, the net chemical structure in the perovskite is very complex, due hexagonal, rhombohedral or tetragonal distortions. These deviations can result in a cationic or anionic non stoichiometry.

For lanthanum manganite, the transition Mn^{3+} à Mn^{4+} is accompanied by cationic vacancies generations and for known oxygen excess related to necessary stoichiometry.

Conclusions

We have examined co-precipitation of a stoichiometric Co/La, Mn/La and Ni/La mixed

hydroxide, in which simultaneous oxidation of Co (II), Mn (III) and Ni (II) was induced by co-addition of an oxidizing agent. High-area samples can be obtained by this method only if the hydroxide gel is dehydrated in a controlled manner by washing with a water-miscible nonaqueous solvent. Subsequent calcinations afforded a crystalline $LaCoO_3$, $LaMnO_3$ and $LaNiO_3$ powder with perovskite structure and a surface area determined by the calcination temperature.

It was verified that the $LaCoO_3$ catalyst presented more efficiency to oxidation reactions when compared to $LaMnO_3$ and $LaNiO_3$. The $LaCoO_3$ presented the highest specific surface.

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