Synthesis and Characterization of LaNi\textsubscript{x}Co\textsubscript{1-x}O\textsubscript{3} Perovskites via Complex Precursor Methods

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ABSTRACT

This work presents a study on the synthesis of LaNi\textsubscript{x}Co\textsubscript{1-x}O\textsubscript{3} perovskites via complex precursor methods. Perovskite oxides with the composition LaNi\textsubscript{x}Co\textsubscript{1-x}O\textsubscript{3} were synthesized by chelating precursor and polymeric precursor methods using nickel and/or cobalt nitrates, lanthanum nitrate, ethylene glycol, citric acid, and EDTA as starting source. The obtained perovskite were characterized by thermogravimetric analysis, infrared spectroscopy, X-ray diffraction and the morphology of the samples were investigated by N\textsubscript{2} adsorption experiments and average medium particle size. TG curves and FTIR spectra were particularly useful in establishing of the optimal calcination temperature of the precursor powders. X-ray diffraction patterns revealed the formation of the perovskite structure in all samples prepared by both synthesis method and after calcinations at 700\textdegree C. The results showed that the preparation method resulted in oxides with the intended structure. The specific surface area values were influenced by preparation method.

Keywords: LaNi\textsubscript{x}Co\textsubscript{1-x}O\textsubscript{3} Perovskites, EDTA, Complex Precursor Methods

1. Introduction

The perovskite-type oxides have received much attention in the last years because of their potential application as electrode materials in solid oxide fuel cells, as gas sensors, in various interesting reactions, such as in the steam reforming and in the dried reforming of hydrocarbons, in the catalytic combustion and as oxygen-permeable membranes [1-4]. Such materials have various advantages as: wide variety of composition and constituent elements keeping essentially the basic structure unchanged, bulk structure can be characterized well, their surface can be fairly well estimated taking advantage of this well-defined bulk structure, their valency, stoichiometry and vacancy can be varied widely and huge information on physical and solid-state chemical properties has been accumulated [5-7].

A perovskite-type mixed oxide can be described by the general stoichiometric formula ABO\textsubscript{3}, where A represents a lanthanide or alkaline earth ion and B a transition metal ion trivalent, generally. The perovskite lattice can accommodate multiple cationic substitutions with only small changes since the value of the structure factor (\(t\)) is between 0.75 and 1 [8]. In this structure, the properties are mainly determined by the occupancy of B sites, which usually are partially substituted [8-9].

The properties studied for the different perovskite oxides are potentially influenced by the synthesis method, calcination conditions (temperature, time and atmosphere) and substitutions of A and/or B sites [5-7,10]. The effects of these variables have been studied in order to optimize the performance of the material. The properties of perovskite can be enhanced by the substitution of lanthanum by strontium [11-12] or even cerium [13-14]. However, the catalytic activity of perovskites is mainly determined by the type of metal that occupies the B sites and the partial substitution of those sites [8-9,15-17]. Substitutions in the A and/or B sites can be cause the formation of defects that modify the catalytic properties [15,18].

Several methods have been used so far to prepare these materials, such as freeze-drying, spray-drying, co-precipitation, hydrothermal synthesis and combustion of metal-organic precursors [19-21]. Chelating ligands which contain carboxylate groups or carboxylate and aliphatic amine groups are essential in the water-soluble complex precursor synthesis route. Citric acid (containing carboxylate groups) or ethylenediaminetetraacetic acid (EDT-
TA) (containing carboxylate and aliphatic amine groups) were often used before in the synthesis of perovskite oxide. In this work, LaNiCoO₃ perovskites were synthesized by polymeric precursor method (PP) and chelating precursor method (PQ). The effects of chelating agents on the synthesis procedure and the evolution of crystalline phase have been investigated. These methods normally involve three sequential steps: preparing an aqueous solution of chelated complexes, concentrating the solution to form a gel, and pyrolyzing the gel to produce an amorphous oxide powder.

2. Experimental

Synthesis of the perovskites by chelating precursors (PQ) method:

LaMO₃ (M = Ni or Co) perovskites were synthesized by chelating precursors method using lanthanum, nickel, and cobalt nitrates, citric acid, and ethylenediaminetetraacetic acid (EDTA) as chelating agent. Citrate aqueous solution were prepared from stoichiometric amounts of La(NO₃)₃·6H₂O, Ni(NO₃)₂·6H₂O and Co(NO₃)₂·6H₂O and citric acid in 1:2 molar ratio (metal:citric acid). EDTA aqueous solution was prepared separately by continuous stirring until complete dissolution. This solution was added slowly to citrate solutions under constant mixing for 15 minutes with pH = 9. With addition of EDTA solution the resultant color was changed. Such solutions were added to obtain a precursor solution in which M-EDTA molar ratio was 1:1 (M = metal = La and Ni or Co). After achieving complete dissolution, the resultant solution was dried in a stove at 160°C for 3 h. After the precursor solution was maintained under vacuum producing a viscous mass. The resultant material was heated treated at 220°C for 30 minutes at a heating rate of 10°C/min. The sponge-like green resin was formed. This solid resin precursor was calcined at 700°C for 4 h at a heating rate of 10°C/min.

Synthesis of the perovskites by polymeric precursors (PP) method:

Perovskite oxides with the composition LaNiCo₁₋ₓO₃ (0.4 ≤ x ≤ 0.6; or x = 1) were synthesized using the precursor polymeric method [22]. Solutions of cobalt citrate and nickel citrate were prepared from Co(NO₃)₂·6H₂O, Ni(NO₃)₂·6H₂O and citric acid-AC (molar ratio of 2.5) under constant stirring at 70°C for 30 min. Stoichiometric contents of La(NO₃)₃·6H₂O solid were mixed with nickel citrate solutions at 70°C for 20 min. The cobalt citrate solution was then added under similar conditions. After complete mixing, the temperature was slowly increased to 90°C, at which point ethylene glycol was added in the ratio of 60:40 (citric acid: ethylene glycol). The resulting solution was maintained at that temperature for 2 h under constant magnetic stirring. A gel was then formed and subsequently heat-treated at 300°C for 2 h resulting in the precursor powders. These materials were calcined at 700°C for 4 h at a heating rate of 10°C/min.

3. Results and Discussion

Thermal analysis has been found to yield information on the decomposition temperatures of oxides as also about its thermal stability [23]. Thermogravimetric curves of LaMO₃ (Ni or Co) heated treated at 220°C and prepared by PQ method are shown in Figure 1(a). TG curves showed an initial mass loss of about 21% in the temperature range of 30-315°C that is attributed to water loss, EDTA initial decomposition and citrate/nitrate decompositions. A second loss weight of 39% can be observed in the range 315-540°C which is due EDTA decomposition given perovskite oxide, sodium carbonate and sodium oxide. For comparison, TG/DTG curves for EDTA pure are shown in the Figure 1(b). The curves shown typically four regions of mass loss in the temperature range studied. EDTA thermo decomposition starting at 30°C and following until 750°C. In the temperature range of 750-850°C there is formation of a stable product that was attributed to sodium carbonate and/or sodium oxide. The residue of pure EDTA decomposition at 773°C for 2 hours was characterized by XRD (Figure not shown) and was observed the formation of predominantly sodium carbonate. It can be seen from Figure 1a that the decomposition of EDTA molecules in the LaMO₃ (Ni or Co) heated treated at 220°C and prepared by PQ method starts at different temperature than in EDTA pure. TG/DTG curves of the EDTA residue obtained by calcinations at 773°C for 2 hours (Figure not shown) showed an initial mass loss of about 9% in the temperature range of 80-108°C that was attributed to water loss. A second loss weight of about 90% in the temperature range of 860-1200°C was attributed to decomposition of sodium carbonate, revealing the predominant presence of this material in the temperature range of 750 at 860°C. For the samples heated treated at 220°C, the complexation of nickel or cobalt and lantha-
num ions with EDTA ligand influence on the EDTA inter-
actions and consequently in their decomposition tem-
perature. Therefore, in these samples the temperature 
required for EDTA decomposition is at 540°C (Figure 
1(a)) and the residue is composed perovskite oxide, 
sodium carbonate and sodium oxide. A loss mass observe 
at temperature up to 850°C is due of sodium carbonate 
decomposition.

TG curves of LaNi_{x}Co_{1-x}O_{3} (0.4 \leq x \leq 0.6; x = 1) heated 
treated at 300°C and prepared by PP method are shown in 
Figure 1c. The first step took place at about 30°C with the 
onset of decomposition of the residual material synthesis 
and following until 350°C. Full decomposition of residual 
material occurred between 350 and 650 °C, followed by 
perovskite oxide formation.

For the samples LaNi_{x}Co_{1-x}O_{3} (0.4 \leq x \leq 0.6; x = 1) 
calcined at 700°C and prepared by PP method, TG curves 
not shown loss mass in the range of 30-900°C.

For the other hand, for the samples LaMO_{3} (Ni or Co), 
calcined at 700°C and prepared by PQ method (Figure not 
shown), TG curves showed that the thermal decomposi-
tion took place in two steps stabilizing at temperatures 
high than 1100°C. The mass loss observed between 
30-140°C was attributed to several simultaneous decom-
position reactions of the residual material of the synthesis 
process. The samples still showed another decomposition 
step above 850°C which can be attributed to decomposi-
tion of carbonates compounds formed.

Figure 2(a) shown FTIR spectra for the samples 
LaMO_{3} (Ni or Co), heated treated at 220°C and prepared 
by PQ method. Several bands were observed in such 
spectra with central point at 1654 cm^{-1}, 1473 cm^{-1}, 866 
cm^{-1} and 600 cm^{-1} which can be attributed to the N-H, C = 
O, C-N, N-O and metal-O bonds [24,25]. The bands due 
EDTA vibrations still were observed in the calcined 
samples at 700°C(Figure not shown). Such results indi-
cated that the temperature and time of calcinations were 
not sufficient for complete decomposition of residual 
material of the synthesis process.

FTIR spectra of LaNi_{x}Co_{1-x}O_{3} (0.4 \leq x \leq 0.6; x =1) 
heated treated at 300°C and prepared by PP method 
showed bands between 1643-1538 and at 1410, 1249, 
1067 and 642 cm^{-1} (Figure 2(b)). The bands observed at 
1643-1538 and 1410 cm^{-1} were assigned to the asymmet-
ic and symmetric carbonyl group stretching vibrations of 
ionized carboxylate. The bands at 1249 and 1067 cm^{-1} 
could be attributed to nitrate ions. These bands were no 
longer observed as the materials were calcined at 700°C, 
suggesting the decomposition of the residual material of 
the synthesis process.

X-ray diffraction patterns of the precursor powders 
prepared by polymeric precursor and chelating precursor 
methods revealed the presence of amorphous structures. 
The formation of crystalline phases can be seen from the 
patterns of powders calcined at 700°C (Figure 3). For the 

Figure 1. TG curves for (a) LaMO_{3} (M = Ni or Co); (b) 
EDTA and (c) LaNi_{x}Co_{1-x}O_{3} 
samples LaNi_{x}Co_{1-x}O_{3} (0.4 \leq x \leq 0.6; x = 1) calcined at 
700°C and prepared by PP method (Figure 3(b)), all the
samples consisted of single-phase materials exhibiting the perovskite structure, except for a minor phase observed on the LaNi_{0.5}Co_{0.5}O_{3} sample. The perovskite structure was characterized by rather intense peaks at 2θ = 33.1°, 47.4° and 59.5°. All perovskite peaks were attributed to rhombohedral unit cells, space group R3c (JCPDS 32-0296). According to XRD data, no significant changes occurred in the lattice parameters of the perovskite structure due to partial substitution of Ni for Co in its B sites. Such result was expected since the ionic radii of Ni^{2+} and Co^{3+} are rather similar. XRD also revealed that the structure of the resulting perovskite is similar to that of non-substituted lanthanum nickelate or cobalt perovskites [26-27]. Moreover, powders prepared by the polymeric precursor method depicted similar structure compared to the same powders prepared by other methods.

Well-resolved X-ray patterns were obtained for the samples LaMO_{3} (Ni or Co), calcined at 700°C and prepared by PQ method (Figure 3(a)) clearly suggesting the formation of a highly crystallized powder. For these samples, X-ray diffraction patterns showed peaks at 2θ = 32.4°, 46.7° and 58.1° which were attributed to perovskite structure [13]. All perovskite structure peaks identified were indexed as rhombohedral system. Peaks referent to carbonate sodium and sodium oxide also were observed suggesting that the crystallinity is not a function of the monophase structure. Carbonate phase also was confirmed by FTIR and TG data. Therefore, the perovskite structure crystallizes from amorphous precursors and simultaneously occurs the formation of intermediate phase which can be decomposed at high temperatures. The LaNi_{0.5}Co_{0.5}O_{3} sample. The perovskite structure was characterized by rather intense peaks at 2θ = 33.1°, 47.4° and 59.5°. All perovskite peaks were attributed to rhombohedral unit cells, space group R3c (JCPDS 32-0296). According to XRD data, no significant changes occurred in the lattice parameters of the perovskite structure due to partial substitution of Ni for Co in its B sites. Such result was expected since the ionic radii of Ni^{3+} and Co^{3+} are rather similar. XRD also revealed that the structure of the
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Table 1 shows the results of the crystallite size of the perovskite phase. The crystallite size was calculated by the Scherrer laws. The crystallites are smaller when the perovskites are synthesized by PQ method when compared with the perovskite synthesized by PP method. In the Table 1 also is shown the specific surface area values and average medium particle size for all the perovskites. For the samples LaMO$_3$ (Ni or Co), calcined at 700°C and prepared by PQ method, the surface area were smaller than 137 m$^2$/g. These values not are characteristics for the perovskite type oxides prepared by conventional synthesis method. This result is a consequence of the presence of carbonate phase showed in the XRD analysis. From the results showed in the Table 1 also is possible to see that with the substitution of nickel by cobalt practically not provokes greats changes in the surface area. Such result was expected since the ionic radii of Ni$^{3+}$ and Co$^{3+}$ are rather similar. The surface area for the samples LaNi$_x$Co$_{1-x}$O$_3$ (0.4 ≤ x ≤ 0.6; x = 1) calcined at 700°C and prepared by PP method were lower than 15 m$^2$/g. These values are characteristics for the perovskite type oxides prepared by polymeric precursor method and from the calcinations conditions used.

Figure 4 shown SEM micrographs for all perovskites samples calcined at 700°C and prepared by PQ and PP methods. SEM micrographs showed non-uniform particles with sizes ranging from 2 to 20 μm. Such distribution in particle size may be attributed to the preparation method and calcination temperature range used. The perovskites prepared by PQ and PP methods showed similar non-uniform particles when were compared to the same powders prepared by other methods.

4. Conclusions

This work was carried out to investigate the effect of the preparation methods in the perovskite structure formation. The effect of partial substitution of Ni for Co in the B sites of LaNiO$_3$ perovskites on the structural, morphological and surface properties also was studied. In accordance with TG curves and FTIR spectra, all organic residual material of the synthesis process decomposed up to 650°C for the precursor powders synthesized by polymeric precursor method. For the other hand, for the precursor powders prepared by chelating precursor method, all organic residual material of the synthesis process also decomposed up to 650°C, but in this case the decompositions lead to the formation of secondary phase in this temperature.

X-ray diffraction patterns revealed the formation of the rhombohedral perovskite structure in all samples prepared by both synthesis method and after calcinations at 700°C. The results showed that the preparation method resulted in oxides with the intended structure. Minor phases attrib-
uted to impurities were observed in the LaNi_{0.5}Co_{0.5}O_{3} prepared by polymeric precursor method and in all the samples prepared by chelating precursor method, which was attributed to carbonate phase.

In the perovskites prepared by PP method, the replacement of Ni by Co did not cause significant changes in the lattice parameters. The perovskites prepared by PP method were characterized by relatively wide particle size distributions with particles ranging from 2 to 20 µm and specific surface area about 15 m²/g. The perovskites prepared by PQ method showed similar structure compared to the same powders prepared by other methods, having advantage strength how a little particle size and surface area higher 100 m²/g.

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