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$LaCoO_3$ formation from precursors obtained by water-based sol–gel method with citric acid

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Abstract In the present work the $LaCoO_3$ formation from gel precursors obtained by water-based sol–gel method with citric acid was studied. As precursors La and Co nitrates were used. The obtained gels were analyzed by TG/DTA and TG/AGE. The decomposition of the gels takes place in two main steps with the evolution of the same volatile compounds (H_2O, CO_2 si NO_2) leading to the conclusion that two types of bonding of the components in the gels occurred. The decomposition of the gels takes place up to 400 °C. The gels thermally treated at 600 °C lead to single pure perovskite rhombohedral phase of lanthanum cobalt oxide ($LaCoO_3$).

Keywords Sol–gel processes · $LaCoO_3$ · TG/AEG · Phase formation

Introduction

Perovskites are mixed oxides of general formula ABO_3, where both A and B metal ions can be partially substituted, leading to a wide variety of compounds. These compounds are often characterized by oxygen non-stoichiometry, which determines interesting catalytic properties for many reactions [1, 2]. Traditionally, such mixed oxides have been prepared through a calcination-milling procedure, leading to low surface area, poorly active materials. To overcome this limit, several techniques were developed, among which the so called citrate or tartrate sol–gel method allows to obtain relatively high surface area, up to two orders of magnitude higher than for the samples prepared by calcination-milling procedure [3].

In the preparation of transition metals oxide powders, monoliths, and thin films, the wet chemistry processing has been used extensively during the last few years. These materials posse high purity, ultra homogeneity, and large surface area [4].

Delmon [5] discuss the strategy of heterogeneous catalysts preparation that has been for many years a dynamic field of sub-nanotechnology and remains so nowadays. Among other methods the so-called ‘citrate process’ and its variants are considered of wide application.

Sinquin et al. [6] tried to control by infrared spectroscopy (FTIR) and thermogravimetric analysis (DTA-TG) the different steps of the formation of $LaMO_3$ perovskites ($M = Co$, Mn) using a sol–gel like method with propionic acid solvent.

Nakayama et al. [7] prepared $LaCoO_3$ by greenish heteronuclear complex, hydrothermal and coprecipitation techniques and showed that the thermal decomposition (TG) occurred in several steps.

Rane et al. [8] prepared the metal oxide by hydrazine method starting with hydroxide, oxalate, and citrate precursors.

In the present work the lanthanum cobalt oxide was synthesized by sol–gel method using nitrates as inorganic precursors. Citric acid (CA) was used as chelating agent. The sol–gel method using chelating agent is a useful technique because it presents the advantage of a good stoechiometric control, good particle size distribution, low temperature, and short period for calcinations [9].

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In one of our previous paper [10] the preparation of $LaCoO_3$ starting with nitrate salt and citric acid as chelating agent and its electrical and catalytic properties was studied.

The main objective of this work was to establish the formation mechanism of the $LaCoO_3$ powder from precursors obtained by sol–gel method by inorganic–carboxylic route.

Experimental

Precursors gel preparation

In the present work the $LaCoO_3$ formation from gel precursors obtained by water-based sol–gel method with citric acid was studied.

Lanthanum cobalt oxide was prepared from gel precursors obtained by sol–gel method, inorganic–carboxylic route. A lanthanum cobalt citrate precursor with La:Co:CA = 1:1:1 was realized by the following preparation procedure: an aqueous solution of 0.25 M of $Co(NO_3)\cdot 6H_2O$ and 0.25 M of $La(NO_3)_3\cdot 6H_2O$ was realized. To this solution solid citric acid was added and the mixture was intensively stirred, until a clear solution was obtained. The chart of procedure used to prepare the solution and powder of $LaCoO_3$ is presented in Fig. 1.

The monocomponent La-citric and Co-citric gels were also obtained by a similar procedure.

Gel and powder characterization

The UV-VIS spectra of the obtained gels were recorded using a PERKIN ELMER Lambda 35 UV-VIS Spectrometer.

The FTIR spectra of the gels were obtained using a Nicolet Spectrometer.

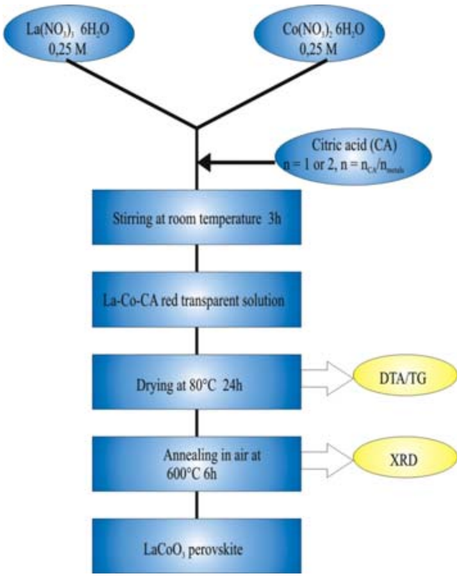

Fig. 1 Chart of preparation $LaCoO_3$

The thermal behavior of the precursor gels were determined by TG/DTA using a NETZSCH STA 409C/CD instrument coupled with a Balzers Thermastar GSD 300D mass spectrometer, in Al_2O_3 crucibles and in air atmosphere and the maximum temperature was set at 740 °C and the heating rate was of 5 °C/min.

The structural evolution of the annealed samples were evaluated by X-ray diffraction, using a CuKα ($\lambda = 0.1540$ nm) radiation source in a BRUKER AXS D4 ENDEAVOR X-ray diffractometer. The diffraction angle (2θ) ranging between 10° and 90° was scanned.

Results and discussion

In the experimental conditions presented above an amorphous red gel was obtained.

Based on the literature data [11] the following gelation mechanism could be considered:

(1) Dissolution of metal salts in water

In the salts solution with pH = 2 aquo-cations are formed:

$$La(NO_3)_3 \xrightarrow{\text{dissolution}} La^{3+} + 3(NO_3)^{1-} \xrightarrow{\text{solvation}} \left[La(H_2O)_6\right]^{3+} + \left[(NO_3)^{1-}\right]_3$$

$$Co(NO_3)_2 \xrightarrow{\text{dissolution}} Co^{2+} + 2(NO_3)^{1-} \xrightarrow{\text{solvation}} \left[Co(H_2O)_6\right]^{2+} + \left[(NO_3)^{1-}\right]_2$$

(2) Complexation and chemically controlled condensation in the presence of citric acid

$$\left[La(H_2O)_6\right]^{3+} + x(C_6H_5O_7)^{3-} \rightarrow \left[La(C_6H_5O_7)_x(H_2O)_{6-x}\right]^{3-x}\{[(NO_3)^-]_3(H_2O)_x\}$$

$$\left[Co(H_2O)_6\right]^{2+} + y(C_6H_5O_7)^{3-} \rightarrow \left[Co(C_6H_5O_7)_y(H_2O)_{6-y}\right]^{2-y}\left\{[(NO_3)^-]_2(H_2O)_y\right\}$$

(3) Formation of metals-citric acid chelate

$$\left[La(C_6H_5O_7)_x(H_2O)_{6-x}\right]^{3-x}\left\{\left[(NO_3)^{1-}\right]_3 (H_2O)_x\right\} + \left[Co(C_6H_5O_7)_y(OH_2)_{6-y}\right]^{2-y}\left\{\left[(NO_3)^{1-}\right]_2(H_2O)_y\right\} \rightarrow \left[LaCo(C_6H_5O_7)_{y+x-z}(OH_2)_{6-y-x}\ (NO_3)_{3Z}^{1-}\right] \times \left[(C_6H_5O_7)_Z(NO_3)_2^{1-}\right] \cdot x + yH_2O$$

The UV-VIS and FT-IR spectra of the obtained gel are presented in Figs. 2 and 3, respectively.

The UV-VIS spectrum present a charge transfer band (CT) at 356 nm assigned to the transfer of 3d orbitals of Co^{2+} to the 2*p* orbitals of the oxygen from the NO_3^- ion. The band with a maximum located at 532 nm is assigned to the $^4T_{1g} \rightarrow {}^4T_{1g}$ (P) for the Co^{2+} in an octhaedral geometry.

In the case of FTIR spectrum the carbonyl stretchings were observed between 1724 and 1451 cm^{-1} indicating the ionization of all the carboxyl groups, leading to complex formation [12, 13]. According to the literature data, the frequency separation between the asymmetric stretching ν_{asym}(COO) vibration and symmetric stretching ν_{sym}(COO) vibration $\Delta\nu = 273$ cm^{-1} suggests that acetate anions act as bridging monodentate ligands. The band at 1383 cm^{-1} is assigned for NO_3^- vibration.

DTA/TG analysis of the obtained gel is presented in Fig. 4. The total mass loss is 68%. It starts at 80 °C with absorbed water evolution and occurs stepwise. Over the temperature of 400 °C there is a low change in mass loss slope without thermal effects. On the DTA curve, a strong exothermic effect, with a maximum at 350 °C is observed, indicating that the thermal events can be primarily associated with the gelic compounds decomposition accompanied with the burning out of the organic residues.

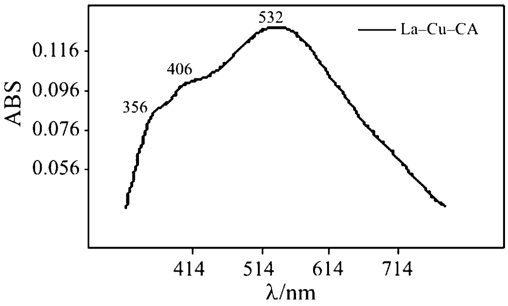

Fig. 2 UV-VIS spectrum of the La-Co-CA gel

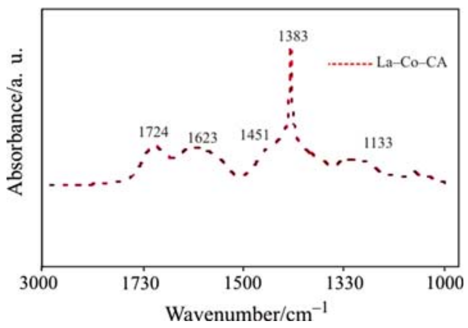

Fig. 3 FTIR spectrum of La-Co-CA gel

Based on the thermal behavior of the binary gel, the thermal behavior of the monocomponent gel was also studied. The TG/DTG/DTA curves of the monocomponent gel are presented in the Fig. 5a for Co-CA and in the Fig. 5b for La-CA.

An important exotermal effect in the case of Co nitrate-citric acid (Co-CA) gel could be observed that appears at 322 °C, while for the La nitrate-citric acid (La-CA) gel a similar effect at 418 °C occurs. The main decomposition effect of the binary La-Co complex (La-Co-CA) gel lies between the decomposition effects of the monocomponent

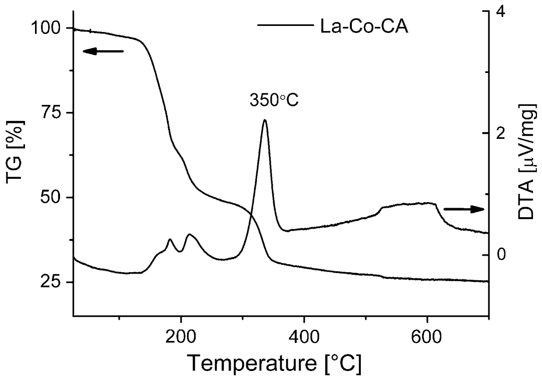

Fig. 4 The DTA/TG curves of the thermal decomposition of La-Co-CA gel

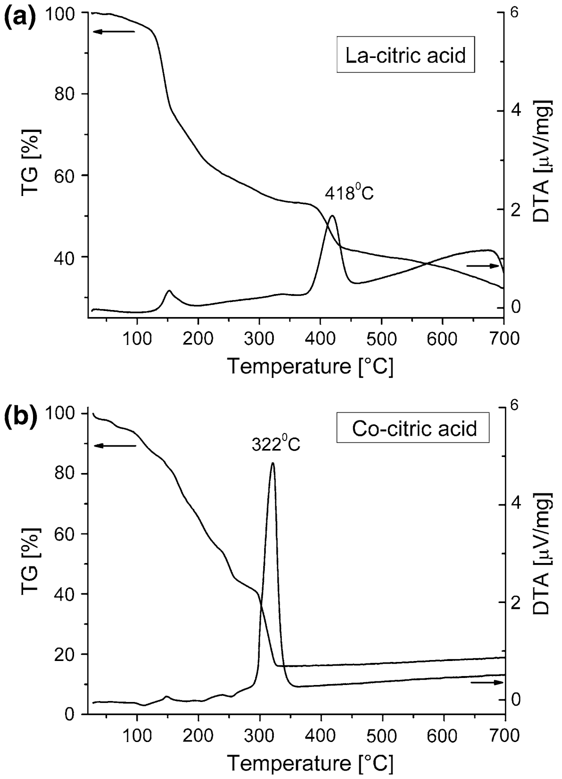

Fig. 5 The TG/DTA curves of the thermal decomposition of monocompoment gels. **a** Co-CA. **b** La-CA

complexes, leading to the conclusion that in the case of binary system not a mixture of phases occurs, but a complex gel was formed.

The thermal decomposition of the gel precursors after drying at 80 °C was followed by simultaneous thermal analysis (thermogravimetry and differential thermal analysis) coupled with a mass spectrometer for the analysis of evolved gases (EGA).

The TG/EGA curves are presented in Figs. 6, 7, and 8.

The TG/AEG results show the decomposition of the complex gel at two different temperatures (200 and 350 °C), with the evolution of the same gases (NO_2, CO_2, and H_2O) that means that the water, citric acid, and nitric reagents are bound in two different ways in the complex.

The initially proposed formula based on literature date was the following:

$$\left[\mathrm{LaCo(C_6H_5O_7)}_{y+x}(\mathrm{H_2O})_{6-y-x}\right]\left[(\mathrm{NO_3})^{1-}\right]_5 \cdot x + y\mathrm{H_2O}$$

In this formula citric acid is bound in the position of a coordinated ligand.

But, based on the TG/AEG results the real formula could be the following:

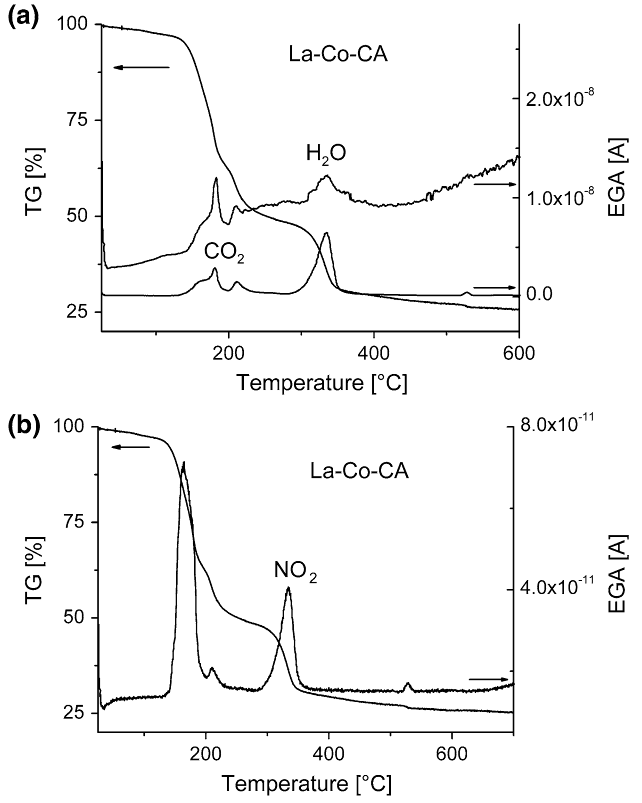

Fig. 6 TG/EGA curves of La-Co-CA gel. **a** H_2O and CO_2 evolution. **b** NO_2 evolution

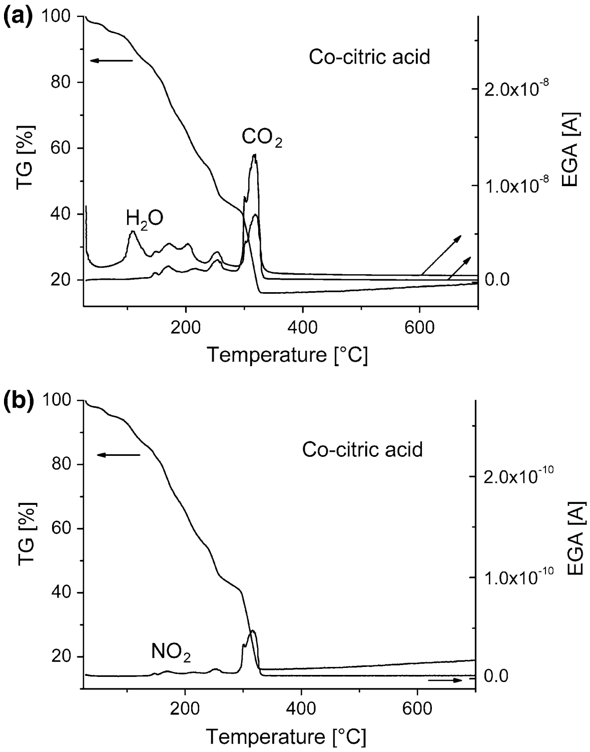

Fig. 7 TG/EGA curves of La-CA gel. **a** H_2O and CO_2 evolution. **b** NO_2 evolution

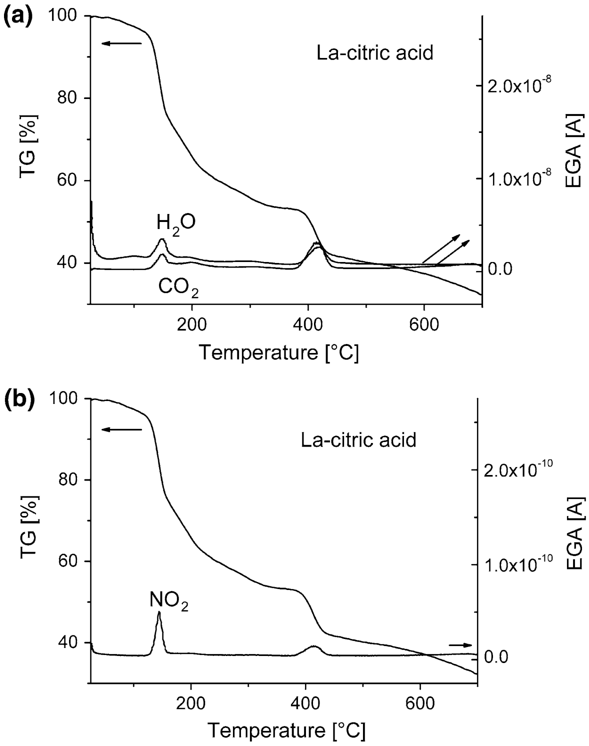

Fig. 8 TG/EGA curves of Co-CA gel. **a** H_2O and CO_2 evolution. **b** NO_2 evolution

$$\left[LaCo(C_6H_5O_7)_{y+x-z}(H_2O)_{6-y-x}\ (NO_3)^{1-}_{3Z}\right]$$
$$\left[(C_6H_5O_7)_Z(NO_3)^{1-}_2\right]\cdot x+yH_2O$$

In this formula citric acid and the nitrate are bound in two positions as weekly bound ligands and as coordinated ligands.

The decomposition of the complex gel occurs in the following steps:

$$\underbrace{[LaCo(C_6H_5O_7)_{y+x-z}(OH_2)_{6-y-x}\ (NO_3)_{3Z}{}^{1-}]}_{II}\ [\underbrace{(C_6H_5O_7)_Z(NO_3)_2{}^{1-}}_{I}]\cdot x+yH_2O$$

In the first step, in the range of 150–200 °C, the total mass loss was 28.00% and the weakly bound ligands are eliminated;

In the second step, in the range of 200–400 °C, the total mass loss was 28.50% and the coordinated ligands are eliminated; one may assume that at 400 °C the gel precursor decomposition is finished.

In the third step, in the range of 400–700 °C, the total mass loss was 6.00% and could be assigned to the evolution of the gases retained on the resulted oxide nanoparticles.

The corresponding thermal effects for the binary and monocomponent gel precursors are summarized in Table 1.

Based on the thermal behavior of the complex gel, the thermal treatment to obtained $LaCoO_3$ was the following: heating rate of 1 °C/min up to 400 °C; 1 h plateau and heating rate of 5 °C/min up to 600 °C; 6 h plateau.

In Fig. 9 the XRD patterns of $LaCoO_3$ thermally treated at 600 °C are presented. The single pure rhombohedral phase of lanthanum cobalt oxide was obtained when the gel was thermally treated at 600 °C for 6 h (JCPDS 84-0848).

The X-ray diffraction results evidenced that the pure phase of $LaCoO_3$ with rhombohedral structure was obtained at 600 °C.

Table 1 DTA/TG results of gel precursors

Sample	Temperature range/°C	Gases evolved	Thermal effects/°C		Mass loss/%	Assignment
			Endo	Exo		
La-Co-CA	20–200	H_2O CO_2 NO_2	100.0	180.0	28.0	Evolution and oxidation of the weakly bounded ligands
	200–400	H_2O CO_2 NO_2		211.0 350.0	28.5	Evolution and oxidation of the coordinated ligands
	400–700	CO_2 NO_2		550.0	6.00	Evolution of the organics resulted by decomposition and absorbed on surface of oxide powders
					Σ = 62.50	
Co-CA	20–200	H_2O CO_2 NO_2	110.0 197.5	150.0	32.50	Evolution and oxidation of the weakly bounded ligands
	200–400	H_2O CO_2 NO_2	250.3	322.0	50.0	Evolution and oxidation of the coordinated ligands
	400–700	–	–	–	0	
					Σ = 82.50	
La-CA	20–200	H_2O CO_2 NO_2	–	150.0	33.20	Evolution and oxidation of the weakly bounded ligands
	200–400	H_2O CO_2 NO_2	–	418.0	14.40	Evolution and oxidation of the coordinated ligands
	400–700	–	–	–	20.60	Evolution of the organics resulted by decomposition and absorbed on surface of oxide powders
					Σ = 68.20	

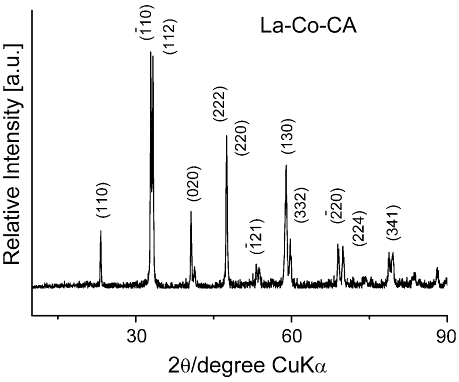

Fig. 9 The XRD patterns of $LaCoO_3$, thermally treated at 600 °C, Al holder

Conclusions

$LaCoO_3$ was prepared from precursors obtained by sol–gel method using citric acid as chelating agent and nitrates as metal precursors.

The UV-VIS spectroscopic investigations of the obtained La-Co-CA complex gel have shown that the Co^{2+} ion is present in octhaedral geometry, while the FTIR spectroscopy suggests that the citric acid act as bridging monodentate ligands.

The TG/DTA coupled with mass spectrometry has shown the complex composition of the obtained gels and their decomposition in several steps.

By adequate thermal treatment, based on the TG/DTA results, pure phase of $LaCoO_3$ with rhombohedral structure was obtained at 600 °C.

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