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Characterization of $LaCoO_3$ powders obtained by water-based sol–gel method with citric acid

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Abstract

$LaCoO_3$-based materials are studied because they exhibit interesting, electrical, magnetic and catalytic properties. In this contribution, $LaCoO_3$ powders were synthesized by sol–gel method in aqueous medium starting from metal nitrates or acetates, and citric acid as the chelating agent at room temperature. The relation between the reactions in solution, crystallization pathway and morphology is discussed. The dried powders were amorphous. Their thermal decomposition occurs stepwise upon heating to 400 °C for nitrate or 500 °C for acetate-based precursors, respectively. Pure perovskite $LaCoO_3$ phase is formed after heating at 600 °C in the case of nitrates while in the case of acetates separation of phases occurs when 2 mol of citric acid are used. The choice of the precursor influences the morphology of the powders heated at 600 °C. The nitrate-based powders are composed of agglomerates of fine particles while the acetate-based powders mainly consist of gel fragments. Some preliminary electrical and catalytic properties are also presented.

Keywords: Sol–gel processes; Electron microscopy; X-ray method; Perovskites; $LaCoO_3$

1. Introduction

The perovskites are mixed oxides of general formula ABO_3, where both A and B metal cations can be partially substituted leading to a wide variety of compounds. These materials can be considered strategic materials due to their electronic, magnetic, optical and catalytic properties.[1]

$LaCoO_3$-based materials exhibit interesting electrical, magnetic and catalytic properties. $LaCoO_3$ can be produced by using a number of methods including conventional ceramic powder technology which leads to low surface area, poorly active materials, requires high temperatures and long calcination periods. To overcome these limitations, several techniques were developed, including sol–gel alkoxides processing route and citrate or tartrate sol–gel aqueous processing route.[2] The citrate sol–gel process has some potential advantages over other methods: besides allowing the homogenous mixing of the components at the atomic scale, it also makes possible the formation of films or fibres from gel, which is of technological importance.[3] The sol–gel method using a chelating agent (like polyethylene glycol, citric acid or polyacrilic acid) is considered a useful technique because it presents the advantages of allowing a good stoichiometric control, obtaining good particle size distributions, low temperature and short periods for calcinations.[4]

In this research, powders of $LaCoO_3$ prepared by the sol–gel method from non-alkoxide precursors and citric acid as a chelating agent were obtained.

2. Experimental

The precursors used are $La(NO_3)_3{\cdot}6H_2O$ and $Co(NO_3)_2{\cdot}6H_2O$ or $La(CH_3COO)_3$ and $Co(CH_3COO)_2{\cdot}4H_2O$, respectively, which were weighted in equimolar amounts and dissolved in distilled water (0.25 M). Citric acid was added to this solution after 10 min of mixing in a molar ratios of citric acid/total cations of 1 or 2. The resulted solution was stirred at room temperature for 3 h leading to a red transparent solution, when starting with nitrate and a violet one, when starting with acetates. The solutions were kept at 80 °C for 24 h and amorphous gels were obtained. The gels were annealed in air at 600 °C for 6 h. The heating rate was 1 °C/min up to 400 °C

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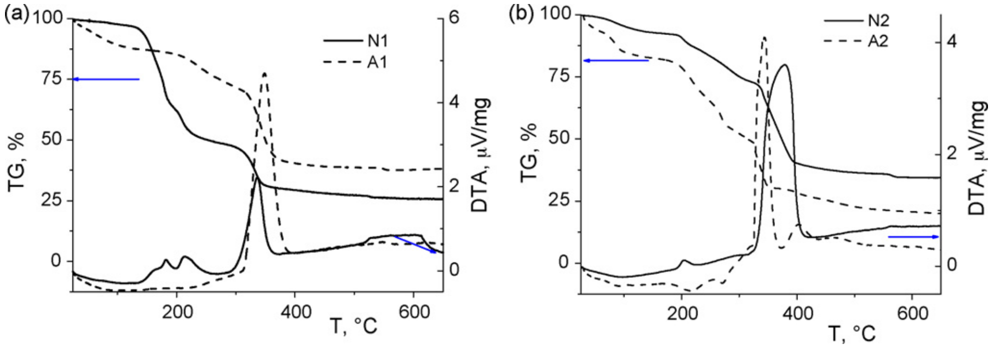

Fig. 1. The DTA/TG curves of the thermal decomposition of the N1 and A1 (a) or N2 and A2 (b) samples.

and 5 °C/min up to 600 °C. According to the type of metal precursors used (nitrate N or acetate A) and the citric acid/total cations ratio (1 or 2) the obtained samples were named N1 and N2 for nitrate precursors and A1 and A2 for acetate precursors, respectively.

3. Characterization

The structural characterization of the gel was carried out by IR spectroscopy by using a PERKIN ELMER FT-IR Spectrometer 1720× and fluoro lube or paraffinum oil. The thermal behaviour of the samples was determined by TG/DTA by using a NETZSCH STA 409C/CD instrument coupled with a mass spectrometer, in Al_2O_3 crucibles and in air atmosphere. The maximum temperature was set at 740 °C and the heating rate was 5 °C/min. The annealed samples were evaluated by X-ray diffraction by using a Cu Kα (λ = 0.1540 nm) radiation source in a BRUKER AXS D4 ENDEAVOR X-ray diffractometer. The diffraction angle (2θ) ranged between 10° and 90°. The particle size and morphology of the samples was characterized with a JEOL JSM-5800 scanning microscope and by electron transmission microscope (TEM) using a JEOL 200 CX electron microscopes working at 200 kV. The ac electrical conductivity of the sample was measured in situ, in operando conditions, by using a special reaction cell coupled to a semi-automatic RLC bridge TESLA BM 484 (at 1592 Hz) and the differential step technique (DST).[5,6] It consists in measuring the temperature dependence of conductance G in gas flow, during successive linear heating-cooling of the same sample between 20 and 400 °C in different atmospheres, according to a specific protocol; this is coupled with permanent monitoring of the composition of the inlet/exit gas by GC. In this case the protocol was: DHe1, 2, DO(1), DHe3, CT, DHe4 and DO(2), where DHe and DO abbreviate dry helium and oxygen, respectively, and CT represents the propylene–air mixture (1:22) used in the catalytic test.

4. Results and discussion

When using nitrate precursors red amorphous gels were obtained, while starting with acetates the obtained gels were amorphous and had a violet colour.

Table 1 presents the assignments of the vibration bands of the IR spectra of the dried gels.

All the dried gels presented the broad vibration band between 3700 and 3100 cm^{-1} assigned to the structural OH groups and the water vibration band at about 1600 cm^{-1}, which overlap the carbonyl asymmetric stretching band. In our cases, the carbonyl stretching bands were observed between 1707 and 1415 cm^{-1} indicating the ionisation of all the carboxyl groups leading to complex formation.[7,8] According to the literature data, the frequency separation between the asymmetric stretching ν_{asym}(COO) vibration and symmetric stretching ν_{sym}(COO) vibration of $\Delta\nu = 165$ cm^{-1} (in cases of nitrate-based samples)

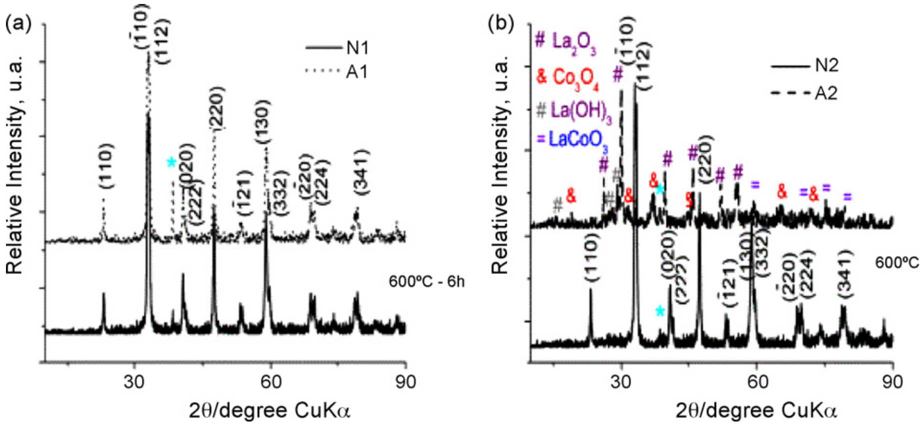

Fig. 2. (a and b) X-ray diffraction patterns of the samples annealed at 600 °C for 6 h, (*) Al sample holder.

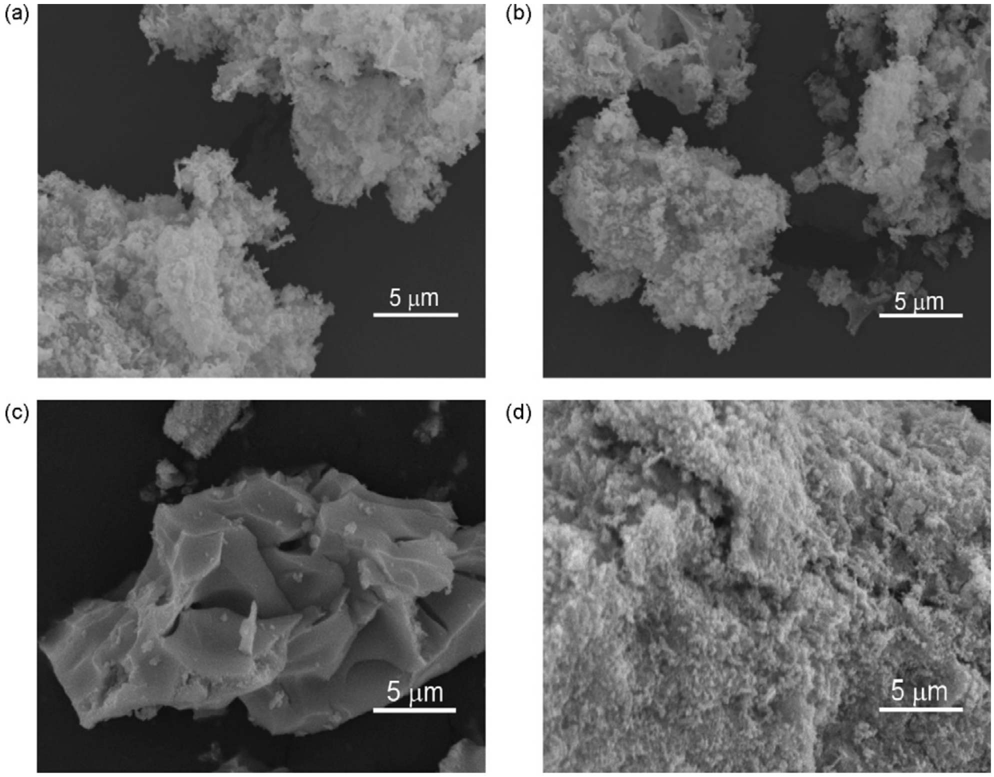

Fig. 3. SEM images of the samples thermally treated for 6 h at 600 °C, (a) N1, (b) N2, (c) A1 and (d) A2.

and of $\Delta\nu = 157\,\mathrm{cm}^{-1}$ (in the case of acetate-based samples), suggests that acetate anions act as bridging bidentate ligands.

The thermal decomposition of the N1 and A1 and of the N2 and A2 powder precursors after drying at 80 °C is present in Fig. 1(a and b).

All dried precursors lose weight stepwise. The choice of the starting compounds influences the pathway of decomposition. Above 400 °C for nitrate-based and above 500 °C for acetate-based gels there is no pronounced weight loss.

On the DTA curves, a strong exothermic effect in the range 320–370 °C, with maximum at ∼340 °C is observed for all samples, indicating that the thermal events can be primarily associated with the nitrate decomposition and the burn out of organic species in the powder.

Based on TG/DTA results, the dried gels were annealed up to 600 °C, as mentioned in Section 2, resulting in a black powder.

The XRD data of the thermally treated gels are presented in Fig. 2(a and b) and the FT-IR spectroscopic results in Table 1.

The single pure perovskite rhombohedral phase of lanthanum cobalt oxide was obtained when N1, N2 and A1 gels were thermally treated at 600 °C for 6 h (JCPDS 84-0848). In the case of A2 a mixture of phases was obtained, namely La_2O_3, $La(OH)_3$, Co_3O_4 and $LaCoO_3$ in low amount. This behaviour is under further investigation.

The IR spectroscopic results (Table 1) confirmed the XRD data showing that the vibration bands assigned to the precursors vanished and the vibration band assigned to the oxide network developed.

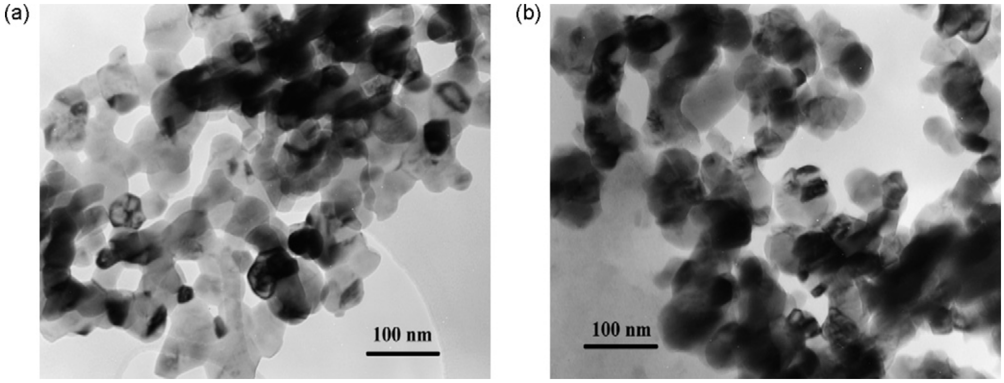

Fig. 4. TEM images of the samples N1 (a) and A1 (b) after thermal treatment for 6 h at 600 °C.

Table 1
IR spectroscopic date on the dried and thermally treated gels

N1		N2		A1		A2		Vibration mode	Assignments
Room temperature	600 °C	Room temperature	600 °C	Room temperature	600 °C	Room temperature	600 °C		
3350	–	3350	–	3326	–	3326	–	νOH	Structural OH group
–	–	–	–	3200	–	3200	–	νOH	
1640	–	1707	–	–	–	–	–	ν_{asym}(COO)	Carbonyl asymmetric stretching
1580	–	1571	–	1566	–	1566	–	ν_{asym}(COO)	Carbonyl asymmetric stretching
1415	–	1415	–	1409	–	1409	–	ν_{sym}(COO)	Carbonyl symmetric stretching
	–	–	–	1257	–	1257	–	νCOOH	Introduced by the citric acid
1033	–	1033	–		–	–	–	νC—OH	
	–	–	–	912	–	–	–	νCH_2	
813	–	813	–	–	–	–	–	νCH_2	
–	–	–	–	–	–	625	–	νCo—O	Co—O in octahedral coordination
–	–	–	–	–	588	588	588	νLa—O	La—O in heptahedral coordination
–	573	–	573	–	–	–	–	νLa—O	La—O in dodecahedral coordination
–	–	–	–	–	–	–	530	νCo—O	Co—O in tetrahedral coordination

The SEM micrographs of the same samples, presented in the Fig. 3(a–d) show fine particles, strongly aggregated, with a morphology depending on the type of the precursors used. In the case of the powders obtained starting with acetates (A1 and A2) pieces of gel were obtained while in the case of powders obtained starting with nitrates (N1 and N2) a more porous structure was obtained.

The TEM micrographs recorded on the N1 and A1 powders, presented in the Fig. 4(a and b), have confirmed the formation of $LaCoO_3$ particles with perovskite structure and their tendency to agglomerate. The aggregates formed are porous and consist of crystallites of about 50 nm.

Some preliminary investigations on the electrical and catalytic properties of the thermally treated N1 powder were also performed in situ, in operando conditions.

Between 20 and 400 °C the sample behaves as an n-type semiconductor (Fig. 5). Three distinct ranges for the dependence of conductance G on temperature could be noticed: (i) in the low temperature range (up to approximately 150 °C), G is almost temperature independent; (ii) between 150 and 220 °C G increases moderately with temperature and is fluctuating, while (iii) above 200–220 °C the G increases sharply, showing also a peak, with more or less pronounced intensity depending on the nature of the heating cycle (in dry He—DHe or O—DO).

The propylene oxidation to CO_2 during CT run (in propylene–air mixture) resulted in higher G values above 200 °C, indicating the surface reduction in presence of hydrocarbon (in spite of the presence of oxygen in the feed). This statement is supported by data measured in DHe4 and by the decrease of G on reoxidation with oxygen in DO (2) cycle. The surface reduction indicates that propylene oxidation occurs by Mars van Krevelan (redox) mechanism, involving lattice oxygen participation. The rather low propylene conversion (maximum around 35–40% Fig. 6), coupled with surface reduction indicates that the lattice oxygen mobility in the bulk is low in this temperature range and the participation of the lattice oxygen is limited to the surface layer.

As shown in Fig. 6, the onset of the oxidation activity was detected around 130 °C (with very low conversion to CO_2); the conversion to CO_2 increases sharply above 150 °C in good rela-

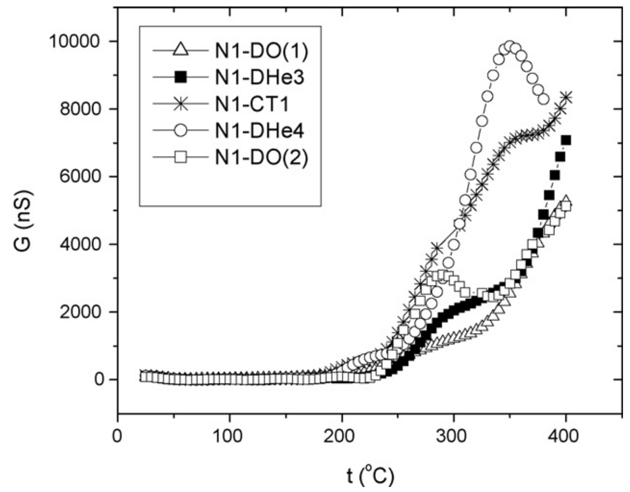

Fig. 5. Temperature dependence of conductance G during heating in various atmospheres.

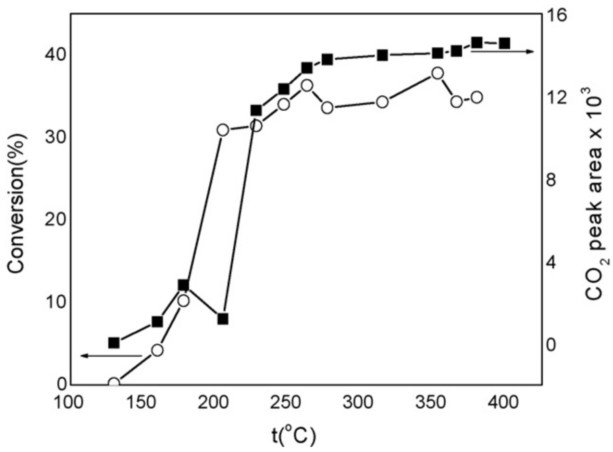

Fig. 6. Catalytic activity in propylene combustion (C_3H_6:air = 1:22, τ = 1.2 s) for N1 sample.

tion with the increase of electronic conductivity around this temperature (see Fig. 5, CT run).

Better catalytic performances are expected by using higher O_2/hydrocarbon ratios, as reported by other authors, good activities in total oxidation of VOC were obtained for $LaCoO_3$ in the case of reach-in-oxygen feeds (e.g.O_2/VOC as 100/1).[9]

5. Conclusions

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

In all cases the dried gels obtained were amorphous and presented the characteristic IR vibration bands assigned to the reagents used in the reaction.

The thermal decomposition of the dried gels occurs stepwise upon heating to 400 °C for nitrate-based or 500 °C for acetate-based precursors, respectively, with a major exothermal effect at about 340 °C.

Different crystalline phases were obtained by thermal treatment, depending on the starting composition of the sol–gel solutions.

Pure perovskite $LaCoO_3$ phase is formed after heating at 600 °C for samples prepared starting with nitrates (N1, N2) and for A1 (prepared with acetates), while sample A2 is a mixture of La_2O_3, $La(OH)_3$, Co_3O_4 and $LaCoO_3$ in low amount. This behaviour is under further investigation.

The choice of the precursor influences also the morphology of the powder.

Some preliminary electrical and catalytic investigations performed on the N1 powder indicated that up to 400 °C the sample behaves as a n-type semiconductor. Propylene deep oxidation occurs by Mars van Krevelen (redox) mechanism. Based on conductivity data, the lattice oxygen mobility is relatively low up to 400 °C.

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