Decomposition study of Ni–La–Mg–O precursors using thermal analysis

Robson Santana Lima · Arnaud Victor dos Santos · Fabiano Vargas Pereira · Marluce Oliveira da Guarda Souza

Abstract The thermal decomposition process of La_2O_3/MgO (La/Mg = 2, 1 and 0.5) supported nickel (15% mass/mass Ni) precursor was investigated. Thermal analysis results show distinct processes of decomposition of the samples in accordance with the composition. The mass loss at higher temperature is associated to distinct stages of decomposition of lanthanum precursors. The thermal analysis results agree with the FTIR spectra showing change in the band corresponding to carbonates and nitrates species. XRD results also confirmed the precursor's decomposition. It can be concluded that the thermal decomposition of La_2O_3–MgO-nickel precursor depends on the La/Mg ratio and of the residual species.

Keywords Lanthanum and magnesium oxide · Catalyst preparation · Thermal decomposition

Introduction

The properties of rare earth elements and their characteristics have been largely studied, aiming the use of these materials as supports in several reactions [1–5]. Several studies quote the use of lanthanum oxide either as catalytic support or as dopant in several reactions for hydrogen generation, such as natural gas and ethanol steam reforming, partial oxidation of natural gas, and methane reforming using carbon dioxide [1, 5]. The characteristics of lanthanum oxides may be altered by adding alkali metal oxides in small quantities or in amounts enough to obtain mixed systems. Among the alkaline earth oxides used to obtain mixed systems with lanthanum oxide, magnesium oxide [2, 3] associated to systems mainly based on lanthanum, magnesium, and nickel have been recently studied regarding their use in natural gas reforming reactions [2].

New formulations are proposed in some studies concerning the development of nickel based catalysts, supported on mixed lanthanum and magnesium oxides; assessing the effect the obtained system has on the properties. It is known that the systems based on Ni/MgO and Ni/La_2O_3 may produce a solid solution ($Ni_{1-x}Mg_xO$) and a phase of perovskite kind ($LaNiO_3$), respectively, among other phases, after the precursor's thermal decomposition [3]. Meanwhile, the nature of phases and the interaction of NiO with the respective support vary according to the precursor composition [3].

In this study, thermal decomposition was studied for precursors based on: Nickel (15% mass/mass), lanthanum and magnesium, varying the La/Mg ratio. Precursors were obtained by a co-precipitation carried out from the metallic nitrate solutions, using carbonate and/or potassium hydroxide solutions as precipitants.

Experimental

Samples preparation

The mixed solids based in nickel (15% mass/mass), lanthanum, and magnesium (La/Mg (molar) = 2, 1, and 0.5) were prepared by precipitation method from nickel, lanthanum, and magnesium nitrate solutions, using a potassium hydroxide solution and potassium carbonate solution,

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with an excess of 10%. During the experiments, the potassium and carbonate hydroxide solution was slowly added to the precursor salt solution under stirring at 60–65 °C and pH 10–10.5. The suspension obtained was aged at 60–65 °C for 2 h. The solid was then separated by filtration, rinsed with water and filtrated. The gel was then dried at 80 °C for 24 h and calcined under air at 600 °C, for 4 h. Solids without lanthanum and/or magnesium were also obtained for comparison, using only potassium hydroxide solution as precipitating agent. Sample obtained: NL—catalyst precursor based on nickel and lanthanum hydroxide; NM—catalyst precursor based on nickel and magnesium hydroxide. NLM, N2LM, NL2M—catalyst precursor based on nickel and lanthanum and magnesium hydroxide, La/Mg ratio 1/1; 2/1 and 1/2, respectively. Samples calcined: NLO—catalyst based on nickel and lanthanum oxide; NMO—catalyst based on nickel and magnesium oxide. NLMO, N2LMO, NL2MO—catalyst based on nickel and lanthanum and magnesium oxide, La/Mg ratio 1/1; 2/1 and 1/2, respectively.

Samples characterization

The nickel content in solids was determined by elemental analysis, performed in a scanning electron microscope JEOL equipped with an EDS detection system. The crystalline phases were identified by X-ray powder diffraction, carried out in a Shimadzu model XRD 6000, using Cu K_α radiation generated at 40 kV and 30 mA. The FTIR spectra were obtained using a Varian Cary 5G equipment. Thermal analysis (TG/DTG) experiments were performed in air (30 mL min^{-1}) over the temperature range 25–1,000 °C, at heating rate 10 °C min^{-1} using a SHIMADZU TGA-50. The sample mass was 20 mg. The DSC experiments were performed in air (30 ml min^{-1}) over the temperature range 25–550 °C using a SHIMADZU DSC 50.

Results and discussion

From the elemental analysis it was found that solids with around 15% (mass/mass) of nickel were obtained.

Figure 1 and Table 1 show the results obtained from DSC method to the precursors. By analyzing the results, it can be observed that the curves related to the NL sample show endothermic events at temperatures lower than 100 °C, followed by mass loss observed through TG and DTG curves at the same temperature range (Fig. 2a, b), which can be associated to elimination of physisorbed species. Endothermic events with maximum at 272 and 328 °C are observed through DSC curve (Fig. 1). The DTG curve shows event of mass loss with maximum at 270 °C corresponding to the one observed through DSC. The
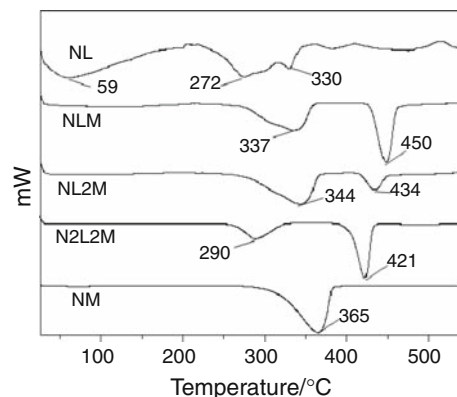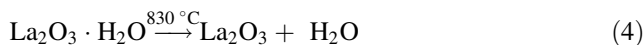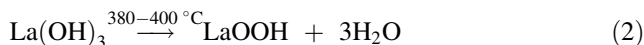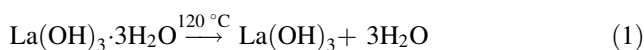
Fig. 1 DSC precursor results

Table 1 Variation of the energy involved in each occurrence of the catalysts precursors' decomposition

	Temperature/°C	ΔH/kJ g^{-1}	Temperature/°C	ΔH/kJ g^{-1}
NL	276.65	−82.20	328.75	−10.48
N2LM	289.81	−116.23	424.05	−227.82
NLM	336.62	−210.27	448.84	−150.35
NL2 M	343.72	−359.20	435.36	−70.88
NM	365.37	−1107.44	–	–

ΔH involved in each mass loss event

thermal change observed at 328 °C probably corresponds to progressive mass loss shown by TG and DTG curves at the same temperature range. The events mentioned can be related to the precursor to the first steps of lanthanum hydroxide, La(OH)$_3$, which is the prevailing phase at NL system according to X rays diffractograms (Fig. 3a). The FTIR spectrum of NL sample shows band at 3,606 cm^{-1} attributed to OH groups (Fig. 4a). It is well known from the literature that the thermal decomposition of lanthanum hydroxide takes place in two or more different stages, represented by Eqs. 1–4 [1, 6, 7].

$$\text{La(OH)}_3 \cdot 3\text{H}_2\text{O} \xrightarrow{120\,°\text{C}} \text{La(OH)}_3 + 3\text{H}_2\text{O} \tag{1}$$

$$\text{La(OH)}_3 \xrightarrow{380-400\,°\text{C}} \text{LaOOH} + 3\text{H}_2\text{O} \tag{2}$$

$$2\text{LaOOH} \xrightarrow{580\,°\text{C}} \text{La}_2\text{O}_3 \cdot \text{H}_2\text{O} \tag{3}$$

$$\text{La}_2\text{O}_3 \cdot \text{H}_2\text{O} \xrightarrow{830\,°\text{C}} \text{La}_2\text{O}_3 + \text{H}_2\text{O} \tag{4}$$

The steps as well as the corresponding decomposition temperatures of lanthanum hydroxide can be influenced by the preparation method and presence of other ions [1, 6, 7].
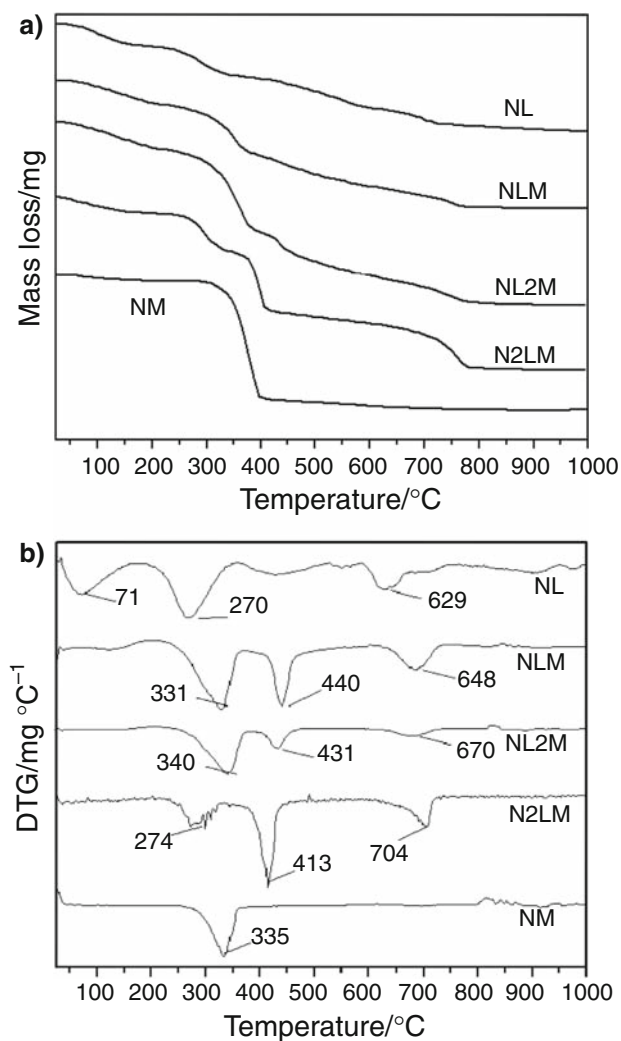
Fig. 2 **a** TG and **b** DTG precursor results

* La(OH)$_3$ † Mg(OH)$_2$ ◊La$_2$O$_2$CO$_3$

■LaOOH;○ La$_2$O$_3$;♦ La$_2$O$_2$CO$_3$; ▼ La(OH)$_3$; □ LaNiO$_3$;
▲La(NiO$_3$)$_3$;● MgO; △ MgO$_4$; ▽ Mg(OH)$_2$; ◊MgO.4NiO.6O

Fig. 3 DRX results: **a** precursors, **b** catalysts. JPSDC: Mg(OH)2 86-0441; La(OH)3 83-2034; La2O2CO3 25-0424; LaOOH 77-2349; La2O3 83-1355; La(NO3)3 84-1112; LaNiO3 88-0633; MgO 78-0430; MgO.4NiO.6O 34-0410

The mass loss observed in DTG curves at 626 °C for the nickel lanthanum system can be related to the decomposition of additional residual nitrate species in samples (Fig. 3) [8]. The presence of NO$_3^-$ species is observed through NL sample FTIR spectrum (Fig. 4a) with corresponding bands at 833 and 1,052 cm^{-1}, besides a wide band with several signals at the range of 1,200–1,650 cm^{-1} [1]. Calcination leads to change in bands position and intensity as observed in NLO sample spectrum (Fig. 4b) indicating that during the heating there are changes in the nitrate species.

A single peak can be observed in the curve corresponding to the NM sample, which is related to the thermal decomposition of magnesium hydroxide at 365 °C, the prevailing phase observed through DRX [3].

DSC curves associated to precursors of mixed catalysts (Fig. 1) show two peaks for decomposition of samples at temperatures higher than the ones observed in the nickel–lanthanum system with higher energy (Table 1). In the first
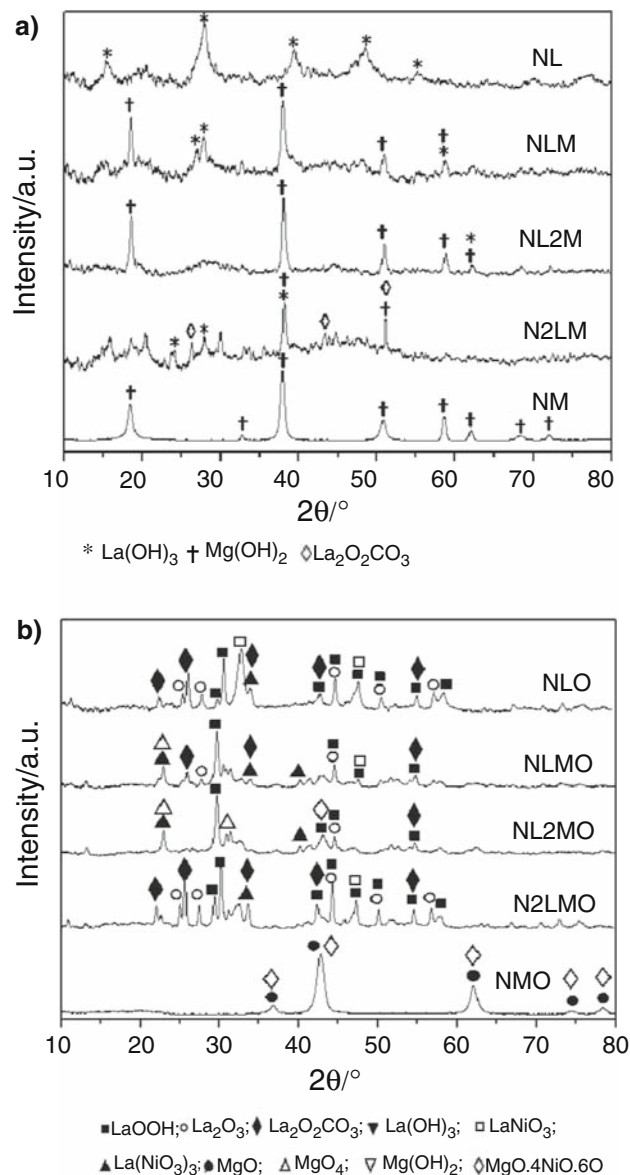
occurrence observed, temperature and energy increased together with the magnesium concentration in samples (Table 1) indicating that, in these precursors, the species formed were more difficult to be decomposed. Meanwhile, the energy involved in the decomposition of mixed precursors is lower than the energy necessary to decompose nickel–magnesium hydroxide. These results can be associated to the phases formed observed by X-ray diffraction before and after calcination of different samples (Fig. 3a, b). It can be observed that the increase in magnesium amount alters the precursors' diffractograms profile so that NL2M sample profile is the closest one to NM sample
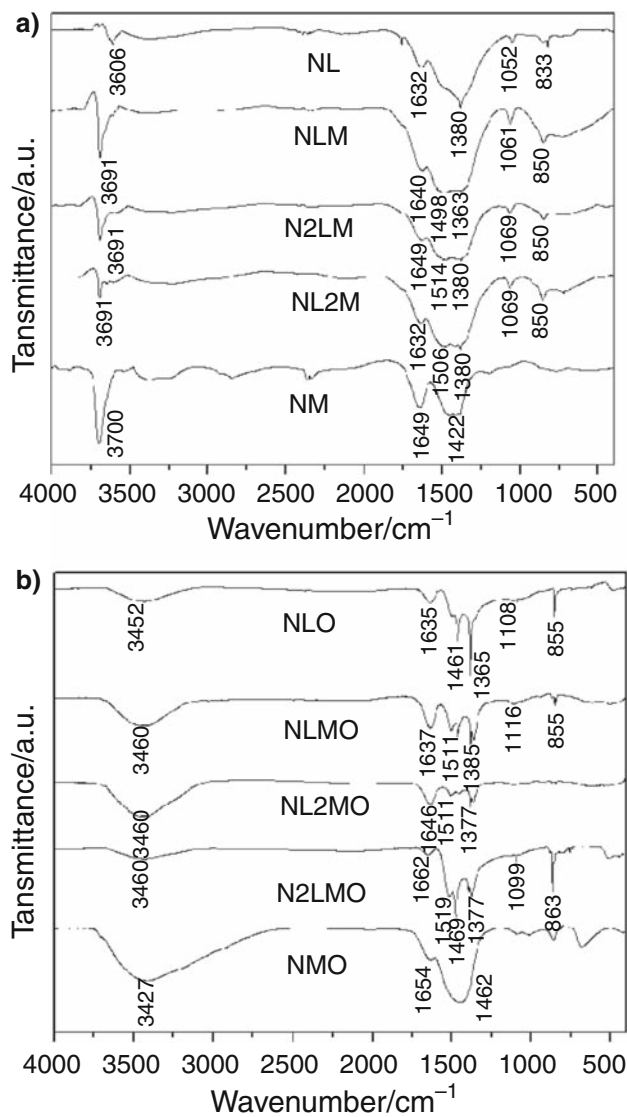
Fig. 4 FTIR results: **a** precursors, **b** catalysts

Table 2 Carbon content in samples of mixed catalyst precursors (Ni–La–Mg–O), before and after calcination

Precursors		Catalysts	
Sample	Carbon content/%	Sample	Carbon content/%
NL	0.67	NLO	1.39
NLM	2.61	NLMO	2.09
N2LM	3.18	N2LMO	1.93
NL2 M	2.31	NL2MO	1.60
NM	0.40	NMO	1.35

and carbonate species in the precursors and the modifications after calcination were also confirmed by X-ray diffraction (Fig. 3a, b). FTIR spectra obtained before and after calcination of precursors showed modifications on the bands related to carbonate and nitrate species (1,200–1,650 cm^{-1} range, mainly) (Fig. 4a, b). Narrower bands are observed in the region of 1,200–1,650 cm^{-1} in solid spectra obtained after calcination, including the samples obtained without the use of carbonate, NLO, and NMO, related to the way the species are linked in the crystal [9, 10]. Those results are explained considering that the carbonate species in the calcined material can be originated by three different ways: the permanence of carbonate even after calcination of mixed oxides, the adsorption of CO_2 from the atmosphere from the bonding with O^{2-} and OH^- like types and as impurity of reactants [1, 10]. The partial decomposition of carbonate species in the mixed systems and the adsorption of CO_2 from the atmosphere in NLO and NMO systems were confirmed by the carbon analyses, obtained before and after calcination of precursors, observing that calcination led to diminishing of the carbon concentration (Table 2).

The shifting of mass loss events, observed at 626 °C in the NL sample curve to higher temperatures in the mixed precursors' curves can be a consequence of the side decomposition of nitrate and carbonate species. Some species of lanthanum carbonate are decomposed according to steps I and II, at temperatures ranging from 420 to 550 °C, and according to III with temperatures ranging from 670 to 710 °C [10].

$$La_2(CO_3)_3 \xrightarrow{I} La_2O(CO_3)_2 \xrightarrow{II} La_2O_2CO_3 \xrightarrow{III} La_2O_3$$
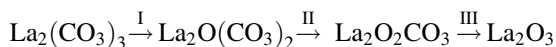
Conclusions

It can be concluded that even when the precursors of mixed catalysts with nickel, lanthanum, and magnesium are complex systems, the recognition of some thermal properties was possible, which is necessary to facilitate deeper studies about catalysis. The influence of La/Mg system molar ratio has on the decomposition process is highlighted

(Fig. 3a). In mixed systems, obtained after calcination of precursors, phases related to lanthanum oxide (La$_2$O$_3$) and perovskite (LaNiO$_3$) were formed (Fig. 3b). However, the peak intensity corresponding to perovskite was lower than the one observed with the nickel/lanthanum oxide system, probably due to interactions between nickel and magnesium oxides (Fig. 3b). The X ray diffractogram (Fig. 3b) of nickel/magnesium oxide is characteristic of the solid solution (Ni$_{1-x}$Mg$_x$O) [3].

The thermal effects observed occurred together with a mass loss corresponding to the decomposition of several species of the mixed precursors' components of lanthanum, nickel, and magnesium, which include carbonate species as well as the residual hydroxyls and nitrate from the starting salts, once potassium carbonate was used in the synthesis of the precursors of mixed oxides. The presence of nitrate

in this system, the energy involved increases in events taking place at lower temperatures. Moreover, the decomposition process is influenced by the phase composition of the catalysts obtained through calcination.

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