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LANTHANUM NITRATE DECOMPOSITION BY BOTH TEMPERATURE PROGRAMMED HEATING AND CITRATE GEL COMBUSTION

Comparative study

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Thermal decomposition of lanthanum nitrate to lanthanum oxide was carried out by both temperature programmed heating (TPH) and citrate-gel combustion. The temperature programmed heating was carried out under flow of oxidizing (air), neutral (nitrogen) and reducing (25 vol.% hydrogen+argone mixture) gases, and the processes were controlled by simultaneous thermogravimetry and differential thermal analysis. It was shown that hydrogen atmosphere helps to reduce temperatures of all decomposition steps. The results of TPH were utilized to check the nature of residues in the products of lanthanum nitrate–to-oxide conversion performed via citrate-gel combustion technique.

Keywords: *anhydrous lanthanum nitrate, lanthanum oxide, sol–gel preparation, temperature programmed decomposition, thermal properties*

Introduction

Lanthanum oxide has numerous applications in various fields of industry: as a component of catalysts in automobile exhaust-gas converters [1, 2], as a catalyst support [2–4], particularly in methanol production [4] and as a component of ceramics [5], and its synthesis in a form of fine dispersion presents now an exciting research area. A way to produce pure La_2O_3 on a small (laboratory) scale may be the thermal decomposition of either nitrates, or other thermally degradable lanthanum compounds, like acetylacetonates [6] or other complex compounds with organic ligands [7, 8]. The early thermogravimetric investigations of lanthanum nitrate-hexahydrate decomposition have been published in the period 1956–60 by Wendlandt *et al.* [9–11]. Significantly later, in 1977, Gobichon *et al.* studied thermal decomposition of $La(NO_3)_3 \cdot 6H_2O$, $La(OH)_2NO_3 \cdot H_2O$ and $La(NO_3)_3$ under flow of both moist air and nitrogen [12].

Recently, gel combustion technique, which may be used for rapid synthesis on large scale, was developed to synthesize either simple or mixed oxide products. For instance, Xuchen *et al.* [13], produced the O_2–sensing $LaNiO_3$ film via citrate-gel combustion technique. Jugovic *et al.* [14] synthesized intercalate compound $LiMn_2O_4$ by glycine-nitrate method. Jiao *et al.* [15] prepared the electrochromic NiO thin film by a slow combustion of gel obtained by heating the solution of nickel chloride and citric acid in butanol. Most recently, Wang *et al.* synthesized $LaFeO_3$ perovskite by glycine-combustion method [16].

In this work, lanthanum nitrate decomposition to La_2O_3 was studied by TG/DTA methods under flow of various gases, in order to compare the already known decomposition steps in oxidizing (air) and neutral (nitrogen) atmosphere [9–11], to the ones under reducing (25% H_2 in argone) atmosphere, considered here for the first time. In view of the results of these measurements, the recommendations were derived how to obtain pure La_2O_3 via gel-combustion technique at minimum overheating.

Experimental

Preparation of anhydrous lanthanum nitrate for thermal amalysis

Analytical grade Merck $La(NO_3)_3 \cdot 6H_2O$ was dried by heating at 200°C during 2 h under flow of argone. As already known [12], the dehydration of lanthanum nitrate-hydrates in an inert atmosphere becomes complete after a slow heating up to 180°C, while anhydrous salt is thermally stable up to 250°C. Anhydrous salt was then transferred into thermobalance, and subjected to simultaneous thermogravimetry and differential thermal analysis. The flow of pure nitrogen and

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25 vol% H_2+Ar mixture (the purity of gases was 99.995 vol%) was provided using high-pressure tanks, while the flow of ambiental air was provided by means of gas compressor.

Preparation of La_2O_3 by gel combustion procedure

The synthesis of La_2O_3 via gel-combustion procedure started with the preparation of a solution of La-nitrate and citric acid. The equation of combustion of citric acid is: $2C_6H_8O_7+9O_2=12CO_2+8H_2O$. Assuming that during fast combustion nitrate ion presents the exclusive source of oxygen, to satisfy the stoichiometry of the reaction, 3.6 moles of nitrate groups (i.e. 1.2 mol of $La(NO_3)_3$) should be used against 1 mol of citric acid, as published elsewhere [17].

Lanthanum nitrate and citric acid were dissolved in water in an above mentioned mole ratio. The solution was heated on water bath in an open glass beaker, until a homogeneous and transparent gel obtained on the bottom. The heating was then continued in an oven. Before the temperature of 300°C was achieved, the gel self-ignited, and an ignition front propagated fastly through the whole mass, leaving a white flaky product in the beaker. This product was then analysed by TG/DTA in both reducing and air atmosphere, and by X-ray diffraction.

Instruments

Simultaneous thermogravimetric and differential thermal analysis was performed by TA SDT 2060 device.

The X-ray diffractograms were taken by Phillips, PW 1710 device using Cu LFF line of wavelength 0.154 nm.

Results and discussion

Figure 1 presents the TG curves of anhydrous lanthanum nitrate decomposition under nitrogen, air and (25% H_2+Ar) atmospheres, while Fig. 2 presents the first derivative of the TG curves, recorded under nitrogen and reducing atmospheres. These diagrams are discussed in the following sections.

Thermal analysis of anhydrous lanthanum nitrate decomposition under flow of nitrogen and air

The dehydrated $La(NO_3)_3$ is very hygroscopic, and thus it readsorbed some water during introduction into TG/DTA device. The differences in initial amount of absorbed water is the only reason of the scatter in final mass readings in Fig. 1.

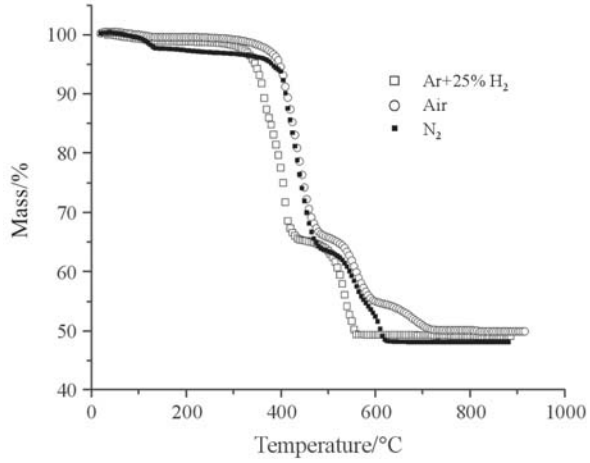

Fig. 1 TG curves of dehydrated lanthanum nitrate in different atmospheres, at heating rate 15°C min^{-1} and at gas flow rate 90 mL min^{-1}

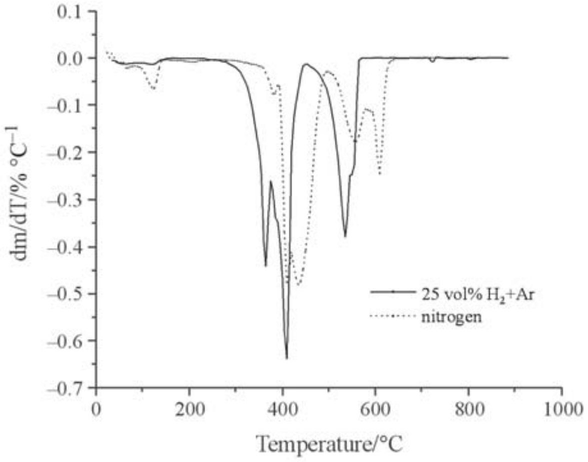

Fig. 2 DTG curves of thermal decomposition of $La(NO_3)_3$ in nitrogen and 25% H_2+Ar; heating rate 15°C min^{-1}, gas flow rate 90 mL min^{-1}

The curves recorded under flow of nitrogen confirm the three main decomposition steps reported elsewhere [10]:

(I) $La(NO_3)_3 \rightarrow LaONO_3+(N_2O_5)$[**]
(350 to 470°C)

(II) $3LaONO_3 \rightarrow La_3O_4NO_3+(N_2O_5)$
(470 to approx. 570°C)

(III) $2La_3O_4NO_3 \rightarrow 3La_2O_3+(N_2O_5)$
(570 to 610°C)

The relative mass loss corresponding to the first step, amounting to 33.5%, agrees well with the value 33. 3%, calculated on the basis of chemical formulae.

[**] Here the formula in parentheses symbolizes the equilibrium mixture of gaseous products of thermal decomposition of N_2O_5 [18].

Under air flow, the step (III) is accompanied by decomposition of lanthanum oxy-carbonate:

$$\text{(III')}\ La_2O_2CO_3 \rightarrow La_2O_3 + CO_2$$
(between 600 and 700°C)

$La_2O_2CO_3$ appears as an intermediate compound in early stages of the step (III), as a consequence of high reactivity of La_2O_3 with atmospheric CO_2 [19], supported by elevated temperature.

Thermal analysis of anhydrous lanthanum nitrate decomposition under flow of 25% H_2+Ar

In reducing atmosphere, all the decomposition steps (I–III) are shifted more than 60°C toward lower temperatures, and proceed at somewhat different route in comparison to the ones observed in nitrogen and air. The main reason for both of these features is the formation of water as a new reaction product. Namely, according to the mass-spectrometric investigations, the products of nitrate decomposition in nitrogen and air atmospheres are N_2O_3, NO_2, NO, N_2O and O_2 [18]. Since the free energy of formation of each of nitrogen oxide is small and positive, and free energy of water formation presents a very high negative value (–294.3 kJ mol^{-1}) [20], in a hydrogen atmosphere, most probably pure nitrogen and water are the final reduction products, according to the reaction: $N_2O_5+5H_2 \rightarrow N_2+5H_2O$. Free energy of water formation helps that the reactants surmount the activation barrier of decomposition of oxynitrates, shifting all decomposition steps toward lower temperatures. An additional consequence of water formation is an obvious splitting of the step I, (observed under both nitrogen and air flow in the temperature range 350–470°C as a unique step), into two distinguishable parts: that taking place between 300 and 380°C and that taking place between 380 and 420°C, as visible very well in Fig. 2. Since in the first temperature range the existence of $LaOH(NO_3)_2$ is allowed [12], we assume that in this temperature range $La(NO_3)_3$ decomposition is accompanied by decomposition of $LaOH(NO_3)_2$, which appears through the equilibrium $La(NO_3)_3+H_2O \leftrightarrow LaOH(NO_3)_2+HNO_3$. Under both nitrogen and air flow, the first step is barely visible, and in this case $LaOH(NO_3)_2$ may originate exclusively from hexahydrate dehydration. Further to this, reduction atmosphere prevents the formation of intermediate compound $La_3O_4NO_3$, since the corresponding decomposition step is practically absent in the TG curve. Thus, the step II in reducing atmosphere leads immediately to La_2O_3, according to the equation: $2LaONO_3 \rightarrow La_2O_3+(N_2O_5)$ and consequently, the whole decomposition procedure ends at only 550°C. Figure 3 shows an additional consequence of the use of reducing atmosphere. Namely, while in nitrogen and air all the decomposition steps are endothermic, under hydrogen atmosphere, thanks to a very negative value of enthalpy of water formation, all steps become exothermic.

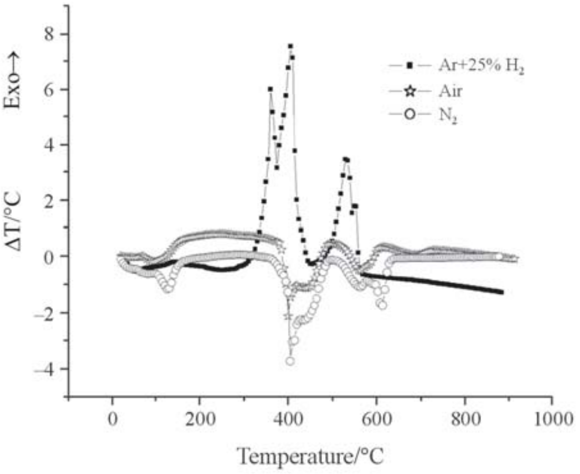

Fig. 3 The DTA curves of dehydrated lanthanum nitrate, recorded simultaneously with TG curves shown in Fig. 1. The gas flow rate was 90 mL min^{-1}, heating rate 15°C min^{-1}

Thermogravimetric analysis of lanthanum oxide obtained by gel-combustion procedure

As described in the experimental section, after combustion of gelled citric acid+lanthanum nitrate complex, the white flacky product was obtained, which is expected to be pure La_2O_3. In order to test the completeness of nitrate→oxide conversion, the three randomly taken samples of the gel-combustion product were analysed by TG, two ones in reducing (25% H_2+Ar) atmosphere, and one in air.

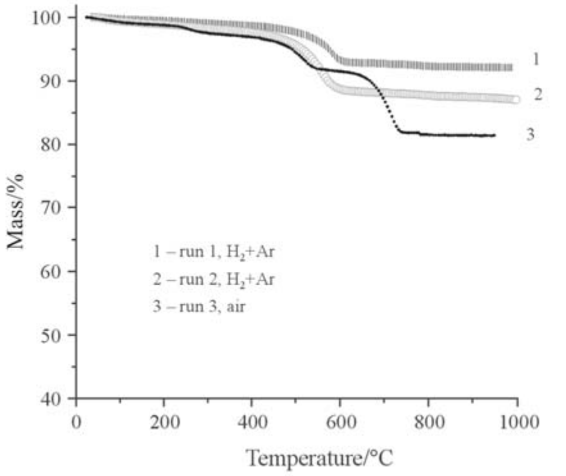

Fig. 4 The TG curves of product obtained by lanthanum nitrate/citric acid gel-combustion. Three randomly taken samples were analysed (runs 1–3). Gas flow rate 90 mL min^{-1}, heating rate 15°C min^{-1}

Figure 4 evidences that the samples of the product of gel-combustion, undervent to TG analysis, display an additional mass loss during heating. Thus one may conclude that La_2O_3 obtained by citrate-gel combustion contains impurities. The mass loss is very slow up to 450°C, and, probably one deals in this temperature range with the deliberation of adsorbed and absorbed water and with hydroxide decomposition. More pronounced mass loss, amounting to 5–8% of the initial mass, commences at nearly 500°C in all atmospheres, and, regarding the Fig. 1, may be attributed to the decomposition of residual $LaONO_3$. Since, the TG curves 1 and 2 in Fig. 4 indicate that the decomposition process does not complete up to 550°C, (unlikely to the TG curves in Fig. 1 for reducing atmosphere), but exceeds to approx. 600°C, one may conclude that not only $LaONO_3$, but also other impurities are present in the gel-combustion product. The comparison of TG curves in Fig. 4 to those in Fig. 1 allow to assume that the presence of $La_2O_2CO_3$ may be responsible for the enlargement of limiting decomposition temperature up to 600°C in reducing atmosphere. The appearance of $La_2O_2CO_3$ is not surprising, having in mind the facts that during gel-combustion CO_2 is evolved in large amounts, and lanthanum oxide is reactive with CO_2 [19]. Since H_2+Ar mixture, used as reducing atmosphere, does not contain CO_2, it is reasonable to expect that in this atmosphere the equilibrium $La_2O_2CO_3 \leftrightarrow La_2O_3+CO_2$ is shifted to right side, and thus the decomposition of residual $La_2O_2CO_3$ may be finished up to 600°C. However, when air flow was used (run 3 in Fig. 4), the presence of CO_2 turns the decomposition equilibrium to left, and consequently, even 700°C is required to complete $La_2O_2CO_3$ decomposition.

Before and after the temperature programmed heating was performed, the product of gel combustion was investigated by X-ray diffraction too, and the results are shown in Fig. 5. As one can see, the diffractogram of original product shows quite low relative intensity, and its noise-like character indicates a completely amorphous phase. After annealing up to 900°C (in reducing atmosphere) at a heating rate 15°C min^{-1}, a diffractogram was registered which corresponds to ordered La_2O_3 (ASTM table 05-0602) indicating that purification by heating leads also to particle crystallization, accompanied by increase in mean particle diameter.

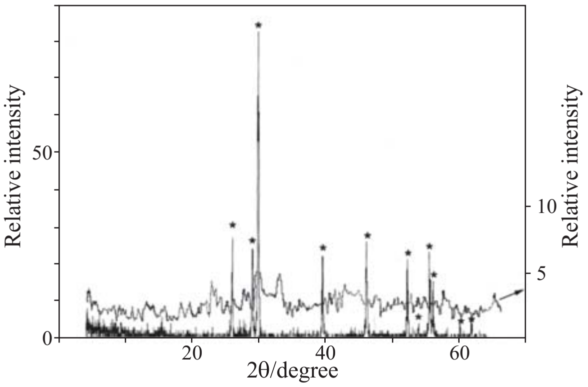

Fig. 5 The X-ray diffractograms of La_2O_3 produced by citrate gel combustion, before (upper random line, right-side intensity axis), and after heating in reducing atmosphere up to 900°C at a heating rate 15°C min^{-1} Asterix denotes the line of La_2O_3

Conclusions

By comparing thermogravimetric curves of decomposition of anhydrous lanthanum nitrate recorded under flow of air and nitrogen, to the one recorded under flow or 25% H_2+Ar, it has been concluded that the appearance of water among reaction products when reducing atmosphere is used, modifies the decomposition route registered in other two atmospheres, emphasizing the appearance of $La(OH)(NO_3)_2$, and suppressing the appearance of $La_3O_4NO_3$ intermediates. Reducing atmosphere also enables the decomposition to be completed at the lowest temperature of only 550°C. The last finding was attributed to the decrease of activation energy of decomposition on account of free energy of formation of water. The study of $La(NO_3)_3$ decomposition under controlled both temperature and atmosphere, enabled to estimate thermogravimetrically that $LaONO_3$ and $La_2O_2CO_3$ present the impurities in lanthanum oxide obtained by lanthanum nitrate/citric acid gel combustion. An additional heating of this product up to 600°C in a CO_2-free atmosphere may be recommended in order to purify La_2O_3 and keep simultaneously the lowest degree of its crystallinity. The purification by heating in air is also possible, but minimum temperature of 700°C is required.

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