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Combustion synthesis of lanthanum chromite starting from water solutions: Investigation of process mechanism by DTA–TGA–MS

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Abstract

The mechanism of combustion synthesis of lanthanum chromite was investigated by carrying out simultaneous differential thermal analysis (DTA), thermal-gravimetric analysis (TGA) and quadrupole mass spectrometry measurements (MS). The whole process was found to involve several phenomena: urea and nitrates thermal decomposition, exothermal reactions occurring directly between nitrates and urea as well as between their decomposition products, final reaction between solid oxides. In order to better understand the complex calorimetric, thermal-gravimetric and mass spectrometric curves, the behaviour on heating of each single reagent as well as that of binary mixtures, made by combining urea with each single nitrate, were also studied. Combustion synthesis was performed either under an oxidizing atmosphere or under an inert one. Chemical reactions possibly occurring during this combustion synthesis have been proposed on the basis of MS analysis of gaseous reaction products. The effect of using an excess of sacrificial fuel jointly with the addition of ammonium nitrate was also investigated.

Keywords: Combustion synthesis; $LaCrO_3$; Perovskites; Powders-chemical preparation; Reaction mechanism

1. Introduction

Since the preparation of α-alumina foam by rapidly heating a solution of aluminium nitrate and urea,[1] quite a number of advanced materials have been prepared by means of combustion synthesis.[2] For example, a variety of useful oxides such as yttria,[3,4] ceria,[4,5] zirconia,[4,6,7] zinc oxide,[8,9] iron oxide,[10] thoria,[11] aluminates,[12–15] chromites,[16–19] ferrites,[20,21] manganites,[19,22] titanates[23,24] etc. has been obtained using this technique.

Briefly, combustion synthesis consists of bringing an aqueous solution, containing suitable metal salts (nitrates are generally preferred because of their good solubility in water) and a proper organic fuel, to temperatures in the range of 400–600 °C. The mixture starts boiling, then it ignites and an exothermal, self-sustaining and very fast chemical reaction takes off, resulting in a dry, usually crystalline, fine oxide powder.

A key feature of this technique is that the heat required to drive the synthesis is provided for the main part by an exothermal reaction occurring among the reagents, thus greatly reducing the amount of heat that has to be supplied by an external source. Actually, metal nitrates can also be decomposed by simple calcination into metal oxides, upon heating to or above their decomposition temperature; afterwards these oxides can further react together giving new substances. But, in this case, a constant external heat supply is necessary, to maintain the system at the high temperature required to accomplish the appropriate reaction. On the contrary, the combination of nitrates with a sacrificial fuel causes the ignition of this mixture of precursors at a rather low temperature as well as the advance of an exothermal reaction, that provides itself the heat necessary for the synthesis. In this way the system is not forced to stay at high temperature for a long period of time, thus preventing particles sintering.

In addition, as the reagents are mixed in an aqueous solution, this method enables a good chemical homogeneity of the system, which leads to a nearly instantaneous reaction.

Thus, combustion synthesis provides an interesting alternative to other elaborate techniques because it offers several attractive advantages such as: simplicity of

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experimental set-up; surprisingly short time between the preparation of reactants and the availability of the final product; cheapness due to energy saving.

If on one hand the combustion synthesis is an efficient, quick and straightforward method for the preparation of oxide materials, on the other hand the mechanism of the process in terms of reactions involved is quite complex. Besides, it has been shown that the properties of the resulting oxide powders (crystalline or amorphous structure, crystallite size, purity, surface area, particle clustering and agglomeration, etc.) strongly depend on the processing parameters adopted.[25]

Most of previous investigations reported in the literature dealt with the properties of final products and were aimed at evaluating the influence exerted by the composition of the reactant mixture on both phase composition and microstructure of the oxides obtained. For example, product characteristics were observed to depend on the kind of sacrificial fuel used[12,13,24] as well as on the adoption as precursors of acetates instead of nitrates;[13] these characteristics were also found to change with both the nitrates/fuel ratio and the concentration of precursors in the water solution.[3,5,16]

Despite these extensive investigations, the mechanism of the combustion synthesis is still not well understood, probably owing to the short synthesis times and the great number of parameters that influence the process. At any rate its knowledge entails great importance in order to control the characteristics of the final products. Three main possible mechanisms, which differ in kind and succession of chemical reactions involved in this complex process, were expounded in the literature. Kingsley et al.[1] suggested that during the first step of combustion synthesis the thermal decomposition of urea and aluminium nitrate occur simultaneously. Urea decomposes initially to biuret and ammonia and, at higher temperatures, to cyanic acid (HCNO) trimer, while aluminium nitrate decomposes to amorphous alumina and nitrogen oxide. According to those authors, afterwards, final gas phase reactions between combustible species (like ammonia and cyanic acid) and oxides of nitrogen occur, causing the appearance of a flame. Li et al.[12] and Chandramouli et al.[11] also support this theory. On the contrary, Segadaes et al.[8,15,23] suggested that the overall combustion reaction could be dismembered into partial reactions of thermodynamic significance, among which a combustion reaction between the fuel and the oxygen produced in the decomposition of the nitrates supplied the heat needed for the synthesis reaction. Suresh et al.[10] suggested that a direct reaction between a metal nitrate and a sacrificial fuel occurs during combustion synthesis. This last reaction results in the complete fuel consumption and, being exothermal and authocatalytic once ignited, goes to completion without taking any heat from external sources.

Some attempts of investigating, in an indirect way, the progress of combustion synthesis reactions by using calorimetric and thermal-gravimetric techniques are reported in literature,,[11,14,20,24] while experimental results about the gases developed during the advancement of the process are not yet available.

Actually, the combination of calorimetry and thermal-gravimetry with the simultaneous analysis of gaseous reaction products is a powerful tool, suitable for better understanding the mechanism of combustion synthesis.

The present study is just aimed at investigating by all these techniques the chemical reactions occurring during a combustion synthesis. In order to understand the role played by each reagent, in this work, the behaviour on heating of each single reagent was firstly studied; afterwards, the reactions which happen when two, three or more reagents (nitrates and fuel) are mixed together were investigated.

The case of lanthanum chromite ($LaCrO_3$) combustion synthesis was chosen as an example of a quite complex synthesis, involving both nitrate–fuel and oxide–oxide reactions.

In addition, this chromite is known to be suitable for practical applications as a catalyst; recent studies[26] have pointed out its good catalytic activity in diesel soot abatement (activity even better than those displayed by other perovskite catalysts like $LaMnO_3$ and $LaFeO_3$).

Owing to the disagreement found in literature about the role of the atmosphere under which the process is carried out, experimental investigations were performed both in oxidising environment (air) and in inert one (argon).

2. Experimental

The present investigation about combustion synthesis of lanthanum chromite was carried out by using as reagents: lanthanum nitrate hexahydrated (99.9%, Alfa), chromium nitrate nonahydrate (99%, Aldrich), ammonium nitrate (98 + %, Aldrich) and urea (99.5%, Alfa).

Lanthanum and chromium nitrate were used as cationic sources for oxide preparation, urea as sacrificial fuel and ammonium nitrate as an additional substance able to react with urea, thus increasing the heat emission without altering the chemical composition of the final product (combustion aid).

Simultaneous thermal-gravimetric analysis and differential thermal analysis (TGA/DTA Mettler-Toledo) were used for investigating the combustion synthesis process. The gas exiting the TGA/DTA cell was analysed by a quadrupole mass spectrometer (MS Balzers). In this way, sample weight variation, heat involved in the process and gaseous reaction products were simultaneously detected during a temperature scan.

TGA/DTA runs were carried out from 25 to 600 °C with a heating rate of 20 °C/min, as preliminary experiments proved this heating rate suitable for giving at the same time significant and understandable results as regards both TGA and DTA.

However this heating rate (20 °C/min) is quite different from the typical one adopted in combustion synthesis. In fact, during a combustion synthesis a crucible containing the reagent solution is placed into an oven, set at a constant temperature between 400 °C and 600 °C. In this way the heating rate of the precursor mixture is the highest one allowed by the oven temperature and the thermal capacity of the system made of crucible plus solution. In order to make sure that different heating rates do not modify the synthesis product, samples of lanthanum chromite were prepared placing the reagent solution either in an oven kept at 600 °C or in an oven whose temperature was increased from 25 to 600 °C (heating rate of 20 °C/min). X-ray diffraction patterns of samples prepared in these two different conditions (Fig. 1A) show that the product resulting from combustion synthesis does not depend on which of these methods is adopted for the ignition of the reagent mixture. Lanthanum chromite powders, resulting from the combustion reactions, were characterized by transmission electron microscopy (TEM) (Fig. 1B) thus revealing submicrometric (or even nanometric) particle dimensions.

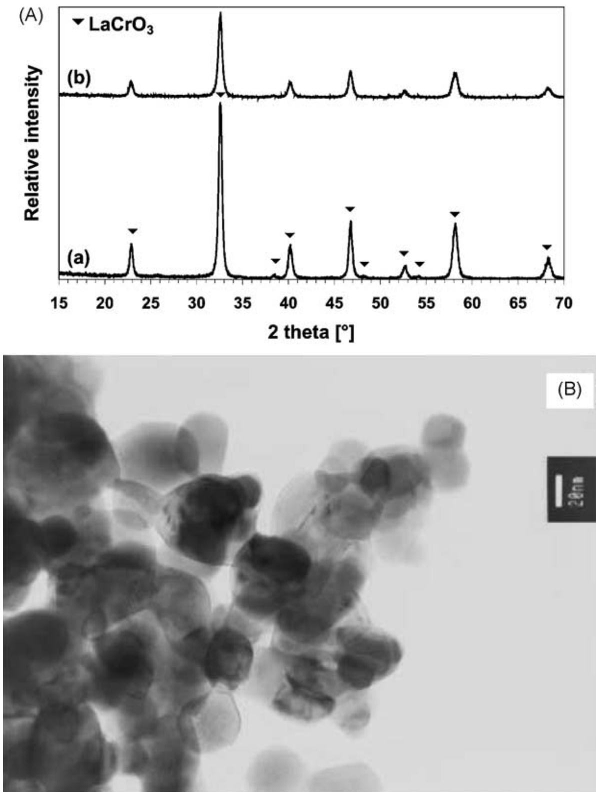

Fig. 1. Characterization of lanthanum chromite powders. (1A) X-ray diffraction: (a) prepared in an oven kept at 600 °C; (b) prepared by heating with 20 °C/min rate. (2B) transmission electron microscopy.

TGA/DTA tests were performed both in air and under argon (gas flow 50 ml/min in every case) in order to investigate the possible influence of the atmosphere on the process.

When argon was used, a preliminary isothermal step (30 min at 25 °C) was included before the heating step, to take away completely the air entered into the calorimetric cell during the insertion of the specimen in the sample holder.

The behaviour on heating of each single reagent (lanthanum nitrate, chromium nitrate, ammonium nitrate and urea) was firstly investigated. To this purpose samples (weighing 10–20 mg) of each raw reagent, put inside a 70 μl alumina crucible, were submitted to a temperature run and analysed by simultaneous TGA–DTA–MS.

Afterwards, the behaviour of binary mixtures, made of a nitrate plus the fuel, was studied. Pairs of reagents (lanthanum nitrate–urea, chromium nitrate–urea, ammonium nitrate–urea) were dissolved in distilled water. An amount of 10–20 mg of these solutions was put inside a 30 μl steel crucible and then dried into an oven at 80 °C for 15 min. Operating with solutions assured a good homogeneity of reagent mixtures, while drying was necessary in order to prevent the evaporation of an excessive amount of water during the calorimetric test. These binary mixtures were submitted to combustion process during a temperature scan in the TGA–DTA–MS equipment. For sample preparation a stoichiometric molar ratio between nitrate and urea was adopted, according to the possible following equations:

$$2\,\mathrm{La(NO_3)_3}+5\,\mathrm{CO(NH_2)_2} \rightarrow \mathrm{La_2O_3}+5\,\mathrm{CO_2}\uparrow+8\,\mathrm{N_2}\uparrow+10\,\mathrm{H_2O}\uparrow \quad (1)$$

$$2\,\mathrm{Cr(NO_3)_3}+5\,\mathrm{CO(NH_2)_2} \rightarrow \mathrm{Cr_2O_3}+5\,\mathrm{CO_2}\uparrow+8\,\mathrm{N_2}\uparrow+10\,\mathrm{H_2O}\uparrow \quad (2)$$

$$3\,\mathrm{NH_4NO_3}+\mathrm{CO(NH_2)_2} \rightarrow \mathrm{CO_2}\uparrow+4\,\mathrm{N_2}\uparrow+8\,\mathrm{H_2O}\uparrow \quad (3)$$

The above stoichiometry results from an oxidizing to reducing valency balance, as suggested by the propellant chemistry and used by the majority of authors.

These exothermal reactions took place very quickly, involving the rapid formation of a rather large quantity of gaseous species. In order to avoid that these gases may drag any amount of solid product when they leave the specimen under analysis, a lid with a little hole was screwed on the crucible containing the sample. In this way the gaseous species left the crucible and were transported by the carrier gas (air or argon) to the mass spectrometer, while the solid product was forced to remain inside the crucible.

Finally, samples prepared by drying solutions containing all the substances needed for the combustion synthesis of lanthanum chromite (lanthanum nitrate–chromium nitrate–urea) were heated in the DTA–TGA–MS equipment. Reagents were mixed according to the stoichiometric ratios needed for the occurrence of the reaction:

$$La(NO_3)_3+Cr(NO_3)_3+5\ CO(NH_2)_2 \rightarrow LaCrO_3 + 5\ CO_2\uparrow + 8\ N_2\uparrow + 10\ H_2O\uparrow \quad (4)$$

To conclude this study, an energized synthesis, with enhanced exothermal character, was also investigated. This can be easily done by adding to the ternary mixture, prepared according to the stoichiometry of Eq. (4), extra amounts of both urea and ammonium nitrate, thus allowing an extra amount of heat to develop following the occurrence of exothermal reaction (3). The practice of adding an excess of fuel[12,15] or both fuel and ammonium nitrate,[19,23] has already been adopted in the preparation, by combustion synthesis, of various mixed oxides. Consequently, in order to counteract a partial urea loss (due to thermal decomposition before mixture ignition) and to provide an extra amount of heat, a further sample was prepared by drying 10-20mg of a solution containing $La(NO)_3\ 6H_2O$, $Cr(NO)_3\ 9H_2O$, NH_4NO_3 and $CO(NH_2)_2$ according to the molar ratio 1:1:3:35/2. In this mixture urea is present in a large excess in order to assure, in spite of its thermal decomposition, the fuel necessary for reactions (3) and (4).

3. Results and discussion

3.1. *TGA–DTA–MS investigation of single reagents*

When a single substance (among those used for combustion synthesis of lanthanum chromite) was submitted to a temperature scan in TGA–DTA–MS equipment only melting and thermal decomposition phenomena were observed. In addition, these substances underwent the same kind of transformation whichever was the atmosphere adopted: oxidizing atmosphere (air) or inert one (argon). This result proves that oxygen present in air does not react with urea (or with nitrates, of course) in the temperature range between 25 °C and 600 °C. Thus, the discussion that follows refers to experiments performed both under oxidizing and inert environments. Anyway, only little differences in onset and peak temperature and in sample weight variation were sometimes observed depending whether DTA end TGA measurements were performed under air or argon flow. At any rate, some differences were expected to occur, because the presence in the instrument furnace of gases with rather different density and thermal conduction (like air and argon) can very likely slightly affect the response of the equipment.

3.1.1. *Lanthanum nitrate*

Fig. 2 (A and B) shows the TGA–DTA curves and the MS curves of gaseous species (detected in the gas ensuing from the TGA–DTA equipment) emitted as a consequence of $La(NO_3)_3\ 6H_2O$ thermal decomposition. The first endothermic peak in DTA thermogram (T_{onset} at about 67 °C, as the average of several experiments) is due to the sample melting, in agreement with the literature.[27] Melting phenomena seems to occur during dehydration, as water was already detected by the mass spectrometer at this temperature.

Concerning the nitrate decomposition, it is possible to single out two different steps: before 325 °C weight losses are associated only with water emissions while after 325 °C weight losses are associated only with NO_2 an O_2 emissions. Then, thermal decomposition of $La(NO_3)_3\ 6H_2O$ happens in two different stages: dehydration to $La(NO_3)_3$ and further decomposition to La_2O_3. The experimental mass loss recorded by TGA measurements up to 325 °C (25%, in average), agrees well with the theoretical value of 24.9% corresponding to complete dehydration to $La(NO_3)_3$. Similarly, the weight loss observed at 600 °C (60%) agrees well with the theoretical value of 62.3% corresponding to a complete decomposition to La_2O_3.

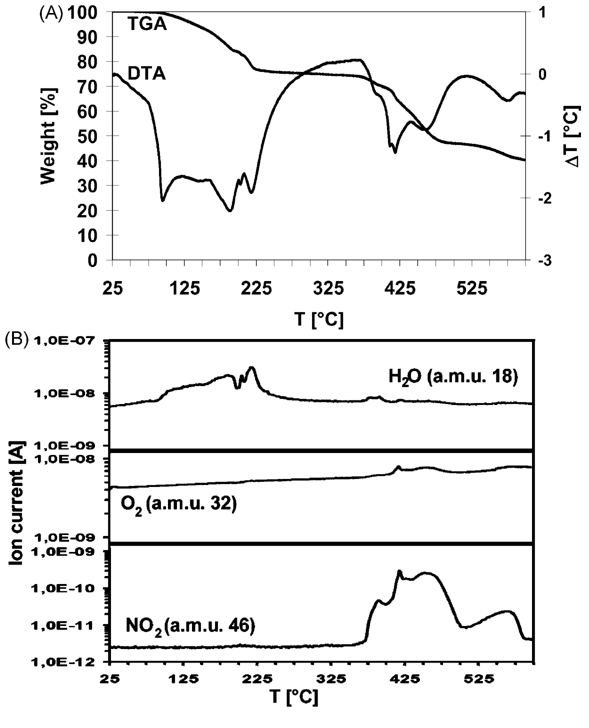

Fig. 2. Decomposition of lanthanum nitrate: (2A) TGA–DTA curves; (2B) MS curves.

Both these decomposition steps are related with endothermic effects in the DTA curve. The endothermic peaks in the DTA trace, as well as the peaks due to water and nitrogen oxide emissions in the corresponding MS curves, are structured, showing that these decomposition phenomena occur in a complex way. TGA–DTA curves show that dehydration occurs in two main endothermic steps ($T_{\text{peak, 1}} \cong 180$ °C and $T_{\text{peak, 2}} \cong 215$ °C) according to equations:

$$La(NO_3)_3\ 6H_2O \rightarrow La(NO_3)_3\ XH_2O + (6-X)\ H_2O \tag{5}$$

$$La(NO_3)_3\ XH_2O \rightarrow La(NO_3)_3 + X\ H_2O \tag{6}$$

If $X=2$, theoretical weight loss calculated for reaction (5) (16.6%) agrees well with the experimental value of 16%, observed after the first dehydration peak.

Above 325 °C, decomposition also takes place in various stages, as shown by the structured endothermic peak observed in the range 350–500 °C. Actually, according to the literature[27] above 330 °C only $LaONO_3$ is formed, at 370 °C La_2O_3 begins to form besides $LaONO_3$ and after 400 °C La_2O_3 is the only stable product. According to this, the structured peak can be tentatively attributed to the following reactions:

$$La(NO_3)_3 \rightarrow LaONO_3 + 2\ NO_2 + 1/2\ O_2 \tag{7}$$

$$2\ La(NO_3)_3 \rightarrow La_2O_3 + 6\ NO_2 + 3/2\ O_2 \tag{8}$$

$$2\ LaONO_3 \rightarrow La_2O_3 + 2\ NO_2 + O_2 \tag{9}$$

3.1.2. Chromium nitrate

Fig. 3 (A and B) shows the TGA–DTA curves (from 25 to 600 °C) and the corresponding MS curves which depict the emission of gaseous species during $Cr(NO_3)_3\ 9H_2O$ thermal decomposition.

The first endothermic peak in DTA trace ($T_{\text{onset}} = 65$ °C) is due to sample melting.[27] Melting phenomena seems to occur during dehydration, as weight loss and water emission were simultaneously observed.

The main weight loss showed by the TGA curve, occurring in the range between 75 °C and 275 °C, is associated with two tightly overlapped endothermic peaks in the DTA thermogram. These two peaks correspond rather fairly to emissions of water and NO_2, respectively. The curves obtained by mass spectrometry show that at first the sample loses water only, while, at higher temperatures, water emission is accompanied by NO_2. Then, dehydration starts first according to reaction (10), and afterwards, while dehydration is still occurring, decomposition begins according to reaction (11).

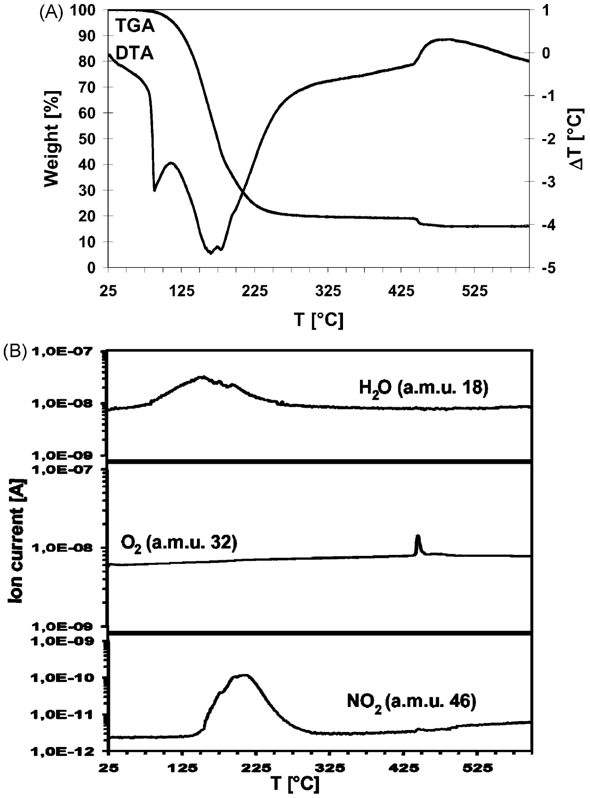

Fig. 3. Decomposition of chromium nitrate: (3A) TGA–DTA curves; (3B) MS curves.

$$Cr(NO_3)_3\ 9H_2O \rightarrow Cr(NO_3)_3 + 9\ H_2O \tag{10}$$

$$Cr(NO_3)_3 \rightarrow CrO_3 + 3\ NO_2 \tag{11}$$

Sample weight loss at 275 °C (77 wt.%) agrees well with the theoretical value of 75% corresponding to a complete transformation of nitrate into CrO_3. In addition, it is confirmed that chromium nitrate starts decomposition at rather low temperatures.[27]

A further reaction step, corresponding to both a weight loss and an exothermal phenomenon, occurs in the range 425–475 °C. It can be attributed to reaction (12), which leads to the formation of Cr_2O_3, a compound stable only above 400 °C.[27,28]

$$2\ CrO_3 \rightarrow Cr_2O_3 + 3/2\ O_2 \tag{12}$$

The sharp peak observed at 475 °C in the oxygen MS curve, during experiments performed under argon, and the cumulative sample weight loss of 81 wt.% (equal to the theoretical one for transformation of $Cr(NO_3)_3\ 9H_2O$ into Cr_2O_3) strengthen this conclusion.

3.1.3. Ammonium nitrate

TGA–DTA curves as well as MS curves for the gaseous species evolved during the decomposition of NH_4NO_3 are shown in Fig. 4 (A and B).

The first three endothermic phenomena observed in the DTA trace can be attributed to polymorph transformations and sample melting, because they are accompanied neither by change in weight nor by formation of gaseous substances.

In fact, under ordinary pressure (P = 1atm) ammonium nitrate may exist in several stable polymorph modifications as shown below:[27]

$$\text{ROMBOEDRAL} \xrightarrow{32.1\,^{\circ}\text{C}} \text{ORTHOROMBIC} \xrightarrow{84.2\,^{\circ}\text{C}}$$

$$\text{TETRAGONAL} \xrightarrow{125.2\,^{\circ}\text{C}} \text{CUBIC}$$

Besides the above mentioned transitions, a metastable one at about 45–50 °C has also been reported.[29]

Possibly, both the first ($T_{\text{onset}} \cong 53$ °C) and the second ($T_{\text{onset}} \cong 128$ °C) endothermic peaks in the DTA curve correspond to polymorph transformations. The first wide peak might be due to either the metastable transformation or the orthorhombic-tetragonal one, while the second may refer to the tetragonal–cubic transformation. According to the literature,[27] the third endothermic peak in DTA curve ($T_{\text{onset}} \cong 170$ °C) is due to melting of ammonium nitrate.

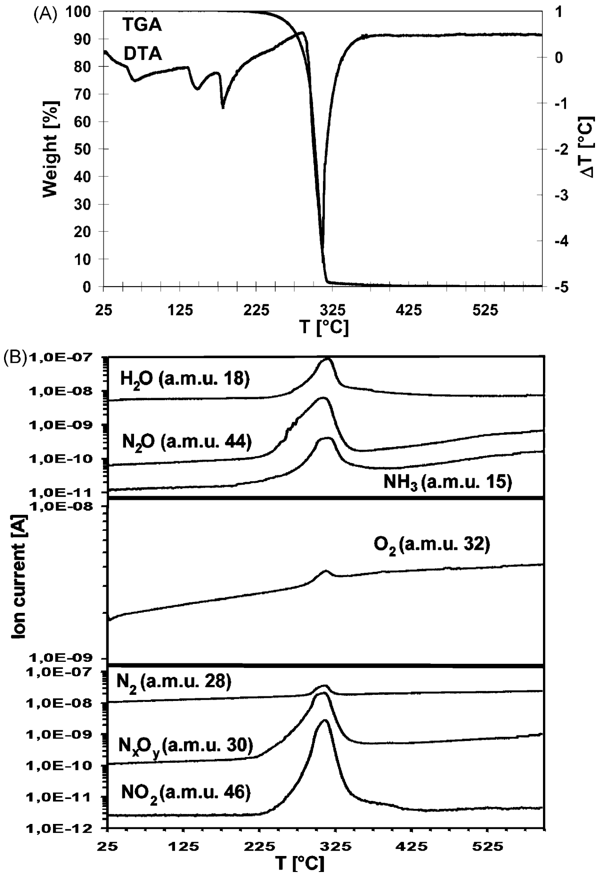

Fig. 4. Decomposition of ammonium nitrate: (4A) TGA–DTA curves; (4B) MS curves.

As regards the ammonium nitrate decomposition, only a sharp weight decrease (starting at 200 °C) leading to the complete vanishing of the sample, was observed in the TGA curve. Simultaneously only a shallow endothermic phenomenon was detected by DTA. This result seems rather surprising because, according to the literature,[29] ammonium nitrate thermal decomposition can occur in a complex way. However, as for most energetic materials, ammonium nitrate decomposition pathway was found to depend upon various factors like pressure and other experimental conditions (sample size, rate of heating, sample purity, presence of foreign substances). Some of the possible reactions of decomposition[29] are reported below:

$$NH_4NO_3 \rightarrow NH_3 + HNO_3 \tag{13}$$

$$HNO_3 \rightarrow NO_2 + 1/2\ H_2O + 1/4\ O_2 \tag{14}$$

$$NH_4NO_3 \rightarrow 1/2N_2 + NO + 2\ H_2O \tag{15}$$

$$NH_4NO_3 \rightarrow N_2O + 2\ H_2O \tag{16}$$

Previous investigations[29] pointed out the influence of heating rate on the decomposition pathway, namely that endothermic surface decomposition occurs [according to reactions (13) and (14)] at high heating rate, while exothermal bulk decomposition occurs [according to reactions (15) and (16)] at a slow one.

As the DTA curve shows that the whole decomposition process has an endothermic character, it must be inferred that ammonium nitrate undergoes decomposition mainly according to reactions (13) and (14), at least in the experimental conditions adopted in this work. All the gaseous products arising from those reactions (NH_3, NO_2, H_2O and O_2) were observed by mass spectrometry. On the other hand, as N_2, N_2O and N_xO_y were also detected in the gaseous mixture flowing out from the TG–TDA cell, reactions (15) and (16) have to occur as well.

Even though thermal decomposition of ammonium nitrate involves several chemical reactions, these reactions occurred simultaneously leading to the completion of the decomposition within a narrow range of temperature.

3.1.4. Urea

Fig. 5 (A and B) shows the TGA–DTA curves, with the corresponding gaseous species formed during $CO(NH_2)_2$ thermal decomposition.

DTA trace shows three main endothermic phenomena. The first sharp endothermic peak ($T_{onset} \cong 133$ °C), which is not related neither to weight loss nor to gas emission, is due to sample melting.[30] The following two endothermic phenomena, which on the contrary involve both weight loss and formation of gaseous species, are caused by decomposition reactions occurring in various, but well distinguishable, steps.

Several different pathways have been reported[30–32] for urea thermal decomposition, which involves the formation of many complex compounds. It is well established that urea decomposes primarily into ammonia and isocyanic acid (HCNO), but in addition to this, the highly reactive isocyanic acid easily undergoes several secondary reactions which result in the formation of larger molecules. Trimerization leads to cyanuric acid [$(HCNO)_3$] and addition of isocyanic acid to urea gives biuret ($H_2NCONHCONH_2$). Other compounds which can form are ammelide ($C_3H_4N_4O_2$), ammeline ($C_3N_5H_5O$), melamine ($C_3H_6N_6$).

The urea sample underwent a first decomposition step in the temperature range 154–263 °C; this process happened with strong sample weight loss, sharp endothermic effect and vigorous gas emission. On the basis of both literature data and analysis of gaseous species evolved, this stage of the decomposition process can be related to the following reactions:

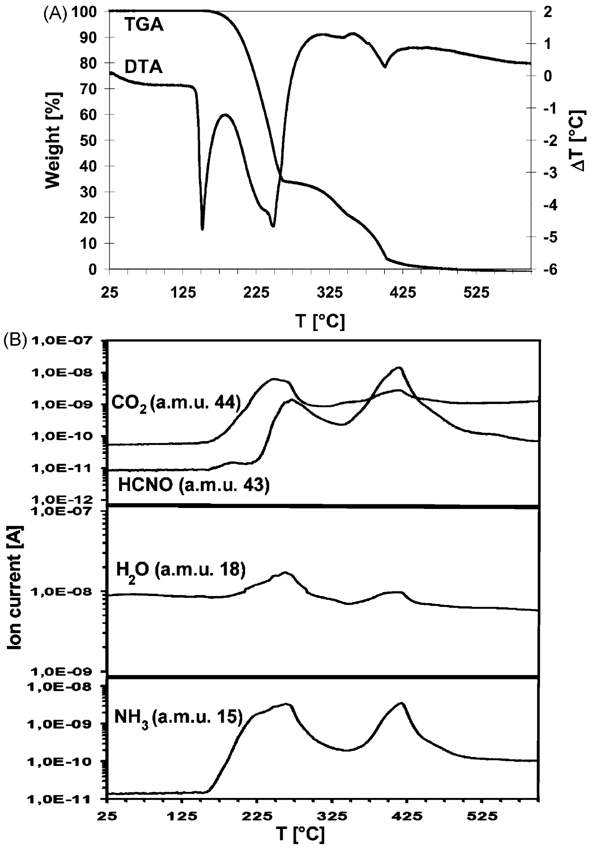

Fig. 5. Decomposition of urea: (5A) TGA–DTA curves; (5B) MS curves.

$$CO(NH_2)_2 \rightarrow NH_3 + HCNO \quad (17)$$

$$CO(NH_2)_2 + HCNO \rightarrow H_2NCONHCONH_2 \quad (18)$$

$$H_2NCONHCONH_2 + HCNO \rightarrow (HCNO)_3 + NH_3 \quad (19)$$

$$H_2NCONHCONH_2 + HCNO \rightarrow C_3H_4N_4O_2 + H_2O \quad (20)$$

$$HCNO + H_2O \rightarrow CO_2 + NH_3 \quad (21)$$

In fact, the DTA peak is structured, showing that more than one chemical reaction is occurring during decomposition, and the reaction products formed in this temperature range (NH_3, HCNO, CO_2, H_2O) are compatible with all the reactions (17)–(21).

Afterwards, the sample weight almost did not change with temperature increase from 263 to 282 °C. Then a further decomposition occurred, with a sample mass loss and an endothermic effect. A possible pathway could be:

$$(HCNO)_3 \rightarrow 3HCNO \quad (22)$$

$$(HCNO)_3 + NH_3 \rightarrow C_3H_4N_4O_2 + H_2O \quad (23)$$

$$HCNO + H_2O \rightarrow CO_2 + NH_3 \quad (21a)$$

All these reactions agree with the gaseous species detected by mass spectrometer.

At a temperature higher than 400 °C, the final mass loss can be tentatively attributed to ammelide ($C_3H_4N_4O_2$) sublimation.

Unfortunately, it was not possible to detect by MS the presence of high molecular weight substances like ammelide and biuret, because they condensed in the capillary tube that makes the connection between TGA–DTA and MS.

This last experiment conducted on a sample of pure urea has a central role for the comprehension of the reactions involved in a combustion synthesis process. Actually, it reveals that urea, submitted to rising temperature, has the same thermal decomposition both in air and argon thus laeding to the conclusion that the air oxygen is not able to ignite an exothermal combustion reaction of urea. Hence, the exothermal reaction observed in the combustion synthesis processes must originate from the mixture of nitrates with urea.

3.2. TGA–DTA–MS investigation of binary mixtures made of a single nitrate and sacrificial fuel (urea)

No differences were noticed in TGA–DTA–MS experimental results when binary mixtures made of each single nitrate and urea were submitted to a temperature run under an air flow or an argon one. For this reason and because only an argon atmosphere enables the accurate observation of N_2 emission, only the results obtained under inert atmosphere will be reported in this section.

3.2.1. Lanthanum nitrate plus urea mixture

Fig. 6 (A and B) shows TGA–DTA results and the corresponding gaseous species formed during the heating of a sample made of lanthanum nitrate and urea, mixed together with a ratio suitable for allowing the reaction (1) to occur.

Endothermic effects due to melting of both lanthanum nitrate and urea (placed at 70 and 133 °C, respectively) are not distinguishable from background noise in DTA curve of Fig. 6A, probably because the insufficient amounts of each of these two substance in the mixture examined (amounts lower than that adopted in experiments carried out on single reagents).

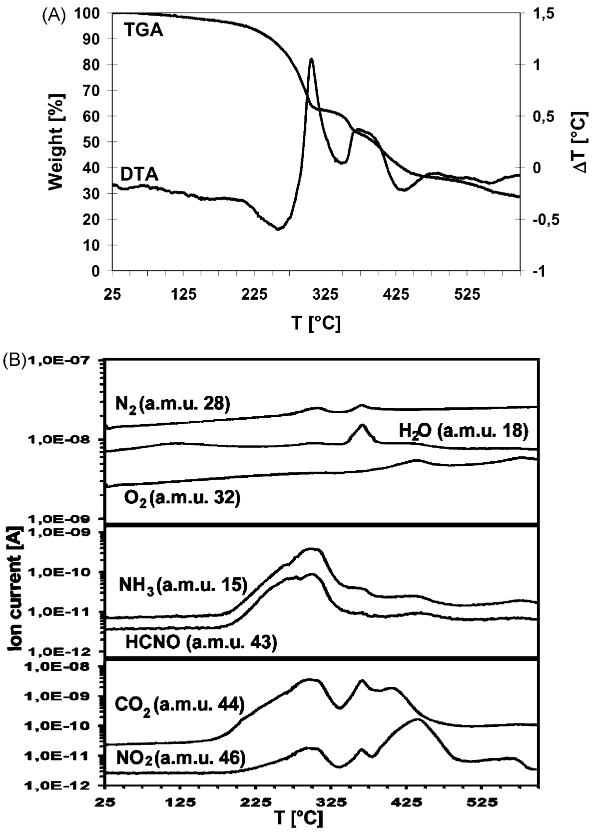

Fig. 6. Reaction between lanthanum nitrate and urea: (6A) TGA–DTA curves; (6B) MS curves.

TGA curve shows a progressive weight loss starting from about 70 °C. This weight loss becomes progressively faster with the temperature increase (in the temperature range 70–263 °C) and corresponds to an endothermic effect in DTA curve. On the basis of the results showed in the previous section of this paper, it can be concluded that this weight loss is due to dehydration of lanthanum nitrate (starting at about 70 °C) and partial decomposition of urea. This conclusion is strengthened by the detection by MS of gaseous species related to dehydration (H_2O) and arising from urea decomposition according to reactions (17)–(21) (CO_2, NH_3 and HCNO). The emission of these gases is stroger at higher temperature, when a first exothermal peak appears in DTA thermogram and the weight loss decrease becomes more rapid. Exothermal effects can be only caused by reactions between nitrate and urea or between nitrate and compounds arising from urea decomposition. This means that decomposition and combustion reactions happen simultaneously, at least at temperatures between 263 °C and 325 °C. Owing to the urea depletion in the sample, combustion synthesis cannot occur any longer according to the reaction:

$$2\,La(NO_3)_3 + 5\,CO(NH_2)_2 \rightarrow La_2O_3 + 5\,CO_2 + 8\,N_2 + 10\,H_2O \quad (1a)$$

As regard the gaseous species detected by mass spectrometer, it must be reminded that NH_3 and HCNO only come from urea decomposition [reactions (17)–(21)], CO_2 and H_2O from both urea decomposition and reaction urea–lanthanum nitrate, while N_2 can be formed only after a reaction between urea and lanthanum nitrate [reaction (1a)]. Since the MS curve of N_2 shows here a very weak peak only, the sharp exothermal phenomenon can not be exclusively attributed to reaction (1a). In addition there is an evident formation of NO_2, which cannot be again explained by reaction (1a), or by urea decomposition [reactions (17)–(21)], or by lanthanum nitrate decomposition [reactions (7)–(9)] which starts only at higher temperature (above 325 °C). In order to explain both the well evident exothermal feature of the process and the marked emission of NO_2 it is possible to assume reactions (24) and (25):

$$2\,La(NO_3)_3 + CO(NH_2)_2 \rightarrow La_2O_3 + 6\,NO_2 + CO_2 + N_2 + 2H_2O \quad (24)$$

$$2\,La(NO_3)_3 + 2\,HCNO \rightarrow La_2O_3 + 6\,NO_2 + 2\,CO_2 + N_2 + H_2O \quad (25)$$

It must be pointed out that reaction (24) needs a fuel/lanthanum nitrate molar ratio of 1:2, while for reaction (1a) this ratio is 5:2. Because of the partial decomposition of urea, the amount of this reagent becomes lower than the stoichiometric quantity needed for reaction (1a). Accordingly, it seems more realistic to describe the combustion synthesis with reaction (24) and (25), that is assuming that lanthanum nitrate simltaneously reacts with urea directly and with cyanic acid (urea decomposition product) as well.

The heat emission keeps on at higher temperatures, as shown by the exothermal broad peak with a plateau in the range of temperatures 367–390 °C. This last exothermal peak seems to be structured, showing that combustion occurs in a complex way. This second exothermal phenomenon is related to formation of NO_2, CO_2, H_2O and N_2, while at the same time emission of NH_3 and HCNO (possibly due to urea decomposition) becomes here very weak. On the basis of the sharp MS peaks for N_2 and H_2O, it can be inferred that both reactions (1a) and (24) occur, thus consuming the remaining amount of urea in the sample.

The further weight loss showed by TGA curve above 416 °C and the corresponding endothermic phenomenon, which involves the formation of a significant amount of NO_2 accompanied by a lower amount of O_2, may be attributed to reactions (7)–(9). Actually, as urea undergoes partial decomposition before reacting with lanthanum nitrate, the part of this last reagent not consumed by direct reaction with urea or urea's products of decomposition must finally undergo thermal decomposition.

3.2.2. *Chromium nitrate plus urea mixture*

Fig. 7 (A and B) shows the TGA–DTA response with the corresponding gaseous species emitted during heating of a sample made of chromium nitrate and urea, mixed according to the stoichiometry of reaction (2).

The TGA curve shows that sample weight loss begins at 72 °C and, at the same time, only slight and progressively increasing water emission is detected by mass spectrometer; thus this weight loss is due to dehydration of chromium nitrate.

Starting from about 150 °C, the weight loss rate increases and exothermal phenomena take place.

Both TGA and DTA curves are structured: firstly the rates of heat emission and of weight change are rather low, then, starting from about 235 °C, they greatly increase. It can be concluded that decomposition reactions (of chromium nitrate and urea) preferentially occur below 235 °C, while above this temperature combustion is the main process.

As regards the gaseous species, the same assumptions done in the discussion of lanthanum nitrate/urea system may be adopted: NH_3 and HCNO are only related to urea decomposition, NO_2 arises either from nitrate decomposition or nitrate/urea reaction and N_2 presence shows that urea and chromium nitrate react according to Eq. (2).

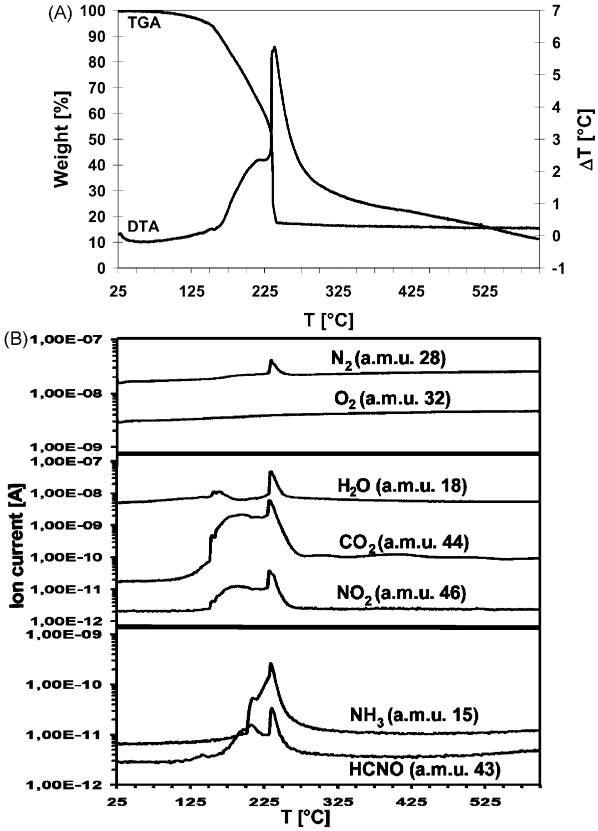

Fig. 7. Reaction between chromium nitrate and urea: (7A) TGA–DTA curves; (7B) MS curves.

Emission curves of NH_3 and HCNO show that urea decomposition occurs simultaneously with the exothermal combustion reactions at every temperature.

Below 235 °C, as nitrogen emission is not well evident, in order to explain both the well defined exothermal character of the process and the marked emission of NO_2 it is possible to assume the following reactions:

$$2\ Cr(NO_3)_3 + CO(NH_2)_2 \rightarrow Cr_2O_3 + 6\ NO_2 + CO_2 + N_2 + 2H_2O \tag{26}$$

$$2\ Cr(NO_3)_3 + 2\ HCNO \rightarrow Cr_2O_3 + 6\ NO_2 + 2\ CO_2 + N_2 + H_2O \tag{27}$$

However above 235 °C reaction (2) certainly occurs, as a sharper peak for nitrogen formation is clearly observed in the MS curve.

Thus, also in the case of Cr_2O_3 combustion synthesis a part of the urea put in the reactant mixture undergoes thermal decomposition before having a chance of reacting directly with chromium nitrate; at any rate this last compound can react with one of the urea decomposition products (namely HCNO).

3.2.3. Ammonium nitrate plus urea mixture

Fig. 8 (A and B) shows TGA–DTA response as well as the gaseous species emitted during heating of an ammonium nitrate–urea mixture, prepared adopting a molecular ratio in agreement with the stoichiometry of reaction (3).

According to the TGA curve, only a slight sample weight loss happens from about 150 to 250 °C. This weight loss is very likely due to thermal decomposition of both urea and ammonium nitrate (respectively beginning at about 150 and 200 °C). Actually, the gaseous species resulting from thermal decomposition of either urea (HCNO, NH_3 and CO_2) or ammonium nitrate (N_xO_y and NH_3) were detected by MS in this temperature range. No thermal effect was detected by DTA owing to the small amount of decomposing substances and the possible simultaneous occurrence of decomposition endothermic reactions [reactions from (17) to (21)] as well as of decomposition exothermal ones [reactions (15) and (16)]. The main exothermal effect and the main weight decrease occur from 250 °C onwards. This last phenomenon is chiefly caused by direct reactions between urea and ammonium nitrate. As NO_2 and N_2 (in addition to H_2O and CO_2) were found above 250 °C in the gas flowing out from the calorimetric equipment, combustion has to occur according to both equations:

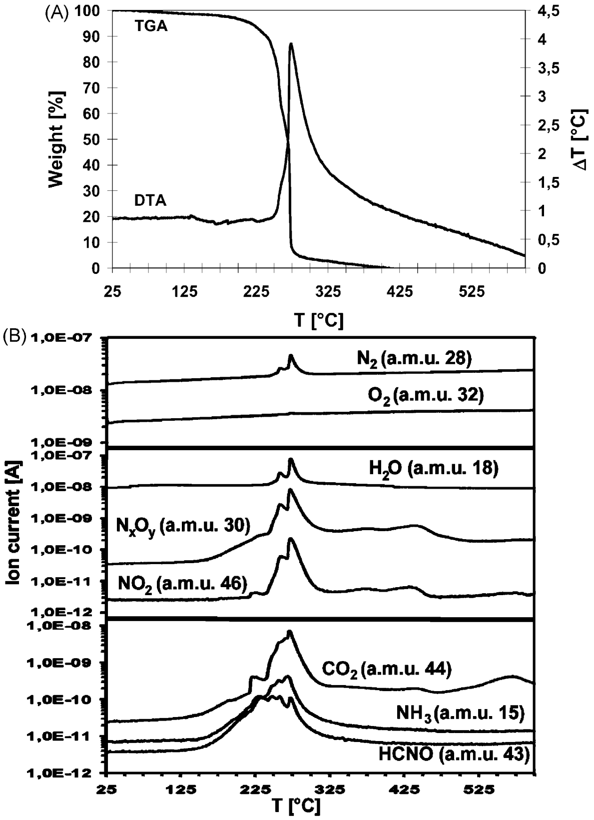

Fig. 8. Reaction between ammonium nitrate and urea: (8A) TGA–DTA curves; (8B) MS curves.

$$3\ NH_4NO_3 + CO(NH_2)_2 \rightarrow CO_2 + 4\ N_2 + 8\ H_2O \tag{3a}$$

$$7\ NH_4NO_3 + CO(NH_2)_2 \rightarrow 2NO_2 + CO_2 + 7\ N_2 + 16\ H_2O \tag{28}$$

The MS curve for HCNO and NH_3 show that thermal decomposition of reagents also take place simultaneously with the combustion process.

All the experimental results obtained by investigating the behaviour of binary mixtures (made of a single nitrate and urea) point to the conclusion that urea undergoes a partial thermal decomposition, thus becoming not completely available for the main combustion reaction with nitrates. On the other hand, it is apparent that at least one of the decomposition products thus obtained can itself react with nitrates.

Probably, this is the reason why, in order to obtain pure products, a rather large excess of urea is necessary.

However, this excess of sacrificial fuel does not result in an increase of the system temperature, because urea is not able to react with the oxygen of air. Actually, the oxidant material needed for the reaction with the fuel was found to come from the nitrates, since the process develops in the same way when using an oxidizing or an inert gaseous atmosphere.

Then direct reaction between urea and nitrates and thermal decomposition of urea are competitive reactions which occur simultaneously. The fraction of urea that really reacts directly with nitrates very likely depends on the heating rate of the reactant mixture, that is on the time necessary for reaching the ignition temperature.

Probably, the direct reaction becomes the main phenomenon occurring in particular experimental conditions, as proposed by Suresh et al.,[10] while if urea decomposition occurs to some extent, also reactions between HCNO and nitrates or between HCNO and nitrogen oxide (arising from nitrate decomposition) happen, as suggested by other authors.[1]

Anyway, the thermal decomposition of reagents makes the control of the process rather puzzling. To this purpose it seems more convenient to reach the temperature suitable for direct urea–nitrate reaction in a time as short as possible. Possibly such decomposition processes might be avoided by changing sacrificial fuel or precursor salts.

3.3. TGA–DTA–MS investigation of mixtures containing three or more reagents

The synthesis of lanthanum chromite was performed both under air and argon, by mixing chromium nitrate, lanthanum nitrate and urea in molar ratios suitable for allowing the reaction (4) to happen. In perfect agreement with the results discussed up to this point, no differences were observed by TGA–DTA–MS during lanthanum chromite synthesis whichever was the gaseous atmosphere adopted. This combustion synthesis was also carried out using an excess of urea and with the addition of ammonium nitrate, that is operating with a four component mixture of reagents.

3.3.1. Synthesis of lanthanum chromite with three reagent mixture

The influence of the presence, inside the mixture with the sacrificial fuel (urea), of both chromium and lanthanum nitrates can be pointed out by comparing DTA curves showing the behaviour of binary and ternary mixtures (Fig. 9). The simultaneous presence of these two nitrates in the reactant mixture resulted in a sort of compromise between the behaviour of each mixture containing a single nitrate and urea.

As seen previously, lanthanum nitrate is able, by itself, to react with urea according to reactions (24) and (25) only at high temperatures (263–390 °C), when a certain quantity of the initial urea is already decomposed and while the fuel decomposition is still going on. The occurrence of decomposition and combustion reaction at the same time, results in a wide and not very marked exothermal peak [curve (b) in Fig. 9]. On the contrary, chromium nitrate begins to react with the sacrificial fuel according to reactions (26) and (27) at lower temperatures (150 °C), showing a stronger exothermal peak in the DTA curve [curve (a) in Fig. 9].

When both lanthanum and chromium nitrates react with urea [curve (c) in Fig. 9] a broaden and structured exothermal peak appears in DTA curve, in an intermediate range of temperatures (216–356 °C) with respect to thermal effects given by reactions of single nitrates with urea. This means that the presence of chromium nitrate, which reacts earlier with urea in a strong exothermal way, may rise the sample temperature locally, thus promoting the reaction among lanthanum nitrate and urea and causing the completion of the final endothermic reaction between lanthanum and chromium oxides:

$$Cr_2O_3 + La_2O_3 \rightarrow 2LaCrO_3 \qquad (29)$$

The irregular shape of the exothermal peak observed in the DTA curve for the three component system shows that the combustion synthesis occurs in a complex way, involving several reactions. This feature is confirmed by the MS curves for the gaseous species ensuing from the TGA–DTA equipment (Fig. 10A and B).

The emission of NO_2, CO_2, N_2 and H_2O while the exothermal effect occurs is consistent with the occurrence of combustion reactions, but the simultaneous presence of NH_3 and HCNO, arising from urea decomposition, lead to the conclusion that urea only partially react directly with the nitrates. This conclusion is further strengthened by the poor concentration of N_2 in the gaseous mixture of reaction products.

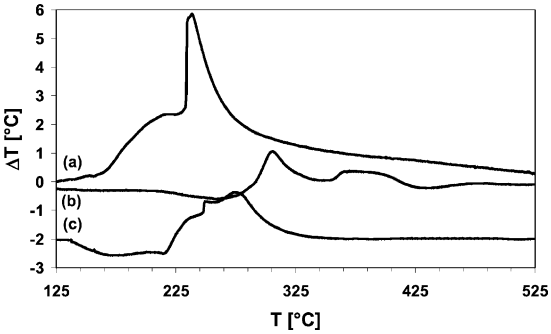

Fig. 9. DTA curves of (a) chromium nitrate–urea binary mixture, (b) lanthanum nitrate–urea binary mixture and (c) chromium nitrate–lanthanum nitrate–urea ternary mixture.

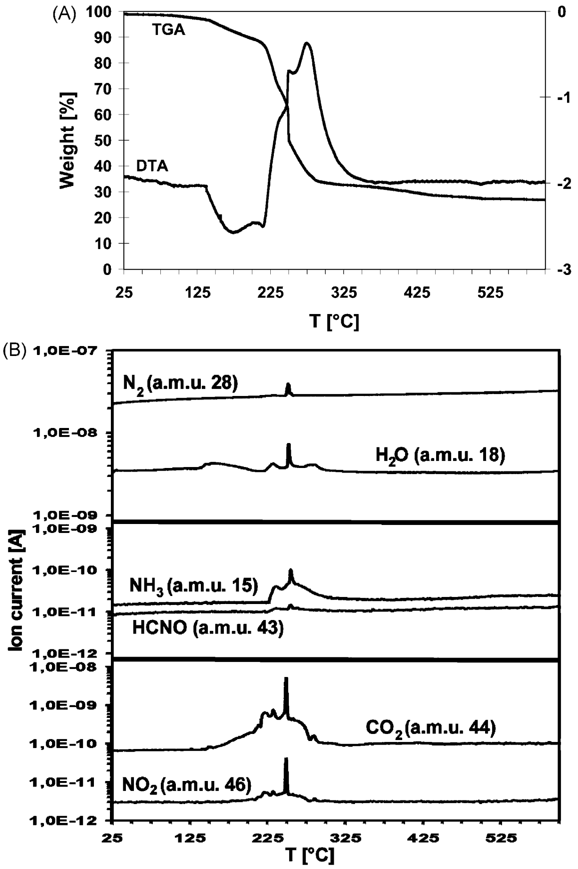

Fig. 10. Reaction between lanthanum nitrate, chromium nitrate and urea: (10A) TGA–DTA curves; (10B) MS curves.

3.3.2. Synthesis of lanthanum chromite with four reagent mixture

The addition of ammonium nitrate (and of an excess of urea too) to the three component system would increase the total amount of substances which react with urea just above the ignition temperature for the lanthanum nitrate–chromium nitrate–urea mixture. Actually, ammonium nitrate begins to react with urea at 250 °C, giving a strong and short heat emission. In other words it may act as an additional energetic source for the synthesis (a "combustion aid", as suggested by Segadaes et al.[23]). In addition, both ammonium nitrate and urea partially undergo thermal decomposition before 250 °C, forming gaseous species which can easily react together,[1] thus giving a contribution to the reagent mixture ignition. Finally, the reaction between ammonium nitrate and urea leads to the formation of gaseous products only, which do not affect the purity of the resulting lanthanum chromite.

A confirmation of the predicted influence of the presence of ammonium nitrate in the mixture can be pointed out by comparing DTA curves, as shown in Fig. 11. When ammonium nitrate is present among the reagents the sample temperature, some time after ignition, increases more quickly, and the combustion rapidly reaches the end. In this last case the exothermal peak in the DTA thermogram is not structured any more and the sample weight loss happens almost instantaneously (Fig. 12 A), thus confirming that the different steps of the process, which lead to the synthesis of lanthanum chromite, take place in a very short time.

The MS curves show that thermal decomposition of ammonium nitrate and urea happens before than most of heat involved in the whole process is emitted (Fig. 12B). At any rate, the presence of CO_2 in the outlet gas well below 225 °C and the corresponding deflection of the DTA curve in the exothermal direction shows that combustion phenomena already begin to happen just above 150 °C.

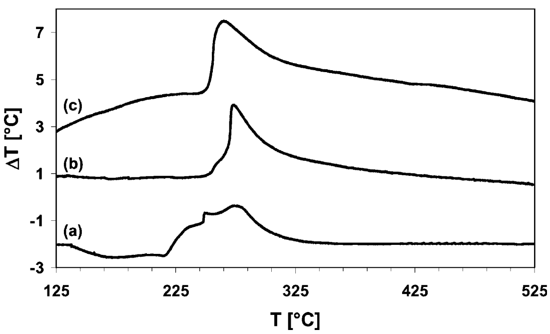

Fig. 11. DTA curves of (a) chromium nitrate–lanthanum nitrate–urea mixture, (b) ammonium nitrate–urea mixture and (c) chromium nitrate–lanthanum nitrate-ammonium nitrate–urea mixture.

4. Conclusions

Pure, well crystallized lanthanum chromite powders (with a significant fraction of particles having submicrometric size) were prepared by combustion synthesis starting from water solutions. Combustion synthesis happened, during heating of these solutions, through several reactions, which occur either between the sacrificial fuel and the reactant nitrates or between the decomposition products arising from both fuel and nitrates.

Thermal effects, changes in sample weight and kind of gaseous reaction products were found not to depend on the presence of oxygen in the gaseous atmosphere under which the experiments were performed, which proves that the oxydant material necessary for combustion comes from the reagents contained in the solution.

As part of the urea undergoes thermal decomposition before the starting of combustion reactions (observed at about 235 and 275 °C in the case of chromium and lanthanum nitrates, respectively) depletion of fuel in the reagent mixture easily occurs. As a consequence of this depletion, the direct reaction between urea and each nitrate is forced to happen according to a modified stoichiometry (fuel:nitrate molar ratio of 1:2 instead of

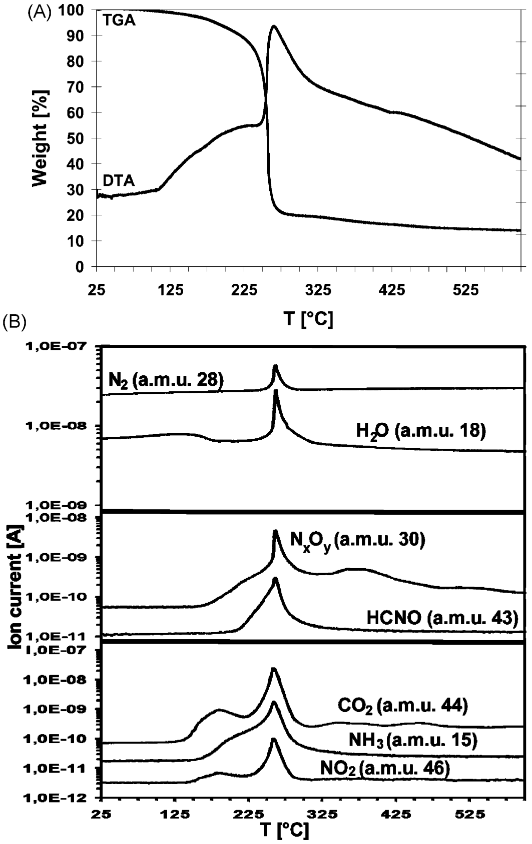

Fig. 12. Reaction between lanthanum nitrate, chromium nitrate, ammonium nitrate and urea: (12A) TGA–DTA curves; (12B) MS curves.

5:2), which also results in the formation of NO_2 in addition to N_2, as a reaction product.

Also chromium nitrate thermal decomposition starts (at about 150 °C) below the ignition temperature for combustion synthesis giving gaseous NO_2.

On the other hand, NO_2 (arising from decomposition of any nitrate) is itself an oxidant species which can exothermally react with urea decomposition products (NH_3 and HCNO).

In addition, the combustion synthesis can also go on through secondary reactions between HCNO and nitrates.

Thus, combustion synthesis is a complex process which cannot be described by one chemical reaction only.

The thermal decomposition of both sacrificial fuel and chromium nitrate, as well as the occurrence of secondary reactions, render the control of the process very difficult.

Nevertheless, as urea decomposition just produces gaseous species, to use an excess of urea seems to be the best way for obtaining a pure product.

Besides, the combustion reaction between chromium nitrate and urea begins a few degrees above the beginning of chromium nitrate decomposition, probably owing to the formation of very active gaseous species. Hence, thermal decomposition sometimes can be regarded as a way to ignite the combustion reaction.

Furthermore, an addition of ammonium nitrate to the reactant mixture is also suitable for bringing the combustion synthesis to completion rapidly and at a rather low temperature. Actually this compound provides a strongly exothermal direct reaction with urea starting from about 250 °C.

Generally speaking, the addition to the reactant mixture of proper substances, able to react with the fuel at low temperature in a strong exothermal manner, seems to be an effective method to lower down the ignition temperature, to increase the synthesis speed and to hinder detrimental secondary reactions of thermal decomposition.

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