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The influence of combustion synthesis conditions on the α-Al_2O_3 powder preparation

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Abstract Fuel type and fuel/aluminium nitrate molar ratio proved to be of great importance during the preparation of α-Al_2O_3 powders. A stoichiometric amount of urea (U) enabled the formation of α-Al_2O_3 with a surface area of 24 m^2/g directly from the combustion reaction. Monoethanolamine, triethylenetetramine, trishydroxymethylaminomethane, and triethanolamine yield amorphous powders. This behaviour was explained by the reaction mechanism, which requires the simultaneous decomposition of metal nitrate and fuel, as shown by thermal analysis. The use of 50% of the stoichiometric amount of U was unable to trigger a combustion reaction. The resulting powder was amorphous and had a surface area of 424 m^2/g. A parabolic correlation between the surface area of combustion-synthesized powder and the U/aluminium nitrate molar ratio was found. Due to U consumption during the hydrolysis side-reaction, 50% of U excess above the stoichiometric ratio is required in order to maximize the exothermic effect of the combustion reaction. The use of U excess higher than 150% of the stoichiometric ratio not only increases the surface area of the powder, but also changes the phase composition: as the U excess increases the proportion of α-Al_2O_3 decreases and the amount of γ-Al_2O_3 increases.

Introduction

Corundum, α-Al_2O_3, represents a ceramic material with significant technological importance. Mainly this is due to its versatile features, such as: excellent mechanical strength at room temperature and high temperature, hardness and abrasion resistance, high melting point, chemical inertness, thermal shock resistance, large band-gap and so on. Such unique properties made corundum one of the most commonly used materials for various applications: cutting tools [1], electronic components and substrates [2], abrasives, bioceramics [3], refractory materials, composite materials [4], spark-plugs, ballistic armours [5], thermoluminescent dosimeters [6] and so on.

Taking into account the market increasing demands for alumina ceramics as well as the failure of the traditional Bayer process to provide high surface area α-Al_2O_3 powders, several soft chemical methods have been suggested: precipitation [7], spray pyrolysis [8], sol–gel [9], organic precursors [10], Pechini [7] and so on. Nevertheless, these methods require many sophisticated techniques and time-consuming procedures, which are obstacles to reproducibility, cost and reliability of the final powder. In addition, α-Al_2O_3 powders are obtained after annealing the various precursors above 1100 °C.

A possible solution to some of the above-mentioned problems could be the solution combustion synthesis, which has attracted significant attention in the past few years [11]. Briefly, this method involves the development of a highly exothermic redox reaction amongst an oxidizing agent, typically metal nitrates and various reducing agents, called fuels [11–13]. The initiation of the combustion process is done by rapidly heating the precursor solution containing the desired raw materials up to 500 °C. The exothermic nature of the combustion reaction ensures

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the self-propagating character of the process as well as the formation of the desired compound. The most important advantages of this process are: low energy requirements (no additional annealing is necessary), time saving (the entire process takes only a few minutes) and environmentally friendly (the combustion reaction by-products are N_2, CO_2 and H_2O).

Several authors reported the formation of single-phase α-Al_2O_3 powders using urea [14–16], carbohydrazide [17] or hydrazine [18] as fuels, without any subsequent thermal treatments. At the same time, other authors reported that glycine [19, 20] or citric acid [21, 22] yields an amorphous powder, which after annealing above 1100 °C turns into α-Al_2O_3. In addition, in this case the formation of α-Al_2O_3 is preceded by the intermediate formation of γ-Al_2O_3.

This study aims to investigate the formation of α-Al_2O_3 powders by solution combustion synthesis. The emphasis is on the effects of using various fuels and different fuel/metal nitrate molar ratios, showing that these parameters have major consequences on the characteristics of the resulting powder. An ignition mechanism for the combustion reaction is suggested.

Materials and methods

In all the experiments Merk analytical reagents were used as raw materials. $Al(NO_3)_3 \cdot 9H_2O$ was used as oxidizing agent. Urea (U), monoethanolamine (MEA), triethylenetetramine (TETA), trishydroxymethylaminomethane (THAM) and triethanolamine (TEA) were used as fuels. Batches were designed in order to obtain 7.140 g of Al_2O_3. The assumption was made that combustion reactions reach completion, meaning that the gaseous by-products are CO_2, H_2O and N_2. After dissolving 52.500 g of $Al(NO_3)_3 \cdot 9H_2O$ in 20.00 mL of distilled water in a porcelain evaporating dish, the stoichiometric amount of fuel was added according to each recipe: sample U (21.000 g), sample MEA (9.74 mL), sample THAM (12.100 g), sample TETA (7.45 mL), sample TEA (8.44 mL). The molar composition of various Al_2O_3 preparation recipes based on using different fuels is presented in Table 1.

The effect of fuel/metal nitrate ratio was also investigated by using various U/aluminium nitrate molar ratios. The amounts of U used in these recipes were: 10.500 g of U (fuel-lean sample, sample U50), 21.000 g of U (stoichiometric sample, sample U100), 31.500 g of U (fuel rich sample, sample U150), 42.000 g of U (fuel rich sample, sample U200), 52.500 g of U (fuel rich sample, sample U250), 63.000 g of U (fuel rich sample, sample U300). The resulting solutions were rapidly heated to 350 °C in an electric nest causing water evaporation and the ignition of the combustion reaction. All samples underwent combustion except for the TEA sample and the fuel-lean sample, which failed to ignite. The velocity of combustion reactions was quantified by measuring the time gap between the initiation of the combustion reaction and its ending.

Thermal behaviour of precursor mixtures was monitored by thermal analysis, using a TGA851/LF/1100 Mettler instrument. The investigated temperature range was 25–600 °C, with a 10 °C/min heating rate, in air static atmosphere and alumina crucibles.

Loss on ignition (LOI) of combustion-synthesized powders was used to compare the exothermicity of different combustion reactions. Theoretically, in the case of a complete combustion reaction the resulting powder should have no LOI. Higher LOI means a lower combustion temperature reached during the combustion process, whereas lower LOI denotes a higher combustion temperature. LOI was determined by annealing the combustion residue at 1000 °C for 1 h.

In the case of combustion-synthesized powders CNH elemental analysis was carried out by “Dynamic Flash Combustion” using an Elemental Analyzer EA 1108 according to ASTM D 5373-02 2007 standard test procedures. An EAGER 200 data system was connected to the thermo-conductivity detector, and a Porapack PQS chromatography column was used for N_2, CO_2 and H_2O separation.

The evolution of crystalline phases was monitored by XRD, using a Bruker D8 Advance System, $Cu_{K\alpha}$ monochromated radiation (0.15406 nm) operating at 40 kV, 40 mA, and a scanning rate of 3°/min. The morphology of the powders was investigated by SEM analysis, using a FEI

Table 1 Molar composition of precursor mixtures designed for α-Al_2O_3 preparation

Sample	Raw material composition of precursor mixtures (molar ratio)					
	$Al(NO_3)_3$	CH_4N_2O	C_2H_7NO	$C_4H_{11}NO_3$	$C_6H_{18}N_4$	$C_6H_{15}NO_3$
U	2	5	–	–	–	–
MEA	2	–	30/13	–	–	–
THAM	2	–	–	10/7	–	–
TETA	2	–	–	–	5/7	–
TEA	2	–	–	–	–	10/11

Inspect S instrument. BET (Brunauer, Emmett and Teller) surface area measurements were performed using a Micromeritics ASAP 2020 instrument and nitrogen as adsorption gas.

Results and discussion

The influence of fuel type

In the first part of the experiments, the influence of fuel type on the features of the resulting powders as well as the correlation of these results with the combustion reaction development was studied. The redox reactions assumed to take place during the combustion process are described by Eqs. 1–5.

$$2Al(NO_3)_3+5CH_4N_2O \rightarrow Al_2O_3 + 5CO_2 + 10H_2O + 8N_2 \quad (1)$$

$$2Al(NO_3)_3+30/13C_2H_7NO \rightarrow Al_2O_3 + 60/13CO_2 + 105/13H_2O + 54/13N_2 \quad (2)$$

$$2Al(NO_3)_3+10/7C_4H_{11}NO_3 \rightarrow Al_2O_3 + 40/7CO_2 + 55/7H_2O + 26/7N_2 \quad (3)$$

$$2Al(NO_3)_3+5/7C_6H_{18}N_4 \rightarrow Al_2O_3 + 30/7CO_2 + 45/7H_2O + 31/7N_2 \quad (4)$$

$$2Al(NO_3)_3+10/11C_6H_{15}NO_3 \rightarrow Al_2O_3 + 60/11CO_2 + 75/11H_2O + 38/11N_2 \quad (5)$$

Table 2 shows the experimental results concerning the influence of fuel type on the combustion synthesis of alumina powders using stoichiometric fuel/metal nitrate molar ratios. One can see that there are significant dissimilarities in terms of combustion reaction velocity and combustion type. In the case of U, the combustion process was very energetic, characterized by the incandescence of raw material mixture and the presence of bright flames. In the case of TEA, there was no sign of a visible combustion reaction; instead, reddish-brown gases could be seen, indicating the decomposition of aluminium nitrate.

MEA generated a combustion reaction faster than U, but not as vigorous. No flames could be seen in this case and the resulting powder had a black colour (Fig. 1). THAM and TETA exhibited an intermediate behaviour. In these cases the combustion process was of smouldering type. The fundamental difference between smouldering and flaming combustion is that the combustion temperature and heat released during a smouldering process are much lower compared to those in a flaming combustion. Consequently, the features of the resulting powders are highly dependent on the combustion reaction type.

U is the only fuel that yields a white powder (Fig. 1). The other powders exhibited colours varying from grey to black, which indicates the presence of residual carbon (certified by the CNH elemental analysis) originating from the incomplete oxidation of fuel (Table 2). The LOI of the resulting powders gives important clue about the exothermic nature of combustion reactions.

The white powder prepared by using U had a surface area of 24 m^2/g and exhibited the lowest LOI and negligible amounts of CNH, which is consistent with the bright incandescence and the flaming-type combustion process (Table 2). XRD analysis revealed that the only crystalline

Table 2 The influence of fuel type during the preparation of α-Al_2O_3 powders

Sample	Fuel	T^a (°C)	Reaction time (s)	Combustion type	LOI (wt%)	CNH content (wt%)		
						C	N	H
U	CH_4N_2O	133	55	Flaming	1.7	0.03	0.02	0.15
MEA	C_2H_7NO	171	30	Non-flaming	16.1	2.68	0.78	1.50
THAM	$C_4H_{11}NO_3$	220	120	Smouldering	20.1	7.86	1.18	1.70
TETA	$C_6H_{18}N_4$	266	240	Smouldering	21.4	2.11	0.39	3.11
TEA	$C_6H_{15}NO_3$	335	–	No combustion	35.3	7.83	1.17	3.42

[a] T stands for the decomposition temperature of fuels [23]

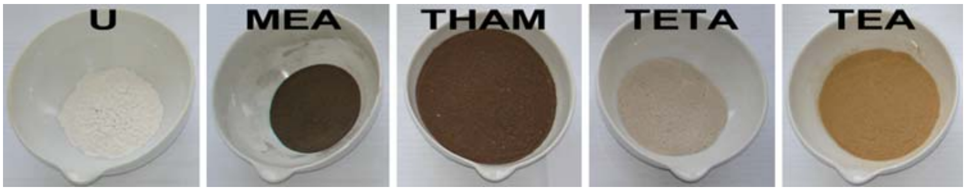

Fig. 1 Images of combustion-synthesized powders, obtained from $Al(NO_3)_3 \cdot 9H_2O$ and various organic fuels

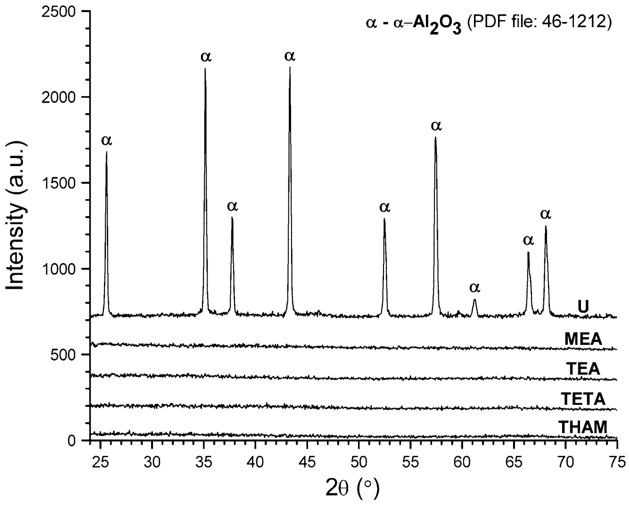

Fig. 2 XRD patterns of the powders prepared by using different fuels

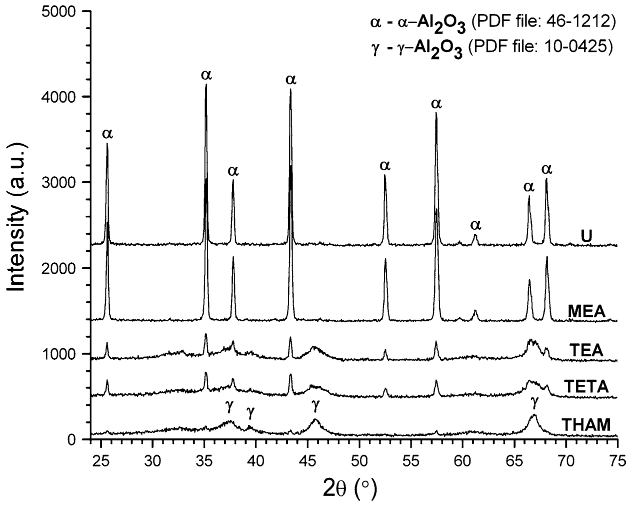

Fig. 4 XRD patterns of the alumina powders after annealing at 1000 °C for 1 h

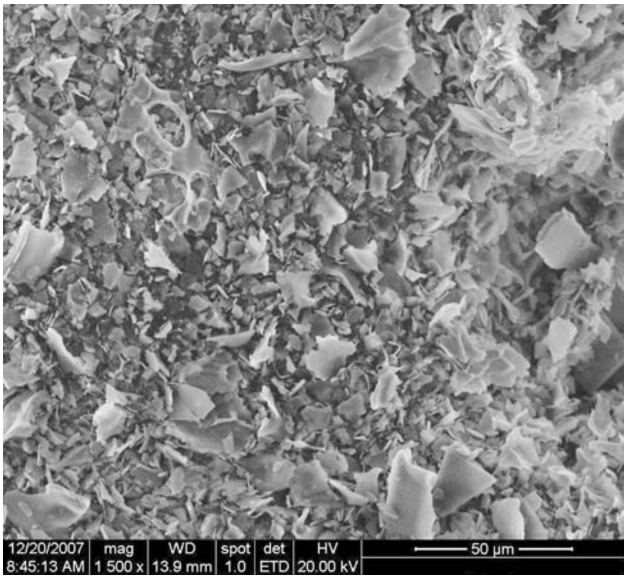

Fig. 3 SEM image of α-Al_2O_3 prepared from $Al(NO_3)_3$ and U

phase present on the diffraction pattern is α-Al_2O_3 (Fig. 2). SEM investigations evidenced that most of the α-Al_2O_3 grains are rugged, smaller than 30 μm and have a flakes-like aspect (Fig. 3).

Unlike U, the other fuels lead to the formation of amorphous powders. The high losses on ignition of these powders as well as the significant CNH content (Table 2) point towards an incomplete reaction and thus a combustion temperature lower than the one reached in the case of U.

After annealing at 1000 °C for 1 h, the amorphous powders crystallize; the complete burning of carbonaceous material is achieved (Fig. 4). In the case of sample U, no variation of the phase composition could be seen; in the case of the powders prepared from aluminium nitrate and MEA, THAM, TETA or TEA, the modifications are obvious.

The amorphous powder obtained by using MEA as fuel turned into single-phase α-Al_2O_3 after annealing. On the other hand, THAM leads after annealing to the formation of single-phase γ-Al_2O_3. In the case of samples prepared by using TETA or TEA a mixture of γ-Al_2O_3 and α-Al_2O_3 was obtained (Fig. 4). These results are in agreement with those reported by other authors [19–22], which have shown that the powders resulting from the combustion reaction of aluminium nitrate with glycine or citric acid are initially amorphous and the complete polymorph transition of γ-Al_2O_3 to α-Al_2O_3 requires annealing above 1100 °C.

Considering the above-mentioned observations, one can conclude that the combustion type and the characteristics of the resulting powders depend to a decisive extent on the nature of the selected fuel. On the other hand, the different behaviours of aluminium nitrate/fuel binary mixtures reveal an affinity for aluminium nitrate with respect to certain fuels. Amongst the tested fuels, U has been found to be the best fuel for aluminium nitrate, since this is the only one that allows the formation of α-Al_2O_3 (high-temperature polymorph modification of Al_2O_3) directly from the combustion reaction (Fig. 2), without requiring further annealing as happens in the case of MEA, TEA, TETA or THAM.

In order to explain the predilection of aluminium nitrate with respect to different fuels, thermal analysis investigations were used. In the first place the heating behaviour of $Al(NO_3)_3 \cdot 9H_2O$ was studied. Thermal decomposition of $Al(NO_3)_3 \cdot 9H_2O$ proceeds mostly over the interval 110–200 °C, being preceded by the crystal hydrate melting (Fig. 5).

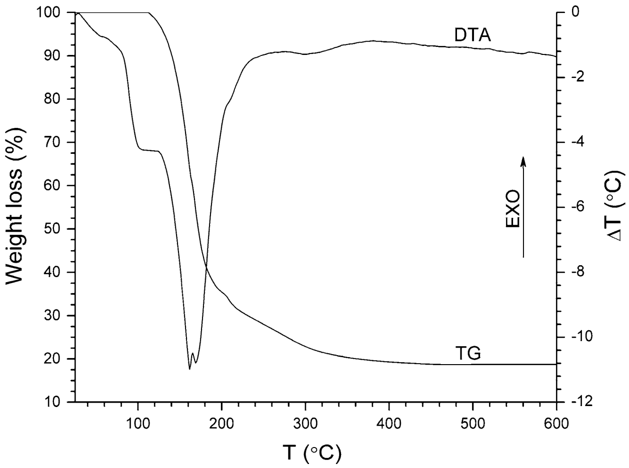

Fig. 5 TG and DTA curves of aluminium nitrate nonahydrate, $Al(NO_3)_3 \cdot 9H_2O$

The total weight loss of the sample is 81.3% that roughly corresponds to $Al(NO_3)_3 \cdot 9H_2O$ stoichiometry (86.4%). The sharp and split character of the endothermic peak (162 and 169 °C)—which accompanies the mass loss on the TG curve—suggests the parallel evolution of several processes. Pacewska and Keshr [24] obtained similar results, showing that the decomposition rate of aluminium nitrate below 160 °C is much higher than above 160 °C. As a matter of fact, according to Speight [23] thermal decomposition of aluminium nitrate takes place at 135 °C. Dehydration, hydrolysis and destruction of nitrate groups take place below 160 °C, whereas the dehydroxylation of hydroxy salts, formed during the decomposition as a consequence of hydrolytic processes, takes place above 160 °C [24].

Figure 6 depicts the heating behaviour of the precursor mixture consisting of aluminium nitrate and MEA. It may be noticed that the initiation and the evolution of the combustion reaction—marked out by the presence of a strong exothermic effect (212 °C) on the DTA curve—are preceded by an endothermic effect (189 °C), which may be attributed to the aluminium nitrate partial decomposition (Fig. 5) as well as to the MEA boiling (Table 2). Although both thermal effects are accompanied by weight loss on the TG curve, one may note that during the combustion reaction the weight loss becomes definitely more pronounced. The contamination of the powder with residual carbon is confirmed by the weight loss of the sample, which continues up to approximately 500 °C. Beyond this temperature the powder does not suffer any other transformations.

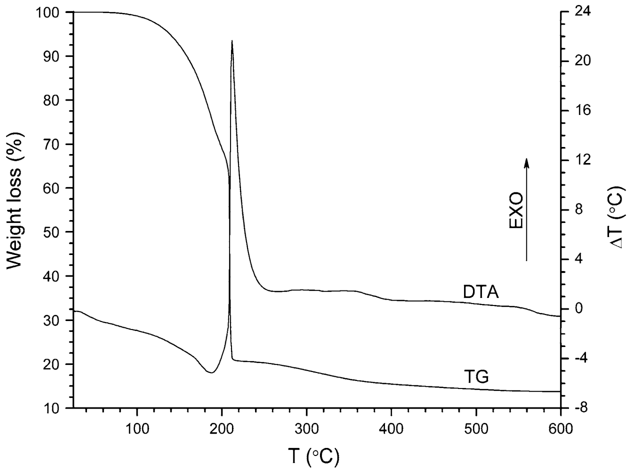

Fig. 6 TG and DTA curves of the precursor mixture consisting of $Al(NO_3)_3$ and MEA

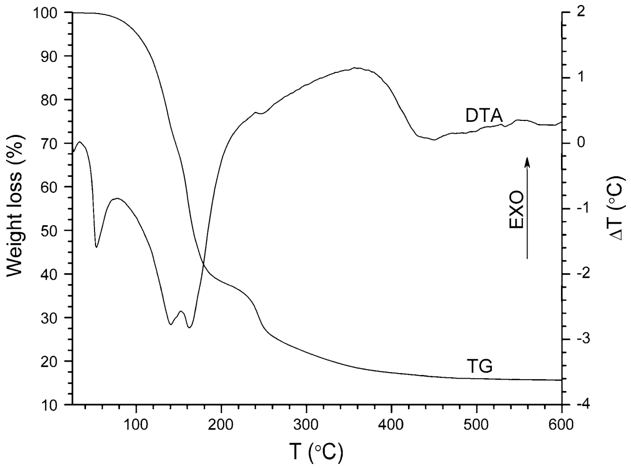

Fig. 7 TG and DTA curves of the precursor mixture consisting of $Al(NO_3)_3$ and TEA

Thermal behaviour of the precursor mixture consisting of aluminium nitrate and U could not be pursued by thermal analysis. In this case the combustion reaction was so violent that the sample was thrown out of the crucible. However, it may be inferred that if in the case of MEA the exothermic effect is so pronounced (Fig. 6) and still the resulting powder is amorphous (Fig. 2), and exhibits a black colour, in the case of U the combustion process is far more intense, since a white crystalline powder of α-Al_2O_3 is obtained.

Figure 7 presents the TG and DTA curves of the precursor mixture containing aluminium nitrate and TEA. The general profile of the DTA curve confirms the experimental observations in relation to the absence of a visible combustion reaction between TEA and aluminium nitrate. In this case an amorphous light brown powder was obtained. The endothermic effect from 53 °C, which is not accompanied by weight loss, indicates the melting of the precursor mixture originally found in a solid state. The important weight loss that occurs within the range of 100 to 200 °C is characterized by the presence of a split endothermic effect (141 and 162 °C), which resembles very much the one from the DTA curve of $Al(NO_3)_3 \cdot 9H_2O$ (Fig. 5). The very weak exothermic process, which takes place with maximum speed at 356 °C, may be assigned to TEA self-ignition. The very low intensity of this process could be explained by the presence of Al_2O_3, which dilutes the TEA burning process.

The results of thermal analysis corroborated with LOI and phase composition of the resulting powders suggest that the ignition of combustion reactions is preceded by the decomposition of $Al(NO_3)_3$ and fuel. From this point of view, combustion reactions evolve more energy as the decomposition temperature of metal nitrate and fuel are closer. As noted in Table 2, when the fuel decomposition temperature increases, combustion reactions become less intense, as confirmed by the evolution of the resulting phase composition and the increasing LOI.

The suggested mechanism explains why the combustion reaction between aluminium nitrate and U is the most intense one in terms of energy. U has a decomposition temperature of 133 °C that is precisely in the temperature range in which aluminium nitrate decomposes with maximum speed (Fig. 5). The overlapping of the decomposition temperatures of aluminium nitrate and U triggers a very energetic combustion reaction that yields α-Al_2O_3 powder with negligible LOI.

It is worth mentioning that other fuels able to generate α-Al_2O_3 powders directly from the combustion reaction, such as carbohydrazide [17] or hydrazine [18], decompose at similar temperatures: 152 and 114 °C, respectively. On the other hand, glycine [19, 20] or citric acid [21, 22]—which decomposes at 240 and 175 °C, respectively—give smouldering combustion with aluminium nitrate, leading to the formation of amorphous powders.

MEA, which boils at 171 °C, generates a shorter combustion reaction than U, leading to the formation of a black amorphous powder with considerable LOI (Table 2). Since most of the aluminium nitrate decomposes up to 160 °C, the fuel/aluminium nitrate molar ratio shifts from the stoichiometric value towards higher values. Therefore, when fuels with higher decomposition temperatures are used, such as MEA, THAM or TETA, at the time of the combustion ignition the real amount of aluminium nitrate is lower than the stoichiometric one.

Moreover, the aluminium oxide generated by the decomposition of aluminium nitrate does not participate to the redox process, but acts as ballast, consuming a fraction of the combustion reaction enthalpy. The global result of these phenomena is reflected by the combustion evolution, characterized by the appearance of a weak incandescent area and long reaction time. If the fuel decomposition temperature is too high when compared to aluminium nitrate decomposition temperature, as in the case of TEA, practically no combustion occurs.

Maximizing the exothermic effect associated with a combustion reaction requires a rational fuel selection. This fuel selection must take into account the heating behaviour of both metal nitrate and fuel. Thus, it is recommended to use fuels that decompose virtually in the same temperature range as the metal nitrate does. In the case of aluminium nitrate, such fuels are U, carbohydrazide and hydrazine.

The influence of fuel/metal nitrate molar ratio

The importance of fuel/metal nitrate molar ratio was already emphasized to a certain extent by showing that increasing this ratio ends up in lowering the combustion temperature. As a result, the probability of obtaining the designed crystalline compound is considerably diminished. Considering that amongst all tested fuels, U gave the best results, in the second part of determinations the influence of U/aluminium nitrate molar ratio was investigated.

Experimental results presented in Table 3 indicate that the velocity of combustion reactions is strongly influenced by the U/aluminium nitrate molar ratio.

Except for sample U50, where no combustion took place, one may notice that the use of higher U/aluminium nitrate molar ratios accelerates the combustion reaction evolution (Table 3). The absence of the combustion reaction in sample U50 is confirmed by the high LOI (38.6%) of the yellow powder and by its amorphous character (Fig. 8). Although in the case of sample U50 no genuine combustion reaction occurred, some chemical transformations, such as U hydrolysis and the thermal decomposition of aluminium nitrate into aluminium oxide and nitrogen oxides, took place within the precursor mixture. It is the decomposition of aluminium nitrate, in the absence of

Table 3 The effect of CH_4N_2O:$Al(NO_3)_3$ molar ratio on the formation of α-Al_2O_3 powders

Sample	CH_4N_2O:$Al(NO_3)_3$	Reaction time (s)	Colour of the powder
U50	5:4 (1.25; Fuel-lean)	No combustion	Yellowish
U100	5:2 (2.50; Stoichiometric)	55	White
U150	15:4 (3.75; Fuel-reach)	40	White
U200	10:2 (5.00; Fuel-reach)	27	White
U250	25:4 (6.25; Fuel-reach)	23	Grey
U300	15:2 (7.50; Fuel-reach)	20	Grey

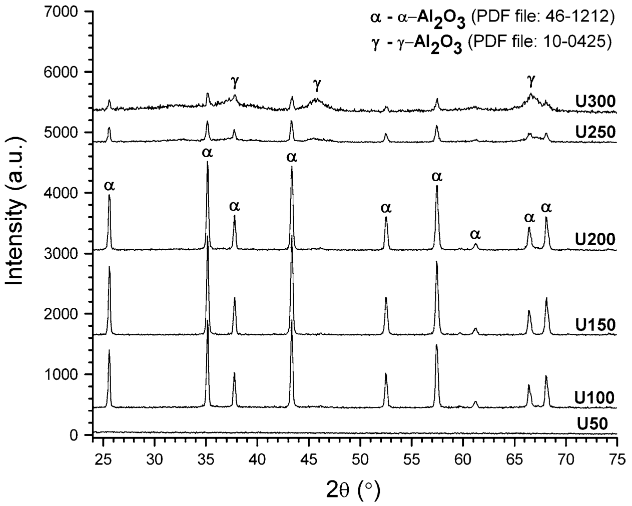

Fig. 8 XRD patterns of the powders prepared with different U/Al$(NO_3)_3$ molar ratios

combustion reaction, which generated an amorphous powder with high surface area (424 m^2/g), as Pacewska and Keshr [24] have already reported.

Both the surface area and LOI of the powders prepared by using various U/aluminium nitrate molar ratios are highly depending on the temperature reached during the redox reaction: higher combustion temperature leads to lower surface area and lower LOI. As a result, by considering the above-mentioned parameters a comparative appreciation of the exothermic nature of combustion reactions was made. The plot of BET surface area of combustion-synthesized powders against the U/aluminium nitrate molar ratio is shown in Fig. 9. A similar profile was observed in the case of the dependence of LOI as a function of U/aluminium nitrate molar ratio (Fig. 10).

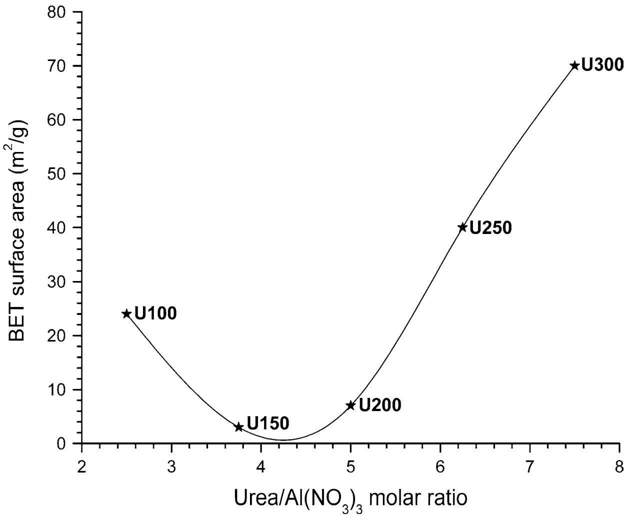

Fig. 9 The evolution of BET surface area as a function of U/Al$(NO_3)_3$ molar ratio

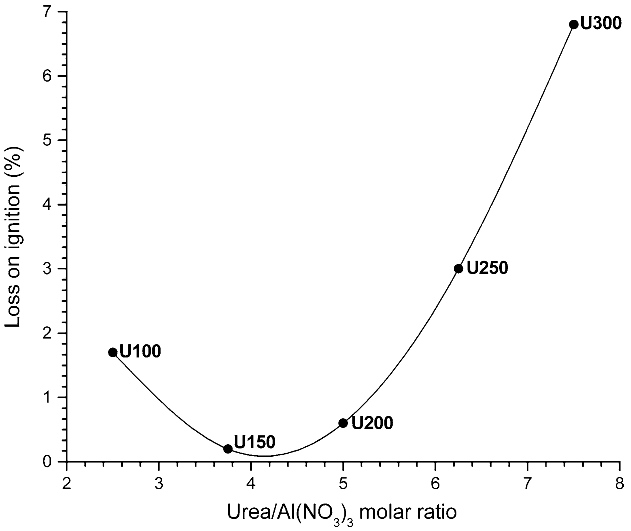

Fig. 10 The evolution of LOI as a function of U/Al$(NO_3)_3$ molar ratio

From the thermodynamic point of view the maximum temperature reached during combustion reaction corresponds to the use of a stoichiometric fuel/metal nitrate ratio [15]. Any deviation from the stoichiometric ratio involves a decrease in the combustion temperature. Nevertheless, both the surface area (Fig. 9) and LOI (Fig. 10) indicate a shift of the maximum combustion temperature from the stoichiometric (U100) value towards higher U/aluminium nitrate molar ratios (U150).

A possible explanation for the deviation of the maximum combustion temperature could be the U hydrolysis [25] side-reaction, which takes place above 80 °C according to Eq. 6

$$CH_4N_2O + H_2O \rightarrow CO_2 + 2NH_3 \tag{6}$$

During the heating of a stoichiometric amount of U and aluminium nitrate (U100) some of the U is consumed due to the hydrolysis process. By the time combustion occurs, the ratio between U and aluminium nitrate has decreased below the stoichiometric one. As a result, the combustion temperature does not reach the maximum predicted value, but is high enough to ensure the formation of single-phase crystalline α-Al_2O_3 (Fig. 8).

Using 50% of U excess (sample U150) is meant to compensate the U loss during the hydrolysis side-reaction. Therefore, during the ignition process the actual U/aluminium nitrate ratio is closer to the stoichiometric value, which is reflected by the lowest surface area and LOI of the resulting powder. In this case the combustion reaction was so vigorous that the porcelain-evaporating dish broke into pieces. Unlike recipe U150, in the case of sample U200 even after the hydrolysis process the amount of U is still higher than the stoichiometric one.

The excess of U present at the time of combustion reaction initiation acts as a ballast, lowering the combustion temperature.

As a result, by comparison to sample U150, sample U200 yields a powder with higher surface area (Fig. 9) and higher LOI (Fig. 10).

Using an even higher excess of fuel (recipes U250 and U300) contributes to a more significant decrease in the combustion temperature, which has direct repercussions on the characteristics of the resulting powders. A first difference that could be noticed was the grey colour of the powders, which suggests the presence of residual carbon (C^0). The origin of residual carbon is the C^{4+} from U, which reduces to C^0 due to the reducing atmosphere caused by the high excess of fuel. In addition there was a pronounced increase in the surface area and LOIs of the as-prepared powders.

Essential changes may also be observed in the phase composition of powders U250 and U300. Evident that in these cases the intensity of the α-Al_2O_3 diffraction peaks decreased dramatically. Moreover, simultaneously with the decrease in the α-Al_2O_3 diffraction peaks γ-Al_2O_3 appears on the diffraction patterns (Fig. 8). Both the phase composition and the α-Al_2O_3 crystallinity degree of combustion-prepared powders are in agreement with the evolution of surface area and LOI. The intensities of the I_{100} peak of α-Al_2O_3 from $2\theta = 35.152°$ (Fig. 8) expressed in arbitrary units vary according to Eq. 7:

$$\begin{aligned} &\mathrm{U100}\,(1476) < \mathrm{U150}\,(1658) > \mathrm{U200}\,(1493) \\ &\quad > \mathrm{U250}\,(383) > \mathrm{U300}(216) \end{aligned} \tag{7}$$

Based on the above-mentioned results one could conclude that the fuel/aluminium nitrate molar ratio largely influences the phase composition and the surface area of combustion-prepared powders.

Conclusions

Aluminium nitrate reacts very differently with U, MEA, TETA, TEA and THAM. This behaviour may be explained by the combustion reaction ignition-mechanism, which requires the simultaneous decomposition of both metal nitrate and fuel.

The features of the powder prepared using various fuels vary in a wide range. While U allows the formation of α-Al_2O_3 powder with a surface area of 24 m^2/g directly from the combustion reaction, the other fuels yield amorphous powders. After annealing at 1000 °C for 1 h, the powder obtained by using MEA crystallizes into α-Al_2O_3, whereas the powder prepared by using THAM crystallizes into γ-Al_2O_3. The powders resulting from the combustion reaction of aluminium nitrate with TETA or TEA turn after annealing into a mixture of γ-Al_2O_3 and α-Al_2O_3.

In addition to the fuel type, the fuel/aluminium nitrate molar ratio proved to be of great importance. The use of only half of the stoichiometric amount of U is unable to ensure the development of a combustion reaction. The resulting powder obtained in this case was amorphous and had a surface area of 424 m^2/g.

A parabolic correlation between surface area-LOI of combustion-synthesized powder and U/aluminium nitrate molar ratio was found. Due to the U partial consumption during the hydrolysis side-reaction, 50% of U excess is required in order to favour full combustion reaction and reduce the LOI. The use of U excess above 150% of the stoichiometric ratio increased the surface area of the final powder. However, in this case the phase composition of the powder changes, as the U excess increases the proportion of α-Al_2O_3 decreases and the amount of γ-Al_2O_3 increases.

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