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Peculiarities of $CaO{\cdot}6Al_2O_3$ Formation by using Low-Temperature Combustion Synthesis

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The preparation of calcium hexaaluminate, $CaO{\cdot}6Al_2O_3$, by solution combustion synthesis was achieved. It was shown that calcium nitrate and aluminium nitrate develop an essentially different behaviour with respect to urea or β-alanine: urea is the most suitable fuel for aluminium nitrate, whereas β-alanine is more appropriate for calcium nitrate. An innovative alternative for the combustion synthesis was presented: instead of using a single fuel for both metal nitrates, a two-fuel mixture containing the most suitable fuel for each metal nitrate was used. It was proved that by using the fuel mixture containing both urea and β-alanine, the exothermic effect of the combustion reaction was maximized, which ensured the direct formation of pure $CaO{\cdot}6Al_2O_3$ without the need of any additional calcination. Further thermal analysis of the powder evidenced that at around 600 °C the as-synthesized $CaO{\cdot}6Al_2O_3$ undergoes polymorphic transformation. The use of a single fuel, urea or β-alanine, does not allow the straight formation of pure calcium hexaaluminate, as X-ray diffraction analysis showed. Urea leads to the formation of a calcium hexaaluminate contaminated with α-Al_2O_3 whereas β-alanine leads to the formation of an amorphous reaction product, which after annealing at 900 °C with 1 h soaking time turns into γ-Al_2O_3.

Introduction

Binary compounds of the CaO–Al_2O_3 oxide system are very important, especially due to their hydraulic activity. However, unlike all other calcium aluminates, calcium hexaaluminate, $CaO{\cdot}6Al_2O_3$ (CA_6) also called hibbonite, does not become hydrated in the presence of water, so it does not exhibit hydraulic properties.

In contrast, $CaO{\cdot}6Al_2O_3$ can be regarded as a member of the β-alumina family. It has a magnetolumbite structure-type consisting of spinel blocks and conduction layers, which are stacked alternatively to form a layered structure.[1] As a consequence of its structure, calcium hexaaluminate shows interesting electrical and optical properties, and it can be used as a host network to obtain phosphor materials.[2–5] Another major application of $CaO{\cdot}6Al_2O_3$ is closely related to its refractory properties: it melts incongruently at 1885 °C by turning into a mixture α-Al_2O_3 and a liquid phase.

Calcium hexaaluminate was recently introduced as a new synthetic dense refractory aggregate for refractories. It was proved that refractory materials based on calcium hexaaluminate can be a solution for applications in areas suffering from aluminium penetration and corundum growth.[6] Pabbruwe et al. speculated that the presence of $CaO{\cdot}6Al_2O_3$ in alumina ceramic implants has positive effects on stimulating the osteoclastic activity at the bone–ceramic implant interface.[7] More than that, Maschio and Pezzotti reported that the composite materials containing alumina and a small fraction of $CaO{\cdot}6Al_2O_3$ maintain the same properties after aging for 30 d at 35 °C in aqueous or physiological solution, and there is no sign of interaction between calcium hexaaluminate and the aging media.[8] Other applications of calcium hexaaluminate include its use as a catalytic substrate[9] or as a protective coating layer and fibre,[10,11] and it also forms various composite materials.[1,8,12]

As a result of the wide variety of applications of $CaO{\cdot}6Al_2O_3$, there is a constant interest in the synthesis and characterization of this oxide compound. As it is well known, the synthesis of calcium hexaaluminate requires prolonged heat treatments at elevated temperatures through a ceramic route, which often involves repetitive grinding, compaction and annealing.

For instance, starting from a stoichiometric mixture of alumina and calcium carbonate, Sanchez-Herencia et al. reported the formation of single-phase calcium hexaaluminate only after thermal treatment at 1650 °C for 3 h.[13] As the formation of pure single-phase $CaO{\cdot}6Al_2O_3$ is difficult to achieve, there is continuous search for the development of new unconventional synthesis methods that should be able to ensure the formation of calcium hexaaluminate at lower temperatures, within shorter soaking times.

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Until now, various authors have undertaken the study of several unconventional synthesis methods. Callender et al. reported the thermolysis of calcium carboxylate–alumoxanes at 1400 °C to yield pure crystalline $CaO{\cdot}6Al_2O_3$.[14] Cinibulk and Hay studied the formation of $CaO{\cdot}6Al_2O_3$ starting from alumina sols that contained calcium acetate and noticed that after annealing at 1400 °C the resulting product was a mixture of $CaO{\cdot}6Al_2O_3$, α-Al_2O_3 and $CaO{\cdot}2Al_2O_3$.[10] Cinibulk used a polymeric sol for the formation of pure single-phase $CaO{\cdot}6Al_2O_3$ at 1300 °C in 1 h.[15] Lazău et al. managed to obtain pure $CaO{\cdot}6Al_2O_3$ after calcination of calcium and aluminium glyoxylate at 1000 °C for 1 h; the glyoxylate resulted from the oxidation of 1,2-ethandiol by calcium and aluminium nitrates.[16]

It was proved that under certain conditions, the solution combustion synthesis allowed the direct formation of the desired oxide compound without any subsequent calcination.[17,18] In this case, the formation of the crystalline oxide compound was achieved due to the development of a strong exothermic self-propagating redox reaction between the desired metal nitrates – the oxidizing agent – and a reducing agent, which is called the fuel. The initiation of the combustion reaction is usually done by the rapid heating of the homogeneous aqueous solution containing the raw material mixture at temperatures below 500 °C. During the development of this exothermic redox reaction, the temperature often exceeds 1000 °C, so that it can promote the formation of the designed oxide compound without any additional calcination.

However, according to Taş, the combustion synthesis with the use of a single fuel, such as urea, glycine or carbohydrazide, leads to the formation of pure-phase $CaO{\cdot}6Al_2O_3$ only after heating the combustion synthesized powder at 1200 °C for 48 h.[19]

In this context, the aim of the paper is to present an efficient solution for the direct formation of pure single-phase calcium hexaaluminate by combustion synthesis: the use of a two-fuel mixture containing the most suitable fuel for each metal nitrate.

Results and Discussion

The Reactivity of $Al(NO_3)_3$ with respect to Urea and β-Alanine

Within the first step, the reactivity of aluminium nitrate with respect to urea (U) and β-alanine (β-Ala) was investigated according to Reactions (1) and (2).

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

$$2Al(NO_3)_3 + 2C_3H_7NO_2 \rightarrow Al_2O_3 + 6CO_2 + 7H_2O + 4N_2 \quad (2)$$

As seen in Table 1, there is a great difference between the reaction of aluminium nitrate with urea [Reaction (1)] and that with β-alanine [Reaction (2)].

Table 1. The behaviour of $Al(NO_3)_3$ with respect to urea and β-alanine.

Fuel	Reaction time [s]	Colour of the resulting powder	Crystalline phases identified on the XRD patterns
Urea	10	white	α-Al_2O_3
β-Alanine	240	black	amorphous

Whereas the reaction of $Al(NO_3)_3$ with urea is accompanied by the appearance of a bright-orange flame that lasts 10 s, the reaction of $Al(NO_3)_3$ with β-alanine is a smouldering combustion process – dark red incandescence – that lasts 240 s.

The black colour of the powder obtained when β-alanine was used reflects the incomplete evolution of the combustion reaction, which is in agreement with the amorphous character of this powder (Figure 1). In contrast, the powder obtained by using urea as a fuel had a white colour and consisted of well-crystallized corundum, α-Al_2O_3 (Figure 1).

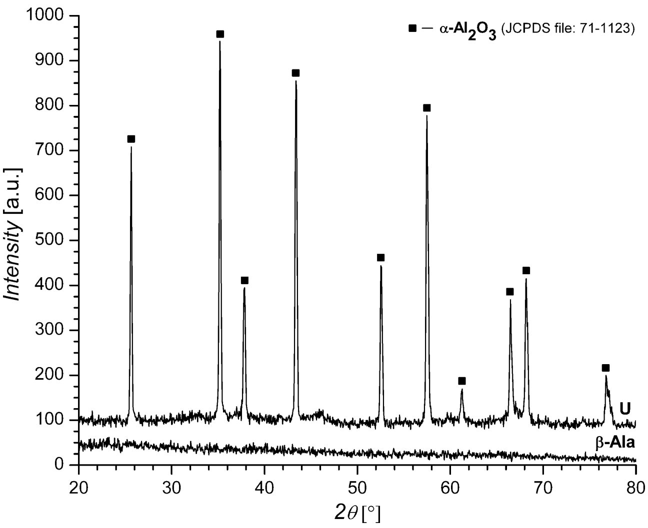

Figure 1. The X-ray diffraction patterns of the powders obtained from $Al(NO_3)_3$ with urea and β-alanine as fuels, respectively.

The Reactivity of $Ca(NO_3)_2$ with respect to Urea and β-Alanine

As a second step, a similar experiment was performed to determine which fuel was the most appropriate for calcium nitrate: urea [Reaction (3)] or β-alanine [Reaction (4)].

$$Ca(NO_3)_2 + 5/3CH_4N_2O \rightarrow CaO + 5/3CO_2 + 10/3H_2O + 8/3N_2 \quad (3)$$

$$Ca(NO_3)_2 + 2/3C_3H_7NO_2 \rightarrow CaO + 2CO_2 + 7/3H_2O + 4/3N_2 \quad (4)$$

The experimental determinations (Table 2) showed that calcium nitrate does not react with urea by a combustion reaction.

Table 2. The behaviour of $Ca(NO_3)_2$ with respect to urea and β-alanine.

Fuel	Reaction time [s]	Colour of the resulting powder	Crystalline phases identified on the XRD patterns
Urea	no reaction	white	$Ca(NO_3)_2{\cdot}nH_2O$ where $n = 0, 2, 4$
β-Alanine	0	white	CaO, $CaCO_3$

This observation is also supported by the X-ray diffraction analysis, which evidenced that the only crystalline phases identified on the XRD pattern of the resulting white powder was $Ca(NO_3)_2$, which crystallized with a variable amount of water (Figure 2).

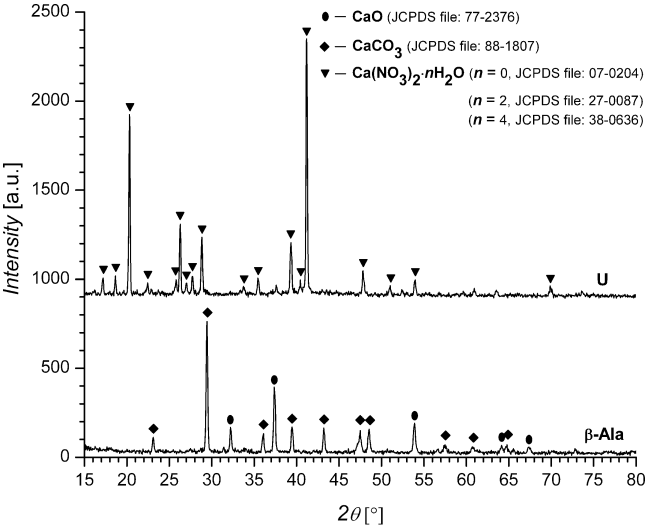

Figure 2. The X-ray diffraction patterns of the powders obtained from $Ca(NO_3)_2$ with urea and β-alanine as fuels, respectively.

In this case, the absence of a combustion reaction can be explained by urea hydrolysis [Reaction (5)], which took place before the raw-material mixture could reach the initiation temperature.

$$CH_4N_2O + H_2O \rightarrow CO_2 + 2NH_3 \qquad (5)$$

Unlike urea, which does not react with calcium nitrate by a combustion reaction, the reaction of β-alanine with calcium nitrate is extremely violent. Actually, in this case, the combustion reaction is practically an explosion (Table 2). The resulting white powder proved to be a mixture of CaO and $CaCO_3$ (Figure 2). The formation of $CaCO_3$ can be explained by taking into account the alkaline character of CaO as well as the weak-acid character of CO_2, which results from the combustion reaction.

The Synthesis of $CaO{\cdot}6Al_2O_3$

By comparing the reactivities of aluminium nitrate and calcium nitrate towards one of the fuels it becomes obvious that there is a predilection of metal nitrates for certain fuels. Aluminium nitrate reacts very fast with urea and considerably slower with β-alanine (Table 1), whereas calcium nitrate reacts explosively with β-alanine and does not react with urea (Table 2).

On the basis of these preliminary results, it can be concluded that among urea and β-alanine, urea is a fuel more suitable for aluminium nitrate, whereas β-alanine is more adequate for calcium nitrate. By starting with these experimental observations, it has to be emphasized that the use of a single fuel − either urea or β-alanine − would not represent the most efficient solution for calcium hexaaluminate combustion synthesis. However, for the sake of comparison, a traditional combustion synthetic recipe was designed that involves the use of a single fuel [for urea, see Reaction (6); for β-alanine, see Reaction (7)].

$$Ca(NO_3)_2 + 12Al(NO_3)_3 + 95/3CH_4N_2O \rightarrow CaAl_{12}O_{19} + 95/3CO_2 + 190/3H_2O + 152/3N_2 \qquad (6)$$

$$Ca(NO_3)_2 + 12Al(NO_3)_3 + 38/3C_3H_7NO_2 \rightarrow CaAl_{12}O_{19} + 38CO_2 + 133/3H_2O + 76/3N_2 \qquad (7)$$

The innovative element consists in the use of a two-fuel mixture containing both urea and β-alanine: urea for aluminium nitrate and β-alanine for calcium nitrate [Reaction (8)].

$$Ca(NO_3)_2 + 12Al(NO_3)_3 + 2/3C_3H_7NO_2 + 30CH_4N_2O \rightarrow CaAl_{12}O_{19} + 32CO_2 + 187/3H_2O + 148/3N_2 \qquad (8)$$

The experimental results concerning the synthesis of calcium hexaaluminate are presented in Table 3.

As seen in Table 3, the combustion reaction occurs in all three samples. Nevertheless, there are important variations regarding the evolution of the combustion reactions: the colour of the resulting powder, their losses on ignition and the phase composition of the resulting powder. Urea, for instance, reacts with the mixture of calcium nitrate and aluminium nitrate designed for the synthesis of $CaAl_{12}O_{19}$ (sample 1) in 50 s. Because aluminium nitrate reacts with urea in 10 s (Table 1), the slower development of the combustion reaction in this case can be explained by the presence of calcium nitrate, which as was already shown does not react with urea (Table 2). The resulting powder was white in colour and consisted of $CaO{\cdot}6Al_2O_3$ and α-Al_2O_3 (Figure 3). These observations are in agreement with the evolution of the combustion reaction, which reflects itself in the insignificant losses on ignition of this powder (1.6%).

Table 3. The experimental results concerning the combustion synthesis of CA_6.

Sample number	Fuel	Reaction time [s]	Colour of the resulted powder	Loss on ignition [%]
1	urea	50	white	1.6
2	β-alanine	180	dark grey	21.5
3	urea + β-alanine	20	white	0.1

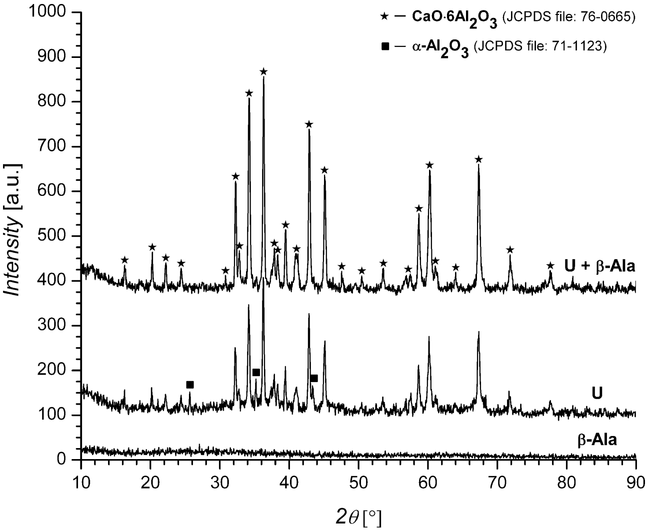

Figure 3. The X-ray diffraction patterns of the resulting combustion powders obtained from $Ca(NO_3)_2$, $Al(NO_3)_3$ and various fuels (samples 1, 2, 3).

The reaction of β-alanine with $Ca(NO_3)_2$ and $Al(NO_3)_3$ (sample 2) lasted 180 s and evolved as a smouldering combustion process. By taking into consideration that the reaction of calcium nitrate with β-alanine is extremely violent (Table 2), this long combustion reaction time can be explained by the delay effect of aluminium nitrate. Alternatively, as aluminium nitrate reacts with β-alanine in 240 s (Table 1), it can be inferred that the addition of calcium nitrate – even in small quantities, which is necessary for $CaAl_{12}O_{19}$ formation – leads to faster development of the combustion reaction. The resulting powder is amorphous (Figure 3) and dark grey in colour, which indicates the presence of residual carbon originating from the incomplete development of the combustion reaction. The presence of the residual carbon was certified by means of thermal analysis (Figure 4).

As can be seen from the DTA curve (Figure 4), between 500 and 660 °C there is an exothermic effect accompanied by a significant mass reduction, which can be attributed to carbon oxidation. By taking into consideration that after being annealed at 900 °C for 1 h the amorphous powder turns into γ-Al_2O_3, it can be assumed that the exothermic effect from 930 °C is correlated with the crystallization of γ-Al_2O_3. Nevertheless, this exothermic effect overlaps with an endothermic effect – accompanied by a weak weight loss – that can be attributed to the decomposition of amorphous $CaCO_3$ generated during the combustion reaction.

The important weight loss, which is shown by the TG curve up to 500 °C may be a consequence of the gradual endothermic elimination of moisture from an amorphous aluminium oxy–hydroxide, which is highly probable to be formed during the smouldering-type combustion reaction. The amorphous character of the powder as well as the significant loss on ignition (21.5%; Table 3) are in excellent consistency with the smouldering-type evolution of the combustion reaction, which suggests that the temperature within the reactant system was not very high.

The reaction of calcium nitrate and aluminium nitrate with the two-fuel mixture, urea + β-alanine (sample 3), lasts 20 s, which is considerably faster than the previous recipes where a single fuel was used. In addition, the reaction was accompanied by the appearance of a bright glowing incandescent combustion front, which turned the clear solution into a white fluffy powder. X-ray analysis pointed out that the only crystalline phase present on the XRD pattern was $CaO{\cdot}6Al_2O_3$ (Figure 3). The total loss on ignition of the resulting white powder was 0.1% (Table 3), which reflects the complete evolution of the combustion reaction, and this value is in agreement with the formation of the desired crystalline phase, $CaO{\cdot}6Al_2O_3$. The thermal behaviour of the resulting sample 3 showed no significant transformations, except for an endothermic effect around 600 °C (Figure 5).

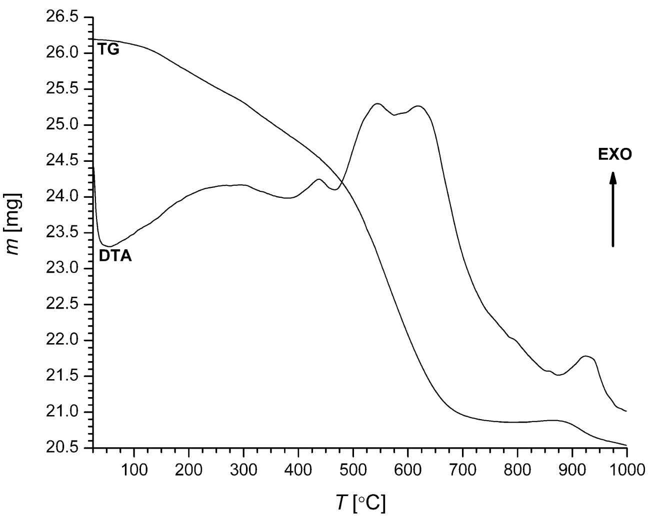

Figure 4. Thermal behaviour of the powder obtained from $Ca(NO_3)_2$, $Al(NO_3)_3$ and β-alanine as the fuel (sample 2).

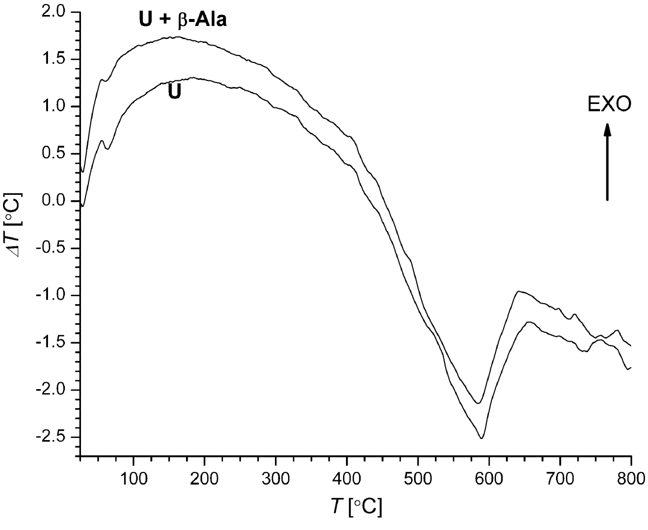

Figure 5. The DTA curves of the powders obtained by using urea and a urea/β-alanine fuel mixture (samples 1 and 3).

Because this endothermic effect is not accompanied by a weight variation, the only possible explanation for this behaviour is that $CaO{\cdot}6Al_2O_3$ undergoes polymorphic transformation. The hypothesis of $CaO{\cdot}6Al_2O_3$ polymorphic transformation is also supported by the fact that this endothermic effect – situated around 600 °C – appears in all the samples with $CaO{\cdot}6Al_2O_3$ content (samples 1 and 3). Moreover, during the thermal analysis investigations of the precursor solution mixture consisting of calcium nitrate, aluminium nitrate, urea and β-alanine, the same endothermic effect was identified on the DTA curve (Figure 6). The strong endothermic effect from 175 °C can be attributed to the partial thermal decomposition of aluminium nitrate. The exothermic effect situated between 260 and 440 °C reflects the evolution of the combustion reaction process. However, it is obvious that at 300 °C there is also an endothermic effect, which suggests a possible unstable evolution of the combustion reaction.

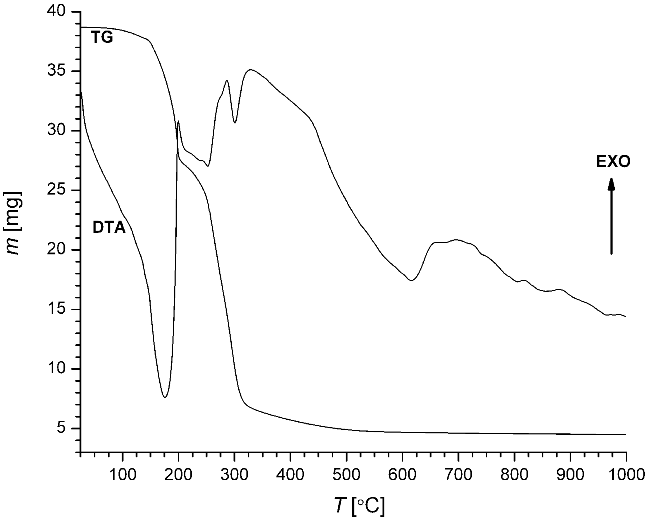

Figure 6. Thermal behaviour of the precursor mixture consisting of $Ca(NO_3)_2$, $Al(NO_3)_3$, urea and β-alanine.

The X-ray diffraction patterns of the powders after being annealed at 900 °C for 1 h are depicted in Figure 7. In the case of sample 1, which was obtained by using urea as the fuel, even after annealing at 900 °C with 1 h soaking time there were still traces of α-Al_2O_3 alongside $CaO{\cdot}6Al_2O_3$. After annealing the amorphous powder obtained by using β-alanine as fuel (sample 2), one could notice the formation of poorly crystallized γ-Al_2O_3.

On the basis of the evolution of the crystalline phases in the samples where a single fuel was used, it can be inferred that higher annealing temperatures are required to guarantee the formation of $CaO{\cdot}6Al_2O_3$ as a single, monomineral phase. From this point of view, these results are quite similar to those reported by Taş, according to which the formation of pure calcium hexaaluminate by combustion synthesis with the use of a single fuel requires annealing at 1200 °C for 48 h.[19]

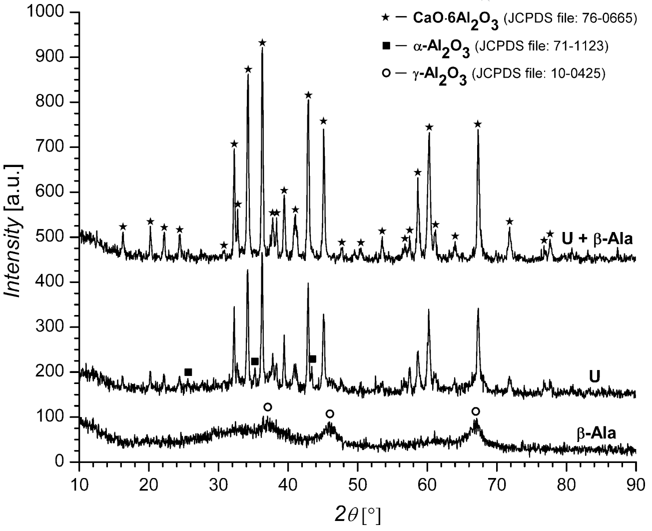

Figure 7. The X-ray diffraction patterns of the powders after being annealed at 900 °C for 1 h.

In contrast, sample 3, which was obtained by using a urea/β-alanine fuel mixture, showed no significant transformations after annealing at 900 °C for 1 h, as the only crystalline phase is the one that resulted from the combustion reaction: $CaO{\cdot}6Al_2O_3$. This means that during the combustion reaction, the existing thermal conditions within the reactant system containing $Ca(NO_3)_2$, $Al(NO_3)_3$ urea and β-alanine are at least equivalent with a subsequent thermal treatment at 900 °C with 1 h soaking time.

In these circumstances, it becomes evident that the use of a single fuel, urea or β-alanine, does not represent a rational solution for the combustion synthesis of $CaO{\cdot}6Al_2O_3$. In contrast, the use of a urea/β-alanine fuel mixture leads to the direct formation of $CaO{\cdot}6Al_2O_3$ without the need of any additional thermal treatment. Moreover, by comparing the average crystallite size of $CaO{\cdot}6Al_2O_3$ directly resulting from the combustion reaction (samples 1 and 3), it can be seen that the $CaO{\cdot}6Al_2O_3$ crystallites obtained by using a mixture of urea/β-alanine are larger than the $CaO{\cdot}6Al_2O_3$ crystallites obtained by using urea alone as the fuel (Table 4).

Table 4. The average crystallite size of the resulting $CaO{\cdot}6Al_2O_3$.

Sample	Fuel	Average crystallite size [nm]
1	urea	29.0
2	β-alanine	–
3	urea + β-alanine	32.6

Because Reaction (8) (sample 3) lasts 20 s and Reaction (6) (sample 1) lasts 50 s (Table 3), the increase in size of the $CaO{\cdot}6Al_2O_3$ crystallites from sample 3 could be interpreted as a consequence of a higher combustion temperature. In other words, the smaller $CaO{\cdot}6Al_2O_3$ crystallites resulting from sample 1, as well as the presence of undesired α-Al_2O_3, reflect a lower combustion temperature relative to sample 3.

Conclusions

It was shown that calcium nitrate and aluminium nitrate display different behaviours towards urea and β-alanine. In other words, there is a predilection of these metal nitrates for certain fuels: urea is the most suitable fuel for aluminium nitrate, whereas β-alanine is more appropriate for calcium nitrate. As a consequence, the use of a fuel mixture containing both urea and β-alanine leads to the maximization of the exothermic effect associated with the combustion reaction, which ensures the direct formation of pure single-phase $CaO{\cdot}6Al_2O_3$ without the need of additional calcination. In this way, the outstanding advantages of using solution combustion synthesis are once again emphasized: whereas calcium hexaaluminate preparation by ceramic methods requires annealing at 1650 °C for 3 h, the use of a urea/β-alanine fuel mixture in a new solution combustion synthesis procedure ensures the formation of pure calcium hexaaluminate after the initiation of the combustion reaction at 300 °C within a few seconds only and without any subsequent thermal treatment.

As a result of the differences in reactivities exhibited by calcium nitrate and aluminium nitrate towards the two fuels, the use of a single fuel, urea or β-alanine as it is usually done worldwide – does not allow the direct formation of pure $CaO{\cdot}6Al_2O_3$. Urea leads to the formation of calcium hexaaluminate contaminated with undesired α-Al_2O_3, which does not disappear even after having annealed the sample at 900 °C with a 1 h soaking time. Alternatively, β-alanine leads to the formation of an amorphous reaction product, which turns into γ-Al_2O_3 after annealing at 900 °C for 1 h.

Experimental Section

The starting raw materials $Ca(NO_3)_2{\cdot}4H_2O$, $Al(NO_3)_3{\cdot}9H_2O$, urea (CH_4N_2O) and β-alanine ($C_3H_7NO_2$) were all purchased from Merck, Germany (pro analysi purity). Alongside the well-known recipes involving the use of a single fuel (samples 1 and 2) a fuel mixture consisting of urea and β-alanine (sample 3) was also used. In this last case, the dosage was done assuming that aluminium nitrate will react exclusively with urea, whereas calcium nitrate will react exclusively with β-alanine. Moreover, it was assumed that the gaseous byproducts of the combustion reaction are: CO_2, H_2O and N_2. Stoichiometric metal nitrate/fuel molar ratios have been used in all samples. The recipes were designed each time in order to obtain 0.015 mol (10.020 g) of calcium hexaaluminate, $CaO{\cdot}6Al_2O_3$. Appropriate amounts of calcium nitrate [3.540 g $Ca(NO_3)_2{\cdot}4H_2O$] and aluminium nitrate [67.500 g $Al(NO_3)_3{\cdot}9H_2O$] were dissolved in a minimum volume of distilled water (10.0 mL). Subsequently, according to each recipe, the requested stoichiometric amount of fuel was added to the clear solution containing the dissolved metal nitrates: sample 1 (28.500 g urea), sample 2 (16.910 g β-alanine), sample 3 (27.000 g urea and 0.890 g β-alanine). Afterwards, the capsules (Φ = 20 cm) with the samples were placed on a preheated electric nest (300 °C) in order to promote water evaporation and the initiation of the self-propagating combustion reaction. The space of time between the initiation of the combustion reaction and its finalization was carefully measured in each case. The heating behaviour of the resulting powders as well as of the precursor mixture consisting of calcium nitrate, aluminium nitrate, urea and β-alanine (sample 3) was monitored by thermal analysis by using a TGA851/LF/1100 Mettler derivatograph. The investigated temperature range was 25–1000 °C with a heating rate of 10 $°C\,min^{-1}$ in an air atmosphere and alumina crucibles. Losses on ignition were determined after annealing the resulting powders at 900 °C with 1 h soaking time. The evolution of the crystalline phases was monitored by XRD by using a Bruker D8 Advance System, Ni filtered $Cu_{K\alpha}$ radiation. The crystallite size was determined on the basis of the XRD patters by using Sherrer's Equation [Equation (9)]:

$$D = \frac{0.9{\cdot}\lambda}{\beta{\cdot}\cos\theta} \tag{9}$$

where: D is the crystallites size in nm, λ is the radiation wavelength ($Cu_{K\alpha}$, 0.15406 nm), β is the full width at half of the maximum in radians and θ is the Bragg angle.

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