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Application of New Organic Fuels in the Direct $MgAl_2O_4$ Combustion Synthesis

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The paper presents a new version of $MgAl_2O_4$ solution-combustion synthesis, based on the individual reactivity of $Mg(NO_3)_2$ and $Al(NO_3)_3$ with respect to various fuels. Beside the traditionally used fuels (urea, glycine, β-alanine), new organic reducing agents [monoethanolamine, triethanolamine, tris(hydroxymethyl)aminomethane and triethylenetetramine] have also been used. The study of the individual reactivities of $Mg(NO_3)_2$ and $Al(NO_3)_3$ with respect to each of the previously mentioned fuels suggested that there is a predilection of the two metal nitrates for certain fuels: urea is the optimum fuel for $Al(NO_3)_3$, whereas monoethanolamine represents the most suitable fuel for $Mg(NO_3)_2$. It has been shown by X-ray diffraction and thermal analysis that the use of a single fuel in the $MgAl_2O_4$ low-temperature combustion synthesis leads to the formation of an amorphous powder. In this case, the formation of pure crystalline $MgAl_2O_4$ requires a subsequent thermal treatment at 900 °C with 1 h soaking time. On the other hand, the use of fuel mixtures containing urea and monoethanolamine or urea and β-alanine proved to be the rational solution for the direct formation of $MgAl_2O_4$. It has been shown that, by using the above-mentioned fuel mixtures, one can obtain pure nanocrystalline $MgAl_2O_4$ straight from the combustion reaction, no additional calcination being necessary.

Introduction

The magnesium spinel, $MgAl_2O_4$, is an oxide compound, which exhibits a wide variety of valuable properties: high melting point (2135 °C), good thermal shock resistance, low thermal expansion coefficient, low thermal conductivity, high mechanical strength both at room temperature and elevated temperature, good chemical inertness. Because of these valuable properties, $MgAl_2O_4$ represents a ceramic material frequently used in many different applications: catalysts support,[1] humidity sensors,[2–4] nuclear technique,[5] refractory materials,[6,7] dentistry[8] etc.

One of the major problems that appear during the fabrication of this kind of materials is related to the synthesis of cheap high-reactivity $MgAl_2O_4$ powders. That is why one of the major research directions in the field of materials science is represented by the development of new more efficient synthesis methods. As a result, several different methods have been suggested for the $MgAl_2O_4$ synthesis: the ceramic method,[9,10] mechanochemical synthesis,[11,12] sol-gel,[13–15] thermal decomposition of complex combinations,[16,17] coprecipitation,[18,19] Pechini,[20] SHS (*s*elf-propagating *h*igh-temperature *s*ynthesis)[21] etc. Yet, in all these methods the formation of crystalline magnesium aluminate, $MgAl_2O_4$, as a single phase can be achieved only after subsequent thermal treatments are applied.

In addition, all these methods exhibit a number of major drawbacks, such as long-lasting powder processing time, contamination, and high energy consumption. Still, the most important negative aspect is that the resulted powder does not exhibit the features of a highly reactive ceramic powder: small (nano) grain size, narrow particle size distribution, low agglomeration tendency, regular (round) particle shape, high purity and compositional homogeneity.

A possible solution to all these problems is represented by the use of low-temperature combustion synthesis. The method relies on the exploitation of the combustion reaction enthalpy, which is taking place when rapidly heating an aqueous solution containing the desired metal nitrates – oxidizing agents – and various organic compounds with nitrogen content, which act as reducing agents, as fuels. The highly exothermic nature of the reaction ensures the self-propagating character of the combustion process, and – under certain conditions – the temperature reached within the reactant system is high enough to promote the formation of the desired compound without any additional annealing.

Despite the high potential displayed by this method, many authors failed to present a systematic approach towards fuel selection and a logical extension of the synthetic procedures. Therefore, all the articles reporting the combustion synthesis of magnesium aluminate recommend the use of a single fuel for both metal nitrates, magnesium

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nitrate and aluminium nitrate: urea,[22–25] citric acid,[26] alanine,[16] sucrose.[23–25]

According to the results reported by these authors[16,22–26] the reaction product obtained right from the combustion reaction is amorphous or poorly crystalline, often being contaminated with residual carbon originating from the incomplete evolution of the combustion reaction. As a consequence, the formation of $MgAl_2O_4$ as a single crystalline phase is achieved only after annealing the previously combustion-synthesized powder.

By using a wide range of new organic fuels, this paper presents an original and systematic approach concerning the steps which should be followed in order to ensure the straight formation of $MgAl_2O_4$ by low-temperature combustion synthesis. It has been demonstrated that the key feature for the rational elaboration of the recipes is represented by the rational selection of the fuel, which should be done by considering the individual reactivity of each metal nitrate.

Results and Discussion

Individual Reactivities of $Al(NO_3)_3$ and $Mg(NO_3)_2$ with Respect to Different Fuels

The first step in the $MgAl_2O_4$ combustion synthesis was the study of the individual reactivities of $Al(NO_3)_3$ and $Mg(NO_3)_2$ with respect to each of the seven fuels taken into consideration: urea (U), glycine (Gly), β-alanine (β-Ala), monoethanolamine (MEA), triethanolamine (TEA), tris-(hydroxymethyl)aminomethane (THAM) and triethylenetetramine (TETA). As far as we know, the last four organic compounds have never been used as fuels in the $MgAl_2O_4$ combustion synthesis. With this purpose, stoichiometric binary mixtures have been designed: $Al(NO_3)_3$/fuel and $Mg(NO_3)_2$/fuel.

The main parameters, which have been monitored, were: the combustion reaction time, the phase composition of the resulting powders as well as the average crystallite size. The results of the experimental determinations have shown that both metal nitrates, $Al(NO_3)_3$ and $Mg(NO_3)_2$, exhibit a very different behaviour with respect to the fuels taken into consideration (Table 1).

Table 1. Individual reactivities of $Al(NO_3)_3$ and $Mg(NO_3)_2$ with respect to each of the fuels taken into consideration.

Fuel	Combustion reaction time [s]	
	$Al(NO_3)_3$	$Mg(NO_3)_2$
CH_4N_2O (U)	10	–
$C_2H_5NO_2$ (Gly)	60	4
$C_3H_7NO_2$ (β-Ala)	240	0
C_2H_7NO (MEA)	30	40
$C_6H_{15}NO_3$ (TEA)	–	25
$C_4H_{11}NO_3$ (THAM)	120	20
$C_6H_{18}N_4$ (TETA)	240	5

In other words, there is a predilection of $Mg(NO_3)_2$ and $Al(NO_3)_3$ for certain fuels. For instance, by comparing the velocity of the combustion reactions between $Al(NO_3)_3$ and the fuels taken into consideration (reactions 1–7), one can notice that urea reacts the fastest with $Al(NO_3)_3$, in just 10 s, whereas TEA does not react with $Al(NO_3)_3$ (Table 1).

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

$$2\ Al(NO_3)_3 + 10/3\ C_2H_5NO_2 \rightarrow Al_2O_3 + 20/3\ CO_2 + 25/3\ H_2O + 14/3\ N_2 \quad (2)$$

$$2\ Al(NO_3)_3 + 2\ C_3H_7NO_2 \rightarrow Al_2O_3 + 6\ CO_2 + 7\ H_2O + 4\ N_2 \quad (3)$$

$$2\ Al(NO_3)_3 + 30/13\ C_2H_7NO \rightarrow Al_2O_3 + 60/13\ CO_2 + 105/13\ H_2O + 54/13\ N_2 \quad (4)$$

$$22/10\ Al(NO_3)_3 + C_6H_{15}NO_3 \rightarrow 11/10\ Al_2O_3 + 6\ CO_2 + 15/2\ H_2O + 19/5\ N_2 \quad (5)$$

$$2\ Al(NO_3)_3 + 10/7\ C_4H_{11}NO_3 \rightarrow Al_2O_3 + 40/7\ CO_2 + 55/7\ H_2O + 26/7\ N_2 \quad (6)$$

$$14/5\ Al(NO_3)_3 + C_6H_{18}N_4 \rightarrow 7/5\ Al_2O_3 + 6\ CO_2 + 9\ H_2O + 31/5\ N_2 \quad (7)$$

Moreover, based on the XRD patterns (Figure 1) of the combustion-synthesized powders obtained from $Al(NO_3)_3$ and each of the seven fuels, one can easily observe that urea is the only fuel that leads to the straight formation of crystalline α-Al_2O_3, which is the high-temperature polymorph modification of Al_2O_3.

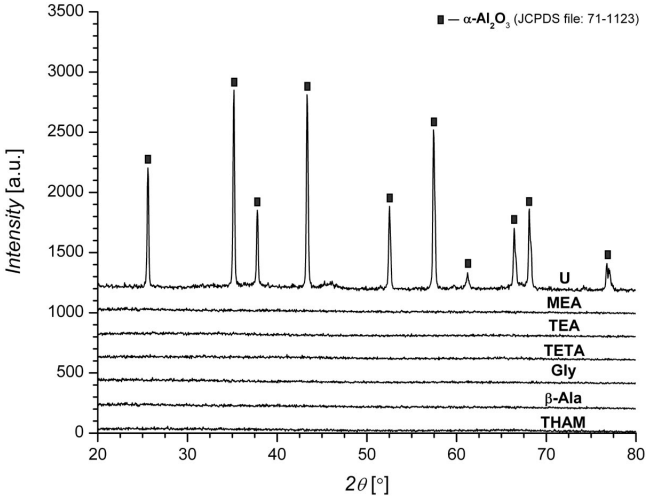

Figure 1. X-ray diffraction patterns of the powders prepared from $Al(NO_3)_3$ and various fuels using solution-combustion synthesis.

In the case of using urea as fuel, the formation of α-Al_2O_3 as a single crystalline phase and the white colour of the resulting powder reflect the high temperature reached within the raw material mixture. On the other hand, all the other fuels lead to the formation of amorphous grey powders (Figure 1), suggesting that the temperature within the reactant system was not as high as in the case of urea.

Considering the very essence of the combustion synthesis – the formation of the desired crystalline phase due to the strong exothermic effect of the combustion reaction – it becomes obvious that in case of $Al(NO_3)_3$, among all the

tested fuels, urea is the only one that allows the formation of α-Al_2O_3 directly from the combustion reaction.

Starting from this particular case of the combustion reaction between $Al(NO_3)_3$ and urea, most of the authors that dealt with the combustion synthesis of various oxide compounds reached the false conclusion that urea is a suitable fuel for any metal nitrate, so it may be used as fuel under any circumstances.[27]

In reality, the situation is different: urea, the most suitable fuel for $Al(NO_3)_3$, does not react with $Mg(NO_3)_2$ (reaction 8) (Table 1).

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

$$Mg(NO_3)_2 + 10/9\ C_2H_5NO_2 \rightarrow MgO + 20/9\ CO_2 + 25/9\ H_2O + 14/9\ N_2 \quad (9)$$

$$Mg(NO_3)_2 + 2/3\ C_3H_7NO_2 \rightarrow MgO + 2\ CO_2 + 7/3\ H_2O + 4/3\ N_2 \quad (10)$$

$$Mg(NO_3)_2 + 10/13\ C_2H_7NO \rightarrow MgO + 20/13\ CO_2 + 35/13\ H_2O + 18/13\ N_2 \quad (11)$$

$$Mg(NO_3)_2 + 10/33\ C_6H_{15}NO_3 \rightarrow MgO + 20/11\ CO_2 + 25/11\ H_2O + 38/33\ N_2 \quad (12)$$

$$Mg(NO_3)_2 + 10/21\ C_4H_{11}NO_3 \rightarrow MgO + 40/21\ CO_2 + 55/21\ H_2O + 26/21\ N_2 \quad (13)$$

$$Mg(NO_3)_2 + 5/21\ C_6H_{18}N_4 \rightarrow MgO + 10/7\ CO_2 + 15/7\ H_2O + 31/21\ N_2 \quad (14)$$

As a matter of fact, the X-ray analysis of the resulting powder confirmed the absence of the combustion reaction (8), showing that the main crystalline phase present, as shown in the diffraction pattern, is $Mg(NO_3)_2$ (Figure 2).

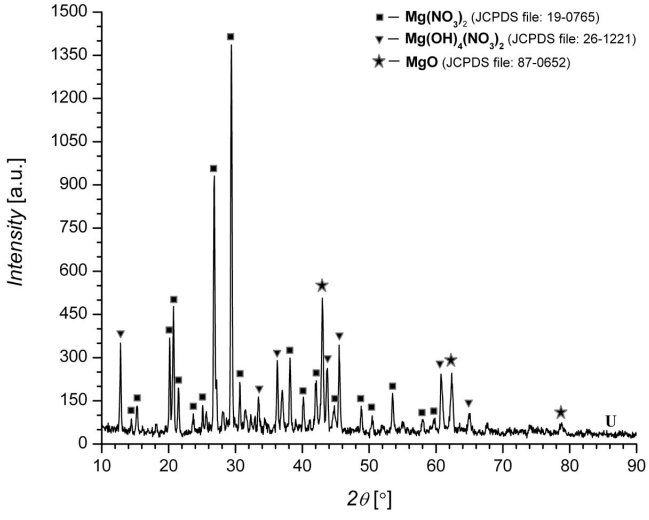

Figure 2. X-ray diffraction pattern of the powder prepared from $Mg(NO_3)_2$ and urea by solution-combustion synthesis.

All the other fuels (reactions 9–14) react with $Mg(NO_3)_2$ leading to the formation of fine white powders. Unlike $Al(NO_3)_3$, which reacts very slowly with β-alanine or TETA, $Mg(NO_3)_2$ reacts very fast with TETA and explosively with β-alanine (Table 1). This experimental observation emphasizes once again that there are significant dissimilarities concerning the behaviour of $Mg(NO_3)_2$ and $Al(NO_3)_3$ with respect to the same fuel.

If in the case of $Al(NO_3)_3$ the choice of the most suitable fuel does not raise special problems – since urea is the only reducing agent that allows the direct formation of α-Al_2O_3 – in the case of $Mg(NO_3)_2$ the situation is not that simple. Mainly, this is due to the fact that except for urea, all the other fuels lead to the formation of single-phase MgO, periclase (Figure 3).

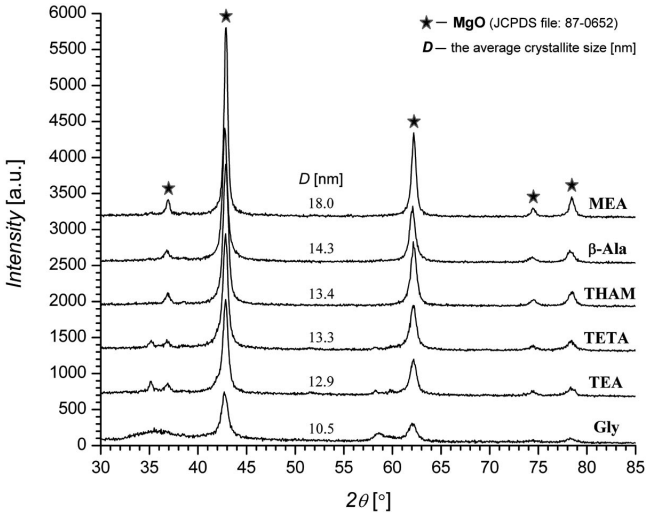

Figure 3. X-ray diffraction patterns of the powders prepared from $Mg(NO_3)_2$ and different fuels by solution-combustion synthesis.

In order to establish the most appropriate fuel for $Mg(NO_3)_2$, it had been assumed that the average crystallite size of MgO obtained by using different fuels reflects the global effect of all the parameters which govern the nucleation and crystal growth processes specific to the combustion synthesis [Equation (15); D = average crystallite size, $\Delta_r H$ = reaction enthalpy, τ = duration of the combustion reaction, V = amount of combustion-generated gases].

$$D = f(\Delta_r H, \tau, V) \quad (15)$$

Taking into account this criterion, it becomes obvious that the most appropriate fuel is the one that leads to the formation of the largest crystallites. From this point of view, it can be seen (Figure 3) that the most suitable fuel for $Mg(NO_3)_2$ is MEA, followed by β-alanine. Another reason, which stands for the use of MEA instead of β-alanine is linked to the practical evolution of the combustion reaction. While β-alanine reacts explosively with $Mg(NO_3)_2$, so that most of the resulting powder is taken away by the combustion gases, MEA reacts in a considerably more controllable manner, allowing the total recovery of the reaction product (Table 1).

On the other hand, one can notice that MEA, which is the most appropriate fuel for $Mg(NO_3)_2$, does not lead to the same spectacular results when mixed with $Al(NO_3)_3$, since the resulting powder, in this last case, is amorphous (Figure 1). These preliminary experimental results confirm the hypothesis that there is a predilection of metal nitrates

for certain fuels. This means that fuels which react very vigorously with $Mg(NO_3)_2$ do not necessarily react with $Al(NO_3)_3$ as well and vice versa (Table 1).

$MgAl_2O_4$ Low-Temperature Combustion Synthesis

Starting from the experimental results presented above, which have proven that $Mg(NO_3)_2$ and $Al(NO_3)_3$ exhibit a completely different behaviour with respect to the same fuel, the next step consisted in the $MgAl_2O_4$ combustion synthesis. Nine procedures have ben designed: the first seven procedures correspond to the initial version of the combustion synthesis involving the use of a single fuel (reactions 16–22) whereas procedures 8 and 9 are the optimised ones, where two-fuel mixtures have been used: urea and MEA (reaction 23), urea and β-alanine (reaction 24). These fuel mixtures were designed by using the most suitable fuel for each metal nitrate. The most important experimental results concerning the combustion synthesis of $MgAl_2O_4$ are presented in Table 2.

$$Mg(NO_3)_2 + 2\ Al(NO_3)_3 + 20/3\ CH_4N_2O \rightarrow MgAl_2O_4 + 20/3\ CO_2 + 40/3\ H_2O + 32/3\ N_2 \quad (16)$$

$$Mg(NO_3)_2 + 2\ Al(NO_3)_3 + 40/9\ C_2H_5NO_2 \rightarrow MgAl_2O_4 + 80/9\ CO_2 + 100/9\ H_2O + 56/9\ N_2 \quad (17)$$

$$Mg(NO_3)_2 + 2\ Al(NO_3)_3 + 8/3\ C_3H_7NO_2 \rightarrow MgAl_2O_4 + 8\ CO_2 + 28/3\ H_2O + 16/3\ N_2 \quad (18)$$

$$Mg(NO_3)_2 + 2\ Al(NO_3)_3 + 40/13\ C_2H_7NO \rightarrow MgAl_2O_4 + 80/13\ CO_2 + 140/13\ H_2O + 72/13\ N_2 \quad (19)$$

$$Mg(NO_3)_2 + 2\ Al(NO_3)_3 + 40/33\ C_6H_{15}NO_3 \rightarrow MgAl_2O_4 + 80/11\ CO_2 + 100/11\ H_2O + 152/33\ N_2 \quad (20)$$

$$Mg(NO_3)_2 + 2\ Al(NO_3)_3 + 40/21\ C_4H_{11}NO_3 \rightarrow MgAl_2O_4 + 160/21\ CO_2 + 220/21\ H_2O + 104/21\ N_2 \quad (21)$$

$$21/20\ Mg(NO_3)_2 + 21/10\ Al(NO_3)_3 + C_6H_{18}N_4 \rightarrow 21/20\ MgAl_2O_4 + 6\ CO_2 + 9\ H_2O + 31/5\ N_2 \quad (22)$$

$$Mg(NO_3)_2 + 2\ Al(NO_3)_3 + 10/13\ C_2H_7NO + 5\ CH_4N_2O \rightarrow MgAl_2O_4 + 85/13\ CO_2 + 165/13\ H_2O + 122/13\ N_2 \quad (23)$$

$$Mg(NO_3)_2 + 2\ Al(NO_3)_3 + 2/3\ C_3H_7NO_2 + 5\ CH_4N_2O \rightarrow MgAl_2O_4 + 7\ CO_2 + 37/3\ H_2O + 28/3\ N_2 \quad (24)$$

As seen in Table 2, the behaviour of these samples is quite different. In some cases, such as samples 1 and 5, the combustion reaction does not even occur, as one could expect by taking into consideration that these procedures involve the use of urea, which does not react with $Mg(NO_3)_2$, or TEA, which does not react with $Al(NO_3)_3$ (Table 1). By comparison, in other cases (samples 4, 8 and 9) the combustion reaction ends in less than 60 s.

Another very important aspect is the colour of the combustion-synthesized powders. From this point of view it needs to be emphasized that in all procedures involving the use of a single fuel (samples 1–7) the resulting powders do not present the white colour specific for $MgAl_2O_4$. Moreover, loss on ignition exhibited by these powders represent hard evidence that the combustion reactions either did not occur (samples 1 and 5) or occurred but did not reach completion (samples 2–4, 6 and 7). For instance, the additional thermal analysis of the yellowish powder resulting in the case of using urea as fuel (sample 1) confirms the absence of the combustion reaction (Figure 4).

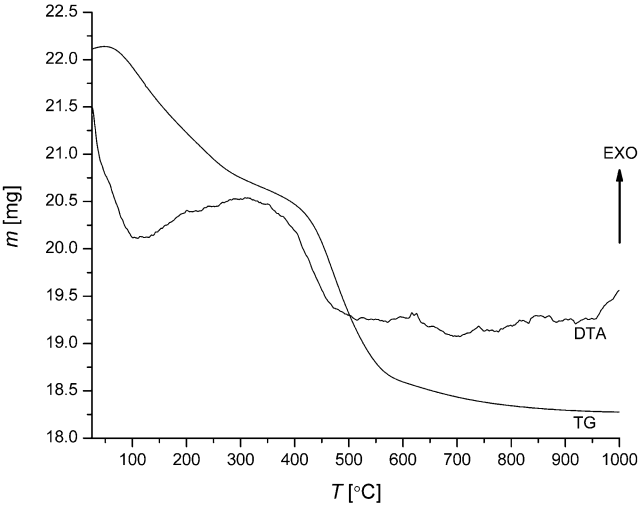

Figure 4. Thermal analysis of the powder prepared by using urea as fuel (sample 1).

The endothermic effect accompanied by a weight loss, which takes place at about 100 °C, can be assigned to the residual moisture removal. In addition, the sample displays another important weight loss at about 460 °C, which can be assigned to the decomposition of unreacted $Mg(NO_3)_2$ (Figure 4). This observation is in excellent consistency with the preliminary results according to which urea does not react with $Mg(NO_3)_2$ (Table 1). In this case, $Mg(NO_3)_2$ acts as an inhibitor, as a diluting medium, preventing the occurrence of the combustion reaction between $Al(NO_3)_3$ and urea.

Table 2. Experimental results regarding the $MgAl_2O_4$ combustion synthesis.

Sample	Fuel	Reaction time [s]	Colour of the resulting powder	Loss on ignition [%]
1	U	–	yellowish	16.4
2	Gly	140	grey	23.5
3	β-Ala	120	grey black	20.9
4	MEA	55	light grey	11.5
5	TEA	–	grey	40.1
6	THAM	180	black	29.2
7	TETA	300	mustard	25.0
8	U + MEA	50	white	1.2
9	U + β-Ala	60	white	2.1

In the case of sample 3 obtained by using β-alanine as fuel, the grey black colour of the powder denotes the partial evolution of the combustion reaction. In this case, as well as in the case of all the other samples involving the use of a single fuel, the combustion reaction is a smouldering one, the sample hardly reaching a dark red incandescence.

Thermal analysis of the powder prepared by using β-alanine as fuel (sample 3) has shown that the dark colour of the sample is due to the presence of carbonaceous material (Figure 5). The sample presents an important weight loss accompanied by an exothermic effect at about 550 °C, which can be assigned to the oxidation of carbonaceous material. The weight loss from 815 °C can be assigned to the decomposition of amorphous aluminium oxy-hydroxide, which is probably generated during the evolution of the smouldering combustion reaction.

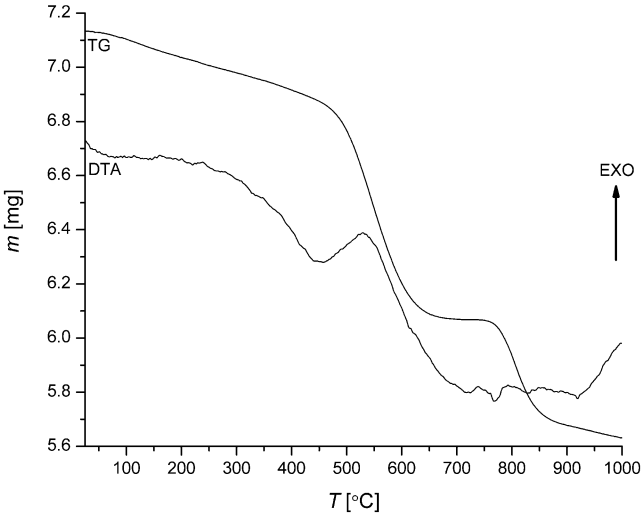

Figure 5. Thermal analysis of the powder prepared by using β-alanine as fuel (sample 3).

The X-ray diffraction presents evidence that all powders obtained by using the traditional version of the combustion synthesis, involving the use of a single fuel (samples 1–7) are amorphous (Figure 6). This is in excellent agreement with the results obtained by means of thermal analysis as well as with the experimental observations concerning the evolution of the combustion reactions presented in Table 2. From this point of view, these results are in consistency with those reported by other authors.[16,23–26]

The amorphous character of the powders obtained by using a single fuel represents conclusive evidence, which stands for the hypothesis that $Mg(NO_3)_2$ and $Al(NO_3)_3$ exhibit an essentially different behaviour with respect to the same fuel. As a result, when a single fuel is used for the synthesis of $MgAl_2O_4$, be it MEA – the most suitable fuel for $Mg(NO_3)_2$ – or be it urea – the most appropriate fuel for $Al(NO_3)_3$ – one of the two metal nitrates will act as a moderator or as an inhibitor of the combustion reaction.

This behaviour leads to a dramatic decrease of the combustion temperature, which is responsible for the amorphous character of the resulting powders (Figure 6). It needs

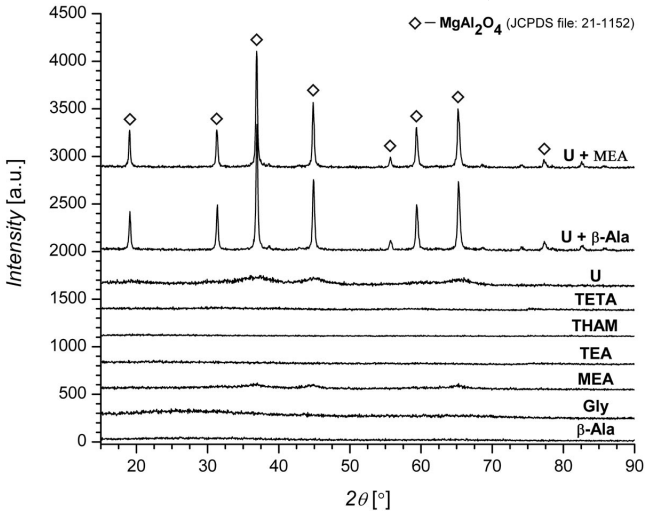

Figure 6. X-ray diffraction patterns of the powders prepared from $Mg(NO_3)_2$, $Al(NO_3)_3$ and various organic fuels.

to be emphasized that this behaviour of the mixtures consisting of $Mg(NO_3)_2$, $Al(NO_3)_3$ and a single fuel does not represent an isolated case; similar results were obtained by using new organic fuels (samples 4–7).

As a consequence, it becomes evident that the use of a single fuel does not represent the most efficient solution for the $MgAl_2O_4$ synthesis, since the most important advantage of the combustion synthesis – the formation of the desired crystalline phase, $MgAl_2O_4$, due to the strong exothermic effect associated to the combustion reaction, without additional annealing – is virtually cancelled.

On the other hand, it is expected that by replacing the use of a single fuel (samples 1–7) with the use of two-fuel mixtures (samples 8 and 9) containing the most suitable fuel for each metal nitrate – urea for $Al(NO_3)_3$ and MEA or β-alanine for $Mg(NO_3)_2$ – would maximize the exothermic effect of the combustion reaction. As far as we know, this is an entirely novel approach, concerning the $MgAl_2O_4$ combustion synthesis.

Unlike the combustion reactions where a single fuel has been used (sample 1–7), which evolve as smouldering combustion reactions – slow and incomplete – the procedures using fuel mixtures (samples 8 and 9) develop a completely different behaviour (Table 2): the combustion reactions (23) and (24) are faster and much more vigorous. As a matter of fact, in the samples where fuel mixtures were used the intensity of the combustion reaction is so high that the raw material mixture reached a bright glowing incandescence within seconds, and the porcelain dish broke.

Another argument, which stands for the incomparable higher exothermic effect of reactions (23) and (24) is represented by the loss on ignition of the white resulting powders: 1.2% in case of sample 8 and 2.1% in the case of sample 9 (Table 2). In addition, further thermal analysis investigations confirmed that the combustion reactions reached completion, the only thermal effect being the one assigned to the removal of the absorbed moisture.

Thermal analysis of the precursor mixture consisting of $Al(NO_3)_3$, $Mg(NO_3)_2$, urea and β-alanine (sample 9) allowed the determination of some of the processes and phenomena which are taking place during the heating of the raw material mixture. As can be seen from Figure 7, the combustion reaction appears on the DTA curve at about 300 °C as a strong exothermic effect, which is accompanied by a significant weight loss on the TG curve. The two endothermic effects, which are preceding the combustion reaction, can be assigned to the partial thermal decomposition of aluminium nitrate (175 °C) and urea (250 °C), respectively.

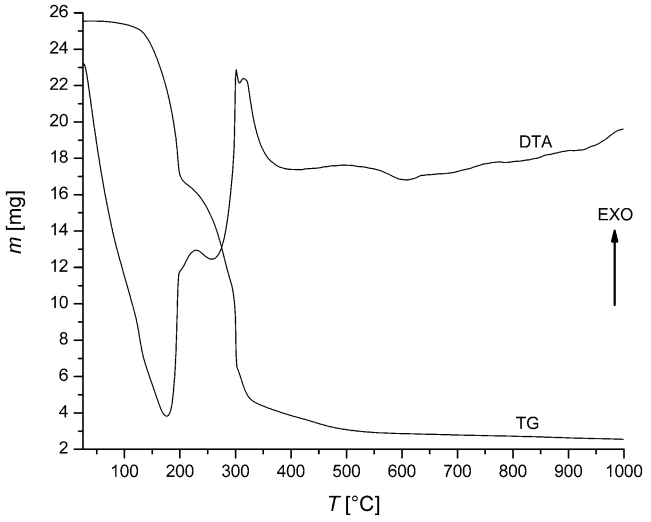

Figure 7. Thermal behaviour of the precursor mixture containing $Al(NO_3)_3$, $Mg(NO_3)_2$, urea and β-alanine (sample 9).

This observation suggests that the initiation of the combustion reaction is taking place between the gaseous decomposition products of aluminium nitrate and urea, triggering afterwards the reaction of magnesium nitrate with β-alanine.

Unlike samples 1–7, where a single fuel has been used and the resulting powders were all amorphous, samples 8 and 9, involving the use of fuel mixtures, are the only samples whose procedures allow the straight formation of crystalline $MgAl_2O_4$ as a single phase (Figure 6).

This means that the exothermic effect, which occurs during the combustion reactions containing fuel mixtures (reactions 23 and 24), is considerably more intense than the one occurring in the traditional combustion reactions involving the use of a single fuel (reactions 16–22).

Concerning the average crystallite size of the as-synthesized $MgAl_2O_4$ (Table 3) one can observe that it is in the range of nanometers. However, it can be seen that the $MgAl_2O_4$ crystallites resulting in the case of sample 8 are larger than the ones resulting in case of sample 9.

Table 3. Average crystallite size (D) and average reticular parameter (a) of the combustion-synthesized $MgAl_2O_4$.

Sample	Fuel	D [nm]	a [Å]
8	U + MEA	27.5	8.070
9	U + β-Ala	26.2	8.063

This evolution of the average crystallite size can be easily explained by taking into consideration that, as it was already confirmed, MEA is a more suitable fuel for $Mg(NO_3)_2$ than β-alanine (Figure 3). As a result, using the fuel mixture containing urea and MEA (sample 8) leads to the development of the fastest and the most exothermic combustion reaction, ensuring the formation of pure nanocrystalline $MgAl_2O_4$ within just 50 s (Table 2).

As one can see from Figure 8, after annealing at 900 °C for 1 h, all samples consist of crystalline magnesium spinel, $MgAl_2O_4$. This behaviour suggests that in case of samples 1–7, where a single fuel was used, the combustion temperature reached within the reactant system was far below 900 °C.

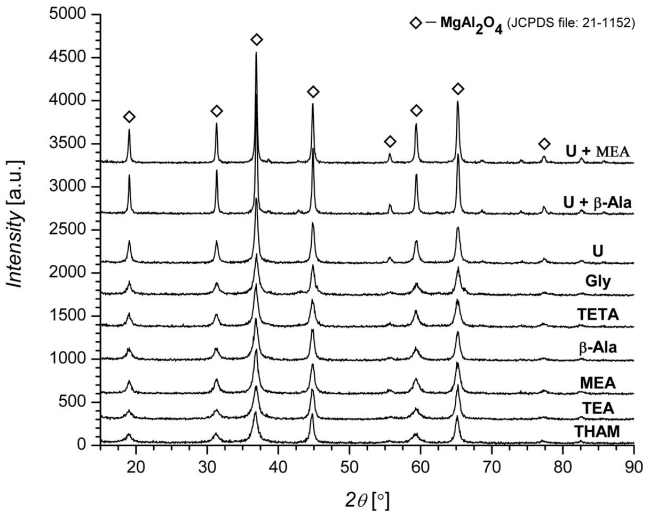

Figure 8. X-ray diffraction patterns of the combustion-synthesized powders after annealing at 900 °C for 1 h.

Nevertheless, even after annealing at 900 °C, the $MgAl_2O_4$ crystallites (Table 4) obtained by using a single fuel (samples 1–7) are significantly smaller than the $MgAl_2O_4$ crystallites resulting straight from the combustion reactions (Table 3) involving the use of fuel mixtures (samples 8 and 9).

Table 4. Average crystallite size (D) and average reticular parameter (a) of $MgAl_2O_4$ after annealing at 900 °C for 1 h.

Sample	Fuel	D [nm]	a [Å]
1	U	17.9	8.071
2	Gly	12.3	8.069
3	β-Ala	12.2	8.082
4	MEA	10.5	8.083
5	TEA	9.4	8.081
6	THAM	10.0	8.101
7	TETA	11.8	8.086
8	U + MEA	27.5	8.075
9	U + β-Ala	26.9	8.069

Moreover, by comparing the $MgAl_2O_4$ crystallite size before (Table 3) and after annealing (Table 4) in case of samples 8 and 9, where fuel mixtures were used, one can notice that there are no major differences. This means that when fuel mixtures are used (samples 8 and 9), the additional thermal treatment practically has no influence on the crystallinity degree of $MgAl_2O_4$ already formed during the combustion reaction (Figure 6). In other words, during the combustion reactions (23) and (24) the existing thermal conditions within the reactant system containing $Mg(NO_3)_2$, $Al(NO_3)_3$ and one of the two fuel mixtures (samples 8 and 9) are at least equivalent with a subsequent annealing at 900 °C with 1 h soaking time.

Analysis of the results presented in Table 4 shows that in case of samples 1–7 the crystallinity degree of $MgAl_2O_4$ obtained after annealing at 900 °C with 1 h soaking time – appreciated by the average crystallite size – is strongly depending on the fuel nature. Concerning the reticular parameter, it may be said that the calculated values are relatively close to the standard value, presented in the JCPDS file 21-1152 (a = 8.083 Å) for well-crystallized magnesium spinel, $MgAl_2O_4$.

Conclusions

Alongside the most often used fuels (urea, glycine, β-alanine) new organic fuels have been tested with nitrogen content [monoethanolamine, triethanolamine, triethylenetetramine and tris(hydroxymethyl)aminomethane] in order to enlarge the fuel range.

It has been shown that these organic compounds can be successfully used as fuels in $MgAl_2O_4$ combustion synthesis.

The study of the individual reactivities of $Mg(NO_3)_2$ and $Al(NO_3)_3$ with respect to each of the previously mentioned fuels indicated that there is a predilection of the two metal nitrates for certain fuels: urea is the most adequate fuel for $Al(NO_3)_3$, whereas monoethanolamine or β-alanine are the most suitable fuels for $Mg(NO_3)_2$.

During the $MgAl_2O_4$ combustion synthesis it was confirmed that the use of a single fuel – as it is predominantely described in the literature – does not represent the optimum solution, since in these cases the combustion-synthesized powders are amorphous. In order to obtain the desired crystalline phase, $MgAl_2O_4$, by using a single fuel, an additional annealing at 900 °C for 1 h is mandatory.

The use of fuel mixtures containing the most suitable fuel for each metal nitrate – monoethanolamine or β-alanine for $Mg(NO_3)_2$ and urea for $Al(NO_3)_3$ – proved to be the rational solution for the $MgAl_2O_4$ combustion synthesis. This new approach ensures the formation of pure nanocrystalline $MgAl_2O_4$ straight from the combustion reaction, no other additional annealing being necessary.

It has been established that the most important aspect, which must be taken into account during the rational elaboration of the procedures for the $MgAl_2O_4$ combustion synthesis, is the predilection of the two metal nitrates with respect to different fuels.

Experimental Section

The starting raw materials were all from Merck, Germany and of pro analysis purity: $Mg(NO_3)_2{\cdot}6H_2O$, $Al(NO_3)_3{\cdot}9H_2O$, urea (U), glycine (Gly), β-alanine (β-Ala), monoethanolamine (MEA), triethanolamine (TEA), tris(hydroxymethyl)aminomethane (THAM), triethylenetetramine (TETA). Within the framework of the preliminary study concerning the individual reactivities of $Mg(NO_3)_2$ and $Al(NO_3)_3$, stoichiometric ratios of metal nitrate/fuel binary mixtures were used, considering reactions (1–14). All the procedures were designed in order to obtain 0.070 mol of MgO (2.800 g), and Al_2O_3 (7.140 g) respectively. In the second part of the paper, within the framework of $MgAl_2O_4$ combustion synthesis, seven procedures were designed involving the use of a single fuel (samples 1–7). In addition, two different fuel mixtures were also used: urea and monoethanolamine (sample 8), urea and β-alanine (sample 9). In these cases, dosages were used with the assumption that $Al(NO_3)_3$ will react exclusively with urea, whereas $Mg(NO_3)_2$ will react exclusively with monoethanolamine or β-alanine. Moreover, it was assumed that the gaseous by-products of the combustion reaction are CO_2, H_2O and N_2. In all samples stoichiometric metal nitrate/fuel molar ratios were used, according to reactions (16–24). The procedures were designed in order to obtain 0.070 mol (9.940 g) of magnesium aluminate, $MgAl_2O_4$. Appropriate amounts of magnesium nitrate (17.920 g) and aluminium nitrate (52.500 g) were dissolved in a minimum volume of distilled water (10.00 mL) in a porcelain evaporating dish with a diameter of Φ = 20 cm. Subsequently, according to each procedure, the requested stoichiometric amount of fuel was added to the clear solution containing the dissolved metal nitrates: sample 1 (28.000 g of urea), sample 2 (23.333 g of glycine), sample 3 (16.613 g of β-alanine), sample 4 (12.98 mL of monoethanolamine), sample 5 (11.25 mL of triethanolamine), sample 6 [16.133 g of tris(hydroxymethyl)aminomethane], sample 7 (9.93 mL of triethylenetetramine), sample 8 (21.000 g of urea and 3.25 mL of monoethanolamine), sample 9 (21.000 g of urea and 4.153 g of β-alanine). Afterwards, the porcelain dish was placed in 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. The heating behaviour of the resulting powders, as well as of the precursor mixtures consisting of $Mg(NO_3)_2$, $Al(NO_3)_3$, urea and β-alanine were monitored by thermal analysis, using a TGA851/LF/1100 Mettler thermobalance. The investigated temperature range was 25–1000 °C, with a 10 °C/min heating rate, in air-static atmosphere and alumina crucibles. Losses on ignition were determined after annealing the as-synthesised powders at 900 °C with 1 h soaking time. The evolution of the crystalline phases was monitored by XRD, using a Bruker D8 Advance System, Ni-filtered Cu-K_α radiation. The crystallite size was determined based on the XRD patterns, using Scherrer's Equation (25), where D = crystallites size in nm, λ = radiation wavelength (Cu-K_α, λ= 0.15406 nm), β = full width at half of the maximum in radians, θ = Bragg angle.

$$D = \frac{0.9{\cdot}\lambda}{\beta{\cdot}\cos\theta} \tag{25}$$

The peaks used for the crystallite size determination were the ones corresponding to the following *hkl* planes: 311, 400, 440, 220, 111 and 511. Taking into account the cubic symmetry of $MgAl_2O_4$, the reticular parameter, a, was calculated with Equation (26), where *hkl* = Miller indices for the same crystal-lattice planes as those used for D calculus (311, 400, 440, 220, 111 and 511).

$$a = d_{hkl}(h^2 + k^2 + l^2) \tag{26}$$

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