Technical aspect for oxidation of magnesium and aluminum nitrates to manufacture nano- and micro-sized MgAl_2O_4 spinel by combustion method

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Abstract: In the present investigation, the nano- and micro-sized powders were synthesized by stoichiometric contents of magnesium and aluminum nitrates using combustion–oxidation method. The study was conducted over a wide range of operating conditions, in terms of fuel ratio and calcination temperature. The characteristics of magnesium aluminate powders were studied by differential thermal analysis and thermogravimetry (DTA–TG), Brunauer–Emmett–Teller (BET), X-ray diffraction (XRD), and transmission electron microscopy (TEM) techniques. The thermal stability of powders was evaluated by calcination at different temperatures. Differences of the specific surface areas were related to the composition and crystallite size. The importance of fuel ratio and calcination temperature to achieve the nano- and micro-sized oxide was discussed in detail. The fuel ratio of 0.56 and calcination at 800 °C provided the conditions to achieve the nano-scale magnesium aluminate powders, smaller than 20 nm. The application of presented algorithm can be an important tool for control of particle size in the nano- and micro-scale.

Keywords: magnesium aluminate spinel; oxidation; nano-crystallite; combustion; calcination

1 Introduction

Recently, magnesium aluminate (MgAl_2O_4), which is a ceramic composition, is employed at different engineering fields. The important properties that make magnesium aluminate as a superior material are high melting point (2135 °C), relatively low density (3.58 g/cm³), excellent transmittance in the wavelength of 0.25–5.0 μm, high bending strength (180 MPa) and Vickers hardness (16 GPa), inertness in acidic environments, low thermal expansion coefficient

($9 \times 10^{-6} (\text{°C})^{-1}$ between 30 and 1400 °C), and high thermal shock resistance [1]. Several applications were reported for magnesium aluminate, and numerous technologies were developed for manufacturing spinel powders depending on application. The control of particle size plays an important role in the application demand. The major applications of this composition can be summarized as: (i) catalyst support especially for high temperature reactions [2,3]; (ii) fabrication of refractory [4,5]; (iii) manufacture of optical devices and sensors [6,7]; (iv) advance applications such as electrochemical fields, dentistry, and reinforcing fibers [6].

MgAl_2O_4 is crystallized in the cubic form in which the oxygen atoms are arranged in a cubic close-packed

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lattice [8]. Different techniques were developed for production of MgAl_2O_4 particles. High energy ball milling process is the oldest technology for the direct fabrication of magnesium aluminate spinel in the micro-scale [9–12]. In general, the wet-chemical process [6], precipitation method [13], sol–gel route [14–16], polymerized complex method [17], microwave [18,19], and pyrolysis [20] techniques were reported as processes for the preparation of spinel. Depending upon the method used, particles with the various morphology, stoichiometry, and level of crystallinity have been produced. These factors essentially affect the quality of final product through the influence on the thermal behavior, mechanical characteristics, and electrical and optical properties.

Although, the sol–gel method using polyvinyl alcohol for polymerizing was developed for the synthesis of high surface area MgAl_2O_4 spinel precursors, this technique involved quite long processing time. As the contrary solution, combustion synthesis has emerged as a simple, fast, and economically viable procedure to prepare pure and nano-structured powders. This quick, straightforward process can be used to synthesize homogeneous, high-purity crystalline powders including ultrafine particles with a broad range of particle size. In this technique, an aqueous solution containing the desired metal ions and a suitable fuel is prepared. A viscous gel is obtained during the heat treatment and exothermic reaction which take place rapidly, leading to formation of fluffy powders. The calcination of autoignition product increases the crystallinity of spinel. The combustion technique is an inexpensive method that allows the preparation of highly purified, nano-sized crystalline powders at lower calcination temperatures in significantly shorter time [21–30].

Urea–formaldehyde [21], urea and triethylenetetramine mixture [22], sugar–urea [23], glycine [24], starch [25], alanine [14], citrate [26–28], and polyacrylamide [29] were used as fuels in the combustion synthesis of nano-scale MgAl_2O_4 powders. Generally, in the combustion process, a thermally induced redox reaction takes place between cations and fuel. The metal nitrates act as cation sources, whereas organic compounds are employed as fuels. Although MgAl_2O_4 spinel with high surface area was produced at relatively low temperature by urea–formaldehyde, the fuels like glycine and starch can be economically applied for production of nano-sized spinel which is not only cost-effective, but it also reduces the

environmental risk due to generation of nontoxic gases. Glycine, which is one of the simple amino acids, is known to act as a complexing agent for a number of metal ions [30], because it contains a carboxylic acid group at one end and amino group at the other end. Moreover, glycine molecules can effectively maintain the compositional homogeneity among the constituents.

The calcination of precursor yields dense particles with high crystallinity, while the initial powders contain amorphous phase. On the other hand, the increment in calcination temperature increases the rate of grain growth and consequently affects the crystalline structure of material. The morphology and particle size of spinel should be considered in calcination of precursor to achieve nano-sized particles. The optimization of spinel preparation and calcination conditions promises the direction to obtain nano-sized particles. Although different fuels were employed for production of MgAl_2O_4 , the effect of fuel ratio on crystallite size, morphology, and purity of product was not studied fundamentally. The compromise between fuel ratio and calcination temperature should be taken into account in production of spinel. In this article, the effects of above factors on technical characteristics of powders were investigated to optimize the procedure for achieving pure nano-sized particles.

2 Experimental procedure

2.1 Materials and powder preparation

Magnesium nitrate, $\text{Mg}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, and aluminum nitrate, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, both manufactured by Sigma-Aldrich Company, were used as starting materials. The purity of nitrate salts was above 99 wt%. Glycine, $\text{NH}_2\text{CH}_2\text{COOH}$ (produced by the same company, 99.5 wt%), was applied as fuel. 61.2 g magnesium nitrate and 227.2 g aluminum nitrate were dissolved in 300 mL de-ionized water, and the molar ratio of Mg/Al was considered to be 0.50.

The lean and rich contents of glycine were considered to evaluate the effect of fuel amount on technical characteristics of final product. The appropriate amounts of glycine were added to the prepared solution for adjusting the fuel/ NO_3 molar ratio at levels of 0.56 and 0.75, corresponding to 4.5 and 6.0

moles of glycine, respectively. After stirring for 30 min and considering the industrial feasible condition, the pH of solutions was controlled at level of 7.0 by slowly dropping ammonia and continuously stirring by magnetic mixer. The homogeneous solutions were heated at 110 °C on a hot plate to form viscous precursors. The temperature of the obtained precursors was raised to 300 °C by electrical furnace. The smoldering-type ignition causes the decomposition, generating a large volume of gas. The combustion occurs as flaming, gas phase reaction, or smoldering, solid–gas reaction. The flaming-type combustion can endure for seconds or maximum 1 min, while the smoldering type is extinguished in a few seconds. During the smoldering-type combustion, the material underwent foaming followed by decomposition and it lasted for almost 7 min, but in flaming-type combustion, vigorous ignition occurred for less than 1 min. The obtained powders were crushed and calcined in an electrical kiln at 600, 800, 1000, and 1200 °C for 1 h. The complete powder preparation steps are illustrated in Fig. 1.

Fig. 1 Preparation chart of MgAl₂O₄ spinel in nano-scale.

2.2 Powder characterizations

In order to investigate the effect of fuel ratio on thermal decomposition of viscous precursors, the thermo-analytical measurements were carried out with simultaneous differential thermal analysis and thermogravimetry (DTA–TG) instrument (Model 409, Netzsch, Germany). The heating rate was fixed at 10 °C/min and air was used as purge gas. Approximate 10 mg of each precursor was placed in a ceramic pan and the thermal treatment was performed from room temperature to 600 °C. In order to better evaluate the ignition of fuel after calcination, the residual hydrogen, carbon, and nitrogen amounts were determined by elemental analysis (Carlo Erba, Model EA 1110, Italy).

The synthesized powders were characterized by X-ray diffraction (XRD) technique (X'PERT PRO, Philips Research Laboratories, the Netherlands) in the diffraction angle range of 10°–80° using Cu K α radiation. The crystallite size, D , was estimated by the Scherrer equation [31]:

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (2)$$

where β is the breadth of observed diffraction peak at its half intensity, k is the so-called shape factor which usually takes a value of 0.9, θ is the Bragg angle, and λ is the radiation wavelength (0.15406 nm).

The specific surface area of powders was determined by low-temperature nitrogen adsorption method (Brunauer–Emmett–Teller (BET) technique, Gemini 2360 Apparatus, Micromeritics, Norcross, GA, USA) after degassing under vacuum at 150 °C. Each experiment was repeated three times and the entire experimental procedure was found to give satisfactory reproducible results.

Finally, transmission electron microscopy (TEM, JEM 2010, JEOL, Tokyo, Japan) was used in characterizing particle morphology. The sample was prepared by dispersing the powders in de-ionized water and then placing a drop of suspension on a copper grid with a transparent polymer followed by drying in laboratory oven.

3 Results and discussion

3.1 Combustion evaluation

The combustion mechanism of precursors prepared with different fuel ratios was studied by thermal

analysis. The DTA–TG curves of precursors synthesized with fuel ratios of 0.56 and 0.75 are shown in Figs. 2 and 3, respectively. The weight losses of samples up to 230 °C were 13.0 and 18.0 wt% which are due to the dehydration of precursors. As shown in these figures, the distinct mass loss centered at 280 °C is observed for precursors. The organic material ignition occurs in the narrow temperature range of 230–280 °C. In this temperature range, the weight losses of 69.0 and 58.0 wt% are recorded for precursors synthesized using fuel ratios of 0.56 and 0.75, respectively. The thermo-gravimetric analyses show great weight losses, 16.0 and 18.0 wt%, in the temperature range of 280–600 °C, respectively.

With increasing temperature from 500 to 600 °C, the negligible changes are observed which confirm the thermal stability of powders in this temperature range. Indeed, the sharp exothermic peak is related to the

burning of glycine as the following reaction:

The ammonium nitrate also reacts with glycine according to

The generated heat due to decomposition of fuel causes the formation of spinel phase at relatively lower temperatures:

The exothermic decomposition of precursors is accompanied by evolution of various gases such as CO_2 , N_2 , and water vapor. The samples show incandescent flame growing after autoignition. The combustion leads to the decomposition of compounds, and the precursors become approximately carbon free above 600 °C. The DTA–TG data give a strong evidence for the adoption of 280–300 °C as the initiation temperature. Overall, the following reaction can be considered for synthesis of magnesium aluminate spinel:

where m is the mole number of glycine used in preparation of precursor. Theoretically, for synthesis of 1.0 mol MgAl_2O_4 , 1.78 moles of glycine is required without getting oxygen from air. When the glycine amount is smaller than stoichiometric value, the combustion reaction cannot be performed completely and part of metal ions remain in final product. However, oxygen would be involved to ensure the complete combustion of fuel if the glycine amount is larger than 1.78 moles. The glycine combustion enthalpy can be expressed as [32]:

$$\Delta H^\circ = (\sum n\Delta H_f^\circ)_{\text{products}} - (\sum n\Delta H_f^\circ)_{\text{reactants}} \quad (7)$$

where n is the mole number of the reactants and products. Also, ΔH_f° is the formation enthalpy. Using the thermodynamic data, the enthalpy of combustion can be calculated. The combustion enthalpy for reactions with fuel ratios of 0.56 and 0.75 are about −2376 and −3168 kJ/mol, respectively. As expected, the enthalpy increases substantially with fuel ratio.

In order to identify the composition of remained organic materials in synthesized products, the elemental analyses were completed by determination of residuals

Fig. 2 DTA–TG curves of precursor prepared by fuel ratio of 0.56.

Fig. 3 DTA–TG curves of precursor prepared by fuel ratio of 0.75.

of carbon, hydrogen, and nitrogen contents in the powders. Table 1 reports the amounts of the individual elements for precursors prepared using different fuel ratios. The carbon content is reduced sharply up to 800 °C and reached to constant value when fuel-lean is applied. The reported data indicate that the content of nitrogen strongly depends on fuel ratio before calcination and falls down to a minimum value when calcination is performed at 1000 °C. The increment in calcination temperature improves removal of hydrogen. Although temperature plays an important role in the removal of carbon and hydrogen, these variations are much more marked at 1200 °C. On comparing elemental data, it is found that the calcination of powders at 1000 °C satisfactorily decreases organic contents

Figure 4 indicates the XRD patterns of materials prepared with fuel ratio of 0.56 and calcined at four temperatures. The main peaks of MgAl_2O_4 (JCPDS 01-075-1796) are observed at 2θ of 37.26°, 44.91°, and 65.35°. With increase in calcination temperature, the peaks of magnesium aluminate become more intense and sharper above 800 °C, indicating a continuous increase in the degree of crystallization. Furthermore, the peaks of MgO (JCPDS 00-045-0946) appear at 2θ of 43.47°, 62.26°, and 74.25°. It is noteworthy that temperature has remarkable effect on the partial re-crystallization of magnesium oxide. The peak intensities of Al_2O_3 (2θ : 35.27°, 52.67°, and 57.58° according to JCPDS 01-081-2266) are weak when calcination is performed at 1000 °C, demonstrating that the small content of alumina is crystallized at this temperature. When temperature is raised to 1200 °C, the peak intensities of MgAl_2O_4 increase drastically accompanied with an obvious increase in crystallite size of MgO and Al_2O_3 . The XRD patterns indicate that the negligible amounts of Mg and Al cannot be well arranged in a close-packed cubic lattice and appear in

Fig. 4 XRD patterns of precursor prepared by fuel ratio of 0.56 and calcined at different temperatures.

oxide forms at high calcination temperature.

The XRD analysis was also performed on the powders prepared with fuel ratio of 0.75. The XRD patterns which perfectly match with JCPDS 01-075-1796 are represented in Fig. 5. The crystallinity of MgAl_2O_4 increases after heat treatment at 800 and 1000 °C. However, the calcination at 1000 °C causes the growth of crystals in comparison to that at 800 °C. The fuel-rich causes the high intensity that is directly related to the crystallinity of powders. The highest crystallinity of MgAl_2O_4 is achieved after calcination at 1200 °C. The MgO peaks appear at 1000 °C and the increase in peak intensities of MgO and Al_2O_3 is related to re-crystallization process. These results confirm that the re-crystallization of MgO and Al_2O_3 is independent of fuel ratio. There are clear differences between the crystallinity of powders prepared with different fuel ratios. The crystallinity of MgAl_2O_4 prepared with fuel ratio of 0.75 is comparable with that synthesized by low fuel ratio in all studied temperatures. The powders prepared at low fuel ratio indicate the low crystallinity when it was heated at 800 °C. The increase in fuel ratio positively affects the crystallinity due to increment in the combustion enthalpy.

$\text{NH}_3^+\text{CH}_2\text{COO}^-$ is dominant species at neutral condition [33], and the interaction between the ions of hydroxides and glycine occurs via $-\text{COO}^-$ groups. The interaction is beneficial for dispersion of ions and facilitates the reaction between the solid and gas,

Table 1 Elemental analysis of powders as a function of fuel ratio and temperature (Unit: wt%)

Element	Temperature (°C)				
	As-obtained	600	800	1000	1200
Fuel ratio: 0.56					
Carbon	4.42	2.25	1.11	0.53	0.52
Nitrogen	1.41	0.60	0.12	0.0	0.0
Hydrogen	1.83	1.42	0.90	0.50	0.0
Fuel ratio: 0.75					
Carbon	7.80	2.62	0.89	0.56	0.25
Nitrogen	3.65	0.89	0.12	0.0	0.0
Hydrogen	2.02	1.38	0.91	0.47	0.0

Fig. 5 XRD patterns of precursor prepared by fuel ratio of 0.75 and calcined at different temperatures.

consequently. Therefore, the thermal decomposition needs higher energy and the smoldering-type combustion is observable in this condition. The negligible amounts of Mg and Al are not well arranged in a close-packed cubic lattice and remain free. These cations are re-crystallized at higher calcination temperatures as oxides. Magnesium aluminate spinel is synthesized by the solid state reaction between sources of MgO and Al₂O₃ at higher temperatures. Formation of magnesium aluminate spinel from its constituent oxides is diffusion controlled process of Al³⁺ and Mg²⁺ ions through a relatively immobile oxygen lattice of spinel. At lower temperatures, surface diffusion of alumina is predominant and bulk diffusion is predominant at higher temperatures. Moreover, the bulk diffusion cannot be performed at temperatures lower than 1200 °C. Therefore, MgO and Al₂O₃ remain unreacted. As a result, the intensities of reflections related to oxides increase concomitantly with rise in the calcination temperature.

The exact particle nucleation and growth of crystals are not clear at low calcination temperature <600 °C due to formation of abundant amorphous phase. The crystallite size of MgAl₂O₄, which is estimated using the Scherrer equation, is shown in Fig. 6 as a function of temperature and fuel ratio. An increase in the crystallite size is observed for synthesized powders with increment in calcination temperature. In the studied cases, the variation in crystallite size can be divided into two distinguished domains. When

Fig. 6 Crystallite size of MgAl₂O₄ as a function of calcination temperature and fuel ratio.

calcination is carried out at 800 °C, the crystallite size is found to be about 14 nm and independent of fuel ratio. When the precursor is prepared with high content of glycine and calcination is performed at 1200 °C, the crystallite size reaches a maximum value due to surface diffusion and formation of necks between the particles. Regardless of the effect of fuel ratio on crystallite size, the calcination above 1000 °C causes the further nucleation/growth of nano-crystals.

The specific surface area data determined by nitrogen adsorption are presented in Fig. 7 as a function of temperature and fuel ratio. An increase in the glycine amount leads to a marked decrease in the specific surface area at lower temperatures. The maximum surface area is obtained for precursor prepared with low content of glycine and a sharp decrease appears after calcination at 600 °C. This result is in accordance with the sintering of amorphous particles. The specific surface area of the mentioned precursor increases slightly due to heat treatment at 800 °C in which the nano-sized crystals are formed. The calcination at 1000 °C reduces the surface area to 51.2 m²/g, corresponding the crystallite size of 19 nm. As shown in Fig. 7, the variation of powder surface area prepared with high amount of glycine is similar to that synthesized by low fuel ratio. Between the crystallized powders, the maximum surface area of 60.2 m²/g is obtained for the sample calcined at 800 °C and the minimum value of 7.6 m²/g is related to powders heated at 1200 °C.

The surface area reaches minimum value when heat treatment is performed at 1200 °C and is not affected by

Fig. 7 Specific surface area of synthesized powders as a function of calcination temperature and fuel ratio.

fuel ratio at this temperature. For combustion synthesis, the structure of products is mainly determined by the combustion enthalpy. It is well known that the products with small particles and large specific surface area are obtained at lower calcination temperatures. Since the combustion is not an adiabatic process in studied method, the crystallite size and specific surface area are related to the following factors: (i) the heat released by combustion reaction increases with fuel content and larger combustion heat results in a higher combustion temperature. (ii) The shorter duration of combustion is another reason for grain growth because the heat dissipated in a short time is small and the most of the produced energy is imposed on product. The duration of combustion is mainly affected by the fuel content. (iii) The released gas content is directly related to the fuel ratio. Furthermore, the gas evolution prevents the inter-particle contact and hinders particle growth. The competition from the above factors determines the powder characteristics. At the same time, these factors are connected to the fuel content. For instance, different variations are observed in crystallite size. For the fuel-rich reaction, the amount of evolved gas is large and the duration of combustion energy is long. The combustion enthalpy also is high when fuel ratio is considered to be 0.75. The released energy and duration time are predominant; thereby it is easy to understand the variation in crystallite size of MgAl_2O_4 .

The specific surface area plot versus the crystallite size of MgAl_2O_4 is indicated in Fig. 8. The surface area decreases with the crystallite size to minimum value of $7.2 \text{ m}^2/\text{g}$, in which the calcination temperature is 1200°C . The sharp increase in the crystallinity is

Fig. 8 Variation of specific surface area with the crystallite size.

registered in the crystallite size of 40–50 nm. Another significant change occurs between 14 and 20 nm. The heat treatment between 800 and 1000°C causes a decrease in specific surface area. It is worth noting that the nano-sized MgAl_2O_4 powders can be synthesized by calcination of precursors prepared with different fuel ratios of 0.56 and 0.75, in temperature range of 800– 1000°C . By considering the agglomeration of particles, it is better to carry out the precursor preparation with fuel ratio of 0.56 and in order to achieve the maximum specific surface area, the calcination temperature should not exceed than 800°C .

The morphologies of the MgAl_2O_4 particles synthesized by different fuel ratios and calcined at 800°C are represented in Fig. 9. The morphology of particles is observed to be more regular in shape with size in the range of 10–20 nm. The TEM observations are in agreement with the result obtained by Scherrer equation (Fig. 6).

4 Conclusions

A series of magnesium aluminate powders were prepared through the glycine–nitrate combustion technique. A solution containing magnesium and aluminum nitrates was prepared with Mg/Al mole ratio of 0.50. The appropriate amounts of glycine were added to adjust the fuel/ NO_3 ratio at levels of 0.56 and 0.75. The viscous gels were obtained by heating the solutions at 110°C and MgAl_2O_4 spinel was synthesized by oxidation. The thermal behaviors of powders were evaluated by calcination at different temperatures of

Fig. 9 TEM micrographs of powders synthesized by fuel ratios of (a) 0.56 and (b) 0.75 (calcined at 800 °C).

600–1200 °C. The glycine–nitrate combustion method was found to be a simple, fast, and effective technique for manufacturing nano- and micro-sized magnesium aluminate spinel. The combustion process and physico-chemical characteristics of powders are greatly influenced by the glycine amount and

calcination temperature. It is absolutely impossible to achieve the pure nano-scale particles when calcination is performed at temperatures higher than 1000 °C due to re-crystallization of MgO and Al₂O₃. Although the nano-sized MgAl₂O₄ with regular shape of 10–20 nm is obtainable by synthesis of precursors at studied fuel ratios, the specific surface area of powders produced with low content of glycine is larger than one prepared with fuel ratio of 0.75. In order to avoid agglomeration, both of fuel ratio and calcination temperature should be controlled at appropriate levels. The synthesis of spinel according to the presented algorithm can provide not only the economical method for production of MgAl₂O₄ in the nano- and micro-scale but also reduce the environmental risk.

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