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New synthesis methods of $MgAl_2O_4$ spinel

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Abstract

The paper presents a study concerning the influence of the precursors upon the synthesis temperature, particle size and morphology of the $MgAl_2O_4$ spinel. With this view there have been used by comparison three synthesis methods: thermal conversion of the heteropolynuclear complex combination resulted from the oxidation reaction of 1,2-ethanediol with Mg and Al nitrates; combustion method based on the exothermal redox reaction of Mg and Al nitrates with an adequate fuel (urea, glycine, β-alanine) and sol–gel method, starting from aluminium isopropoxide and Mg nitrate. The obtained samples have been characterized by X-Ray diffraction and scanning electron microscopy.

Keywords: Spinels; Precursors – organic; Sol–gel processes; Combustion synthesis

1. Introduction

The magnesium aluminate, $MgAl_2O_4$ crystals present spinel structure, thus a lot of important properties used in industrial applications. The high melting point (2135 °C), the mechanical strength at high temperatures, chemical inertness and good thermal shock resistance are considerable properties which confer to the $MgAl_2O_4$ usability in the metallurgical, electrochemical, radiotechnical and chemical industrial fields.[1–3]

The production of high purity and high reactivity $MgAl_2O_4$ is influenced by the synthesis method. Although the conventional method, based on the mechanical oxide and/or salt mixtures calcination is the most used for the $MgAl_2O_4$ synthesis,[4,5] it has some inconveniences like high synthesis temperatures, even when mineralizer,[6] additives like ZnO[7] or sintering aid as $AlCl_3$[8] is being used. Another inconvenient is the high number of operations (milling, mixing, consecutive firing), which can impurify the produced material.

Many unconventional methods like: precipitation method,[9] the aerosol method,[10] the citrate–nitrate route,[11,12] classical sol–gel method[13,14] or modified sol–gel route by combining gelation and coprecipitation processes[15] were used to produce $MgAl_2O_4$ spinel.

The literature references also present the methods used for obtaining $MgAl_2O_4$ by pyrolysis of aluminium and magnesium complex compounds with trietanolamine,[16] PVA evaporation technique[3] or the combustion synthesis, using urea and sucrose as fuel.[1,2,17]

In the previous papers,[18–21] we have evidenced certain advantages of the organic precursors method based on the thermal decomposition of the heteropolynuclear complex combination resulted from the oxidation reaction of 1,2-ethanediol by the metallic nitrates by comparison with other unconventional methods. The aim of this work consists in the synthesis of $MgAl_2O_4$, using this method and the accomplishment of a comparative study relative to sol–gel route and combustion method taking into consideration the advantages and disadvantages of that.

2. Experimental procedure

2.1. Organic precursor's method

Organic precursor's method based on magnesium and aluminium glyoxylate preparation through 1,2-ethanediol oxidation with magnesium and aluminium nitrates.

The aqueous solution of aluminium and magnesium nitrates and the 1,2-ethanediol dosed in stoichiometric proportion was heated in air up to 100 °C. Previous studies[18–21] assigns the

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following reactions to the synthesis of complex combination:

$$Al(NO_3)_3 + H_2O \rightarrow Al(OH)(NO_3)_2 + HNO_3 \quad (I)$$

$$3C_2H_4(OH)_2 + 2\,Al(OH)(NO_3)_2 + Mg(NO_3)_2 \xrightarrow{\text{solution}} Al_2Mg(OH)_2(C_2H_2O_4)_3.xH_2O + 6NO + 6H_2O \quad (II)$$

$$NO + 1/2O_2 \rightarrow NO_2 \quad (III)$$

During the reactions, white powder formation takes place. After complete emission of nitrogen dioxide the reaction product was washed out with acetone–water mixture and filtered.

2.2. Combustion method

Combustion method is based on the redox reaction between aluminium and magnesium nitrate (oxidant reactants) and an adequate fuel (reductive reactant). The used fuels were urea, glycine and β-alanine, in order to study the influence of their reducing characteristics and chain length on the synthesis temperature and of the crystallite size. An important influence in the combustion method has the reducer and oxidizer agent ratio, while it determine the temperature and reaction time, control the degree of conversion, the phase formations, particles morphology and the nature of the agglomerates.

Stoichiometric metal nitrate and fuel ratio was used, taking into consideration the electrons changes involved in the redox reactions, considering that the resulted gases are: CO_2, H_2O and N_2.

The magnesium and aluminium nitrate aqueous solutions mixed with the fuel (urea, glycine, respectively β-alanine) were heated up to 100 °C, for the water evaporation. The dried product was heated on a hot plate at about 300 °C in open system, where ignition took place, resulting dry, white and very fragile foam that easily crumbled into powder.

2.3. Sol–gel method

Aluminium triisopropoxide - $Al(O^iC_3H_7)_3$ (Merk) was used, as aluminium source and magnesium nitrate - $Mg(NO_3)_2 \cdot 6H_2O$ (Chimopar Bucureşti), as magnesium source. The aluminium triisopropoxide was hydrolyzed with water, 8 h at 80 °C using 1:200 molar ratio. Nitric acid – HNO_3 65% (Reidel Haën) was used as peptization agent at: alkoxide/HNO_3 = 1/1 molar ratio. The magnesium nitrate was dissolved in isopropanol and added to the sol during continuously stirring and after addition, the temperature was raised gradually up to 110 °C. The formed gel was dried in a drying stove at 150 °C and subsequently ground.

All the prepared samples were annealed in electric furnace for 1 h between 500 and 1000 °C.

The evolution of the phase composition of the samples after the thermal treatments has been monitored by XRD (Bruker's D8 Advanced system) using Ni filtered CuK_α radiation. The crystallite size was determined from the XRD patterns using the Sherrer Eq. (1).

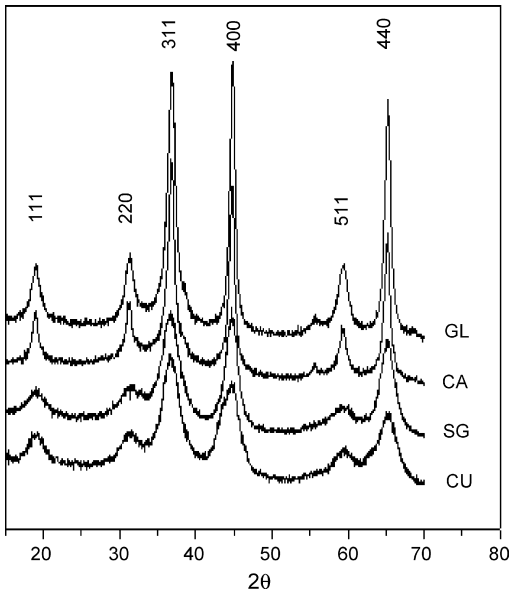

Fig. 1. The X-Ray diffraction patterns of some of the studied samples annealed at 700 °C.

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

D – represents the crystallite size in nm, λ – CuK_α (0.15406 nm) radiation wavelength, β – the full width at half of maximum in radian and θ – the Bragg-angle.

The particles morphology and size were examined by SEM photomicrographs (Philips ESEM XL 30 electron microscope using secondary-electron photomicrographs).

3. Results and discussion

The X-Ray diffraction patterns analysis points out that, the formation of $MgAl_2O_4$ spinel starts at temperatures lower than 500 °C, regardless of the synthesis method. Fig. 1 presents the X-Ray diffraction patterns of the samples annealed at 700 °C for 1 h obtained by the magnesium and aluminium glyoxylate (GL) thermal decomposition, by the combustion method using urea (CU) and β-alanine (CA) as fuel and sol–gel method (SG).

A close analysis of Fig. 1 leads to the following observations:

The diffraction patterns prove that at 700 °C the spinel phase is present regardless of the used synthesis method. The spinel phase crystallinity, according to the intensity and broadness of diffraction peaks and to the synthesis method, alternates as follows: the most intense peaks presents the GL sample where magnesium and aluminium glyoxylate precursor was used and CA sample obtained using combustion method when β-alanine as fuel was used. Poorly intense and broader peaks could be observed on SG sample, obtained by sol-gel method and on CU, combustion method sample obtained with urea fuel. Increasing the annealing temperature, the increase of diffraction peaks intensity can be observed.

The crystallites size was calculated for samples obtained at 700 °C, by different synthesis methods. For GL, CU and SG

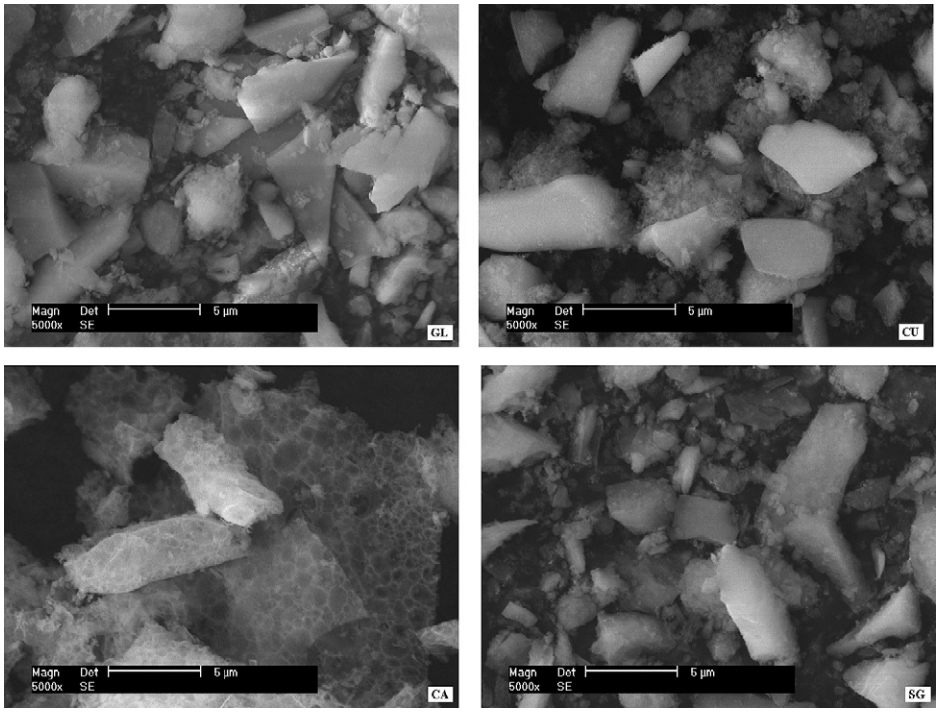

Fig. 2. SEM photomicrographs of $MgAl_2O_4$ obtained using different synthesis methods: glyoxylate precursor (GL), combustion with urea as fuel (CU), combustion with β-alanine as fuel (CA), and sol–gel (SG).

Table 1
Crystallites size (D_{av}) and the reticular parameter (a_{av}) calculated for $MgAl_2O_4$ obtained at 700 and 900 °C, using different synthesis methods

Sample	Temp. (°C)	D_{av} (nm)	a_{av} (Å)
GL	700	8.34	8.0780
GL	900	9.89	8.0924
CU	700	3.45	8.0742
CU	900	5.12	8.0812
CA	700	10.36	8.0882
SG	700	4.37	8.0593
SG	900	6.14	8.0776

samples the crystallites size was calculated for 900 °C too. The data were calculated using Sherrer relation taking into consideration the diffraction peaks of the following crystal-lattice planes: (1 1 1), (2 2 0), (3 1 1), (4 0 0), (5 1 1) and (4 4 0). The average crystallites sizes (D_{av}) are presented in Table 1. The experiments (measurements and calculations) indicate the increase of the crystallites size when the annealing temperature is increased, for the samples obtained using the same method.

The cell parameter (a) was calculated for the $MgAl_2O_4$ phase for the samples annealed at 700 °C, (produced with different synthesis methods) and also for GL, CU and SG samples annealed at 900 °C. The cell parameter (a) was calculated using the following Eq. (2):

$$a = d_{hkl}(h^2 + k^2 + l^2)^{1/2} \quad (2)$$

where *hkl* are the Miller indices, for the same crystal-lattice planes as used for *D* calculus. The average size of the cell parameter (a_{av}) is presented in Table 1. The calculated values are quite similar to those from references, where $a = 8.0831$ Å (21–1152 JCPDS file[22]) for the well crystallized spinel $MgAl_2O_4$. The differences between the calculated cell parameters (a_{av}) of the spinel obtained by different methods are unessential.

The SEM photomicrographs of $MgAl_2O_4$ obtained using different methods at 700 °C (SG, GL, CU and CA samples) are presented in Fig. 2.

Based on the SEM photomicrographs, the following remarks can be pointed out: the samples obtained using different synthesis methods, at 700 °C, lay out significant differences, concerning the particles size, and especially their shape and dimensional distribution; in the case of combustion method using β-alanine (CA) the most rounded particles with narrow-range of size associated in agglomeration can be observed.

Taking into consideration that the spinel obtained through sol–gel method displays the smaller crystallites size (determined using X-Ray diffraction) and on the other hand the spinel obtained from combustion method using β-alanine displays the larger size, the conclusion that there is no correlation between the crystallite size (respectively the crystal-lattice ordering) and particles sizes, can be educed.

4. Conclusions

(1) The obtained results prove that the magnesium aluminate ($MgAl_2O_4$) formation takes place at low temperature, about 500 °C in all of the used unconventional methods. The X-Ray diffraction patterns prove that at 700 °C the spinel phase is present and the spinel phase crystallinity alternate with the used synthesis method.
(2) The $MgAl_2O_4$ crystallites size differs according to the synthesis method between 3.45 nm for combustion with urea

fuel and 8.34 nm for that of aluminium and magnesium glyoxylate calcinations, respectively 10.36 nm for combustion with β-alanine at 700 °C.

(3) The nature of the fuel used in the combustion method greatly influences the crystallites size: the longer the chain of the molecule – the larger the crystallites formed.

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