



Synthesis of MgAl_2O_4 by Gelatin Method: Effect of Temperature and Time of Calcination in Crystalline Structure

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Magnesium aluminate can be obtained by the methods: ceramic method, sol-gel, co-precipitation, hydrothermal and combustion. However, this work presents a simple and low cost route to obtain MgAl_2O_4 through the gelatin method. The main objective was to use gelatin as an organic precursor and to verify the influence of temperature and time of calcination on the structural and morphological properties of obtained materials. Al and Mg nitrates were used as metal precursors with Al/Mg = 2 ratio. Samples were calcined as follows: 700 °C, 900 °C and 1100 °C during 2 and 4 h. The powders were characterized by TGA, XRD and SEM. A single phase material with a crystallinity of 39.18 - 90.40% and crystallite size in the range of 12.4 to 55.5 nm was obtained. The materials exhibited morphology in the form of plates and small agglomerates. It was found that increasing temperature and time of calcination favored the growth of crystallites and increased crystallinity.

Keywords: *Magnesium aluminate, gelatin method, thermal treatment, catalytic support.*

1. Introduction

Magnesium aluminate spinel (MgAl_2O_4) has a cubic crystalline structure and general formula AB_2O_4 . It is well known and studied in the area of ceramic materials since it presents a potential combination of mechanical, physical and chemical properties^{1,2}. Thus, MgAl_2O_4 is widely required for several industrial applications and has recently been used as a support in the preparation of heterogeneous catalysts^{3,4}, mainly those used in strongly endothermic reactions such as dry reforming of methane^{3,5-7}.

The solid-state ceramic reaction method has traditionally been the most used in the preparation of MgAl_2O_4 ⁸, however it has the disadvantages of being a high-energy route and producing materials with inadequate physico-chemical properties for catalytic applications⁹. Therefore, efforts have been made to improve the synthesis methods in order to obtain MgAl_2O_4 nanometric powders with high purity and chemical homogeneity, for a more efficient control of its properties and potentialization of its applications.

In microwave assisted combustion method the variation of synthesis parameters implies on the formation of undesirable secondary phases and affect the crystallinity and crystallite size of the material obtained. However, MgAl_2O_4 with higher degree of crystallinity (66.60%) and small crystallite sizes (23.86 nm) can be obtained after adjustment of synthesis and calcination variables at 900 °C for 3 h¹⁰.

In turn, uniform and nanometric monophasic MgAl_2O_4 powders with crystallites of about 11 nm and low degree of crystallinity can be obtained by the modified sol-gel method (Pechini) with subsequent calcination at 800 °C for 2 h¹.

In recent years, the use of natural gelatin as an organic precursor for the synthesis of mixed oxides with spinel¹¹ and perovskite¹²⁻¹⁴ structure has received special attention because it is a low cost, easy to acquire and nontoxic material, as well as it allows to obtain materials with well-defined structure and morphology. In principle, the amino acids present in the natural gelatin interact with the metal ions present in the aqueous solution to form a resin. The resin obtained is thermally treated to remove organic material at low temperatures and calcination at higher temperatures to form the material crystalline phase. The gelatin method appears as

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an alternative method of synthesis, but with few reports of its use on the synthesis of magnesium based aluminates. In these cases, acids were used on the synthesis as well as long periods of calcination (12 h)¹⁵⁻¹⁷. However, considerations on the structural and morphological properties of these materials are not presented. Thus, the aim of this work was to synthesize MgAl_2O_4 using gelatin as organic precursor, as well as to evaluate the effect of different temperatures and calcination times on the formation of spinel crystalline structure.

2. Materials and Methods

2.1. Synthesis

The synthesis of MgAl_2O_4 was performed using Al and Mg nitrates (Sigma-Aldrich) as starting material and commercial gelatin as organic precursor at a weight ratio of 1:1:2 (gelatin:Mg:Al). Initially, deionized water was heated at 60 °C. Gelatin was added slowly and stirred for 30 min to ensure a total dissolution. Then, suitable amounts of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (98.0%) and $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (98.0%) were added and the mixture was kept under stirring until complete dissolution. The temperature was slowly increased to 90 °C, keeping the stirring until gel formation. The resulting gel was pretreated in a muffle furnace at 350 °C for 2 h at a heating rate of 10 °C min^{-1} . A sample of the precursor powder was submitted to thermogravimetric analysis and the remaining powder was calcinated at a 10 °C min^{-1} in air atmosphere at different temperatures and times (700 °C, 900 °C and 1100 °C during 2 and 4 h). The synthesized materials were characterized by different techniques.

2.2. Characterization

The thermal behavior of the samples were measured by thermogravimetric analysis in a SDT - Q600 thermal analysis system from TA Instruments, under air atmosphere, varying the temperature from 30 to 900 °C at a heating rate of 10 °C min^{-1} . The formation of the crystalline structure was investigated by X-ray diffraction (XRD), by the powder method on a Shimadzu equipment (XRD-7000) using Cu-K α radiation (1.5409 Å) with 2θ values ranging from 10° to 80°, operating at 2° min^{-1} with 0.02° step. The morphology of the material was observed by scanning electron microscopy on a SSX-550 Shimadzu equipment, equipped with tungsten filament. The crystallinity was calculated using the XRD-7000 Shimadzu Software.

3. Results and Discussions

Figure 1 shows the thermogravimetric curve of natural gelatin. A mass loss of 99.33% corresponding to three characteristic events was observed: (A) 30 to 190 °C,

associated with water loss; (B) 190 to 433 °C, related with the decomposition of amino acids fragments of easy degradation, essentially proline; and (C) 433 to 620 °C regarding the elimination of amino acids of difficult degradation, mainly glycine¹⁴. Figure 2 shows the thermogravimetric curve of MgAl_2O_4 precursor powder pre-calcinated at 350 °C for 2 h. A mass loss of 25.93% corresponding to three different events was observed: (A) 30 to 322 °C, associated to water loss and elimination of proline residues; (B) 322 to 611 °C and (C) 611 to 800 °C, can be related to glycine degradation and the decomposition of Mg and Al metallic nitrates to form the MgAl_2O_4 phase¹². Higher temperature was required to break the bonds between the organic glycine radicals and the metal ions of the precursor salts, as can be seen in the thermogravimetric curve of precursor powder. Similar behavior was observed in obtaining the perovskites PrCoO_3 and PrNiO_3 by the gelatin method¹³.

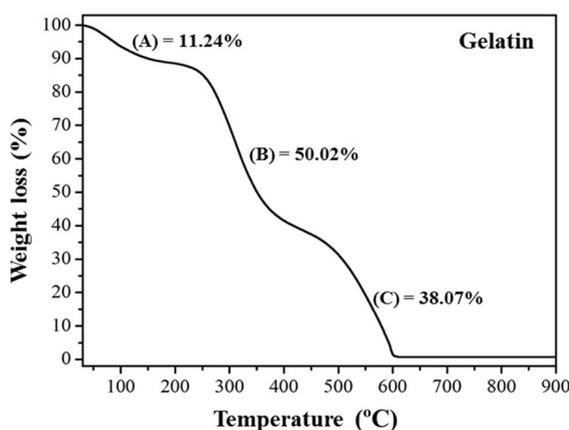


Figure 1. Thermogravimetric curve of natural gelatin.

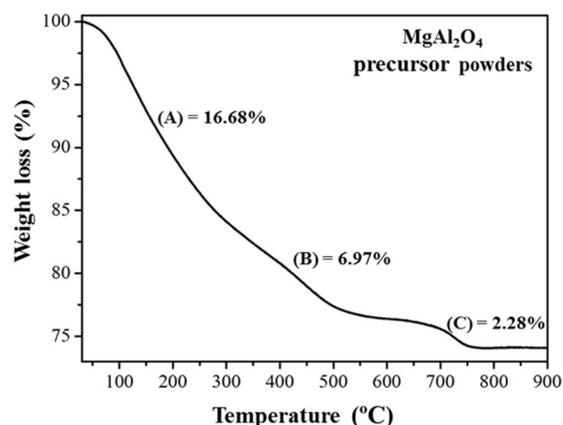


Figure 2. Thermogravimetric curve of MgAl_2O_4 precursor powders.

Figure 3 shows the X-ray diffractograms of the synthesized materials. All materials show characteristic diffraction peaks corresponding to the crystallographic planes of MgAl_2O_4 spinel of cubic structure and Fd-3m symmetry (JCPDS No.

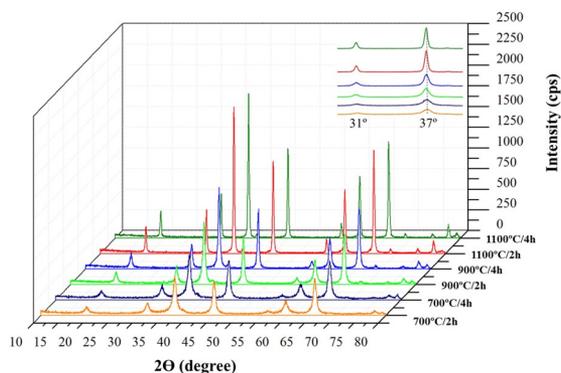


Figure 3. XRD patterns of MgAl_2O_4 powders.

073-1959). According to the XRD patterns all materials are monophasic (MgAl_2O_4 spinel), revealing the efficiency of gelatin as an organic precursor to obtain pure magnesium aluminate. The higher intensity peak observed at $2\theta = 37^\circ$ (of the standard chart), referring to (311) reflection, confirms that the degree of crystallinity increased following an overall trend ($700^\circ\text{C}/2\text{h} < 700^\circ\text{C}/4\text{h} < 900^\circ\text{C}/2\text{h} < 900^\circ\text{C}/4\text{h} < 1100^\circ\text{C}/2\text{h} < 1100^\circ\text{C}/4\text{h}$). Moreover, it was observed that the main peak (311) was slightly shifted to lower diffraction angles as the heat treatments were intensified (Figure 3 magnified). This indicates the possibility of preparing more crystalline materials by using more severe heat treatments.

The average crystallite size (D), calculated from the most intense X-ray diffraction peak (311) using Scherrer's equation¹⁸ is given by equation (1)

$$D = \frac{0.89\lambda}{\beta \cos\theta} \quad (1)$$

where λ is the X-ray wavelength of 1.5409 \AA , β the full width at half maximum (FWHM) of the diffraction peak and 2θ is the Bragg's diffraction angle. CeO_2 was used as instrumental pattern. The lattice parameter of cubic magnesium aluminate was calculated based on the X-ray diffraction patterns using equation (2),

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

where d_{hkl} is the interplanar distance associated with the respective Miller indices (hkl) and a is the lattice parameter.

Figure 4 shows the curve of the effect of temperature and calcination time on the degree of crystallinity and crystallite size of the synthesized magnesium aluminate. In general, the values of these measurements increased with temperature and time of heat treatment. With respect to crystallinity, it was observed that the temperature has a greater influence than the calcination time. In turn, significant differences were observed with respect to the crystallite size for samples calcinated at temperatures above 900°C . The crystals grow slowly up

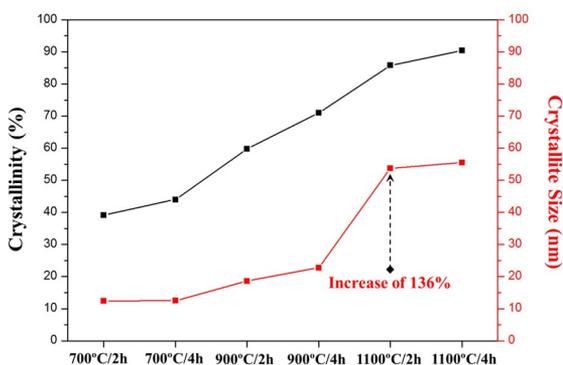


Figure 4. Effect of temperature and time of calcination on crystallinity and crystallite size.

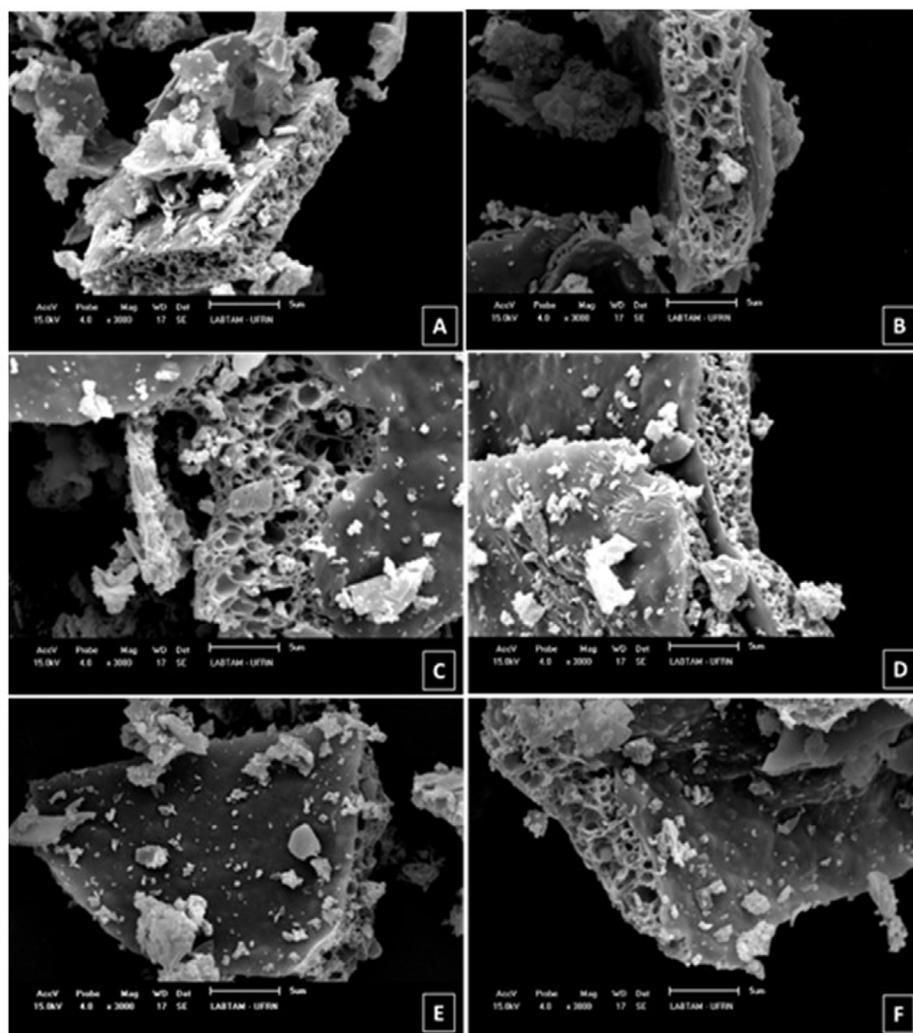
to 900°C and rapidly between 900°C and 1100°C , which gives a 136% increase in crystallite size (Figure 4). This is due to the surface diffusion phenomena that can activate and promote neck-forming sintering between calcined particles above 900°C ¹⁹. This result showed that the MgAl_2O_4 powders prepared by the gelatin method can be used as catalysts supports in the range of 700 and 900°C ^{5,20-22} without any major modifications in the crystallite size.

Interestingly, this result may be important for preparing catalysts, since the deposition of the metal phase on MgAl_2O_4 support can be performed at temperatures below 900°C without significant changes in the crystallite size, allowing the obtaining of catalysts with different levels of metal-support interaction.

The lattice parameters calculated for the MgAl_2O_4 powders prepared were: $a = b = c = 0.801814, 0.803923, 0.804384, 0.805436, 0.805767, 0.806199 \text{ nm}$ for samples calcined at $700^\circ\text{C}/2\text{h}, 700^\circ\text{C}/4\text{h}, 900^\circ\text{C}/2\text{h}, 900^\circ\text{C}/4\text{h}, 1100^\circ\text{C}/2\text{h}, 1100^\circ\text{C}/4\text{h}$, respectively (Table 1). For all samples, slight changes were observed in the lattice parameters and this can be attributed to the presence of lattice strain that modify with the thermal treatments. It is possible to observe a slight increase in the volume of crystalline structure as the sample is calcined at higher temperature, which can be attributed to the increase of the particle size as the sample undergoes heat treatment^{23,24}. The intensification of the diffraction peaks (Figure 3) and the growth of the crystallites (Figure 4) may be related to the internal strains resulting from the thermal energy supplied, which results in the formation of larger grains at higher temperatures^{23,25}. According to the results presented in Table 1 for MgAl_2O_4 synthesized by the sol-gel² and flash pyrolysis²⁶ methods, it can be seen that the values of the lattice parameters and the cell volume of the crystalline structure for the samples obtained are slightly higher than those observed in this study. The heat treatment at 1100°C in this work caused internal stresses in the MgAl_2O_4 structure similar to those observed in the literature for calcination of 700 and 900°C . This indicates the strong influence of the synthesis method and the type of organic precursor on the structural properties of MgAl_2O_4 powders.

Table 1. Lattice parameter from the obtained XRD data.

References	Sample	h k l	Lattice parameter (nm) a = b = c	d_{hkl} (nm)	V (nm ³)
JCPDS card	01-073-1959	(3 1 1)	0.804998	0.242716	0.521656
This work	700°C/2h	(3 1 1)	0.801814	0.241756	0.515491
	700°C/4h	(3 1 1)	0.803923	0.242392	0.519570
	900°C/2h	(3 1 1)	0.804384	0.242531	0.520464
	900°C/4h	(3 1 1)	0.805436	0.242848	0.522508
	1100°C/2h	(3 1 1)	0.805767	0.242948	0.523153
	1100°C/4h	(3 1 1)	0.806199	0.243078	0.523994
Ref. 2	700°C/1h	(3 1 1)	0.805930	0.242997	0.523470
	900°C/1h	(3 1 1)	0.807760	0.243549	0.527044
Ref. 26	700°C/2h	(3 1 1)	0.806000	0.243018	0.523607
	900°C/4h	(3 1 1)	0.808000	0.243621	0.527514


Figure 5. SEM images of MgAl_2O_4 . A) 700 °C/2 h, B) 700 °C/4 h, C) 900 °C/2 h, D) 900 °C/4 h, E) 1100 °C/2 h and F) 1100 °C/4 h.

Finally, Figure 5 shows the micrographs of the obtained powders. The micrographs reveal that the particles are formed by porous plates. In this case, temperature and time did not significantly influence morphology.

4. Conclusions

Single phase MgAl_2O_4 spinel-type powders were successfully obtained by the gelatin method. The effect of temperature and calcination time affects the structure of the powders, mainly the crystallinity. For the crystallite size, temperatures up to 900 °C do not affect significantly. However, the increase observed in the lattice parameters and in the volume of crystalline structure confirms the effect of calcination on the structure of MgAl_2O_4 obtained. From a simple and low cost route it was possible to obtain a very promising material for catalysis and other industrial applications.

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