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Characterization of $ZnAl_2O_4$ Spinel Obtained by Hydrothermal and Microwave Assisted Combustion Method: A Comparative Study

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In this work, zinc aluminate spinel was prepared by two methods of directly synthesis (without calcination): microwave assisted combustion and hydrothermal method. The materials were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and N_2-adsorption/desorption isotherms. The XRD patterns confirmed the formation of cubic $ZnAl_2O_4$ spinel structure with no secondary phases for both synthesis routes, whereas the hydrothermal method yielded powders with crystallite size 3 times smaller (6.9 nm), as compared to the powders produced by microwave assisted combustion method (25.6 nm). The micrographs revealed agglomerated powders with plate-like morphologies for both routes. Nitrogen adsorption/desorption isotherms (BET) revealed higher surface area (183 $m^2.g^{-1}$) and greater pore volume (0.173 $cm^3.g^{-1}$) for $ZnAl_2O_4$ powders prepared by the hydrothermal method.

Keywords: *Zinc Aluminate, Hydrothermal Method, Microwave Assisted Combustion*

1. Introduction

Zinc aluminate, $ZnAl_2O_4$, is a ternary oxide with spinel structure that has drawn considerable attention in the past years as an advanced material due to its combination of desirable properties: high mechanical strength, high thermal and chemical stability, low sintering temperature, low surface acidity, wide band gap and excelent optical properties[1-3] with various applications. Therefore, it is currently being used as high temperature material, sensors, eletronic and optical materials, as well as catalysts and catalyst support[4-8]. In general, many methods of synthesis have been used for the preparation of $ZnAl_2O_4$ oxide, which include co-precipitation[9-10], modifed citrate sol-gel[11], microwave combustion[3,12], hydrothermal[13-14], sol–gel[15], polymeric precursor[16] and solid state route[17].

Among the several preparation methods, microwave assisted combustion synthesis is one of the most effective, fast, simple and energy efficiency method for the synthesis of metal oxide based materials, producing high purity and chemically homogeneous powders[3,6]. Metal precursors and fuel (mostly organic compounds like urea, citric acid, glycine, carbohydrazide or alanine) in an appropriate stoichiometric ratio controls the combustion process in accordance with the propellant chemistry principles, producing a very fast and exothermic chemical reaction to form the material[12,18].

The hydrothermal method is a wet chemical solution technique and stands out by using low temperatures to produce directly nanometric powders with high surface areas, narrow size distribution and crystals with great perfection without the need of subsequent thermal treatments[19-20]. The high surface area and a porous structure of $ZnAl_2O_4$ are of great importance for catalytic purposes.

The synthesis method can greatly affect the characteristics and properties of materials. In this context, the aim of this work was to carry out a comparative study of the synthesis of $ZnAl_2O_4$ prepared without calcination by hydrothermal and microwave assisted combustion method. Besides, the present work aims to study the influence of the synthesis methods on the structural, morfological and textural parameters of $ZnAl_2O_4$ powders. The powders produced were characterized

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by the following techniques: X-ray diffraction (XRD), scanning electron microscopy (SEM) and N_2-adsorption/desorption isotherms.

2. Materials and methods

All chemicals used in the present study were of analytical grade and used as received without further purification. $Al(NO_3)_3 \cdot 9H_2O$ (Sigma-Aldrich), $Zn(NO_3)_2 \cdot 6H_2O$ (Sigma-Aldrich) and urea CH_4N_2O (Vetec) were used as starting materials.

2.1. Microwave Assisted Combustion Synthesis

Zinc nitrate and aluminum nitrate were used as precursors and urea as a fuel in this method. The compounds were dissolved separately in de-ionized water and mixed together in a glass becker at room temperature under constant stirring to obtain a homogeneous solution. The fuel to oxidizer ratio (F/O) was equal to 1 as per the concept used in propellant chemistry. The homogeneous solution was placed inside a domestic microwave-oven and exposed to irradiation for 5 min at 900 W output power, and frequency of 2.45 GHz. Initially, the solution boiled and underwent dehydration followed by decomposition with the evolution of gases[12]. After ignition started, a rapid flame took place resulting in a solid final product that was denoted as $ZnAl_2O_4$_MC.

2.2. Hydrothermal Synthesis

Zinc nitrate and aluminum nitrate were used as precursors and urea as a basic source in this method. First, zinc nitrate, aluminum nitrate and urea were dissolved in de-ionized water to form a transparent solution under magnetic stirring. The Zn:Al molar ratio and the Zn:Urea molar ratio were maintained as 1:2 and 1:10, respectively. Then, the above solution was transferred into a 100 mL Teflon-lined stainless steel autoclave, which was further sealed and kept at 180 °C in an electrical oven for 24 h. The final pH value of the reaction solution was ~10. After being cooled to room temperature, the product was filtered, thoroughly washed with water until the pH value of the filtrate was neutral[13]. Then, the resulting precipitate was dried at 80 °C overnight and denoted as $ZnAl_2O_4$_H.

2.3. Characterization

The structural characterization of the $ZnAl_2O_4$ spinel powders were determined by X-ray powder diffraction (XRD) in a Shimadzu XRD 7000 apparatus with Cu-Kα radiation at λ = 1.540 Å for 2θ values ranging from 20° to 80°, operating at 2°.min^{-1} with 0,02° step. The morphological characteristics of the powders were analyzed by scanning electron microscopy in a Shimadzu SSX550 microscope, operating with 15 kV and equipped with tungsten filament. Previously, the samples were coated with a thin layer of gold. The textural characteristics of the samples (surface area, pore size, and pore volume) were determined by the adsorption and desorption of nitrogen in a Micromeritics ASAP 2020 apparatus using BET and BJH methods. The pore size distributions were derived from the desorption branches of the isotherms using Barret–Joyner–Halenda (BJH) method. Prior to measurements samples were degassed at 200 °C for 10 h.

3. Results and discussions

The XRD patterns of the $ZnAl_2O_4$_H and $ZnAl_2O_4$_MC samples are shown in Figure 1. Both diffractograms consist of a single crystalline phase, showing characteristic diffraction peaks corresponding to (220), (311), (222), (400), (331), (422), (511), (440), (620) and (533) reflections of cubic $ZnAl_2O_4$ spinel structure (JCPDS No. 05-0669). This indicates that there is a complete formation of the spinel phase in both samples synthesized in the experimental conditions employed in this work. No diffraction peaks related to secondary phases or impurity were detected. The $ZnAl_2O_4$_MC sample presented more intensive and sharper diffraction peaks ($FWHM_{311}$ = 0.2558) revealing its higher crystallinity degree and bigger crystallite size; whereas the $ZnAl_2O_4$_H sample presented broader and less intense peaks ($FWHM_{311}$ = 0.2362) indicating its smaller crystallite size and fine particule nature. The lattice parameters and average crystallite size of the samples are listed in Table 1. The average crystallite size (D), calculated from the most intense X-ray diffraction peak (311) using Scherrer's equation[21] is given by equation (1)

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

where, λ is the wavelength of the X-ray source, β the full width at half maximum (FWHW) of the diffraction peak and 2θ, the diffraction angle. The lattice parameter of cubic zinc aluminate was calculated based on the X-ray diffraction patterns using equation (2),

$$\alpha^2 = d_{hkl}^2 (h^2 + k^2 + l^2) \qquad (2)$$

where, a is the lattice parameter, d_{hkl} the interplanar spacing corresponding to the Miller indices, h, k, and l the miller indices[21]. The results show that the crystallite sizes are in nanometers scale, 25.6 nm and 6.9 nm, for $ZnAl_2O_4$_MC and $ZnAl_2O_4$_H, respectively. As the working temperature is relatively low in the hydrothermal synthesis, this method leads to the formation of smaller crystallites[22]. Whereas, $ZnAl_2O_4$_MC powders present larger crystallite sizes, probably due to the large amount of heat released during combustion reaction[3]. These values are similar to those for zinc aluminate

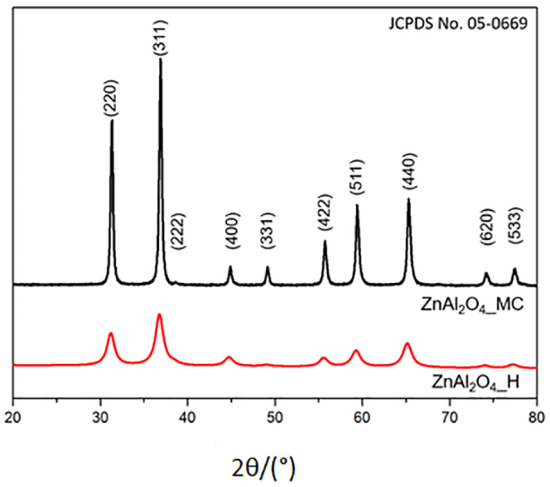

Figure 1. XRD patterns of $ZnAl_2O_4$ powders.

Table 1. Structural and textural data for $ZnAl_2O_4$ powders.

	$ZnAl_2O_4$_MC	$ZnAl_2O_4$_H
Crystallite size (nm)	25.6	6.9
Lattice parameter (Å)	8.0779	8.1121
Surface area ($m^2.g^{-1}$)	5.3	183.5
Average pore size (nm)	10.9	3.4
Total pore volume ($cm^3.g^{-1}$)	0.011	0.173

obtained by Anand et al. (20 nm)[23] and Chen et al. (6–7 nm)[13] using the microwave combustion method and hydrothermal method, respectively. The lattice parameters of (8.1121 Å) and (8.0779 Å) for $ZnAl_2O_4$_H and $ZnAl_2O_4$_MC respctively, are very close to the theoretical value of gahnite (8.0848 Å) mentioned in the PDF file JCPDS 05-0669.

The micrographs of $ZnAl_2O_4$_MC and $ZnAl_2O_4$_H powders obtained by scanning electron microscopy (SEM) are shown in Figure 2. The powders prepared via hydrothermal method (Figure 2a) resulted in smaller particles measuring between 1 and 21 µm. While the powders obtained by microwave combustion method (Figure 2b) resulted in larger particles, measuring between 3 and 95 µm. The micrography of $ZnAl_2O_4$_H (Figure 2a) revealed agglomerated particules with shaped plate type morphology and small aggregates on the surface of bigger clusters[22]. SEM image of $ZnAl_2O_4$_MC (Figure 2b) revealed the presence of plate-like aggregates with irregular surface and porous structures. This morphology is typical for combustion synthesized powders due to the large volume of gases released during combustion reaction and the high temperature reached within the reaction mixture[3]. The morphology of the powders depends strongly on the synthesis method used. For example, Du et al.[24] obtained $ZnAl_2O_4$ powders with polyhedral morphology prepared by solid state route. Motloung et al.[5] describe zinc aluminate powders with rod-like-needles morphology prepared by citrate sol-gel. $ZnAl_2O_4$ powders with semi spherical morphology can be obtained by sol-gel[25] and co-precipitation[26] methods.

Figure 3 shows the N_2 adsorption/desorption isotherms of the $ZnAl_2O_4$ samples. According to IUPAC classification, both samples have a type IV isotherm and H2 hysteresis, which are typical for mesoporous materials[27]. The mesoporous structure was confirmed by the analysis of pore size distribution (see insert in Figure 3), which shows the spectra of the pore diameter in the mesoporous region for both samples. The pore size distribution curves display a narrow unimodal distribution with an average pore size of approximately 3.4 nm and 10.9 nm (see Table 1) for sample $ZnAl_2O_4$_H and $ZnAl_2O_4$_MC, respectively. In addition, $ZnAl_2O_4$_H sample exhibit higher total pore volume (0.173 $cm^3.g^{-1}$) compared to $ZnAl_2O_4$_MC sample (0.011 $cm^3.g^{-1}$) as shown in Table 1.

The surface area was measured via the N_2 physisorption technique calculated by the BET method. The results, listed in Table 1, show that the average area for the $ZnAl_2O_4$_MC sample was 5.3 $m^2.g^{-1}$, which is compatible with the average area of powders obtained via microwave-assisted combustion synthesis[28]. However, BET surface area of only 5 $m^2.g^{-1}$, is

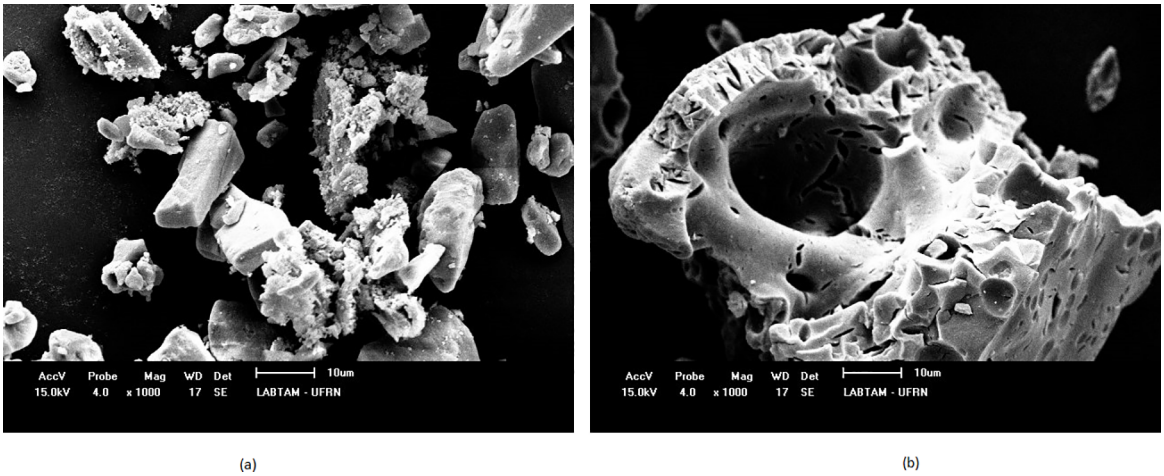

Figure 2. SEM images of (a) $ZnAl_2O_4$_H and (b) $ZnAl_2O_4$_MC powders.

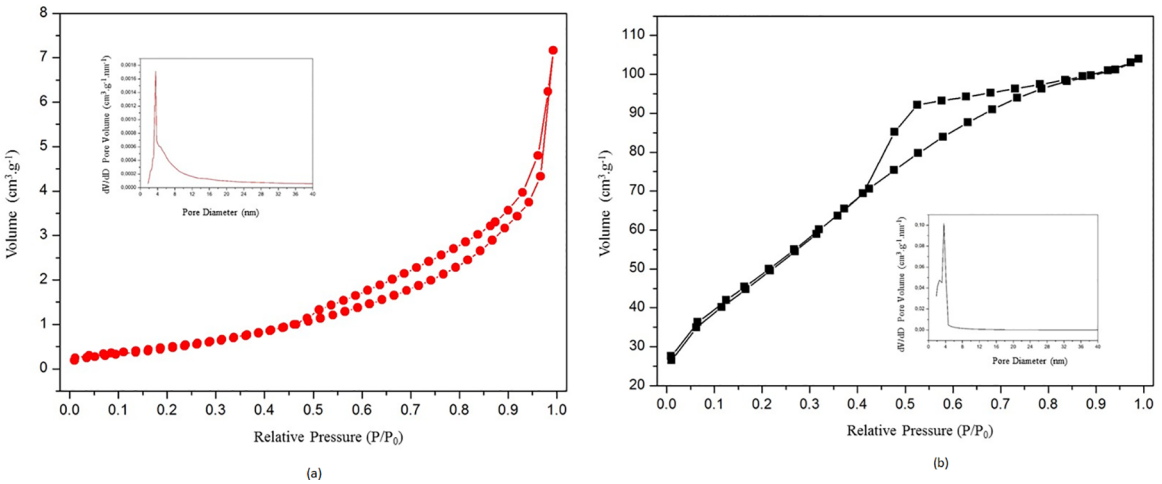

Figure 3. N_2 adsorption/desorption isotherms and (insert) pore diameter distribution of (a) $ZnAl_2O_4$_MC and (b) $ZnAl_2O_4$_H powders.

quite small, especially for catalysis applications[14,18]. The most probable explanation for this result might be the large amount of heat released during combustion reaction[3]. The BET surface area of $ZnAl_2O_4$_H sample was 183.5 $m^2.g^{-1}$, indicating that $ZnAl_2O_4$ prepared by hydrothermal method exibit high surface area, which is in agreement with the average area of powders obtained via hydrothermal synthesis[14,29,30]. Since the temperature is relatively low in the hydrothermal synthesis, this method leads to the formation of nanometric powders with high surface area, which is of great importance for catalytic purposes since it allows a greater accessibility of reactant molecules to the catalyst[31]. Ballarini et al.[9] tested the catalytic activity of Pt-$ZnAl_2O_4$ powders on the n-butane dehydrogenation reaction. They concluded that the $ZnAl_2O_4$ powders with larger BET surface area presented the best catalytic performance[9].

4. Conclusions

Single phase $ZnAl_2O_4$ spinel-type powders have been successfully prepared in a direct procedure without calcination by hydrothermal method and microwave assisted combustion method. Depending on the method chosen, powders with different physical properties were obtained. Due to the large amount of heat released during the combustion reaction, the resulted $ZnAl_2O_4$_MC powder presented a small BET surface area (5.3 $m^2.g^{-1}$) and an average crystallite size of 25.6 nm. Whereas, the hydrothermal method yielded powders with surface area 30 times higher (183.5 $m^2.g^{-1}$) and crystallite size 3 times smaller (6.9 nm), as compared to the powders produced by microwave assisted combustion method, once the working temperature in the hydrothermal synthesis is relatively low. Both samples showed a strong tendency to agglomerate with plate-like morphology powders.

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