

# Preparation of ZnAl<sub>2</sub>O<sub>4</sub> Catalytic Support by Combustion Reaction: Influence of Type of Heating Source

E. Leal<sup>\*</sup>, K. M. S. Viana<sup>\*\*</sup>, R. H. G. A. Kiminami<sup>\*\*\*</sup>, D. C. Barbosa<sup>\*\*\*\*</sup>, S. M. P. Meneghetti<sup>\*\*\*\*</sup>, A. C. F. M. Costa<sup>\*</sup>, H. L. Lira<sup>\*</sup>

<sup>\*</sup> Department of Materials Engineering – UFCG, Avenue Aprígio Veloso - 882, Bodocongó, 58109-970, Campina Grande, PB, Brazil, elvialeal@gmail.com

<sup>\*\*</sup> Faculty of Materials Engineering – UFPA, Marabá, PA, Brazil, kalinesouto@yahoo.com.br

<sup>\*\*\*</sup> Department of Materials Engineering – UFSC, São Carlos, SP, Brazil, ruth@power.ufscar.br

<sup>\*\*\*\*</sup> Department of Chemistry – UFAL, Maceió, AL, Brazil, smpm@qui.ufal.br

## ABSTRACT

The aim of this work is to evaluate the esterification activity of ZnAl<sub>2</sub>O<sub>4</sub> catalysts obtained by different ways of heating (plate, muffle furnace and microwave oven) during the combustion synthesis using urea as reducing agent, and nitrates of zinc and aluminum as oxidants. All samples were characterized by XRD, particle size distribution, nitrogen adsorption (BET/BJH) and SEM, and then, they were forwarded to the catalytic tests on the biodiesel esterification. XRD results showed that all catalysts presented the formation of a cubic structure of ZnAl<sub>2</sub>O<sub>4</sub> spinel. The heating way had a great influence on the structural and textural features of ZnAl<sub>2</sub>O<sub>4</sub>, such as crystallite size and surface area, whose values were of 27, 35 and 16 nm, and 15, 9 and 57 m<sup>2</sup>/g for the catalysts I, II and III, respectively. All catalysts presented morphology in irregular plates shape (SEM) and formation of particle agglomerates with a narrow size distribution. For all catalysts tested, very low reactions profits were observed.

**Keywords:** zinc aluminate, combustion, characterization, esterification.

## 1 INTRODUCTION

Oxide spinels comprise a very large group of structurally related compounds many of which are of considerable technological significance. Among them, zinc aluminate (ZnAl<sub>2</sub>O<sub>4</sub>), with typical normal spinel structure AB<sub>2</sub>O<sub>4</sub>, is of interest due to its combination of desirable properties such as high mechanical resistance, high thermal stability, low temperature sinterability, low surface acidity and better diffusion [1].

These powders of zinc aluminate find applications in industrial ceramics due to high performance and refinement. It also has proved interesting for catalytic applications, such as cracking processes and synthesis of alcohols and biodiesels [2, 3].

Recently, ZnAl<sub>2</sub>O<sub>4</sub> has been prepared by solid state-reaction [4] or wet chemical routs such as co-precipitation [5], sol-gel [6] and hydrothermal method [1]. Among the different synthesis methods used to obtain ZnAl<sub>2</sub>O<sub>4</sub> with

nanosized particles, combustion reaction stands out as a promising technique, because it is a self-sustaining method that allows reaching temperatures that ensure the crystallization and phase formation in short period of time [7].

This work reports the preparation of ZnAl<sub>2</sub>O<sub>4</sub> catalyst by combustion reaction using three kind of heating source (a spiral resistance, a muffle furnace and a microwave oven). The effect of heating source on the structure and morphology of the produced powders and their catalytic activity on the esterification process in biodiesel preparation were investigated.

## 2 EXPERIMENTAL

To obtain the ZnAl<sub>2</sub>O<sub>4</sub> catalysts were used the following materials: aluminum nitrate [Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O], zinc nitrate [Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O] and urea [CO(NH<sub>2</sub>)<sub>2</sub>], all of them with 98% of purity. The proportion of each reagent was calculated based on the theory of propellants and explosives, in order to produce the stoichiometric ratio between oxidizer/reductor equal to 1 ( $\Phi_e = 1$ ), where  $\Phi_e$  is the elemental stoichiometric coefficient [8]. The mixture was placed in a vitreous silica crucible and subjected to different heating sources (I - a spiral resistance; II - a muffle furnace; and, III - a microwave oven) so that promote an ignition followed by combustion.

During the synthesis carried out in the spiral resistance and the muffle furnace were measured the parameters of combustion flame time and temperature, using a stopwatch (Vítese) and an infrared pyrometer (Raytek RAYR3I ± 2°C), respectively. Unable to determine the temperature and time of flame of the synthesis reactions carried out in the microwave oven, since it is formed by a Faraday cage, these were performed in a power of 100% during 10 minutes.

The samples were characterized by X-ray diffraction in a Shimadzu LAB 6000 diffractometer in a scan 2 $\theta$  range of 20-80°, using CuK $\alpha$  radiation ( $\lambda=1,5418\text{\AA}$ ). The values of surface area, diameter and volume pore were obtained by nitrogen adsorption, using a Quantachrome NovaWin2 system (NOVA 3200). Surface area was determined using the BET model while to determine the radius and volume pore was used the BJH theory. The average particle size

was calculated from BET data using the equation (1) [9]. The agglomerate size distribution was determined using a CILAS 1064 LD particle size analyzer. The morphology of the powders also was analyzed by scanning electronic microscopy in a Philips XL30 FEG SEM microscope.

$$D_{BET} = \frac{6}{D_t \cdot S_{BET}} \quad (1)$$

where,

$D_{BET}$  represents the spherical diameter (nm);  $D_t$  is the theoretical density ( $\text{g}/\text{cm}^3$ );  $S_{BET}$  corresponds to the surface area ( $\text{m}^2/\text{g}$ ).

$\text{ZnAl}_2\text{O}_4$  catalysts were employed in esterification reactions and the percentage of biodiesel formed (FAME = fatty acid methyl ester) was determined by gas chromatography. The catalysts were tested using methanol and fatty acids derived from soybean oil, in the following reaction conditions: molar ratio of methanol/fatty acid/catalyst = 400/100/1, reaction time of 1 hour and temperature of 160 °C.

### 3 RESULTS

Fig. 1 shows the X-ray diffractograms of the  $\text{ZnAl}_2\text{O}_4$  catalysts prepared by combustion reaction using the different heating sources.

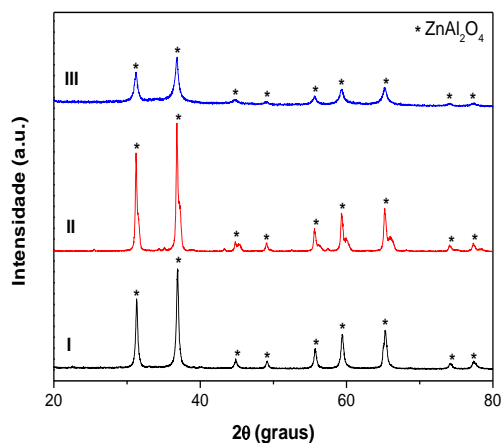


Figure 1: X-ray diffractograms of  $\text{ZnAl}_2\text{O}_4$  catalysts. I – spiral resistance; II - muffle furnace; and, III - microwave oven.

The observed diffraction peaks in all the recorded XRD patterns correspond to those of the standard patterns of cubic  $\text{ZnAl}_2\text{O}_4$  spinel (JCPDS, No. 05-0669) under the form of the guanine mineral. These peaks can be indexed as (220), (311), (400), (331), (422), (511), (440), (620) and (533) diffractions.

The crystallite size from XRD was calculated from X-ray line broadening of the (311) diffraction line located  $2\theta = 36.87^\circ$  and using the Scherrer equation [10]. The crystallite size of the catalysts I, II and III was calculated to be 27, 35 and 16 nm, respectively. The ratios of peak

intensities of all prepared powders were not the same. Comparing the XRD spectra with the flame temperatures and times measured during the synthesis performed in the spiral resistance and in the muffle furnace, whose values were of 895 and 941 °C, and 27 and 21 seconds, respectively, it is observed that the higher the flame temperature reached in synthesis, more intense the peaks in the diffractograms spectra (Fig. 1). This shows that the higher the combustion temperature the greater the energy supplied to the growth of crystals.

Despite not have been performed the measurement of the flame temperature in the synthesis performed in the microwave oven, it was possible to observe through XRD spectra of the catalyst III the presence of peaks with broad bases and low intensity, that probably is a strong indicative that the combustion temperature generated in the microwave oven synthesis was lower than the temperatures generated in the synthesis performed in the spiral resistance and in the muffle furnace, which led to a crystallite size 41% and 54% nether to the crystallite sizes obtained to the catalysts I and II, respectively.

Fig. 2 shows the curves of the equivalent spherical diameter of the agglomerates as a function of the cumulative mass for the  $\text{ZnAl}_2\text{O}_4$  catalyst.

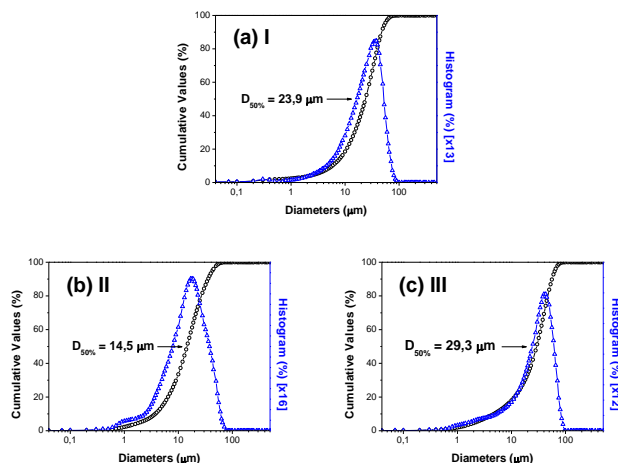


Figure 2: Granulometric distribution of the  $\text{ZnAl}_2\text{O}_4$  catalysts. (a) I – spiral resistance; (b) II - muffle furnace; and, (c) III - microwave oven.

These curves suggest the formation of particle agglomerates with a narrow median size distribution. It was also observed that the catalysts produced in the spiral resistance (I) and microwave oven (III) showed an agglomerates distribution a little narrower and with a slight displacement of the curve to the right, indicating a cumulative mass increase in the median diameter of agglomerates ( $D_{50\%}$ ), whose values were of 23.9 and 29.3  $\mu\text{m}$ , respectively. The other hand, the median diameter of agglomerates ( $D_{50\%}$ ) referring to the catalyst produced in the muffle furnace (II) was the lower, with a value of 14.5  $\mu\text{m}$ .

This difference in the agglomerates sizes is also a result of the combustion temperature achieved during synthesis, since higher temperatures favor the formation of denser agglomerates, constituted by pre-sintered particles and without interparticle porosity, which can lead to the formation of more compact powders. The lower temperatures favor the formation of less dense agglomerates and with interparticle porosity. Costa et al. [7] when evaluated the influence of glycine and urea on the synthesis of  $ZnAl_2O_4$  catalyst by combustion reaction using a hot plate as heating source (480°C) observed a wide agglomerates size distributions, with median diameters ( $D_{50}$  %) of 12.5 and 28.2  $\mu\text{m}$ , respectively. Comparing our value referring to the catalyst (I) obtained in the spiral resistance, which was 23.9  $\mu\text{m}$ , with the value obtained from the authors above regarding the  $ZnAl_2O_4$  synthesized with urea, whose value was of 28.2  $\mu\text{m}$ , it can be said that variations in synthesis conditions have great influence in the agglomerates size.

Table 1 shows the surface area, pore radius, pore volume and particle size referring to  $ZnAl_2O_4$  catalysts. It can be observed that the catalysts obtained in the spiral resistance (I) and in the muffle furnace (II) presented a low surface area when compared with the catalyst obtained in the microwave oven (III), whose value was 57  $\text{m}^2/\text{g}$ . Probably, this is explained in fact this heating source (microwave oven) have provided less energy for the particles growth, since size was 23 nm. It is observed that the larger the particle size the smaller the surface area presented. All catalysts (I, II and III) presented a mesoporous characteristic, with pore radius ranging from 17.3 to 19.2  $\text{\AA}$ . The pore volume had a small variation between the values 0.014 and 0.024  $\text{cm}^3/\text{g}$ , with minimum belonging to the catalysts I and II, and maximum to the catalyst III.

Catalisador	$S_{\text{BET}}$ ( $\text{m}^2/\text{g}$ )	$R_p$ ( $\text{\AA}$ )	$V_p$ ( $\text{cm}^3/\text{g}$ )	$D_{\text{BET}}$ (nm)
I	15	19.2	0.014	87
II	9	19.0	0.014	151
III	57	17.3	0.024	23

Table 1: Surface area ( $S_{\text{BET}}$ ), pore radius ( $R_p$ ), pore volume ( $V_p$ ) and particle size ( $D_{\text{BET}}$ ) to  $ZnAl_2O_4$  catalysts.

Fig. 3 shows the nitrogen adsorption/desorption isotherms of the  $ZnAl_2O_4$  catalysts. According to the IUPAC classification [12], all  $ZnAl_2O_4$  catalysts showed type IV isotherm profiles, suggesting a characteristic of mesoporous material (pores with ratio ranging from 10 to 250  $\text{\AA}$ ). Regarding the hysteresis, these catalysts also showed hysteresis loop of type H3 mixed with H2, indicating the presence as much of pores of slit-shaped originating in the particle aggregates, as pores open and closed with strangulations typical of an irregular morphology of bottle type [13]. Zawadzki et al. [14] synthesized  $ZnAl_2O_4$  by microwave assisted solvothermal

conditions using zinc acetate, aluminium isopropoxide and 1,4-butanediol as precursors, and observed through textural analysis a  $N_2$  adsorption/desorption isotherm similar to presented in this study, i.e. also of type IV and with a well-developed hysteresis loop of type H2, suggesting a material with basically mesoporous characteristic. Despite this similarity, the authors also observed a surface area, pore volume and pore radius of 133  $\text{m}^2/\text{g}$ , 0.18  $\text{cm}^3/\text{g}$  and 24  $\text{\AA}$ , respectively. I.e. values of surface area and pore volume higher than those obtained in this work.

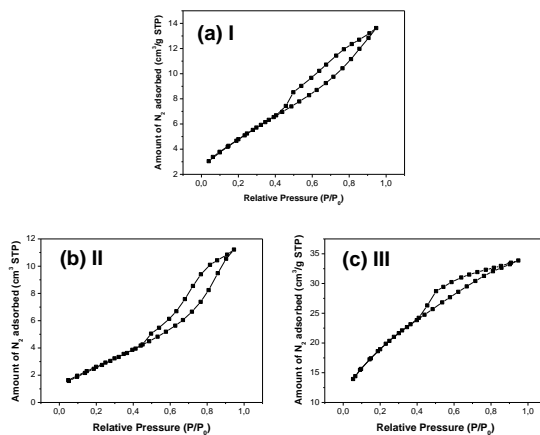


Figure 3:  $N_2$  adsorption/desorption isotherms for the  $ZnAl_2O_4$  catalysts. (a) I – spiral resistance; (b) II - muffle furnace; and, (c) III - microwave oven.

The SEM micrograph in Fig. 4 shows the morphology of the  $ZnAl_2O_4$  catalysts according to heating sources used in the combustion reaction.

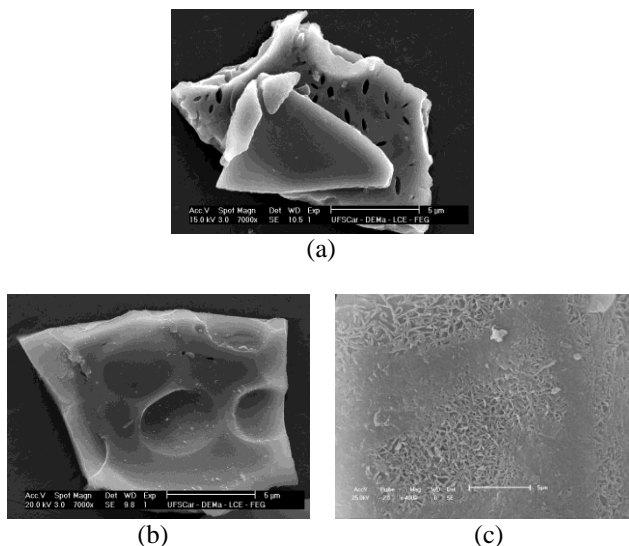


Figure 4: SEM micrographs of  $ZnAl_2O_4$  catalysts. (a) I – spiral resistance; (b) II - muffle furnace; and, (c) III - microwave oven.

The micrograph referring to the catalyst obtained in spiral resistance (Fig. 4a) reveals the formation of agglomerates in the irregular plates form with rigid aspect (pre-sintered particles), sizes larger and smaller than 5  $\mu\text{m}$ , and presence of large pores in slit form and uniform sizes, which probably were caused by the difficult gases release during the synthesis. The micrograph referring to the catalyst obtained in muffle furnace (Fig. 4b) shows the presence of a large agglomerate in the irregular rigid block form with approximately 10  $\mu\text{m}$ . Although present a rigid aspect, this appears being composed by linked fine particles. The micrograph of the catalyst obtained in the microwave oven (Fig. 4c) shows the formation of a large agglomerate in plate form (rigid aspect) and presence of sections with fibrous aspect, providing a greater presence of pores with irregular shapes and sizes. According to Singh et al. [11], this non-uniformity in the shape could be related to the non-uniformity in the distribution of temperature and mass flow in the combustion flame.

Table 2 shows the reaction yield obtained from the esterification of fatty acids with methanol, in the presence of  $\text{ZnAl}_2\text{O}_4$  catalysts. The presented results are compared to the reaction performed without catalyst, since the esterification reaction is self-catalytic. Thus, taking the results evaluated by the difference of profit between the reactions performed with and without catalyst, it was observed very low reactions profits for all catalysts. It was observed that the catalyst III despite having presented the larger surface area, this resulted in a lower reaction profit when compared to reaction without catalyst. Therefore, we assume that these low values of profit was not only a consequence of the low surface area values, but probably had interference from the nonuniformity of size and shape of particles or agglomerates, which leads to nonuniformity in size and shape of pores.

Reaction	FAME (%)
I	48
II	47
III	41
without Catalyst	45

Table 2: Profit obtained in the esterification reaction of fatty acids obtained from soybean oil referring to the different catalysts.

## 4 CONCLUSIONS

According to the results obtained in this work, it can conclude that changes in the  $\text{ZnAl}_2\text{O}_4$  synthesis conditions, as the heating source used, led to significant changes in structural and morphological characteristics of the material. The synthesis performed in the microwave oven was most efficient to obtain powder with higher surface area and smaller crystallite size. The catalysts were not efficient in the conditions of esterification reactions tested, taking their

morphological characteristics decisive interference in this behavior.

## 5 ACKNOWLEDGEMENTS

The authors are grateful to RENAMI / CNPq, CNPq / Multi-user case: (402561/2007-4), PROCAD / NF-CAPES, PRO-Engineering-CAPES, CNPq and CAPES for the financial support.

## REFERENCES

- [1] M. Zawadzki, Solid State Sciences 8, 14, 2006.
- [2] T. El-Nabarawy, A.A. Attia and N. Alaya, Materials Letters 24, 319, 1995.
- [3] C.T. Alves, H.M.C. Andrade, L.S. Bastos, L.S. Macêdo, S.A.B.V. Melo and E.A. Torres, In: 8th World Congress of Chemical Engineering, Montreal, 2009,
- [4] S.K. Sampath and J.F. Cordaro, Journal of the American Ceramic Society 81, 649, 1998.
- [5] G.F. Hetting, H. Worl, H.H. Weiter and Z. Anorg. Allg. Chem. 283, 207, 1956.
- [6] M.A. Valenzuela, P. Bosh, G. Aguilar-Rios, A. Montoya and I. Schifter, Journal of Sol-Gel Science and Technology 8, 107, 1997.
- [7] A.C.F.M. Costa, D.A. Vieira, R.P.T. Lula, R.H.G.A. Kiminami and L. Gama, In: 17<sup>o</sup> CBECIMat, 2339, 2006.
- [8] S.R. Jain, K.C. Adiga and V. Pai Verneker, Combustion and Flame, 40, 71, 1981.
- [9] J.S. Reed, Principles of Ceramics Processing, 2a ed., 1994.
- [10] H. Klung and L. Alexander, In X-ray diffraction procedures, Wiley, New York, EUA, p. 491, 1962.
- [11] V. Singh, R.P.S. Chakradhar, J.L. Rao and D.-K. Kim, Journal of Luminescence, 128, 394, 2008.
- [12] IUPAC, International Union of Pure and Applied Chemistry, Handbook, v. 2, n<sup>o</sup> 2, 1976.
- [13] S.J. Gregg and K.S.W. Sing, Adsorption, Surface Area and Porosity, 2nd ed., Academic Press, London, 1982.
- [14] M. Zawadzki, W. Staszak, F.E. López-Suárez, M.J. Illán-Gómez and A. Bueno-López, Applied Catalysis A: General, 371, 92, 2009.