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Use of Ni-Zn Ferrites Doped with Cu as Catalyst in the Transesterification of Soybean Oil to Methyl Esters

Joelda Dantas[a]*, Jakeline Raiane D. Santos[a], Rodrigo Bruno L. Cunha[a], Ruth Herta G. A. Kiminami[b], Ana Cristina F. M. Costa[a]

[a]*Synthesis Laboratory of Ceramic Materials – LabSMaC, Department of Materials Engineering, Federal University of Campina Grande – UFCG, CEP 58109-970, Campina Grande, PB, Brazil*
[b]*Department of Materials Engineering, Federal University of São Carlos – UFSCar, CEP 13565-905, São Carlos, SP, Brazil*

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The purpose of this work is to evaluate the performance of $Ni_{0.5}Zn_{0.5}Fe_2O_4$ ferrite doped with 0.1 and 0.4 mol of Cu as a catalyst for the transesterification of soybean oil to biodiesel, using methanol. The samples were characterized by X-ray diffraction, nitrogen adsorption and scanning electron microscopy. The reaction was performed for 2 hours at a temperature of 160 °C, using 10 g of soybean oil, a molar ratio of oil: alcohol of 1:20, and 4% (w/w) of catalyst. The product of the reaction was characterized by gas chromatography, which confirmed conversion to methyl esters. The diffraction patterns showed the presence only of $Ni_{0.5}Zn_{0.5}Fe_2O_4$ ferrite phase with a crystallite size of 29 nm. The samples doped with 0.1 and 0.4 mol of Cu showed a surface area and particle size of 22.17 m^2g^{-1} and 50.47 nm; and 23.49 m^2g^{-1} and 47.64 nm, respectively. The morphology of both samples consisted of brittle block-shaped agglomerates with a wide particle size distribution. A comparative analysis of the two catalysts indicated that the catalyst doped with 0.4 mol of Cu showed the better performance, with a conversion rate of 50.25%, while the catalyst doped with 0.1 mol of Cu showed 42.71% conversion.

Keywords: *biodiesel, transesterification, NiZn ferrite, copper, catalysts*

1. Introduction

Metal oxide spinel type ferrites have proved to be very important for catalysis, and the literature describes the favorable performance of ferrites obtained via combustion synthesis with potential application in biodiesel production[1,2]. On a laboratory scale, various chemical synthesis methods are known to obtain ferrites, aiming the development of new materials or the optimization of the existing materials characteristics. Among these are the hydrothermal synthesis[3], the conventional ceramic method[4] and thermal cracking[5]. However, the combustion reaction synthesis has received special attention because its easy procedure, do not require multiple processing steps, do not use sophisticated equipment, it's quick, it's possible a reproducibility of the product and its achievement in batches (semi-pilot scale lab)[6].

Biodiesel, a renewable source of energy increasingly used for the total or partial substitution of fossil diesel[7], offers numerous advantages for the environment, society and the global economy. Many chemical processes are used in biodiesel production, including transesterification, esterification, cracking or pyrolysis. The transesterification reaction is a widely used process to transform raw materials with high levels of fatty acids into biodiesel. However, the homogeneous and heterogeneous catalysts that trigger this reaction have several limitations. Therefore, research has increasingly focused on new catalytic systems that can promote high activity, easy separation and recovery, and inhibit the corrosion of processing equipment[8].

Among these new systems with potential applications are nanoscale solids, whose large surface area increases the contact between catalyst and substrate, enabling them to be recovered and reused in other reaction processes[9]. Thus, heterogeneous catalysts play a fundamental role in the chemical reaction of transesterification, since they accelerate the reaction that converts fatty acids from triacylglycerides (vegetable oil) into the corresponding methyl esters of fatty acids (biodiesel). In view of these advantages, this study aimed to evaluate the performance of $Ni_{0.5}Zn_{0.5}Fe_2O_4$ nanoferrites doped with 0.1 and 0.4 mol of Cu^{2+} as catalysts in the transesterification of soybean oil with methanol to produce biodiesel.

2. Material and Methods

The synthesis of nanoferrites obtained via combustion reaction involved mixing salts of metal ions as oxidizing reagents (nickel nitrate, zinc, copper and iron) and urea as reducing agent to form a redox solution. The initial composition of the solution was calculated based on the total valence of oxidizing and reducing reagents, using the concept of propellant chemistry[10]. The reactions were performed in a stainless steel container, which was heated directly on a ceramic base with a coil resistance until self-ignition and subsequent combustion occurred.

*e-mail: joeldadantas@yahoo.com.br

Samples of nanoferrites were characterized by X-ray diffraction (SHIMADZU XRD-6000 diffractometer), using CuKα radiation, $\lambda = 1.542$ Å, a voltage of 40 kV, 30 mA current and scanning from 15 to 85. The crystallite size was calculated from the X-ray line broadening (d_{311}) by deconvolution of the secondary diffraction line of polycrystalline cerium (used as standard), using the Debye-Scherrer equation[11]. The specific surface area of the nanoferrites was determined by the BET (Brunauer, Emmett and Teller) nitrogen adsorption method, using a Micromeritics ASAP 2020 surface area porosity analyzer. The morphological aspects of the nanoferrites resulting from the combustion reaction were analyzed using a scanning electron microscope (SEM, SHIMADZU SSX-550 Superscan) operating at 15 kV.

The transesterification reactions were performed in a pressurized stainless steel reactor with a usable volume of 80 mL, equipped with borosilicate glass sleeves and a thermocouple input tube connected to a manometer. Stirring and heating were performed on a heating plate with magnetic stirring. The molar ratio of methyl alcohol to fatty acid was 20: 1, using 4 wt. (%) of catalyst relative to fatty acid. The reactions were performed at 160°C for 2 hours. The products of the transesterification reaction were analyzed in a Varian 450-GC gas chromatograph equipped with a flame ionization detector (FID) operating at 380 °C, using a Varian capillary column stationary phase Select Biodiesel for Glycerides + RG (Ultimetal) (15 m × 0.32 mm × 0.45 µm). The initial injection temperature was 100 °C and that of the GC was 180 °C.

3. Results

Figure 1 shows the diffractograms of the $Ni_{0.5}Zn_{0.5}Fe_2O_4$ nanoferrites doped with 0.1 mol and 0.4 mol of Cu^{2+}. Note the presence of major peaks characteristic of the inverse spinel structure, as evidenced by the appearance of the main peak $2\theta = 35.5°$, according to the crystallographic form indicated in JCPDS card no. 52-0278. Note the peaks of high intensity and high basal width of all the reflections, indicating the crystallinity of the samples and their characteristic nanostructure. Both samples showed a crystallite size of about 29 nm, confirming the efficiency of the combustion reaction of the materials. These results are consistent with the work of Batoo and Ansari[12], who studied ferrite nanoparticles with a basic composition of $Ni_{0.7-x}Cu_{0.3}Zn_xFe_2O_4$ synthesized by self-combustion and obtained a single phase and a crystallite size of 28 to 32 nm.

Table 1 lists the values of specific surface area (S_{BET}), particle size (D_{BET}) and the ratio of particle to crystallite size (Tc) of the $Ni_{0.5}Zn_{0.5}F_2O_4$ nanoferrites doped with 0.1 mol and 0.4 mol Cu^{2+}. These data indicate that the two nanoferrites showed very similar surface area values, although the surface area of the nanoferrite doped with 0.4 mol of Cu^{2+} was 5.52% larger than that of the nanoferrite doped with 0.1 mol of Cu^{2+}. The specific surface areas listed in Table 1 indicate that, in general, that of the $Ni_{0,1}Cu_{0,4}Zn_{0,5}Fe_2O_4$ nanoferrite was higher, thus favoring a reduction in particle size. In addition, the ratio of particle size to crystallite size (D_{BET}/tc) showed a slight increase at the higher Cu^{2+} doping, thus indicating that the respective particles tend to be monocrystalline.

Figure 2 shows the morphology of the nanoferrites. The micrographs indicate that the two nanoferrites were generally composed of irregular block-shaped agglomerates with a brittle appearance, i.e., fine particles loosely bound with little porosity due to the flue gas. This confirms the results of the aforementioned analysis of particle size determined from the surface area measurements. Costa et al.[13], who synthesized and characterized Ni-Cu-Zn ferrites, also

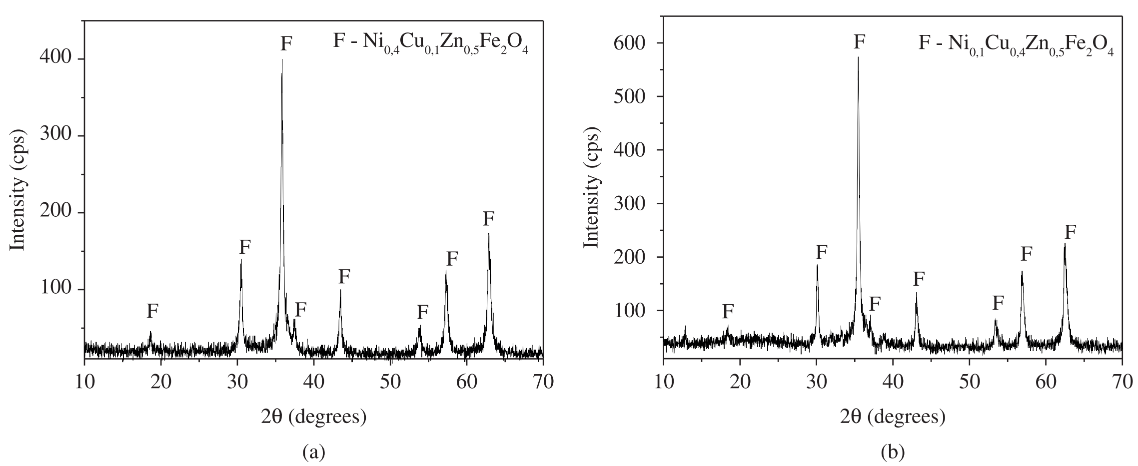
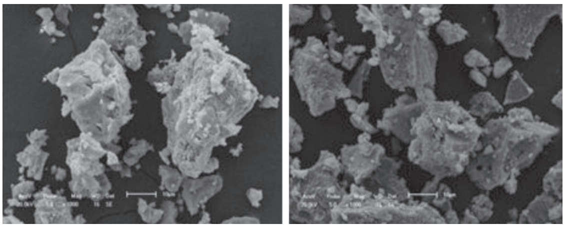


Figure 1. X-ray diffractograms of nanoferrites with: (a) 0.1 mol and (b) 0.4 mol of Cu^{2+}.

Table 1. Surface area, particle size and ratio of particle size to crystallite size.

Nanoferrites	Surface area (BET) ($m2g^{-1}$)	Particle size (DBET) (nm)	DBET/Tc*
Ni0,4Cu0,1Zn0,5Fe2O4	22,17	51	1.8
Ni0,1Cu0,4Zn0,5Fe2O4	23,49	48	1,7

*Tc = Crystallite size.



(a) (b)

Figure 2. SEM micrograph with magnified 1000× for: (a) 0.1 mol and (b) 0.4 mol Cu^{2+}.

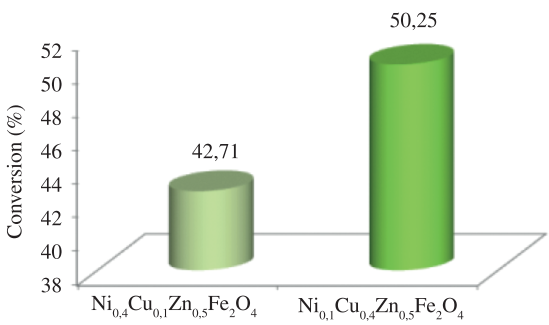


Figure 3. Conversion to methyl ester of nanoferrites.

reported a morphology consisting of soft agglomerates of nanoparticles smaller than 100 nm. Our results were also consistent with those reported by these authors regarding the particle size of the materials determined by BET.

Figure 3 illustrates the results achieved by using nanoferrites as catalysts to obtain biodiesel. The nanoferrite doped with 0.4 moles of Cu^{2+}, whose specific surface area was slightly higher than that doped with 0.1 moles of Cu^{2+}, achieved a higher conversion rate. This was probably due to its larger specific surface area, which is an important characteristic of a good catalyst. This finding is supported by reports in the literature that, when it comes to catalysts, the larger the area available to the reactants, the greater the conversion of products provided diffusive phenomena are not involved[14]. In general, it was observed that both evaluated nanoferritas has shown satisfactory conversions on tested conditions and it's possible therefore to be considered as a new promising catalysts aiming in the biodiesel production.

4. Conclusions

The combustion reaction synthesis was efficient for processing $Ni_{0.5}Zn_{0.5}Fe_2O_4$ nanoferrites doped with Cu^{2+}, yielding the desired phase with a crystallite size of 29 nm. The best conversion result was obtained with nanoferrite doped with 0.4 moles of Cu^{2+}, and a correlation was identified between specific surface area and the percentage of conversion achieved. The catalysts tested under the conditions of this study show a promising potential for use in transesterification reactions of soybean oil to methyl.

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