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Magnetic nanocatalysts of $Ni_{0.5}Zn_{0.5}Fe_2O_4$ doped with Cu and performance evaluation in transesterification reaction for biodiesel production

J. Dantas [a,*], E. Leal [a], A.B. Mapossa [b], D.R. Cornejo [c], A.C.F.M. Costa [a]

[a] Federal University of Campina Grande, Synthesis of Ceramic Materials Laboratory – LabSMaC, Science and Engineering of Materials Postgraduate, Aprígio Veloso Avenue – 882, Bodocongó, 58109-970 Campina Grande, PB, Brazil

[b] Institute of Applied Materials, Department of Chemical Engineering, University of Pretoria, Private Bag X20, Hatfield 0028, Pretoria, South Africa

[c] University of São Paulo, Institute of Physics, 05508-900 São Paulo, SP, Brazil

HIGHLIGHTS

- $Ni_{0.5-x}Cu_{0.5-x}Zn_{0.5}Fe_2O_4$ nanocatalysts magnetic heterogeneous synthesized by combustion reaction.
- Dependence of structural, morphology and magnetism of the nanocatalyst in relation to the content of Cu^{2+}.
- Magnetic nanocatalysts promising for biodiesel production.

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ABSTRACT

It was proposed in this work to investigate the Cu^{2+} ions doping influence in the structure, morphology and magnetic properties of nanoferrites $Ni_{0.5}Zn_{0.5}Fe_2O_4$ for their application in methyl transesterification of soybean oil to biodiesel production. The nanoferrites with $Ni_{0.5-x}Cu_xZn_{0.5}Fe_2O_4$ composition ($0.0 \leqslant x \leqslant 0.4$) were synthesized by combustion reaction using a conical reactor with production of 10 g per batch and characterized by X-ray diffraction, textural analysis by N_2 adsorption, magnetic measurements, thermal analysis by temperature-programmed desorption, and biodiesel analysis by gas chromatography. All compositions resulted in the single phase of the inverse spinel type $B(AB)_2O_4$ and adsorption/desorption isotherms of the same profile, classified as type V, with hysteresis loop type 3 (H3). However, the increase of Cu ions doping from 0.0 to 0.4 mol caused a reduction of 37% in the surface area values and 36.4% in the saturation magnetization value. However, this reduction remained the ferrimagnetic characteristic and that is still strongly attracted by a magnet. The Cu ions presence has also facilitated an increase of 5.5–85% in the conversion values in methyl esters obtained from soybean oil transesterification. These results indicate the potential application of NiZn nanoferrite compositions doped with Cu^{2+} as heterogeneous nanocatalysts to produce biodiesel.

1. Introduction

The study of ternary oxides with magnetic characteristics, type spinel ferrites, has attracted immense attention from the scientific community because of its properties and new technological applications, especially when the particle size approaches to the nanoscale, as it enables their properties control such as the magnetic anisotropy and the saturation magnetization. In general, the transport properties of nanomaterials are largely controlled by the particle size than the particle itself. For this reason, magnetic materials have explored a wide range of applications, such as in the fields of drug carriers [1,2], contrast agents [3,4], DNA separation [5,6], telecommunication [7] and brown pigments [8,9] therefore they are gradually replacing conventional materials.

Awati et al. [10] they reported that soft magnetic materials with a particle size in the nanometer range are now in evidence and the interest is due to their unique magnetic properties that differ considerably from the bulk material that is why they have become technology very important.

In catalysis field the magnetic nanoparticles can act as heterogeneous catalysts promising, because the nanoscale structures

* Corresponding author.
E-mail address: joeldadantas@yahoo.com.br (J. Dantas).

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manipulation provides nanocatalysts obtaining with a larger amount of active chemical sites, thereby promoting a surface area expansion. Netto et al. [11] they reported that the nanoparticles have large surface area and high mass transfer area, ideal criteria for a catalysis support. In catalysis, the greater evidence in nanomagnetics materials points are their high surface area, recovery facility through the magnetic field (magnet), the reusing and the presence of basic or acidic active sites [12,13]. Moreover, usually heterogeneous catalysts are separated from the reaction means by intense filtration steps and/or centrifugation, thereby, much research has been devoted to the development of easily separable heterogeneous catalysts where in this item the magnetic nanocatalyst become even more attractive and preponderant.

Although the application of magnetic materials in heterogeneous catalysis of many industrial chemical processes is already consolidated an unheard field in this area is the catalytic processes application for clean energy production, such as biofuels. A biofuel primary example is biodiesel that is obtained from renewable biomass such as vegetable oil and animal fat in the presence of an alcohol and the transesterification and esterification are the main chemical production processes where it is necessary to use catalysts which act to reduce the necessary energy to occur the reaction and this contributes to decrease the reaction time. The catalysts also assist in a better reaction yields obtaining because they increase the amount of end product.

In this way, the advantages of heterogeneous catalysts obtained at nanometric scale added to the magnetic property, constitute an appropriate and pertinent contribution to the chemical reactions of transesterification for biodiesel production. In addition, heterogeneous catalysts become even more advantageous when they are spinel-type, since they allow a great cationic mobility, where their original crystalline structure may have substitution of chemical elements for other elements of same structure, that are similar in terms of electronegativity, valence and radius size. For example, it is possible to mention the Ni-Zn ferrite, which can be doped with different metal ions and thus obtain a set of new properties, which when used in transesterification may contribute to higher conversions in biodiesel. This is supported by Akhtar et al. [14], that the substitution of metal ions in the Ni-Zn spinel structure may result in an adjustment of the structural, morphological and magnetic properties, respectively. Recently, the substitution of Cu and Zn contents are used to achieve high versatility in the properties of these materials.

Therefore, doping with Cu contributes significantly to the sum and improvement of properties in the catalytic processes. Nickel catalysts are efficient in catalytic processes due to the great abundance of nickel and its low cost. However, for example, in the work of Ambursa et al. [15], the authors reported research on hydrodeoxygenation of bio-oil using Ni, and found that Ni exhibits low corrosion resistance due to the acidity of the bio-oil, and this may affect its activity and stability during the process. To solve this problem, the addition of Cu has been used to increase the activity and stability of the Ni catalyst, and improve its reducing properties. Li et al. [16], studied the formation of coke on the surface of Ni/HZSM-5 and Cu-Ni/HZSM-5 catalysts during hydrodeoxygenation of bio-oil, and reported that the Ni catalyst is only capable of activating hydrogen and significantly inhibiting polymerizations of unsaturated hydrocarbons, reducing their concentrations during the process. However, the formation of coke on the surface of Ni catalysts cannot be avoided, while the presence of Cu can improve the Ni dispersion and reduce the size of Ni particles, and thus favor the elimination of coke, since the hydrogen molecules moved on Cu are easily desorbed due to the lower dissociation barrier when compared to Ni. This manifests that addition of Cu is beneficial to the catalytic process.

In this context and on the understanding that contributions corroborate to increase the researches consolidation in the search for new heterogeneous catalytic species that gather together characteristics such as recovery facility, renewability, reuse, presence of more active sites in their surface area and still to collaborate to mitigate environmental damage it has been objectified in this study to evaluate the Cu^{2+} ions doping influence in the structure, morphology and magnetic nanoferrites properties of $Ni_{0.5}Zn_{0.5}Fe_2O_4$ for their application in methyl transesterification of soybean oil for biodiesel production.

2. Experimental

2.1. Materials and methods

The basic composition nanoferrites $Ni_{0.5-x}Cu_xZn_{0.5}Fe_2O_4$ ($0.0 \leqslant x \leqslant 0.4$) were synthesized by combustion reaction and it involved a metal ions salts mixture as oxidizing reagents (nickel nitrate hexahydrate - $Ni(NO_3)_2{\cdot}6H_2O$, zinc nitrate hexahydrate - $Zn(NO_3)_2{\cdot}6H_2O$, iron(III) nitrate nonahydrate - $Fe(NO_3)_3{\cdot}9H_2O$ and copper(II) nitrate trihydrate - $Cu(NO_3)_2{\cdot}3H_2O$), and urea - $CO(NH_2)_2$ as reducing agent, to form a redox solution. All reagents with a purity between 98 and 99%. The solution initial composition was calculated based on the total valence of the oxidizing and reducing reagents using the propellants and explosives chemistry concepts [17,18]. The reactions were performed in a conical reactor designed to produce nanomaterials with capacity of 10 g/batch [19].

For the transesterification reactions was used refined soybean oil, purchased in local commerce, whose physico-chemical characteristics comparing to the National Agency of Sanitary Surveillance (ANVISA) values are shown in Table 1.

2.2. Characterizations

The reactions products were characterized by X-ray diffraction (XRD) in a X-ray diffractometer from Shimadzu, model XRD 6000 (Cu Kα radiation source, λ = 1.542 Å, a voltage of 40 kV, current of 30 mA and scanning from 15 to 85 °C). The crystallite size was calculated from the extension X-ray line (d_{311}) by the secondary diffraction line deconvolution of the polycrystalline cerium (used as standard) using the Scherrier equation [20].

To determine the surface area it was used the adsorption nitrogen/helium method developed by Brunauer, Emmett and Teller (BET) using a machine model ASAP 2420, brand Micromeritics. This technique was also used to determine the particles size (equivalent spherical diameter) by Reed equation [21]. The pore volume and pore diameter were determined by the theory developed by Brunauer, Joyner and Halenda (BJH).

The magnetic property was evaluated by determining of the magnetic hysteresis loops (M × H) using an alternating gradient magnetometer (AGM). By means of the M × H curves it was possible to determine some magnetic parameters values, such as the coercive field (Hc), remanent magnetization (Rm), saturation magnetization (Sm) and magnetic losses estimated from the area

Table 1
Results of the characterization of the refined soybean oil, compared to the expected values taken as reference.

Oil characterization	Determined value	Established value ANVISA[a]
Iodine level (g I_2/100 g)	138.6	120.0–141.0 [a]
Acidity level (% oleic acid)	0.06	<0.3 [a]
Specific mass 20 °C (kg/m^3)	921	919–925 [a]

[a] Value established by ANVISA.