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Synthesis of zinc oxide by microwave hydrothermal method for application to transesterification of soybean oil (biodiesel)

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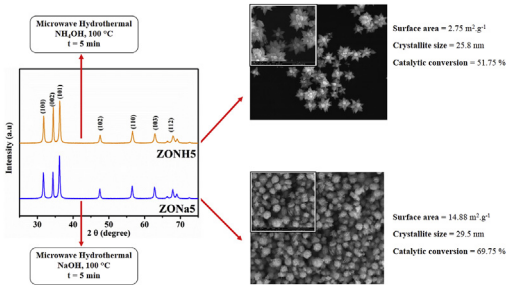
HIGHLIGHTS

- ZnO was synthesized by MH method in only 5 min.
- The powders morphology is completely influenced by mineralization agent.
- ZONa5P showed activity of 77.82% for the conversion of soybean oil into biodiesel.

GRAPHICAL ABSTRACT



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ABSTRACT

ZnO nanostructures were synthesized by microwave hydrothermal treatment using two different mineralization agents (NaOH and NH_4OH), and were evaluated as catalysts for biodiesel synthesis. The materials were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and Brunauer-Emmett-Teller (BET) surface area analysis. The XRD patterns indicated the formation of the hexagonal wurtzite phase in both samples. SEM analysis showed completely different morphologies based on the mineralization agent employed. The ZnO nanostructures synthesized with NaOH (ZONa5 and ZONa5P) presented plate-like agglomerates, resulting in a quasi-spherical morphology, whereas the materials synthesized with NH_4OH (ZONH5 and ZONH5P) presented a flower-like morphology. The ZONa5P sample showed an activity of 77.82% for the catalytic conversion of soybean oil into biodiesel by transesterification using methanol.

1. Introduction

The properties of zinc oxide make it highly exploitable in technological applications, and the high and direct band gap at ambient temperature, along with the high bond energy excitation, contribute to its thermal stability. This amphoteric oxide is widely applied in photoelectronic devices, including flat screen surfaces, electronic gadgets, and transparent conductors for solar cells [1–5]. It proved to be an excellent material for gas detection, where oxidative and reductive processes may be employed to detect gases

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at the parts per million (ppm) or higher level [6], and has also been applied to the detection of acetylene at levels below one ppm [7]. Moreover, several studies have reported the photocatalytic activity of ZnO powder [8–10].

ZnO is an amphoteric transition-metal oxide employed as heterogeneous catalyst for the esterification of free fatty acids (FFAs) and the transesterification of triglycerides [11]. It efficiently catalyses the conversion of a wide range of feedstocks, such as palm oil [12], rapeseed oil [13], and soybean oil [14,15], for biodiesel production. However, only few studies report the use of this catalyst in biodiesel synthesis. Zinc oxide has been prepared through various synthetic routes; however, these routes generally require high temperatures (such as in the combustion method [16]) or the use of lengthy procedures, resulting in laborious operations [17]. The conventional hydrothermal (HC) method uses low temperatures, but requires long synthesis times. Yaqi et al. [8] synthesized ZnO by the HC method using NaOH as a mineralization agent and isopropanol as a solvent; the reaction system was treated at 180 °C for 24 h. Zhang et al. [7] produced micro ZnO discs from a solution with a controlled stoichiometry of zinc chloride, citric acid, NaOH, and deionized water, treated at 200 °C for 20 h. Various syntheses based on this method required several hours for completion or the use of templates to generate the catalyst [18,19]. Kormaneni et al. [20] introduced microwave irradiation in the conventional hydrothermal process and termed this technique microwave hydrothermal (MH) method. This approach led to an increase in the crystallization kinetics by one or more orders of magnitude, resulting in reduced reaction times as compared to the HC method. Several studies have employed the MH method for rapid preparation of various materials with different morphologies [21–25]. Various zinc oxide morphologies have been obtained by the MH method, including nanowires, nanoflowers, hexagonal, conical rods, nanorods, and stars [26–28]. In general, the different morphologies of zinc oxide, obtained by the MH method, were generated by addition of organic substances, such as templates or structure-modifying agents (hexamethylenetetramine (HTMA), ethylenediamine, polyvinylpyrrolidone, and polyethylene glycol (PEG)), to the reaction medium. In this study, we report the synthesis of zinc oxide with diverse morphologies via the MH method at low temperatures, within an extremely short synthesis time, and without the use of templates or organic solvents. For comparative purposes, we also report the use of polyethylene glycol 400 to observe the influence of this template on the morphology of zinc oxide.

Heterogeneous catalysts are of great interest for application in biodiesel production because their use in the transesterification reaction would greatly simplify and reduce the phase separation and purification steps [29]. Because of these advantages, the development of catalysts that are in a different phase compared to the other reactants is a very active and dynamic area of research [30–32]. The MH method is a promising approach as it uses a low temperature and short synthesis time, thus saving energy for catalyst production.

The aim of this study is to synthesize single-phase zinc oxide with different morphologies by the MH method using various mineralization agents, without using surfactants, structure-modifying agents, or templates, and by applying a low temperature for a short time. The morphology achieved by this method is compared with the powder morphology achieved with and without the PEG 400 template. To illustrate the catalytic effect, the synthesized material is applied to the transesterification of soybean oil with methanol (biodiesel).

2. Materials and methods

2.1. Synthesis

Initially, four solutions (9×10^{-3} mol) of zinc nitrate ($Zn(NO_3)_2 \cdot 6H_2O$; 98%, SIGMA-ALDRICH) were prepared. For each solution, the required quantity of salt was homogenized in 132 mL of deionized water under constant stirring at room temperature (~25 °C) to achieve complete dissolution. To one of these solutions, an 8 mL aliquot of NaOH solution (5 mol L^{-1}, 98%, VETEC) was added. For another solution, prepared in the same manner, a different mineralization agent was used; in this case, 5 mL of NH_4OH (28–30%, A.C.S., VETEC) was added. To the other two similarly prepared solutions, 3.6 g of PEG 400 (U.S.P., Synth) was added. The amount of PEG 400 was calculated to achieve a ratio of 1 mol PEG to 1 mol zinc cations (Zn^{2+}). All the precursor solutions were transferred into a sealed Teflon autoclave and placed in a domestic microwave, and were separately subjected to the same microwave-assisted hydrothermal treatment (f = 2450 MHz, maximum power = 800 W), i.e., each synthesis was performed at 100 °C for 5 min at a heating rate of 20 °C min^{-1}. No autogenous pressure was produced. After the microwave-assisted hydrothermal treatment, a white precipitate was formed, which was washed repeatedly until neutral pH was achieved. Subsequently, the material was collected and transferred to an oven for drying at 110 °C for 12 h. The samples in which sodium hydroxide and ammonium hydroxide were used as mineralizing agents are hereafter termed ZONa5 and ZONH5, respectively. The samples to which PEG 400 was added are denoted as ZONa5P and ZONH5P.

2.2. Characterization

The obtained powders were characterized by X-ray diffraction (XRD) using a SHIMADZU (XRD 6000 model) instrument with Cu-Kα radiation (λ = 1.5418 Å) in the 2θ range from 5 to 85° with 0.02° increments. The peaks in the XRD patterns were indexed using ICDD 36–1451. The lattice parameters were calculated using the least squares refinement from Rede 93 developed at Unesp, Araraquara–SP, Brazil. The average crystallite size was estimated from Scherrer's equation using the full width at half maximum (FWHM) of the most intense peak (101). The morphology of the agglomerates of the obtained samples was observed using a scanning electron microscope (FEG-SEM Philips, XL30). The textural characteristics of the samples (surface area, pore size, and pore volume) were determined by the nitrogen adsorption and desorption technique using the Brunauer, Emmett and Teller (BET) and Barret, Joyner and Halenda (BJH) methods and an ASAP 2000 Micromeritics apparatus.

2.3. Catalytic test

The soybean oil transesterification reaction with methanol (CH_3OH, P.A, VETEC) was performed in a 50 mL stainless steel bath reactor, which was magnetically stirred (1000 rpm) under autogenous pressure. The catalyst performance was evaluated under the following reaction conditions: temperature = 180 °C; soybean oil/methanol molar ratio 1:20; reaction time = 3 h; 2% w/w of catalyst (referenced to the amount of soybean oil). A 10 g sample of soybean oil was used for the performance evaluation of all catalysts. After each test, the system was cooled at room temperature and the catalyst was separated by centrifugation. A portion of the heterogeneous mixture was placed in a separation funnel. The less dense phase, which contains the fatty acid methyl ester (FAME) mixture, was separated, and the excess methanol was removed. This phase was analysed by gas chromatography using a Varian 450c instrument with a flame ionization detector and a capillary column as the stationary phase (Varian Ultimetal "Select Biodiesel Glycerides RG"; dimensions: 15 m × 0.32 mm × 0.45 μm). The internal standard used for calculating the FAME yield, expressed in terms of weight percentage, was provided by Varian. A blank test was carried out.

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