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Biodiesel obtained by ethylic transesterification using CuO, ZnO and CeO_2 supported on bentonite

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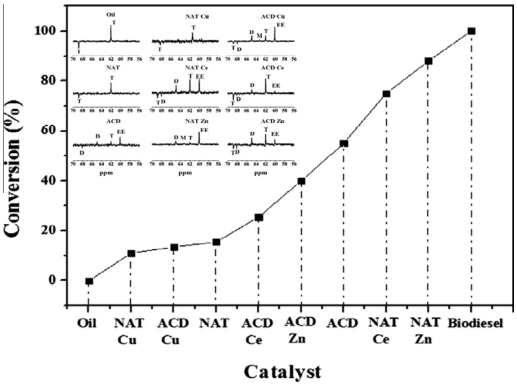
HIGHLIGHTS

- Montmorillonite was impregnated with different oxides for biodiesel synthesis.
- Biodiesel was obtained by ethylic transesterification, while most papers use the methylic one.
- More than 80% conversion was obtained in a green chemistry process using ZnO impregnated on natural bentonite.

GRAPHICAL ABSTRACT



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ABSTRACT

This research aims to study the feasibility of using bentonite clays in their natural form, acidified and impregnated with CuO, ZnO and CeO_2 by a microwave-assisted solvothermal method, for use in the production of biodiesel. Characterization of the materials confirmed impregnation on the bentonite. Transesterification reactions were performed using the ethylic route at 200 °C in a Parr reactor for 1, 2 and 4 h. The results indicated that acidified bentonite led to the conversion of triacylglycerides into esters in addition to small amounts of diacylglycerides and monoacylglycerides. However, this material does not lead to the homogeneous impregnation of the oxides on its surface. For the natural bentonite, almost no conversion was obtained for the pure material, but a homogeneous impregnation with zinc oxide was attained, leading to 88% conversion after 4 h of a catalytic test.

1. Introduction

Natural clays have been used in catalytic reactions. For instance, K-10 montmorillonite and HB zeolite were used as catalysts in the

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methylic transesterification of *Pongamia pinnata* oil at 120 °C for 24 h. Conversions of 47% and 59% were obtained, respectively [1,2].

The structural properties of clay minerals can be modified by different methods or can be used as supports for the deposition of catalysts. The use of a catalytic support aims to increase the surface area and improve the dispersion of the active phase leading to more active sites [2,3]. In the present work, a bentonite was used as a support for ZnO, CuO and CeO_2.

ZnO is a material with promising results in the synthesis of biodiesel, with conversions up to 96% depending on the method of synthesis and the reaction conditions during transesterification [4]. Karmee and Chadha [1] obtained an 83% conversion in the methylic transesterification of *Pongamia pinnata* oil at 120 °C for 24 h. The simultaneous synthesis of nanometric ZnO and biodiesel was performed by the solvothermal reaction of vegetable oils and zinc nitrate in methanolic media with conversion of almost 97% [5]. Zinc was also used as a salt for the methanolic transesterification of castor oil [6,7]. ZnO was also mixed with other oxides, as CaO, La_2O_3 or SiO_2 for the transesterification reaction [8–12].

CuO has been mixed with other oxides and used in the synthesis of biodiesel from cooking oil. CuO–CeO_2 mixed oxides led to 92% conversion [13]. Caland et al. [14] obtained ~84% conversion using CuO–Al_2O_3 for the methanolic transesterification of babassu oil. CuO was supported on SrO for the transesterification reaction in addition to the selective hydrogenation of hempseed oil [15].

CeO_2 has been used as a support or mixed with other oxides for the methanolic transesterification of different oils. For instance, CeO_2–CaO mixed oxides were used as catalysts by Thitsartarn and Kawi [16] for the methanolic transesterification of palm oil with 95% conversion and also by Kawashima et al. [17], with 80% conversion. Ramírez et al. [18] obtained 56% conversion after 1 h of reaction for CeO_2 impregnated on MgO in the transesterification of cooking oil. In other studies, CeO_2 was used as a support for CaO in the methylic transesterification of soybean oil. [19,20].

In the present work, ZnO, CuO and CeO_2 were deposited on bentonite using the microwave-assisted hydrothermal/solvothermal method of synthesis, which has been widely used to obtain nanometric materials with different compositions [21]. The transesterification reaction was performed by the ethylic route because Brazil produces ethanol from sugar cane, which leads to a very green fuel.

2. Materials and methods

2.1. Synthesis of the catalytic system

The natural (NAT) and acid (ACD) clays were provided by BETONISA S.A. ZnO and CuO solutions were prepared separately using acetates as precursors ($Zn_2(CH_3COO)_2{\cdot}H_2O$ and $Cu(CH_3COO)_2{\cdot}H_2O$, respectively) under ethanolic media and CeO_2 was obtained using $Ce(SO_4)_2{\cdot}4H_2O$ in aqueous media. All of the suspensions were obtained after alkalinization by NH_4OH. The bentonite was added to the suspension containing the cations under constant stirring for 20 min and solvothermalized/hydrothermalized in a microwave reactor at 100 °C for 15 min. The precipitated material was washed with distilled water in a centrifuge until neutralization at pH = 7 and dried at 100 °C for 5 h. Samples were named based on the bentonite used as the support (NAT for the natural one and ACD for the acid one) and the symbol of the cation present in each oxide.

Powders were characterized by X-ray diffraction in an XRD 6000 instrument from Shimadzu using K_α (Cu) radiation ($\lambda = 1.54$), a step scan of 0.03°/s and a 2θ range of 3–80°. Analyses of the surface area were performed by N_2 adsorption using the BET equation. Measurements were taken in a BELSORP II instrument. FE-SEM micrographs were performed using a FEG-VP Zeiss Supra 35 instrument.

For the catalysts NAT, ACD, NAT Zn and ACD Zn, the acid sites were determined by the n-butylamine adsorption/desorption, according to the methodology described by Silva et al. [22], except for the activation temperature which was done at 200 °C instead of 400 °C, due to the clay dehydroxylation reaction which takes place between 400 and 500 °C. Quantification of the n-butylamine adsorbed/chemisorbed on the acid sites was performed by thermosorption using thermogravimetry measurements by a Mettler 851 TG/SDTA equipment. For this calculation the mass loss assigned to dehydroxylation was subtracted from the total mass loss. The analyses were carried out in alumina crucibles containing ca. 10 mg of sample pre-adsorbed with n-butylamine. High purity nitrogen was used as carrier gas was with a flow of 25 mL min^{-1}. Samples were heated with a rate of 10 °C min^{-1} up to 850 °C.

2.2. Catalytic test

Synthesis of the biodiesel was performed using ethyl alcohol and soybean oil in a molar ratio of 12:1. The catalysts were used in a concentration of 5% m/m. Reactions were performed in a Parr reactor, model 4561, with a capacity of 300 mL. The reagents were placed in the reactor and heated to 200 °C at a heating rate of 2 °C min^{-1} under stirring at a speed of 600 rpm. The final pressure varied from 300 to 330 psi. Samples of 35 mL were removed from the reactor after 1, 2 and 4 h. These samples were centrifuged for separation of the catalysts and then transferred to a decantation balloon, where they were washed and dried at 80 °C under vacuum.

The biodiesel samples were characterized by kinematic viscosity measurements using a Julab viscometer, model V18, with a Cannon Fenske glass capillary immersed in a water bath at 40 °C. ^1H NMR spectra were obtained on a GEMINI 300BB VARIAN spectrometer operating at a frequency of 200 MHz. Conversion of the oil into biodiesel was evaluated based on the integrated peaks of the spectra [23–25] according to the methodology developed by Ghesti [24]. The concentration of the ethylic esters was determined using a gas chromatograph with a flame ionizing detector (GC-FID) from Shimadzu, model CGMS-2010, with an automatic sampler and a split injector. The capillary column Durabond – DB-23 (Agilent Technologies) was used. Helium was used as the carrier gas with a flow rate of 30.0 mL min^{-1} and an injection volume of 0.5 μL. The temperature of the FID detector was 380 °C.

3. Results and discussion

3.1. Synthesis of the catalysts

The XRD patterns of the pure and impregnated bentonites are presented in Fig. 1 and Table 1. The presence of smectite was confirmed, in addition to quartz and minor amounts of illite and kaolinite. One peak assigned to CeO_2 was identified at 28°, which confirmed the formation of the fluorite phase. Superposition of the peaks assigned to CuO and ZnO with those of the smectite made identification of these phases difficult. Moreover, this behavior may be related to the formation of ZnO and CuO with low crystallinity, which would lead to low-intensity peaks in the XRD patterns.

After deposition of the oxide on the bentonite, a significant decrease in the intensity of the (001) peak of the smectite can be observed, in addition to its dislocation to larger angles, which indicate that the interlamellar distance decreased. This behavior can be assigned to the intercalation of H_3O^+ molecules among the lamellae being exchanged with hydrated Na^+ cations.