

Research Article

One-Step Synthesis of CaO-ZnO Efficient Catalyst for Biodiesel Production

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Biodiesel is the best candidate for fuel oil replacement, and to obtain it, heterogeneous catalysts offer large advantages: they can be separated from the product and reused. This work reviews a novel one-step synthesis of CaO-ZnO catalytic particles suitable for biodiesel production. The catalyst is synthesized using an original simple method that involves mixing of ZnO with CaCO₃ and subsequent calcination. The CaO-ZnO microparticles obtained present an average size of 2 μm. This material shows the characteristic crystallographic cubic structure of CaO and the hexagonal phase of ZnO. The temperature-programmed reduction experiment evidences an interaction between CaO and ZnO. Moreover, the infrared spectroscopy shows typical bands of these compounds. The catalyst shows high biodiesel yield, up to 73% in the first cycle and 64% in the second one. In this work, the synthesis of an efficient CaO-ZnO catalyst with a huge potential is revealed, which could be an economic alternative to produce biodiesel.

1. Introduction

Nowadays, searching for a renewable and alternative energy source is an important task due to the continuous increase in energy demand, the depletion of fossil fuel resources, the global warming, and the environmental pollution. The biodiesel (BD), fatty acid methyl esters (FAMES), has been accepted worldwide as a renewable fuel alternative to the fossil diesel [1]. FAMES are obtained by the transesterification of triglycerides (vegetable oils or animal fats) with methanol using catalysts [2]. FAMES can be used as a substrate for the preparation of additives for diesel fuels and provide an environmentally friendly alternative to conventional diesel [2–4]. It is well known that the mechanism of the transesterification reaction to obtain biodiesel is the same for both alcohols: ethanol and methano. However, ethanol allows obtaining BD with better characteristics for the diesel engine: high cetane number and small cloud point

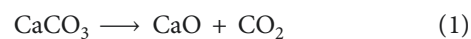
[5–7]. Moreover, ethanol produces more environmentally friendly biodiesel than methanol because its combustion produces fewer amounts of CO, particles, and NOx. There are several kinds of catalysts (acid, basic, heterogeneous, and homogeneous) to produce biodiesel [8–13]. Basic homogeneous catalysts (sodium hydroxides or alkoxides) are frequently used for the transesterification of triglycerides in an industrial scale. However, these catalysts have serious disadvantages; for example, they are neither recyclable nor environmentally friendly and lead to formation of biodiesel and glycerol contaminated with sodium or potassium ions [14, 15] and they also produce soaps. Furthermore, these catalysts are deactivated when the feedstock presents a humidity level of more than 0.3 wt.% and/or the free fatty acid (FFA) level are higher than 0.5 wt.% [16]. Therefore, the use of homogeneous catalysts to produce biodiesel requires very pure raw materials. The nonedible oils, animal fat, cooking oils, or waste oils used as raw materials for the

biodiesel production are less expensive than edible oils and reduce the cost of biodiesel production [17–20]. However, these oils usually contain high amounts of FFAs (up to 12% by weight) and humidity (~3% by weight), and also a homogeneous base catalyst cannot be used for transesterification [21]. In order to achieve a solution to the abovementioned problems, the researchers have developed heterogeneous basic catalysts, which show several advantages over homogeneous ones. The main advantages are that they present a better catalytic performance and an easy separation from the reaction products. Moreover, they maintain its activity independently to the humidity content and the quantity of FFA in the feedstock, and they can also be recycled [4]. Additionally, the heterogeneous catalyst most frequently used for the transesterification reaction is calcium oxide, mainly due to its lack of toxicity and low cost [22–25]. The activity of pure CaO could be improved by preparing the oxide in the nanocrystalline form [26] or by potassium or lanthanum ion impregnation [22, 27, 28]. Hassan et al. found that a 2.0 M calcium precursor has high catalytic activity and it obtained 81% FAME yield within 3 h of the reaction [29]. Among the transition metal oxides, ZnO is another most studied catalyst [30–32]. In a recent work, a screening of the performance of ZnO and CaO catalysts showed that a conversion at 6 h for the transesterification reaction using soybean oil and methanol was 38% and 24%, respectively [33]. The performance of the ZnO/Li catalyst was tested using soybean oil esterified with methanol. Using this catalyst leads to a conversion efficiency of 96% in 3 h of reaction time [34]. Also, the preparation of CaO-ZnO has been reported by the coprecipitation method, varying the atomic ratio Ca/Zn [35]. The CaO-ZnO powder mixture has been used as a heterogeneous catalyst for the transesterification of soybean oil using methanol [36–38]. However, the proposed synthesis methods involve several steps to obtain the catalyst. In this work, a simple synthesis of CaO-ZnO catalysts, in only one step, is proved.

2. Materials and Methods

2.1. Preparation of Catalyst (CaO-ZnO). CaO-ZnO catalysts were prepared by adding 1 g of ZnO to 50 mL of a 2 M CaCO₃ aqueous solution. Such a ratio of Zn/Ca was chosen considering exploratory assays. A further increment of Zn concentration not showed a higher conversion in the transesterification reaction. As it was previously reported by Kumar and Ali [39], an increase of Zn content can affect the catalyst base strength. The prepared suspension was stirred for 3 hours. After that, this suspension was dried in an oven at 120°C for 24 hours. Afterwards, the obtained solid was calcined at 850°C in a muffle. The catalyst synthesis was performed from ambient temperature to 100°C with a heating rate of 4°C·min⁻¹; in a first plateau, the sample was kept at 100°C during 75 minutes and then the temperature was raised to 850°C at 3.5°C·min⁻¹. Once this temperature was reached, a second plateau was performed during 180 minutes. Finally, the temperature was reduced to 20°C with a cooling ramp of 3°C·min⁻¹.

The calcination temperature causes the decomposition of carbonate as it is shown in equation (1). This new material is synthesized in one step. Such *in situ* synthesis produces an intimate contact of the ZnO with the CaO during the calcination.



2.2. Catalyst Characterization. The catalyst was characterized using scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), X-ray diffraction analysis (XRD), Fourier transform infrared spectroscopy (FTIR), BET surface area, and thermal programmed reduction (TPR).

2.2.1. Scanning Electron Microscopy and Analysis of X-Ray Scattering. SEM micrographs were obtained by using a LEOGENESIS VP 1450 microscope. The samples were placed on aluminium pegs and sputtered with gold. The SEM equipment was operated under high vacuum, and the measurements were obtained using an accelerating voltage of 8 kV. Also, the elemental analyses were determined by energy dispersive spectroscopy (Genesis EDS probe).

2.2.2. Particle Size Distribution. The particle size distribution was determined employing a Sedigraph 5100 analyser. The device uses X-rays to detect the concentration of particles based on Stokes' law. The absorption of X-rays is directly proportional to the mass of the particles. The well-dispersed sample was placed for the cell analysis, where a beam of X-rays initially determines the amount of larger particles and then it registers particles of smaller sizes.

2.2.3. X-Ray Diffraction (XRD) and Thermal Programmed Reduction (TPR). The diffractogram of the catalyst was obtained on a Rigaku diffractometer operated at 30 kV and 20 mA, using K α radiation ($\lambda = 0.15418$ nm) at a speed of 3°C min⁻¹ between $2\theta = 20^\circ$ and 80° .

The TPR analysis was performed with a differential scanning calorimeter equipped with a cooling device (Netzsch DSC-204-F1-Phoenix). The catalyst (5 mg) was dried for 2 h at 650°C and reduced at 25 to 650°C (5°C·min⁻¹), with 5% H₂/N₂ mixture. The H₂ concentration in the effluent was monitored with a thermal conductivity detector. The TPR curves were obtained from 100°C to 590°C using N₂ liquid, at a scanning rate of 10°C·min⁻¹.

2.2.4. Fourier Transform Infrared Spectroscopy (FTIR). In order to verify the presence of characteristic absorption bands of CaO and ZnO, the FTIR spectra were collected by using a Nicolet Impact 410 spectrometer in transmission mode, from KBr pellets of solid samples; a total of 200 scans were averaged at a resolution of 4 cm⁻¹.

2.2.5. BET Surface Area. The surface area was measured with a Micromeritics Gemini V analyser by adsorption of

nitrogen at -196°C on 100 mg of a sample previously degassed at 250°C for 16 h under flowing N_2 .

2.2.6. Biodiesel Synthesis. In order to synthesize BD, ethanol 99.4% v/v (EtOH) was provided by BIO4 S.A. (Río Cuarto, Argentina); the soybean oil was kindly provided by OLCA S.A.I.C. (General Cabrera, Argentina). The synthesis was performed in a two-necked round-bottom flask equipped with a reflux condenser and a magnetic stirrer. The heating of the reactive mixture was conducted by using a hot water bath (60°C) using a crystallizer with glycerol-water (90 : 10 v/v). Then 20 g of semirefined (degummed and neutral) soybean oil and the catalyst was placed into the flask at a ratio of 10% w/w and 30% w/w, respectively.

The oil and the catalyst were dispersed in EtOH 99.4% v/v. The quantity of EtOH was calculated to achieve an oil/alcohol molar ratio of 1 : 40. The temperature of the mixture was controlled at 60°C . The reactant system was kept under vigorous stirring (c.a. 800 rpm) for 6 hours. The catalyst was separated by centrifugation, and then the reaction mixture was transferred to a 250 mL decantation ampoule. At room temperature, phase separation was observed, an upper phase: ethyl ester (BD), and a bottom phase: glycerol. The latter was separated, quantified, and discarded, while the first phase (after ethanol evaporation in a rotary evaporator: 70°C , 20 torr, 1 h) was used for BD characterization. The yield of biodiesel (%EE) was calculated as presented in Eq. (2), being m_{oil} the mass of vegetable oil and m_{BD} the biodiesel mass:

$$\% \text{ EE} = \frac{m_{\text{BD}}}{m_{\text{oil}}} 100. \quad (2)$$

Free glycerol (FG) and total glycerol (TG) were determined by AOCS method Ca 14-56. Pro-analysis chloroform, glacial acetic acid 99.5% v/v, periodic acid, potassium iodide, potassium dichromate, potassium hydroxide, and hydrochloric acid were purchased from Cicarelli, while ethyl alcohol (EtOH) 95% v/v was obtained from Porta S.A., Argentina. All measurements were performed in duplicate with independent samples.

2.2.7. Catalyst Leaching Studies. The leaching of the reactive groups Ca(II) and Zn(II) was determined using atomic absorption spectroscopy (Varian 50AA spectrometer). Once the reaction was finished, the solid catalysts were separated by centrifugation (3000 rpm, 30 min). Then, the solution was mineralized by HNO_3 for 8 h. Ca(II) was determined at 422.7 nm with an N_2O /acetylene mixture, whereas Zn(II) was determined at 213.9 nm using an air/acetylene mixture.

2.2.8. Reusability. In order to study the reusability, the catalyst regeneration was performed by washing the used CaO-ZnO catalyst with ethyl alcohol and hexane, followed by calcination in a muffle furnace at 300°C for 3 hours to remove any remaining alcohol, oil, or biodiesel. Then, the BD production was carried out following the procedure depicted in Section 2.2.6.

3. Results and Discussion

3.1. Characterization of the Catalyst. The synthesis procedure employed to obtain the CaO and ZnO particles produces a relatively uniform size distribution as it is shown in Figure 1. The average of the particle size achieved is approximately $2 \mu\text{m}$.

The SEM images (Figures 2(a) and 2(b)) of the catalyst show that the synthesized material presents particles of different sizes ranging from c.a. $1 \mu\text{m}$ to $20 \mu\text{m}$. However, most of the particles present the size of c.a. $2 \mu\text{m}$. The quantitative analysis results from EDS were used to determine the following composition: Ca 44.58%, Zn 20.81%, and O 34.62%. The image of the material indicates that the particles are formed by agglomeration of microparticles and nanoparticles generated during the calcination process (Figure 2). In addition, the external rugosity enhances the superficial area, allowing more available active sites for the catalytic process.

The measured specific surface area obtained was $10.3 \text{ m}^2 \cdot \text{g}^{-1}$, and this value is in agreement with another similar catalyst synthesized recently (7 to $11 \text{ m}^2 \cdot \text{g}^{-1}$) [29, 33].

The catalyst X-ray diffraction analysis is shown in Figure 3. The diffractogram reflects the characteristic peaks at c.a. 34.4° , 36.2° , 47.6° , 56.7° , and 62.7° , which correspond to a cubic crystallographic form of CaO (JCPDS 821 691), and peaks at c.a. 31° , 34° , 36° , 47° , 27° , 64° , 67° , 68° , and 69° (JCPDS 891 397), which match to the hexagonal phase of ZnO. These results confirm that the particles are formed by a combination of the two oxide phases CaO-ZnO.

In Figure 4, the TPR experiment of the mixture (CaO + ZnO) shows the typical peaks of the CaO (at c.a. 340°C) [40] and the ZnO (at c.a. 290°C and 500°C) [41]. On the other hand, the profile of the CaO-ZnO catalyst shows a peak at c.a. 330°C and a shoulder at 490°C , showing a TPR curve different than CaO + ZnO. Based on this result and considering the XRD diffractogram data, it is possible to ensure that the particles of the CaO-ZnO catalyst do not present the same physicochemical characteristics compared with the mixture of the two oxides CaO + ZnO.

The FTIR spectrum of the catalyst is shown in Figure 5. The spectrum shows a weak absorption band at 875 cm^{-1} that reveals the presence of carbonate [42]. It has been demonstrated that the contact of the CaO reactive surface area with air during calcination produces a considerable amount of CO_2 and H_2O . These compounds are adsorbed on the CaO surface in the form of free -OH and carbonate species (fundamental bands at 1465 , 874 , and 712 cm^{-1}) [42]. The characteristic band of the O-H stretching vibration of $\text{Ca}(\text{OH})_2$ is located at 3643 cm^{-1} , and the bands at 2965 and 2880 cm^{-1} are attributed to the O-H groups from H_2O [43, 44]. Moreover, the band at 1080 cm^{-1} is attributed to the Zn-O-H bending vibration [36]. The absorption peaks recorded at 400 – 600 cm^{-1} could be considered to be of Zn-O stretching [45]. Since the infrared spectrum shows the characteristic band of ZnO and CaO, it is possible to ensure that catalysts are formed by both compounds.

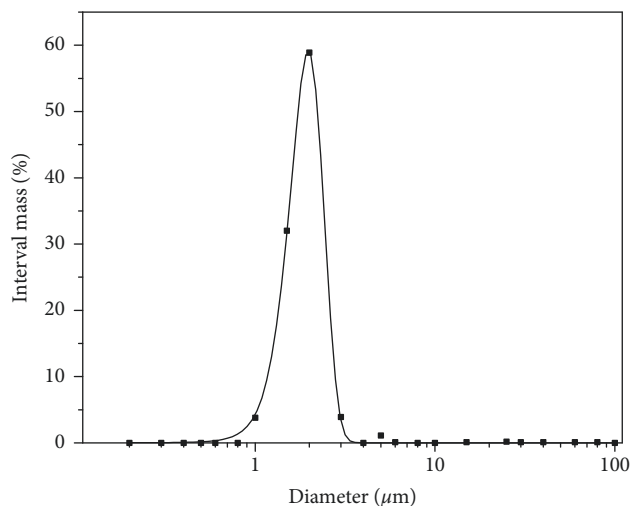


FIGURE 1: Particle size distribution of the CaO-ZnO catalyst.

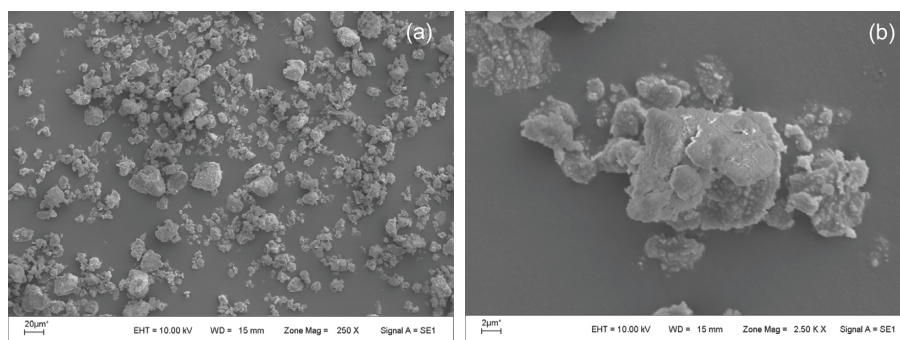


FIGURE 2: SEM images of the fresh catalyst.

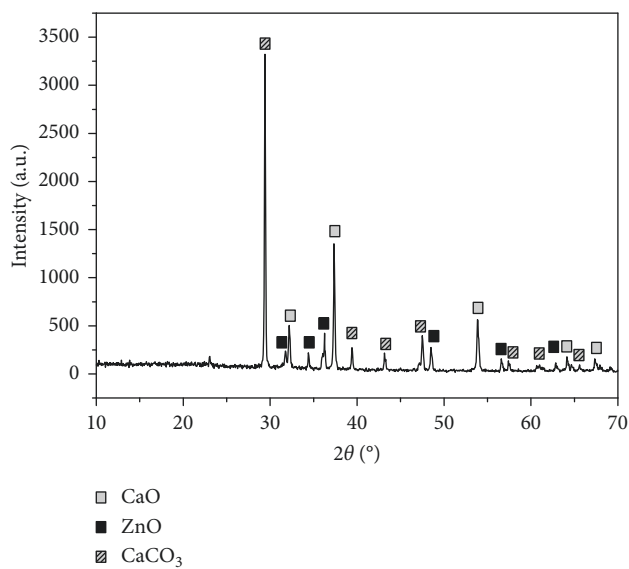


FIGURE 3: XRD diffractogram of the CaO-ZnO catalyst.

3.2. *Biodiesel Synthesis.* The biodiesel synthesis was performed as described in the experimental section. After the reaction, the phases were separated, the excess of alcohol was

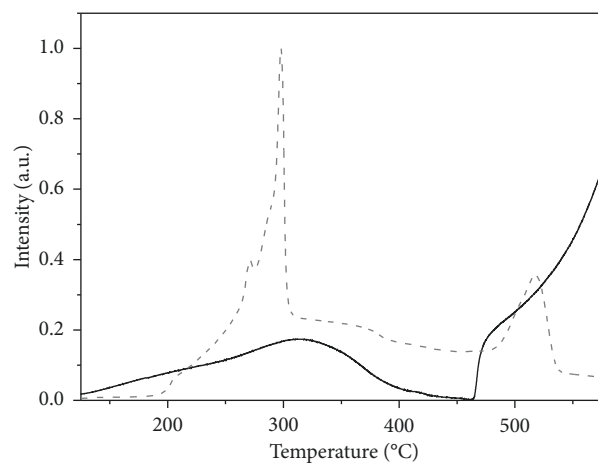


FIGURE 4: Temperature-programmed reduction experiment: CaO + ZnO oxide mixture (dotted line); CaO-ZnO catalyst (continuous line).

removed, and the amounts of both phases were weighed to estimate the conversion of esters according to equation (2). The results are shown in Table 1.

From the analysis of the results, it can be concluded that a change in the catalyst/oil ratio (10 and 30% w/w) does not

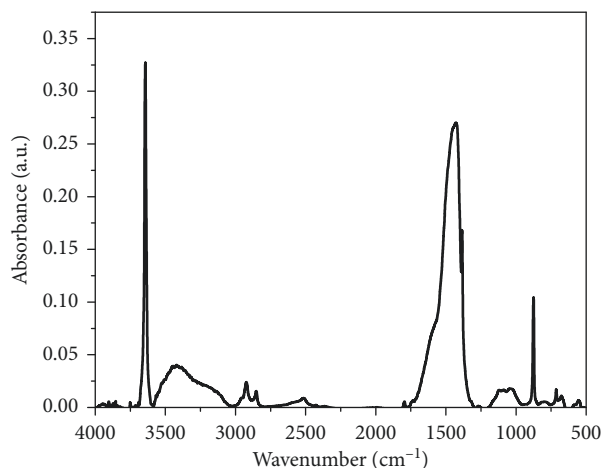


FIGURE 5: Infrared spectra of the CaO-ZnO catalyst.

TABLE 1: Percentage of ethyl esters generated by biodiesel synthesis using mixed CaO-ZnO as a catalyst.

Catalyst	% EE
Fresh (10%)	73 ± 0.5
Fresh (30%)	77 ± 0.6
Washed (10%)	64 ± 0.7

Reaction conditions: oil/alcohol molar ratio 1 : 40, 60°C, and 800 rpm for 6 hours.

improve the BD conversion (Table 1). For this reason, it is more efficient and economical to produce BD with only 10% w/w catalyst.

Considering that the regeneration and reuse of the catalyst is one of the most important aspects in industrial applications, the catalyst reusability for BD production was studied. The CaO-ZnO catalyst reused yields 64% EE (Table 1). These results show that the catalyst presents high performance and it is possible to reuse it without a significant activity loss.

The Ca(II) and Zn(II) concentration obtained by atomic absorption spectroscopy in the reaction mixture was 0.31% w/w and 0.15% w/w, respectively. These results allow concluding that the leaching of the catalyst is negligible and the decrease in the yield may be due to the catalyst poisoning.

For the experiment with 10% catalyst, the found values of free and total glycerol, according to AOCS method Ca 14-56, for the fresh catalyst (TG 1.18 ± 0.03%, FG 0.83 ± 0.01%) and the washed catalyst (TG 1.40 ± 0.03%, FG 1.00 ± 0.02%), were similar. These results demonstrate the good performance of the reused catalyst for the BD production.

Furthermore, the SEM image of the reused (washed) catalyst does not show structural changes in the surface as compared to the fresh catalyst (Figure 6).

Alba-Rubio et al. have reported a similar zinc oxide catalyst manufactured from the thermal decomposition of zinc oxalate impregnated with different amounts of calcium oxide [46]. The ZnO-CaO catalysts synthesized by these authors were thermally activated at 1073 K. The FAME yield was ≈80% in 5 h (using ZnO and CaO 4 wt.%)

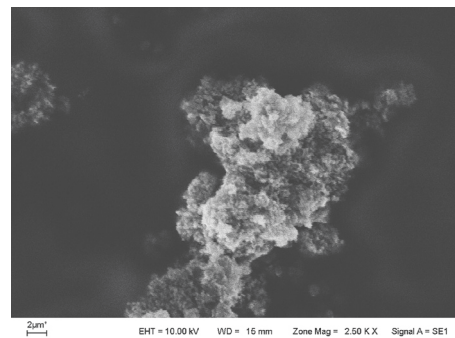


FIGURE 6: SEM image of the recovered catalyst.

and ≈50% (using ZnO and CaO 6 wt.%) in 3 h using methanol [46, 47].

It is known that the synthesis of esters using methanol produces better yields than using ethanol. Nearly employing half quantity of the catalyst and one hour less of reaction, the final yield is almost the same as that obtained in our experiments. However, the efforts to substitute nonrenewable (fossil) raw materials for sustainable ones, such as ethanol, are well known [48].

Recently, Hassan et al. [29] found similar results. The synthesis of FAMEs catalyzed by CaO showed conversions of 64–81% employing different concentrations of precursors in the catalyst synthesized by the sol-gel method. The BD reaction conditions were as follows: 60°C for 3 hours, ratio of palm oil to methanol 1 : 9, and 4% of CaO. The similar conversions achieved by these authors, with a lower concentration of catalyst and a lower alcohol-to-oil ratio compared to this work, can be explained with greater efficiency due to the active sites distributed in an improved mesoporous structure produced by the synthesis route of the used catalyst and the use of methanol instead of ethanol, which is well known as a less efficient alcohol for the transesterification reaction [29, 48].

The catalyst prepared by Navas et al. [33] was synthesized by precipitation of the precursors: calcium, magnesium, and zinc nitrates in the presence of alumina and then by calcination at 600–750°C. The biodiesel synthesis was carried out using 5 wt.% catalyst under the following reaction conditions: oil-to-methanol ratio 1 : 6, 6 hours of reaction time, and 60°C. It is remarkable how the presence of alumina increases the FAME conversion for all the precursors used, mainly for MgO (13%–60%). In the case of CaO catalyst, the conversion varies from 38% without alumina to 50% by adding alumina prior to the calcination step. It seems that the supported oxides in the alumina provide higher concentration of basic sites and the catalyst is more efficient [47].

The results presented in this work are comparable to those published elsewhere and show an acceptable performance of ethanol as alcohol for the transesterification of vegetable oils using this new heterogeneous CaO-ZnO catalyst prepared in a single step.

These promising results can be taken as a starting point for new developments and optimization of reaction conditions, catalyst preparation, and heterogeneous transesterification reaction.

4. Conclusion

In the present study, an easy one-step synthesis of a novel material to generate a biodiesel catalyst is shown. In addition, it is demonstrated that ethanol is an appropriate alcohol to use as a short-chain alcohol in substitution to methanol. The CaO-ZnO particles of the synthesized catalyst are $2\ \mu\text{m}$ in size. The procedure of synthesis presents an enormous advantage over other techniques due to the CaO-ZnO catalyst is manufactured in only one step. Moreover, this catalyst presents a good performance for the biodiesel synthesis using ethanol. Also, the catalyst can be reused as it maintains its catalytic activity and morphological properties.

Data Availability

The data supporting the conclusions in this work are included in this manuscript. Other datasets generated and analysed during the current work are available from the corresponding author on reasonable request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

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