International Journal of Chemistry Studies
www.chemistryjournal.in
ISSN: 2581-348X
Received: 28-07-2022, Accepted: 14-08-2022, Published: 31-08-2022
Volume 6, Issue 2, 2022, Page No. 42-46

Biodiesel synthesis from used cooking oil via one-step process of green CaO based solid catalyst and its reused

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Abstract
Catalysts can increase the reaction rate in biodiesel synthesis. The biodiesel synthesis from used cooking oil (low-grade oil, LGO), green CaO from eggshell as a solid catalyst support is potential to be used as a catalyst in a one-step esterification-transesterification reaction. This study aims to utilize a solid catalyst supported by CaO prepared from activated chicken egg shells with KOH solution and loading TiO_2/H for biodiesel synthesis from LGO in a one-step reaction and its reused. The solid catalyst of CaO/K-TiO_2/H was characterized by active sites functional groups, crystallinity, and surface morphology as well as tested for synthesizing biodiesel from LGO. Results showed that the biodiesel yield using fresh catalyst was 93.89%, 78.24% for reused-1 catalyst, and 60.98% for reused-2 catalyst. The solid catalyst of CaO/K-TiO_2/H had the potential to be developed for the synthesis of biodiesel from LGO in one-step process and can be reused.

Keywords: biodiesel, CaO/K-TiO_2/H solid catalyst, eggshell, reused catalyst, low-grade oil

Introduction

Biodiesel synthesis can be done in several ways, namely direct oil mixing, pyrolysis, micro-emulsion, and transesterification. The transesterification is the most popular method, because it is easiest to do under normal conditions, provides high conversion efficiency and the best quality compared to other methods [1]. In the transesterification method, biodiesel can be synthesized by reacting oil and short chain alcohol (methanol) with the presence of a catalyst [2, 3, 4]. Catalysts are indispensable in the transesterification reaction, because it serves to accelerate the methyl ester formation (biodiesel) [2].

The solid catalysts were chosen to overcome property weaknesses of the liquid catalyst. The strength of solid catalysts including the biodiesel production process using only a few units of separation and product purification so it becomes more efficient [4, 5]. In addition, solid catalysts are also non-corrosive, environmentally friendly, and can be regenerated after use, so it can be reused [6]. Meanwhile, the advantage of a bifunctional solid catalyst has both surface acid and base sites of the catalyst, which can functioning at the same time [7]. The bifunctional solid catalyst makes it possible to catalyze the esterification and transesterification reactions continuously, so the process of biodiesel synthesis from low-grade oil with free fatty acids more than 1% can be simplified into one-step process [8].

The use of solid catalysts for biodiesel synthesis has been widely studied. Utilization of solid K/TiO_2 catalyst for the esterification method of biodiesel synthesis from canola oil [9]. Istadi *et al*. (2015), examined performance of K_2O/CaO-ZnO catalyst for soybean oil transesterification into biodiesel [10]. Meanwhile, according to Carlucci *et al*. (2019), solid catalyst of sulfated-TiO_2 is suitable to be developed for the esterification reaction [11]. He *et al*. (2016) and Carlucci *et al*. (2019) reported that the compound of sulfated-TiO_2 had a super-acid property which is good for the esterification reaction [12, 11]. However, all the utilization of their solid catalysts are only for esterification or transesterification reactions and not yet for continuously esterification-transesterification reactions (one-step reaction).

Calcium oxide (CaO) is good solid catalyst for transesterification reactions in biodiesel synthesis. CaO has many advantages including insoluble in methanol, high activity, relatively longer shelf-life, and cheap [13]. However, when pure CaO is used, it still has weaknesses, namely it is quickly hydrated and easily carbonated at room temperature, and when mixed with methanol is quickly forms a paste, so the role of the catalyst becomes less stable. As a result, the conversion of oil into biodiesel decreases [14]. This weakness can be overcome by utilizing the CaO-matrix from culinary waste (green CaO), which is structurally more stable than pure CaO. Green CaO as an environmentally friendly matrix can be obtained from waste, including crab shells, bones, and eggshell. The high content of CaO in eggshell can be used as support of solid catalyst for biodiesel synthesis.

In this study, the solid catalyst with CaO-matrix from chicken eggshell was developed with KOH impregnation to form CaO/K as a source of surface base sites and loading TiO_2/H as source of a surface acid sites to form a bifunctional catalyst. The bifunctional solid catalyst was used for the one-step esterification-transesterification reaction of used cooking oil (low-grade oil) into biodiesel. Furthermore, the testing of the reused catalyst to the biodiesel yield.

Materials and Methods

Materials

In this the experiments were used chicken eggshell and LGO collected from culinary waste in Gianyar-Bali, KOH (99.8% purity), TiO_2 (98% purity), sulfuric acid (95-97% purity), and methanol (99.9% purity).

Methods

The synthesis of CaO/K-TiO_2/H catalyst. (1) Green CaO is prepared from eggshell (in powder) by decomposition of thermal. A hundred g of green CaO is mixed with 200 mL of distilled water and solution of 1.25 M KOH 25 mL and then stirred for 3 hours. Its component is repeatedly washed until free of base residual, furthermore dried at 110°C for 5 hours and calcinated at 600ºC for 5 hours [15] as CaO/K. (2) The prepared TiO_2/H, 10 g TiO_2 powder is impregnated with sulphuric acid solution of 200 mL of 0.5 M and stirred by medium stirring speed of a magnetic stirrer for 24 hours. Then, it is repeatedly washed until free of sulphate ions and filtered using Whatman 1 filter paper. Next, it was calcinated at 500ºC for 4 hours [16]. (3) CaO/K-TiO_2/H composite is prepared by physical mixing-calcination method. The TiO_2/H is mixed evenly with CaO/K of 1:3 mass ratio in a porcelain dish and added distilled water in 1:2 ratio, then calcinated at 550ºC for 3 hours. The prepared composite is characterized such as surface functional groups by using FTIR (Fourier transform infrared), crystallinity by XRD (X-ray diffraction), and surface morphology by SEM (scanning electron microscope).

The CaO/K-TiO_2/H activity testing into biodiesel synthesis. Synthesis of biodiesel in a one-step esterification and transesterification process is conducted using solid catalyst of CaO/K-TiO_2/H at catalyst concentrations to oil of 5%; molar ratios of oil/methanol of 1:9; and 60 minutes reaction times. This step is done at 65ºC and low scale mixing intensity [17]. Synthesized biodiesel is calculated as percent yield $= \frac{amount\ of\ synthesized\ biodiesel}{amount\ of\ oil} x\ 100$ [18].

The biodiesel functional groups is analyzed by FTIR. After the catalytic process, the used catalyst was regenerated by washing with 95% ethanol in several times, then filtered and dried at 110°C for 3 hours. The obtained reused catalyst is tested its activity for the synthesis of biodiesel.

Results and Discussion

Catalysts characteristics

The results of the analysis of catalyst active sites functional groups using FTIR are presented in Figure 1. The FTIR analysis of the catalyst (Figure 1) was carried out at wavenumber of 500-4000 cm^{-1}. The spectra showed that presence of O-H band in area around 3600 cm^{-1}, which appeared at 3637.90 cm^{-1}, stretching band of C-O in calcium carbonate compound appeared at wavenumber of 1461.38 cm^{-1}. The TiO_2/H (-O-Ti) absorption appeared weakness at wavenumber of 1056.07 cm^{-1} [19].

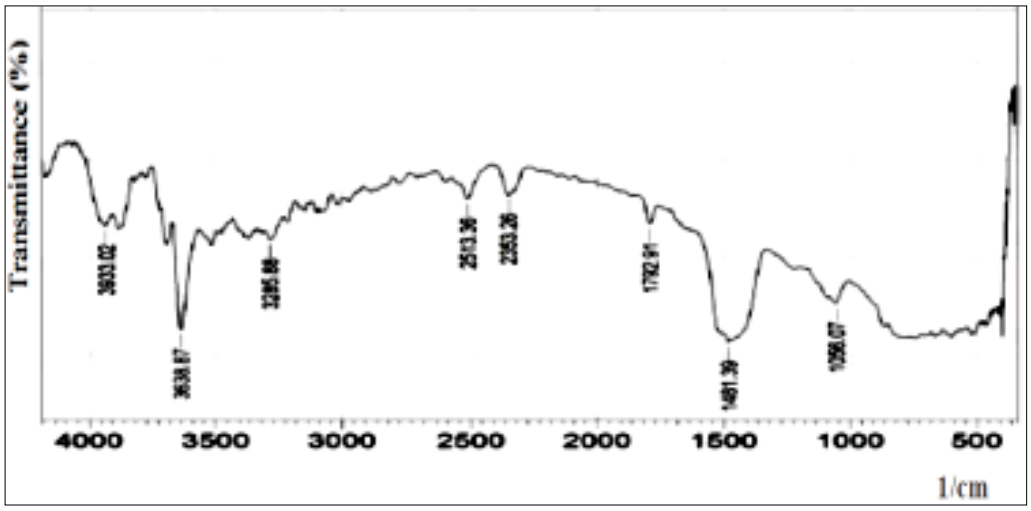

Fig 1: Fuctional groups of CaO/K-TiO_2/H fresh catalyst

The crystallinity of catalyst from the XRD analysis is presented in Figure 2. The XRD patterns showed that CaO, K (K_2O), and TiO_2 are all classified as crystalline and semi-crystalline. The K_2O appears at 2θ of 32.04º and 2θ of 33.91º have relative intensity of 39.84% and 62.94%, respectively. Meanwhile, TiO_2 appeared at 2θ of 25.22º and 34.12º has a relative intensity of 100 and 44.39%, respectively and its relative intensity is less than 6.50% was at 2θ of 35.92º; 38.47º; and 39.31º. The TiO_2/H appears at of 2θ 57.34º has 2.15% relative intensity which tendency to form semi crystalline. It means that K_2O and TiO_2 entered into the CaO structure. This is well agreement with Fadhil's research (2017) that TiO_2/H tends to form crystalline and semi crystalline [20].

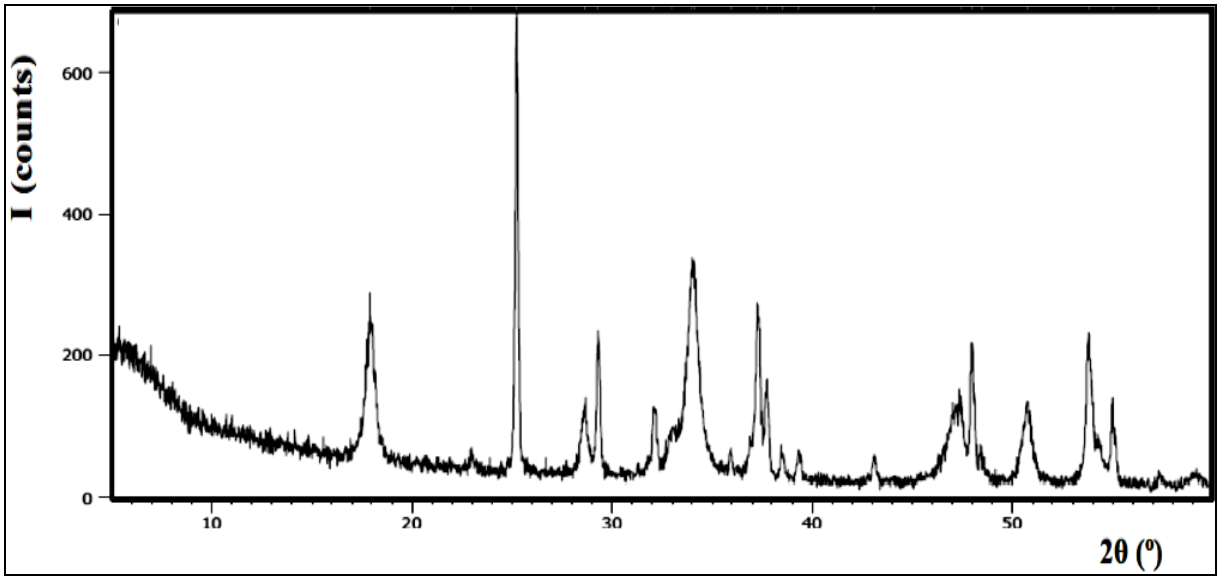

Fig 2: XRD diffractogram of CaO/K-TiO_2/H catalyst

The surface morphology of catalyst using SEM is presented in Figure 3. The surface morphology of CaO/K-TiO_2/H catalyst showed that porous structure, irregular in shaped particles, and approximately in spherical [15, 21].

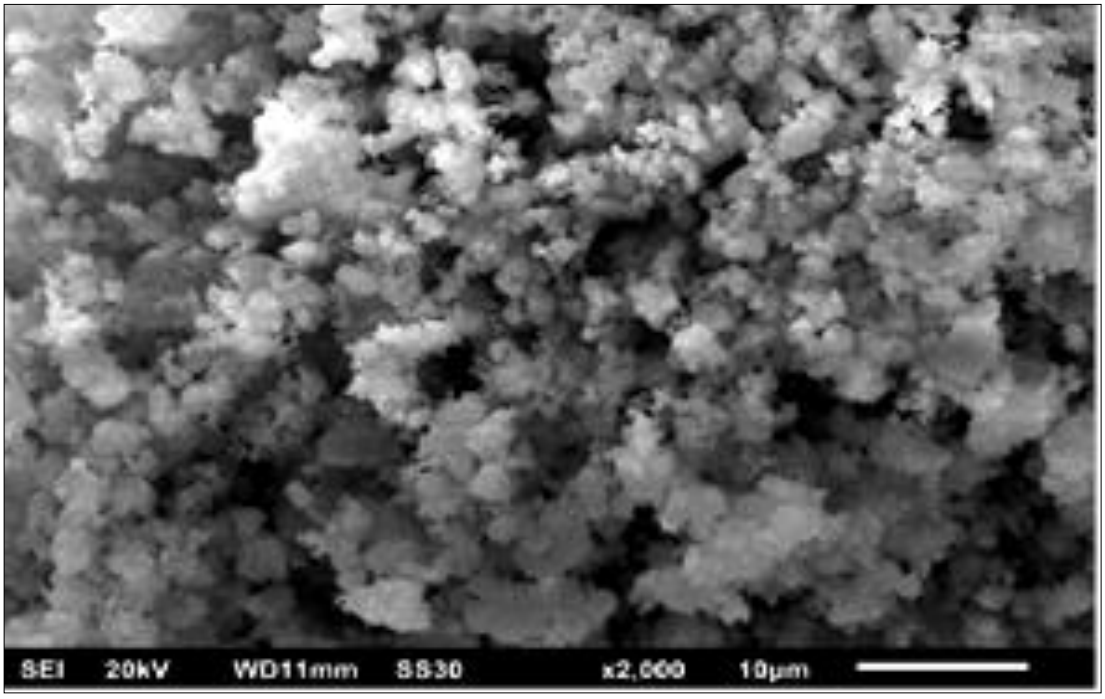

Fig 3: Surface morphology of CaO/K-TiO_2/H catalyst at magnification of 2000x

Activity test of reused catalyst

Table 1: Biodiesel yield of testing reused catalyst

Cycle	Biodiesel yield (%)
1 (Fresh catalyst)	93.89
2 (Reuse-1 catalyst)	78.24
3 (Reuse-2 catalyst)	60.98

The results of reused catalyst activity from the fresh catalyst decreased 15.65% in reused-1 catalyst and 32.91% in reused-2 catalyst to biodiesel yield. The decrease in biodiesel yield is caused by the role of catalyst which has decreased its activity. Although the activity of the catalyst has decreased to the biodiesel yield obtained, the catalyst still provides its function in converting oil into biodiesel.

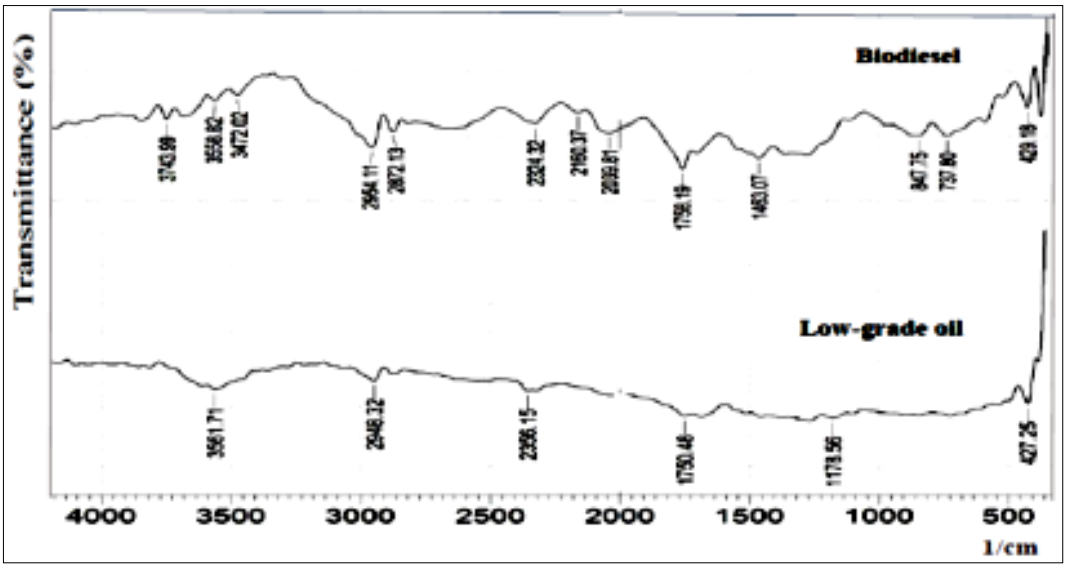

Fig 4: Fuctional groups of low-grade oil and biodiesel

Based on the FTIR analysis (Figure 4), it was found that presence of biodiesel functional groups more complex than in low-grade oil. Functional group of O-C=O appears at wavenumber of 2160.37 cm^{-1}, functional group of -CH_3 at 1463.07 cm^{-1}, and functional group of C-O or O-CH_3 at 700-800 cm^{-1}. It means that methyl ester (biodiesel) has been successfully formed from the conversion of low-grade oil (triglycerides) in the presence of solid catalyst.

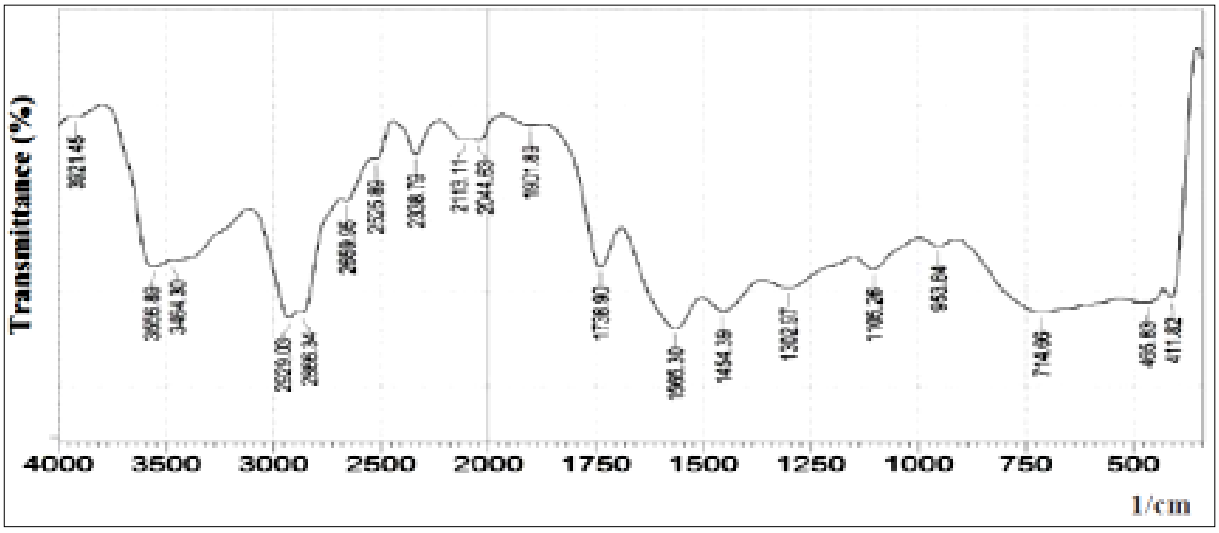

Fig 5: Fuctional groups of CaO/K-TiO_2/H reused catalyst

The result of FTIR analysis of reused catalyst (Figure 5) showed that it was an addition of functional groups compared to the fresh catalyst (Figure 1). The addition of functional groups is thought to be caused by the presence of methanol and oil (triglycerides) compounds that have been bound to the catalyst surface during the catalytic process. The presence of O-C=O functional group appears at wavenumber of 2113.11 cm^{-1} as a functional group of oil trapped on the surface of catalyst. Meanwhile, functional groups of -CH_3 appeared at a wavenumber of 1454.39 cm^{-1} and O-CH_3 at 714.66 cm^{-1} due to the binding of methoxide groups on the catalyst surface. Its functional groups are formed because of the initial stage of catalyst interacted with methanol and oil.

Conclusion

The results showed that the biodiesel yield using the fresh catalyst was 93.89%, 78.24% for reused-1 catalyst, and 60.98% for reused-2 catalyst. Based on the results of reused catalyst characterization with FTIR, appeared new functional groups due to adsorption of methanol and oil have been formed. Therefore, the solid catalyst of CaO/K-TiO_2/H has the potential to be developed for the biodiesel synthesis from low-grade oil in one-step and can be reused.

Acknowledgement

Thanks to the Institute of Research and Community Service of Udayana University through the Faculty of Mathematics and Natural Sciences was research funding from PUPS scheme of year 2021.

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