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Research Article

Reusability and Stability Tests of Calcium Oxide Based Catalyst (K_2O/CaO-ZnO) for Transesterification of Soybean Oil to Biodiesel

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Abstract

This paper was purposed for testing reusability and stability of calcium oxide-based catalyst (K_2O/CaO-ZnO) over transesterification reaction of soybean oil with methanol to produce biodiesel. The K_2O/CaO-ZnO catalyst was synthesized by co-precipitation method of calcium and zinc nitrates followed by impregnation of potassium nitrate. The fresh and used catalysts were tested after regeneration. The catalysts were characterized by Scanning Electron Microscopy (SEM), X-ray Diffraction (XRD), and BET Surface Area in order to compare the catalyst structure between the fresh and used catalysts. The catalyst testing in transesterification proses was carried out at following operating conditions, i.e. catalyst weight of 6 wt.%, oil to methanol mole ratio of 1:15, and temperature of 60 oC. In addition, metal oxide leaching of K_2O/CaO-ZnO catalyst during reaction was also tested. From the results, the catalysts exhibited high catalytic activity (80% fatty acid methyl ester (FAME) yield after three-cycles of usage) and acceptable reusability after regeneration. The catalyst also showed acceptable stability of catalytic activity, even after three-cycles of usage.

Keywords: K_2O/CaO-ZnO; biodiesel production; transesterification process; reusability; stability

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1. Introduction

Biodiesel has become a great attention recently to replace the conventional fossil fuel based diesel. Biodiesel, consisting of fatty acid methyl ester (FAME), offers a solution to fossil fuel depletion and environmental degradation issues due to its ability to be renewed and biodegraded easily [1,2]. Application of biodiesel in diesel engine exhibited better degradation characteristic and lower emissions of carbon monoxide (CO), carbon dioxide (CO_2), total hydrocarbons (THCs), particulate matter (PM), and volatile organic compound (VOC) [3]. However from economics point of view, the biodiesel is not comparable with the petroleum based diesel due to its high production cost and feedstock price. Thus, many researchers have investigated on how to reduce the cost of biodiesel production. One of the efficient ways was

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by using heterogeneous catalytic transesterification reaction [1, 2].

Homogeneous catalysts, such as: NaOH, KOH, H_2SO_4, and H_3PO_4, were typically used for the transesterification reaction, although having a few disadvantages in costing of washing and purification processes. On the other hand, the use of the heterogeneous catalyst can avoid the homogeneous catalyst-based problem, because the heterogeneous catalyst can be separated from the liquid products easily and can be designed to give higher activity, selectivity and longer catalyst lifetimes. Previous researchers highlighted the reusability test of catalyst which makes it environmental friendly [1, 4]. However, some drawbacks were existed in the heterogeneous catalyzed transesterification process, i.e. metal oxide leaching that caused deactivation of the active sites and resulted to product contamination and slower reaction rate, and higher reaction temperature required [5]. Among the solid catalysts, the base catalyst is normally accepted as an efficient system because the biodiesel could be synthesized under mild conditions [6].

In the pioneering works by several researchers, CaO-based catalysts were used as a heterogeneous catalyst for the transesterification of vegetable oil to produce biodiesel due to its economical advantages and highly active (biodiesel yielded >90%) [6]. Development of CaO-based catalyst is undertaken by increasing their surface area and basicity in order to enhance the biodiesel yield. In this research, combining CaO and ZnO by co-precipitation method could improve the catalyst surface area. Promoting the catalyst with K_2O may increase its basicity as well as covering basicity instead of decreasing CaO content due to leaching [7, 8]. However, proper composition of the metal oxides (CaO, K_2O, and ZnO) should be investigated in detail.

Therefore, this study is purposed to test the stability and reusability of the K_2O/CaO-ZnO catalyst by considering basicity, surface area, and yield of biodiesel in order to enhance the economical point of view. The catalyst was characterized by SEM-EDX, XRD, and BET Surface Area to evaluate its structural changed during the transesterification process. The stability and reusability of the catalyst was performed by considering the biodiesel yield with respect to its surface properties.

2. Materials and Method

2.1. Materials

In this research, soybean oil (Happy-Indofood) and methanol (99.9%, Merck) were used as raw materials. The following chemicals, i.e. $Zn(NO_3)_2.4H_2O$ (98.5%, Merck), $Ca(NO_3)_2.4H_2O$ (99%, Merck), KNO_3 (99%, Merck), and Na_2CO_3 (99%, Merck), were used as precursors for catalysts preparation.

2.2. Catalyst preparation

The K_2O/CaO-ZnO catalyst was prepared according to the conventional coprecipitation and impregnation methods [9]. The required amounts of $Ca(NO_3)_2.4H_2O$ and $Zn(NO_3)_2.6H_2O$ were dissolved in deionized water to make 1 M solution. Solution of Na_2CO_3 2 M was added slowly into the mixed solution with vigourously stirred. pH of the solution was adjusted to 10 by adding NaOH 1 M solution. The obtained precipitate was aged for 24 h at temperature of 60 ^{o}C while stirring. The solid product was filtered and washed by deionized water until alkali free, and dried at 110 ^{o}C overnight in an oven (Memmert). The dried solid catalyst was calcined at 800 ^{o}C for 3 h in a box furnace (Ney Vulcan) and produced the CaO-ZaO solid catalyst. Thereafter, the solid catalyst was impregnated in the solution of KNO_3 1 M for 1 h while stirring and was dried in an oven (Memmert) at 110 ^{o}C overnight. The K_2O/CaO-ZaO solid catalyst were obtained after calcination at 800 ^{o}C for 3 h in the box furnace (Ney Vulcan).

2.3. Catalyst characterization

Crystal structure of the catalysts (active carbon and modified-carbon), before and after used, were analyzed by XRD (X-Ray Diffraction, Shimadzu XRD-7000) with Cu-Kα radiation (k = 1.54 Å) operated at 30 mA and 30 kV. The sample was scanned at the boundary between 10° to 90° with a scanning speed of 2 °/minute. Furthermore, diffractogram or peak was compared to the data from JCPDS (Joint Committee of Diffraction Data) library or literatures to determine the compounds contained in the catalyst. The Brunauer-Emmer-Teller (BET) surface area and pore size analyzer of the catalyst were determined using nitrogen adsorption-desorption isotherms (at 77 K) over Quantachrome Nova Instruments. The samples were out gassed for 5 h at 300 ^{o}C (573 K) under vacuum pressure (6.58×10^{-5} Torr) prior to the sorption measurements.

2.4. Transesterification reaction test

Mole ratio of methanol to soybean oil was kept at 15:1 and the amount of catalyst was 4 wt.% of the total mixed materials. The soybean oil was weighed and heated to 60 °C. The catalyst and methanol were weighed and also heated to 60 °C in the three-necked flask. Thus, the heated soybean oil was added and the transesterification reactions were performed at 60 °C for 4 h in a 500 mL three necked flask equipped with a water cooled reflux condenser, a thermometer, a heating mantle, and an impeller equipped with motor. After that, the reaction was stopped by cooling down the reactor to room temperature. The products were placed in a separatory funnel overnight to ensure that phase of FAME, glycerol, and catalyst were separated completely. Afterward, the obtained catalyst was washed by organic solvent and filtered. The used catalyst was re-activated by washed by hexane-methanol method and filtered, drying at 110 °C overnight and calcining at 800 °C for 3 h.

Concentration of the methyl esters was determined by using a GC-MS (QP2010S SHIMADZU), equipped with AGILENT HP 5 MS column (30 m × 0.25 mm i.d., 0.25 µm film thickness) and helium as a gas carrier. The FAME contain was quantified according to EN 14103 method [4]. The biodiesel and FAME yields were determined using Equations (1) and (2). The biodiesel was also tested for its standard quality, such as: kinematic viscosity and acid value, by ASTM D 445 and AOCS Cd 3d-63 methods, respectively. In Equations (1) and (2), the %FAME was derived from the peak area of GC-MS analysis. $\rho_{biodiesel}$ denotes density of biodiesel, $V_{biodiesel}$ denotes volume of biodiesel product, and m_{feed} denotes mass of soybean oil feed.

$$Biodiesel\ Yield\,(\%) = \frac{(\rho_{biodiesel}).(V_{biodiesel})}{(m_{feed})}x100\% \quad (1)$$

$$FAME\,Yield\,(\%) = \frac{(\%FAME).(\rho_{biodiesel}).(V_{biodiesel})}{(m_{feed})}x100\% \quad (2)$$

2.5. Reusability and stability test

An experimental work to evaluate stability of the catalysts was conducted. The leached test of catalyst was observed under the same conditions as used in the transesterification reaction by using fresh and used catalyst. After the treatment, the catalyst was removed by filtration from mother liquor. The phase of methanol-glycerol was separated and the amount of leached Ca was measured using colorimetric method.

The reusability of catalyst was investigated at similar reaction condition by repeating the transesterification reaction several times using the used catalyst form previous reaction process. The catalyst was separated from the previous reaction mixture, washed with hexane-methanol, and then dried at 60 °C [10]. The resulted solid catalysts were calcined at 800 °C for 3 h in a box furnace and were used for further transesterification reaction tests.

3. Results and Discussion

3.1. Catalyst characterization

XRD characterization was intended to determine the crystal structure and phases in the catalysts. The XRD patterns of catalysts, fresh and used 2% K_2O/CaO-ZnO, were shown in Figure 1. The XRD diffractogram of CaO gave intensified and narrowed peaks at 2θ degree of 17.2°, 27.2°, 28.7°, 50.5°, 52.7°, and 67.9° (JCPDS File No. 37-1497) [11]. Meanwhile, the XRD pattern of ZnO showed crystallite phases at 31.7°, 34.4°, 36.24°, 47.5°, 56.5°, 62.8°, and 67.8° (JCPDS File No. 36-1451) [11]. In addition, the impregnation of 2% K_2O loading showed additional small intensity peaks at 2θ degree 25.88° and 75.36° which is presented on the surface of catalyst. The small intensity of K_2O detected peak was due to too small concentration of K_2O which in turn it dispersed evenly. Based on the XRD pattern of fresh and used catalysts, increasing of CaO intensity at 2θ degree 17.2°, 27.2°, and 28.7° by leaching of methanol eventually the catalyst has better crystallinity. However, diffraction peak of CaO and ZnO on both catalysts showed similar pattern but the little different peaks were shown which may be due to modified CaO and ZnO ratio content (see Table 3) in the catalyst (JCPDS File No.47-1701; 77-2176) [12].

Scanning Electron Microscopy was used to determine of the morphology of catalyst surfaces. Figure 2 shows the SEM images of both

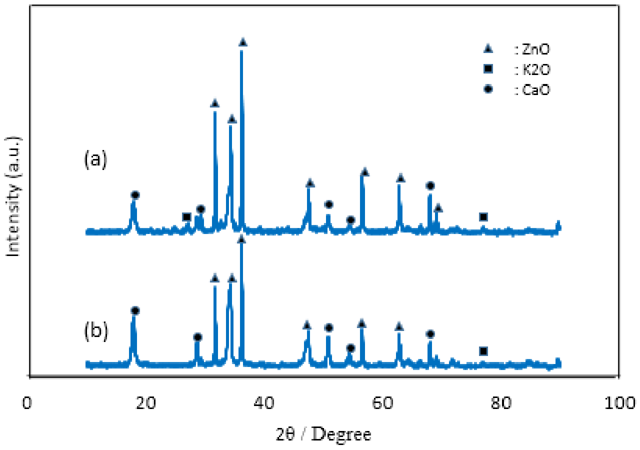


Figure 1. XRD pattern of catalysts: (a) Fresh catalyst of 2% K_2O/CaO-ZnO, (b) Three cycles used catalyst of 2% K_2O/CaO-ZnO

catalysts indicating particles with irregular shape sizes ranging from 0.5-2 μm. Some of them are bonded together as aggregates. The smaller size of the grains and aggregates could provide a higher specific surface area [13]. It can be inferred that surface morphology of the used catalyst could be maintained after three-cycles of used for transesterification process. From qualitative analysis by SEM-EDX study supported that the presence of 2 wt.% K_2O and CaO to ZnO catalyst was evidenced. The presence of K_2O observed on the fresh catalyst was suggested distributing the K_2O component evenly on the catalyst surface. Meanwhile for the used catalyst, there was no detected K_2O found. In this matter, the presence of K_2O may be lost during the transesterification process because of too low concentration of this oxide. Decreasing the CaO to ZnO ratio with respect to before and after used catalyst were 2.28:1 and 1.76:1, respectively (by EDX measurement) as inline in result of other researchers [5].

Surface area of the fresh and the three-cycles used of 2% K_2O/CaO-ZnO catalysts were listed in Table 1. From the table, it is indicated that surface area of the three-cycles used catalyst showed better than the fresh catalyst. In transesterification process, calcium as active component of the catalyst may be leached to methanol phase. Previous researchers reported that the surface area of their catalysts decreased steadily when the Ca^{2+} content (measured by EDX) in the mixed CaO-MgO catalysts increased [5]. This fact indicates that the BET surface area corroborates well with the crystallite size, in which a large crystallite size of the catalysts will reduce the surface area. Excessive CaO phases may cause saturation or filling of pores in catalyst composite, which contribute to reducing catalyst surface area.

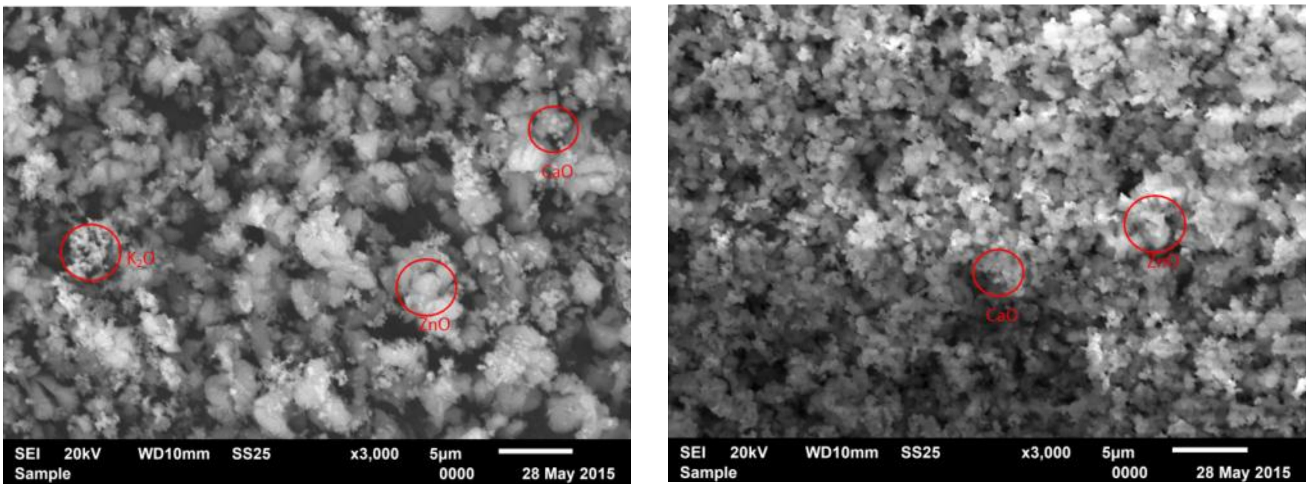
3.2. Catalysts performance testing for transesterification of soybean oil to fatty acid methyl ester

Performances of the catalysts on transesterification of soybean oil to fatty acid methyl esters were listed in Table 2 including the characteristics of soybean oil raw material. From the table, the catalyst has good performance to produce biodiesel with the yield higher than 80%.

Decreasing CaO content in the catalyst is due to leached by methanol reactant as indicated in Table 3. Meanwhile, decreasing the biodiesel yield in second-cycle catalyst usage may be due to decreasing the CaO content during the

Table 1. BET Surface Area of fresh and three-cycles used 2% K_2O/CaO-ZnO catalyst

Catalysts	Average pore diameter (nm)	Surface area (m^2/g)	Total pore volume (cm^3/g)
Fresh catalyst	36.01	3.094	0.02786
Three cycles used catalyst	31.44	4.669	0.03670



(a) (b)

Figure 2. Scanning Electron Microscopy images of 2% K_2O/CaO-ZnO catalyst: (a) fresh catalyst; (b) after three cycles of used

transesterification process as shown in the XRD and SEM-EDX results. The FAME yield after three-cycle used is better than other cycles as shown in Table 2. This trend was due to abundant of CaO content which may cause free phase and saturation in catalyst pores which in turn decreasing the catalyst surface area as suggested by other researchers [5]. The Ca content in the catalyst probably creates a free phase causing the leaching of Ca content during the transesterification process. The better surface area causes better activity in FAME yield and selectivity. Azis & Maulana [8] has proved that adding K_2O as promoter makes better activity and selectivity of the K_2O/CaO-ZnO catalyst. As shown in 3rd cycle of usage, the FAME yield was equal to the yield of biodiesel inferring 100% selectivity. The phenomenon may be due to the role of K_2O content promotion replacing the lost CaO content in previous cycles usage due to leaching in methanol. Therefore, the K_2O promoter takes place the role of base sites activity and selectivity.

3.3. Reusabilty and stability tests

The catalyst stability plays an important role in determining the economical point of views of the heterogeneous catalysts in large-scale biodiesel production. The 2% K_2O/CaO-ZnO catalyst was tested its reusability and stability over several consecutive three-cycles usage after washing and thermal treatment steps. The results indicated that the catalyst has consistent activity up to three-cycle usage after simple regeneration as listed in Table 2. The decreasing catalytic activity during the three repeating usage may be caused by following reasons: (i) leaching of calcium content from active sites into methanol phase; (ii) poisoning of the catalyst active sites by the reaction medium (oil, biodiesel and/or glycerol) which reduced contact area between base sites and reactants; and (iii) collapsing catalyst structure [3].

Leaching test of the 2% K_2O/CaO-ZnO catalyst with respect to Ca active component in methanol was listed in Table 3. The leaching test was conducted by colorimetric analysis method. From Table 3, it is showed that the Ca content was found in methanol phase after transesterification process in the first (408 ppm), second (520 ppm) and third runs (408 ppm) of biodiesel production, which suggested that a little bit of Ca component was leached in the reaction medium. The CaO leaching phenomenon affects on reducing catalytic activity during each stability test.

Table 2. Catalyst performance on transesterification reaction and the FAME product characteristics based on SNI (*Standar Nasional Indonesia*)

Run/Cycle	Biodiesel Yield (%)	FAME Yield (%)	Density (g/ml)	Kinematic Viscosity (mm/s, 313K)	Acid Number (mg KOH/g)
1st	98.80	41.17	0.885	2.43	0.50
2nd	92.98	37.88	0.883	2.27	0.57
3rd	84.82	84.82	0.878	2.49	0,51
SNI Standard of biodiesel	-	-	0.85-0.89	2.3-6	<0.8
Soybean Oil Raw Material	-	-	0.93	23.37	0.76

Table 3. Leaching test of Ca component of catalyst during transesterification process. *Ca/Zn mole ratio was measured by EDX results and leaching test data

Number of Run	Ca content in methanol phase (ppm)	Ca/Zn mole ratio*
Fresh	0	2.28
1st cycle run	408	2.27
2nd cycle run	520	1.58
3rd cycle run	408	1.57

4. Conclusions

In this study, a K_2O/CaO-ZnO catalyst was developed and tested according to its stability during the transesterification reaction process. From the testing, the 2% K_2O/CaO-ZnO catalyst showed promising for transesterification of soybean oil with methanol to produce biodiesel which having good catalytic activities with biodiesel yield was higher than 80%. The catalyst has also relatively good stability during the stability-reusability test with the yield of FAME higher than 80%. Component of calcium may be leached during the reaction process which replacing its role by promoting the reaction using K_2O promoter.

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