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## Characterization of K<sub>2</sub>O/CaO-ZnO Catalyst for Transesterification of Soybean Oil to Biodiesel

I. Istadi <sup>1)\*</sup>, Sebastianus A. Prasetyo <sup>1)</sup>, Tito S. Nugroho <sup>1)</sup><sup>1)</sup> Laboratory of Chemical and Process Engineering, Department of Chemical Engineering, Diponegoro University, Jln. Prof. Soedarto, Kampus Undip Tembalang, Semarang, 50275 Indonesia.**\*Corresponding author : [istadi@che.undip.ac.id](mailto:istadi@che.undip.ac.id) (I. Istadi)**

**ABSTRACT:** In this study, heterogeneous solid base catalysts (K<sub>2</sub>O/CaO-ZnO) were developed and characterized for transesterification of soybean oil to biodiesel. In the catalyst, CaO-ZnO prepared by coprecipitation was promoted by K<sub>2</sub>O by impregnation method. The catalysts were characterized by using X-Ray Diffraction (XRD) and Brunauer Emmett Teller (BET) surface area. The catalysts were compared to ZnO and CaO-ZnO catalysts to study their activities in the transesterification process under suitable conditions (reaction temperature of 60 °C, catalyst loading of 6 wt.%, methanol to oil molar ratio of 15:1, and reaction time of 4 h). From the catalyst testing results, the 2 wt.% K<sub>2</sub>O/CaO-ZnO showed the highest catalytic activity with Fatty Acid Methyl Ester (FAME) yield of 81.08 %. The incorporation of K<sub>2</sub>O on the CaO-ZnO catalyst enhanced the catalytic transesterification activity due to increasing its basicity and surface area.

**Keywords:** heterogeneous solid base catalyst; K<sub>2</sub>O/CaO-ZnO; biodiesel; transesterification; soybean oil.

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### 1. Introduction

Biodiesel is one of popular alternative energy in the world due to biodegradable and renewable fuel, non-toxic and lower emissions of CO. Some of studies have been investigated to produce biodiesel with different kinds of vegetable oils, such as palm oil, soybean oil, rapeseed oil, castor seed oil and cooking oil, as raw materials by transesterification process. The transesterification process was catalyzed by homogeneous catalysts (acid or base), enzymes, and heterogeneous catalysts (solid acid or solid base) [1]. The usage of homogeneous base catalysts, i.e. NaOH and KOH, for transesterification has much problems due to soap formation during reaction leading to difficult separation process [1-2]. The usage of homogeneous acid catalysts, i.e. sulfuric, hydrochloric, and sulfonic

acid, were better for the transesterification process in terms of solving difficulties in the homogeneous catalysis, but it showed lower biodiesel yield. Recently, many researches have focused on heterogeneous (solid acid or solid base) catalysts [1-2].

One of the most used catalysts is CaO as it has many advantages such as low price, long catalyst life, high activity and requires only moderate reaction conditions, although some disadvantages were found in the CaO catalyst which is low surface area and leaching [3]. Therefore, combination of CaO and ZnO metal oxides is interesting to be studied as a catalyst for transesterification process. Improving the basicity by doping by K<sub>2</sub>O was also proposed in this paper. The catalysts were tested on the activity performance in the transesterification between methanol and soybean oil.

## 2. Experimentals

### 2.1. Materials

In this research, soybean oil (Happy-Indofood having acid number of 1.12 mg KOH / g and 0.56% FFA) and methanol (99.9%, Merck) were used as raw materials. The following chemicals, i.e. Zn(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (98.5%, Merck), Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (99%, Merck), KNO<sub>3</sub> (99%, Merck), and NH<sub>4</sub>OH (25%, Merck), were used as precursors for catalyst preparation.

### 2.2. Catalysts Preparation

ZnO catalyst was prepared by calcination of Zn(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O at 600 °C for 3 h in a muffle furnace (Neo Vulcan). The CaO-ZnO (Ca/Zn = 1/3) catalyst was made by mixing solutions of Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O 2 M and Zn(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O 2 M and stirred. After that, NH<sub>4</sub>OH solution was dropwised to the mixed solution until coprecipitation was occurred. The coprecipitated gel was then washed by distilled water. Therefore, the resulted solid was dried in an oven (Memmert) at 110 °C overnight. The dry solid was then calcined at 600 °C for 3 h in a muffle furnace (Neo Vulcan). A part of the resulted solid catalyst was then impregnated to a solution of KNO<sub>3</sub> 2 M, and dried in an oven (Memmert) at 110 °C overnight. Thus the solid was calcined in a muffle furnace (Neo Vulcan) at 600 °C for 3 h. All CaO-ZnO catalysts in this paper have Ca:Zn = 1:3 (molar ratio).

### 2.3. Catalysts Characterization

The catalysts were characterized by powder X-Ray Diffraction (XRD) and Brunauer-Emmer-Teller (BET) surface area. In the XRD method, Cu-K $\alpha$  radiation (40 kV and 40 mA) by Bruker in the 2 $\theta$  angle of 10° - 90° was employed to generate diffraction patterns from powder crystalline samples at ambient temperature. The XRD pattern analysis was identified by Powder Diffraction File database (JCPDS).

Specific surface area and pore size distribution of the catalysts were determined by AsiQwin Automated Data Acquisition and Reduction at 77.35 K N<sub>2</sub> adsorption with gas sorption. Before analysis, the amount of gas in the catalyst was removed by heating (degassing) at a temperature of 300 °C and 6.58.10<sup>5</sup> mmHg for 12.4 h. For analysis of the catalyst surface area and pore size distribution, the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods were used, respectively.

### 2.4. Catalysts Testing

Testing of the catalysts was conducted by transesterification reaction in a set of three-neck flask 500 ml as a reactor and equipped with impeller, temperature controller, and reflux cooling system. The catalytic reaction was carried out at 60°C for 4 h. The catalysts tested were ZnO, CaO-ZnO, 2 wt.% K<sub>2</sub>O/CaO-ZnO, and 5 wt.% K<sub>2</sub>O/CaO-ZnO. Catalyst loading of 6 wt.% and methanol to oil molar ratio of 15:1 were used in the catalyst testing. After the reaction finished, the biodiesel product (FAME) was separated after aged for 24 h forming 3 layers (residual methanol, FAME, and glycerol as well as used solid catalyst). The resulted FAME biodiesel was characterized and identified using GC-MS (SHIMADZU) equipped with Agilent DB-1 column and helium as a gas carrier.

## 3. Result and Discussion

### 3.1. Catalysts Characterization

XRD characterization is aimed to determine the nature and crystal structure of the catalysts as depicted in Figure 1. From the figure, XRD diffractogram of CaO catalyst shows intensity of the peak at 2 $\theta$  angle of 17.4°, 26.3°, 28.13°, 32.2°, 33.5°, 37.3°, 46.7°, 53.8°, 63.5°, 66.7°, 79.1°, and 87.9° (JCPDS File No. 37-1497) [3]. Meanwhile, the ZnO catalyst has sharp diffraction pattern in the 2 $\theta$  angle of 31.8°, 34.46°, 36.3°, 47.6°, 56.6°, 62.9°,

66.37°, 69.2°, 71.9°, 76.8°, 80.8°, and 89.7° which is categorized as ZnO wurtzite hexagonal phase (JCPDS File No. 36-1451) as appeared in Figure 2 [3]. Diffractions of CaO-ZnO catalyst in Figure 3 shows a similar pattern with ZnO catalyst which may be due to lower CaO content in the catalyst. The impregnation of K<sub>2</sub>O on the surface of CaO-ZnO catalyst with K<sub>2</sub>O loading of 2 and 5 wt.% shows additional small intensity peak at 2θ angles of 23.08° and 28.98° as well as 26.16°, 33.2°, 40.7° which is assigned to the presence of distributed K<sub>2</sub>O on the catalyst surface (JCPDS File No. 47-1701; 77-2176) [5].

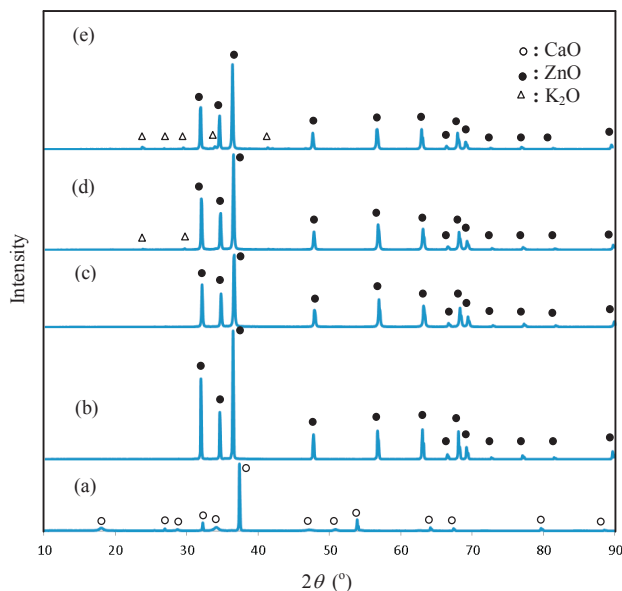
Surface area, total pore volume, and average pore diameter were characterized by BET method as reported in Table 1. From the table, surface area of each catalyst can be sorted from highest to lowest as follow: 2 wt.% K<sub>2</sub>O/CaO-ZnO > ZnO > CaO-ZnO > 5 wt.% K<sub>2</sub>O/CaO-ZnO. It is shown that doping of K<sub>2</sub>O on the CaO-ZnO increases the surface area of catalyst significantly. The increasing surface area of the catalyst may be due to increasing the number of base active sites and leads to enhancing the catalyst activity in transesterification process as reported by Yan *et al.* [6]. ZnO metal oxide has a small surface area (only 5.71 m<sup>2</sup>/g) and there is no base sites on the surface of ZnO as inline with results of Taufiq-Yap *et al.* [3]. The ZnO metal oxide has low total pore volume (0.0057 cm<sup>3</sup>/g) indicating low number of active pores.

In the catalyst testing, ZnO showed lower catalyst activity in the transesterification process. Combination of ZnO with lower content of CaO is able to enhance the total pore volume and shows a better activity for the transesterification process. However, the FAME yield is still low for the transesterification process which may be due to lower basicity of the catalyst [7]. From Table 1, it is reported that the surface area of CaO-ZnO is smaller than ZnO which may be due to failure of modifying the ZnO crystal structure by CaO to form basic site required by the transesterification process [8]. Alonso *et al.* [8] found that calcination temperature to activate CaO catalyst is 800-900 °C. This finding is corroborated to XRD analysis as depicted in Figure 1 in which the ZnO crystal diffraction is more dominant than CaO in the CaO-ZnO catalyst.

**Table 1.** BET surface area, total pore volume, and average pore diameter of the catalysts

Catalysts	$S_{BET}^a$ (m <sup>2</sup> /g)	$V_{meso}^b$ (cm <sup>3</sup> /g)	Pore Diameter <sup>c</sup> (nm)
2 wt.% K <sub>2</sub> O/ CaO-ZnO	28	0.03	2.0
5 wt.% K <sub>2</sub> O/ CaO-ZnO	1.6	0.007	1.7-10.3
CaO-ZnO	3.35	0.015	2.52
ZnO	5.71	0.0057	2.53

<sup>a</sup> BET surface area; <sup>b</sup> Total pore volume (mesoporous); <sup>c</sup> Average pore diameter (BJH method)



**Fig. 1.** XRD pattern of catalysts: (a) CaO, (b) ZnO, (c) CaO-ZnO, (d) 2 wt.% K<sub>2</sub>O/CaO-ZnO, and (e) 5 wt.%

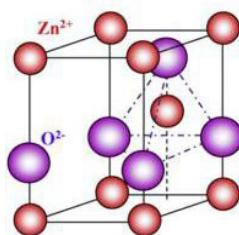
K<sub>2</sub>O/CaO-ZnO

Fig. 2. Hexagonal wurtzite ZnO crystal [4]

Promotion of K<sub>2</sub>O oxide on the surface of CaO-ZnO catalyst is able to increase the catalyst surface area significantly as reported in Table 1. It can be seen that 2 wt.% K<sub>2</sub>O/CaO-ZnO has the highest surface area (28 m<sup>2</sup>/g) and the highest total pore volume (0.03 cm<sup>3</sup>/g) among other catalysts. The incorporation of K<sub>2</sub>O with suitable loading is able to improve the surface area due to increasing total pore volume which in turn providing opportunity to increase the number of base active sites. However, when K<sub>2</sub>O loading is increased to 5 wt.%, the surface area of the catalyst decreases to 1.6 m<sup>2</sup>/g. The depreciation of surface area is caused by covering the catalyst active site by K<sub>2</sub>O dopant at to high loading of K<sub>2</sub>O. However, the incorporation of K<sub>2</sub>O could enhance basicity of the catalyst as required by transesterification process. Therefore, significant increasing yield of FAME (biodiesel) may be due to enhancing the catalyst basicity and surface area by the role of K<sub>2</sub>O doping.

### 3.2. Catalysts Performance for Transesterification of Soybean Oil to Fatty Acid Methyl Ester

Performances of the catalysts on the transesterification of soybean oil to fatty acid methyl esters are listed in Table 2 including the characteristics of soybean oil raw material. Among the catalysts, 2 wt.% K<sub>2</sub>O/CaO-ZnO shows better FAME yield than others. This significant increasing yield of FAME (biodiesel) may be due to enhancing the catalyst basicity and surface area by role of K<sub>2</sub>O doping as revealed by the XRD and BET surface area characterization results. In contrary, covering base active sites on high K<sub>2</sub>O loading catalyst decreases the yield of FAME. From Table 2, the biodiesel product has characteristics within the selected range of *Standar Nasional Indonesia* (SNI) standard.

The incorporation of K<sub>2</sub>O on the CaO-ZnO catalyst shows high catalytic activity on transesterification process may be due to presence of strong basic site as predicted mechanism revealed in Figure 3. This prediction is inline with previous researchers finds in which the O-K bonding can increase the activity of the catalyst in the transesterification process [11-13]. Declining yield on higher K<sub>2</sub>O loading on the catalyst due covering basic active sites by K<sub>2</sub>O dopant is corroborated to results of Wen *et al.* [14]. From Figure 3, surface O<sup>2-</sup> receives donor of the H<sup>+</sup> from CH<sub>3</sub>OH and becomes CH<sub>3</sub>O<sup>-</sup> (Equation 1). This form has very strong basicity and high catalytic activity in the transesterification reaction [15]. Equation (2) shows the carbonyl atom of the triglyceride molecules attract methoxide anion of the catalyst surface -O-Ca-O-Zn-O-K and form a tetrahedral ion in which R<sub>1</sub> is an alkyl chain. The tetrahedral ion attacks H<sup>+</sup> ion from the surface of the catalyst -O-Ca-O-Zn-O-K- as shown in Equation (3). In Equation (4), the tetrahedral ions can also react with methanol to produce methoxide anion [14]. Dissociation reaction of the tetrahedral ion to form biodiesel and alcohol is occurred as revealed in Equation (5). The correlation of the presence of basic sites, basicity and surface area on the catalyst to the FAME yield is inline with the results of Yoo *et al.* [16].

**Table 2.** Catalyst performance on transesterification reaction and FAME product characteristics\* SNI : Standar Nasional Indonesia

Catalyst	FAME Yield (%)	Density (g/ml)	Kinematic Viscosity (mm <sup>2</sup> /s, 313 K)	Acid Number (mg KOH/g)
2 wt% K <sub>2</sub> O/CaO-ZnO	81.08	0.90	3.07	0.1122
5 wt% K <sub>2</sub> O/CaO-ZnO	74.52	0.90	4.60	0.3366
CaO-ZnO	45.56	0.90	5.29	0.4488
ZnO	41.62	0.90	5.64	0.4488
SNI Standard of biodiesel *	-	0.85-0.89	2.3-6.0	<0.8
Soybean Oil Raw Material	-	0.92	23.37	1.122

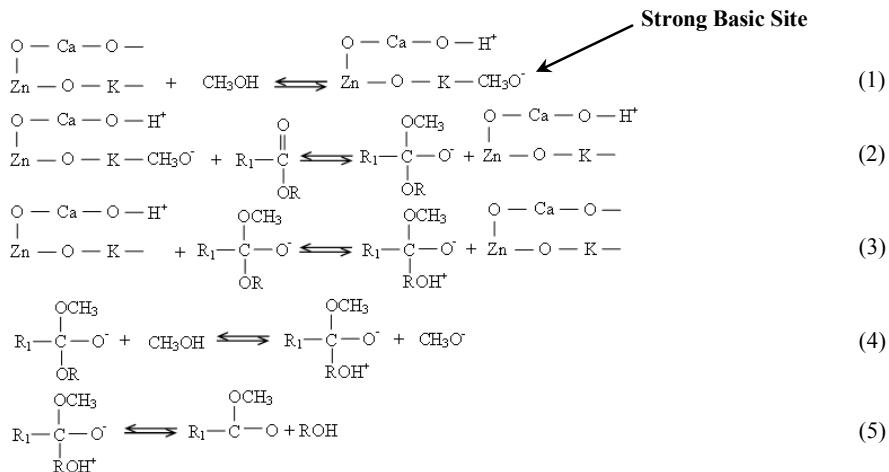


Fig. 3. Prediction of transesterification reaction mechanism using K<sub>2</sub>O/CaO-ZnO catalyst

Contents and composition of FAME in biodiesel products are characterized by using Gas Chromatography-Mass Spectrometry (GC-MS). The result of GC-MS spectrum of biodiesel product is presented in Figure 4. Meanwhile, the components identification and composition of biodiesel product derived from the GC-MS spectrum are listed in Table 3.

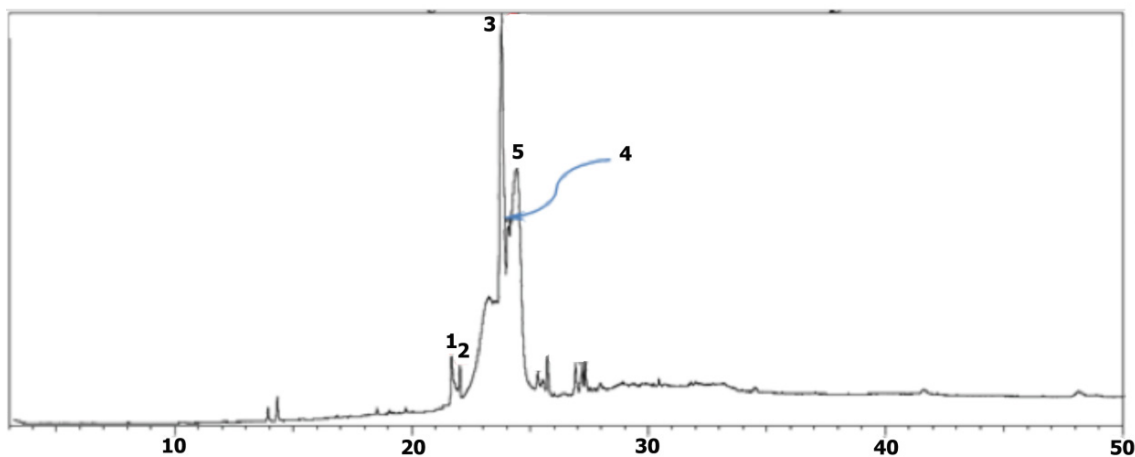


Fig. 4. GC-MS chromatogram of biodiesel product

Table 3. Identification and composition of the biodiesel product using GC-MS

Peak	Molecular Weight	Formula	Component	Composition (%)
1	270	C <sub>17</sub> H <sub>34</sub> O <sub>2</sub>	Hexadecanoic acid methyl ester	4.43
2	270	C <sub>17</sub> H <sub>34</sub> O <sub>2</sub>	Hexadecanoic acid methyl ester	1.93
3	266	C <sub>17</sub> H <sub>30</sub> O <sub>2</sub>	Hexadecadienoic acid methyl ester	33.89
4	298	C <sub>19</sub> H <sub>38</sub> O <sub>2</sub>	Octadecanoic acid methyl ester	10.59
5	280	C <sub>18</sub> H <sub>32</sub> O <sub>2</sub>	9,12-Octadecadienic acid methyl ester	49.16
Total				100

#### 4. Conclusion

In this study,  $K_2O/CaO-ZnO$  catalyst was developed and tested its catalytic activity for transesterification of soybean oil to FAME. The 2 wt.%  $K_2O/CaO-ZnO$  catalyst showed the promising catalytic activities on the transesterification process in which the FAME yield is 81.08%. Significant increasing yield of FAME may be due to enhanced catalyst basicity and surface area by the role of  $K_2O$  incorporation on the  $CaO-ZnO$  catalyst.

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