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Research Article

Synthesis of CaOZnO Nanoparticles Catalyst and Its Application in Transesterification of Refined Palm Oil

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Abstract

The CaOZnO nanoparticle catalysts with Ca to Zn atomic ratios of 0.08 and 0.25 have been successfully synthesized by co-precipitation method. The catalyst was characterized by X-ray Diffraction (XRD) analysis provided with Rietica and Maud software, Scanning Electron Microscopy (SEM) and Fourier Transform Infrared spectroscopy (FT-IR), and its properties was compared with bare CaO and ZnO catalysts. The phase composition estimated by Rietica software revealed that the CaO catalyst consists of CaO and $CaCO_3$ phases. The estimation of the particle size by Maud software, showed that the particle size of all catalysts increased by the following order: $ZnO<CaOZnO_{0.08}<CaOZnO_{0.25}<CaO$. The SEM images showed that all catalysts have different morphology and size. The catalytic activity of CaO, ZnO, $CaOZnO_{0.08}$ and $CaOZnO_{0.25}$ has been studied on transesterification of Refined Palm Oil (RPO) with methanol at 65 °C for 3 hours. It was found that the conversion of triglyceride, yield of methyl ester, turnover number (TON) and turnover frequency (TOF) of $CaOZnO_{0.08}$ are higher than $CaOZnO_{0.25}$. This result confirmed that the particle size of the catalysts play an important role in this study. © 2014 BCREC UNDIP. All rights reserved

Keywords: CaOZnO co-precipitation; transesterification; refined palm oil; yield of methyl ester; TON-TOF

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1. Introduction

Nowadays, biodiesel has gained much attention of researchers as a major renewable energy source. Biodiesel is environmentally friendly, renewable, sulfur-free, non-toxic and possess a high cetane number as well as low viscosity. The most common way to produce biodiesel is by transesterification process using homogeneous strong bases catalysts such as NaOH and

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KOH [1]. The advantages of these catalysts are high catalytic activity under mild operating conditions (65 °C, 1 atm). However, it has several drawbacks such as high corrosion, difficulty in product separation and recovery due to high basicity. A high amount of waste water obtained during the biodiesel production also poses a great disadvantage [2,3]. Thus, the use of heterogeneous catalysts is an alternative route to reduce the cost of biodiesel production as the catalyst is easily separated from the reaction mixture, reusable and less corrosive [2]. Alkali metal oxides catalyst supported on Al_2O_3 such as Na/NaOH/γAl_2O_3 has a base strength (H^-= 37) which is very active for the transesterification reaction of vegetable oils. The Na/NaOH/γAl_2O_3 catalysts show a similar conversion with homogeneous catalysts, NaOH with a 94% conversion [4] but the active oxide component is very hygroscopic and easily soluble in methanol, resulting in less suitable applications in the industry.

CaO catalyst has been studied extensively for transesterification reactions due to its high catalytic activity, low-cost, high base strength (H^- = 26.5) [5] and slight solubility in methanol. Other oxides or alkaline earth metal hydroxides such as SrO and $Ba(OH)_2$ fully dissolve in reaction mediums, causing a difficulty in separation of the catalyst from reaction products. CaO is very active for transesterification and a small amount of CaO can be dissolved in the reaction medium and the surface sites of the catalyst can be poisoned when in contact with air to form groups of carbonates or hydroxyl [6]. In addition, supported calcium is also required to eliminate the leached calcium that inhibits the catalytic activity during biodiesel production [7].

Combination of CaO and ZnO (CaOZnO) catalyst in sun flower seed oil transesterification reactions yield the same alkyl ester produced by CaO with 90% conversion [7]. The advantage of using mixed CaOZnO catalyst than pure CaO is the resultant dissolution of CaO in the reaction medium but this can be eliminated due to the strong interaction between the catalyst and support with respect to the CaOZnO catalyst. The CaO supported on ZnO catalyst can be synthesized either by impregnation or co-precipitation method. The catalyst synthesized by co-precipitation method shows a higher conversion of triglycerides (94.2%) compared to impregnation method (90%) [8]. This proves that the synthesis methods employed to produce the CaOZnO catalysts used in this study influences greatly the physical and chemical properties of the resulting catalyst, thus affecting the activity of the catalyst in the transesterification reaction positively [7].

One way to maximize the activity of heterogeneous catalysts is by increasing the concentration of the active surface. Based on a previous study, it can be concluded that the catalyst with a high concentration of the active site is not easily obtained by impregnation method. Wang *et al.* [9] found that the CaO-ZrO_2 catalysts prepared by co-precipitation method have a higher base strength than those prepared by impregnation method. The CO_2 curves of *TPD* desorption peak for CaO-ZrO_2 catalysts prepared by impregnation method appear at temperatures below 200 °C while for those synthesized by co-precipitation method, the CO_2 curves appear at a temperature of 475 °C. The catalyst with high concentration of active sites generally results in a low specific surface area, thus affecting the productivity of the catalyst in a transesterification reaction. The surface area of the catalyst can be increased by reducing the particle size, such as by synthesizing the nanoparticle size catalyst. In the transesterification reaction of vegetable oil by using a small particle size catalyst, a high amount of methyl ester was obtained [8]. In previous studies, ZnO nanoparticle catalysts were prepared by urea hydrolysis method [11] and precipitation of zinc acetate with oxalic acid in aqueous solvent and the resulted particle sizes are between 22-25 nm [12].

The Ca to Zn atomic ratio also play an important role in the determining the activity of a catalyst in transesterification reactions. The CaOZnO catalysts were synthesized with varied Ca to Zn atomic ratios, from 0.25 to 4 and the obtained particle sizes increased from 0.2 to 9.7 µm. The CaOZnO catalyst with Ca to Zn atomic ratio of 0.25 produced 93.5% of methyl ester, which is higher than those with other atomic ratios. The smaller the particle size of CaOZnO catalyst, the higher the surface area required for higher catalytic activity, thus producing a higher yields of methyl ester [8]. In this study, the CaOZnO nanoparticle catalysts were synthesized by co-precipitation method, the effect of Ca to Zn atomic ratios with respect to the particle size and catalytic activity of the catalyst were investigated during the transesterification reaction of refined palm oil for biodiesel production.

2. Experimentals

2.1. Synthesis of CaOZnO Catalysts

For the preparation of the catalyst with Ca:Zn atomic ratio of 0.25, 0.02M

$Ca(CH_3COO)_2.H_2O$ and 0.08 M $Zn(CH_3COO)_2.2H_2O$ was mixed with deionized water, separately. Then the two solutions were mixed until homogeneous. The zinc and calcium oxalate precipitates were obtained after the addition of 0.15 M $H_2C_2O_4.2H_2O$ aqueous solution under stirring at 160 rpm for 12 h at room temperature. After centrifuged, the precipitates were collected and washed with deionized water and acetone. The precipitates were dried in an oven at 120 °C overnight. Prior to use as a catalyst, the solids were calcined at 800 °C for 6 h. The same procedure was followed to prepare the CaOZnO catalyst with a Ca to Zn atomic ratio of 0.08.

In this study, CaO and ZnO were used as references. For CaO, 0.1 M $Ca(CH_3COO)_2.H_2O$ and 0.15 M $H_2C_2O_4.2H_2O$ mixed with deionized water while for ZnO, 0.1 M $Zn(CH_3COO)_2.2H_2O$ and 0.15 M $H_2C_2O_4.2H_2O$ were used besides deionized water. Each mixture was stirred at 160 rpm for 12 h at room temperature. The solid product obtained after being centrifuged was washed with deionized water and acetone before drying in the oven at 120 °C overnight. Prior to its use as a catalyst, the CaO was calcined at 800 °C for 6 h and for ZnO and the calcination was done at 450 °C for 6 h.

2.2. Solid Characterizations

The X-ray diffraction technique (XRD) was carried out using a *X-Ray Diffraction Phillips Expert*. The diffractometer employing CuKα radiation to generate diffraction patterns from powder crystalline samples at ambient temperature. The CuKα radiation (λ = 1.5405 Å) was generated at 40 kV and 30 mA in the range of 2θ = 1.5 to 40 ^{o} with a scan speed of 0.02°/sec. The Rietica and Maud software were used to estimate the phase composition and crystal sizes from XRD pattern. Fourier transform infrared (FTIR) spectroscopy was done on a Shimadzu *Instrument Spectrum One* 8400S spectrometer, with 2 cm^{-1} spectral separation, at 20 °C. The surface morphology and particle size of solid samples were determined by scanning electron microscopy (JEOL SEM Model JSM-5800LV).

2.3. Transesterification Reaction

Transesterification reaction was performed in a 250 ml three-neck round bottom flask equipped with a reflux condenser to avoid the evaporation of alcohol. A magnetic stirrer was used to control the movement of the reaction mixture, with stirring speed of 1250 rpm to eliminate the effect of external mass transfer. The reactor was placed in the oil bath equipped with temperature controller. 17 g of refined palm oil was added to methanol in a glass reactor with a molar composition 1:30, followed by 0.5 g of CaOZnO catalyst (3%wt) after being activated in a tubular furnace with N_2 flow at temperature 800 °C for 1 h. The mixture was heated at temperature 65 °C for 3 h.

The reaction was stopped by the addition of diluted HCl solution containing twice the stoichiometric amount required to neutralize CaO. After a few minutes, the dichloromethane was added and the mixture was stirred before being transferred to a separating funnel and forms two layers. The upper layer contained dichloromethane, ester, mono, di, and triglycerides and methyl esters while the lower layer contained glycerol, methanol, residual HCl and $CaCl_2$. The ester layer was separated and pretreated with dichloromethane. The dichloromethane was removed from the organic layer by rotary evaporator at 60 °C. The physical characteristics of the organic layer obtained from CaO, $CaOZnO_{0.08}$ and $CaOZnO_{0.25}$ samples are close to the physical characteristics of ester. This can be shown by the viscosity of the organic layer of the three catalyst samples which are thinner than the viscosity RPO. The methyl ester content in the organic layer of CaO, $CaOZnO_{0.08}$ and $CaOZnO_{0.25}$ are higher than those in the ZnO sample. Then, the organic layers of the three samples (CaO, $CaOZnO_{0.08}$ and $CaOZnO_{0.25}$) were analyzed using gas chromatography (GC).

3. Results and Discussion

3.1. Characterization

3.1.1. X-Ray Diffraction

Figure 1 shows the XRD pattern of the calcined samples. For ZnO sample, the diffraction peaks appear at 2θ =31.8, 34.4, 36.2, 47.5 and 56.6˚ which assigned to ZnO phase with hexagonal structure type [12]. Some phases such as $ZnCO_3$ did not exist, indicating that the ZnC_2O_4 was perfectly decomposed into ZnO during calcination at 400 °C. For CaO, the diffraction pattern shows the presence of $CaCO_3$ phase which appears at 2θ = 29.4˚ and the multiple peaks at 2θ =32.2, 37.4, 53.9, 64.1 and 67.4˚ which was assigned to CaO phase with cubic structure [13]. $CaOZnO_{0.08}$ and $CaOZnO_{0.25}$ only show two diffraction peaks representing the CaO and ZnO phases. The CaO and ZnO phases in both samples are similar to the phase of ZnO deposited on the pure CaO. Therefore, it can be concluded that the

$CaOZnO_{0.08}$and $CaOZnO_{0.25}$ catalysts do not have specific structure, but they represent a cluster set of CaO and ZnO oxides in the sediment particles. The absence of $CaCO_3$ phase in the $CaOZnO_{0.08}$ and $CaOZnO_{0.25}$ samples confirms that the deposition of ZnO on the CaO catalyst significantly reduces the decomposition temperature of $CaCO_3$ to CaO. The lower the calcination temperature required to decompose the $CaCO_3$ phase, the lower the energy that is used in the preparation of the active catalysts. These results are similar with the study that was conducted by El-Shobaky and Mostafa [14]. In that study, they reported that the addition ofa small amount of Zn to the MgO and Fe_2O_3 can lower the decomposition temperature of $MgCO_3$ which is from 520 °C to 375 °C. The higher amount of Zn causing the catalyst to release more H_2O and CO_2 in the decomposition of zinc carbonate ($ZnCO_3$) to ZnO, at the same time facilitates the decomposition of $CaCO_3$ to CaO. The pores that formed consequently by the decomposition of $ZnCO_3$ to ZnO allowed for the heat transfer into the particle thus producing the diffusion of gases [8].

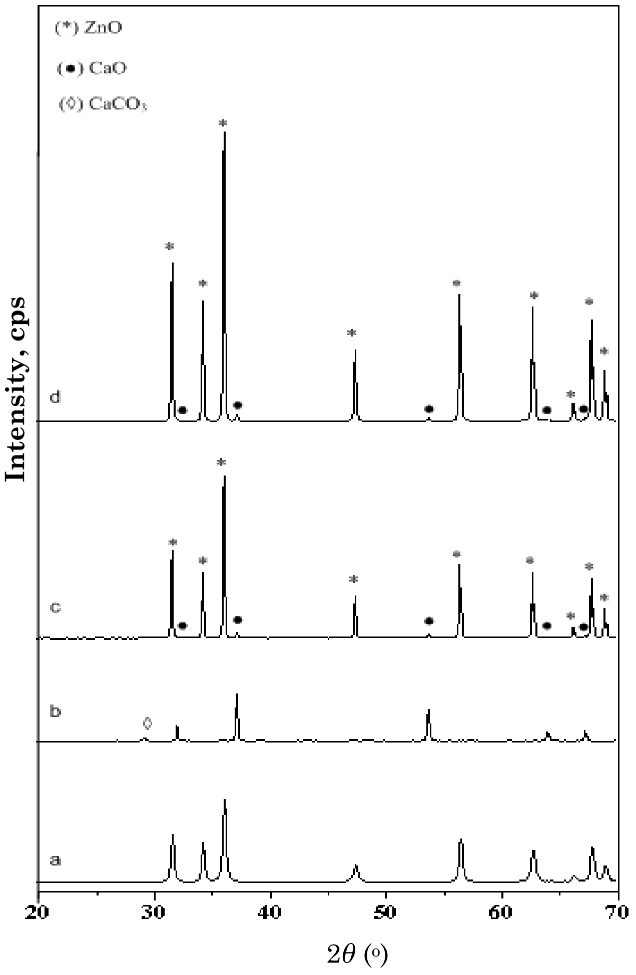

Figure 1. XRD pattern of ZnO (a), CaO (b), $CaOZnO_{0.08}$ (c) and $CaOZnO_{0.25}$ (d) after calcination at 800 °C.

The phase composition of the calcined CaO, $CaOZnO_{0.08}$ and $CaOZnO_{0.25}$ samples estimated by Rietica software are shown in Table 1. From the table, we can see that the CaO sample shows the highest amount of CaO phase which is 88.7%, but there is still a trace of the $CaCO_3$ phase. There are two possibilities that can explain the presence of $CaCO_3$ phase; $CaCO_3$ is not fully decomposed to CaO at 800 °C of calcination temperature, or recarbonation of CaO to $CaCO_3$. It was reported that the CaO catalyst is rapidly hydrated and carbonated by contact with room air and few minutes are enough to chemisorb significant amounts of H_2O and CO_2 [6].

The estimated size of the crystal obtained from XRD data were calculated by MAUD (Material Analysis Using Diffraction) software as shown in Table 2. The estimated size of the ZnO calcined at 400 °C is 31.0 nm while for $CaOZnO_{0.08}$ and $CaOZnO_{0.25}$ which were calcined at 800 °C, the size are 60.1 and 73.0 nm, respectively. The increase in calcination temperature from 400 to 800 °C led to agglomeration of clusters which is due to the sintering process. This result is in agreement with the previous study [8], who reported that the ZnO nanoclusters derived from a mixture of $CaCO_3$

Table 1. Phase composition of the calcined samples estimated by Rietica software.

Sample	Phase composition (wt%)		
	CaO	$CaCO_3$	ZnO
CaO	88.7	11.3	-
$CaOZnO_{0.08}$	18.7	-	81.3
$CaOZnO_{0.25}$	12.2	-	87.8

Table 2. Crystal size of the calcined samples estimated by MAUD software

Sample	Crystal size (nm)		
	CaO	$CaCO_3$	ZnO
CaO	190 (10)*	30 (3)*	-
$CaOZnO_{0.08}$	93 (8)*	-	60 (6)*
$CaOZnO_{0.25}$	101(7)*	-	73 (5)*
ZnO	-	-	31 (2)*

*Numbers in parentheses are the estimated standard deviations of the last significant digit.

and $ZnCO_3$ precipitated when calcined at 700 °C and 900 °C and the crystal size increased from 26.6 to 41.3 nm. For CaOZnO sample, the ZnO that was added to the CaO sample reduced the particle size of the catalyst. It was also reported that, the more ZnO was added, the very easily the $CaCO_3$ decomposed, thus reducing the thermal energy that was needed for that process [8].

3.1.2. Scanning Electron Microscopy

Figure 2 shows the SEM images of the ZnO, CaO and $CaOZnO_{0.25}$ samples. The ZnO sample appears as small spherical homogeneous solid particles with an average particle size smaller than CaO and $CaOZnO_{0.25}$. The CaO sample appears as a collection of clot and general form of spherical particles with larger size than ZnO and $CaOZnO_{0.25}$. For the $CaOZnO_{0.25}$, the particles are not uniform, consisting of spherical particles with random sizes. These results are significant with the estimated crystal size which shows that ZnO crystals in ZnO sample are smaller than those in the $CaOZnO_{0.25}$ sample. The XRD patterns also show that the intensity of ZnO phase in ZnO sample is lower than those for $CaOZnO_{0.25}$ which means that the crystal size of ZnO sample is smaller than $CaOZnO_{0.25}$. For the CaO sample, the estimated

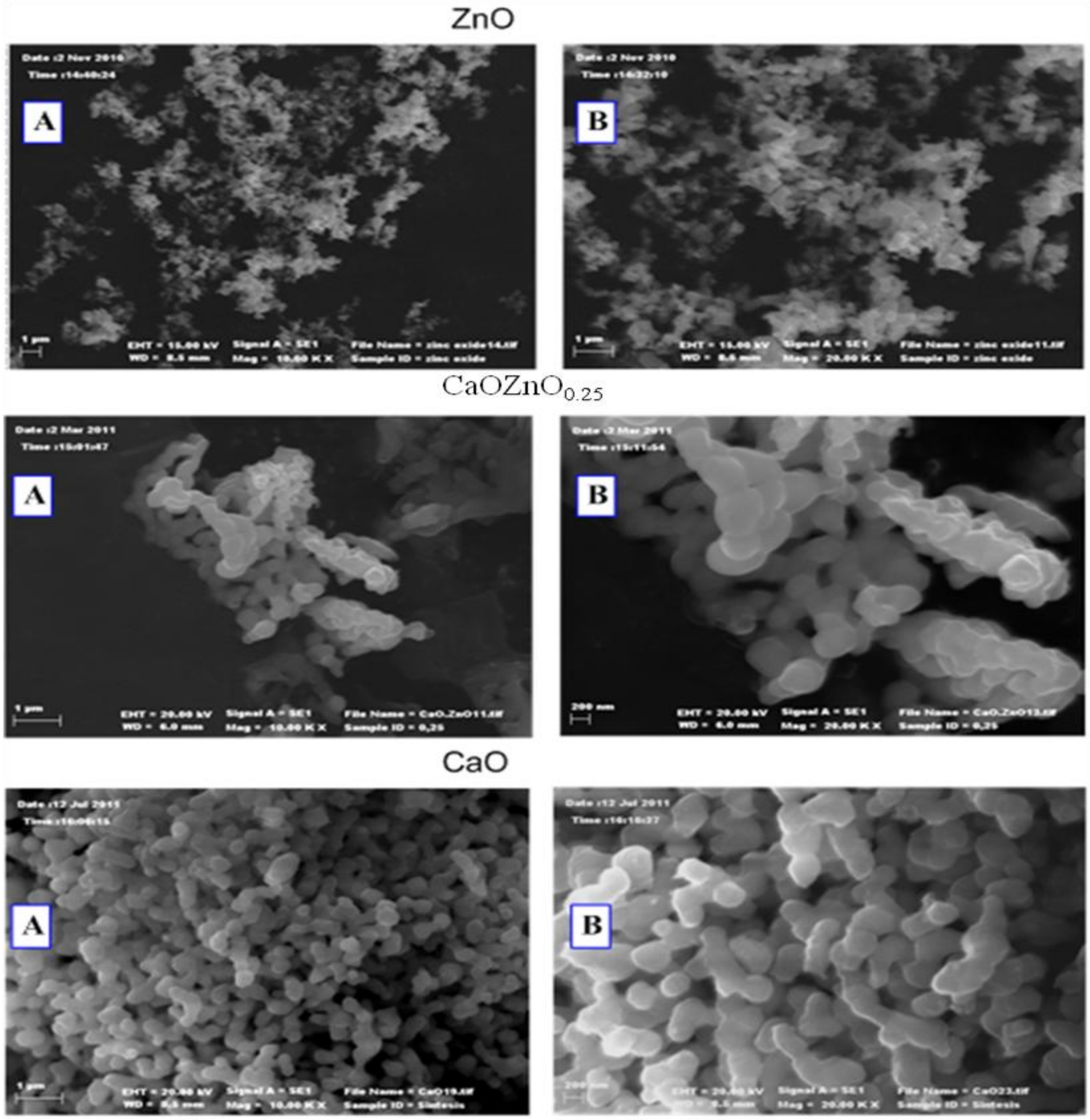

Figure 2. SEM Images of ZnO; $CaOZnO_{0.25}$ and CaO with different of magnification (A and B)

Table 3. The functional groups presence in the ZnO, CaO, $CaOZnO_{0.08}$ and $CaOZnO_{0.25}$ samples.

Sample	Wavenumber (cm^{-1})			CaO	CaO-ZnO
	Hydroxyl	Carbonyl	ZnO		
ZnO	3433, 1639	-	486	-	-
CaO	3645, 3433, 1647	1797, 1778, 1523, 1411, 875, 713	-	405	-
$CaOZnO_{0.08}$	3641, 3444, 1650	1790, 1597, 1411, 875	-	-	482
$CaOZnO_{0.25}$	3641, 3433, 1639	1793, 1743, 1415, 875	-	-	443

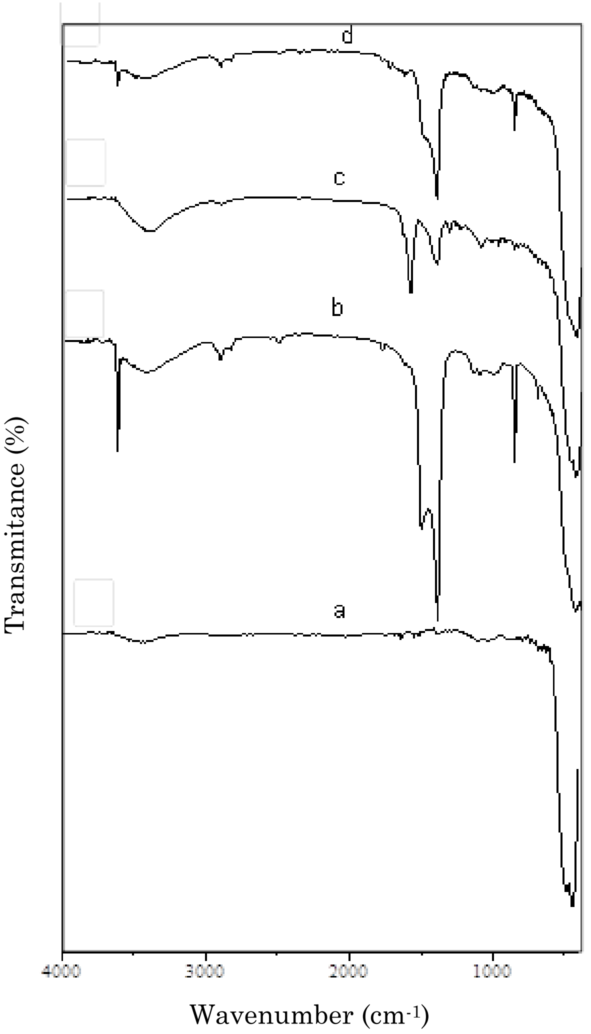

Figure 3. FTIR spectra of ZnO (a), CaO (b), $CaOZnO_{0.25}$ (c) and $CaOZnO_{0.08}$ (d) after calcination.

size of the CaO crystal is greater thanthat in $CaOZnO_{0.25}$, which further supports the SEM result.

3.1.3. Fourier Transform Infrared Spectroscopy

The FTIR analysis was done to identify the functional groups present in the compound. Figure 3 shows the FTIR spectra of ZnO, CaO, $CaOZnO_{0.08}$ and $CaOZnO_{0.25}$ at wavenumbers between 4000-400 cm^{-1}. The infrared spectra of ZnO sample showed bands at 3433, 1639, and 486 cm^{-1}. The band at 1639 cm^{-1} is assigned to the O-H bending mode of water molecules absorbed on the surface of ZnO. The broad band centered at 3433 cm^{-1} is related to the O-H stretching modes of water absorbed on the surface of ZnO while the band at 486 cm^{-1} indicates the stretching vibrations of Zn-O (υZn-O) [15]. For CaO sample, a band with a sharp peak at wavenumbers 3645 cm^{-1} is assigned to the O-H stretching vibration of $Ca(OH)_2$. The broad band centered at 3433 cm^{-1} is related to the O-H stretching vibration of H_2O, indicating the presence of water absorbed on the surface of CaO. These results are related with the previous study [6] which stated that the CaO is rapidly hydrated by contact with room air. The CaO sample also displays band at 1647 cm^{-1} which indicate the O-H bending mode of water molecules absorbed physically on the surface of CaO.

FTIR spectra of $CaOZnO_{0.08}$ and $CaOZnO_{0.25}$ samples show the bands similar to the IR spectra of CaO sample. The band at 3641 cm^{-1} confirms the presence of the O-H stretching vibration of Ca $(OH)_2$ in both CaOZnO samples. The broad band centered at 3433 cm^{-1} is related to the O-H stretching vibration of theH_2O, indicating the presence of water absorbed on the surface ofsamples. This suggests that the surfaces of CaO on the CaOZnO samples are also easily hydrated. The carbonyl group (C = O) in both samples are appeared at 1790 cm^{-1} band while O-H bending mode of water molecules ab-

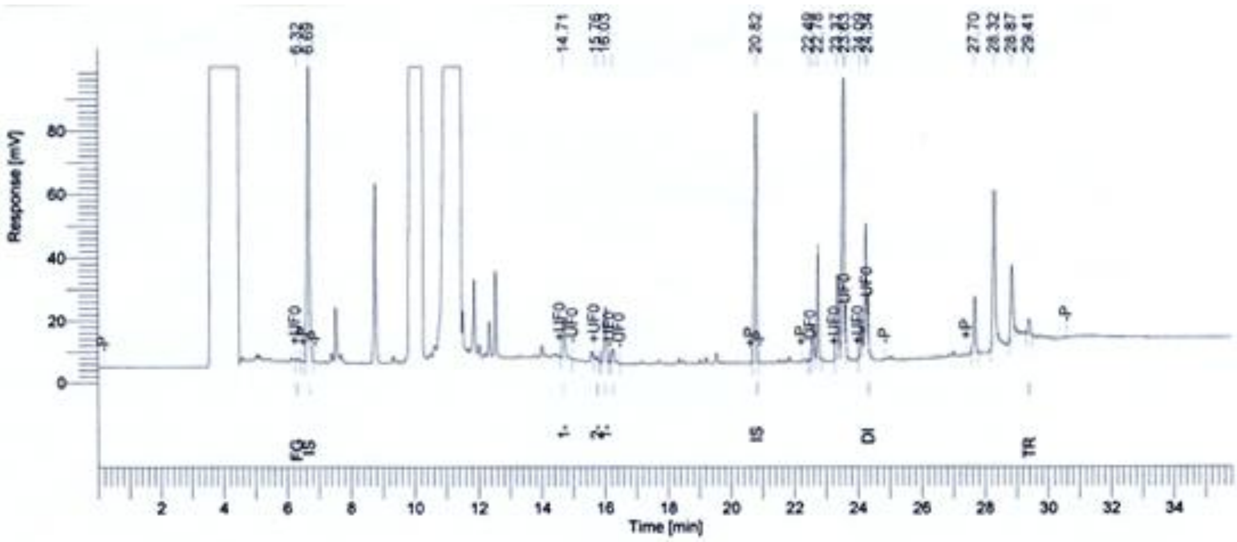

Figure 4. Chromatogram of RPO transesterification reaction with methanol using CaO catalyst at t = 3 hours.

Table 4. Composition products of RPO transesterification with methanol using CaO, $CaOZnO_{0.08}$ and $CaOZnO_{0.25}$ catalysts at t = 3 hours reaction

Catalyst	Composition of the RPO transesterification products (% mass)					
	Gly	M-G	D-G	T-G	Tot gly	ME
CaO	0.003	0.32	1.39	0.75	0.37	96.49
$CaOZnO_{0.08}$	0.003	0.96	2.09	1.12	0.67	93.57
$CaOZnO_{0.25}$	0.011	0.46	6.56	2.02	1.30	87.55

Note: Gly= free glycerol, M-G= monoglycerides, D-G= diglycerides, T-G=triglycerides, Tot gly= total glycerol, ME= methyl ester

sorbed physically on the surface solids represented by the band at 1650 cm^{-1}. The bidentate and monodentate carbonate are appeared at the bands 1597 and 1411 cm^{-1} for $CaOZnO_{0.08}$ sample and at 1510 and 1415 cm^{-1} for $CaOZnO_{0.25}$. Albuquerque et al [13] reported that in the IR spectra of the MgCa oxides catalyst with different molar ratios of Mg/Ca, the presence of a large and sharp band in the region 1400-1600 cm^{-1} is assigned to bidentate and monodentate carbonate. The band at 875 cm^{-1} is interpreted as carbonate groups [6] while the bands at 482 and 443 cm^{-1} in both samples are related to the vibrational modes of ZnO and CaO [7]. The functional groups of ZnO, CaO, $CaOZnO_{0.08}$ and $CaOZnO_{0.25}$ samples are summarized in Table 3.

3.2. Catalytic Performance

3.2.1. Influence of Catalysts

The chromatogram of the product of refined palm oil (RPO) transesterification reaction with methanol by using CaO-based catalyst is shown in Figure 4. Determination of the types of compounds that appear on the chromatogram was done in accordance with DIN EN 14105 procedures. The procedures were used to determine the levels of free glycerol, mono-, di-, and triglycerides in the methyl ester of a fatty acid.

Chromatogram peaks appeared after 35 minutes of analysis. The peaks are as a result of the culmination of the compounds present in the organic layer. Chromatogram peaks that appear in Figure 4 can be described as follows: 1 peak appearing at *t*R about 6 minutes, 1 peak appearing at *t*R about 7 minutes, between 8-12 minutes, four peaks appearing at *t*R 14-16 minutes, 1 peak appearing at *t*R about 20 minutes,

Table 5. The relationship between the active sites and the conversion of triglycerides, TON, yield of methyl ester, and TOF.

Catalyst	Amount of active site catalyst x10^{-3} (mole) [a]	Conversion of triglycerides (%) [b]	TON (hour^{-1}) [c]	Yield of methyl ester (%) [d]	TOF (hour^{-1}) [e]
CaO	7.92	99.25	0.80	96.49	0.24
$CaOZnO_{0.08}$	6.75	98.88	0.95	93.57	0.27
$CaOZnO_{0.25}$	6.72	97.98	0.93	87.55	0.26
ZnO	6.14	83.72	0.86	75.26	0.24

[a] Amount of active site catalyst calculated as the moles of catalyst (composition phase from Table 1 x 0.5 g / molar mass)

[b] Conversion of triglycerides calculated as (initial moleof triglycerides - mole of triglycerides) / initial mole of triglycerides x 100%

[c] TON is calculated as initial mole of triglycerides reduced with mole of triglycerides rest) per amount of active sites per time

[d] Yield of methyl ester from Table 4

[e] TOF is calculated as mole of methyl ester per amount of active sites per time

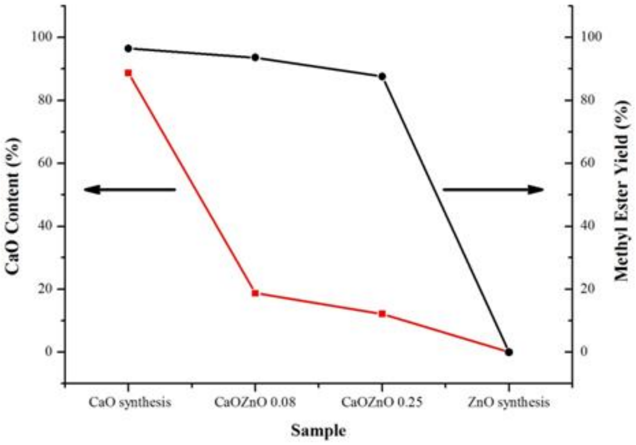

Figure 5. The relationship between the yields of methyl ester (%) with the content of CaO in the CaO, $CaOZnO_{0.08}$; $CaOZnO_{0.25}$ and ZnO catalysts.

9 peak appeared at *t*R 22-24 minutes and 4 peaks appearing at *t*R between 27-29 minutes. The identification of the peaks was based on the standard solution of each component that first injected which are as follows: 1 peak appearing at *t*R = 6.32 minutes is the peak of free glycerol. The peak of the internal standard 1,2,4-butanetriol 1 appears at *t*R = 6.692 minutes. Methyl ester peaks appear in 8-12 minutes. The peak at *t*R = 16.033 minutes is the culmination of monoglycerides, whereas the peak at *t*R = 20.823 minutes are peaks of 1,2,3-tricaproylglycerol (tricaprin) as an internal standard 2. The peak at *t*R = 24.095 minutes and *t*R = 29 160 minutes is the culmination of diglycerides and triglycerides.

Based on the data from the chromatogram shown in Figure 4, the composition of the transesterification products such as methyl esters, monoglycerides, diglycerides, triglycerides and glycerol as residual by-products can be calculated. The following equation can be used to calculate the yield of glycerol, monoglycerides, diglycerides, and triglycerides:

$$\text{Yield of i compound(\%)} = \left[a_i x(\frac{\sum A_i}{A_{ei}}) + b_i \right] x \left(\frac{M_{ei}}{m} \right) x100$$

where *i* is the compound of glycerol, monoglycerides, diglycerides, and triglycerides, a_i is the slope of the linear regression equation of the calibration curve of *i* compound, b_i is the intercept of the linear regression equation of the calibration curve for *i* compound, A_i is the area of *i* compound, Ae_i is the standard area 1 for glycerol and standard area 2 for mono-, di-, and triglycerides, Me_i is the standard mass 1 for glycerol and a standard mass 2 for mono-, di-, and triglycerides and m is the mass of the sample injected to the GC.

The total glycerol (TG) can be calculated by the equation:

$$TG(\%) = G + 0.255 \ x\, M + 0.146\, x\, D + 0.103\, x\, T$$

where G is the yield of glycerol, M is the yield of monoglycerides, D is the yield of diglycerides and T is the yield of triglycerides. Yield of ester can be calculated by the equation:

$$\text{Yield of Methyl Ester (\%)} = \frac{(10.4 - TG)}{10.4} x100$$

where 10.4 is the yield value for methyl ester palmitic and TG is total glycerol (%).

The calculated yields of triglycerides, diglycerides, monoglycerides, methyl esters and glycerol are summarized in Table 4. The three catalysts produced about 0.003 to 0.011% of glycerol yield, followed by monoglyceride (0.3 to 0.9%), diglycerides (1.3 to 6.5%), triglycerides (0.7 – 2%) and the highest yield is methyl ester which is between 87-96%.The presence of glycerol in the organic layer indicates that the extraction process is not complete. However, the amount is smaller compared to monoglycerides, diglycerides, triglycerides, and methyl ester. The yield of methyl ester increases significantly when compared to the intermediates product, which indicates that the transesterification reaction for 3 hours using all three catalysts is quite successful. These results are similar with previous study [16], which reported that the concentration of di- and monoglycerides increased at the beginning of the reaction and decreases at the end of the reaction, followed by the rise in the amount of methyl ester.

For transesterification reaction using ZnO catalyst, the organic layer are still in solid oil/clumping form, so it cannot be injected to the gas chromatography (GC). The determination of methyl ester product was done by using titration method. The yield of methyl esters obtained by this method is 74.8% which is the lowest compared to other three catalysts.

Table 4 also shows the methyl ester yield from transesterification reaction of refined palm oil using ZnO, CaO, $CaOZnO_{0.08}$ and $CaOZnO_{0.25}$ catalysts. The ZnO, CaO, $CaOZnO_{0.08}$ and $CaOZnO_{0.25}$ catalysts produced 74.8%, 96.49%, 93.57% and 87.55 % of methyl ester, respectively. Based on the graph, the yield of methyl ester decrease by the following order; CaO > $CaOZnO_{0.08}$> $CaOZnO_{0.25}$> ZnO, and it is influenced by the content of CaO in the catalyst, where the amount of CaO in CaO catalyst > $CaOZnO_{0.08}$> $CaOZnO_{0.25}$. The relationship between the yield of methyl ester and CaO content in the catalysts are shown in Figure 5. Based on the figure, the yield of methyl ester generated from the four catalysts are between 75-100% while the content of CaO in each catalyst are from 0 - 89%.

The graph shows that the higher content of CaO in the catalyst, the higher yield of methylesters produced. The CaO is the main base site which is responsible in the transesterification reaction of the catalysts. In the $CaOZnO_{0.08}$ and $CaOZnO_{0.25}$ catalysts, transesterification reaction is affected by the incorporation of CaO and ZnO. Although ZnO possesses a weaker base than CaO, but with the merger of ZnO to CaO catalyst, the base strength can be increased. The base strength of CaOZnO catalyst has been investigated by Alba-rubio *et al.* [7] and Taufiq-Yap *et al.* [17]. In their studies, they concluded that based on the TPD-CO_2 result, the CaOZnO mixed oxide shows the higher base strength than the pure metal oxides, namely ZnO and CaO. The stronger base site is derived from ZnO which prompted the displacement of electrons from a metal surface to metal CaO, thus increases the base strength of the catalyst.

3.2.2. Analysis of TON and TOF catalyst

Catalytic activity is partly influenced by the number of the active sites and particle size of the atoms involved in chemical reactions. The value of this activity are demonstrated by the parameter turnover number (TON) and turnover frequency (TOF). The higher value of TON and TOF of a catalyst, the higher catalytic activity which means the catalyst is more productive. The TON and TOF parameters were also used to investigate the level of the catalyst productivity in transesterification reaction of RPO with methanol. The turnover number (TON) is defined as the initial reactant (mol) minus final reactant (conversion of triglycerides) divided by the number of the active catalyst and the reaction time. While TOF is defined as the moles of product (yield methyl ester) divided by the number of the active catalyst and the reaction time. In this study, the active catalyst is assumed to be the total of metal moles in the catalysts that react, analogous to the definition of TON that the turn over number is defined as moles of product divided by moles of the solid metal.

Table 5 shows the relationship between the amount of the active sites and the conversion of triglycerides, TON, methyl ester yield, and TOF of the catalysts. The amounts of the active sites for all samples are about 6.14 x 10^{-3} to 7.92 x 10^{-3} moles. The triglycerides conversions are from 83.72 to 99.25%, which is higher than the yield of methyl ester (75-96%). The productivity of all catalysts as measured by TON and TOF parameters are about 0.8 to 0.9 $hours^{-1}$ and 0.23 to 0.27 $hours^{-1}$, respectively. The TON and TOF values are decreasing by the following order; $CaOZnO_{0.08}$> $CaOZnO_{0.25}$>ZnO>CaO.

As we mentioned earlier, the catalytic activity are influenced by the particle size of the catalyst. The small particle size of the catalyst increases the surface area resulting in a growing number of collisions, thus affecting the productivity of a catalyst. Based on Table 2, the particle size of the sample increases in the following order: ZnO < $CaOZnO_{0.08}$ < $CaOZnO_{0.25}$ < CaO. The yield of methyl ester, triglyceride conversion, TON and TOF values of $CaOZnO_{0.08}$ are higher than $CaOZnO_{0.25}$. This result is predicted because the smaller particle size of the catalyst, the higher number of active sites, which resulted in increasing yields of methyl ester and triglyceride conversion.

Based on Table 2 and 5, it is shown that the $CaOZnO_{0.08}$ and $CaOZnO_{0.25}$ catalysts are more productive than CaO and ZnO catalysts, which are due to the higher amount of active sites present in both samples. These results are also supported by TON and TOF values for all samples. The ability of $CaOZnO_{0.08}$ and $CaOZnO_{0.25}$ give rise in conversion and yield which could be attributed to the interaction between the two metals (CaO and ZnO). This result is in agreement with the research that was conducted by Taufiq-Yap *et al.* [17] which studied the behavior of the solid catalyst from a mixture of two metal oxides (CaMgO and CaZnO) and compared with CaO, MgO, and ZnO (as reference catalysts) in transesterification reaction. In that study, the particle size of CaOZnO is smaller than CaO catalyst, resulting in the higher surface area (S_{BET}) of the catalyst.

4. Conclusions

The CaOZnO nanoparticle catalysts with Ca to Zn atomic ratios of 0.08 and 0.25 were successfully synthesized. The diffraction of CaO shows the presence of 11,3 wt% $CaCO_3$ detected by Rietica Software. The estimation of the particle size by Maud software, showed that the particle size of all catalysts increased by the following order: ZnO < $CaOZnO_{0.08}$ < $CaOZnO_{0.25}$ < CaO. The conversion of triglyceride, methyl ester yield, turnover number (TON) and turnover frequency (TOF) of $CaOZnO_{0.08}$ are higher than $CaOZnO_{0.25}$. The higher activity of $CaOZnO_{0.08}$ is probably due to the increased surface area of smaller crystal.

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References

[1] Mc Neff, C.V., Mc Neff, L. (2008). A Continuous System for Biodiesel Production. *Applied Catalytic A: General*, 343: 39-48.

[2] Carmo, A.C., Luiz K.C., Carlos E.F., Longo, E., José R.Z, Geraldo N. (2009). Production of Biodiesel by Esterification of Palmitic Acid over Mesoporous Aluminosilicate Al-MCM-41. *Fuel*, 88: 461-468.

[3] Alonso, D.M, Mariscal, R., Granados, M. L., Maireles-Torres, P. (2008). Biodiesel Preparation Using Li/CaO Catalysts: Activation Process and Homogeneous Contribution. *Catalysis Today*, 30: 1-5.

[4] Kim, H.J., Kang, B.S., Kim, M.J., Park, Y.M., Kim, D.K. (2004). Transesterification of Vegetable Oil to Biodiesel Using Heterogeneous Base Catalyst. *Catalysis Today*, 93-95: 315-320.

[5] Liu, X., He, H., Wang, Y., Zhu, S., Piao, X. (2008). Transesterification of Soybean Oil to Biodiesel Using CaO as a Solid Base Catalyst. *Fuel*, 27(2): 216-221.

[6] Granados, M.L., Poves, M.D.Z., Alonso, D.M., Mariscal, R., Galisteo, F.C., Moreno-Tost, R., Santamaría, J., Fierro, J.L.G. (2007). Biodiesel from Sunflower Oil by Using Activated Calcium Oxide. *Applied Catalysis B: Environmental*, 73: 317-326.

[7] Alba-Rubio, A. C., Santamaria-Gonzalez, J., Josefa M. (2010). Heterogeneous Transesterification Processes by Using CaO Supported on Zinc Oxide as Basic Catalysts. *Catalysis Today*, 149: 281-287.

[8] Ngamcharussrivichai, C., Totarat, P., Bunyakiat, K. (2008). Ca and Zn Mixed Oxide as a Heterogeneous Base Catalyst for Transesterification of Palm Kernel Oil. *Applied Catalysis A: General,* 341: 77-85.

[9] Wang, H., Wang, M., Liu, S., Zhao, N., Wei, W., Sun, Y. (2006). Influence of Preparation Methods on the Structure and Performance of CaO–ZrO_2 Catalyst for the Synthesis of Dimethyl Carbonate via Transesterification. *Journal of Molecular Catalysis A: Chemical,* 258: 308-312.

[10] Cho, Y.B., Seo, G., Chang, D.R. (2009). Transesterification of Tributyrin with Methanol over Calcium oxide Catalysts Prepared from Various Precursors. *Fuel Processing Technology*, 90: 1252-1258.

[11] Yan, S., Mohan, S., DiMaggio, C., Kim, M., Simon Ng, K.Y., Salley, S.O. (2010). Long Term Activity of Modified ZnO Nanoparticles for Transesterification. *Fuel*, 89: 2844-2852.

[12] Kanade, K.G., Kale, B.B., Aiyer, R.C., Das, B.K. (2006). Effect of Solvents on the Synthe-

sis of Nano-Size Zinc Oxide and Its Properties. *Materials Research Bulletin*, 41: 590-600.

[13] Albuquerque, M.C.G., Jimenez, U.I., Santamaria, G.J. (2008). CaO Supported on Mesoporous Silicas as Basic Catalysts for Transesterification Reactions. *Applied Catalysis A: General,* 334: 35-43.

[14] El-Shobaky, G.A., Mostafa A.A. (2003). Solid-Solid Interactions in Fe_2O_3/MgO System Doped with Aluminium and Zinc Oxides. *Thermochimica Acta*, 408: 75-84.

[15] Palomino, A.G.P. (2006). Room-Temperature Synthesis and Characterization of Highly Monodisperse Transition Metal-Doped ZnO Nanocrystals. University of Puerto Rico.

[16] Ma, F., Hanna, M.A. (1999). Biodiesel Production: A Review. *Bioresource Technology*, 70: 1-15.

[17] Taufiq-Yap, Y.H., Lee, H.V., Hussein, M.Z., Yunus, R. (2011). Calcium-Based Mixed Oxide Catalysts for Methanolysis of Jatropha Curcas Oil to Biodiesel. *Biomass Bioenergy*, 35: 827-834.