Preparation and characterization of KF/CaO-MgO catalyst for monoglycerides synthesis

by Indro Sumantri

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RESEARCH ARTICLE

Preparation and characterization of KF/CaO-MgO catalyst for monoglycerides synthesis

Didi Dwi Anggoro*, Lugman Buchori, Indro Sumantri, Herawati Oktavianty

Department of Chemical Engineering, Faculty of Engineering, University of Diponegoro, Jl. Prof. Sudharto, Tembalang, Semarang, 50239, Indonesia

* Corresponding author: anggorophd@gmail.com

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Abstract

A heterogeneous KF/CaO-MgO catalyst was prepared by impregnation method and was characterized by X-ray diffraction, BET and Tanabe method. The effects of weight KF addition, temperature and time of calcination on catalyst preparation were investigated. The influence of basicity value of catalyst was investigated. KF/CaO-MgO catalyst could perform the active sites to produced a high MG yield of 47.96% for 2%w KF addition, at 550 °C of calcination temperature and 2 hours of calcination time. It has a high spesific surface area (110,924 m²/g) that favorable for contact between catalyst and substrates, which effectively improved efficiency of glycerolysis. The high activity of the catalyst was described to the formation of KCaF₃ and MgKF₃ crystals.

Keywords: KF/CaO-MgO catalyst, basicity, impregnation method, glycerolysis, monoglycerides

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INTRODUCTION

To date, monoglycerides (MG) needed by the industry is increasing. MG is widely used as emulsifier, wetting agent, lubricant and so on in the food industries, cosmetics, pharmaceuticals [1, 2], oil well drilling [3], textile [4], packaging [5], plastic processing [6], and material construction [7].

Indonesia is one of the largest producer countries of palm oil in the world. Indonesia's crude palm oil (CPO) production had shown a significant increase over the last 5 years. In 2012, Indonesia had produced palm oil as much as 26 million tons and reached 33.2 million tons by 2016 [8]. More than half of palm oil production is used to meet domestic demand especially the cooking oil industry and the rest is exported. Utilization of palm oil is less effective due to the lack of development in downstream palm oil industries. Palm oil contains 41% saturated fat, 81% palm kernel oil, and 86% coconut oil [10].

Table 1 Composition of fatty acid on palm oil [9].

No	Component	Mass %
1	Myristic Acid	1,1 – 2,5
2	Palmitic Acid	40-46
3	Stearic Acid	3,6-4,7
4	Oleic Acid	39-45
5	Linoleic Acid	7-11

There are several methods of making monoglycerides, among others, through the direct esterification of glycerol and esterification of indirect glycerol by transesterification of glycerol-fitty acid of methyl ester (FAME), glycerolysis, enzymatic reactions and chemical deactivation. Glycerolysis reactions are simpler and more economical because they do not require the process of hydrolyzing fat into fatty acids, the separation of fatty acids,

purification and selective esterification steps as in enzymatic methods [11].

Fig. 1 Glycerolysis reaction [11].

Glycerolysis is an important reaction between glycerol with oils or fats to produce MG. Glycerolysis reactions will run slowly without using catalyst. The existence of catalyst will make the reaction to run quickly and can take place under normal pressure and temperature conditions [12]. The reaction can be carried out in the presence of an acid catalyst or an alkaline catalyst. Reaction with an alkaline catalyst is usually faster [13].

The most common catalyst used in glycerolysis is base catalyst. glycerolysis reactions using a catalyst may use homogeneous or heterogeneous catalysts, each of them has deficiencies and advantages. Comparing to homogeneous catalysts (such as NaOH), heterogeneous catalysts (such as Ca/MgO) have several advantages, such as no production of soap, no need for neutralization and extraction, easier product separation and can be used repeatly. The use of a heterogeneous catalyst may also be increased in activity by modification of the catalyst in the form of a composite or doping to a catalyst. Heterogeneous catalysts consist of two main components, namely as active sites (dopants) and buffers. The active site serves to increase the reaction rate and direct the reaction toward the desired product. The buffer which is generally a porous solid serves as a container for the distribution of the active site so that the catalyst has a larger surface area [14]. The mechanism of base catalyst in transesterification is shown in Fig. 2.

Fig. 2 Transesterification mechanism using base catalyst [15].

Basic strength of a solid surface is defined as the ability of the surface to convert an adsorbed neutral acid to its conjugate base *i.e.*, the ability of the surface to donate electron pair to an adsorbed acid [16]. Base sites in alkaline earth catalysts of oxides are generally caused by the presence of positive metal ion pairs (M²⁺) which have the properties of lewis acid and oxygen ions (O²⁻) which have bronsted base properties. The increasing of basic strength is proportional to the increasing of the activity of alkaline earth oxide metal catalysts as indicated by the increased yield of product [17].

Heterogeneous MgO base catalyst has been applied in the synthesis of MG from the reaction of glycerol with methyl oleate [18, 19]. Based on previous research [20], where MG synthesis by using Ca-doped MgO catalyst showed that Ca-doped MgO catalyst has the potential to develop its activity on glycerolysis reactions by modifying the structure, alkalinity and catalytic area of CaO/MgO. Verziu et al obtained that supported KF catalysts exhibited high catalytic activity for transesterification in which the biodiesel yield was more than 95% [21].

In this study, addition KF as support to KF/CaO-MgO catalyst was expected to obtain a higher yield of MG than other utilizations of heterogeneous catalyst. KF/CaO-MgO catalyst was prepared by impregnation method. The influences of the preparation conditions, such as calcination temperature and time, and weight KF addition on KF/CaO-MgO catalyst, on the activity of catalyst on MG yield were investigated. KF/CaO-MgO catalyst was characterized by X-Ray Difraction, nitrogen adsorption and Tanabe method.

EXPERIMENTAL

Materials

The starting materials for Ca-MgO catalyst were magnesium acetate (Merck), calcium nitrate (Merck), citric acid (technical) and absolute ethanol (EtOH, technical 96%). For catalyst supporting, KF powder was used (Merck), while aquadest/deionized water was used for washing, then glycerol (Merck) and CPO as reactants for glycerolysis process.

KF/CaO-MgO catalyst preparation

Magnesium acetate, calcium nitrate, and citric acid compounds were weighed according to predetermined calculations and dissolved in 95% ethanol, the solution was stirred until clear color was obtained. All three solutions were mixed and distilled at 350 rpm until the soltemperature reached 80°C. The formed gel was heated in an oven at 110°C until it was dried. The catalyst was then smoothed by using mortar and calcined it using furnace for 3 hours with a temperature range of 550°C. Impregnation of MgO-Ca with KF would be achieved by dissolving KF in deionized water then adding Ca-MgO before being stirred for 1 hour. Thereafter, the mixture was exposed to 140°C for 6 hours to remove the water absorbed onto the surface of the catalysts and calcined at various temperatures and time.

Characterization of catalyst structure by X-Ray Difraction

XRD (Panalytical X'Pert Powder, Semarang State University) was used to charaterize the sructural of catalyst. XRD patterns were measured under the following conditions: K_{α} ($\lambda=1,5406$ Å) at 400 kV and 300 mA, $2\theta=10-70^{\circ}$, step size 0.017, and step time 0,5 sec. At first, the sample was smoothed to a very fine powder, then placed on preparations and pressed. It was then placed on the sample holder and irradiated with X-rays. The results obtained (difractogram) would be compared with the JCPDS standard for the compounds.

Characterization of spesific surface area by using nitrogen adsoption

Analysis with Nitrogen Adsorption was carried out in the Integrated Chemical Engineering Laboratory, Diponegoro University, Semarang. Measurement of specific area was carried out by nitrogen adsorption method. Samples of 0.2 grams were treated with nitrogen gas with a flow rate of 30 cm³/min at 200°C for 1 hour and cooled to adsorption and desorption of nitrogen at a temperature of 77°C.

Characterization of catalyst basicity by using Tanabe method

The Tanabe method was analyzed by Chemical Engineering Process Engineering Laboratory, Diponegoro University, Semarang. A gram of sample (catalyst) of 100 - 200 mesh was added into 100 ml erlenmeyer, before 20 mL of benzene and 1 mL of Bromthymol blue (BTB) indicator were added. After that, the solution was titrated with benzoate 0.1N.

Glycerolysis process and MG analysis

Palm oil, glycerol and catalyst (0.1% w KF/w Ca-MgO) were mixed and stirred in a three necked bottom flasks as shown in Fig 3 below. Then the reaction was carried out at 200°C and 700 rpm for 3 hours.

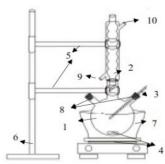


Fig. 3 Schematic diagram for Glycerolysis Process (1- three-necked round-bottomed flask, 2- condenser, 3- thermometer, 4- Magnetic stirrer + hotplate, 5- clamp, 6- stative, 7- oil bath, 8- glass cover, 9- water in, 10- water out.

The result analysis of the monoglycerides synthesis in the form of liquid product was carried out by using Gas Chromatography-Mass Spectrometry (GC-MS). This analysis was used to identify the monoglyceride components. The analysis was carried out with the condition of injector temperature, column temperature and with solvent used n-hexane and helium carrier gas with 1ml/min flow rate. The MS range used was 0 m/z up to 450 m/z.

RESULTS AND DISCUSSION

Characterization of KF/CaO-MgO catalyst and the influence to MG yield

The diffractogram in CaO gave intensity and has peaks at 20: 37.36°; 74.65° and 78.70°, MgO was seen at 20: 42.91° and 62.15°; and Ca(OH)₂ has peaks at 20: 18.19°; 29.39°; 50.77° and 58.74° (JCPDS Data). When impregnated with a variation of % KF and calcination temperature variations were carried out on KF/CaO-MgO

catalyst, there was an additional new intensity for CaKF3 crystals which had peaks at 2θ : 28.28° and 59.32° and MgKF3 crystals with a peak of 2θ : 38.58° , as shown in Fig. 4 below.

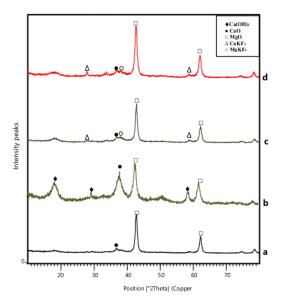


Fig.4 XRD pattern comparison between CaO-MgO catalyst (a); KF/CaO-MgO catalyst (2%w KF, 450°C, 2 h) (b); KF/CaO-MgO catalyst (2%w KF, 500°C, 2 h) (c); KF/CaO-MgO catalyst (2%w KF, 550°C, 2 h) (d)

Variations in KF support concentration, temperature and calcination time indicated differences in intensity and theta shift. When the calcination temperature was below 500°C, there was still Ca (OH)₂ crystals and when the calcination temperature reached 500°C and up to 550°C, new peaks were formed in the form of crystals CaKF₃ and MgKF₃ were the active sites that formed due to the addition of KF as support and high temperature calcination and thus, increasing catalyst activity which influenced on the high yield of monoglycerides produced. Xuan's study confirmed that the addition of KF to heterogeneous catalysts and high calcination temperatures would help to produce crystals of CaKF₃ and MgKF₃ as active sites that could produce higher biodiesel yields due to high catalytic activity [22].

Characterization of specific surface area of KF/CaO-MgO catalyst

The spescific surface area is shown in Table 2 below. Fig. 5 shows the correlation between specific area of the catalyst and MG yield, where at range 83-121 m²/g of surface area, above 30% of MG yield was obtained and when the surface area was above 121 m²/g, the MG yields were getting lower. The higher MG yield was obtained by surface area value of 110 m²/g, this was closed to Wen (2010) result which obtained 109 m²/g of catalyst surface area value that achieved 96,8% of biodiesel yield, meaning that the value of surface area was matched to produce high MG yield in the same condition of temperature and time of calcination [23]. From table 2, surface area which range 83-121 m²/g was resulted by using calcination temperature above 500°C, which obtained high MG yield by 550°C of calcination temperature, but when the temperature reached 584°C, the MG yield was decreased, it was due to the fact that overheating resulted in the surface sintering and the reduction of spesific surface area, which in turn led to the decreased of catalytic activity [24].

Table 2 Surface area value of KF/CaO-MgO catalyst.

Ru n	Calcination Temperatur e (°C)	Calcination Time (hours)	%K F	Surface Area (m²/g)	MG Yield (%)
1	450	2	2	132.456	22.85
2	450	2	4	144.566	26.52
3	450	4	2	152.036	24.31
4	450	4	4	141.128	21.78
5	550	2	2	110.924	47.96
6	550	2	4	84.285	41.65
7	550	4	2	92.362	39.16
8	550	4	4	83.521	36.13
9	416	3	3	154.384	13.98
10	584	3	3	85.481	32.94
11	500	1 h 19 min	3	119.706	44.75
12	500	4 h 40 min	3	98.005	31.78
13	500	3	1.32	121.128	43.36
14	500	3	4.68	94.447	38.58
15	500	3	3	105.946	40.28
16	500	3	3	106.623	35.30

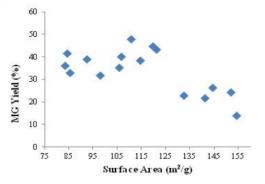


Fig. 5 Correlation between surface area and MG yield.

Conditional optimization of KF/CaO-MgO basicity

Optimization for the catalyst preparation was performed by central composite design of response surface methodology that is shown in Table 3.

Table 3 Basicity value of KF/CaO-MgO catalyst.

Run	Calcination Temp (°C)	Calcination Time (hours)	% KF	Basicity (mmol/g)	MG Yield (%)
1	450	2	2	0.30	22.85
2	450	2	4	0.64	26.52
3	450	4	2	0.54	24.31
4	450	4	4	1.04	21.78
5	550		2	0.84	47.96
6	550	2 2	4	0.98	41.65
7	550	4	2	0.66	39.16
8	550	4	4	1.18	36.13
9	416	3	3	0.28	13.98
10	584	3	3	0.72	32.94
11	500	1 h 19 min	3	0.92	44.75
12	500	4 h 40 min	3	1.16	31.78
13	500	4 n 40 min 3	1.32	0.96	43.36
14	500	3	4.68	1.10	38.58
15	500	3	3	1.06	40.28
16	500	3	3	1.04	35.30
17	CaO-MgO			0.26	36.03

Table 3 shows that the increasing of weight KF obtained to higher catalyst basicity, and compared to unloaded support (CaO-MgO), the KF loaded catalysts have the higher catalyst basicity, indicating that loading KF onto the support material promoted the basic strengths and basicity of the catalysts [25]. The increasing of calcination temperature performed the higher catalyst basicity too, but when the

temperature reached 584°C, the catalyst basicity was lower, due to the changes in the catalyst composition which led to the increasing of catalyst basicity and the formation of new crystals namely CaKF₃ and MgKF₃. According to Wen (2010), the addition of KF led to the formation of CaKF₃ which enhanced catalytic activity of the catalyst [23].

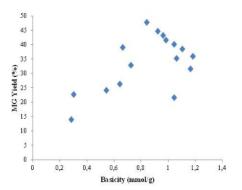


Fig. 6 Correlation between catalyst basicity and MG yield.

Figure 6 shows the correlation between catalyst basicity and MG yield, which optimal MG yield reached at 0.84 mmol/g of basicity and decreased when the catalyst basicity was higher. This was contrary to the greater the basicity, the higher the MG yield. According to Wen's study (2010), when the amount of KF was greater, the catalytic activity was decreased, since KF was supported on CaO, it was evenly distributed on CaO surface if the KF content was lower than a threshold with mono-molecular layer. When the KF content was higher than the threshold, it covered the activity sites, resulting in the decrease of catalytic ability. During the preparation of the solid catalyst, high temperature calcination favors the interaction between carrier and active component to form new crystal, activity sites. However, overheating can result in the surface sintering and the reduction of specific surface area, which in turn leads to the reduction in catalytic activity [23]. The current experiment showed that calcination at 550°C produced highly active catalyst.

Efficiency between CaO-MgO catalyst and KF/CaO-MgO catalyst

The comparison performance between CaO-MgO catalyst and KF/CaO-MgO catalyst is shown in Table 4, in which the loading KF onto the CaO-MgO promoted the basic strengths. By increasing the catalyst basicity, new active sites *i.e.* CaKF₃ and MgKF₃ were produced, that helped the increasing catalyst activity to produce higher MG yield.

Table 4 Comparison performance between CaO-MgO catalyst and KF/CaO-MgO catalyst.

Run	Catalyst	Basicity (mmol/g)	MG Yield (%)
1	CaO-MgO	0.84	36.03
2	KF/CaO-MgO	0.26	47.96

CONCLUSION

KF/CaO-MgO catalyst was prepared by impregnation method, resulting the active sites to produce a high MG yield of 49.76% for 2%w KF addition, at 550°C of calcination temperature and 2 hours of calcination time. It has a high specsific surface area (110.924 m²/g) that was favorable for contact between catalyst and substrates which effectively improved the efficiency of glycerolysis. The high activity of the catalyst was described by the formation of KCaF3 and MgKF3 crystals as the active sites. However, further studies were required to

improve the MG yields by adding purification process in order to develop a commercially useful catalyst for the production of MG.

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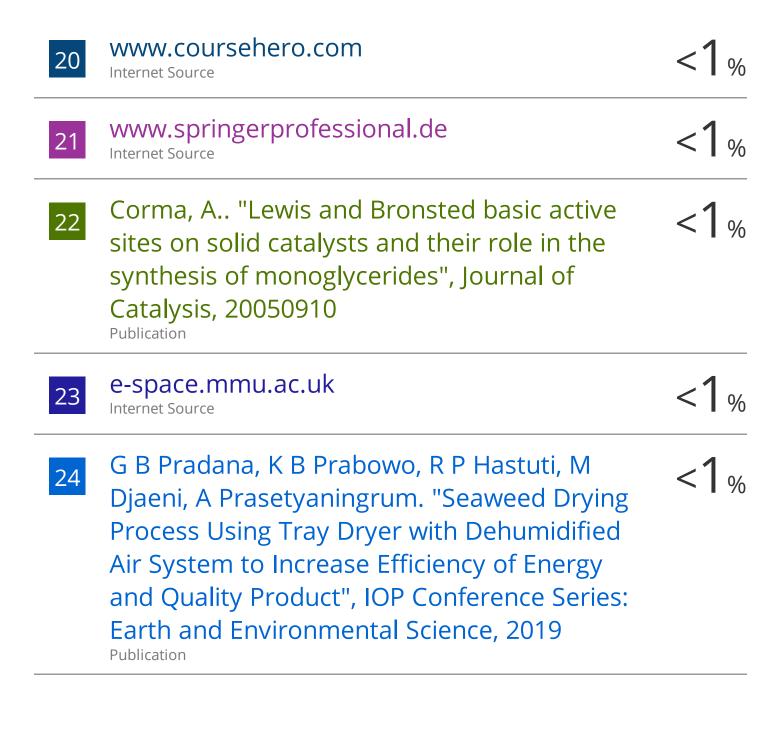
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