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Synthesis of Ca/MgO Catalyst Using Sol Gel Method for Monoglycerides Production

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Abstract. This paper discusses Ca-doped MgO catalysts using Sol-Gel method. The doping of Ca is expected to increase the basicity of the catalyst. The basicity of catalyst has effect on the monoglycerides production by glycerolysis reaction. The Ca/MgO catalyst was prepared by sol gel method by using solution as a precursor. This method was expected to produce a more homogeneous mixture of Mg and Ca. The catalyst was characterized using X-Ray Diffraction (XRD) and the basicity was analyzed using Hammett titration method. The monoglycerides yield was analyzed using Gas Chromatography Mass Spectrometry (GC/MS). Based on Hammett's titration method, the basicity value was calculated in which the largest value was obtained by the dopant concentration of 2% Ca and calcination temperature of 800^0C. The 2% Ca/MgO catalyst that has the highest basicity value was tested for the production of monoglycerides through glycerolysis reaction. This reaction carried on the conditions of 200^0C, the catalyst amount of 0.1% weight of oil, the ratio of glycerol : oil = 3 : 1, reaction time of 3 hours, and stirring speed of 700 rpm. The composition of monoglyceride on oil phase product was 100%, while without catalysts composition was 7.43%.

INTRODUCTION

Monoglycerides is a product with high economic value and the global market of monoglycerides is quite prospective in the future. The monoglycerides used as emulsifiers are about 132,000 ton/year. The functions of monoglycerides are as emulsifiers, emollients, lubricants, and dispersant. The monoglycerides are also applied in the food, pharmaceutical, cosmetic, detergent industries [1], oil well drilling [2], textiles [3], packaging [4], plastic processing [5] and construction materials [6].

The most common process to produce monoglycerides is by catalytic reactions [7, 8]. The advantages of catalyst are to support the speed of the reaction at normal temperature and pressure state [9]. The potential catalyst used in the glycerolysis reaction is the heterogeneous base catalysts.

A heterogeneous base catalyst widely used is Magnesium oxide (MgO). The advantages of MgO catalyst are easily used in the synthesis process, easier to control, the abundant availability, and also relatively inexpensive [9]. The activity of the heterogeneous catalyst can be enhanced by the modification of catalyst in the form of composite mixture or catalyst doping. The Calcium (Ca) doping on MgO is expected to increase the basicity, hence it will be more effective in the monoglycerides synthesis process by glycerolysis reaction.

Mguni (2012) concluded that the sol-gel method is one of heterogeneous catalyst material synthesis methods. The advantage of sol-gel method is its easy preparation. The sol gel method uses the precursor solution, hence it produces a more homogeneous mixture of Mg and Ca. This method produces a catalyst with smaller size and larger surface area. Therefore, this study used sol-gel method for synthesis Ca/MgO catalyst.

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METHODOLOGY

This study used magnesium acetate, calcium nitrate, citric acid, ethanol, benzoic acid, methanol, and phenolphthalein. All chemicals were supplied by Merck. Triglyceride/*Jatropha curcas* oil (JCO) and glycerol technical quality are also from Merck.

Preparation of Ca/MgO Catalyst

Magnesium acetate solids, calcium nitrate and citric acid were weighed according to the calculation and were dissolved in 95% ethanol. The solution was stirred until it was clearly visible. The third solution was mixed and stirred with speed of 350 rpm until the sol was formed. The homogeneous solution was heated at temperature of 80^0C and stirred until the gel was formed. The gel solution was heated in an oven at temperature of 110^0C for 2 hours. The Ca/MgO catalysts were crushed and calcined for 6 hours using a variation of temperature, namely 600^0C, 700^0C and 800^0C.

Characterization of Ca/MgO Catalyst using XRD

Ca-doped MgO catalysts were characterized by using the technique of X-Ray Diffraction (XRD) powder for structure identification. XRD analyze was carried out by PANalytical X'Pert Pro with Cuα (λ= 1.5405 Å), monochromatic radiation of 40 kV and 35 mA, 2θ = 10-90 ^{0}, step of 0.02 ^{0}, and step time of 0.7 seconds. The catalyst sample was mashed up into a very fine powder, then placed on the preparation and pressed. The results were obtained (diffractogram) and subsequently compared to JCPDS standard for MgO compounds. Crystal size was calculated using the Debye-Scherrer equation.

Calculation of The Basicity of Catalyst

Basicity value of catalyst was calculated using Hammett's titration method [10]. Ca/MgO catalysts were weighed as much as 0.1 grams with 3 (three) concentration variations and 3 (three) calcination temperature variations. Subsequently, 10 ml of distilled water was added and the mixture was stirred using a stirrer for 1 hour at speed of ± 125 rpm and filtered. The result was added PP indicator as much as 20 drops until the color turned pink and titrated using 0.01 M benzoic acid solution in methanol solvent. The titration was stopped when the solution was clear again. The titration final volume was recorded then the basicity value of catalyst was calculated.

Testing Catalyst

Ca/MgO catalysts were tested for the production of monoglycerides by glycerolysis reaction. The Ca/MgO catalysts were dissolved in glycerol at temperature of 90°C in stirred glass beaker until it was completely dissolved. JCO was mixed into beaker with mole ratio glycerol and JCO of 3:1. Mix reactants and catalyst were heated at temperature of 150°C and the whole mixture was dissolved. Furthermore, the reaction temperature was increased until the reaction temperature at 200°C and stirring speed of 700 rpm. This reaction condition should be maintained during the reaction time of 3 hours. Upon reaching the desired reaction time, the heating should be stopped and refluxed results cooled down. Reflux result was put into separator to separate the oil phase and the water phase. Furthermore, the oil phase was analyzed using GCMS for known compounds contained and the yield of monoglycerides obtained.

Gas Chromatography Mass Spectrometry (GC/MS) Analysis

The oil phase was analyzed based on the composition and quantity of compounds using gas chromatography (GC) *Varian* brands CP-3800 types and Mass Spectrometry (MS) *Varian* brands Saturn 2200 types. Analysis was done by separating condition injector temperature 310^0C, 150^0C column temperature for 10 min, 150^0C to 300^0C rate of 5^0C/min, 300^0C for 20 minutes (total 60 minutes). The solvent used was n-hexane and carrier gas was helium with a flow rate of 1 ml/min. MS used was in range of 30 m/z to 450 m/z.

RESULTS AND DISCUSSION

X-Ray Diffractogram Result

The results of XRD diffractogram (Figure 1) were compared with the MgO standard (JCPDS 01-1235). The result showed that the synthesized catalyst has typical peaks owned by MgO, namely in theta 36.9^0; 42.9^0; 53.8^0 and 62.9^0. These results were similar with the XRD pattern of the Ca/MgO catalyst from previous research [11], which showed the same typical peak of Ca/MgO catalyst. The XRD diffractograms were observed regarding to the effect of doping metal against 2θ shift that appear on the typical peak of MgO. It indicates the metal in Ca doped MgO catalyst. These results are consistent with Zhi [12], in which the doping metal is affected by 2θ shift.

The difference of Ca concentration and calcinations temperature indicates the effect on difference in intensity and theta shifts. The higher Ca concentration and temperature calcinations have effect on the increase in peak intensity. For example, Ca/MgO catalysts with Ca dopant concentration of 2% and calcination temperature of 800 °C showed the highest absorption intensity at the height of typical theta MgO of 42.9° (1690.93) and 62.3° (699.59). The intensity level has effect on the level of crystallinity, in which the higher the intensity, the higher the crystallinity level.

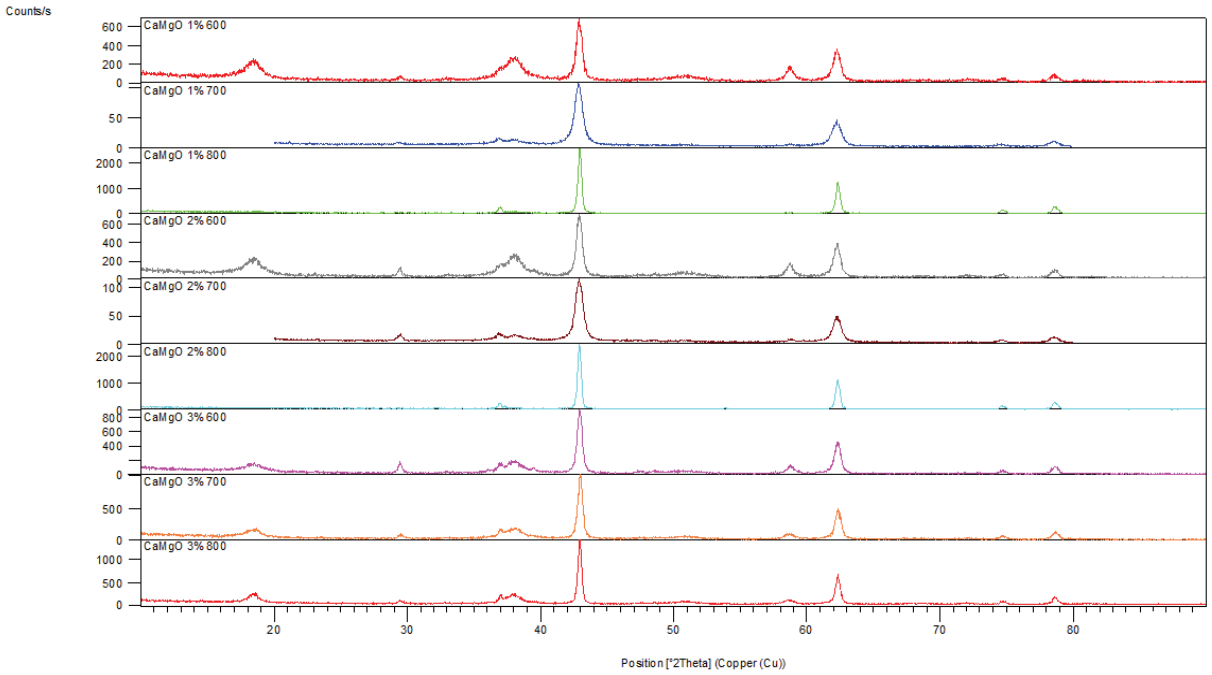

FIGURE 1. The result of measurement analysis of XRD sample variation of Ca dopant concentration of 1%, 2%, 3% and calcination temperature of 600^0C, 700^0C, and 800^0C.

The increase in calcinations temperature causes the strong oxidation reaction of the sample, hence the size of catalyst crystal also increased. The time of calcinations has effect on the size of crystal grain. The longer the calcinations time, the larger the size of crystal grain [13]. It confirms by XRD pattern in which the longer the calcinations time leads to the higher and sharper diffraction peaks. Hence, the half peak width is smaller as the crystal size is inversely proportional to the values of the full width half maximum (FWHM), thus the size of crystal is larger.

The Results of Catalyst Basicity

In this research, the basicity calculation was conducted using Hammett's titration method. The basicity values of various Ca concentrations and calcination temperatures are shown in Figure 2. From the results, the influence of the Ca concentration to the basicity is noticeable. MgO catalyst doped by 1% Ca has the lowest basicity value of 0.015 mmol/g. It shows that the low concentration of Ca leads to fewer Ca ions is able to become the crystal lattice and replace Mg ions. Meanwhile, the higher the Ca dopant concentration, the higher the basicity values along with the increase in the calcination temperature. The highest basicity value of 0.095 mmol/g was obtained by the Ca/MgO catalyst with dopant concentration of 2% and calcination temperature of 800^0C. The increase in Ca dopant concentration (3%) causes the lower basicity value, of 0.035 mmol/g. It is because the crystal condition is too saturated, hence the possibility of replacing Mg ions with Ca ions is also smaller.

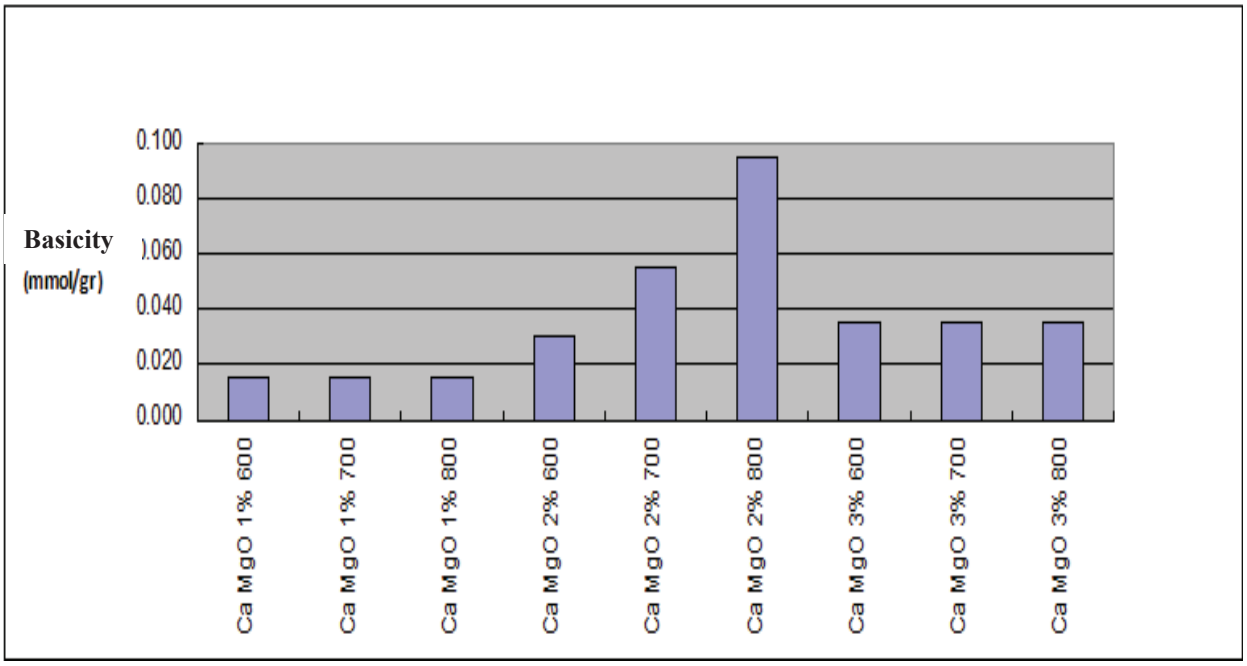

FIGURE 2. The basicity values of Ca/MgO catalyst with different dopant concentration of Ca and calcination temperature.

Ca/MgO Catalyst Testing Result

In this study, Ca doped MgO catalysts (2% Ca/MgO 800^0C) has the highest basicity value, which its catalytic activity was tested in association with monoglycerides synthesis production. The monoglycerides synthesis was made through glycerolysis reaction from reacting triglycerides (*Jatropha curcas* oil) with glycerol. For comparison, glycerolysis reaction was done without using a catalyst. The oil phase products were analyzed using GCMS as shown on Figure 3 and Figure 4.

Figure 3 shows the composition of oil phase product using 2% Ca/MgO catalyst was 100% monoglycerides. It is because the 2% Ca/MgO catalyst has the highest basicity value. It indicates the monoglycerides compound shows specific retention time of 33.085 minutes, with molecular weight of 356. The surface area of the 2% Ca/MgO catalyst was 48.8328 m^2/g.

Figure 4 shows the results of GCMS test on the composition of oil phase product without catalyst. The oil phase product was identified, which consisted of: methyl palmitate, palmitic acid, methyl linoleic, methyl oleic, oleic acid and monoglycerides. The composition of monoglycerides was 7.43%. From these results, it can be concluded that the highest basicity catalyst is proven to be effective in glycerolysis reaction. It is similar with the findings of other studies that the basicity of the catalyst affects the catalyst activity [14].

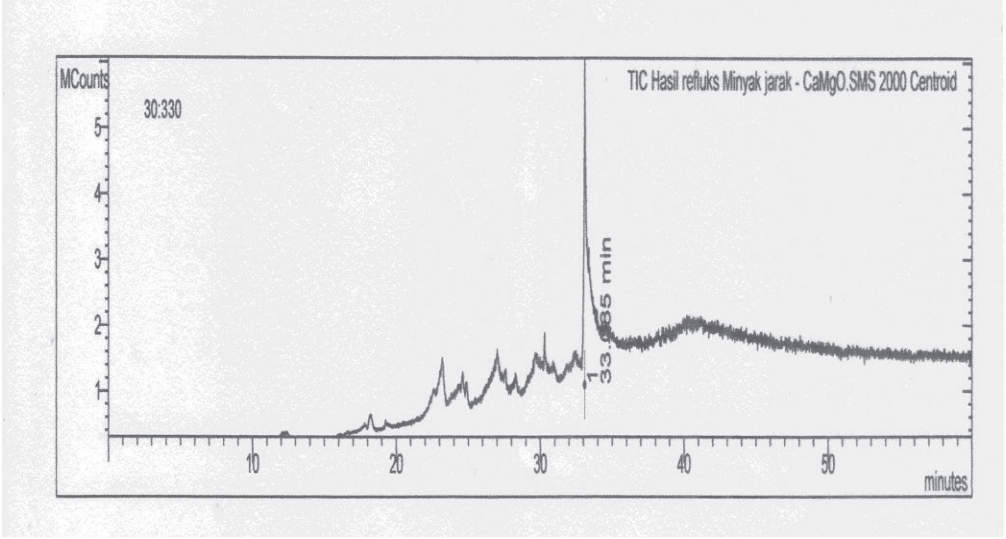

FIGURE 3. Chromatogram of oil phase product using Ca/ MgO catalyst with dopant concentration of Ca 2% and calcination temperature of 800^{0}C.

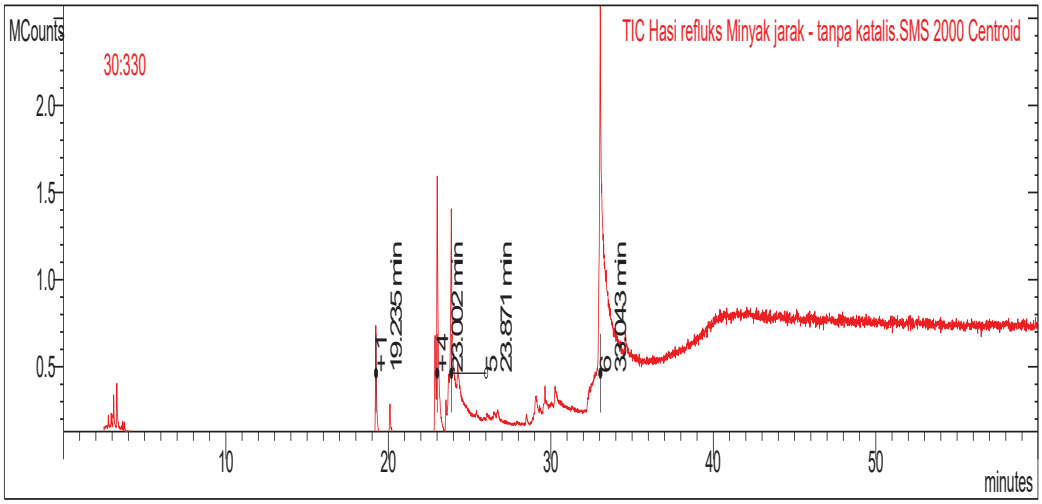

FIGURE 4. Chromatogram of oil phase product without catalyst.

CONCLUSION

Ca/MgO catalyst can be synthesized using sol-gel method. The result of XRD analysis shows that the synthesized catalyst has typical peaks owned by MgO, namely in theta 36.9^0; 42.9^0; 53.8^0 and 62.9^0. The highest basicity value of 0.095 mmol/g was obtained by Ca/MgO catalyst with dopant concentration of 2% and calcination temperature of 800°C. It produces monoglycerides synthesis by glycerolysis reaction. The 100% monoglyceride obtained by using 2% Ca/MgO 800^{0}C. The highest basicity value of catalyst is proven to be effective in glycerolysis reaction.

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REFERENCES

1. U.T. Bornscheuer. Enzyme and MicrobialTechnology 17, 7, 578-586 (1995).
2. D. L. Breeden and R. L. Meyer. U.S. Patent No. 6,884,762 (2005).
3. D. Hough, T. Barclay, I. Drive and W. Merseyside. EPO 107479 A2. (1984).
4. H. G. Franke and D. R. Bittner. U.S. Patent No. 5,512,090 A (1996).
5. M. Rosen, and L. K. Hall. U.S. Patent No. 4,363,891 A (1982).
6. S. Narisawa, Y. Taira, Y. Yoshii, and T. Kondou. U.S. Patent No. 4,434,257 A (1984).
7. WB Setianto, TY Wibowo, H Yohanes, F Illaningtyas, and D.D. Anggoro. IOP Conference Series: Earth and Environmental Science. 65, 1, 012-046 (2017).
8. D.D. Anggoro, W.B. Setianto, T. Wibowo, L. Buchori, F.R. Pratama, and A. Giovanno. Advanced Science Letters. 23, 6, 5602-5604 (2017).
9. L. L. Mguni. Biodiesel Production Over Supported Nano-magnesium Oxide Particles, Ph.D. thesis. University of Johannesburg, 2012.
10. R. Rahul, K. Jitendra, D. Satyarthi, Srinivas. Indian Journal of Chemistry 5OA, 1017-1025 (2011).
11. Y. H. Taufiq-Yap, H. V. Lee, M. Z. Hussein, and R. Yunus. Biomass and bioenergy 35, 827 – 834 (2011).
12. 12. G. Zhi, J. Song, B. Mei, and W. Zhou. Journal of Alloys and Compounds 509, 9133–9137 (2011).
13. 13. B. D. Chullity, *Element of X-ray Diffraction (XRD).* (University of Notre Dame, Massachusetts, 2006).
14. 14. Z. Helwani, M. R. Othman, N. Aziz, J. Kim, and W. J. N. Fernando. Applied Catalysis A: General, 363, 1-10 (2009).