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Methyl Ester Production via Heterogeneous Acid-Catalyzed Simultaneous Transesterification and Esterification Reactions

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Abstract. The heterogeneous acid catalysts (MgF_2 and ZnF_2) have been used to catalyze the simultaneous transesterification and esterification reactions of crude palm oil (CPO) with methanol. Catalysts were synthesized by sol-gel method (combination of fluorolysis and hydrolysis). The physicochemical, structural, textural, thermal stability of the prepared catalysts was investigated by N_2 adsorption-desorption, XRD, FT-IR, SEM and TG/DTG. Both MgF_2 and ZnF_2 have rutile structures with a different phase. The surface area of ZnF_2 is smaller than that of MgF_2, but the pore size and volume of ZnF_2 are larger than those of MgF_2. However, these materials are thermally stable. The performance of the catalysts is determined from the yield of catalysts toward the formation of methyl ester determined based on the product of methyl ester obtained from the reaction. The catalytic activity of ZnF_2 is higher than MgF_2 amounted to 85.21% and 26.82% with the optimum condition. The high activity of ZnF_2 could be attributed to its pore diameter and pore volume but was not correlated with its surface area. The yield of methyl ester decreased along with the increase in molar ratio of methanol/CPO from 85.21 to 80.99 for ZnF_2, respectively.

Keyword. Acid catalyst, crude palm oil, methyl ester, simultaneous transesterification and esterification reactions

1. Introduction

The use of methyl ester based on renewable vegetable oils as a starting material or intermediate for several oleochemical industries such as in the cosmetics, surfactants (MES), plastics, biolubricants, pharmacy, foodstuff, and energy production is considered and proposed as a new alternative in the development of Green-Sustainable chemistry [1-6]. Methyl ester can be obtained from the processing of vegetable oils such as rapeseed oil, jatropha oil, soybean oil, karanja oil, rubber seed oil, safflower oil, and crude palm oil [7-13]. In Indonesia, a source of vegetable oil that is used the most widely is derived from crude palm because it is abundant, cheap, eco-friendly and renewable [14-16].

Methyl ester can be obtained through the transesterification of palm oil and alcohol with a base catalyst such as KOH or NaOH [17]. However, the catalyst is very sensitive to triglyceride which contains high free fatty acid (FFA). FFA reacts readily with a base catalyst to form soap so that the transesterification reaction with the base catalyst cannot be conducted directly. Also, methyl ester can also be obtained by simultaneous transesterification and esterification reactions using a homogeneous

acid catalyst such as H_2SO_4, HF, H_3PO_4, HCl, toluensulfonate acid [18], $SnCl_2$ [19], $AlCl_3$ and $ZnCl_2$ [20]. However, the reaction in homogeneous phase is very dangerous because the acid used as the catalyst is very corrosive. Therefore, the use of the solid phase heterogeneous acid catalyst in simultaneous transesterification and esterification reactions is considered as an alternative to minimize environmental damage [21].

Some solid acids have been tested as catalysts for simultaneous transesterification and esterification reactions. Zirconium oxide is used the most frequently because it has the acidity [22]. Samart et al. reported that the number of acids is one criterion for the selection of catalysts for simultaneous transesterification and esterification reactions [23]. In addition, V_2O_5 phosphate can also be used as a catalyst for simultaneous transesterification and esterification reactions. The ability of V_2O_5 phosphate as a catalyst in this reaction related with the acid side [24]. Synthesis of methyl ester has also been successfully carried out with the MoO_3 supported by SiO_2 as a catalyst [25] and Al_2O_3 [26]. However, the use of catalysts in the above still have disadvantages such as high price e.g. for zirconium, easily deactivated e.g. V_2O_5 phosphate, and the problem of *leaching* to become inactive e.g for MoO_3.

Recently, the fluoride-based materials are one of the solids that are known to have acid side and are often used as catalysts in reactions that require acid side such as in the synthesis of vitamin E [27], vitamin K [28], benzyl benzene [29], and acetylation of glycerol [30]. In addition to having an acid side, the catalytic performances of this catalyst are related to its chemical structure, high surface area, and mesoporous pore diameter [31]. Therefore, we would use fluoride-based materials such as MgF_2 and ZnF_2 as catalysts in the simultaneous transesterification and esterification reactions. The use of MgF_2 and ZnF_2 as catalysts in the reaction of crude palm oil (CPO) with methanol to methyl ester production was due to the similarity between Mg and Zn. In this experiments were demonstrated the synthesis, characterization and catalytic activity of MgF_2 and ZnF_2 as catalysts to methyl ester production by the simultaneous transesterification and esterification reactions.

2. Experimental Method

2.1. Synthesis of catalysts

The MgF_2 material was synthesized by sol-gel method (combination of fluorolysis and hydrolysis). Firstly, Mg turning was dissolved in dry methanol at room temperature for 12 hours and heated under reflux condition for 3 hours. Furthermore, the HF (48%) solution was added and stirred for 3 hours. After the aging process at room temperature, the resulting gel was dried under vacuum at a temperature of 70 ºC for 5 hours. Zn acetate was used as a precursor to prepare the ZnF_2 material. The precursor was dissolved in dry methanol at the room temperature without heated at reflux for 3 hours. Then, the steps were repeated for the synthesis of MgF_2.

2.2. Characterization of Catalyst

All samples were characterized by XRD (X-ray diffractometer) Philips X-Pert with Cu-K_α radiation source (λ = 1.54056) at 30 kV, and the speed of 1°/ min at 2θ = 20-80°. The obtaining XRD patterns were compared by diffractogram of the JCPDS-PDF database. The infrared spectrums were recorded using KBR pellets method in the range of 4000-400 cm^{-1} with an FT-IR Shimadzu spectrophotometer. TG/DTG was performed on METTLER TOLEDO through the sample-holder system (Pt/PtRh10 thermocouple). The pore size and surface area were measured by adsorption-desorption of nitrogen (N_2), while the morphology and topography of samples were observed by Scanning Electron Microscope (SEM). The methyl esters, obtained from the catalytic test, were conducted with HP6890 GC chromatography equipped with FID detector, capillary column, HP 19095N-123-HP INNOWax Polyethylene Glycol, l = 30 m, d = 0.53 mm.

2.3. Catalytic tests

The resulting materials were tested in simultaneous transesterification and esterification reactions to methyl ester production. The crude palm oil (CPO) was obtained from PT Wilmar, Indonesia. Furthermore, the simultaneous transesterification and esterification reactions of CPO with methanol at

molar ratios of methanol to CPO of 10:1, 20:1, 30:1 and 40:1 at a temperature of 150 °C for 5 hours with a stirring speed of 600 rpm and 5 wt.% concentration of CPO as the catalyst were done. Then, the mixtures were centrifuged for 15 minutes, and the residue of methanol was evaporated with a rotary evaporator. The methyl esters were analyzed by GC. The yield of catalysts toward the formation of methyl ester was determined based on the product of methyl ester obtained from the reactions. The yield of methyl ester was calculated using Eq. (1) [32]:

$$\text{Yield}\,(\%) = \frac{\text{weight of methylesters(g)}}{\text{weight of CPO(g)}} \times 100\% \quad (1)$$

3. Results and Discussion

X-ray diffraction techniques were employed to obtain the information about the structure, crystallinity, and composition of the prepared material. Figure 1 shows the XRD patterns of MgF_2 and ZnF_2. As shown in Figure 1, the MgF_2 material has three main peaks at 2θ = 27.29, 40.56 and 53.47, which indexed to the rutile structure. However, the MgF_2 sample has a structural disorder and very broad as presented in Figure 1(a). Figure 1 (b) shows the diffractogram pattern of ZnF_2 sample. As displayed in Figure 1(b), the ZnF_2 catalyst had the main peaks at 2θ = 26.69°, 34.39° and 52.98°, which matched to rutile structure. However, the ZnF_2 has a higher crystallinity structure than MgF_2 with the same structure of rutile.

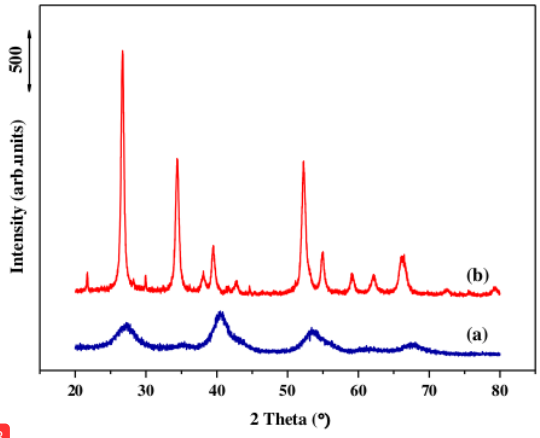

Figure 1. X-ray diffraction patterns of MgF_2 (a) and ZnF_2 (b)

The MgF_2 and ZnF_2 catalysts were also characterized by infrared spectrophotometer (FT-IR). The use of this characterization aimed to determine the chemical bond of MgF_2 and ZnF_2. Figure 2 shows the spectra of MgF_2 and ZnF_2 materials. As illustrated in Figure 2, both MgF_2 and ZnF_2 have the spectral bands at 3000-3700 cm^{-1} (♣), which indicated the presence of the adsorbed H_2O molecules and of bridged –OH group, while the bending vibrations of the H-O-H and OH group at 1640 cm^{-1} (♠) and 792 cm^{-1} (●). The bands at 418, and 490 cm^{-1} (♦) were attributed to Zn-F and Mg-F bending. As presented in Figure 2 (a)-(b), the spectral bands at 1563, 1453, 702, and 615 cm^{-1} referred to acetate group were not seen. Moreover, the bands appearing at 1026 and 945 cm^{-1} in all prepared samples, which were correlated with the existence of C-C and C-H vibrations, also did not appear. These results indicated that these samples were free of acetate group and methanol as precursors and solvents.

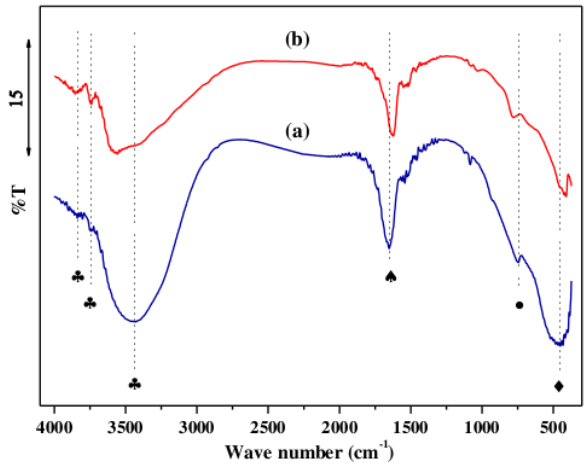

Figure 2. Fourier Transform Infrared (FT-IR) Spectra of MgF_2 (a) and ZnF_2 (b)

The information about the thermal stability of the MgF_2 and ZnF_2 samples was gathered using TG/DTG. Both TG and DTG profiles in Figure 3 and 4 showed that all samples had similar behaviors. The TG/DTG profiles of MgF_2 and ZnF_2 are presented in Figure 3 and 4. As shown in Figure 3 and 4, these samples only had one single destruction phase (150-300 °C) that indicated the loss of the -OH group on the surface of solids. As shown in Figure 3 and 4, it was not appeared the removal of HF, which was usually observed at a higher temperature, i.e. 700 °C (both TG and DTG curves). This result indicated that the MgF_2 and ZnF_2 materials were thermally stable.

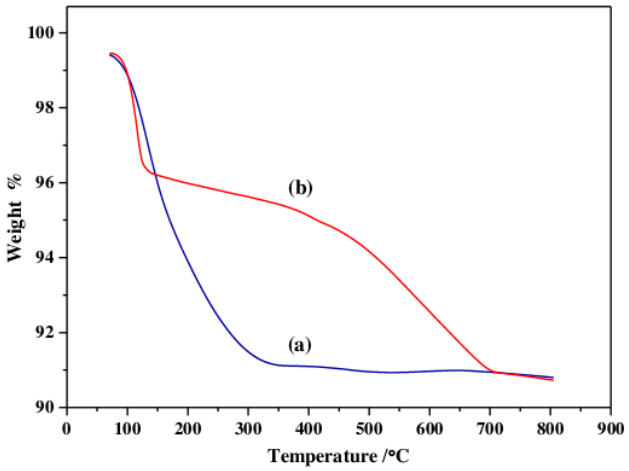

Figure 3. TG profiles of MgF_2 (a) and ZnF_2 (b)

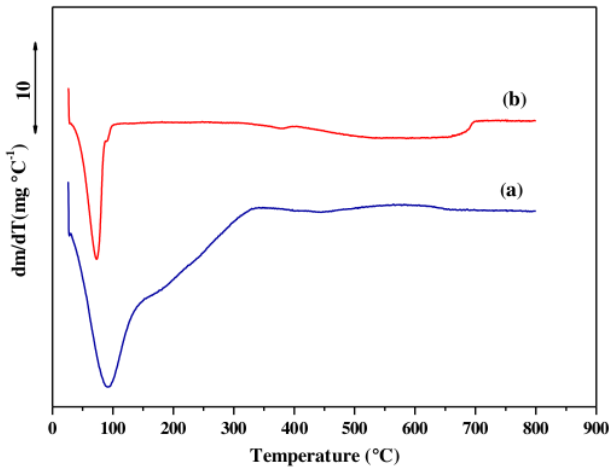

Figure 4. DTG profiles of MgF_2 (a) and ZnF_2 (b)

The porous features of catalysts were measured through the N_2 adsorption-desorption measurements. The N_2 adsorption-desorption isotherms of materials are shown in Figure 5. Based on the IUPAC classification, the MgF_2 has typical IV with H1 hysteresis loop, which showed a specific pore. While the ZnF_2 sample had typical II with H3 hysteresis loop, which referred to pores with non-uniform size. Furthermore, from pore size distribution analysis as shown in Table 1, the pore sizes of MgF_2 and ZnF_2 were 3.63 and 50.16 nm. These results showed that both of MgF_2 and ZnF_2 represent a mesoporous structures. The surface area from BET measurement of MgF_2 and ZnF_2 were 110.973 and 17 m^2/g, respectively.

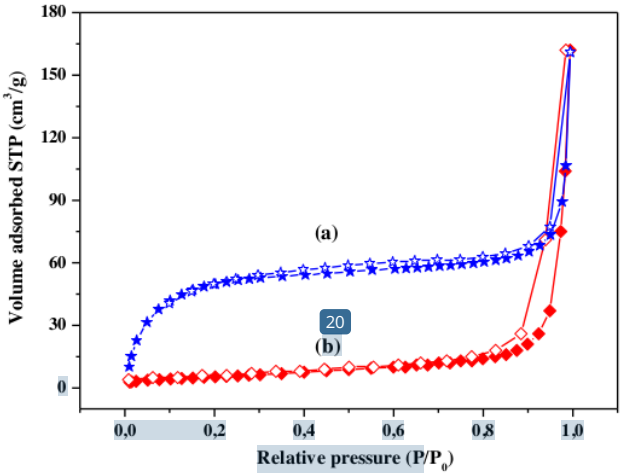

Figure 5. N_2 Adsorption-desorption isotherms of MgF_2 and ZnF_2

Table 1. Physicochemical properties of MgF_2 and ZnF_2

Catalysts	S_{BET} (m^2/g)	Pore diameter (nm)	Pore volume (cm^3/g)
MgF_2	110.973	3.6330	0.1008
ZnF_2	17	50.1568	0.2515

The morphology and topography of the catalysts were observed by Scanning Electron Microscope (SEM). The SEM image of MgF_2 and ZnF_2 is shown in Figure 6. From SEM images, it can be obtained the information that the particle size of MgF_2 and ZnF_2 was around 0.2-3.0 µm, while the morphology of these samples was similar as shown in Figure 7.

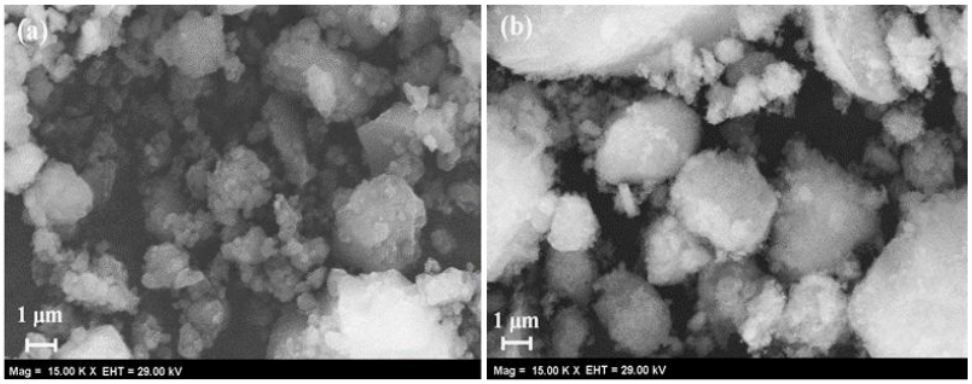

Figure 6. SEM images of MgF_2 (a) and ZnF_2 (b)

The catalytic evaluation of these catalysts in the simultaneous transesterification and esterification reactions was summarized in Table 2. As presented in Table 2, the ZnF_2 catalyst showed a higher methyl ester yield than MgF_2 of 85.21 and 26.82%, respectively. This result indicated that the crystallinity of material had advantages in the reaction with synthesis methyl ester than disorder phase. In addition, the higher activities could also be attributed to the pore diameter and pore volume of ZnF_2. It was clarified that the large pore size of the catalyst was able to adsorb more reactants and resulted in a higher catalytic activity. On the other hand, although the surface area of MgF_2 was greater than that of ZnF_2, it cannot help to improve the contact between the reactant and active site of the catalyst. It was clear that catalytic activity of these catalysts did not correlate with the surface area. Moreover, as shown in Table 2, the reaction had also been carried out with different molar ratio and showed different results. The yield of methyl ester increased together with the increase in molar ratio of CPO to methanol from 13.97 to 85.21% (ZnF_2), respectively. According to the previous research, the molar ratio of CPO to methanol is one of the important variables that influence the yield of methyl ester. Stoichiometrically, this reaction required three moles of methanol to react with one mole of triglyceride to obtain three moles of methyl ester (transesterification) and one mole of methanol to react one mol of free fatty acids to produce one mole of methyl ester (esterification). Therefore, it needed excess methanol for product formation. However, the excess of methanol could increase the polarity of reaction mixtures, and then decrease the yield of methyl ester from 85.21 to 80.99% (ZnF_2), respectively.

Table 2. The catalytic evaluation of the catalysts

Catalysts	Molar ratio	Temperature (°C)	Time (h)	Yield (%)
MgF_2	1:10	150	5	2.16
MgF_2	1:20	150	5	10.59
MgF_2	1:30	150	5	26.82
MgF_2	1:40	150	5	20.27
ZnF_2	1:10	150	5	13.97
ZnF_2	1:20	150	5	54.76
ZnF_2	1:30	150	5	85.21
ZnF_2	1:40	150	5	80.99

4. Conclusion

The synthesis of MgF_2 and ZnF_2 has been successfully prepared by sol-gel process. The resulting samples performed as heterogeneous catalysts in the simultaneous transesterification and esterification reactions for the production of methyl ester. These samples have rutile structure with a different phase (amorphous and crystal). The surface area of ZnF_2 is lower than MgF_2, but the pore size and volume of ZnF_2 are higher than that of MgF_2. However, the catalytic activity of ZnF_2 is greater than MgF_2 of 85.21% and 26.82% with the same reaction condition. In addition, the optimum conditions of reactions for finding the highest yield of methyl ester are obtained at a molar ratio of oil/methanol of 1:30, a reaction temperature of 150 °C for 5 hours with a stirring speed of 600 rpm and 5 wt.% of CPO concentration as a catalyst. The increasing methanol decreased the yield of methyl ester from 85.21 to 80.99% for ZnF_2, respectively.

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