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SYNTHESIS, CHARACTERIZATION, AND APPLICATION OF ZNO/ZSM-5 AS CATALYST IN THE CRACKING PROCESS OF PALM METHYL ESTERS

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Biofuels as environmentally friendly alternative fuels such as biogasoline, biokerosene and others are generally obtained through a cracking process and take place more effectively to attend a catalyst. In this study, the synthesis of ZnO/ZSM-5 aims to obtain a catalyst that can be used in the cracking process of Palm Methyl Esters (PME) into hydrocarbon fuels especially biogasoline. This catalyst is environmentally friendly, easy to separate, has good selectivity, and can increase the conversion of cracking products. The wet impregnation method followed by drying and calcination is the method used to synthesize the catalyst. Furthermore, several analyzes were carried out to determine the characteristics of the catalyst. The analysis is the Scanning Electron Microscopy-Energy Dispersive X-Ray (SEM-EDX), X-Ray Diffraction (XRD), N2 adsorption-desorption with BET-BJH, Temperature Programmed Desorption-NH3 (TPD-NH3) and the Temperature Programmed Reduction (TPR). Based on synthesis results obtained ZnO/ZSM-5 catalyst with ZnO content of 11.77 wt%, 13.61 wt% and 18.22 wt%. The use of this catalyst in the cracking process can result in the conversion of liquid fuel by 88.57%, heavy hydrocarbon (8.57%) and gas product (2.86%).

Key words: ZnO/ZSM-5 catalyst, impregnation, cracking, biogasoline

INTRODUCTION

Biogasoline production has begun to be widely studied and is very appropriate as a solution to find an alternative to gasoline fuel (the result of petroleum fractionation). In general, the cracking process with a catalyst or without a catalyst is used to make biogasoline and the process takes place at high temperatures and pressures [1,2]. Based on several studies on biogasoline reported in the reviews of Zandonai [2] and Xu [3], it turned out that the cracking process with a catalyst showed more effective results than without a catalyst. A catalyst can accelerate the reaction time, reduce the reaction temperature, and make a selective process for the desired reaction.

One catalyst that has a good performance for the cracking of triglycerides into biogasoline is the zeolite catalyst [3,4]. This catalyst is a heterogeneous catalyst which has many advantages because it is easy to separate, environmentally friendly [5,6,7], and does not require additives such as methanol and ethanol [1]. Another advantage is that it can control activity and selectivity. However, it is unfortunate that the resulting product yield is still low so that the zeolite performance is improved by developing metals. These metals include nickel, cuprum, zinc, platinum, paladium and aurum [1,4,8-21]. Not only that, several metal oxides (such as ZnO, NiO, CuO, PbO, MgO, and others) are also applied to zeolite catalysts to determine their performance in various processes that produce biofuels [5-7, 22-24].

Although metal oxide catalysts such as ZnO show good performance, their powder form tends to be released in the reaction mixture. This poses a problem in terms of reviewing the environmental process and regulations. Therefore, Singh and colleagues synthesized new catalysts from ZSM-5 modified with zinc oxide (ZnO) and plumbum oxide (PbO). The hydrothermal precipitation impregnation (HIP) method was used to product ZnO/ZSM-5 (mass ratio 1: 3) followed by drying and calcined from 100°C - 500°C for 3 h. The same method is used to make PbO/ZSM-5 with Pb $(NO_3)_2$ as the precursor. The catalyst performance was evaluated in the process of making biodiesel from jatropha oil and showed that the yield of biodiesel reached 93.8% [5-7].

In another study, the lamellar and pillared forms of ZSM-5 were modified with ZnO and MgO using the impregnation method have been investigated and used for fast pyrolysis process. The pyrolysis raw material is eucalyptus woodchips [23]. Incorporation of 10% wt ZnO (or MgO) into lamellar and pillared ZSM-5 using ethanol solvent, then dried in an oven and then calcined at a temperature of 450 oC for 6 hours. The presence of metal oxides deposited on the zeolite increases the Lewis acid site. The results showed that the catalyst was able to reduce the formation of polyaromatic hydrocarbons and coke and increase the amount of gas yield.

Furthermore, Abdullah has reported his research on the conversion of alcohol to hydrocarbons using the synthetic zeolite catalyst modified with ZnO/NiO [24]. The study results show that this catalyst has high activity and stability against ethanol conversion and hydrocarbon yield and prevents coke formation. The hydrocarbon yield was

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54.7%. The main products are methane, ethylene, propylene, ethyl methyl ether, and toluene.

Based on the description above, the performance of the ZSM-5 catalyst modified with metal oxide in the cracking process of vegetable oil into biogasoline is very interesting to study. Studies on this matter are still underreported. In this study, we synthesized ZnO/ZSM-5 catalyst with $ZnCl_2$ as a zinc precursor and applied it in the cracking process of palm methyl esters (PME) into biogasoline in a fixed bed reactor.

MATERIALS AND METHODS

Material

This study, ZSM-5, or zeolite Secony Mobile-5 catalyst (Si / Al ratio = 80) was obtained from Gongyi City Meiqi Industry & Trade Co., Ltd (China). Zinc chloride (ZnCl2) was purchased from the ROFA laboratory Center, Bandung under the Pudak Scientific brand, and 0.5 M NaOH solution was purchased from Rudang Jaya, Medan.

The cracking raw material is palm methyl esters (PME) facilitated by PT. Wilmar Bioenergy Indonesia, Riau-Indonesia. From the certificate of analysis of PT Wilmar Bioenergy Indonesia, it is known that PME has the following characteristics: the kinematic viscosity at 40°C is 4.457 mm2 / s, the density at 40°C is 856 kg/liter, the acid number is 0.16 grams, and the ester content is 99.1 wt %. The chemical composition of PME consists of oleic ester (52.35%), palmitate ester (33.6%), stearate ester (10.5%), and methyl laurate (3.5%).

Catalyst Preparation

In this research, 3 catalysts were synthesized, ZnO/ZSM-5 (I), ZnO/ZSM-5 (II), and ZnO/ZSM-5 (III). To simplify the name of the catalyst, the ZnO/ZSM-5 (I), ZnO/ZSM-5 (II), ZnO/ZSM-5 (III) are abbreviated as ZZ (I), ZZ (II), and ZZ (III). Each catalyst was synthesized with a different weight percent $ZnCl_2$ (16 wt% - 25 wt%). This catalyst is synthesized using zinc nitrate as a precursor for zinc [5-7, 22-24]. It is different in this study, $ZnCl_2$ was chosen as a precursor because it is cheaper and widely available.

At first, 27.5 grams of zinc chloride ($ZnCl_2$) were dissolved with 500 ml of distilled water in a beaker glass. The solution is heated to a temperature of 90°C using a hot plate and stirred with a magnetic stirrer (speed 500 rpm). Furthermore, ZSM-5 catalyst (Si / Al=80) was added to the solution, heated, and stirred at constant temperature and speed while slowly adding 1 liter of 0.5 M NaOH solution to prevent agglomeration. After 2 h of the reaction process, the solution was precipitated and separated with filter paper. The precipitate was molded into cylindrical pellets (1 cm long and 0.5 cm in diameter), then dried at 100 °C for 3 h in an oven followed by calcination at 450 °C for 4 hours.

Catalytic Cracking Process

The catalytic cracking of PME into biogasoline is carried out in a fixed bed reactor (reactor volume is 6 liters). PME as much as 3.5 liters is cracked at a temperature of 450°C with time variations (40 min - 90 min). The ZnO/ZSM-5 catalyst used was 5 wt% of PME where the mass ratio of ZnO to ZSM-5 was 1:5, 1:6 and 1:7. After being cracked according to the specified time, the final product obtained consists of liquid top product, liquid bottom product, and gas product. The liquid top product is liquid resulting from the condensation of the gas products (output from the top of the reactor). This liquid is called biogasoline if its characteristics are like gasoline (the result of petroleum fractionation).

RESULTS AND DISCUSSION

XRD Analysis

The XRD patterns for the three ZnO/ZSM-5 catalysts are shown in figure 1. Information from the XRD analysis results includes the peak position and intensity. The position indicates the cristal structure of the phase present in the ZnO/ZSM-5 catalyst.

Figure 1 shows the results with a range of 2θ=13°–67°. The three catalysts show almost the same pattern where the main peak is obtained at 2θ=23°. This is like the XRD pattern reported by Zhao for the peak of Zn/ZSM-5 catalysts [11]. The other studies also showed a peak at 2θ=23° for the peak of ZnO/ZSM-5 catalysts [6, 23, 24]. The main peak of each catalyst is ZZ (I) was obtained at 2θ=23.04°, 2θ=23.27° and 2θ=23.9°, then the ZZ (II) catalyst was obtained at 2θ=23.07°, 2θ=23.29°, and 2θ=23.93°. The ZZ (III) catalyst had the highest peak intensity. The amount of ZnO in the ZnO/ZSM-5 increases, it will increase the number of peak intensities.

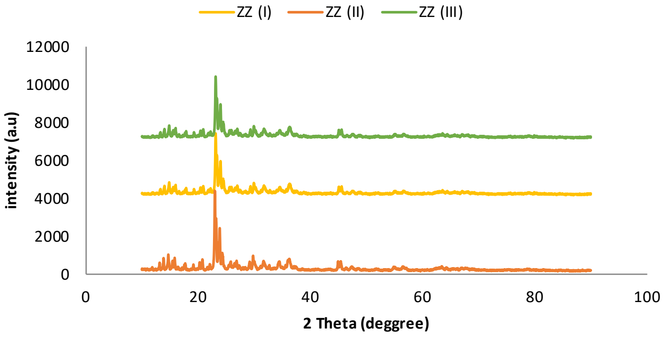


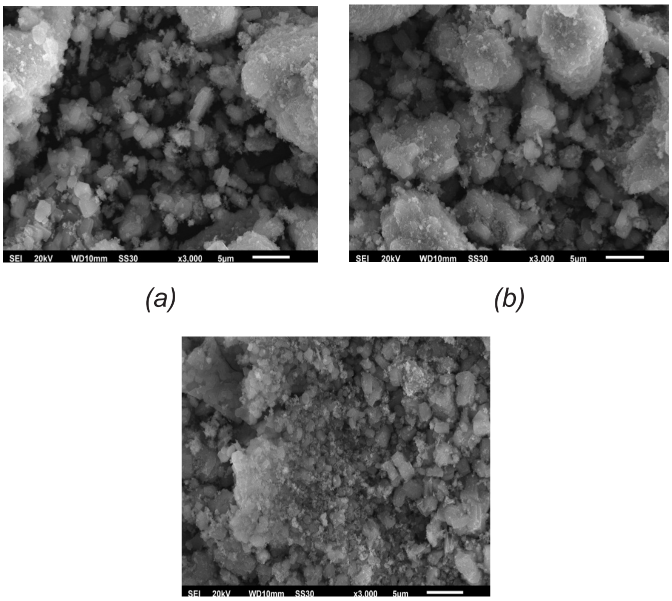
Figure 1: XRD pattern for ZnO/ZSM-5 catalyst

SEM – EDX Analysis

Figure 2.1 – 2.3 are images of SEM analysis showing the surface morphology of ZZ (I), ZZ (II), and ZZ (III) catalyst. The surface of the three catalyst is covered with white crystals. The white crystals covered more of the ZZ (II) catalyst surface with a larger size than other catalysts (fig 2.2). In Figure 2.1, part of the surface of the ZZ (I) catalyst is covered with white crystals of various sizes

and there is also a black shadow showing the carbon (C) on the surface. This is confirmed by the results of the EDX analysis which shows the presence of a carbon component (25.87%). Whereas in Figure 2.3, the surface of the ZZ (III) catalyst is coated with ordinary crystals which are smaller in size.

The components contained in the catalyst are known from the EDX analysis results which can be seen in Table 1. ZZ (I) catalyst contained 11.77 wt % ZnO and 88.23 wt % ZSM-5. ZZ (II) catalyst contained 13.61 wt % ZnO and 86.39 wt % ZSM-5. Furthermore, ZZ (III) catalyst contains 18.22 wt % ZnO and 81.78 wt % ZSM-5.



(a) (b)

(c)

Figure 2: SEM images of (a) ZZ (I), (b) ZZ (II), and (c) ZZ (III)

Component	ZZ (I) (wt%)	ZZ (II) (wt%)	ZZ (III) (wt%)
Silica Dioxide, SiO_2	58.75	66.20	76.35
Alumina oxide, Al_2O_3	1.42	1.41	1.84
Zink Oxide, ZnO	11.77	13.61	18,22
Copper (II) Oxide, CuO	1.69	1.46	1.20
Sodium Oxide, Na_2O	-	2.69	1.90
Carbon, C	25.87	13.03	-
Chloride, Cl	0.50	1.61	0.49

N_2 Adsorption - desorption with BET – BJH Methods

Table 2 shows the pore size, pore volume and surface area of ZZ (I), ZZ (II), ZZ (III). The catalyst surface area decreases as the amount of ZnO in catalyst increases. This may be due to metal oxide particles (ZnO) covering part of the surface of the catalyst so that the results of calculations by the tool show that the surface area of the catalyst is getting smaller [23, 24]. This can be seen in the ZZ (III) catalyst which contains the most ZnO than other catalyst but has the smallest area (SBET = 188.490 m2/g). BET analysis results for ZnO/P-ZSM-5 and ZnO/L-ZSM-5 catalysts were the same as those reported by Fermoso [23]. Abdullah also reported this, where the increasing amount of ZnO made the surface area of the NiO/ZnO/HZSM-5 catalyst smaller [24].

Figure 3 shows the N_2 adsorption-desorption isothermal curves of ZZ (I), ZZ (II), and ZZ (III) catalyst. In this curve the amount of substance adsorbed per unit solid mass (volume) is plotted against the relative equilibrium pressure (P / Po). The curve increases in the catalyst as the relative pressure of the equilibrium increases. Based on the classification of adsorption isotherms recommended by IUPAC (1985), the adsorption isotherm forms of ZZ (I), ZZ (II) and ZZ (III) catalysts are classified into type I and type IV. The curve slowly rises when the relative pressure (P / Po) is low, as well as at medium pressure until it is relatively close to the value of one. Type I is generally represented by micropore solids (< 2 nm), an example of which is the molecular sieve zeolite. Therefore, the ZZ (II) catalyst which has a size of 17.051 Å or 1.7051 nm is included in type I. This is made clear by the new classification of adsorption isotherms based on the IUPAC Technical Report by Thommes et al which classifies the type I adsorption isotherm into 2, namely types I (a) and I (b) which can be seen in Figure 3.1. The adsorption isotherm of ZZ (II) catalyst tends to be of type I (b) with a larger pore size distribution in the micropore range and the possibility of a narrow slit mesopore (<~ 2.5 nm).

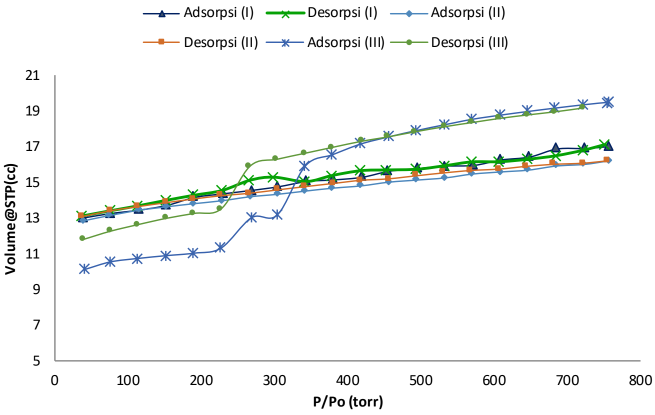


Figure 3: N_2 adsorption – desorption isothermal catalyst curve ZZ (I), ZZ (II), and ZZ (III)

The adsorption isotherm curves of ZZ (I) and ZZ (III) catalysts are included in type IV which has a characteristic that is a plateau at the end of saturation. The curve increases rapidly at low relative pressure (P / Po), then rises quite sharply in the middle and increases rapidly until the relative pressure approaches the value of one. This type is made clear from Figure 3.1 where the two catalysts tend to be Type IV (a) with capillary condensation accompanied by hysteresis [26].

Figure 4 shows the pore size distribution of the ZZ (I), ZZ (II), and ZZ (III) catalysts. Based on IUPAC recommendations (1985), the pore sizes consist of: (a). macropores with a diameter> 50 nm, (b). mesopore with a diameter

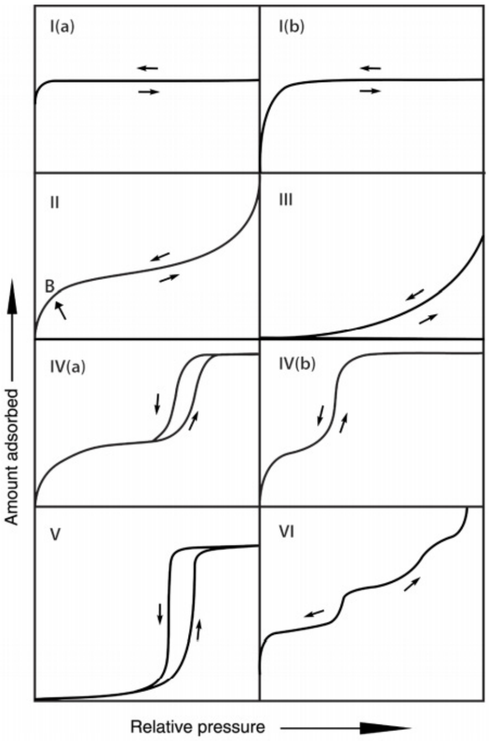


Figure 3.1: Classification of adsorption isoterm [26]

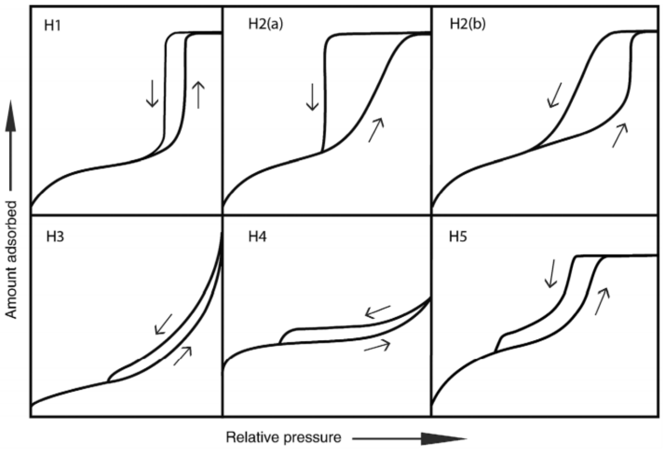


Figure 3.2: Classification of hyteresis loops [26]

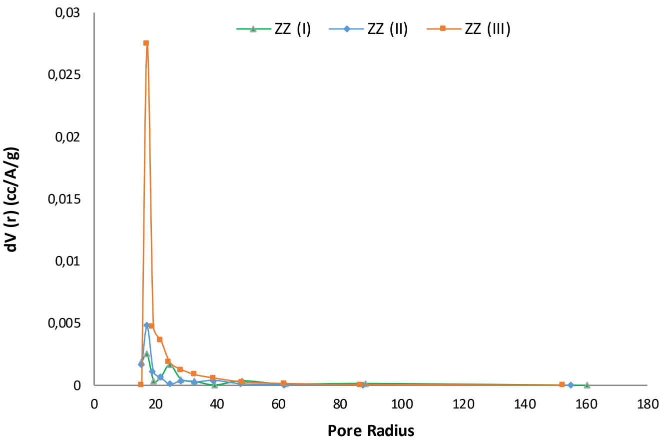


Figure 4: Pore Size Distribution

of 2 - 50 nm and (c). micropores with a diameter of < 2 nm [26]. The measurement results for ZZ (I), ZZ (II) and ZZ (III) catalysts with the BJH adsorption method shown in Figure 4 show that the pore sizes for the three catalysts are around 17 Å or 1.7 nm. This size is classified as a micropore size, where the curve is shown by a red arrow at the peak of the highest graph which is at the size of 17 Å or 1.7 nm. Meanwhile, the pore size distribution is minor in the micropore region (15 Å - 19 Å) and most of it is in the mesopore size (21 Å - 160 Å). This can prove that the hysteria loop that occurs in Figure 3 is due to the presence of mesoporous pores.

TPD-NH$_3$

The catalyst first went through the pretreatment stage by heating it at 40°C for 90 minutes in He (inert) gas conditions. Then proceed with the NH3 adsorption stage (5% in He) carried out at 100 °C for 30 minutes, then blended with He (inert) gas at the same temperature for 30 min. In the last step, NH3 desorption is carried out at a temperature of 100–700°C with a temperature increasing rate of 10°C/minute, then held for 10 minutes at a temperature of 700°C. The whole gas flow rate is 15 cm. TPD-NH3 profiles for ZZ (I), ZZ (II), and ZZ (III) catalysts are shown in figure 5.

The acid site of the ZnO/ZSM-5 catalyst is Bronsted acids and Lewis's acids. According to the Bronsted-Lowry concept of acids and bases, an acid is a substance that can give off positively charged hydrogen ions or protons (H+) Meanwhile Lewis acids are electron-pair acceptors that can include acids that do not contain hydrogen or removable protons [28]. On catalysts, especially solid catalysts, it can be said to have Brønsted acidity when in the solution system the catalyst will dissociate on its surface and produce hydrated protons. The reactants that have proton acceptor properties will be deprotonated on the surface of the catalyst, causing the reactant structure to be unstable and lowering the activation energy when there is a chemical reaction with other reactants.

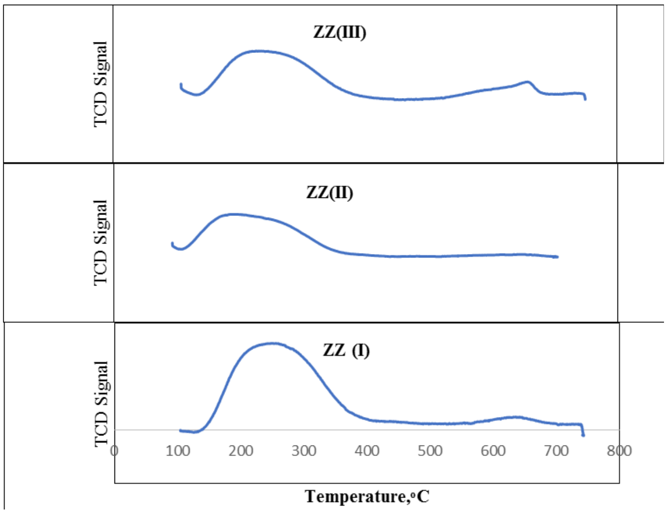


Figure 5: TPD-NH$_3$ Profile for ZZ (I), ZZ (I), and ZZ (III) catalyst

Examples of Bronsted acids and Lewis's acids on the zeolite molecular framework and ZnO/ZSM-5 catalyst are shown in figure 5.1 and fig 5.2.

In the PME cracking process, Brønsted acidity plays an important role in the protonation stage of the reactants and the interaction with pi (π) bonds. The proton (H+) will bind to the hydrocarbon compound whose bond is broken from the methyl ester so that according to the function of the catalyst is selectivity, short chain hydrocarbon compounds can be formed (R1, R2, R3, R4). Role of acid sites in the cracking reaction mechanism of PME can be seen in Figure 5.3.

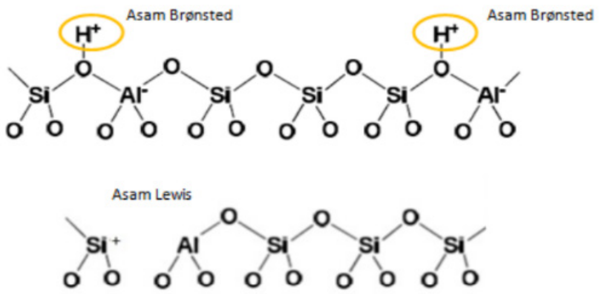


Figure 5.1: Bronsted acids and Lewis's acids in the Zeolite molecular framework [29]

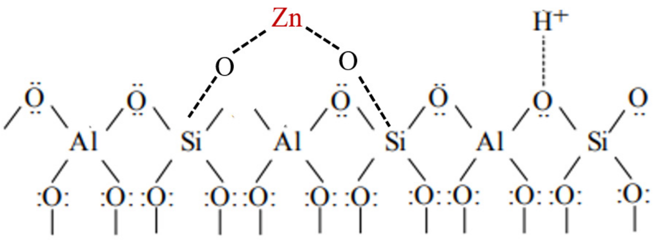


Figure 5.2: Acid sites of ZnO/ZSM-5 catalyst [30, 31]

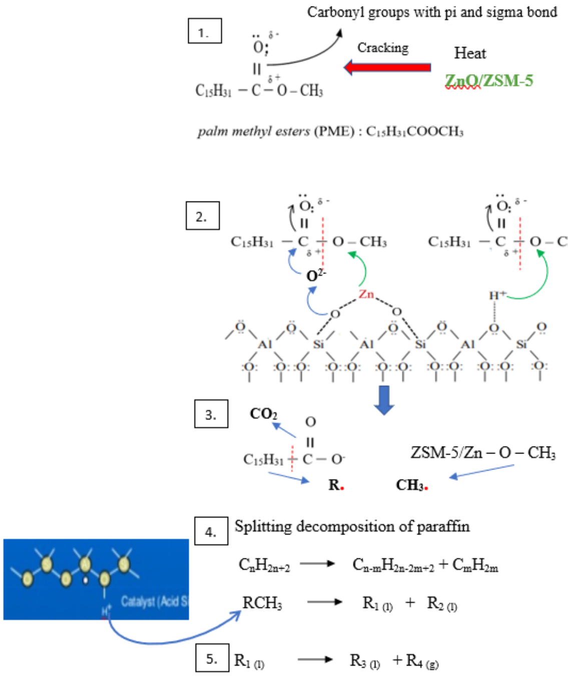


Figure 5.3: Role of acid sites in the cracking reaction mechanism of PME [32, 33]

TPR Analysis

Figure 6. shows the TPR profile of the ZZ (I), ZZ (II), and ZZ (III) catalyst. The area of three catalyst will decrease as the number of ZnO increases. This can be seen from figure 6 where ZZ (III) < ZZ (II) < ZZ (I). ZZ (I) contains the least amount of ZnO (11.77 wt %) but has the largest area based on this analysis (1.44674).

Catalytic Cracking Process

The use of ZZ (I), ZZ (II), and ZZ (III) catalyst in the cracking process affect the conversion of the resulting liquid fuel product. PME cracking is also carried out without the use of a catalyst as a comparison. The number of product conversions can be calculated using equation 1 [25].

$$Conversion=\frac{amount\ of\ biofuel\ collected}{amountofoilused}\times 100\% \qquad (1)$$

From these calculations 1, it is known that the highest conversion is obtained from cracking of PME using ZnO/ZSM-5 (II) catalyst, which is 88.57% (liquid top product), 8.57% (liquid bottom product) and 2.86% (gas product) as shown in Figure 7. The effect of various catalyst on the conversion of top liquid products at different residence times, constant reaction temperature (450 °C), and the ratio ZnO/ZSM-5: PME = 1: 20 is shown in figure 8.

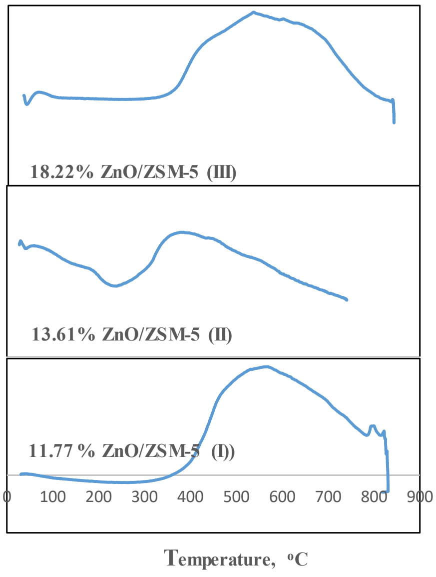


Figure 6: TPR Profile for ZZ (I), ZZ (II), and ZZ (III)

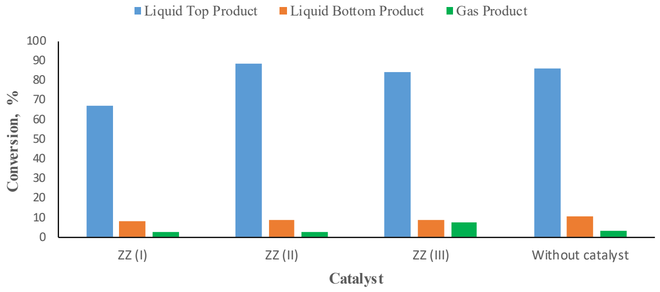


Figure 7: Conversion Graph of PME Cracking Product (T = 450 °C)

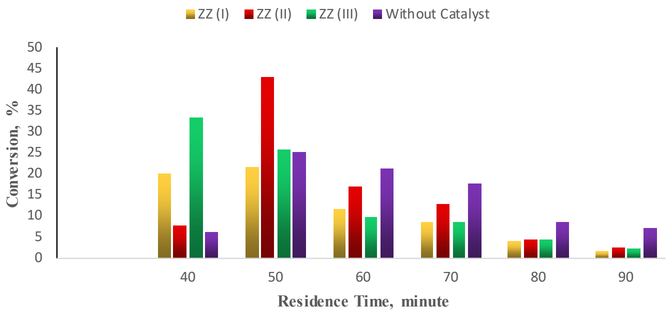


Figure 8: Liquid Top Product Conversion Graph from PME Cracking (T=450°C)

CONCLUSION

The characteristics of the ZZ (I), ZZ (II), and ZZ (III) catalysts after being tested showed differences. From the SEM EDX results, each catalyst has different ZnO content, namely 11.77 wt%, 13.61 wt%, and 18.22 wt%. The surface area of catalyst (SBET) decreases with the increase in the amount of ZnO. This may be due to metal oxide particles (ZnO) covering part of the surface of the catalyst so that the results of calculations by the tool show that the surface area of the catalyst is getting smaller [23, 24]. The acidity of the catalyst greatly affects the activity and selectivity of the catalyst's performance in the cracking process of Palm Methyl ester (PME). This affects the product to be obtained in this study, namely liquid fuel products (short chain hydrocarbons C_5 to C_{10} equivalent to gasoline). The palm methyl ester (PME) cracking reaction requires a catalyst that has a lot of active acid sites so that the liquid product is formed optimally. From the analysis results of TPD for ZnO/ZSM-5 catalyst showed that ZZ (III) has the highest acidity value (0.5833 mmol/g) and produced the highest product conversion (88.57%) compared to others catalyst and without a catalyst.

ASSOCIATED CONTENT

Palm Methyl Esters (PME) is available free of charge from PT. Wilmar Bioenergy Indonesia, Riau-Indonesia.

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