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Research Article

Production of Hydrocarbon (C_7-C_{20}) from Hydrocracking of Fatty Acid Methyl Esters on Pd/Al-MCM-41 Catalyst

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Abstract

The production of hydrocarbon (C_7-C_{20}) and alcohol (C_{11}-$C_{1}9$) from fatty acid methyl esters (FAMEs) compound are produced from the transesterification of the seed oil of the *Nyamplung* that has been conducted by the catalytic hydrocracking using Al-MCM-41 and Pd^{2+}-impregnated-Al-MCM-41 catalysts. The performance of catalysts were compared by various analysis including the acidity that was determined by pyridine and FTIR, the crystal structure observed by XRD, the surface area and pore volume analyzed by BET/BJH, the surface morphology observed by TEM, the metal on the surface of catalyst observed by XPS and the product of the hydrocracking analyzed by GC-MS. Hexagonal structure of the MCM-41(100) was shown in the $2\theta = 3^o$-5^o of the diffractogram. The presence of impregnated Al and Pd observed at the $2\theta = 20^o$ and 34^o, respectively. The Pd/Al-MCM-41 catalyst was more acidic than Al-MCM-41 catalyst. The surface area and pore volume of the catalyst decreased after the impregnation process. The tendency of catalytic hydrocracking of hydrocarbon produced was indicated that more amount of Palladium have more hydrocarbons aliphatic than alcohol. Copyright © 2017 BCREC Group. All rights reserved

Keywords: Biogasoline; Oil seeds; Hydrocracking; Pd/Al-MCM-41

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1. Introduction

The short supply of unrenewable energy has been encouraging scientist to look for the alternative energies. One of the main important route is to produce a biogasoline which can be renewable. Biogasoline is a gasoline which is made from vegetables sources consisting C_4-C_{11} hydrocarbon, which can be linear, cyclic, saturated or unsaturated and could be mixed with ketones and alcohols. In the south coast of Madura Island, *Nyamplung* (*Calophyllum inophyllum*) plants are still available abundantly and its seed oil is rich with triglycerides (around 90 % of dry weight) [1]. The synthesis of fatty acid methyl esters (FAMEs) compounds from seed oil of the Nyamplung through transesterification using Al-MCM-41 catalyst has been reported in our previous paper [2]. The next stage of this proc-

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ess is to convert the FAMEs to biogasoline by a cracking reaction. Catalytic hydrocracking is one type of cracking process that convert FAMEs compounds into hydrocarbon fractions using active acid sites available in the chemical structure of a catalyst.

A well known MCM-41 catalyst has few acid sites but it has advantage in terms of porosity as its pores lie in the mesoporous size. It was reported [3,4] that impregnation of Al metal to the MCM-41, i.e. Al-MCM-41, increased the amount of the acid sites and this lead to a potential material to be used as catalyst in a cracking reaction. Moreover, the change in ratio of Si/Al due to the change of Al component in the structure of the catalyst could influence to the reactivity of the catalyst. Other report Deongseong [5], impregnation of Pd^{2+} on MCM-41 makes an important Pd/SiO_2 ratio and effectively gives different properties in turn. The magnitude of metal impregnated to a catalyst is expected to increase the rate of the reaction involved. Hydrocracking reactions have been reported extensively. Similarly, Deongseong [5] tried to synthesize methanol from carbon monoxide with hydrogen gas to observe the change of the role of Pd metal to the catalyst where it can provide a better conversion than other derivatives of MCM-41. Wang [6] reported the properties and performance of Zr(sulphated)-MCM-41 which managed to catalyze the isomerization of hydrocarbons. Feng [7] and Mastalir [8] reported their study in catalytic activity of Pt-MCM-41 for the catalytic hydrogenation reactions of toluene. In this research, in contrast to Feng and Mastalir, we are focusing increased levels of hydrocarbons and alcohols formed in the process at various catalysts. We have upgrading the Al-MCM-41 by impregnation of various palladium, and conducted catalytic hydrocracking reactions using Al-MCM-41 and Pd/Al-MCM-41 catalysts to obtain biogasoline which its consist of more hydrocarbon and less of alcohol [9]. The cracking has been done within a semi continuous reactor.

2. Materials and Method

2.1 Materials

Paladium chloride (59 % Pd anhydrous), sodium aluminate (PA), tetraethylorthosilicate (PA), and ethyltriamonium bromide (PA) have been supplied by Sigma Aldrich. Phosphoric acid (PA), methanol (99,8 %), n-pentana (95 %), and pyridin (99,9 %) received as it were from Merck. A sample of crude oil of *Nyamplung* (*Calophyllum Inophyllum*) was produced in our laboratory.

2.2 Synthesis of Pd/Al-MCM-41

Catalyst Pd/Al-MCM-41 was synthesized by hydrothermal technique according to the procedure of Papp [10], using a wet impregnation method. The Al-MCM 41 catalyst was soaked in 5 % (w/w) or 10 % (w/w) of $PdCl_2$ solution. All the materials was stirred homogeneously at room temperature in the reactor, then the mixture was heated for 6 h to evaporate the solvent. The process was continued with calcination step. The temperature of the reactor was then increased to 550 ^{o}C in nitrogen atmosphere, changed to normal air after 1 hour, and kept the condition for 6 hours. The final step was to changed nitrogen atmosphere to hydrogen, while kept the temperature at 150 ^{o}C. The red-brown solid was obtained after it was dried and stored in a desiccators for 24 hours prior to be characterized [11].

2.3 Characterization of catalysts

Samples for acidity has saturated steam of pyridine absorption and measured by FTIR. The samples for transmission electron microscopy (TEM) were sonically dispersed in ethanol and transferred to carbon-coated copper grids. TEM observations were conducted using a JEOL 1010 electron microscope. The high resolution transmission electron microscopy (HRTEM) was recorded on a JEOL 2100 microscope operated at 200 kV. The samples were prepared by dipping a carbon film-coated Cu micro grid into the suspension.

X-ray photoelectron spectroscopy (XPS) were acquired on a Kratos Axis ULTRA X-ray photoelectron spectrometer incorporating a 165 mm hemispherical electron energy analyzer and a monochromatic Al Kα (1486.6 eV) radiation at 150W (15 kV, 10 mA). Survey (wide scans were taken at an analyzer pass energy of 160 eV and multiplex (narrow) high resolution scans at 20 eV. Base pressure in the analysis chamber was 1.0 x 10^{-9} Torr and it increased to 1.0 x 10^{-8} Torr during sample analysis. The binding energies were determined using the C1s line at 284.6 eV from adventitious carbon as a reference. Recorded spectra were fitted using Gaussian-Lorentzian curves in order to determine the binding energies of the different element core levels more accurately.

The N_2 adsorption measurements of the calcined samples were performed using a Tristar II 3020. Surface area calculations were carried out using the Brunauer-Emmett-Teller (BET) methods, while pore size distribution was estimated from the desorption branch of the isotherms using the Barrett-Joyner-Halenda (BJH) method. Prior to the measurements, the samples were degassed at 150 °C for 12 h under high vacuum [12].

2.4 Catalytic activity

The *nyamplung* seeds were provided from the coastal area of the southern Bangkalan City of Madura Island. The samples were dried until the moisture content below 5 % and were squeezed using hydraulic press to obtain raw oil of the *nyamplung*. Phosphoric acid was added to carry out degumming process. The transesterification reaction was carried out by the addition of methanol. FAMEs compounds obtained by 98.15 %. The mixture of hydrocarbon and alcohol obtained was placed in a 250 mL round flask with 3 necks. The solution was finally stirred with constant speed at 200 rpm. All products were analyzed using GC-MS Shimadzu [9].

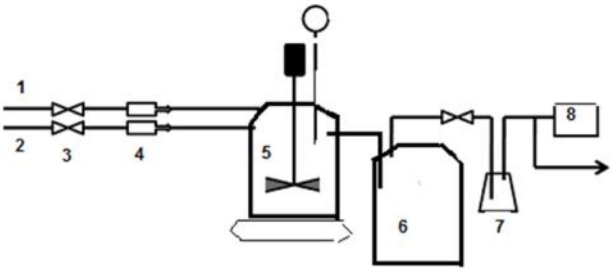

Figure 1. Diagram of catalytic activity setup for catalytic cracking of the FAMEs, 1. N_2 gas inlet; 2. FAMEs inlet; 3. Valve; 4. Mass flow meter; 5. Reactor with stirrer and thermocouple; 6. Cracking reactor; 7. Condenser; 8. GC-MS

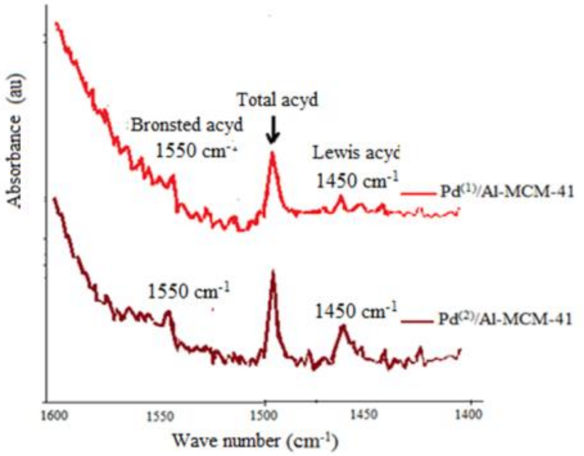

Figure 2. FTIR spectrogram of pyridine adsorption

3. Results and Discussion

3.1 Characterizations

The acidity of catalyst was measured by a pyridin adsorption FTIR as presented in Figure 2. The acidity of catalyst contents tend to increase, while the palladium impregnated in Al-MCM-41 by 65.2 % and 78.2 % whilst the amount of palladium raise two times, respectively. So, it gives an impact on the material properties of the catalyst, resulting in a change in the composition percentage of metallic Al and Si. The performance of the catalyst will subsequently be observed from GC-MS data which show the products of the hydrocracking catalysis. The result of percentage Pd on surface, showed XPS in Figure 3.

The diffractograms of both catalysts are depicted in Figure 4. It shows low angle reflections of the crystal in the field (100), (110), and (200) which are the characteristic angles of Al-MCM-41 catalyst (2θ = 1-5°) together with the very low intensity of Al peak observed at 2θ of 20°. It also shows Pd peak at 2θ of 34 (111), 42, 55, 61° as the result of the Pd impregnation. The decreasing intensity of this 2θ of the mesoporous catalyst Al-MCM-41 indicates that the Pd metal impregnation does not influence the basic structure of the catalyst.

Table 1 describes the characteristics of nitrogen adsorption on the catalysts showing the decrease in surface area and pore volume of Pd modified catalysts. The Al-MCM-41 has larger surface area than Pd/Al-MCM-41. The surface area decreased by 18.99 % as some spaces in the surface were occupied by palladium and the pore volume decreased by 11.98 %. The pore radius of the Pd modified catalyst, how-

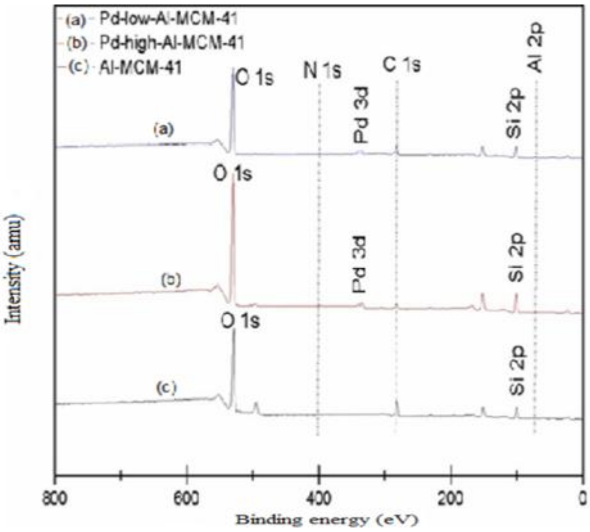

Figure 3. XPS Spectra (a) Pd(1)/Al-MCM-41, (b) Pd(2)/Al-MCM-41 and (c) Al-MCM-41

ever, increased by 0.85 % because palladium may prefer to be adsorbed in the small pore and deposited on the mouth of the small pore.

The morphology TEM of the catalysts was shown in Figure 5. Hexagonal shape still can be observed on both catalysts which have pore holes in the middle indicating the impregnation of the Pd metal that does not damage the basic structure of the silica mesoporous.

3.2 Catalytic testing for cracking process

The chromatogram of the product (FAMEs compounds) of the transesterification reaction can be seen in Figure 6. The chromatogram shows that the FAMEs compounds is 98.15 % consisting of peak (1) 20.86 % methyl palmitic, (2) methyl oleic 59.25 % and (3) 18.04 % methyl stearic. Figure 7 is the chromatograms showing the performance of the Pd$^{(1)}$/Al-MCM-41 (b) and Al-MCM-41 (a) catalysts on catalytic hydrocracking processes, respectively.

The component compounds of the products of the catalytic hydrocracking process for Pd/(1)Al-MCM-41 and Pd(2)/Al-MCM-41 catalyst were shown in Table 2. The hydrocarbon as much as 91.94 % hydrocarbon and 3.24 % alcohol were produced by Pd(1)/Al-MCM-41 catalyst, but 100.0 % were produced by Pd(2)/Al-MCM-41 catalyst, and both of them using 98.15 % FAMEs (methyl palmitic, methyl oleic and methyl stearic) feed from *nyamplung* oil seed. The significant different in this performance was due to the role of the acidity, and pore radius of the catalyst. Although Pd(1)/Al-MCM-41 catalyst have more surface area than Pd(2)/Al-MCM-41, but the catalytic cracking happened in the pore not in surface of catalyst, which the values was quite different. It was clearly seen that the ability of cracking power both of catalyst is powerful. Special interest is processing of a mixture of vegetable and petroleum feedstocks. The authors [11] studying the transformations of a mixture of olefins with paraffins and naphthenes, observed an increase in conversion, i.e. a synergetic effect during their joint transformations. An optimal ratio of vegetable oil (a source of olefins) and vacuum gas oil (paraffins and naphthenes) pro-

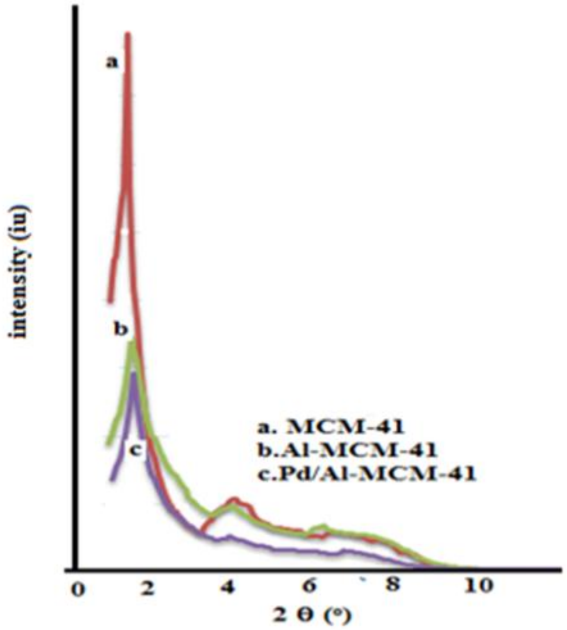

Figure 4. SAXRD diffractogram of the catalysts

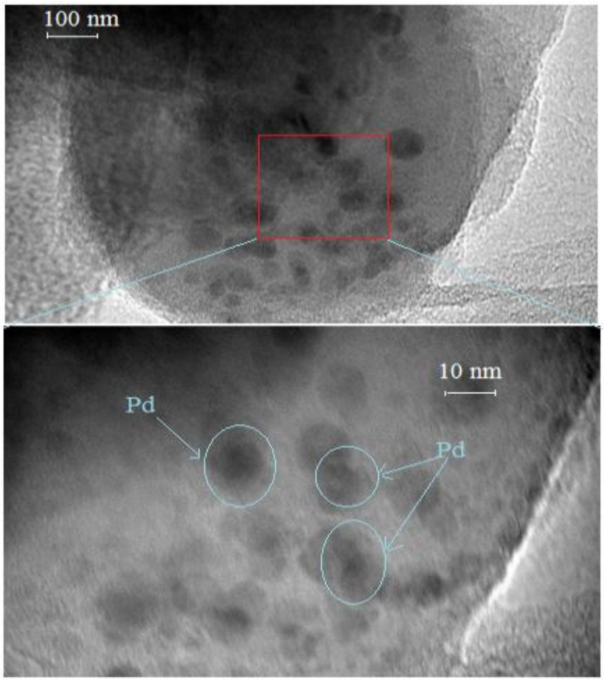

Figure 5. High resolution TEM micrographs of Pd/Al-MCM-41 catalyst

Table 1. Analysis of nitrogen adsorption (BET) and acidity

Catalyst	Surface area (m^2/g)	Pore volume (cc/g)	Pore radius (Å)	Total acidity (mmol/gram)
Pd^{1}Al-MCM-41	576.55	0.5565	37.50	0.0360
Pd^{2}Al-MCM-41	260.93	0.3179	47.50	0.0626

viding a maximum synergetic effect upon transformation of the blend feed should exist. The amount and kind of hydrocarbon were little different because the different of sources, and we can say that the Pd(2)/Al-MCM-41 catalyst more powerful to produce of hydrocarbon by catalytic cracking.

From Figure 8, the curve shows that formation of hydrocarbon and alcohol tends to elevation beside the addition of palladium. The contribution of the active site could be understood from another point of view. For some triglyceride feeds, conversions have difficulty reaching their cracking limits. As heavy molecules have a higher probability of accessing the catalyst surface [13] and relieve the pressure of the surface catalyst by transferring C–H bond. However, the activity of the catalyst has to be controlled by temperature.

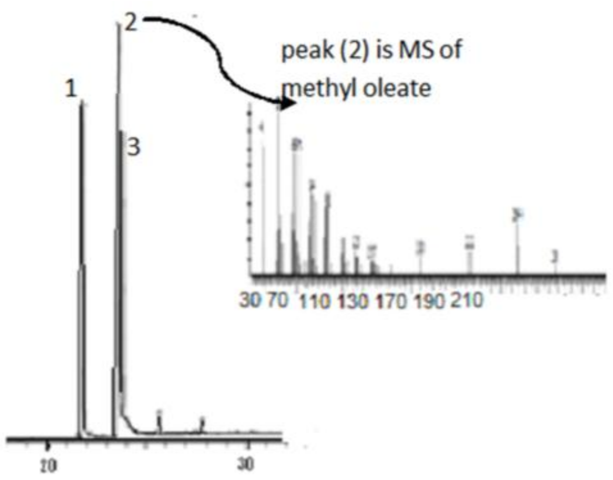

Figure 6. GC-MS chromatograms of FAMEs compounds

Table 2. Summary of compound catalytic hydrocracking reactions

Compound/molecule	$Pd^{(1)}$/Al-MCM41 (%)	$Pd^{(2)}$/Al-MCM41 (%)
C_7 hydrocarbon	3.93	--
C_8 hydrocarbon	-	4.18
C_9 hydrocarbon	-	-
C_{10} hydrocarbon	16.49	-
C_{11} hydrocarbon	40.38	47.56
C_{12} hydrocarbon	16.96	33.93
C_{13}-C_{20} hydrocarbon	14.17	14.33
C_{15}-C_{19} esther	4.82	-
C_{11} alcohol	3.24	-

4. Conclusions

The following conclusion can be drawn from the synthesis of Al-MCM-41 and Pd/Al-MCM-41 catalysts and the catalytic hydrocracking of FAMEs, it is found that Al-MCM-41 and Pd/Al-MCM-41 catalysts synthesized in the same procedure conducted in this research has a different amount content of the acidity. The surface area of the catalyst decreased by 18.99 %, the pore volume decreased by 11.98 % and the pore radius increased by 0.85 % when Pd metal was impregnated to the structure of the Al-MCM-41 catalyst. The acidity as well as the pore size of catalyst a significant role in the catalytic cracking of FAME. The catalytic hydrocracking reactions using Al-MCM-41 and Pd/Al-

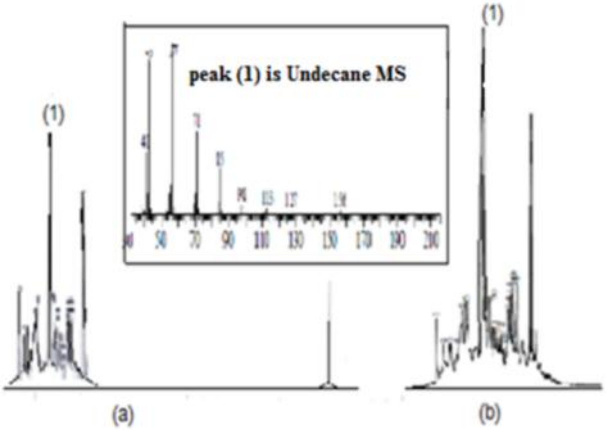

Figure 7. GC-MS chromatograms of the reaction product using $Pd^{(1)}$/Al-MCM-41 (a), and Pd^{2}/Al-MCM-41 (b)

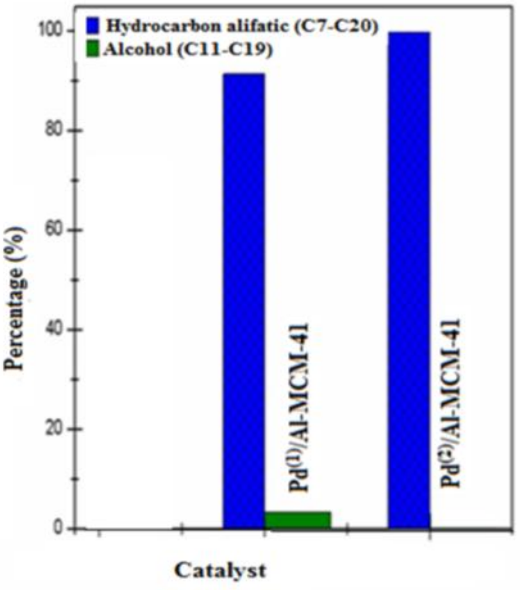

Figure 8. Hydrocracking activity of the different catalysts at 200 °C

MCM-41 catalysts produced different products components. The production of hydrocarbon tends to increase otherwise the production of alcohol tends to decrease when impregnation of palladium put more on the Al-MCM-41 catalyst.

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