THE INFLUENCE OF Pd IMPREGNATION INTO Al-MCM-41 ON THE CHARACTERS AND ACTIVITY FOR BIOGASOLINE PRODUCTION BY CATALYTIC HYDROCRACKING OF FAMEs FROM NYAMPLUNG SEED OIL (*Calophyllum Inophyllum*)

Hendro Juwono[1,2,*], Triyono[2], Sutarno[2], and Endang Tri Wahyuni[2]

[1]*Department of Chemistry, Institut Teknologi Sepuluh Nopember, Kampus ITS Sukolilo, Surabaya 60111, Indonesia*

[2]*Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Gadjah Mada, Jl. Sekip Utara, Yogyakarta 55281, Indonesia*

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ABSTRACT

Biogasoline have been synthesized through catalytic hydrocracking reaction against FAMEs compounds (fatty acid methyl esters) obtained from the transesterification of Nyamplung seed oil. The performance of Al-MCM-41 and Pd/Al-MCM-41 as the catalytic hydrocracking was compared. In this research, the influence of Pd impregnation into Al-MCM-41 catalyst on the characters and catalytic activity has been evaluated. The characters determined were crystallinity by using X-Ray Diffractometer (XRD), Si/Al ratio by Inductively Coupled Plasma (ICP), the acidity by pyridine adsorption, the surface area and pore volume by surface area analyzer and the morphology by Scanning Electron Microscopy (SEM). Catalytic activity was examined for hydrocracking of free fatty acid methyl esters (FAMEs) produced from the transesterification of Nyamplung seed oil, by Hydrogen flowing. The research result showed that impregnation of Pd into Al-MCM-41 has been successfully carried out, which did not destroy the structural morphology of the catalyst. It was also discovered that the Pd impregnation could increase Si/Al ratio and the acidity but it leads to decrease in the catalyst surface area and the volume. Furthermore, Pd impregnated Al-MCM-41 showed superior activity compared to Al-MCM-41 for FAMEs hydrocracking. The superiority was indicated by higher effectiveness and yields selectiveness, that were 100% hydrocarbon composed of C9-C18 that was dominated by C12 emerging the gasoline fraction, compared of that by the results used Al-MCM-41 catalyst that were 97% hydrocarbon consisted of C8-C20 with equal abundance.

Keywords: *biogasoline; oil seeds of nyamplung (calophyllum inophyllum); catalitic hydrocracking; FAMEs; Al-MCM-41; Pd/Al-MCM-41*

ABSTRAK

Telah disintesis biogasolin melalui reaksi katalitik hidrorengkah terhadap senyawa FAMEs (fatty acid methyl esters) yang diperoleh dari hasil reaksi transesterifikasi minyak biji nyamplung. Katalitik hidrorengkah dilakukan dengan membandingkan 2 katalis yang digunakan yaitu Al-MCM-41 dan Pd/Al-MCM-41. Dalam penelitian ini dipelajari pengaruh impregnasi Pd pada katalis Al-MCM-41 terhadap ratio Si dan Al, struktur kristal, keasaman katalis luas permukaan dan volume pori katalis, morfologi permukaan katalis, serta aktivitas katalitik pada hidrorengkah. Ratio Si/Al ditentukan dengan metode ICP, dampak terhadap kekristalan struktur katalis ditentukan dengan XRD, keasaman dengan adsorpsi piridin, luas permukaan dan volume pori dengan surface area analyzer, morfologi dengan SEM dan hasil proses hidrorengkah dengan metode GC-MS. Hasil penelitian menunjukkan bahwa proses impregnasi Pd pada AL-MCM-41 telah berhasil dilakukan sebagaimana ditunjukkan oleh munculnya puncak difraksi pada sudut $2\theta = 34°$. Terimpregnasinya Pd pada Al-MCM-41 telah meningkatkan ratio Si/Al dan keasaman, namun menyebabkan penurunan luas permukaan dan volume pori katalis. Foto SEM memastikan bahwa impregnasi Pd tidak menyebabkan kerusakan kerangka struktur Al-MCM-41. Katalis Pd/Al-MCM-41 menunjukkan aktivitas unggul daripada katalis Al-MCM-41 pada proses hidrorengkah. Keunggulan tersebut ditunjukkan oleh hasil proses yang lebih efektif dan selektif, yaitu berupa hidrokarbon 100% terdiri dari C9-C18 dan didominasi oleh C12 yang merupakan fraksi gasolin, dibandingkan hasil proses dengan katalis Al-MCM-41 yang berupa hidrokarbon 97% terdiri dari C8-C20 dengan kelimpahan yang setara.

Kata Kunci: *biogasolin; minyak biji Nyamplung; katalitik hidrorengkah;senyawa FAMEs; Al-MCM-41; Pd/Al-MCM-41*

* Corresponding author.
Email address : nehin66@chem.its.ac.id

INTRODUCTION

The short supply of unrenewable energy has been encouraging scientist to look for the alternative energies. One of the alternative energy is biogasoline, that can produced from renewable feedstock such as seed of Nyamplung oil containing around 90% of dry weight [1]. For gasoline production from Nyamplung seed oil. The triglycerides in the Nyamplung oil have to be converted into free fatty acid methyl esters (FAMEs) through transesterification in the presence of catalyst, and the used of Al-MCM-41 catalyst has been reported [2]. Then the FAMEs produced were cracked by flowed Hydrogen called hydrocracking. By the addition of catalyst having active acid sites, included MCM-41.

MCM-41 catalyst has porosity lying in the mesopores which was match with the triglycerides size resulted effective catalytic reaction. However, the number of the acid sites provided catalytic activity was relatively low leading to a less effective hydrocracking reaction. The acid sites have been increased by impregnation of Al metal into MCM-41 called Al-MCM-41 [3] but the acid improvement has not been satisfying enough for hydrocracking.

The acid sites improvement in MCM-41 has also been performed by Pt metal impregnation into MCM-41, which was examined for Hydrogenation of *toloune* [4]. Other metal impregnated in MCM-41 was Pd to formed Pd-MCM-41, and it was reported that catalyst was succeeded to catalyzed methanol synthesis from carbon *monooxide* reacted with Hydrogen [5].

In order to get larger number of acid sites of MCM-41 and the high performance in catalyzing FAMEs hydrocracking, in this research, impregnation of Pd into Al-MCM-41 is addressed and the influenced of the impregnation on its characters and activity were also evaluated.

EXPERIMENTAL SECTION

Materials

Palladium chloride, sodium aluminate, tetraethyl orthosilicate, and ethyl triammonium bromide have been supplied by Sigma Aldrich. Phosphoric acid p.a, methanol, n-pentane, and pyridine received as its were from Merck. The sample of Nyamplung seed oil (*Calophyllum Inophyllum*) was produced our laboratory.

Instrumentation

X-Ray Diffractometer (XRD) (Shimadzu), Gas Sorption Analyzer (Quantachrome), Scanning Electron Microscopy (SEM) (Heiss), Inductively Coupled Plasma (ICP) (Teledyne Leeman Labs), Gas Chromatograph - Mass Spectrophotometer (GC-MS)(Shimadzu).

Procedure

Synthesis of Pd/Al-MCM-41

Pd/Al-MCM-41 catalyst was prepared by using wet impregnation procedure continued by hydrothermal step as reported by Deongseong [4], Papp [6], Ruiz [7], Carmo [8], and Okumura [9]. Preparation was carried out by soaking Al-MCM-41 in 5% (w/w) $PdCl_2$ solution, and then the mixture was stirred gently at room temperature until homogen. The mixture was heated for 6 h to evaporate the solvent, and then was continued by calcination in this reactor, in which the temperature was increased to 550 °C in nitrogen atmosphere for 1 h. Then the nitrogen was replaced by air while the calcinations process was going on for 6 h. The air atmosphere was replaced by hydrogen and the process was taking place at temperature 150 °C. And the red-brown solid was obtained. After being dried the solid was stored in a desiccator for 24 h and were ready for characterization.

Characterization of catalysts

The effect of Pd impregnation in Al-MCM-41 on the crystallinity of the catalyst was analyzed using Shimadzu X-Ray Diffractometer (XRD) with Cu Kα radiation at λ = 0.154 nm and then the XRD pattern was recorded at (2θ) was between 3°-60°. The ratio Si/Al and Pd content were determined by using Induced Coupled Plasma (ICP) produced by Teledyne Leeman Labs, and the acidity of both catalysts was determined by pyridine adsorption. Surface area and pore volume were performed using gas sorption analyzer (Quantachrome) in nitrogen atmosphere, and calculated using both KJS and BJA adsorption isotherm method, the morphological structure of the catalyst was observed using Scanning Electron Microscopy SEM (Heiss). The product of the FAMEs hydrocracking were analyzed using Shimadzu GC-MS.

Transesterification and catalytic hydrocracking reactions

The nyamplung seeds were taken 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. The oil was then added with phosphoric acid for degumming process. The transesterification reaction was carried out by the addition of methanol with Al-MCM-41 catalyst to form FAMEs. And the result was 98.15% yield. To produce biogasoline, FAMEs resulted from the transesterification was placed in a 250 mL round flask

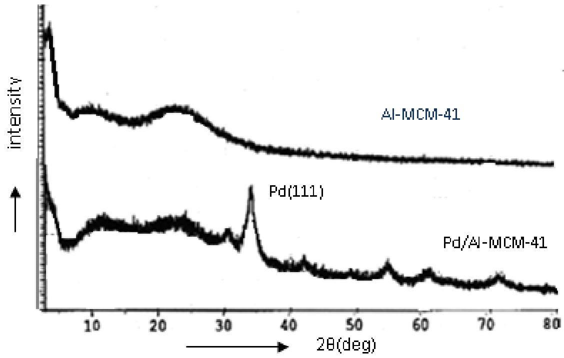

Fig 1. XRD diffractogram of Al-MCM-41 and Pd/Al-MCM-41 catalysts

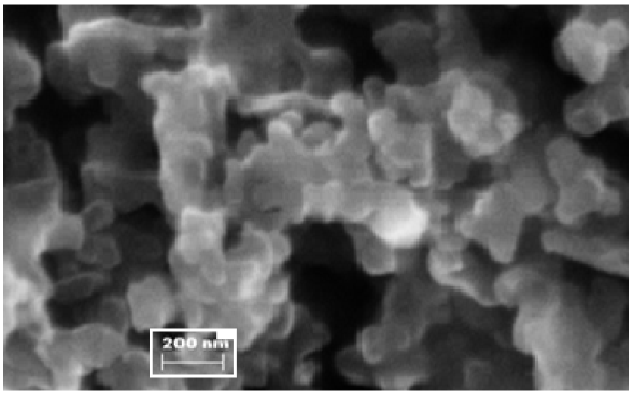

Fig 2. Micrograph SEM (Al-MCM-41)

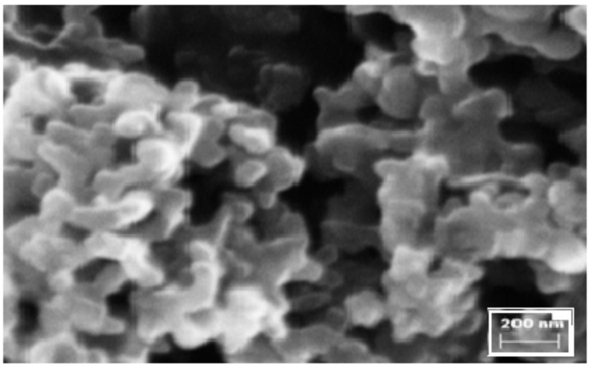

Fig 3. Micrograph SEM (Pd/Al-MCM-41)

Table 1. Al and Si content in the catalyst

Catalyst	Al (%)	Si (%)	Acidity (by Pyridine (mmol/g))
Al-MCM-41	4.81	81.71	0.0284
Pd/Al-MCM-41	6.01	55.30	0.0626

Table 2. The effect of Pd impregnation into Al-MCM-41 on the surface area, pore volume and pore radius

Catalyst	Surface area (m^2/g)	Pore vol (cc/g)	Mean pore radii (Å)
Al-MCM-41	419.934	0.501	15.121
Pd/Al-MCM-41	340.154	0.441	15.249

with 3 necks, connected with reactor hydrocracking was then flown by hydrogen with rate 2 mL/min and temperature of 200 °C.

RESULT AND DISCUSSION

Characterizations

The effect of Pd impregnation into Al-MCM-41 catalyst on its crystallinity structure has been studied using XRD and the pattern recorded was presented as Fig. 1. The figure shows that Al-MCM-41 and the Pd/Al-MCM-41 have similar XRD pattern where peaks at 2θ = 3°–5° and at round 20°, characteristic for MCM-41[4] were observed. It was also seen that Pd impregnation into Al-MCM-41 leads to a slight decreased in the intensity of the peaks, implying an occurrence of very small structural destroyed. In addition, the impregnation also promoted new peaks at 34°, 42°, 55°, 61° that belong to Pd element [7]. It was indicated that Pd has been successfully impregnated in Al-MCM-41.

The effect of Pd impregnation into Al-MCM-41 on the ratio of Si/Al and the acidity content were presented in Table 1.

From the Table, it can be seen that Pd impregnation on Al-MCM-41 has decreased the Si content but made Al content increased, consequently the ratio of Si/Al was decreased. The decreasing of Si/Al ratio or increasing Al caused to increase the acid sites on the catalyst Pd/Al-MCM-41. The acid sites originated from the larger orbital in Pd metal form structural framework of Pd/Al-MCM-41. The increase of the acidity was consistence with the acidity of Pd/Al-MCM-41 measured as presented in Table 1.

The effect of Pd impregnation into Al-MCM-41 on the surface area, pore volume and pore radius were also evaluated and the results were presented in Table 2.

Table 2 indicated that Pd impregnation Al-MCM-41 has been reduced the surface area and the pore volume, though it increased the pore radius. A decrease in the surface area and pore volume may be caused by Pd deposited on the surface as well as entering in the pores of MCM-41. The slight increase of the pore caused by the occupation of the small pore by the impregnation of Pd.

The effect of Pd impregnation into Al-MCM-41 on the morphology of the catalyst was illustrated by Fig. 2 and 3. The Figure showed that hexagonal shapes of Al-MCM-41 and Pd/Al-MCM-41 were observed, that was the characteristic of MCM-41 morphology. It was also seen that Pd impregnation into Al-MCM-41 gave no

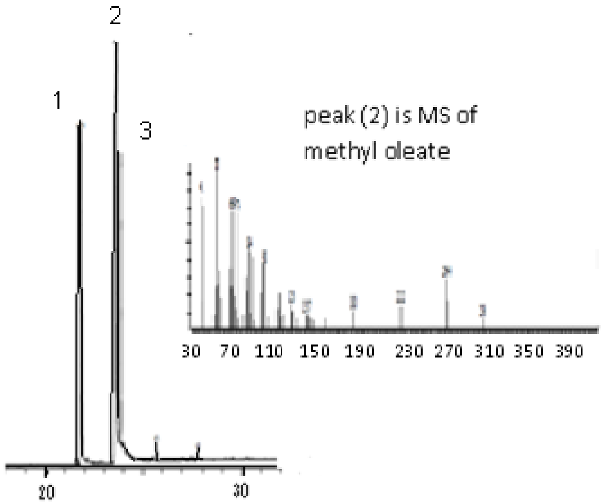

Fig 4. GC-MS chromatograms of FAMEs compounds

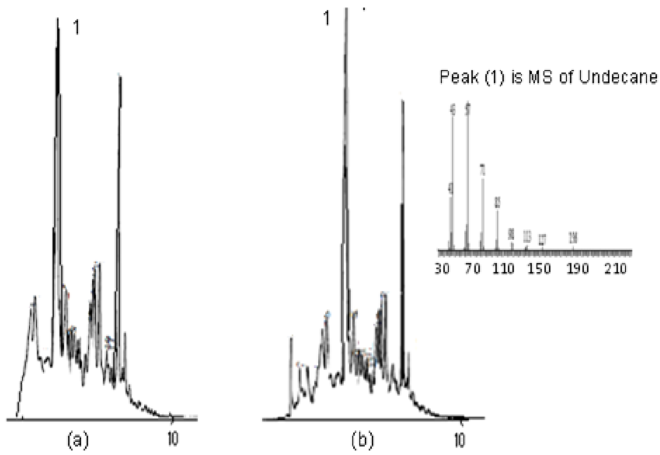

Fig 5. GC-MS chromatograms of the reaction product using Al-MCM-41 (a) and Pd/Al-MCM-41 (b)

Table 3. Product distribution of the catalytic hydrocracking reactions

Compound/molecule	Al-MCM-41 (%)	Pd/Al-MCM-41 (%)
C8 hydrocarbons	1.26	----
C9 hydrocarbons	----	5.14
C10 hydrocarbons	----	10.94
C11 hydrocarbons	47.56	17.62
C12 hydrocarbons	33.93	62.25
C13–C20 hydrocarbons	14.33	4.05
C15–C19 alcohols	2.92	-----

different morphology, implying there was no structural of Al-MCM-41 destroyed.

The Result of Cracking Process

In order to evaluate the effect of Pd impregnation into Al-MCM-41 on the catalyst performance, the catalytic activities of both Al-MCM-41 and Pd/Al-MCM-41 have been tested for FAMEs hydrocracking in the presence of hydrogen gas. The FAMEs was obtained by transesterification of Nyamplung seed oil containing high triglycerides. The transesterification products were identified by GC-MS method, and the chromatogram was presented at Fig. 4.

The Figure showed that three high peaks with total percentage were 98.15% and two other very low peaks that was about 1.85% were observed. From their Mass Spectra, it was indicated that the high peaks belong to (1) 20.86% methyl palmitate, (2) methyl oleate 59.25% and (3) 18.04% methyl stearate that are FAMEs compound. Therefore it was clear that transesterification has been successfully occurred.

The hydrocracking results of the FAMEs with Hydrogen in the presence of Al-MCM-41 and Pd/Al-MCM-41 were indentified by GC-MS, and the chromatograms were displayed as Fig. 5. It can be seen that several peaks with various intensities appear, and from their Mass Spectra interpretation several hydrocarbons can be identified as presented in Table 3.

From the Table, it was found that the FAMEs hydrocracking catalyzed by Al-MCM-41 result in the hydrocracking consisting of C8 and C11 - C19 of the carbon chain, accompanied by small amount of large alcohol compounds (C15 - C19). Furthermore, it was observed that hydrocarbon with C11 - C19 consist of C11 and C12 with equal medium percentage. Meanwhile, by using Pd/Al-MCM-41 catalyst, FAMEs hydrocracking yields only hydrocarbons with narrower distribution that are C9 - C20, which was dominated by C12, emerging gasoline family. By comparing the results, it was clear that Pd/Al-MCM-41 promoted more effective and selective hydrocracking of FAMEs. However, the percentage of C12 hydrocarbon need to be further improved.

CONCLUSION

It was concluded that Pd impregnation into Al-MCM-41 catalyst has been successfully carried out without damaging the structure of Al-MCM-41, by impregnating Pd into Al-MCM-41 to form Pd/Al-MCM-41, Si/Al ratio and the number of acid sites of the catalyst can be increased, but the surface area and pore volume were reduced. Pd/Al-MCM-41 showed better activity in hydrocracking compared to Al-MCM-41 to produce biogasoline. By using Pd/Al-MCM-41, single chain hydrocarbon products consisted of C9 - C18 and dominated by C12 were resulted, meanwhile hydrocarbons with C9 - C20 of the carbon chains and alcohol compounds were produced when Al-MCM-41 was applied.

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