PARTIAL HYDROGENATION OF PALM OIL-DERIVED BIODIESEL OVER Pd/C CATALYSTS

[1]NATTHIDA NUMWONG, [2]NATTAPONG THACHUANGTUMLE, [3]APANEE LUENGNARUEMITCHAI

[1]Catalytic Chemistry Research Unit, Faculty of Science, King Mongkut's Institute of Technology Ladkrabang, 1 Soi Chalongkrung 1, Ladkrabang, Bangkok 10520, Thailand
[2,3]The Petroleum and Petrochemical College, Chulalongkorn University, Soi Chula 12, Phayathai Rd., Pathumwan, Bangkok 10330, Thailand
E-mail: [1]knnatthi@kmitl.ac.th

Abstract— Biodiesel upgrading by partial hydrogenation of polyunsaturated fatty acid methyl esters (FAMEs) derived from palm oil has been investigated on Pd/C catalysts prepared by incipient wetness impregnation (IWI). The effects of type of carbon support [activated carbon and carbon aerogel] and size of support on the catalytic behavior of the Pd/C catalyst were studied. The XRD, BET, FE-SEM, TEM, and CO-chemisorption techniques were used to examine the prepared catalysts. The results showed that Pd supported on different types of carbon support, which possess different pore structures, exhibit different Pd particle size and Pd dispersion that correlate with hydrogenation activity. In addition, particle size of the activated carbon support also has an important effect on the activity of the catalysts. The hydrogenation activity was in this order: Pd/≤40 μm > Pd /850 μm > Pd/granule.

Keywords— Partial Hydrogenation, Pd/C, Biodiesel, Oxidative Stability.

I. INTRODUCTION

Biodiesel or fatty acid methyl ester (FAME) is considered as an alternative for conventional diesel fuel. The advantages of biodiesel over petroleum diesel are: biodegradability, higher flash point, lower sulfur content, lower exhausted emission as well as miscibility with petroleum-based diesel [1–3]. However, properties of biodiesel depend on individual fatty acids in starting oil or fat. The fuel properties and quality of biodiesel are greatly influenced by the number of double bonds present in starting oil [4]. Biodiesel produced from oil that contains higher unsaturated fatty acid composition performs the lower oxidative stability. This low oxidative stability results in easily oxidation of unsaturated FAMEs, which produces peroxides, aldehydes, ketones, and acids that change biodiesel properties and combustion process [2]. In contrast, the higher saturated fatty acid composition, the worse cold flow property becomes. Therefore, the optimization between oxidative stability and cold flow properties by partial hydrogenation of polyunsaturated FAMEs is a promising approach to solve this problem.

Pd supported on carbon materials have been extensively employed as catalysts for hydrogenation reaction because of many advantages e.g. high activity, mild process condition [5], availability of carbon support, and simplicity of recovery of Pd metal by just burning off carbon component [6]. Several publications have addressed the activity of Pd supported on various types of carbon materials such as activated carbon [6–9], nanocomposite carbon [10], carbon nanofibers [11–12], and carbon nanotube [13]. Of many types of carbon materials, activated carbon is still the most commonly used as a catalyst support, because of its large surface area (500–1,200 m^2/g) due to its high degree of microporosity, and low cost [14]. However, in most cases, micropores are often closed with metal particles [8]. Therefore in this work; carbon aerogel, which is a mesoporous material, was used as a catalyst support in order to compare the effect of pore size and structure of support on the activity of the catalysts. Carbon aerogel has a network structure of interconnected nanosized particles [15]. It is highly mesoporous material with extremely low density, large open pore, and high specific surface areas. Moreover, its pore size can be controlled by changing starting materials [16].

On the basis of these facts, this study focused on the catalytic activities of Pd supported on carbon (Pd/C) catalysts for partial hydrogenation of polyunsaturated FAMEs to improve the oxidative stability of palm oil derived-biodiesel. The effects of type and size of carbon support were investigated. Moreover, details in characterization of the Pd/C catalysts by XRD, BET, FE-SEM, TEM, and CO-chemisorption techniques are also reported.

II. EXPERIMENTAL

A. Materials

Commercial activated carbon with particle size ≤40 μm and 850 μm, and granule activated carbon, purchased from Fluka Company were used as a support. Palladium (II) nitrate dihydrate [$Pd(NO_3)_2.2H_2O$] 40% purum was purchased from Sigma Aldrich and used as a Pd precursor. Bisphenol-A (99% purity, Aldrich), formaldehyde (37 wt.% in water, Merck), triethylenetetramine, TETA (98% purity, Fluka), and dimethylformamide, DMF (Lab-Scan) are chemicals for preparing carbon aerogel.

Gases used in the partial hydrogenation experiment

were high purity (99.99%) hydrogen, and high purity (99.99%) nitrogen. Both of them were purchased from Thai Industrial Gases Public Co., Ltd. In addition, feed biodiesel was obtained from Veerasuwan Co., Ltd., Thailand.

Moreover, n-heptane (99.5%, Fisher Scientific) and methyl heptadecanoate (99.7%, Fluka) were used as a solvent and standard for GC.

B. Synthesis of Carbon Aerogel

Carbon aerogel or polybenzoxazine was prepared according to the method of Pekala R.W. [17]. Firstly, bisphenol-A was dissolved in dimethylformamide and stirred for 10 minutes until clear solution was obtained. Secondly, formaldehyde solution was added to bisphenol-A solvent and stirred for 20 minutes in the cooling bath. The third, triethylenetetramine was added into the mixture in the second step and stirred for 1 hour until obtain a transparent yellow viscous liquid. Then, this liquid was aged for 1 day and obtained as benzoxazine aerogel. After that, this aerogel was heated in an oil bath at 80°C for 2 days and then a solid sample was obtained. Then, this solid sample was cut into a dish-shaped and kept in a petri dish at room temperature for 4 days. Finally, the piece of solid benzoxazine aerogel was cured in an oven. After that, it was calcined under N_2 at 800°C for 23 hours. Finally, it was calcined under CO_2 at 900°C for 12 hours.

C. Catalyst Preparation

The 2 wt.% Pd on activated carbon (Pd/AC) and 2 wt.% Pd on carbon aerogel (Pd/CA) were prepared by incipient wetness impregnation (IWI) using $Pd(NO_3)_2.2H_2O$ as a Pd precursor. The catalyst was dried at 110°C for 24 hours and then calcined under N_2 at 500°C for 2 h.

D. Catalyst Characterization

In order to identify the internal structure and crystallinity of the support and catalysts, a Rigaku DMAX2200 X-ray diffractometer was used. CuKα radiation (1.5405 Å) was used as an X-ray source at running conditions for the X-Ray tube of 40 kV and 30 mA. The detector scanned the intensity of a diffracted radiation from the sample as a function of 2θ in the range of 5° to 90° with a scan speed of 5°/sec.

The specific surface area, pore volume, and pore size distribution of the support were determined by N_2 physisorption using a Quantachrome Autosorb-1 MP surface area analyzer. Before analyzing, the sample was heated under vacuum at 250°C overnight to eliminate volatile species that adsorbed on the surface. Pd dispersion of the prepared catalysts was determined by pulse chemisorption of 10.1% CO/He at 50°C, using Temperature Programmed Desorption/Oxidation/ Reduction (TPD/R/O) Ohkura R6015. Prior to measurements, each sample was pretreated with H_2 at 120°C for 1 hour and follow by purging with He at the same temperature for 10 minutes. The Pd dispersion was calculated by assuming a stoichiometry of CO:Pd = 1:1.

Furthermore, Field Emission-Scanning Electron Microscope (FE-SEM), Hitachi Model S4800, was utilized to identify the microstructure and capture the micrograph of catalyst morphology. The distribution of Pd particle size was determined by using Semaphore®.

In addition, the catalyst morphology and dispersion of Pd were examined by Transmission Electron Microscope (TEM), JEOL, JEM-200CX. The catalyst sample was ultrasonically dispersed in 2-propanol solution. After that, this suspension was dropped on a Ni microgrid.

E. Partial Hydrogenation of Polyunsaturated FAMEs

Partial hydrogenation of palm oil-derived polyunsaturated FAMEs was carried out in a 300 mL stainless steel semi-batch reactor at temperature and hydrogen partial pressure of 120°C and 0.4 MPa, respectively. Stirring rate was maintained at 500 rpm to prevent external mass transfer limitation. The flow rate of hydrogen gas was controlled by a mass flow controller at 50 mL/min. Firstly, 1.5 g of catalyst was placed into the reactor. Then, the system was purged with nitrogen to remove the remaining air. After that, 100 g of feed biodiesel was fed into the reactor by a peristaltic pump. The reaction was started by increasing temperature and pressure to the desired points. Finally, the liquid products were collected in every 30 minutes in the first two hours and every hour in the third and fourth hour of reaction.

F. Biodiesel Analysis

FAME composition in biodiesel before and after partial hydrogenation was determined using a Hewlett Packard gas chromatograph 5890 equipped with a flame ionization detector (GC-FID). A DB-WAX (30 m x 0.25 mm) fused-silica capillary column coated with a 0.1 μm film was used. Samples of 0.2 μL was injected under the following conditions: the carrier gas was helium with a flow rate of 2.4 mL/min, the injector temperature is 200°C with a split ratio of 75:1, and the detector temperature is 230°C. The sample was injected at an oven temperature of 130°C. After an isothermal period of 2 min, the GC oven was heated to 220°C at a rate of 2°C/min and held for 15 min with the total running time of 62 min. The FAME composition was identified by reference to the retention time.

Oxidative stability is one of the major issues indicating a content of polyunsaturated FAMEs. The oxidative stability of biodiesel was tested by Metrohm 743 Rancimat. Sample was aged at 110°C under a constant air stream. The oxidative stability corresponds to the period of time passing before FAMEs are degraded to such an extent that the formation of volatile acids can be recorded through an increasing of conductivity. This procedure was developed according to EN 14112.

Furthermore, cold flow properties of biodiesel before and after partial hydrogenation including cloud point and pour point were investigated by using a Tanaka mini pour/cloud point tester Series MCP-102, which was developed according to the ASTM D6749.

III. RESULTS & DISCUSSION

A. Effect of Carbon Support

In this part, Pd supported on activated carbon (Pd/AC) and Pd supported on carbon aerogel (Pd/CA) were investigated for the partial hydrogenation of biodiesel. Fig. 1(a) and (b) show FE-SEM micrographs of the activated carbon and carbon aerogel. It was found that both carbon supports exhibited different pore structure and surface morphology. The activated carbon exhibits a lot of small pores on the surface. On the other hand, carbon aerogel presents a three-dimensional network of interconnected particles, incorporated to open mesopores. The surface area of activated carbon identified by BET surface area analyzer, was 836.6 m^2/g with an average pore diameter of 2.3 nm, whereas; the surface area of carbon aerogel was 280.1 m^2/g, with an average pore diameter of 3.1 nm.

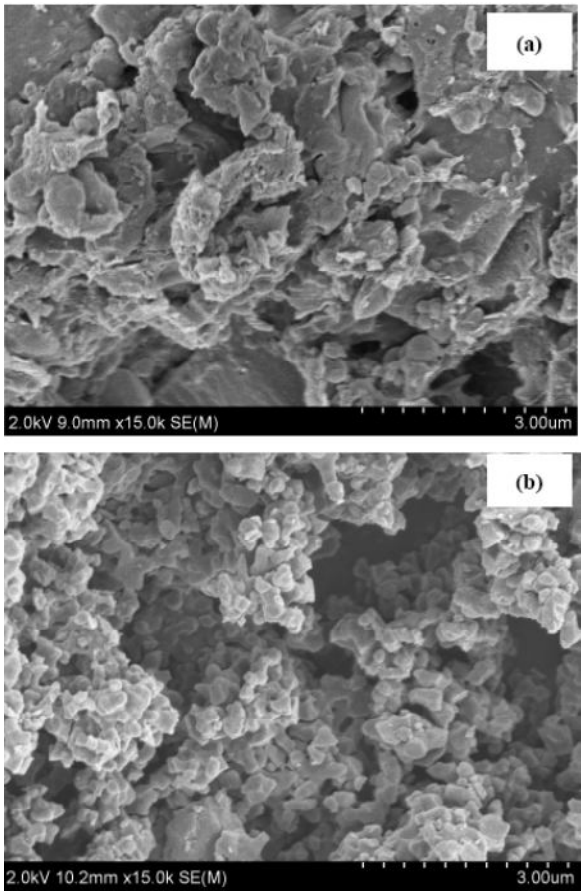

Fig. 1 FE-SEM micrographs of (a) activated carbon and (b) carbon aerogel

The XRD technique determined that Pd supported on both types of carbon support presented four main characteristic diffraction peaks of crystalline Pd including plane (111), (200), (220), and (311) at 2θ of 40.20, 46.80, 68.25, and 82.10, respectively (Fig. 2). The mean particle size of Pd (111) of both catalysts was calculated by applying Scherrer's equation [7]. The Pd particle size of the Pd/activated carbon was 17.75 nm, whereas Pd particle size of Pd/carbon aerogel was 9.97 nm (Table 1). In addition, TEM micrographs of Pd/activated carbon and Pd/carbon aerogel (Fig. 3(a) and (b)) revealed that Pd are well-dispersed on the surface of carbon aerogel, whereas the agglomeration of Pd particles with larger Pd particle size can be observed in Pd/activated carbon catalyst. This is because of the interconnection structure, which incorporated into the open mesopores of carbon aerogel, creates a well dispersion of Pd particles. Moreover, it was found that Pd/activated carbon shows broad Pd particle size distribution, whereas; Pd/carbon aerogel exhibited uniform distribution of Pd particle size, with smaller Pd particle size compared with Pd/activated carbon. This result clearly indicated that the smaller Pd particle size of Pd/carbon aerogel was due to the better dispersion of Pd. After that, Pd dispersion of both catalysts was further determined by CO-chemisorption technique. The Pd dispersion of Pd/activated carbon and Pd/carbon aerogel was 1.98% and 35.09%, respectively (Table 1).

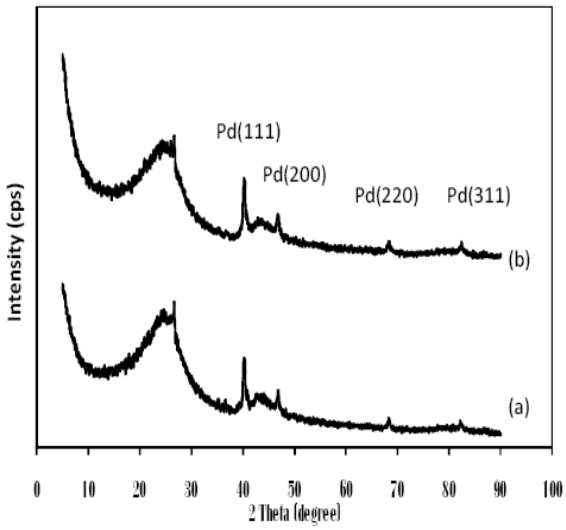

Fig. 2 XRD patterns of (a) Pd/activated carbon, (b) Pd/carbon aerogel

Table 1 Characteristics of carbon supports and Pd/C catalysts.

Catalyst	Surface area (m^2/g)	Pd (111) particle size (nm)	Pd dispersion (%)
Activated carbon (850 μm)	836.6	-	-
Carbon aerogel	280.1	-	-
Pd/≤ 40 μm AC	-	-	2.81
Pd/850 μm AC	-	17.75	1.98
Pd/granule AC	-	-	1.05
Pd/CA	-	9.97	35.09

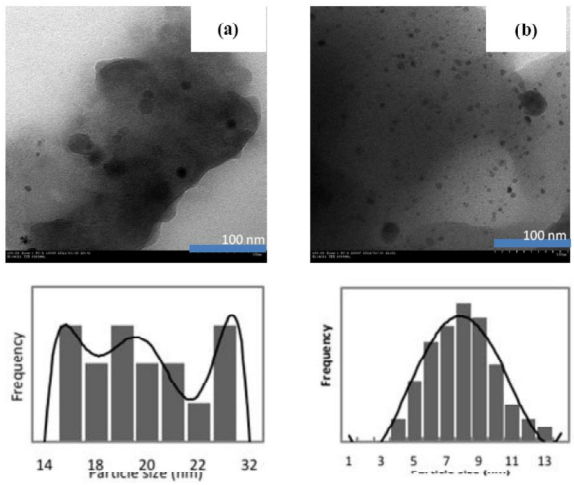

Fig. 3 TEM micrographs and Pd particle size distribution observed by TEM: (a) Pd/activated carbon and (b) Pd/carbon aerogel

In order to compare the performances of Pd/activated carbon and Pd/carbon aerogel catalysts, the partial hydrogenation of palm biodiesel was operated and controlled at the same reaction conditions (120°C, 0.4 MPa, 50 mL/min H_2 flow rate, 500 rpm stirring rate, and 1.5 wt.% catalyst compared to starting biodiesel). The percentages of C18:0, C18:1, C18:2, and other FAMEs (C12:0, C14:0, C16:0, and C22:0) as a function of reaction time, obtained from using both catalysts are shown in Fig. 4. For both catalysts, it evidently showed that the longer the reaction time, the higher the conversion of unsaturated FAMEs (C18:2 and C18:1) while the other FAMEs composition was quite stable. As shown in Fig 4, both catalysts show consecutive hydrogenation behavior from C18:2 to C18:1 and C18:1 to C18:0, respectively. However, Pd/activated carbon presents lower hydrogenation activity compared with Pd/carbon aerogel. Using Pd/activated carbon, C18:2 was gradually hydrogenated to C18:1 (Fig. 4(a)); as it decreased from 5.30% to 0.82%, whereas C18:1 and C18:0 increased from 26.98% to 31.67% and 4.30% to 7.17%, respectively, after 1 h of reaction. After that, at 1.5 h of reaction; C18:2 was completely hydrogenated as there was no significant composition of C18:2 in biodiesel product; while a decrease in C18:1 composition could be observed. On the other hand, Pd/carbon aerogel could rapidly reduce C18:2 and C18:1 from 5.30% to 0.19% and from 26.98% to 15.33%, respectively, after 1 h of reaction; while C18:0 sharply increased from 4.30% to 24.06% in the first hour, and continuously increased to almost 40% after 4 h of reaction (Fig. 4(b)). The higher hydrogenation activity of Pd/carbon aerogel can be explained from the three-dimensional network of carbon aerogel, leading to the smaller Pd particle size, the higher Pd dispersion, and hence the more active surface for hydrogenation of unsaturated FAMEs.

It apparently shows that partial hydrogenation using Pd/activated carbon and Pd/carbon aerogel could improve the oxidative stability of palm oil biodiesel from 1.49 h to 36.00 h and 40.50 h, respectively (Table 2). However, the biodiesel product obtained from using Pd/carbon aerogel exhibited worse pour point and cloud point than that of Pd/activated carbon. This is due to the higher amount of saturated FAME in hydrogenated biodiesel using Pd/carbon aerogel, which provides the higher oxidative stability, but the worse cold flow properties. This suggests that Pd/activated carbon exhibits better partial hydrogenation activity for palm oil biodiesel; where polyunsaturated FAMEs were fully converted into monounsaturated FAME with a minimal increase of saturated FAME.

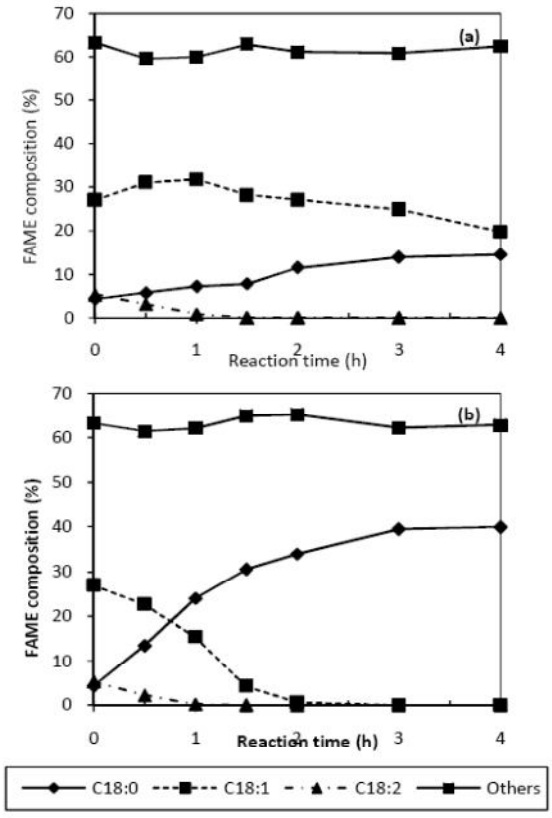

Fig. 4 FAME composition as a function of reaction time using: (a) Pd/activated carbon and (b) Pd/carbon aerogel (Reaction conditions: 120°C, 0.4 MPa, 50 mL/min H_2 flow rate, 500 rpm stirring rate, and 1.5 wt.% catalyst compared with starting biodiesel)

Table 2 FAME composition and fuel properties of biodiesel feed and biodiesel product after 1.5 h of reaction using as Pd/activated carbon and Pd/carbon aerogel

	Biodiesel feed	Biodiesel product after 1.5 h	
		Pd/AC	Pd/CA
FAME composition (%)			
Saturated FAME	67.72	71.89	95.74
Monounsaturated FAME	26.98	28.11	4.26
Diunsaturated FAME	5.30	0.00	0.00
Biodiesel properties			
Oxidative stability (h)	1.49	36.00	40.50
Pour point (°C)	16.0	22.0	25.0
Cloud point (°C)	16.0	23.0	26.0

B. Effect of Particle Size of Carbon Support

The effect of particle size of activated carbon support: ≤40 μm, 850 μm, and granule (3 mm diameter and 7 mm height) on the partial hydrogenation of polyunsaturated FAMEs was investigated. As shown in Table 1, the Pd supported on 40 μm activated carbon shows the highest Pd dispersion. The catalytic activity of these catalysts was investigated by comparing C18 FAMEs composition at the same reaction time (1 h) as shown in Fig. 5. It clearly shows that the hydrogenation activity was decreased in this order: Pd/≤40 μm > Pd/850 μm > Pd/granule, as evidence from the highest and lowest C18:0 composition obtained from Pd/≤40 μm activated carbon and Pd/granule activated carbon, respectively. This can be explained from the large Pd particle size (~17 nm) compared with the pore size of activated carbon support (2.3 nm). Therefore, Pd particles locate outside the pore of carbon and reaction takes place at the outer surface where internal mass transfer limitation can be neglected. Consequently, smaller particle size of carbon support leads to higher amount of active surface for contacting with reactants and higher dispersion of Pd, when compared at the same amount of catalyst used.

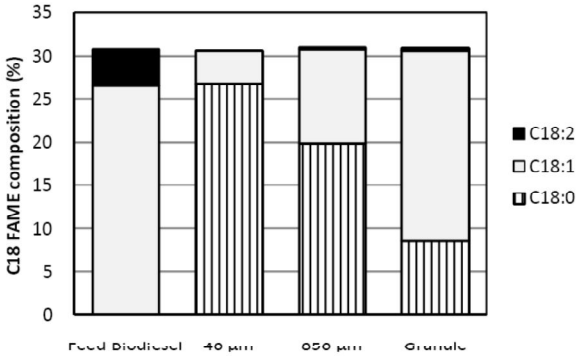

Fig. 5 C18 FAMEs composition of feed biodiesel and hydrogenated biodiesel after 1 h of reaction using Pd supported on activated carbon with different particle sizes (Reaction conditions: 120°C, 0.4 MPa, 50 mL/min H_2 flow rate, 500 rpm stirring rate, and 1.5 wt.% catalyst compared with starting biodiesel)

CONCLUSIONS

Partial hydrogenation of polyunsaturated FAMEs to monounsaturated FAMEs is a promising method, which can improve the oxidative stability of biodiesel. In this study, partial hydrogenation of palm oil-derived FAMEs over Pd/C catalysts was investigated. The results revealed that structure and pore of the carbon support play an important role on Pd particle size and Pd dispersion, and hence hydrogenation activity of the catalyst. The Pd/carbon aerogel, which possessed smaller Pd particle size and higher Pd dispersion, provided higher hydrogenation activity than that of Pd/activated carbon. In addition, due to the location of Pd metals, which locate outside the pore of carbon, where internal mass transfer limitation can be neglected, therefore; the particle size of carbon support has an important effect on the catalytic activity. The Pd on the smallest particle size carbon (≤40 μm) shows the highest hydrogenation activity, which can be explained from its high contacting area and high Pd dispersion.

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