CHAPTER IV
PARTIAL HYDROGENATION OF POLYUNSATURATED FATTY ACID
METHYL ESTERS OVER Pd/C: EFFECT OF CATALYST PREPARATION

4.1 Abstract

Biodiesel upgrading by partial hydrogenation of polyunsaturated FAMEs derived from palm oil has been investigated on Pd/C catalysts prepared by incipient wetness impregnation (IWI). The effects of Pd precursors [$PdCl_2$ and $Pd(NO_3)_2.2H_2O$], catalyst calcination conditions, types 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. Partial hydrogenation activity was found to correlate with Pd particle size. The result showed that $Pd(NO_3)_2.2H_2O$ precursor and calcination under N_2 at 500°C for 2 h exhibited catalyst with Pd particle size of ~17 nm, which provided a good performance for partial hydrogenation of polyunsaturated FAMEs derived from palm oil. In addition, particle size of the activated carbon support also has an important effect on the activity of the catalysts. The hydrogenation activity was decreased in this order: Pd/≤40 μm > Pd /850 μm > Pd/granule. However, differrent types of carbon support, which possess different pore structures did not exhibit different hydrogenation activity.

Keywords: partial hydrogenation, Pd/C, Pd precursor, calcination, biodiesel, oxidative stability

4.2 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 [4]. The fuel properties and quality of biodiesel are greatly influenced by the number of double bonds present in starting oil [5]. 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 [6], availability of carbon support, and simplicity of recovery of Pd metal by just burning off carbon component [7]. Several recent publications have addressed the activity of Pd supported on various types of carbon materials such as activated carbon [7–9], 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 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 material [16].

Furthermore, it is well known that different Pd precursors and catalyst calcination conditions result in the differences in Pd particle size, Pd dispersion, and consequently hydrogenation activity [6]. On the basis of these facts, this study focused on the preparation of Pd supported on carbon (Pd/C) catalysts and their catalytic activities for the partial hydrogenation of polyunsaturated FAMEs to improve the oxidative stability of palm oil derived-biodiesel. The effects of Pd precursors, catalyst calcination conditions, and types of carbon support were investigated. Moreover, details in characterization of the Pd/C catalyst by XRD, BET, FE-SEM, TEM, and CO-chemisorption techniques are also reported.

4.3 Experimental

4.3.1 Materials

Commercial activated carbon with particle size ≤ 40 µm and granule activated carbon, purchased from Fluka Company were used as a support. Two types of Pd precursor: Palladium (II) chloride anhydrous [$PdCl_2$] 60% purum and palladium (II) nitrate dihydrate [$Pd(NO_3)_2.2H_2O$] 40% purum were 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.

4.3.2 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 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.

4.3.3 Catalyst Preparation

The 2 wt.% Pd/C catalysts were prepared by incipient wetness impregnation (IWI) using two types of Pd precursors: $PdCl_2$ and $Pd(NO_3)_2.2H_2O$ The catalysts were dried at 110°C for 24 hours and then calcined at different calcination conditions. Finally, the catalyst was separated into two parts; the first part was used as received, whereas the second part was reduced at 250°C for 3 hours before use in the reaction. The studied parameters can be summarized, as shown in Table 4.1.

Table 4.1 Studied parameters in the effect of catalyst calcination conditions

Calcination Environment	Calcination Temperature (°C)	Used Form	Nomenclature
Under air	300	as-received	air300A
		reduced	air300R
	500	as-received	air500A
		reduced	air500R
Under nitrogen	300	as-received	$N_2$300A
		reduced	$N_2$300R
	500	as-received	$N_2$500A
		reduced	$N_2$500R

4.3.4 Catalyst Characterization

In order to identify the internal structure and crystallinity of the support and catalysts, a Rigaku DMAX2200 X-ray diffractometer was used. CuK_α 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 and catalysts were determined by N_2 physisorption using a Quantachrome Autosorb-1 MP surface area analyzer. Before analyzing, the sample was heated under vacuum atmosphere at 250°C overnight to eliminate volatile species that adsorbed on the surface.

Pd dispersion of the prepared catalysts was determined by pulse chemisorptions 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 hydrogen at 120°C for 1 hour and follow by purging with helium 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.

4.3.5 Partial Hydrogenation of Polyunsaturated FAMEs

Partial hydrogenation of 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 50 ml/min and was controlled by a mass flow controller. Firstly, 1.5 g of Pd/C 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 point. 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. The schematic of the partial hydrogenation experiment is shown in Figure 4.1.
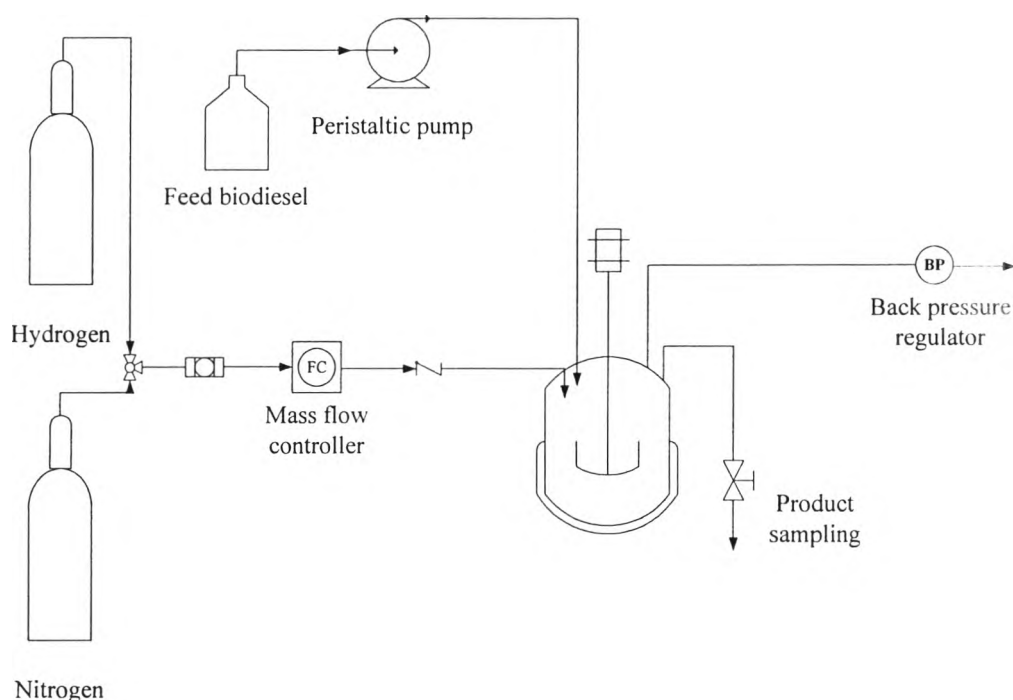
Figure 4.1 Schematic of the partial hydrogenation experimental setup

4.3.6 Biodiesel Analysis

FAME composition in biodiesel before and after partial hydrogenation reaction 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 [18].

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.

4.4 Results and Discussion

4.4.1 Effect of Palladium Precursor

The characteristics of the Pd/C catalysts prepared from two types of palladium precursor [$PdCl_2$ and $Pd(NO_3)_2.2H_2O$] were obtained using: XRD and CO-chemisorption.

Figure 4.2 shows the XRD patterns of activated carbon support and Pd/C catalysts prepared by incipient wetness impregnation (IWI) technique using two types of Pd precursors: $PdCl_2$ and $Pd(NO_3)_2.2H_2O$. The broad signal at about 25°, which is assigned to the amorphous carbon was observed in activated carbon support and all Pd/C catalysts [19]. The four main characteristic peaks of crystalline Pd including plane (111), (200), (220), and (311) at 2θ of 40.20, 46.80, 68.25, and 82.10, respectively, were observed for Pd/C catalyst prepared from $Pd(NO_3)_2.2H_2O$ precursor after calcined under N_2 at 500°C. According to Wu et al. [20]; Pd (111), Pd

(200), Pd (220), and Pd (311) were found after Pd/activated carbon fibers was calcined under N_2. However, the catalyst prepared from $PdCl_2$ did not exhibit any diffraction peaks of Pd. This suggests that Pd particles were highly dispersed on the surface of activated carbon support or the Pd crystallite size of the catalyst prepared from $PdCl_2$ was below the lower limit of XRD detectability (<5 nm) [6]. For the evaluation of hydrogenation activity, mean particle size of Pd was calculated from the peak width at half height of the Pd (111) diffraction peak by applying Scherrer's equation [7]. It shows that the Pd particle size of the catalyst prepared from $Pd(NO_3)_2.2H_2O$ was about 17.75 nm and less than 5 nm for the catalyst prepared from $PdCl_2$ (Table 4.2).
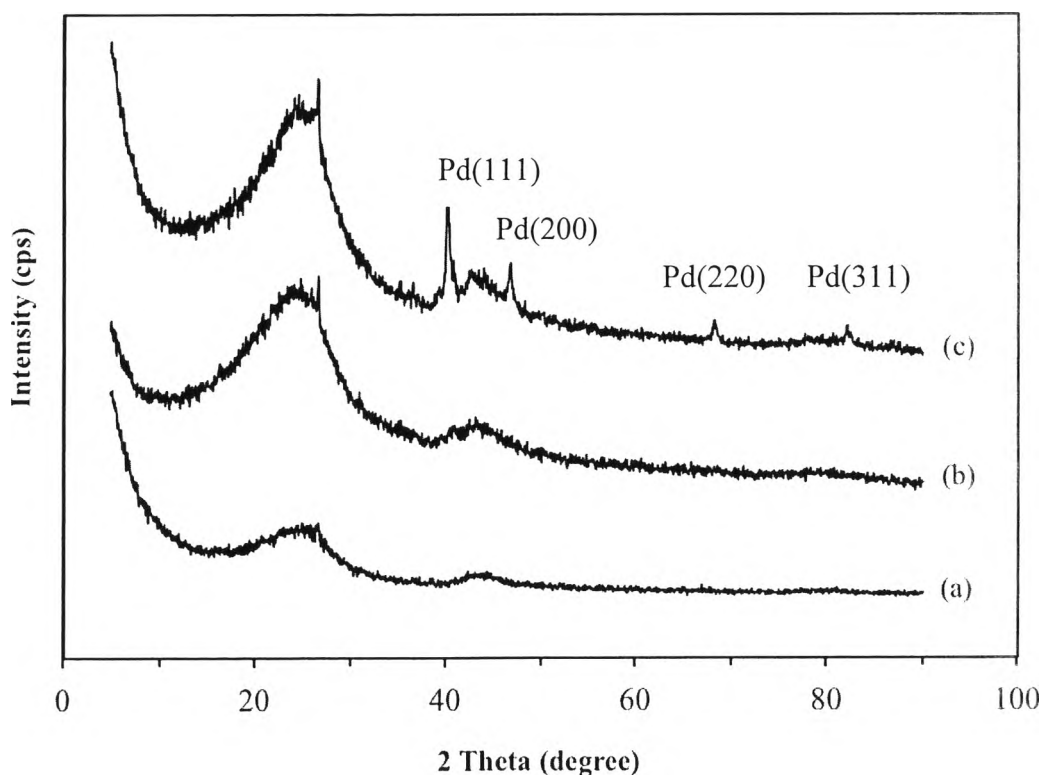
Figure 4.2 XRD patterns of (a) activated carbon support, (b) as received-2 wt.% Pd/C calcined under N_2 at 500°C prepared from $PdCl_2$, and (c) $Pd(NO_3)_2.2H_2O$

Furthermore, CO-chemisorption technique was used to investigate Pd dispersion of the prepared catalysts. The dispersion of Pd for catalyst prepared from $PdCl_2$ was 24.58% and 2.81% for $Pd(NO_3)_2.2H_2O$ (Table 4.2). It evidently showed that the Pd particle size obtained from XRD and Pd dispersion obtained from CO-chemisorption technique revealed a good correlation.

Table 4.2 Characteristics of Pd/C catalysts prepared from different Pd precursors and calcination conditions.

Catalyst	Pd(111) particle size (nm)	Pd dispersion (%)
Effect of Pd precursor		
Pd-Cl$_2$/C[a]	<5	24.58
Pd-NO$_3$/C[b]	17.75	2.81
Effect of calcination condition[c]		
air300A	<5	N/D[d]
air300R	20.24	N/D[d]
air500A	23.68	N/D[d]
air500R	23.68	N/D[d]
N$_2$300A	17.74	N/D[d]
N$_2$300R	17.74	N/D[d]
N$_2$500A	17.75	N/D[d]
N$_2$500R	20.29	N/D[d]

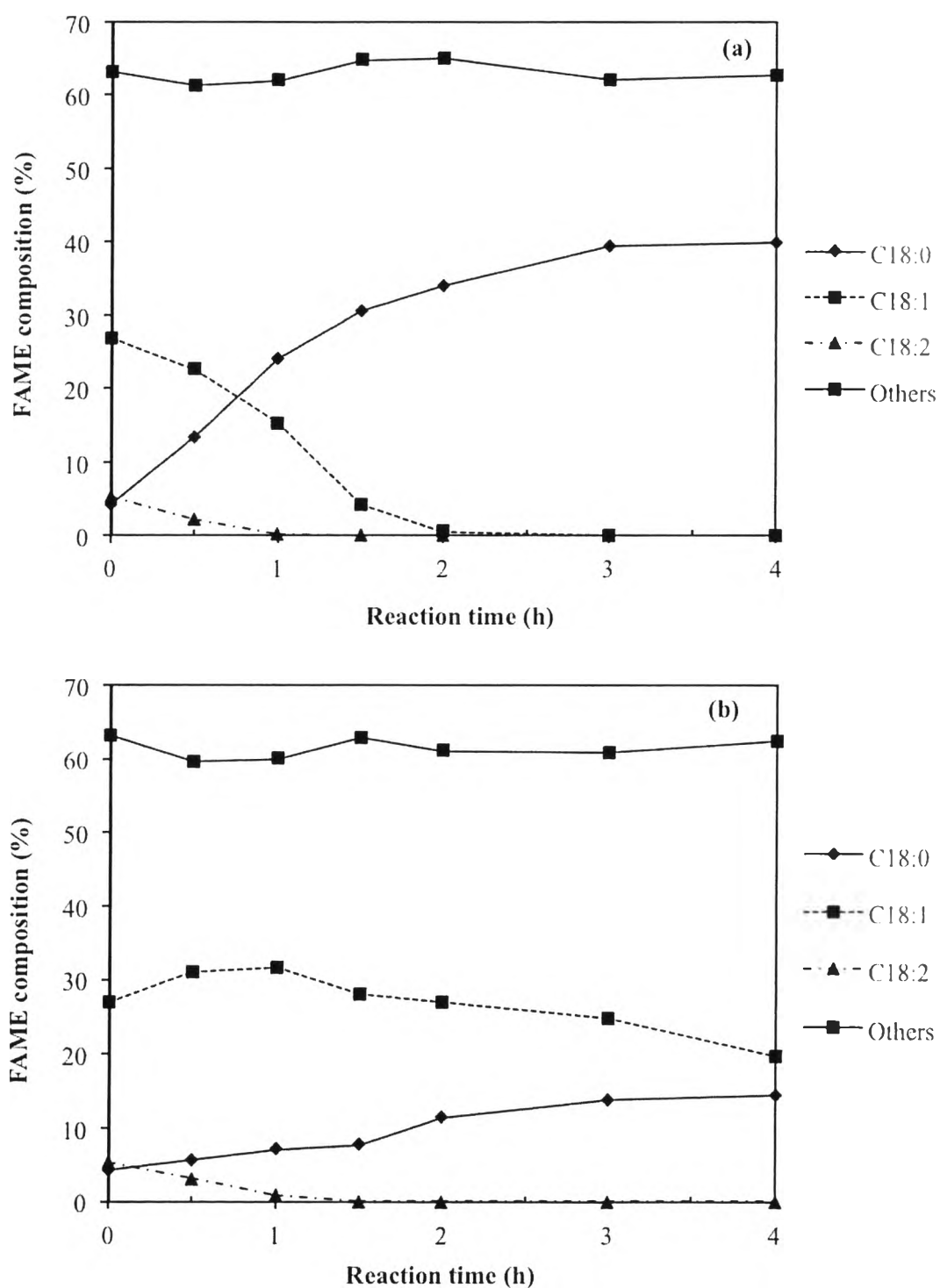[a]As-received Pd/C catalysts calcined under N_2 at 500°C, prepared from $PdCl_2$

[b]As-received Pd/C catalysts calcined under N_2 at 500°C, prepared from $Pd(NO_3)_2.2H_2O$

[c]Prepared from $Pd(NO_3)_2.2H_2O$

[d]Not determined

In order to compare the performances of these two catalysts, the partial hydrogenation reaction was operated and controlled at a condition 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, for both types of Pd precursor are shown in Figure 4.3. For both types of Pd precursor, 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 Figure 4.3(a), the catalyst prepared from $PdCl_2$ precursor 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. For the catalyst prepared from $Pd(NO_3)_2.2H_2O$, C18:2 was gradually hydrogenated to C18:1, as shown in Figure 4.3(b); 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. Sonthisawate *et al.* [4] suggested that the higher amount of saturated FAME, the higher oxidative stability, but the worse cold flow properties. This suggests that biodiesel product after 1.5 h of reaction obtained from using the catalyst prepared from $Pd(NO_3)_2.2H_2O$ will exhibit good biodiesel properties, especially oxidative stability and cold flow properties; where polyunsaturated FAMEs were fully converted into monounsaturated FAME with a minimal increase of saturated FAME.

The FAME composition and some fuel properties of biodiesel feed and biodiesel product after 1.5 h obtained from using the catalysts prepared from both types of Pd precursor are reported in Table 4.3. It apparently shows that partial hydrogenation using Pd/C prepared from $PdCl_2$ and $Pd(NO_3)_2.2H_2O$ can improve the oxidative stability of biodiesel from 1.49 h to 40.50 h and 36.00 h, respectively. These values meet the specification for Thai Standard, which requires ≥ 10 h of oxidative stability. However, the biodiesel product obtained from using $PdCl_2/C$ exhibited worse pour point and cloud point than that of $Pd(NO_3)_2.2H_2O/C$.

Figure 4.3 FAME composition as a function of reaction time using as received-2 wt.% Pd/C calcined under N_2 at 500°C, prepared from: (a) $PdCl_2$ and (b) $Pd(NO_3)_2.2H_2O$ (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 4.3 FAME composition and some fuel properties of biodiesel feed and biodiesel product after 1.5 h of reaction using as received-2 wt.% Pd/C calcined under N_2 at 500°C prepared from $PdCl_2$ and $Pd(NO_3)_2.2H_2O$

	Biodiesel feed	Biodiesel product after 1.5 h	
		Pd-Cl$_2$/C	Pd-NO$_3$/C
FAME composition (%)			
Saturated FAME	67.72	95.74	71.89
Monounsaturated FAME	26.98	4.26	28.11
Diunsaturated FAME	5.30	0.00	0.00
Biodiesel properties			
Oxidative stability (h)	1.49	40.50	36.00
Pour point (°C)	16.0	25.0	22.0
Cloud point (°C)	16.0	26.0	23.0

According to these results, it can be concluded that the catalyst prepared from $PdCl_2$ showed the better catalytic activity in terms of complete hydrogenation, whereas the catalyst prepared from $Pd(NO_3)_2.2H_2O$ exhibited better activity in terms of partial hydrogenation. The higher hydrogenation activity of the catalyst prepared from $PdCl_2$ consistent with its smaller Pd particle size (<5 nm from XRD). Therefore, $Pd(NO_3)_2.2H_2O$ was the suitable precursor for preparation of Pd/C catalyst using in the partial hydrogenation of polyunsaturated FAMEs derived from palm oil and was selected to be used as a Pd precursor for further study.

4.4.2 Effect of Catalyst Calcination Condition

The XRD patterns of Pd/C catalysts prepared from $Pd(NO_3)_2.2H_2O$ precursor, which were calcined under different conditions are shown in Figure 4.4. The broad signal at about of 25°, which is assigned to the amorphous carbon, was observed for all catalysts [19]. There were no significant peaks of PdO or Pd observed in Pd/C catalyst that was calcined under air at 300°C (Figure 4.4(a)). This suggests that PdO or Pd particles were highly dispersed on the surface of activated C

or the PdO or Pd crystallite size of this catalyst was below the lower limit of XRD detectability (<5 nm) [6]. However, the small peak of Pd at 2θ of 40.20° was observed after this catalyst was reduced (Figure 4.4(b)). On the other hand, the catalyst that was calcined under air at 500°C showed sharper and more intense peaks of PdO at 33.90°, 40.90°, 54.80°, 60.20°, 60.85°, and 71.45°, and some small peaks of Pd with the narrower and sharper peak of carbon (Figure 4.4(c)). This suggests that PdO was formed from the oxidation of the Pd precursor [20] and the decomposition of activated carbon support occurred. The result obtained from Thermo Gravimetric Analysis (TGA) evidenced that activated carbon started to degrade at a temperature ~450°C (not shown here). After this catalyst was reduced, the transformation of PdO to Pd occurred as shown in Figure 4.4(d); the four main characteristic peaks of crystalline Pd namely plane: (111), (200), (220), and (311) were observed. In addition, the presence of Pd diffraction peaks also detected for all catalysts that were calcined under N_2 (Figure 4.4(e)–(h)). Moreover, the mean Pd particle size of catalyst calcined under different calcination conditions was also calculated from the peak width at half height of the Pd (111). It evidently showed that the Pd particle size of the Pd/activated C catalysts both calcined under air and N_2 at 500°C was larger than those calcined at 300°C (Table 4.2). This suggests that, the aggregation of Pd particles occurred during the calcination at higher temperature.
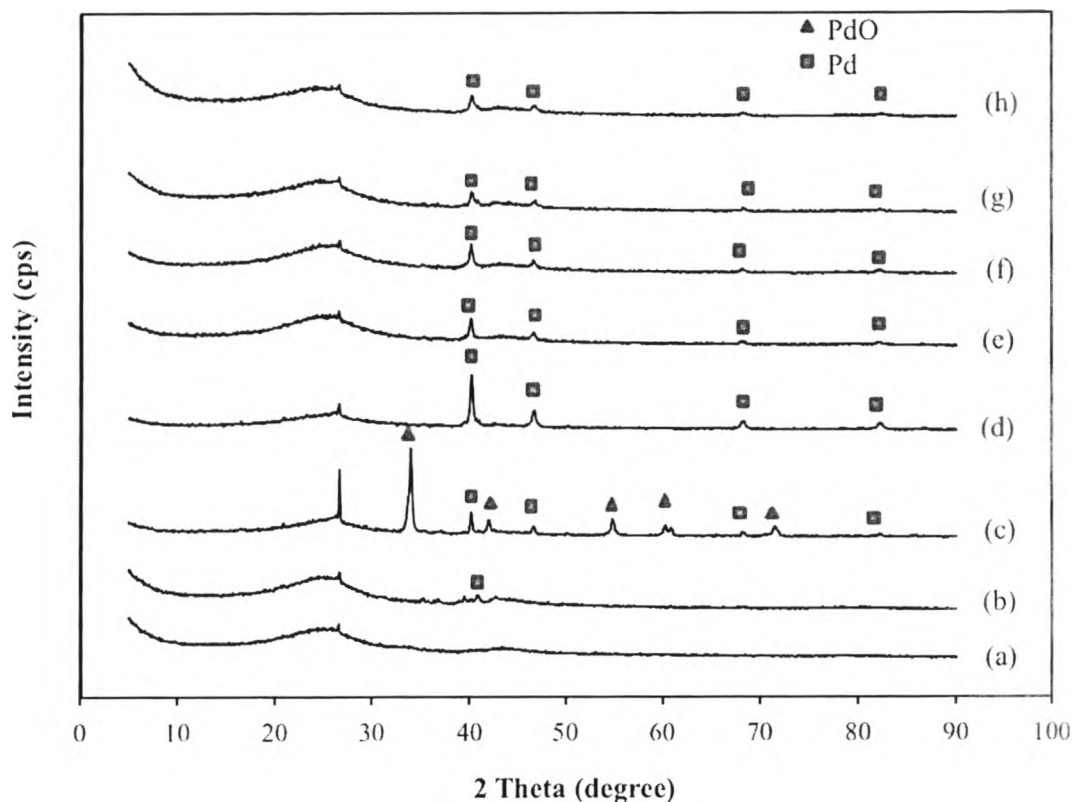
Figure 4.4 XRD patterns of 2 wt.% Pd [Pd(NO₃)₂.2H₂O] prepared under different calcination conditions: (a) calcined under air at 300°C, (b) calcined under air at 300°C and reduced, (c) calcined under air at 500°C, (d) calcined under air at 500°C and reduced, (e) calcined under N₂ at 300°C, (f) calcined under N₂ at 300°C and reduced, (g) calcined under N₂ at 500°C, and (h) calcined under N₂ at 500°C and reduced.

In order to evaluate the performance of the catalysts calcined under different conditions, the FAME compositions in each biodiesel products after reaction time of 1.5 h, operated at the same reaction condition (120°C, 0.4 MPa, 50 ml/min hydrogen flow rate, 500 rpm stirring rate, and 1.5 wt.% catalyst compared to starting oil) were compared as shown in Table 4.4. It obviously showed that all catalysts presented different hydrogenation activities. The catalysts in the reduced-formed (under H₂ at 250°C for 3 h) exhibited better activity in term of partial hydrogenation, which provided higher composition of monounsaturated FAME

(C18:1). In addition, when compared between the catalysts calcined under air with those calcined under N_2, the catalysts that were calcined under N_2 presented better partial hydrogenation property. These catalysts provided the biodiesel products with no significant amount of C18:2 and higher amount of C18:1 when compared with the catalysts that were calcined under air. Moreover, the calcination temperature also affected to the hydrogenation activity of the prepared catalysts. The catalysts calcined at 300°C exhibited higher hydrogenation activity while the catalysts calcined at 500°C showed better property in term of partial hydrogenation and achieved biodiesel products with higher C18:1 composition. According to these results, it can be suggested that Pd particle size plays an important role on the catalytic activity of the catalyst. The catalyst with smaller Pd particle size provided higher conversion and better catalytic activity in term of complete hydrogenation, whereas the catalyst with larger Pd particle size exhibited better property in term of partial hydrogenation.

Table 4.4 Comparison of FAME composition before and after 1.5 h of partial hydrogenation reaction using 2 wt.% Pd/C [Pd(NO$_3$)$_2$.2H$_2$O] calcined under different conditions

FAME	BDF feed	FAME composition (%)							
		After 1.5 h of hydrogenation time							
		air 300A	air 300R	air 500A	air 500R	N$_2$ 300A	N$_2$ 300R	N$_2$ 500A	N$_2$ 500R
C12:0	0.73	0.66	0.70	0.69	0.75	0.79	0.69	0.83	0.70
C14:0	1.71	1.58	1.65	1.64	1.76	1.82	1.63	1.86	1.63
C16:0	60.78	60.54	62.14	62.85	62.08	60.34	62.66	61.23	60.80
C18:0	4.30	30.05	20.77	23.83	20.44	28.34	18.07	7.76	5.00
C18:1	26.98	6.88	14.50	10.77	14.77	8.45	16.64	28.11	29.23
C18:2	5.30	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.37
C22:0	0.20	0.30	0.25	0.23	0.20	0.27	0.30	0.22	0.26

From the above results, it evidently showed that the catalysts calcined under N_2 at 500°C both in as-received and reduced forms ($N_2$500A and $N_2$500R) seem to be suitable for partial hydrogenation of polyunsaturated FAMEs derived from palm oil. The FAME composition of biodiesel as a function of reaction time, obtained from using $N_2$500A and $N_2$500R catalyst were compared as shown in Figures 4.5(a) and (b). It was obviously shown that both $N_2$500A and $N_2$500R catalysts clearly exhibited consecutive hydrogenation reaction from C18:2 to C18:1 and then consequently from C18:1 to C18:0. However, the catalytic activity of $N_2$500R is lower than that of $N_2$500A catalyst. For $N_2$500R catalyst, C18:2 was slowly hydrogenated as shown in Figure 4.5(b); the amount of C18:2 slightly decreased from 5.30% to 1.56% at the fourth hour. When compared with $N_2$500A catalyst, at only 1.5 h of reaction, C18:2 was fully converted into C18:1 with a minimal increase of C18:0. This suggests that the biodiesel product after 1.5 h obtained from using $N_2$500A catalyst will exhibit better oxidative stability than the product that was obtained at 4 h of reaction using $N_2$500R catalyst. In addition, it can be suggested that $N_2$500A catalyst can be stimulated very well under the milder condition. From these reasons, it can be concluded that as received-2 wt.% Pd/C [$Pd(NO_3)_2.2H_2O$] calcined under N_2 at 500°C is the suitable catalyst for partial hydrogenation of polyunsaturated FAMEs derived from palm oil. Moreover, $Pd(NO_3)_2.2H_2O$ and calcination under N_2 at 500°C were selected to be used as Pd precursor and calcination procedure for further study.
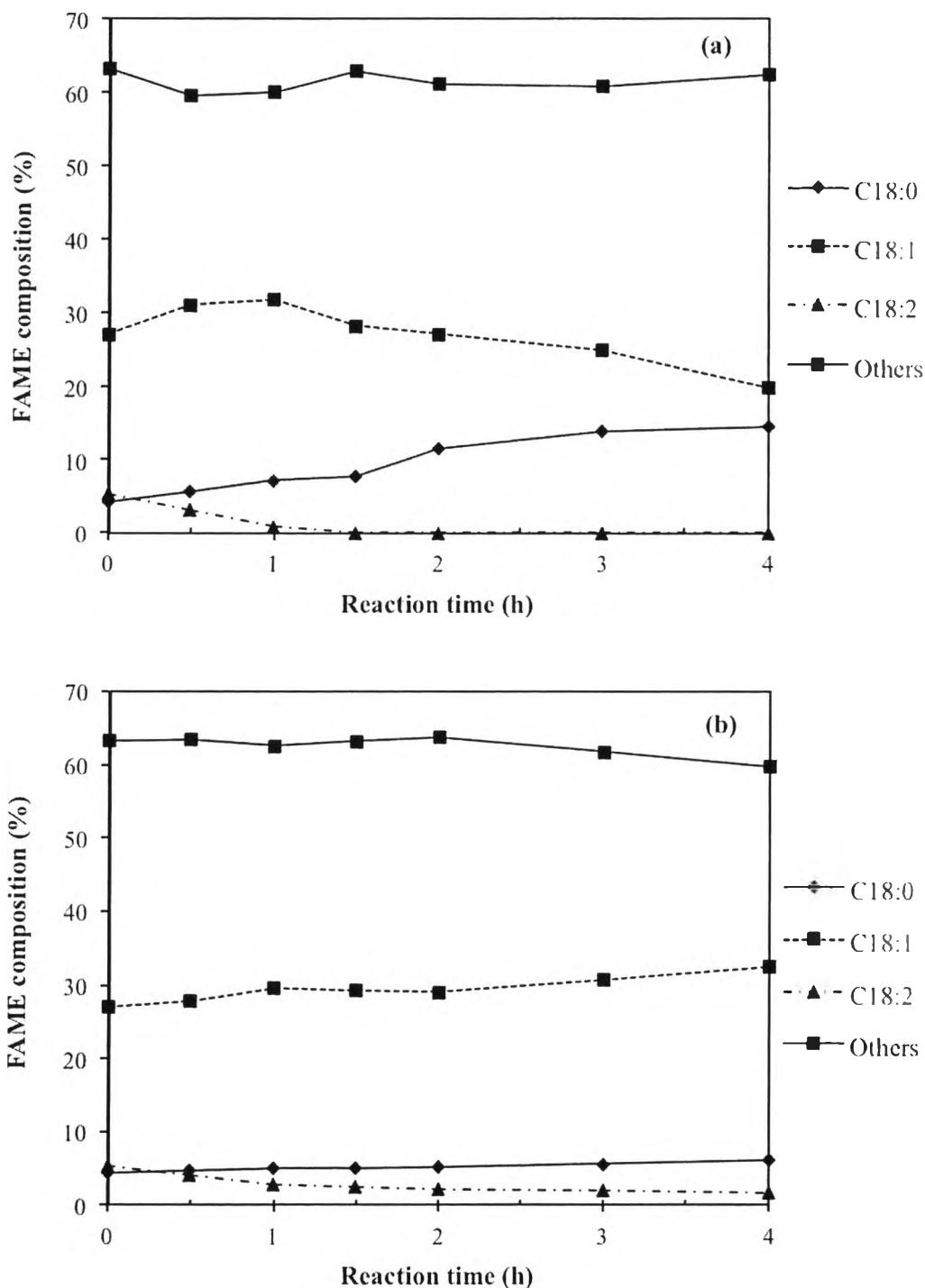
**Figure 4.5** FAME composition of biodiesel as a function of reaction time, obtained from using 2 wt.% Pd/C [Pd(NO₃)₂.2H₂O] calcined under N₂ at 500°C in (a) as-received form and (b) reduced form (Reaction conditions: 120°C, 0.4 MPa, 50 ml/min H₂ flow rate, 500 rpm stirring rate, and 1.5 wt.% catalyst compared with starting biodiesel)

4.4.3 Effect of Type of Carbon Support

In this part, the effect of type of carbon support: activated carbon and carbon aerogel, was investigated for the partial hydrogenation of biodiesel. Figure 4.6(a) and (b) show FE-SEM micrographs of the activated carbon and carbon aerogel support. 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.

Furthermore, the characteristics of Pd supported on activated carbon and carbon aerogel were investigated by many characterization techniques such as XRD, CO-chemisorption, and TEM. 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 (not shown here). 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 4.5). In addition, TEM micrographs of Pd/activated carbon and Pd/carbon aerogel (Figure 4.7(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 on activated carbon catalyst. This is because of the interconnection stucture, which incorporated into the open mesopores of carbon aerogel, creates a well dispersion of Pd particle. 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 2.81% and 35.09%, respectively (Table 4.5).

2.0kV 9.0mm x15.0k SE(M)   3.00um

2.0kV 10.2mm x15.0k SE(M)   3.00um
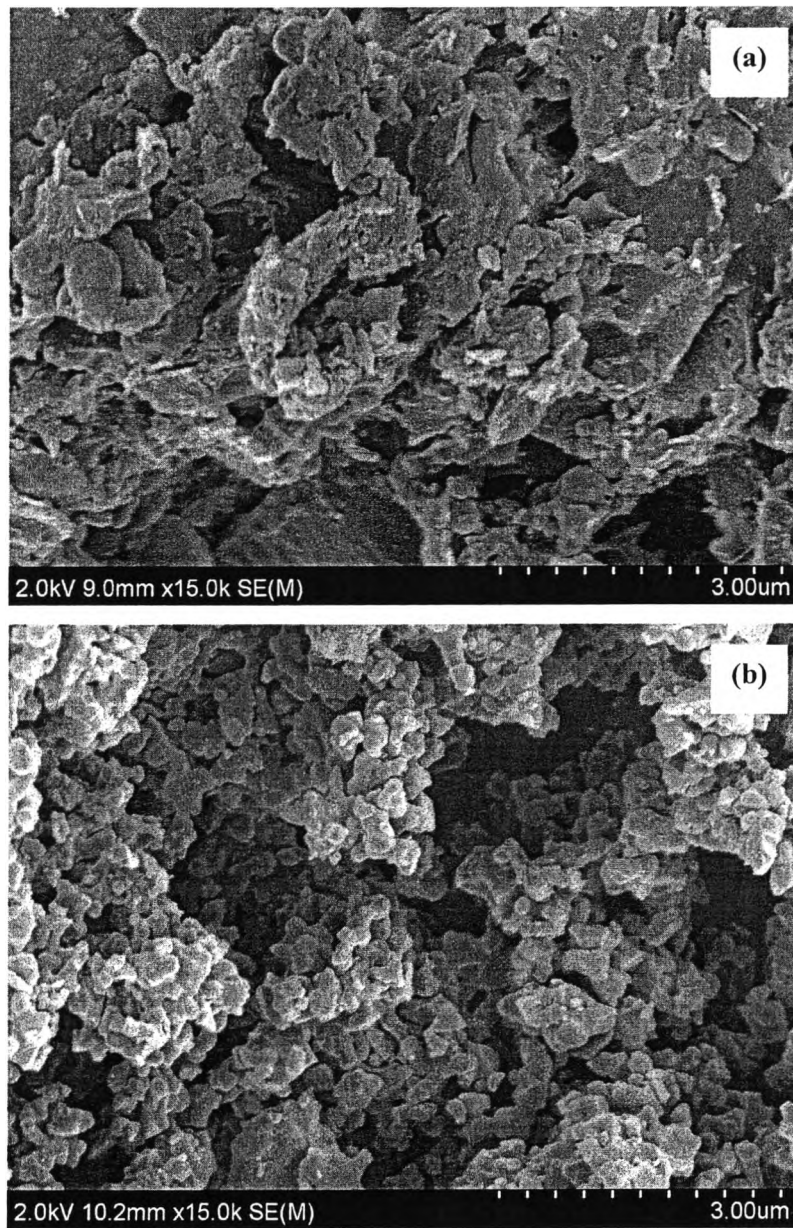
Figure 4.6 FE-SEM micrographs of activated carbon (a) and carbon aerogel (b)

Table 4.5 Characteristics of Pd supported on activated carbon and carbon aerogel.

Catalyst	Pd(111) particle size (nm)	Pd dispersion (%)
Effect of type of carbon support		
Pd/activated carbon	17.75	2.81
Pd/carbon aerogel	9.97	35.09
Effect of size of activated carbon support		
Pd/≤ 40 μm	17.75	2.81
Pd/850 μm	N/D[a]	1.98
Pd/granule form	N/D[a]	1.05

[a]Not determined
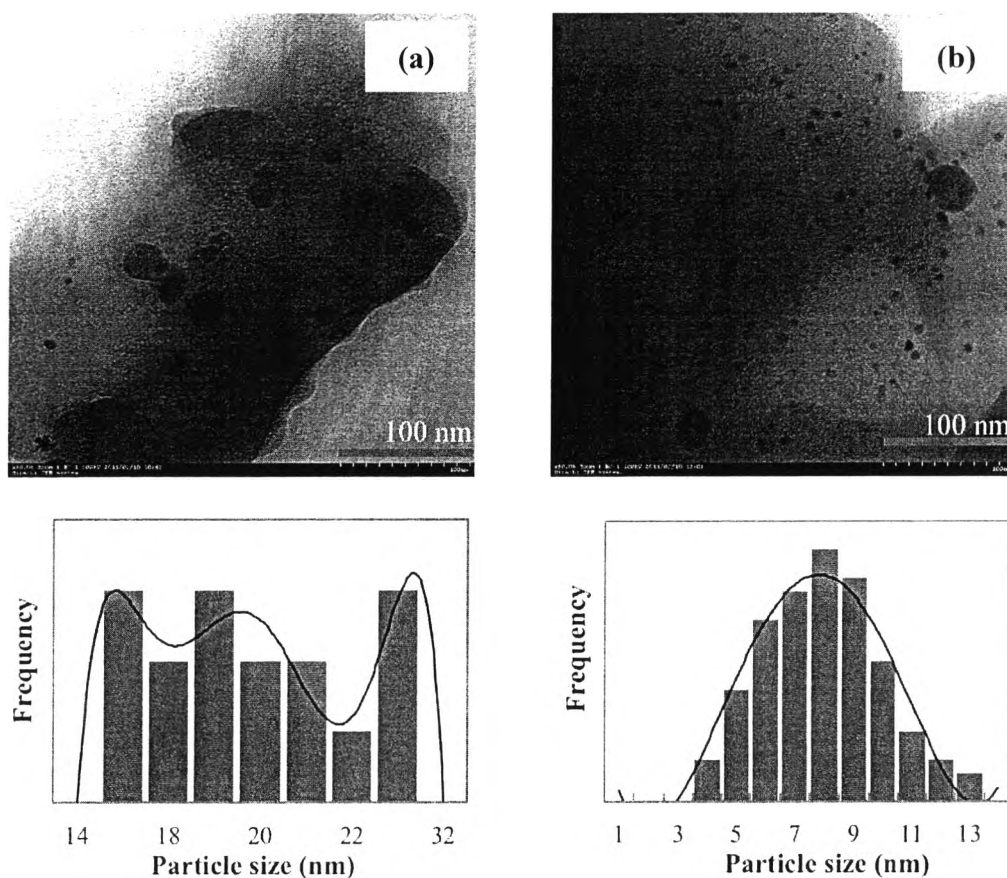
Figure 4.7 TEM micrographs and Pd particle size distribution observed by TEM: (a) Pd/activated carbon and (b) Pd/carbon aerogel

Initially, the hydrogenation activity of carbon supports without Pd loading was investigated at the reaction condition of 120°C, 0.4 MPa, 50 ml/min hydrogen flow rate, and 500 rpm stirring rate. It significantly showed that both types of carbon did not present any hydrogenation activity. Then, the partial hydrogenation of polyunsaturated FAMEs over Pd/activated carbon and Pd/carbon aerogel were carried out at the same reaction conditions. The catalytic activity of these catalysts was determined by examining FAME composition in the product stream during the hydrogenation time as shown in Figure 4.8. It obviously shows that the hydrogenation activities of both catalysts were not significantly different, eventhough both catalysts have different pore structure, Pd particle size, and Pd dispersion. The insignificant effect of support on the hydrogenation activity of the catalyst was also observed by Fernández and co-workers [21]. They studied the hydrogenation of sunflower oil using Pd on Al_2O_3, ZSM-5, and MCM-22 and found that different types of support did not affect the activity of the catalyst. Therefore, commercial activated carbon was selected to be used as a support for the next part due to the ease in preparation point of view.
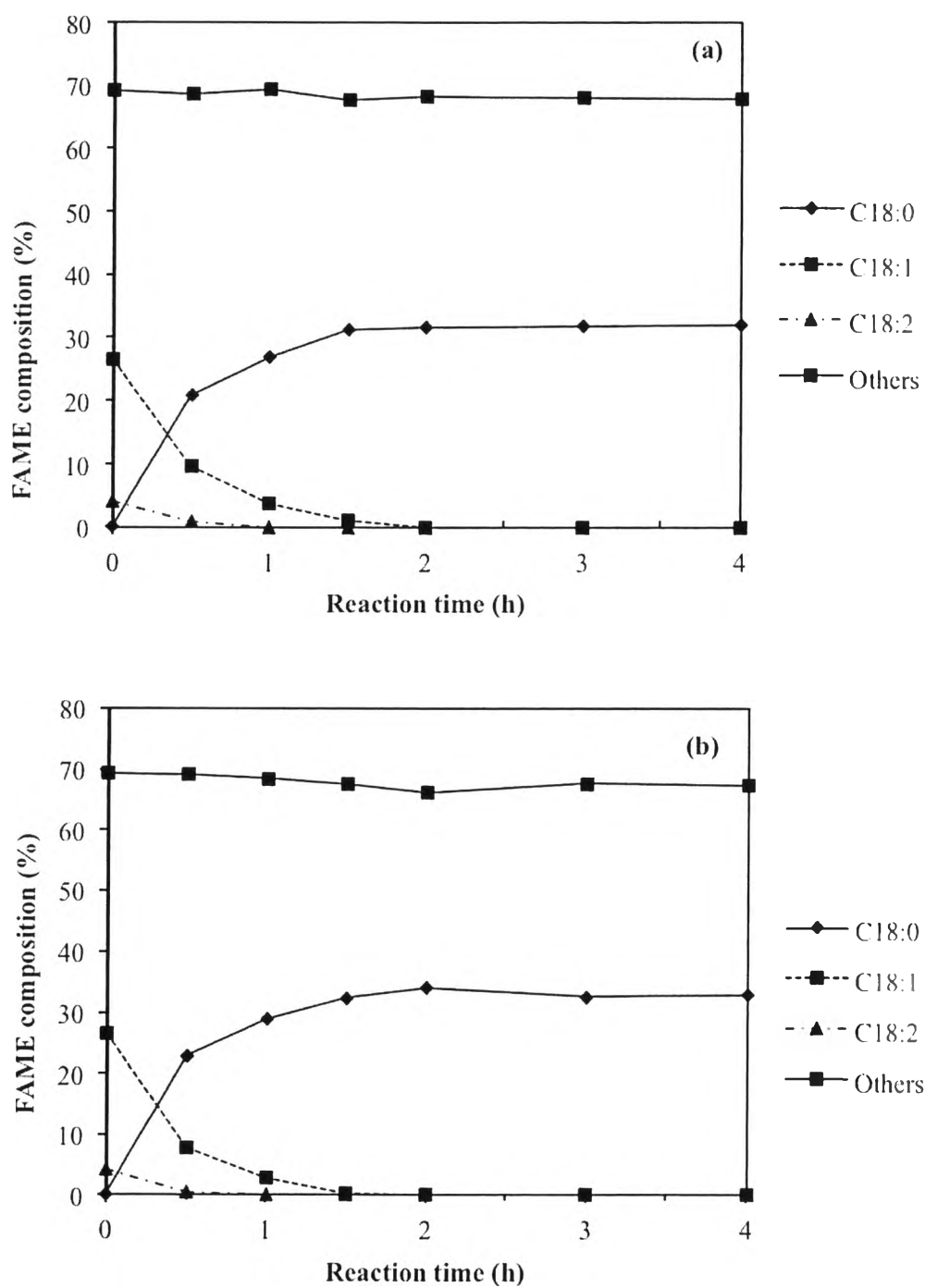
Figure 4.8 FAME composition of hydrogenated biodiesel as a function of reaction time of Pd supported on (a) activated carbon and (b) carbon aerogel (Reaction conditions: 120°C, 0.4 MPa, 50 ml/min H_2 flow rate, 500 rpm stirring rate, and 1.5 wt.% catalyst compared with starting biodiesel)

4.4.4 Effect of Particle Size of Carbon Support

Furthermore, 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 were studied. The Pd dispersion of Pd supported on different particle sizes carbon is presented in Table 4.5. 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 Figure 4.9. It clearly shows that the hydrogenation activity was decreased in this order: Pd/≤40 μm > Pd/850 μm > Pd/granule. As can be seen from the highest and lowest C18:0 composition in Pd/40 μm activated carbon and Pd/granule activated carbon, respectively. This can be explained from the larger of 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 surface for contacting the reactant and higher dispersion of Pd, when compared at the same amount of support used.
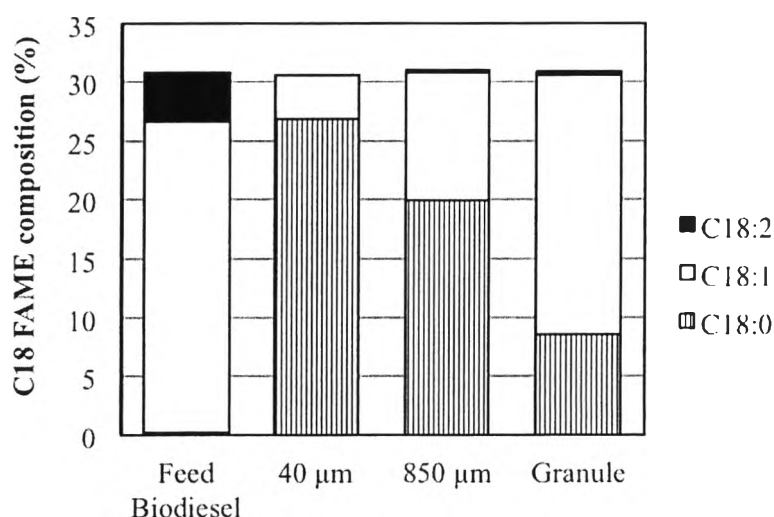
Figure 4.9 C18 FAMEs composition of feed biodiesel and hydrogenated biodiesel after 1 h of reaction using Pd supported on activated carbon with different particle sizes (Reaction conditions: 120°C, 0.4 MPa, 50 ml/min H_2 flow rate, 500 rpm stirring rate, and 1.5 wt.% catalyst compared with starting biodiesel)

4.5 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 effects of Pd precursor, catalyst calcination condition, types of carbon support, and sizes of activated carbon support on the catalytic behavior of Pd/C catalysts were studied. The results revealed that Pd particle size plays an important role on the hydrogenation activity of the catalyst. The $Pd(NO_3)_2.2H_2O$ precursor and calcination under N_2 at 500°C for 2 h provided a good property of Pd/C catalyst for partial hydrogenation of polyunsaturated FAMEs derived from palm oil, which possessed ~17 nm Pd particle size that is suitable for the partial hydrogenation of small amount of polyunsaturated FAMEs in palm biodiesel. 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 ($\leq$40 μm) shows the highest hydrogenation activity, which can be explained from its high contacting area and high Pd dispersion. However, the structure and pore of the support did not show any significant effect on the activity of the catalysts.

4.6 Acknowledgements

4.7 References

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