

Synthesis of Palladium-Platinum Bimetallic Nanoparticles and their Catalytic Activity towards the Hydrogenation Reaction of Palm Olein

Salimah Shafii*, Wu Lihua, M. Ridzuan Nordin and Liew Kong Yong

Faculty of Industrial Science and Technology, University Malaysia Pahang, 26300, Kuantan, Pahang, Malaysia

Abstract

Bimetallic Pd-Pt catalyst was successfully prepared via conventional heating (CH), microwave (MW), and ultrasonic irradiation (US) methods. Bimetallic Pd-Pt nanoparticles stabilized with polyvinylpyrrolidone (PVP) were prepared with molar ratio of PVP to metal, 40:1. Smaller particles sizes with narrow distribution obtained after 30min and 10min with US and MW methods respectively. All the particles are spherical or near spherical in shape.

The average particles size and size distribution for Pd-Pt (US) nanoparticles was 1.28 ± 0.29 nm, while for Pd-Pt (MW) nanoparticles was 1.05 ± 0.21 nm. The average particles sizes of these bimetallic nanoparticles are comparable with the classical CH method, which was 1.23 ± 0.25 nm. Based from the XPS analysis, surface compositions of Pd and Pt show that PdPt(CH) and PdPt(MW) catalyst were enriched with Pd, meanwhile PdPt (US) composition was comparable and it might be in alloy structure formation. The activity of these three catalysts for the hydrogenation reaction of palm olein was studied. The reaction conducted under ambient temperature and atmospheric pressure. A molar ratio of palm olein to catalyst of 25000:1 has been used in the hydrogenation reaction to determine the conversion of linoleate, selectivity of trans-isomer and iodine value (IV) in the hydrogenated palm

olein. After 180 min of reaction, full conversion achieved with Pd-Pt (MW) catalyst, while only 91.4% and 80.6% conversion achieved with Pd-Pt (US) and Pd-Pt (CH) respectively. However, the Pd-Pt (MW) catalyst shows the highest elaidate selectivity after 180 min, which was up to 13.1%, meanwhile the elaidate selectivity of 11.82% and

8.1% for both Pd-Pt (US) and Pd-Pt (CH) respectively. Even though higher conversion of linoleate achieved in short time and lower trans selectivity produced with Pd-Pt bimetallic catalyst. The IV calculated shows that Pd-Pt (MW) catalyst has the lowest IV then followed by Pd-Pt (US) and Pd-Pt (CH) catalysts.

Keywords: Polyvinylpyrrolidone; Platinum; Palladium; Hydrogenation; Palm olein

Introduction

The partial hydrogenation of vegetables is an industrial process that use to obtain a more stable product (which no oxidation on storage), together with a suitable texture and melting-temperature range at human mouth conditions for use as margarine, edible shortenings and baking applications [1,2]. During the hydrogenation process, the carbon double bonds are partially or fully saturated. Unfortunately, the catalytic isomerization of naturally occurring cis isomer to trans isomer fatty acids takes place [3]. In recent years, however it has been published that the intake of trans fatty acids (TFA) adversely affects blood lipid levels. Metabolic and epidemiologic studies confirm the potential role of TFA in increasing the risk of coronary heart disease. Furthermore, on each gram basis the negative health impact of TFA appears to be stronger than that of saturated fatty acids [4,5]. A numbers of alternative have been studied to figure out the ways for substantial reduction of inevitable TFA content in the hydrogenated edible oils such as the electro-catalytic hydrogenation, supercritical fluid hydrogenation, membrane reactor technology, catalytic transfer hydrogenation, and modification including supported precious metals [3]. The investigated catalysts offer various advantages but also have considerable shortcomings.

In this part of work, such modification of precious metals included the use of microwave and ultrasonic irradiation selected and the effects of the catalyst on hydrogenation of palm olein were studied. Obviously, the use of microwave energy to heat chemical reactions has attracted a considerable amount of attention, due to its numerous successful applications in organic synthesis, polymer chemistry, material sciences,

nanotechnology, and biochemical processes [6-10]. A huge number of paper published, had discovered that by using microwave technology can synthesis nanoparticles successfully. The motivation for the use of microwave energy has mainly been to design faster, cleaner and economically more viable methods for synthesis. The super rapid heating and sometimes extreme temperatures observable in microwave chemistry generally lead to faster processes. The transformations that normally required several hours when performed in a solvent at reflux temperature in an oil bath however may reach completion in a few minutes or even seconds using superheated solvent in a seal vessel or microwave reactor [11]. These unique features explained that this heating method has gained its popularity in many different field of chemistry. Mispa and co workers in their previous research in 2010 determined that the electric field applies a force on charged particles, resulted the charged particles started to migrate or rotate. Due to the movement of charged particles, further polarization of polar particles takes place. The concerted force applied by the electric and magnetic

***Corresponding author:** Salimah Shafii, Faculty of Industrial Science and Technology, University Malaysia Pahang, 26300, Kuantan, Pahang, Malaysia, Tel: +6013-977702; E-mail: salimahshafii@hotmail.com

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components of microwaves are rapidly changing in direction, which creates friction and collisions of the molecules, claimed effects of the microwave irradiation include thermal and non-thermal effects [12]. Many papers published about microwave compared with conventional method, shows that microwave synthesis has the advantages of short reaction time, small particles size and high purity [8,9,11,13,14].

On the other hand, the ultrasonic irradiation in particular the acoustic techniques is one of the most useful approaches for acceleration of chemical processes. Acoustic waves with frequencies of more than 20 kHz, can cause structural changes and accelerate chemical reactions [15]. The initiation of most of the sonochemical reactions in aqueous solution applying acoustic vibration was caused by cavitation. Acoustic cavitation is a disturbance of the continuity of a liquid, which connected to the creation, growth, oscillation, and collapse of steam-to-gas bubbles inside the liquid [16,17]. The development of cavitation bubbles follows the sound field in a liquid during the cycles of compression and expansion and stimulated by time-varying pressure. Bubbles either oscillate around their equilibrium position over several expansion or compression cycles or can grow over one or more acoustic cycles to double their initial size and then finally collapse violently [16-18]. Radziuk D et al. [18] report that the tremendous heating or cooling rates of bubbles and transient of high temperature inside hotspot in heterogeneous medium which contained metal nanoparticles, caused it not only to accelerate catalytic activity of metal nanoparticles but also produced smaller size particles that are highly dispersed. Another comprehensive study was on the sonochemical synthesis of colloidal bimetallic Pd-Sn nanoparticles and conducted by Kim et al. [19]. Metals salt of Pd (NH₄)₂Cl₄ and SnCl₂ dissolved in an aqueous ethanol solution containing citric acid, which acts as the stabilizing agent for the bimetallic nanoparticles. Ultrasonic irradiation performed with collimated 20 kHz beam from a ceramic transducer with a titanium amplifying horn directly immersed in the solution and operated with an input power of 42 Wcm⁻² for 2 hours. The bimetallic nanoparticles shape and size were characterized with TEM. Highly dispersed Pd-Sn nanoparticles with sizes of 3-5 nm in average were obtained. Thus, implies that the ultrasonic irradiation method is an effective to form nanoparticles.

The aim of the present work is to synthesized bimetallic nanoparticles of Pd-Pt under ultrasonic irradiation and microwave heating and compared with the conventional heating method. As a lot papers published about the interesting characteristic of bimetallic catalyst compared to monometallic catalyst, it is not only helps to enhance catalytic activity but also increasing the yield of desired product [20,21]. Thus, Pd-Pt catalysts were used in hydrogenation reaction of palm olein to determine the effect of Pd-Pt catalyst especially on catalytic activity and the formation of elaidate (trans fatty acid).

Materials and Methods

Chemicals

Analytical grade or equivalent chemicals: Polyvinylpyrrolidone (PVP), (Mw 40000); methyl oleate (>99%) and methyl elaidate (>99%) (Sigma Aldrich); chloroplatinic acid hexahydrate (Merck, Germany); methanol and hexane AR grade (Merck, Germany); Butan-1-ol (Merck, Germany); anhydrous sodium sulfide and sodium hydroxide (BDH, UK) were used without purification. Palm olein (100% refined palm oil) was obtained from a local supermarket. The fatty acid compositions of the olein were determined to be: 36.11% palmitic, 4.04% stearic, 45.21% oleic, 11.85% linoleic and 0.39% linolenic acid.

Preparation of PVP-stabilized bimetallic Pd-Pt colloidal nanoparticles

PVP-stabilized Pd-Pt bimetal colloids was prepared where 0.0222g PdCl₂ (1.25×10⁻⁴ mol) were converted to H₂PdCl₆·nH₂O by adding 100µl of concentrated HCl, then 0.065g H₂PtCl₆·6H₂O (1.25×10⁻⁴ mol) and 1.11g PVP (1.00×10⁻² mol) was added to the mixture of methanol (130 ml) — distilled water (150 ml) which act as solvent. The solution was mixed in the 500 mL 3-neck round bottom flask. Then, 20 ml of 0.1 M NaOH in methanolic was added drop wise under vigorous stirring. Then the solution was divided into three portions of 100 ml. Each portion was synthesized under different method to produced colloidal metal nanoparticles. Brief descriptions of the different method condition were shown in the Table 1 below. Finally, the final colloidal solution resulted in a dark brown color will be stored in a dark bottle at 4°C [18].

Hydrogenation of palm oil

A constant gas flow rate of 36-37 ml/min of hydrogen gas was used for the whole experiments. The gas flow was first stabilized for 30 min before calibrated thrice. The hydrogenation reaction was performed at ambient temperature and atmospheric pressure. Colloidal catalyst of 0.5 ml (4.17 x 10⁻⁷ mol) and 48 ml of butan-1-ol was fed into the reactor. Next, hydrogen gas flown inside the reaction vessel continuously and the catalyst was activated for 60 min. Finally, palm olein (0.01mol) was injected into the reaction vessel and the reaction started immediately for 180 min. The hydrogenation reactions were done under conventional stirring at the speed of 200 rpm. Partially hydrogenated palm olein were sampled at selected interval; 10 min, 20 min, 30 min, 40 min, 50 min, 60 min, 90 min, 120 min, 150 min, and 180 min.

Analysis method

UV-Visible spectrophotometer (UV-Vis): UV-Vis analysis was using Hitachi U-1800 UV-Visible spectrophotometer. All spectra were taken in the range of 200-700 nm with scan speed of 400 nm/min.

Transmission electron microscopy (TEM): Characterization of the particles size and dispersion were done by using the TEM with LaB₆ source Tecnai G² 20 S-TWIN. Sample for TEM were prepared by placing a drop of a colloidal catalyst onto a perforated carbon copper grid, then the solvent was evaporated for at least 3 min. The average particle size and standard deviation was determined based on that of 250-300 particles, from enlarged photographs via Gatan micrograph software Choo et al. [22].

X-ray diffractometer (XRD): X-Ray diffraction is a strong method to investigate the solid structure of metal nanoparticles. The X-ray diffraction (XRD) patterns of bimetallic Pd-Pt nanoparticles were

Type of method	Synthesized process condition
Conventional heating, Pd-Pt(CH)	This method was done by using oil bath to maintain the refluxing process condition was heated at reflux temperature for 3hr [22,23].
Microwave irradiation, Pd-Pt(MW)	Power of 100 watts was used. Time for the heating was dependent to the color of colloidal solution until it is started to change to dark brown.
Ultrasonic irradiation, Pd-Pt(US)	Ultrasonic bath (ELMA D-78224, type S60H) with frequency of 37kHz was used for this experiment. Temperature of 80°C as it was the maximum temperature for this equipment. Time for the heating was same with the microwave method.

Table 1: Different method and their synthesized process condition.

determined by a Bruker-D8 diffractometer using monochromatized Cu-K α radiation ($\lambda = 1.54056 \text{ \AA}$) operated at 40 kV and 40 Ma and collected by a Vantec-1 detector.

X-Ray photoelectron spectroscopy (XPS): The XPS measurements of the ITO (indium-tin-oxide) substrates were carried out in a VG ESCALAB MK II spectrometer, using a monochromatic Al K α 1486.60 eV as X-ray source. The vacuum in the analysis chamber was maintained at approximately 10^{-8} Pa or lower. All binding energies were referenced to the binding energy of the carbon C 1s peak at 284.0 eV.

Gas Chromatography with FID detector (GC-FID): The hydrogenated palm olein was methylated before analyzed with Agilent-6890 gas chromatograph (GC) equipped with FID detector and a HP-88 capillary column (L , 100m; i.d., 0.25 mm; thickness of film, 0.25 μm). The column temperature was programmed from 185 to 210°C at

2°C.min $^{-1}$ and held at 210°C for 2 min and then raised to 230°C at 3°C.min $^{-1}$ and held for 3 min with helium as carrier gas. Both the injector and detector temperatures were set at 250°C. Methyl oleate and methyl elaidate served as standard for determination of cis- and trans- isomers. Below are the formulas used for calculating linoleate conversion, trans selectivity and iodine value (IV):

Calculations for C18:2 conversions (Brito, 2007)

The C18:2 conversions (linoleate) were determined directly from the GC fatty acid composition using the following formula (Brito, 2007):

$$\text{Conversion } C_{18:2} = \frac{C_{18:2_i} - C_{18:2_0}}{C_{18:2_0}} \times 100\% \quad (C_{18:2_0} = \text{initial value; } C_{18:2_i} \text{ current value})$$

Calculations for trans selectivity

The trans (elaidate) selectivity was determined directly from the GC fatty acid composition using the following formula (D. Pham Minh, 2009):

$$\text{Trans selectivity} = \frac{C_{18:1_{\text{Trans}}}}{C_{18:1_{\text{Trans}}} + C_{18:1_{\text{Cis}}}} \times 100\%$$

Calculations for Iodine Values

The iodine value for oil samples was determined directly from the GC fatty acid composition using the following formula (Xiao, 2007):

$$\text{Iodine value} = [(\% \text{ C18:1} + \% \text{ trans C18:1}) \times 0.86] + [(\% \text{ C18:2} + \% \text{ trans C18:2}) \times 1.732] + [(\% \text{ C18:3} + \% \text{ trans C18:3}) \times 2.616]$$

Results and Discussion

In this part, Pd-Pt bimetallic nanoparticles were synthesized using chemical reduction method as mentioned in the literature. Then, all the metal nanoparticles were reduced by conventional heating (CH), microwave (MW) and ultrasonic irradiation (US). Refluxing-reduction method was done by repeating previous work that has been done before by Yu and Liu [23]. The same method uses to reproduce the previous work and compared with the new preparation method of microwave and ultrasonic irradiation. Comparison was not only based on times required to reduce metal nanoparticles but also the effect on the size and particles distribution, but also its activity towards hydrogenation reaction of palm olein.

Table 2 below shows the time required to produce colloidal

Method	Time
Refluxing*	3 hr
Ultrasonic	30 min
Microwave	10 min

*Following methods from literature [22].

Table 2: Time required for the formation of bimetallic Pd-Pt nanoparticles

nanoparticles for all different methods. For the CH method, it took about 3 hr to produce a homogeneous dark brown colloidal solution of metal nanoparticles [22,23]. On the other hand, ultrasonic and microwave method does not required long time to produce a homogeneous colloidal nanoparticles solution. The result in the Table 2 below shows that bimetallic nanoparticles Pd-Pt took only 10 min and 30 min for microwave and ultrasonic irradiation method respectively. It show that the microwave resulted faster reduction to produced colloidal bimetallic Pd-Pt nanoparticles, followed by ultrasonic irradiation and then the classical heating method.

UV-Vis analysis

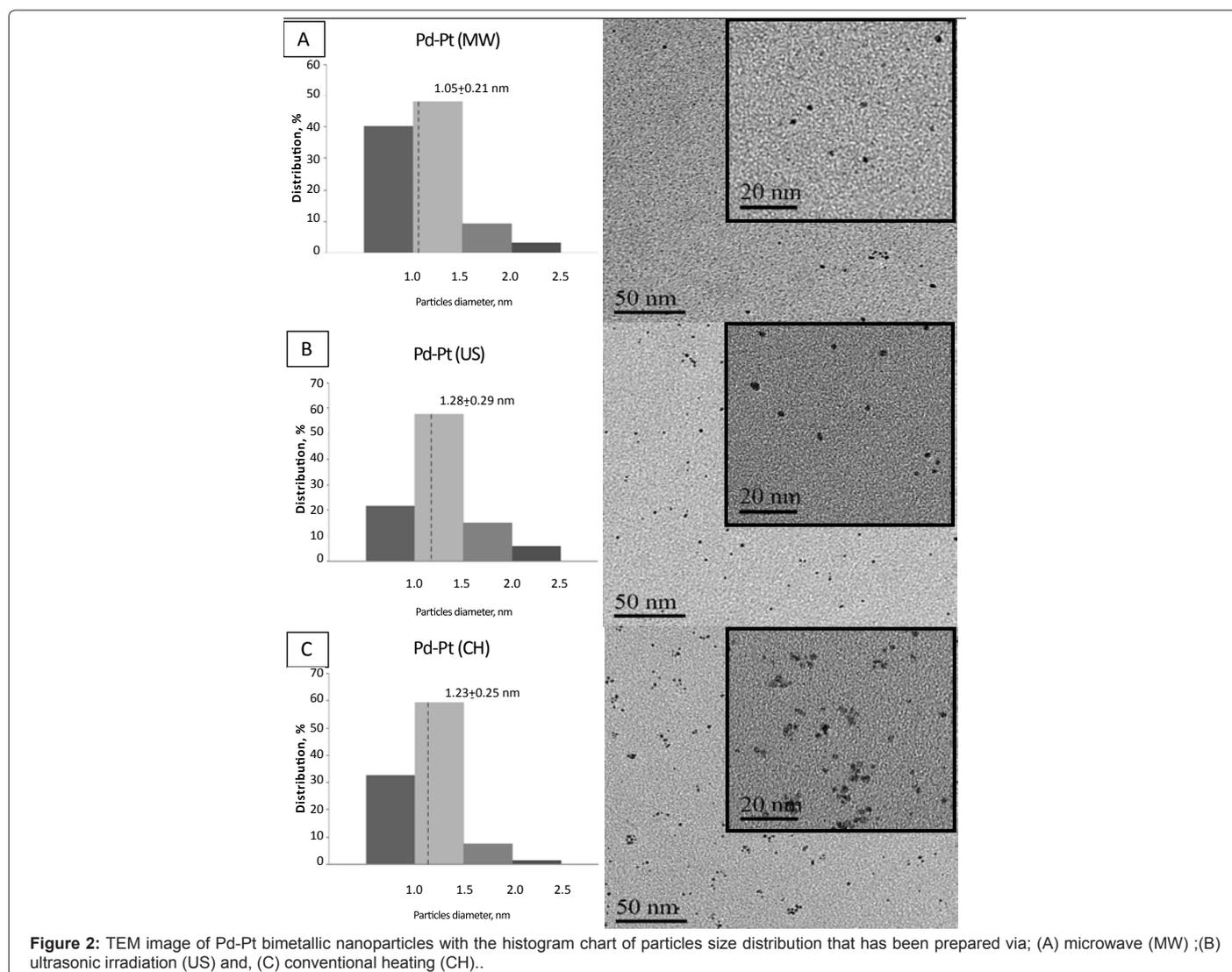
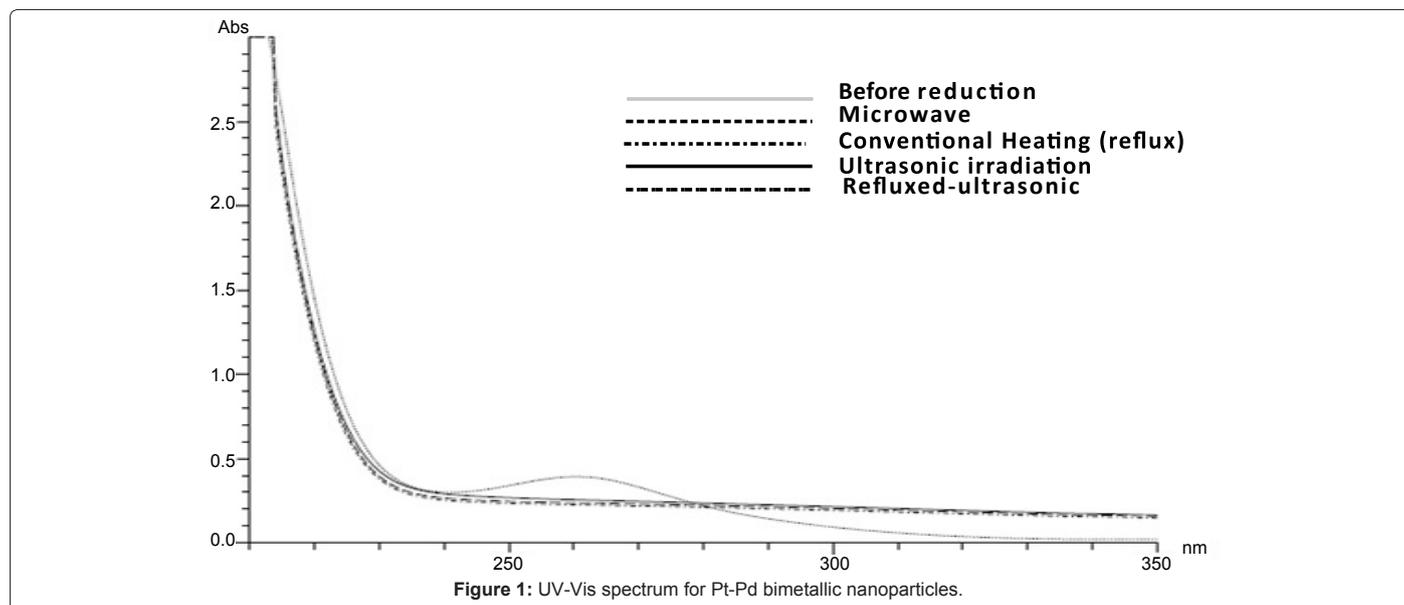
Even though a large number of researches have been reported on the synthesizing bimetallic nanoparticles [11,19,24-26], but the preparation of Pd-Pt stabilized by PVP via microwave and ultrasonic irradiation method has never been reported yet. The UV-Vis spectrums of Pd-Pt (CH), Pd-Pt (MW) and Pd-Pt (US) under different reduction process method shows in Figure 1. All samples including before and after reduction were taken for analysis to determine the changes of reduction processes for both Pd and Pt ions in the solution. A very broad peak was observed before the reduction occurred which indicated that an abundance of metal ions contained in the solution [27]. After the reduction process was completed where it can be determined via visual color changed, the broad peak totally disappeared. It is because of the synthesis of this bimetallic are using the co-reduction method. Where both metal salt of PdCl $_2$ and H $_2$ PtCl $_6$ ·6H $_2$ O, stabilizer and reducing agent are added at the same time and started the reduction process. Besides that, Pd-Pt bimetallic nanoparticles dispersion shows that at shorter wavelengths, the absorbance are the highest, which was described that the formation of smaller size and dispersed bimetallic colloidal nanoparticles [28,29].

TEM analysis

Among the techniques commonly used, transmission electron microscopy (TEM) is indispensable for metal nanoparticles study. Toshima and Yonezawa [30] stated that in their previous work, where noble metal nanoparticles such as Pd and Pt, give high contrast when particles are dispersed on the carbon supported copper grids, thus, the TEM image are much easier to analyze and clearly seen.

Typical micrographs and distribution histograms were shown in Figure 2A-C. The particles are of nanometer sizes with narrow distribution. Microwave-reduction method shows that it has resulted in smallest average particles size than the other methods, followed by ultrasonic irradiation and refluxing method. The average particles size are $1.05 \pm 0.21 \text{ nm}$, 1.28 ± 0.29 and $1.23 \pm 0.25 \text{ nm}$ for MW, US, and CH method respectively. All the TEM images show spherical and nearly spherical in shape and are highly dispersed. Both microwave and ultrasonic irradiation have shown well-improved method in synthesizing metal nanoparticles especially in chemical reduction technique that has been used in this research.

As mentioned previously, that MW method shows smallest



particles size compared to the other method. It can be explained by the microwave heating which allows an instantaneous volumetric and therefore a more rapid heating in comparison with the conventional heating process [11]. The MW technique has demonstrated as a better alternative in synthesizing bimetallic nanoparticles.

On the other hand, it was determined that particles are spherical or near spherical in shape and highly dispersed were also produced by ultrasonic irradiation method. Cavitation bubbles produced the shock wave increased the momentum of metal nanoparticles in the solution and caused them to collide with great force [31,32]. The particles are fracture upon collisions, leading to an overall decrease in the average particles sizes [33].

XPS analysis study

All the Pd-Pt (CH), Pd-Pt (MW), and Pd-Pt (US) samples were analyzed by XPS in order to identify the effect of all different method prepared on the surface composition of both Pd and Pt elements in bimetallic nanoparticles. Figure 3 (A-C) indicates the XPS spectrum for both Pd and Pt elements for each method of catalysts preparation. Both Pd and Pt element spectrums have been deconvoluted. Binding energy (BE) for each element and the Pd-Pt surface composition ratio of Pd to Pt was presented in the Table 3 below.

Pd-Pt (CH) sample shows that Pd spectrums have two peaks in Figure 3 (A1-A2). The binding energy for both peaks are, 335.1 and 341.4 eV assigned to electron form Pd3d_{5/2} and Pd3d_{3/2} orbital respectively. On the other hand, this spectrum can be curve-fitted with a spin orbit-split doublet by having BE at about 342.9 eV (3d_{3/2}) and 337.9 eV (3d_{5/2}) for Pd²⁺ species [34]. At the same table, the BEs for Pt element was also presented. The binding energy signals obtained are

70.9 and 74.2 eV. The Pt⁰ species was found at binding energy signal of 70.9 and 74.2 eV for the 4f_{7/2} and 4f_{5/2} components respectively [35]. The same XPS spectrum also indicated the existence of Pt²⁺ species at BEs of 73.1 (4f_{7/2}) and 76.4eV (4f_{5/2}). Next, the ratio of surface composition of Pd to Pt calculated was 2.7. As the composition of Pd was almost three times higher than Pt, it shows that the Pd enrichment might be to the polymer in anchoring Pt nanoparticles and thus allowing Pd to coalesce onto the Pt nanoparticles. The result shows that this bimetallic catalyst formation described that Pt metal atom had been covered by the Pd metal atom.

The Pd-Pt (MW) sample was presented in single element spectrum of Pd and Pt in Figure 3 (B1-B2). The binding energy of Pd3d_{5/2} and Pd3d_{3/2} electrons amounts are 334 and 340.3 eV respectively, that virtually coincides with the data for palladium in zero-valent metal state [36,37]. However Pd²⁺ species was also observed at BE of 339.3 eV (3d_{3/2}) [38]. This same XPS spectrum was also indicated the presence of oxidized Pt²⁺ species at about Bes of 73.4 and 76.5eV for the (4f_{7/2}) and (4f_{5/2}) component respectively [34,35]. Then the ratio of Pd to Pt surface composition for this sample was 2.5. Like Pd-Pt (CH) samples, it can shows that the Pd has enriched onto the Pt nanoparticles, and resulted higher composition of Pd on the surface of the bimetallic catalyst [30].

The last sample of bimetallic Pd-Pt (US) that is prepared under ultrasonic irradiation was also analyzed with XPS 3(C1-C2). For the Pd metal state element, deconvoluted XPS peaks of are recorded at BEs of 335.1 eV (Pd3d_{5/2}) and 340.5 eV (Pd3d_{3/2}), while Pd²⁺ species was spotted at BEs about 336.2 eV for Pd3d_{5/2} and 342.9 eV for Pd3d_{3/2} components [37]. The zero-valent state of Pt metal species was shown at binding energy signal of 70.7 eV and 74.1 eV for the 4f_{7/2} and 4f_{5/2}

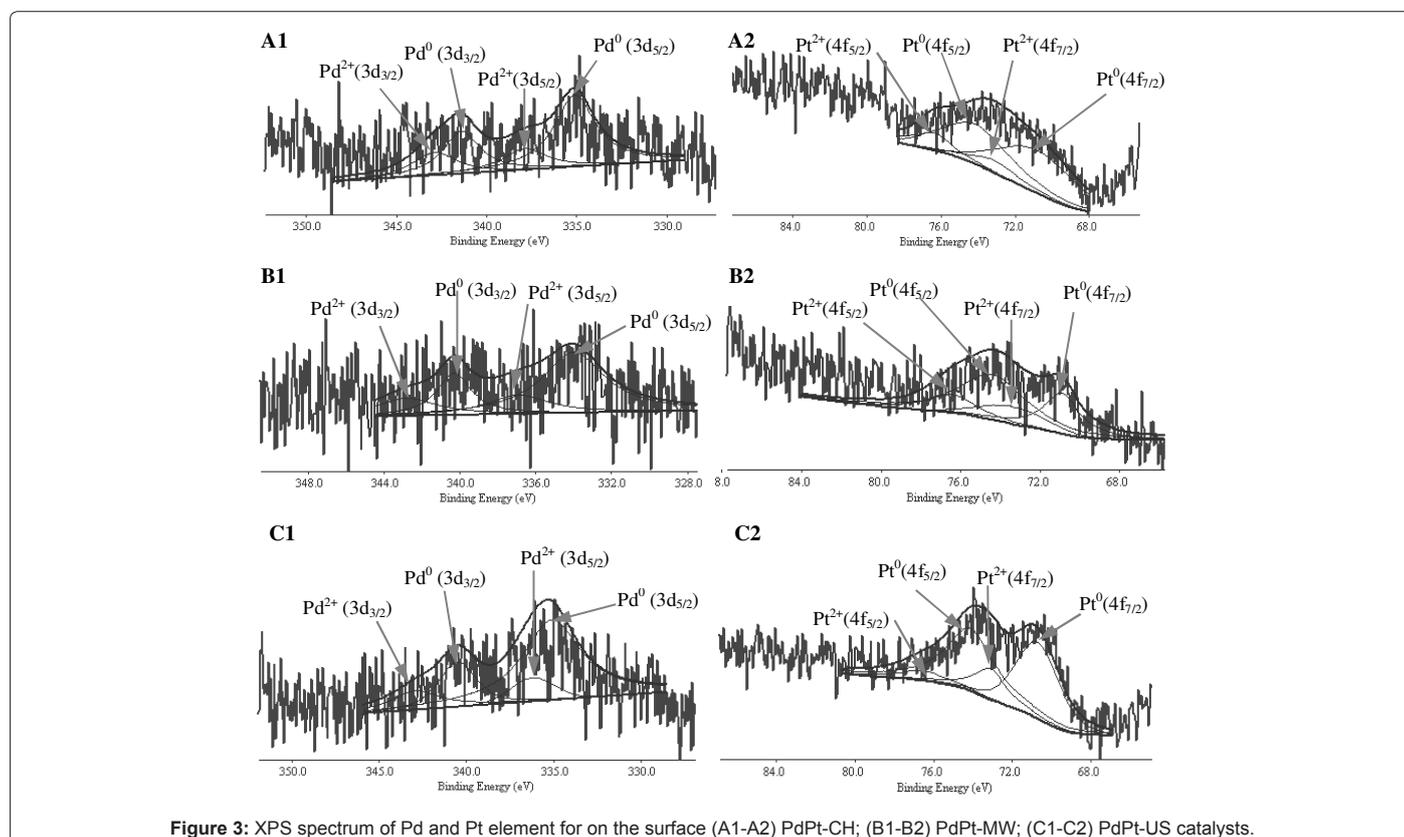


Figure 3: XPS spectrum of Pd and Pt element for on the surface (A1-A2) PdPt-CH; (B1-B2) PdPt-MW; (C1-C2) PdPt-US catalysts.

component respectively. Whereas unreduced Pt²⁺ ions were seen at 73.1 eV for Pt4f_{7/2} and 76.4 eV for Pt4f_{5/2} components [35]. Unlike Pd-Pt (CH) and Pd-Pt (MW) results, the ratio of Pd to Pt surface composition in this sample was 1.2. The surface composition ratio is almost identical; it suggested the alloy formation of bimetallic Pd-Pt (US). The alloy structure formation might be because due to the high intensity of the ultrasonic irradiation that caused the destruction of the bimetallic particles and thus rearrangement of both Pd and Pt atom to form an alloy structure [18,38].

Hydrogenation reaction of palm olein

It is well established that the double bonds in vegetable oils are naturally in cis-conformation. Upon hydrogenation reaction the trans isomer that is thermodynamically more stable are produced. The trans isomer of the fatty acid is unhealthy for consumption and hence their formation in edible fats during hydrogenation must be suppressed as far as possible [2]. Thus, the hydrogenation reaction has been carried out at ambient condition using a direct flow of hydrogen gas (99.5% purity) at a constant flow rate of 36 ml/min through the reaction vessel. This reaction has been done to demonstrate the effect of the Pd-Pt bimetallic catalyst on the composition of partially hydrogenated palm olein.

Figure 4A shows the conversion of C18:2 and selectivity of elaidate (trans-oleic) versus time of reaction for all catalysts of Pd-Pt (CH), Pd-Pt (MW) and Pd-Pt (US) shows the conversion of linoleate and selectivity of elaidate after hydrogenation reaction was conducted with bimetallic PdPt catalyst under conventional stirring method. After

reaction stopped at 180 min, full conversion was achieved with PdPt (MW) catalyst, meanwhile only 91.4 % and 80.6 % conversion were achieved with PdPt (US) and PdPt (CH) respectively. All catalyst shows similar trend, where the conversion of linoleate increased gradually.

On the other hand, it can be seen from the TEM image that although both PdPt (CH) and PdPt (US) catalysts have comparable particles size but PdPt (US) had shows lower linoleate composition compared to PdPt (CH). However, the conversions of linoleate between PdPt (CH) and PdPt (US) from the chart are significantly different. This result occurred maybe due to the well-dispersed of PdPt (US) nanoparticles which in contrary with

PdPt (CH) nanoparticles formation (refer to Figure 4C for TEM study). This aggregated PdPt (CH) nanoparticles caused it to have lower in activity and thus less amount of linoleate hydrogenated [23].

The PdPt(MW) catalyst shows the highest elaidate selectivity after 180 min which up to 13.1%, meanwhile the elaidate selectivity of 11.82% and 8.1% for both PdPt (US) and PdPt (CH) respectively. It can be seen a slightly difference of the elaidate selectivity between catalysts, where the highest selectivity of elaidate obtained with PdPt (MW), followed by PdPt (US) and PdPt (CH) catalyst. Bimetallic PdPt catalyst shows to be less favorable to isomerizes from cis (oleate) to trans (elaidate) conformation thus lower elaidate selectivity obtained for all catalyst.

This may be due to the combination of Pd and Pt characteristics that produced such catalytic activity result. From the previous research,

Sample	Pd3d5/2	Pd3d3/2	Pt4f7/2	Pt4f5/2	Surface ratio (Pd/Pt)
(CH)	335.1(Pd ⁰)	341.4(Pd ⁰)	70.9(Pt ⁰)	70.9(Pt ⁰)	2.7
	337.9(Pd ²⁺)	342.9(Pd ²⁺)	73.1(Pt ²⁺)	73.1(Pt ²⁺)	
(MW)	334.0(Pd ⁰)	340.3(Pd ⁰)	70.9(Pt ⁰)	74.4(Pt ⁰)	2.5
	336.9(Pd ²⁺)	342.8(Pd ²⁺)	73.4(Pt ²⁺)	76.5(Pt ²⁺)	
(US)	335.1(Pd ⁰)	340.5(Pd ⁰)	70.7(Pt ⁰)	74.1(Pt ⁰)	1.2
	336.2(Pd ²⁺)	342.9(Pd ²⁺)	73.1(Pt ²⁺)	76.4(Pt ²⁺)	

Table 3: Binding energy and raw area for each material detected with XPS.

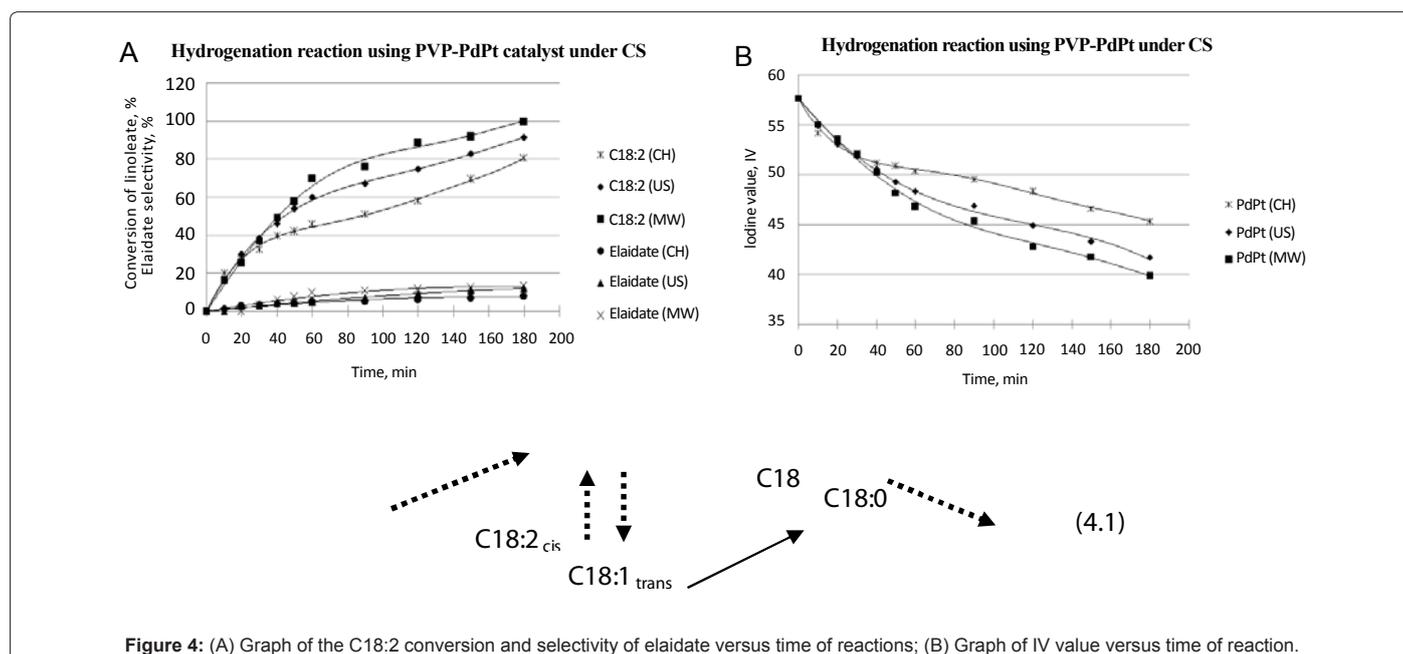


Figure 4: (A) Graph of the C18:2 conversion and selectivity of elaidate versus time of reactions; (B) Graph of IV value versus time of reaction.

Pd shows to be highly active and selective towards monoenes formation rather than Pt catalyst. However, Pd also exhibits higher selectivity towards TFA production than Pt [39]. Thus, in the context of no-TFA production, Pt was viewed as much better for hydrogenation of vegetable oils, as a consequences Pt are favor to produce non-desirable of saturated fatty acid. As a result, the combination of Pd and Pt bimetallic catalyst had shows an interesting result in this part of work. As we know that previously, Pd are highly active on hydrogenation reaction of linoleate, but it is also produced higher trans isomer [23]. However, Pt has the opposite characteristic with Pd catalyst. Thus, the combination of these two noble metals resulted higher activity but lower selectivity of trans isomer.

Figure 4B shows the IV versus time of reaction for all catalyst, Pd-Pt (CH), Pd-Pt (MW) and Pd-Pt (US). The IV for palm olein before hydrogenation reaction was 57. When the reactions proceed, the IV started to decrease slowly as the increasing numbers of double bond were hydrogenated. Based on the Figure 4B, all the catalysts show a similar trend of IV reduction. However, Pd-Pt (CH) and Pd-Pt (US) show a comparable result between each other and both of it have a slightly lower IV than Pd-Pt (MW). After the reaction stopped at 180 min, the IV for Pd-Pt (CH), Pd-Pt (US), and Pd-Pt (MW) are 45, 42, and 40 respectively.

A summary of the reaction pathway with the bimetallic PdPt is described in scheme 4.1 below. The PdPt catalyst favors the hydrogenation for both dienes and monoenes, which was describes by the dash line arrow in the scheme 4.1. Besides that, hydrogenation and isomerization of C18:1 is slightly favorable.

Conclusion

PVP stabilized Pd-Pt bimetallic nanoparticles with average particle sizes range at 1-2 nm were successfully prepared. Synthesis of bimetallic Pd-Pt with microwave and ultrasonic irradiation shows better alternative as a lot of time can be save and small and highly dispersed particles obtained. Interestingly, almost similar nanoparticles characterization achieved compared to classical heating method. The study of catalytic reaction of bimetallic Pd-Pt shows an impressive result. The combination of two noble metals, improved the compositions of partially hydrogenated palm olein, where higher conversion of C18:2 achieved in short time and in addition the elaidate selectivity are also very low. The IV is highly decreased as the reaction proceeds. Further work will be continued to determine the effect of ultrasonic irradiation on the hydrogenation reaction to compare with the conventional stirring.

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