

Activity and selectivity of noble metal colloids for the hydrogenation of polyunsaturated soybean oil

Hwai Peng Choo^a, Kong Yong Liew^{a,*}, Hanfan Liu^b, Chye Eng Seng^a,
W.A. Kamil Mahmood^a, Mohamed Bettahar^c

^a School of Chemical Sciences, Universiti Sains Malaysia, 11800 Minden, Penang, Malaysia

^b Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, PR China

^c Laboratoire de Catalyse Heterogene, Université Henri Poincaré, UMR CNRS 7565, Nancy-1, 54506, Vandoeuvre-les-Nancy, France

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Abstract

Polyvinylpyrrolidone stabilized Pt and Pd colloids with mean particle sizes ranging from 1.5 to 3.1 nm were prepared and are effective catalysts for the selective hydrogenation of polyunsaturated soybean oil at 35 °C and atmospheric pressure. The rate constants for the three stages of hydrogenation from linolenate to linoleate to oleate and to stearate were determined and their ratios, which signify the selectivity were calculated. Pt and Pd catalysts show different rates of hydrogenation towards the double bonds. Pt catalyst has lower oleate selectivity leading to higher yields of saturated product but lower percentage of *trans*-isomer than the Pd catalyst at comparable mean particle size of 1.5 nm. The oleate selectivity increases while the linoleate selectivity as well as the activity decreases with an increase of the mean particle size. An intermediate *trans,trans*-linoleate was detected for the Pt catalyst with larger particle mean size.

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1. Introduction

Noble metal colloids of the Pt group with particles in the nanometer size range have high activity and selectivity at low temperature and pressure as hydrogenation catalysts for various small molecule substrates, such as cinnamaldehyde and halonitrobenzene [1,2]. They were also reported to have high enantiomeric selectivity [3]. These colloids can be prepared by various methods, including electrochemical

and chemical reduction as well as vapor deposition onto polymer or ligand solution matrices which serve as stabilizers to prevent aggregation [4–7]. These high activities are due to their high surface to volume ratios and the quantum size effect.

Vegetable oils are hydrogenated to enhance the stability of the oils as well as to obtain products of desirable properties. The catalysts are usually Raney nickel or Ni supported on silica or alumina. The nickel is known to have toxicity [8] if not completely removed. Vegetable oils are complex mixtures of triglycerides of fatty acids with up to 22 carbons, containing variable number of double bonds in each of the fatty acid chains. It is desirable to selectively hydrogenate the

* Corresponding author. Tel.: +604-6577888x3550;

fax: +604-6574854.

E-mail address: kyliew@usm.my (K.Y. Liew).

polyunsaturated acids to the monoenic level. However, during the hydrogenation, the monoenic acids originally present or formed as products may isomerize to form the *trans*-acids, which are nutritionally inferior to the naturally occurring *cis*-isomers [9]. To replace the supported Ni catalysts, supported noble metals catalysts have been tried as substitute. Although the noble metal catalysts are much more expensive, but because of their much higher activities, lower amount can be used and be recovered and reused [8]. Although it is well known that the activity of metal catalysts increases with a decrease in size to the nanometers range, very few reports have been published on their activities for the hydrogenation of oils and fats. We have previously studied the activity and selectivity of Pt nanoparticles for the hydrogenation of palm olein [10]. The present work reports the results on the hydrogenation of commercial soybean oil at 35 °C and atmospheric pressure, using both polymer-stabilized Pt and Pd nanoparticles as the catalysts.

2. Experimental

2.1. Materials

Polyvinylpyrrolidone (PVP, $M_w = 40,000$), methyl oleate (>99%) and methyl elaidate (>99%) (Sigma); chloroplatinic acid hexahydrate and palladium chloride (Merck, Germany); sodium hydroxide, anhydrous sodium sulfide, methanol, butan-1-ol, boron trifluoride–methanol complex, heptane and carbon disulfide were analytical grade (Merck, Germany) and used as received. Soybean oil was purchased from a local supermarket. The fatty acids compositions were determined using gas chromatograph: 11.7% palmitic, 4.3% stearic, 22.8% oleic, 53.7% linoleic and 7.6% linolenic acids.

2.2. Measurements

TEM micrographs were obtained using a Philips CM12 transmission electron microscope at 80 kV from a drop of the colloidal dispersion onto a copper grid with plastic films and then evaporated off the solvent. The particle diameter and size distribution were measured from the enlarged photographs

of >300 particles using Image Analyst software (SIS Soft-Imaging software GmbH, Germany).

The fatty acid compositions of methylated reaction products were analyzed with a GC-14A gas chromatograph (Shimadzu, Japan) equipped with FID with a TC-wax capillary column (L : 30 m; i.d.: 0.25 mm; thickness of film: 0.25 μ m). The column temperature was programmed from 160 to 200 °C at 5 °C min^{-1} , then raised to 204 °C at 0.5 °C min^{-1} and finally reaching 210 °C at 2 °C min^{-1} and held for 10 min with nitrogen as carrier gas. Both the injection and detection temperatures were set at 250 °C. Palmitic acid served as internal standard. The individual fatty acids were identified by comparing with GC–mass spectrometry (GC–MS). For the quantitative determination of *trans*-isomers, the methyl esters obtained were dried under vacuum and then diluted with CS_2 and injected into a sealed liquid FTIR cell of NaCl window with thickness 0.1 mm using a Perkin-Elmer Infrared Fourier Transform Model 2000 Spectrometer equipped with a computer. The IR spectra at 4 cm^{-1} resolution in the range from 1150 to 900 cm^{-1} and 3100 to 2950 cm^{-1} with five scans were collected. Calibration curve was previously obtained from standard mixtures containing from 3 to 51% *trans*-isomer, prepared from methyl oleate and methyl elaidate with total concentrations of between 20 and 30 mg ml^{-1} [11,12].

2.3. Preparation of polymer-stabilized noble metal colloids

2.3.1. Polymer-stabilized platinum metal colloids (PVP–Pt)

The polymer-stabilized platinum metal colloids with and without added base with molar ratio of PVP:Pt = 40:1 were prepared according to reported method with some modification [13]. The procedure is as follows: 0.555 g PVP (5 mmol as monomeric residue) and 0.065 g $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (0.125 mmol) were dissolved in a mixed solvents of methanol (65 ml)–water (75 ml). The solution was refluxed under air with vigorous stirring for 3 h to obtain a dark-brown homogenous dispersion. During the reaction, 10 ml 0.1 M methanol solution of NaOH was added dropwise. For the other PVP:Pt = 40:1 in which no methanolic NaOH was added, 75 ml each of methanol and water were used.

2.3.2. Polymer-stabilized palladium metal colloids (PVP–Pd)

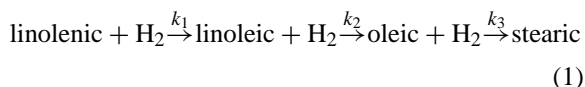
The preparation procedures of the PVP stabilized Pd colloid was the same as in PVP–Pt except that palladium chloride was converted to $\text{H}_2\text{PdCl}_4 \cdot n\text{H}_2\text{O}$ by 0.1 ml of concentrated HCl prior to use. Colloid with molar ratio of PVP:Pd = 40:1 was prepared.

2.4. Hydrogenation of soybean oil

Selective hydrogenation was performed at 35 °C and atmospheric pressure in a closed glass vessel equipped with a magnetic stirrer and a thermostated water bath. The colloidal catalyst and 24 ml butan-1-ol were fed into the reactor. Hydrogen gas was charged several times to replace the air and the catalyst was activated for 60 min with vigorous stirring. The reaction was started immediately after the soybean oil (0.001 mol) was injected. The hydrogen consumption was monitored with a graduated gas burette. The reaction was stopped after 90 min. The partially hydrogenated soybean oils were collected at different intervals and analyzed using GC after the sample were converted into their methyl esters according to a reported method [14].

2.5. Rate constant determination

The hydrogenation scheme is generally depicted as follows:



By taking the concentration of each fatty acids composition and the gas phase partial pressure into account, the reaction rates can then be written as

$$-\frac{d[\text{LL}]}{dt} = k_1[\text{LL}]P_{\text{H}} \quad (2)$$

$$-\frac{d[\text{L}]}{dt} = k_2[\text{L}]P_{\text{H}} \quad (3)$$

$$-\frac{d[\text{O}]}{dt} = k_3[\text{O}]P_{\text{H}} \quad (4)$$

Since hydrogenation of each double bond requires one hydrogen molecule, the overall reaction rate can be

represented as

$$\frac{d[\text{H}_2]}{dt} = (k_1[\text{LL}] + k_2[\text{L}] + k_3[\text{O}])P_{\text{H}} \quad (5)$$

$$\frac{d[\text{H}_2]}{dt} = [\text{catalyst}](k'_1[\text{LL}] + k'_2[\text{L}] + k'_3[\text{O}])P_{\text{H}} \quad (6)$$

where $k_i = k'_i[\text{catalyst}]$ are the respective rate constants, P_{H} is the hydrogen partial pressure and [LL], [L] and [O] are the concentrations of the linolenate, linoleate and oleate, respectively. The rate constants were calculated from Eq. (5) according to a procedure reported previously [10]. The time courses for the hydrogen consumption, changes in linolenate, linoleate and oleate concentrations were fitted with analytical equations that yield the highest correlation coefficients, generally better than 0.999 for the hydrogen consumption and better than 0.98 for the linolenate, linoleate and oleate concentrations. From these equations, the rate of hydrogen consumption and the concentrations of linolenate, linoleate and oleate were obtained at specific time intervals. These values were fitted to Eq. (5) to obtain the rate constants by regression until maximum correlation coefficient was obtained. The three rate constants so obtained were comparable to the values calculated from Eqs. (2) and (4), i.e. the consumption of H_2 gas by each fatty acid, the initial rate of the decrease in linolenate and linoleate concentrations, and the final rate of the decrease in oleate concentration after the linoleate have been depleted, confirming the validity of the method used. The calculated values of k_2 and k_3 were perfectly matched while the k_1 has the same order of magnitude. The selectivity for linoleate from linolenate and oleate from linoleate were then calculated from the ratios of k_1/k_2 and k_2/k_3 , respectively.

3. Results and discussion

3.1. Characterization of PVP stabilized colloids

Two samples of PVP stabilized Pt and one sample of Pd colloids were prepared and characterized by TEM. The TEM micrographs for the Pt and Pd colloids together with their size distributions are shown in Fig. 1a–c. Both the Pt and Pd colloids with methanolic NaOH have comparable mean particles size of 1.5 nm. It is well established that a suitable amount of base

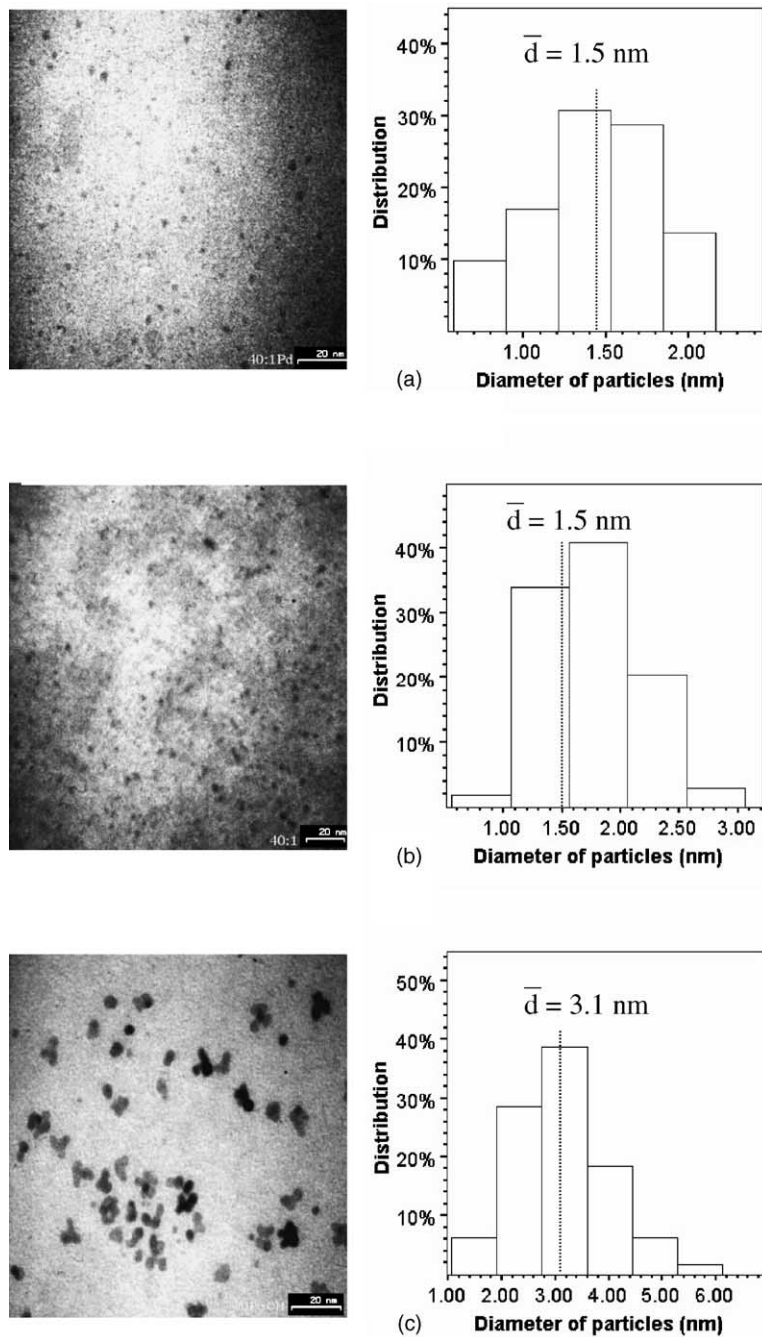


Fig. 1. TEM micrographs and corresponding particle size distribution histograms for molar ratio of PVP:metal = 40:1 (a) Pd; (b) Pt with NaOH; (c) Pt without NaOH. Scale bar: (a–b) 20 nm; (c) 30 nm.

in the reducing system could increase the reduction rate and lead to smaller size of colloidal particles [15]. Hence, the Pt colloid without NaOH has larger mean particle size of 3.1 nm, almost twice that of the Pt colloid with NaOH, with minor aggregation. The size distribution histograms of these samples show that they were narrowly distributed with relative standard deviation of <0.3 . The particles are spherical or near spherical in shape.

3.2. Hydrogenation of soybean oil

The rate of hydrogenation as measured from the hydrogen consumption at 35 °C and atmospheric pressure were compared for the Pt and Pd colloids with comparable mean size of ~ 1.5 nm. The hydrogen consumptions with both catalysts increased nearly linearly initially, corresponding to the hydrogenation of the polyunsaturation with two or three double bonds, and then fell off after some time corresponding to the hydrogenation of the single double bonds. However, as shown in Fig. 2 curves (a) and (b), the initial rate with

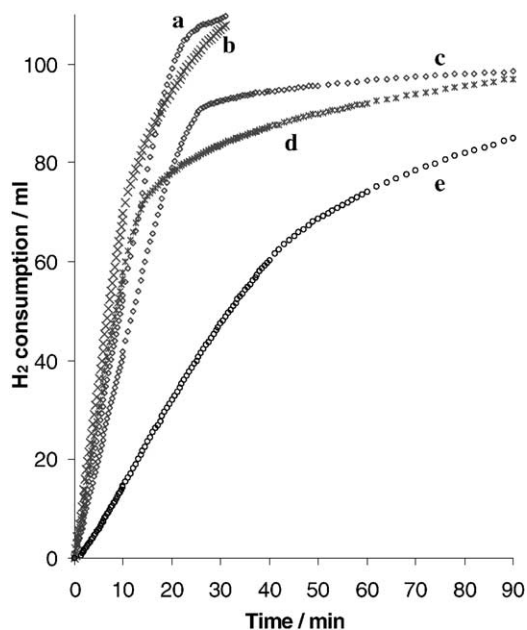


Fig. 2. Hydrogen consumption of soybean oil with molar ratio of PVP:metal = 40:1 as catalyst as a function of times. Reaction conditions—soybean oil: 1.0 mmol; solvent: butanol; initial pressure: 1 atm; temperature: 308 K. (a) 2.34 μmol Pt; (b) 2.34 μmol Pd; (c) 1.17 μmol Pt; (d) 1.17 μmol Pd; (e) 2.34 μmol Pt without NaOH.

Pd was higher than that with Pt as catalyst, while the subsequent reaction rate with Pt was higher than with Pd. This may be attributed to the higher affinity of Pt to the single double bond at the subsequent reaction as shown in Fig. 3, which will be discussed in more detail in the following section. Obviously, Pt and Pd have different activity for the hydrogenation of double bonds hence affect the selectivity. It is also evident that the hydrogenation rate decreased with an increase in the mean particle size of the Pt catalysts from 1.5 to 3.1 nm at similar Pt concentration as shown by curves (a) and (e) in Fig. 2. However, since the number of particles decreased by a factor of 8 and the total surface area decreased by only a factor of 2 as the particle size increased while the hydrogen consumption rate decreased by a factor of 6, it is possible that for the catalyst prepared with NaOH addition the Na^+ ions may have exerted a promotional effect on the activity.

Commercial hydrogenation of vegetable oils usually uses supported Ni catalysts at elevated temperature and pressure. For a typical hydrogenation of soybean oil, using a 0.05% Ni/SiO₂ catalyst at 180 °C near atmospheric pressure in a slurry reactor, the rate was 0.8 mol H₂ h⁻¹ g⁻¹ of Ni [10]. The rates of hydrogen consumption using the colloidal catalysts calculated from data presented in Fig. 1a and b are respectively 45 and 70 mol H₂ h⁻¹ g⁻¹ of Pd and Pt at 35 °C and atmospheric pressure, these values are much higher than the Ni catalysts. These rates are also comparable to the rate of 43 mol H₂ h⁻¹ g⁻¹ for a supported 0.5% Pd catalyst at 102 °C [8].

3.3. Selectivity and rate constants

The changes in concentrations of the constituent fatty acids with reaction time for Pt and Pd as catalysts were determined after being methylated and are shown in Fig. 3. The linolenate was completely hydrogenated within the first 10 min while the linoleate concentration decreased monotonically for both the catalysts in less than 20 min. As the polyunsaturated fatty acids were hydrogenated, the concentration of monoenic oleate increased and reached a maximum value then decreased subsequently to produce the saturated stearate. It is evident that with Pd as the catalyst, the oleate concentration increased more rapidly initially and more than 80% was formed resulted from the faster depletion of the linoleate while only $\sim 63\%$

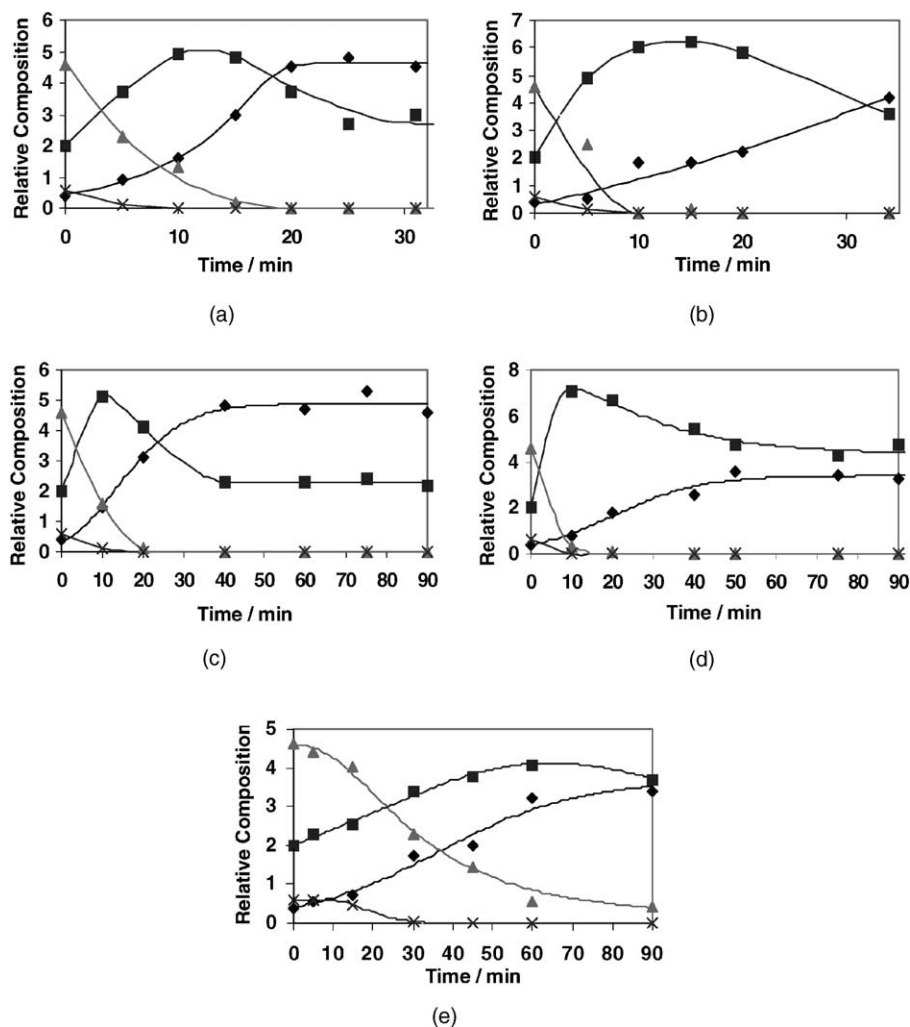


Fig. 3. Relative composition of hydrogenated soybean oil with molar ratio of PVP:metal = 40:1 as catalyst and methyl palmitate as internal standard. Reaction conditions—soybean oil: 1.0 mmol; solvent: butanol; initial pressure: 1 atm; temperature: 308 K. (a) 2.34 μmol Pt; (b) 2.34 μmol Pd; (c) 1.17 μmol Pt; (d) 1.17 μmol Pd; (e) 2.34 μmol Pt without NaOH. (x): Linolenate; (▲): linoleate; (■): oleate; (◆): stearic.

of oleate was formed with Pt as catalyst in ~ 20 min. However, the hydrogenation rate of oleate to saturated stearate with Pd as catalyst was slower than that with Pt hence has a higher selectivity for the monounsaturated product. The stearate concentration increased monotonically to ~ 42 and $\sim 54\%$ with the lower and higher Pd concentrations, respectively. However, the stearate concentration increased rapidly initially then levels off and maintained at the range of 63–68% for

the lower and higher Pt concentrations. Apparently, the effect on the formation of the saturated stearate was more pronounced when lower concentration of Pd catalyst instead of Pt catalyst was used.

As the mean particle size of the Pt catalyst was increased from 1.5 to 3.1 nm, the selectivity in terms of the formation of the monoenic oleate from linoleate was increased. The fatty acids were hydrogenated rather slower with larger particles than with the

Table 1

Rate constants and selectivity for the hydrogenation of soybean oil with different amount of metal from the catalyst PVP:metal = 40:1 at 308 K and atmospheric pressure calculated from Eq. (5) by regression as described in the text

Moles of metal ($\times 10^{-6}$)	k_1^a ($\times 10^2$)	k_2^a ($\times 10^2$)	k_3^a ($\times 10^2$)	k_1/k_2	k_2/k_3	r^b
2.34 Pt	6.24	2.29	1.43	2.7	1.6	0.993
1.17 Pt	16.43	5.99	0.96	2.7	6.2	0.968
2.34 Pd	11.00	4.82	0.74	2.3	6.5	0.957
1.17 Pd	31.46	15.67	1.08	2.0	14.5	0.943
2.34 Pt without NaOH	1.04	0.63	0.14	1.7	4.5	0.988

^a Unit of rate constant is ml H₂ Pa⁻¹ mol⁻¹ s⁻¹ per mole of metal.

^b r : correlation coefficient.

smaller particles, perhaps due to the smaller surface area when the particles are larger. Finally, at 90 min, ~6, ~49 and ~45% of linoleate, oleate and stearate were formed, respectively.

The rate constants for the hydrogenation of the linoleneate, k_1 , linoleate, k_2 , and oleate, k_3 , were calculated and are shown in Table 1 together with the selectivity in terms of the ratio of rate constants. The maximum variation of rate constant for k_1 , k_2 and k_3 were 30 \times , 24 \times and 10 \times , respectively, hence giving rise to the selectivity of linoleate from linoleneate and oleate from linoleate of between 1.7–2.7 and 1.6–14.5, respectively, as the catalysts were changed. It is found that Pd catalyst has higher rate constants of k_1 and k_2 but relatively lower rate constant of k_3 than that of the Pt catalyst. This is consistent with the higher initial hydrogen consumption rate but slower subsequent rate for Pd catalyst as mentioned earlier. At comparable mean size, the selectivity of Pd for the monoenic acid from the polyunsaturated acids was higher than that with Pt while both of them had almost the same selectivity for linoleate from linoleneate. The reaction rate and selectivity are presumably dependent on their unique properties itself. Furthermore, it seems that there was no significant effect on the linoleate selectivity by lowering the catalysts concentration while the oleate selectivity was greatly affected in both Pd and Pt colloids.

For the same metal, Pt catalyst, a change in the particle's mean size caused the selectivity to change beside affecting the activity. The selectivity for the monoenic acid increased from 1.6 to 4.5 with the decrease of linoleate selectivity from 2.7 to 1.7 when the particle's mean size increased. Again, the effect on the selectivity for oleate from linoleate was more prominent when the particle's mean size increased.

However, this change in selectivity may have also been influenced by the presence of Na⁺ ions.

3.4. *Cis–trans isomerization*

The formation of *trans*-isomers of the remaining unsaturation are to be avoided as far as possible for edible oils and fats as they are unhealthy for consumption, desirable catalyst system shall be less active for the isomerization. Most of the double bonds (~96%) in soybean oil are in the *cis*-conformation, which exhibits a distinctive band at ~3006 cm⁻¹. As the hydrogenation advanced, the *trans*-isomer predominantly as elaidate increased as measured at ~966 cm⁻¹ in this study. As shown in Fig. 4, the Pt catalyst produced rather less *trans*-monoenic isomer than that of the Pd as catalyst. The elaidate increased rapidly initially reaching a maximum concentration of ~60% then decreased subsequently to 44 and 34% for both the low and high concentrations of Pd catalyst (Fig. 4b and d). Similar trend was also observed for the high concentration of Pt catalyst with NaOH except that the maximum elaidate concentration was reached at ~16% then decreased to 12.5% (Fig. 4a). For the low concentration, i.e. half of the high concentration of Pt catalyst, the elaidate increased rapidly initially then slowly and steadily to ~23% at 90 min reaction time (Fig. 4c). Thus lowering the catalysts concentration resulted in higher concentration of elaidate.

In the other experiment with Pt catalyst without NaOH, the formation of elaidate profile was similar to that of the low concentration of Pt catalyst except only ~14% of elaidate was formed after 90 min although they have the same initial isomerization rate. Thus, less elaidate was formed for nanoparticles with larger mean size. According to van de Voort et al.

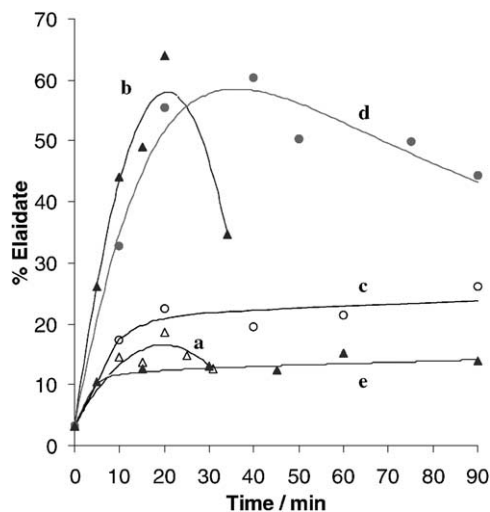


Fig. 4. Percentage of *trans*-isomer in the hydrogenated soybean oil with different catalyst concentration of PVP:metal = 40:1. Reaction conditions—soybean oil: 1.0 mmol; solvent: butanol; initial pressure: 1 atm; temperature: 308 K. (a) 2.34 μmol Pt; (b) 2.34 μmol Pd; (c) 1.17 μmol Pt; (d) 1.17 μmol Pd; (e) 2.34 μmol Pt without NaOH.

[16], the *cis*-band at $\sim 3010\text{ cm}^{-1}$ is made up of the *cis*-double bond of trienic, dienic and monoenic fatty acids without distinctive separation and the *trans*-band at $\sim 970\text{ cm}^{-1}$ is contributed by dienic and monoenic fatty acids. Interestingly, the individual *trans*-band for both the monoenic and dienic double bond was observed in this study. The IR spectroscopic study of the reaction mixtures (Fig. 5) showed that hydrogenation proceeded via an intermediate formation of methyl *cis,trans*- and *trans,trans*-linoleate appearing at ~ 947 and $\sim 989\text{ cm}^{-1}$, respectively, which were slightly shifted as compared to reported absorption peaks (945 and 998 cm^{-1}) [17]. The absorption band of *trans,trans*-linoleate increased rapidly initially then decreased throughout the course of the reaction while the absorption band of *cis,trans*-linoleate increased and decreased slowly as it existed in small amount. As the *cis,trans*- and *trans,trans*-linoleate is thermodynamically more stable, it is expected that the *cis,cis*-linoleate will be hydrogenated faster. Consequently, it can be deduced that the linoleate (>6%) remained at 90 min was mainly the *cis,trans*- and *trans,trans*-isomers (Fig. 3e). It is thus evident that Pt and Pd nanoparticles behave differently. Pt

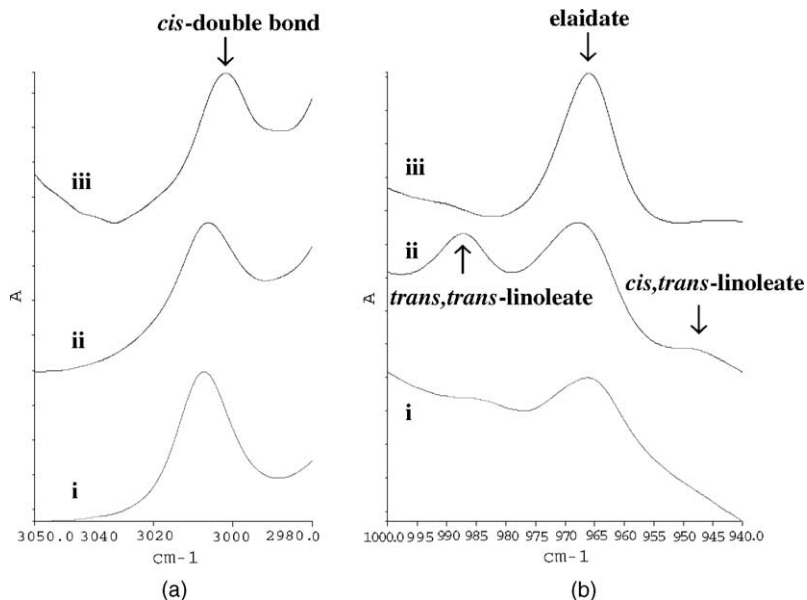


Fig. 5. FTIR spectra of (i) unhydrogenated soybean oil and soybean oil after hydrogenated for 15 min with molar ratio of PVP:Pt = 40:1 as catalyst, (ii) without NaOH, (iii) with NaOH in (a) *cis* and (b) *trans* regions.

nanoparticles have stronger affinity towards the double bonds than Pd nanoparticles. More saturated product and less *trans*-isomer are formed with the Pt catalyst while Pd colloid is more selective for the monoenes but with higher *trans*-isomer content.

4. Conclusions

Hydrogenation of polyunsaturated soybean oil was studied by using PVP stabilized Pt and Pd colloids with mean particle sizes ranging from 1.5 to 3.1 nm as catalysts at 35 °C and atmospheric pressure. The selectivity for hydrogenation of dienes from trienes and monoenes from dienes were calculated from the rate constants to between 1.7–2.7 and 1.6–14.5, respectively. The Pt and Pd with comparable mean size of 1.5 nm showed different catalytic activity to the double bond. The initial hydrogen consumption rate, corresponding to the hydrogenation of the trienic and dienic acids, was higher with the Pd than with Pt as catalyst. However, the subsequent hydrogenation rate, corresponding to the hydrogenation of the monoenic acid, was higher with the Pt as catalyst hence leading to the lower selectivity for monounsaturated oleate than with Pd catalyst. These two metals used had no significant difference on the selectivity of linoleate from linolenate. Further, higher content of elaidate was produced with Pd catalyst than with Pt catalyst. Both the catalysts with lower concentration had relatively lower catalytic activity but superior selectivity for oleate from linoleate without much variation of the linoleate selectivity leading to high yield of elaidate.

The mean particle size increased when no base was added into the reducing system and the activity of the resulting particles decreased. The selectivity for linoleate from linolenate decreased with increase of the selectivity for oleate from linoleate with larger particle. During the hydrogenation, both the intermediate of *cis,trans*- and *trans,trans*-linoleate were detected together with the elaidate. It is deduced that isomerization is suppressed when the hydrogenation rate is fast.

Attempts to recover the colloidal catalysts for reuse by filtration and centrifugation were unsuccessful. Preparation of heterogenized catalysts by depositing the polymer-stabilized noble metal on inert solid support is in progress.

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References

- [1] W. Yu, Y. Wang, H. Liu, W. Zheng, *J. Mol. Catal. A: Chem.* 112 (1996) 105.
- [2] X. Yan, M. Liu, H. Liu, K.Y. Liew, N. Zhao, *J. Mol. Catal. A: Chem.* 170 (2001) 203.
- [3] H. Bönemann, G.A. Braun, *Angew. Chem. Int. Ed. Eng.* 35 (1996) 1992.
- [4] M.T. Reetz, W. Helbig, *J. Am. Chem. Soc.* 116 (1994) 7401.
- [5] H. Hirai, Y. Nakao, N. Toshima, *J. Macromol. Sci. Chem.* A13 (1979) 727.
- [6] G. Sergeev, V. Zagorsky, M. Petrukhina, *J. Mater. Chem.* 5 (1995) 31.
- [7] G. Schmid, V. Maihack, F. Lantmann, S. Peschel, *J. Chem. Soc., Dalton Trans.* (1996) 589.
- [8] V.I. Savchenko, I.A. Makaryan, *Platinum Met. Rev.* 43 (1999) 74.
- [9] D. Kritchevsky, *Chem. Ind.* 15 (1996) 565.
- [10] H.P. Choo, K.Y. Liew, H. Liu, C.E. Seng, *J. Mol. Catal. A: Chem.* 165 (2001) 127.
- [11] B.L. Madison, R.A. Delpalma, R.P. D'Alonzo, *J. Am. Chem. Oil Soc.* 59 (1982) 170.
- [12] A.C. Lanser, E.A. Emken, *J. Am. Chem. Oil Soc.* 65 (1988) 1483.
- [13] W. Yu, M. Liu, H. Liu, J. Zheng, *J. Colloid Interf. Sci.* 210 (1999) 218.
- [14] Anon., *Palm Oil Test Methods*, Palm Oil Research Institute Malaysia, Bangi, 1995, p. 83.
- [15] H. Hirai, *J. Macromol. Sci. Chem.* A13 (1979) 633.
- [16] F.R. van de Voort, A.A. Ismail, J. Sedman, *J. Am. Chem. Oil Soc.* 72 (1995) 873.
- [17] I.K. Chernova, B.N. Bychkov, V.V. Solov'ev, E.I. Filimonova, G.N. Koshel, *Russ. J. Appl. Chem.* 69 (1996) 925.