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Hydrogenation of palm olein catalyzed by polymer stabilized Pt colloids

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Abstract

Polyvinylpyrolidone stabilized Pt colloids with different polymer: Pt ratios with average particle sizes of between 1.4 and 2.9 nm and narrow size distribution were found to be active for the hydrogenation of palm olein at 35°C and atmospheric pressure. The initial hydrogen consumption rate was high, corresponding to the hydrogenation of the linoleate and slowed down thereafter, corresponding to the oleate hydrogenation. The rate constants for the two competing reactions were determined and the selectivity calculated to be between 10 and 100. The particle size of the Pt clusters influences the rate of the diene much more significantly than the monoene. The smaller the average particle size, the higher is the rate for the diene and hence the higher the selectivity. The *trans*-isomer formation was comparative low and was found to be a consequence of the partial saturation of the diene rather than the isomerization of the monoene. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Hydrogenation; Palm olein; Pt nano-cluster; *Cis–trans* isomerization

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1. Introduction

Hydrogenation of vegetable oil is an important process in the oil and fat and the oleochemical industries both to modify the oil's physical characteristics for specific application and to increase its stability towards oxidation and decomposition. Vegetable oils are complex mixtures of triglycerides of fatty acids with 12–22 carbon atoms which may have 0–3 double bonds in each of the hydrocarbon chain. Industrial hydrogenation of palm olein which is the liquid fraction of the semi-solid palm oil, is to convert the trienes and dienes of the constituent fatty acids, respectively linolenic and linoleic, selectively to the monoenes, oleic or to saturation, stearic, for use in frying and baking applications. Nickel catalysts supported on silica, alumina and Raney nickel which is an alloy with aluminum, are generally used in commercial hydrogenation. There are however some concern on the toxicity of traces of nickel remaining in the oil [1,2]. Other catalysts including copper on silica [3], nickel–silver [4], copper chromite [5–8] have been investigated. Noble metal catalysts are not generally used because of their high cost. However, their high activity in small quantity and the possibility of reuse with fixed bed reactor may offset the cost disadvantage. Palladium on carbon has been used for some commercial hydrogenation because of its high linolenic and linoleic activity at low temperature [9,10]. It is also claimed to be cost effective for the production of pure margarine with a novel reactor design [2]. Platinum on carbon had been found to be highly active but with low selectivity producing

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the saturated fat [11]. A more recent report [12] found that a modified platinum on carbon catalyst by incorporating a small amount of ammonia in the hydrogen have high selectivity with low *trans*-isomerization.

Polymer stabilized noble metal nanoclusters for selective hydrogenation of small molecule substrates such as unsaturated aldehydes [13] and hydrocarbons [14,15] have been revived recently. These catalysts were also reported to possess high enantiomeric selectivity [16]. Polymer stabilized platinum has been found to have ~5 times higher activity than Pt/C with increased selectivity for partial hydrogenation of ally alcohol at 25°C and atmospheric pressure [17]. In general, metal nanoclusters have properties and activity that are quite different from the corresponding conventionally prepared supported and unsupported metal catalysts. Their potential as catalyst for selective hydrogenation for the oil and fat and the oleochemical industries is only scarcely being explored.

2. Experimental

2.1. Materials

Analytical grade or equivalent chemicals: Polyvinylpyrrolidone (PVP), ($M_w = 40\,000$); methyl oleate (>99%) and methyl elaidate (>99%) (Sigma, St. Louis); chloroplatinic acid hexahydrate (Beijing Chemicals); methanol and boron trifluoride-methanol complex (Merck, Germany); Butan-1-ol (Fisher, UK); heptane and carbon disulfide (AJAX, Australia); sodium chloride; 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 composition was determined: 40.0% palmitic, 3.7% palmitoleic, 44.3% oleic, 11.7% linoleic and 0.4% linolenic acid.

2.2. Procedures

TEM micrographs were obtained using Philip CM12 transmission electron microscope from a drop of the colloid solution held between two thin plastic films supported on a copper grid and then evaporated off the solvent. The particle diameters were measured from the enlarged photographs. The average particle size and size distribution were obtained from ~300 particles.

The fatty acid composition of methylated reaction products were analyzed using a Hitachi-3000 gas chromatograph (GC) equipped with FID with a Supelcowax capillary column (L, 30 m; i.d., 0.25 mm; thickness of film, 0.25 μm) operated at 210°C with nitrogen as carrier gas. For the quantitative determination of *trans*-isomers, the methyl ester obtained were dried under vacuum and then diluted with CS_2, injected into a sealed liquid FTIR cell of thickness 0.1 mm with NaCl window 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} 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} [18–20].

2.3. Preparation of polymer-stabilized platinum metal colloids (PVP-Pt)

The polymer-stabilized platinum metal colloids were prepared according to reported method [21]. The procedure is as follows: PVP (measured as monomeric residue) and $H_2PtCl_6 \cdot 6H_2O$ were dissolved in a mixture methanol (130 ml) — water (150 ml) as solvent. The solution was refluxed under vigorous stirring for 180 min to obtain a dark-brown homogenous dispersion. During the reaction 20 ml 0.1 M methanol solution of NaOH was added dropwise. Colloids with molar ratio of PVP to Pt = 20:1, 20:2, 30:1 and 40:1 were prepared.

2.4. Hydrogenation of palm oil

Selective hydrogenation was performed at 35°C and atmospheric pressure initially in a closed 380 ml glass vessel equipped with a magnetic stirrer and a thermostated water bath. The colloidal catalyst and 48 ml butan-1-ol were fed into the reactor. Hydrogen gas was charged several times to replace air and the catalyst was activated for 60 min with vigorous stirring. After the palm olein (0.002 mol) was injected the reaction was started. The hydrogen consumption was monitored with a graduated gas burette. The reaction was stopped after 90 min. The partially hydrogenated palm olein were sampled at different intervals and analyzed by GC after the sample was converted into their methyl esters according to reported method [22].

3. Results and discussion

3.1. Particle size distribution

The four samples of the PVP stabilized platinum colloids prepared were characterized by TEM. Typical micrographs and the size distribution histograms are shown in Fig. 1. The particles are of nanometer sizes with narrow distribution and negligible aggregation. The average particle sizes and distributions are 1.75 ± 0.41 nm, 1.38 ± 0.39 nm, 1.51 ± 0.37 nm and 2.94 ± 0.82 nm, respectively for the samples with PVP:Pt ratio of 40:1, 30:1, 20:1 and 20:2. For the first three samples, the average particle sizes are not substantially different from each other and from the values reported for the same catalyst [15] although slightly higher. The average particle size of the last sample is however much larger, at about twice those of the other samples presumably because too little stabilizing polymer was used.

3.2. Rate of hydrogenation

The hydrogen consumption by the refined palm olein in butanol as solvent at 35°C and initial pressure of 1 atm at various times were measured and shown in Fig. 2. During the course of the reaction for selected runs, 1 ml samples were withdrawn at regular intervals, methylated and their compositions determined by GC From Fig. 2 it is seen that the initial hydrogen consumption was rapid, decreasing slightly with time until a point was reached which corresponded approximately to the amount of hydrogen required to hydrogenate the trienes and dienes of the fatty acid ester to the monoenes. The gradient then becomes less steep indicating a slower hydrogen uptake rate corresponding to the hydrogenation of the monoenes. That the abrupt change in the rate of hydrogen consumption was due to the depletion of the polyenes is confirmed from the change in composition of the oil as shown in Fig. 3, which shows that the linoleate was consumed in less than 20 min. It also shows that the monoenic oleate content increased initially, reached a maximum then decreased subsequently while the saturated stearate content increased slowly but monotonically. This is typical of hydrogenation of vegetable oil.

For the least active catalyst with PVP:Pt ratio of 40:1, the change in composition with time is shown in Fig. 4. In this case only very small change in the oleate content was observed up to 90 min reaction time while the linoleate content decreased and the stearate content increased continuously. This is due to the slow rate of oleate hydrogenation coupled with the much higher rate of linoleate hydrogenation which were directly hydrogenated to the stearate without desorbing the oleate. The very slow increase in the oleate concentration may be caused by the larger amount of polymer present which hinder the mobility of the triglycerides from leaving the vicinity of the Pt clusters. Alternatively, the constant oleate concentration may be due to the approximately equal rate of its formation from the linoleate and its conversion to the stearate throughout the course of the reaction. A combination of the two effects is likely to be the cause.

3.3. Rate constants and selectivity

For the hydrogenation of triglyceride oils the individual rate constants for the different unsaturation are generally not determined because of the complexity of the reaction. The selectivity is then determined from a quantity known as the selectivity ratio which is calculated from the ratio of the different hydrogenated products at the end of the reaction [23]. As the relative rate of the reactions for the different unsaturated reactants changed during the course of the reaction, the selectivity ratio so determined depends on the degree of hydrogenation and is not constant. For the present study we determined the rate constants and hence the selectivity based on their ratio.

The initial trienic linolenate in the palm olein is small <0.4% and disappeared shortly after the reaction begun. Thus in the following rate constant determination, linolenate was not taken into consideration. The reaction can then be represented as follows

$$\text{linoleate} + \text{H}_2 \xrightarrow{k_1} \text{oleate} + \text{H}_2 \xrightarrow{k_2} \text{stearate} \tag{1}$$

where the k_s are the respective rate constants. The reaction is generally considered to be first order with respect to the diene or the monoene concentration and

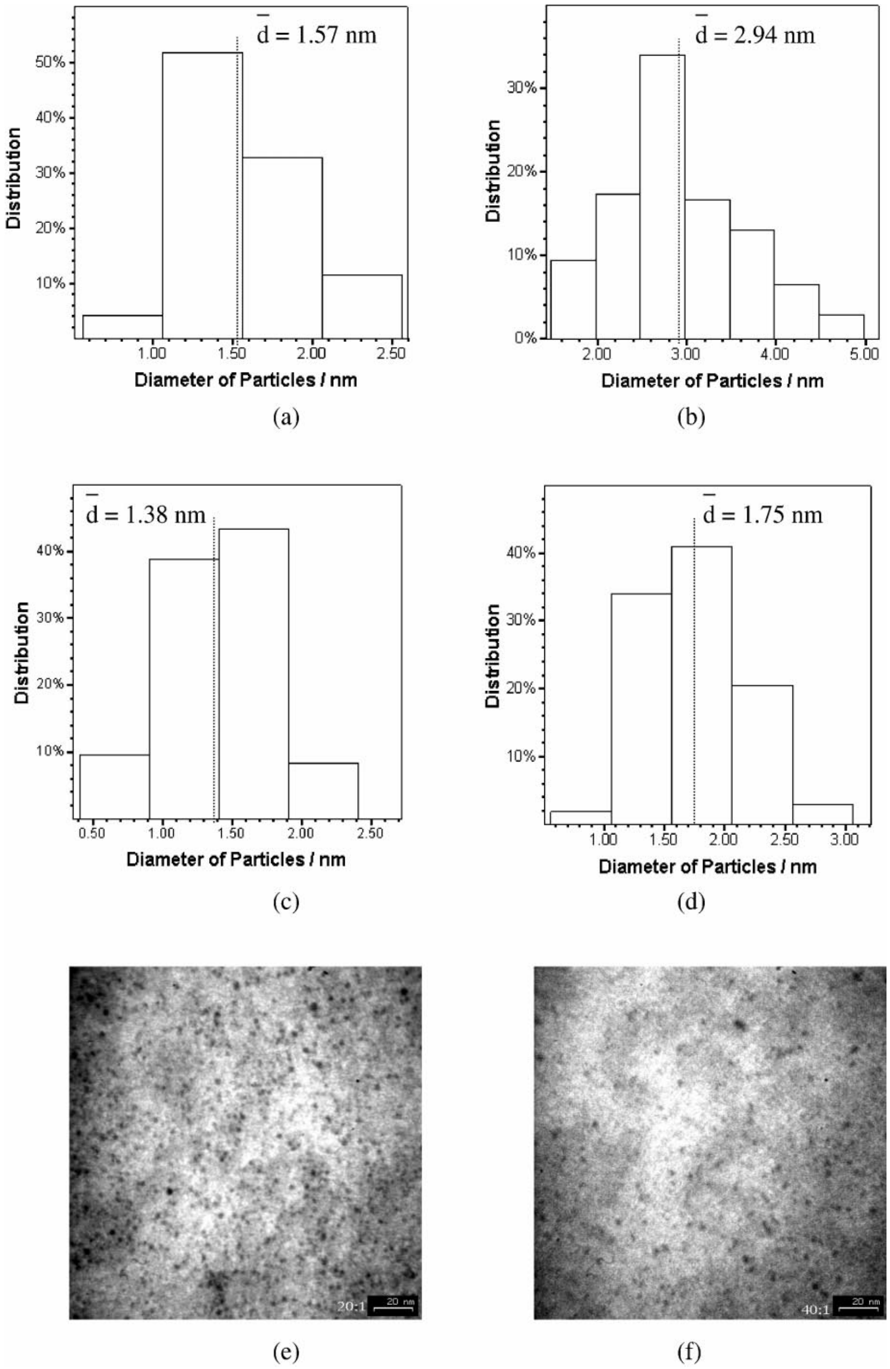

Fig. 1. Particle size distribution histograms of PVP:Pt (a) 20:1; (b) 20:2; (c) 30:1; (d) 40:1 and TEM micrographs of PVP:Pt; (e) 20:1; (f) 40:1.

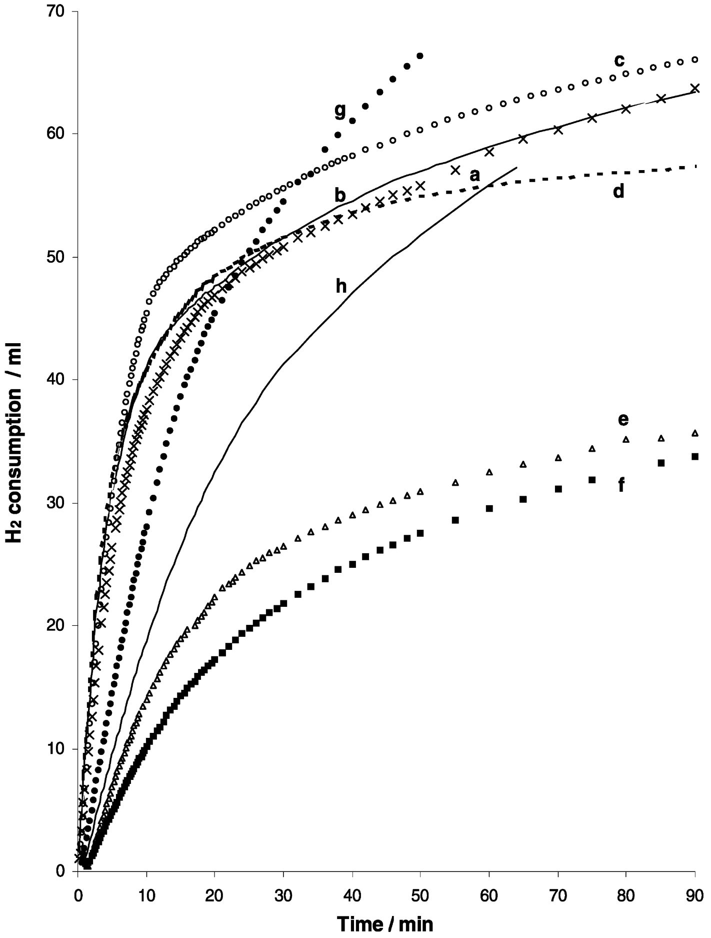

Fig. 2. Hydrogenation of palm oil with different ratios of PVP:Pt. Reaction conditions: palm olein, 2.0×10^{-3} mol; solvent, butanol; initial pressure, 1 atm; temp., 308 K. (a) 4.68×10^{-6} mol Pt (20:1); (b) 7.01×10^{-6} mol Pt (20:1); (c)7.01×10^{-6} mol Pt (30:1); (d) 4.68×10^{-6} mol Pt (30:1); (e) 4.68×10^{-6} mol Pt (40:1); (f) 7.01×10^{-6} mol Pt (40:1); (g) 1.40×10^{-5} mol Pt (20:2); (h) 9.34×10^{-6} mol Pt (20:2).

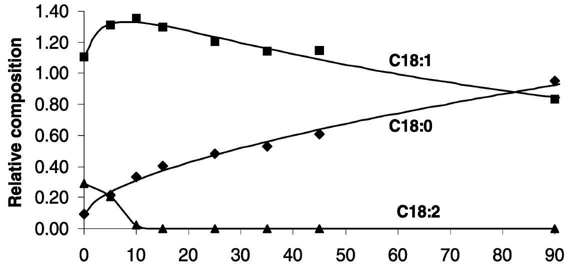

Fig. 3. Relative composition of hyrogenated palm oil by PVP:Pt (30:1), methyl palmitate as internal standard. Reaction conditions: catalyst, 4.68×10^{-6} mol Pt; palm olein, 2×10^{-3} mol; solvent, butanol; initial pressure, 1 atm; temp., 308 K.

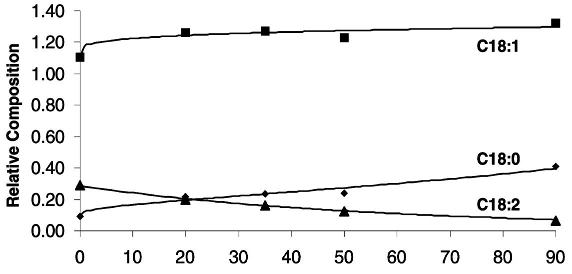

Fig. 4. Relative composition of hyrogenated palm oil by PVP:Pt (40:1), methyl ester as internal standard. Reaction condition: catalyst, 4.68×10^{-6} mol Pt; palm olein, 2×10^{-3} mol; solvent, butanol; initial pressure, 1 atm; temp., 308 K.

dependent on the dissolved hydrogen concentration which in turn depends on its gas phase partial pressure. A 0.5–1 order has been suggested for hydrogen pressure dependence [24]. In this work we assumed a first order dependence. The rate equation can thus be written as

$$\frac{d[H_2]}{dt} = k_1[\text{lin}]P_H + k_2[\text{ole}]P_H \quad (2)$$

where P_H is the hydrogen partial pressure and [lin] and [ole] are the concentrations of the linoleate and oleate.

To evaluate the rate constants in Eq. (2) the following procedure was devised. The time courses for the hydrogen consumption, changes in linoleate and oleate concentrations were fitted with analytical equations that yield the highest correlation coefficents, generally better than 0.995 for the hydrogen consumption and better than 0.97 for the linoleate and oleate. From these equations the rate of hydrogen consumption and the concentrations of linoleate and oleate were obtained at specific time's interval. These values were fitted to Eq. (2) to obtain the rate constants by regression until maximum correlation coefficient was obtained. The two rate constants so obtained were comparable to the values calculated from the initial rate of the decrease in linoleate concentration and the final rate of the decrease in oleate concentration after the linoleate have been depleted, confirming the validity of the method used. The selectivity for linoleate to oleate is then calculated from the ratio of k_1/k_2. The results are shown in Table 1.

It is found that the rate constants for the hydrogenation of the dienes k_1 are more than an order of magnitude higher than that for the subsequent reaction k_2. Further the rate constants for the first stage vary much more widely from 0.3 to 4.3, while the variation for the later stage is much smaller from 0.03 to 0.05 unit (mol-Pt)$^{-1}$ resulting in changes in selectivity of between 10 and 100 as the catalyst was changed.

The rate for this reaction is presumably dependent on the size of the platinum cluster. Qualitatively as the size of the Pt cluster increases for PVP:Pt ratio of 30:1, 20:1, 40:1 to 20:2, the rate constant k_2 are more or less decreasing in the same order, except for the 40:1 catalyst which contains a much larger amount of the stabilizing polymer. The effect on k_2 is much less prominent and no consistent pattern is observed. This caused the selectivity to decrease markedly with increase in catalyst particle size. The selectivity observed for the smaller platinum particles are much higher for the linoleate than that reported for conventional Ni catalysts which were in the region of 20:1 to 58:1 [25,26].

Table 1
Rate constants and selectivity of linoleate to oleate for the hydrogenation of palm olein with various concentrations of PVP:Pt at 308 K

PVP:Pt	Mol of Pt ($\times 10^{-6}$ mol)	k_1[a]	k_2[a]	k_1/k_2	r[b]
20:1	4.68	2.921	0.042	70.0	0.982
20:1	7.01	2.458	0.031	80.5	0.992
30:1	4.68	3.021	0.031	98.7	0.970
30:1	7.01	4.373	0.051	84.9	0.951
20:2	9.36	0.434	0.044	9.8	0.992
20:2	14.01	0.451	0.027	16.5	0.995
40:1	4.68	0.410	0.034	12.0	0.963
40:1	7.01	0.312	0.031	10.2	0.999

[a] Rate constants k_1 and k_2 have unit of ml H_2 Pa^{-1} mol^{-1} s^{-1} per mol-Pt.

[b] r: correlation coefficient.

Supported Ni catalysts on silica or alumina are generally used for commercial hydrogenation of vegetable oils at temperature >160°C and elevated pressure. For a typical hydrogenation of soybean oil with a 0.05% Ni/SiO_2 at 180°C near atmospheric pressure in a slurry reactor, the rate of hydrogenation was found to be 0.0843 min^{-1} corresponding to a rate of $\sim$0.8 mol H_2 h^{-1} g^{-1} Ni [26]. The catalysts was not active at temperature <120°C. With conventional supported noble metals, the activities expressed in terms of iodine number reduction min^{-1} per 1% of catalyst metal for hydrogenation of tall oil fatty acids at atmospheric pressure and 28°C were 5.8 for the 0.05% Pt/C and 72.8 for 0.025% Pd/C [27]. These rates correspond to 2.7 and 34.4 mol H_2 h^{-1} g^{-1} metal, respectively. In a more recent paper [2] the activity for a new supported 0.5% Pd catalyst was measured to be 43 mol H_2 h^{-1} g^{-1} Pd at 102°C at unspecified pressure. The specific activity of the supported Pd catalyst increased markedly with a decrease in Pd loading. The colloidal Pt catalysts studied in this investigation have specific activity of $\sim$12.5 mol H_2 h^{-1} g^{-1} Pt at 35°C and atmospheric pressure with the 20:1 and the 30:1 catalyst systems (Fig. 2 curves a, b, c and d), this is considerably higher than the commercial Ni/SiO_2

and the 0.05% Pt/C and shall be as active as the newly reported supported 0.5% Pd catalyst at similar temperature but less active than the 0.025% Pd catalyst.

Although colloidal noble metal catalysts can be recycled several times by 0.2 μm membrane filtration and to have activities similar to the unused catalysts [28], the recovery of the used catalysts in our experiments are difficult because of entrapment of the catalyst particles in the solid fat formed. Instead, the activity of the used catalyst was studied by injecting fresh sample of the palm olein into the reaction mixture after the initial palm olein has been fully hydrogenated. The rate of hydrogenation observed was about half of the fresh catalysts. The decreased in activeties were likely caused by the presence of the solid fat decreasing the accessibility of the metal particles for the unsaturated triglycerides. Colloidal noble metals on solid support are being prepared and their activities will be studied on recycling.

3.4. *Cis–trans isomerization*

The double bonds in vegetable oils are in the *cis*-conformation. As the *trans*-isomers are thermodynamically more stable they are invariably produced during hydrogenation. The *trans*-forms of the fatty acids are unhealthy for consumption [29,30], their formation in edible fats during hydrogenation shall be suppressed as far as possible. The formation of the *trans*-isomer was thus measured and shown in Fig. 5.

It is seen that the elaidate, the *trans*-isomer of the oleate, increases rapidly initially reaching a value of ∼8% after about 20 min, then levels off as the linoleate was depleted for the active catalyst with PVP:Pt ratio of 20:1. At the same time the oleate concentration decreased as hydrogenation proceeded, the ratio of elaidate to oleate thus increases continuously to 0.31 at 90 min reaction time. For the less active catalyst PVP:Pt ratio of 20:2, similar behavior is observed except that in this case the maximum elaidate concentration at ∼4% is reached later after ∼40 min then decrease slightly. The elaidate to oleate ratio also increased continuously to less than 0.15. In the other run, the maximum elaidate concentration is ∼6% and *trans*:*cis* ratio is <0.3. It thus seems that the *trans*-isomer is produced mainly from the hydrogenation of the linoleate with very little isomerization of the oleate under the reaction condition. The *trans*-isomer formation decreased with decrease in temperature using Pd/C catalyst for the hydrogenation of soybean and sunflower oils to similar iodine value [2,31,32]. The low *trans*-isomer content of the oils produced in this study can be explained by the low reaction temperature.

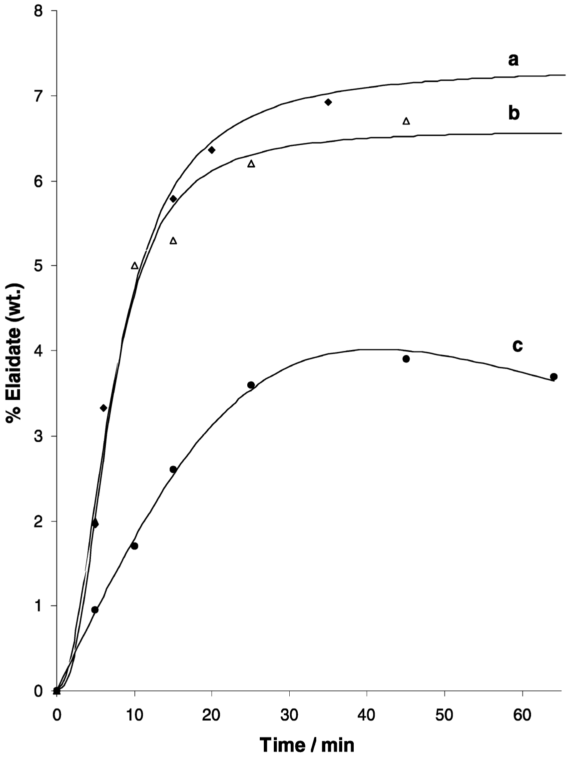

Fig. 5. Percentage of *trans*-isomer in the hydrogenated palm olein with different concentration of PVP:Pt. Reaction condition: palm olein, 2×10^{-3} mol; solvent, butanol; initial pressure, 1 atm; temp., 308 K. Catalyst: (a) 7.01×10^{-6} mol Pt (20:1); (b) 7.01×10^{-6} mol Pt (30:1); (c) 9.34×10^{-6} mol Pt (20:2).

4. Conclusions

PVP stabilized Pt colloids with sizes ranging from 1.3 to 3.0 nm were prepared and are effective catalysts for the hydrogenation of palm olein at low temperature and pressure. The rate constants for the two stages of hydrogenation from linoleate to oleate and to stearate were determined and their ratio which signifies the selectivity, were calculated. The activity as well as their selectivity decreased with increase in the particle size of the platinum nanoclusters. The first stage of the reaction is affected much more than the second stage leading to a change in selectivity. For catalyst system with large amount of the stabilizing polymer the second stage of the reaction can be completely suppressed with the linoleate hydrogenated to the stearate without the intermediate oleate being released into solution. The *cis-trans* isomerization was suppressed due to the low reaction temperature employed resulting in hydrogenated products low in the *trans*-isomer.

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