

Synthesis of chitosan-stabilized platinum and palladium nanoparticles and their hydrogenation activity

M. Adlim, Mohamad Abu Bakar, Kong Yong Liew*, Jamil Ismail

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

Received 23 April 2003; accepted 13 August 2003

Abstract

Chitosan-stabilized Pt (chi-Pt) or Pd (chi-Pd) colloidal nanoparticles catalyst prepared with various chitosan–metal molar ratios and reducing agents were characterized. Chitosan could stabilize Pt and Pd with minimum chitosan:M ratio of 5:1 and 2:1 respectively. The finest and well-dispersed particles of chi-Pt or chi-Pd were obtained when methanol or NaBH₄ were used as the reducing agents. Chi-Pt and chi-Pd reduced by hydrazine gave aggregated particles in all chitosan molar ratios. Chitosan could control particle size of Pt or Pd to within 1.9–2.2 nm when CH₃OH or NaBH₄ was used as the reducing agents. Palladium or Platinum catalysis on cyclooctene hydrogenation gave cyclooctane. Hydrogenation of octene catalyzed by chi-Pd gave octane, 2-octene and 3-octene while chi-Pt prepared by methanol reduction showed 99.99% selectivity and conversion to octane. The catalytic activity of chi-Pt was higher than chi-Pd for both the hydrogenations.

© 2003 Elsevier B.V. All rights reserved.

Keywords: Chitosan; Nanoparticles; Size control; Pt; Pd; Hydrogenation

1. Introduction

Chitosan or poly[β -(1-4)-2-amino-2-deoxy-D-glucon] is a natural polymer isolable from crustacean shell and available commercially. It is applied widely in several industrial and manufacturing processes including waste water treatment, pharmaceutical, medical, food process, agriculture and textile industries [1]. The uses of chitosan in catalyst formulations have been explored. Chitosan–polyvinylpyrrolidone (PVP) composite was used as lipase membrane for enzymatic processing of fats and oil [2]. In the preparation of colloidal nanosized metal catalysts including Pd, Rh, Ru, Pt and Ag, chitosan has been reported as a stabilizer producing particles with relatively large average particle diameters [3,4]. This colloidal catalyst could be supported on inert materials such as silica [5] and synthetic polymers [6] for the preparation of heterogeneous catalyst. Chitosan has also been reported to act as solid matrix for palladium acetate-trisulfate triphenylphosphine catalysts [7].

Metal nanoparticles have interesting and unique properties compared to the larger corresponding metal particles

[8]. Metal particles with nano and uniform sizes have been intensively investigated recently because they have applications in optics, electronics, magnetic devices and as catalysts, photocatalysts, adsorbents and sensors [9–13]. Studies on size control of metal nanoparticles stabilized on polymers, such as polyvinylpyrrolidone and others have been extensively reported [14–20] but there are scarcely report on size control of chitosan stabilize Pt and Pd nanoparticles prepared with different reducing agents.

2. Experimental section

2.1. Materials and equipments

Sodium borohydride (95%, Reidel de Haen), K₂PtCl₄ (99.99%, Aldrich, Germany), octene (99.99%), cyclooctene (99.99%), chitosan of medium molecular weight (~400000, Fluka, Switzerland), hydrazine (99%, BDH, England), PdCl₂ 99.99%, Merck, USA) and Methanol (System, A.C.S. certified grade, Malaysia) were purchased and used without further purification.

Philip CM 12 transmission electron microscope was used to obtain TEM micrographs for determination of particle sizes and size distributions. A drop of the colloid solution

* Corresponding author. Tel.: +60-4-6577-888x3550; fax: +60-4-6574-854.

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

was placed between two thin plastic films supported on a carbon grid under ambient condition except for palladium, which was performed under N₂ atmosphere, followed by solvent evaporation. About 10–20 of the particle images were taken randomly. The individual particle diameters (d_i) were measured from the enlarged micrographs using a computer program “analySIS Docu 2.11” (SIS GmbH, Germany, 1986–1997). The average particle size (d) and standard deviation (σ) were obtained from n_i number of particles ($n_i \geq 300$ particles) and calculated with equations:

$$d = \frac{\sum n_i d_i}{\sum n_i} \quad \text{and} \quad \sigma = \left[\frac{\sum n_i (d_i - d)^2}{\sum n_i} \right]^{1/2}$$

Some notations of experiment conditions are given here. Metal reduced by CH₃OH, NaBH₄ and N₂H₄ are abbreviated as (Pt-me, Pd-me), (Pt-nb, Pd-nb) and (Pt-hz, Pd-hz) respectively. Molar ratio of chitosan:metal was designated as 5:1, 10:1 or 15:1 etc. For example, Pt-me 5:1 means that Pt was reduced by methanol with molar ratio of chitosan:Pt of 5:1. The formation of the colloidal Pt and Pd nanoparticles with each of the reducing agent was followed by using a spectrophotometer.

2.2. Preparation of chitosan-stabilized platinum and palladium colloids (chi-M)

The chitosan-stabilized metal colloids were prepared with modification of the previously reported methods [2]. The procedures were as follows:

Stock solution of palladium chloride was prepared by acidifying 0.1 g of PdCl₂ with concentrated HCl until all the particles dissolved. Then the concentrated HCl was evaporated at about 70 °C. The red residue was dissolved in aqueous acetic acid (10%) in a 25 ml volumetric flask. Stock solution of 10⁻¹ M of K₂PtCl₄ was freshly prepared in a 50 ml volumetric flask. The concentration of platinum or palladium was adjusted to 6.22 × 10⁻⁴ M in all preparations with various chitosan:platinum or palladium molar ratios of 1:1, 2:1, 5:1, 7:1, 10:1 and 15:1. These solutions were prepared as described below.

Chitosan:Pt for molar ratio 5:1 was prepared by dissolving 3.11 × 10⁻³ mol (0.500 g) of chitosan in 88.8 ml of aqueous acetic acid solution (1.5%) and diluted with addition of 90 ml of methanol (99%) with vigorous stirring. Then, 1.12 ml (1.12 × 10⁻⁴ mol) of platinum stock solution was very slowly added to the above solution (total volume became 180 ml) and kept stirring for 1 h. The same procedure was applied for other chitosan molar ratios and for chitosan-palladium.

2.2.1. Methanol reduction

The chitosan–metal solution was refluxed in an oil bath. About 4 ml of the solution was sampled every 30 min, cooled in an ice bath and the absorbance recorded with a UV–VIS spectrophotometer in the range of 700–200 nm.

The reflux was stopped when the absorbance reached maximum.

2.2.2. Sodium borohydride reduction

Metal reduction using sodium borohydride was conducted according to a reported method [21]. Typically, for chitosan:Pt ratio of 5:1, sodium borohydride was added stepwise with increments of NaBH₄/metal ratios and the flask was closed and kept stirring for >2 h. The solution was sampled at every addition of NaBH₄ and the absorbance was recorded. The addition of NaBH₄ was stopped when the absorbance reached maximum. Preparation of chitosan-Pd was done under N₂ atmosphere.

2.2.3. Hydrazine reduction

Two milliliters of N₂H₄ (99%) was transferred into a 100 ml volumetric flask. Then distilled water was added up to the mark. This hydrazine solution was added stepwise into chitosan:Pt solution (5:1) with increment of N₂H₄/metal ratios of 2:1, 3:1, up to, 30:1. After each addition, the solution was stirred for 10 min, sampled and absorbance measured, before the next addition. The addition of N₂H₄ was stopped when the UV–VIS absorbance of the solution was maximum. The same procedure was followed for palladium.

2.3. Chitosan-coated TiO₂ as a support for Pt and Pd nanoparticles

Preparation of chitosan-coated TiO₂ (chi-TiO₂) Pt and Pd were carried out by modified previously reported method [5]. About 0.2080 g of chitosan was dissolved in 346 ml of aqueous acetic acid (1.5%) and diluted with 300 ml of methanol. The solution was stirred until a clear solution formed. About 10 g of TiO₂ (anatase) was suspended in 200 ml of solution of 1:1 aqueous acetic acid (1.5%)–methanol. Using a pipette, the slurry was added dropwise to the chitosan solution and kept stirring vigorously. The mixture was neutralized by addition of sodium hydroxide and the precipitate was filtered and washed with distilled water until neutral. The solid was dried in an oven at 50 °C overnight and dried solid of chi-TiO₂ was ground and dried again in an oven at 110 °C for 1 h.

Exactly 1.000 g of chi-TiO₂ was suspended in 100 ml of methanol–water (1:1) with stirring. Exactly 0.08332 g of PdCl₂ (0.02950 g of Pd) was suspended in 100 ml of ethanol with stirring. The metal–ethanol solution was added to chi-TiO₂ suspension with stirring at room temperature for 24 h. The metal content in the filtrate was determined by AAS. The chi-TiO₂–metal was reduced either by reflux, NaBH₄ or N₂H₄ addition. The residue was filtered and washed several times with water and the last with methanol, dried in an oven at 50 °C for 24 h and at 110 for 1 h. The metal content in this solid were determined with AAS analysis and have about 1% of metal content. Exactly 3.3 × 10⁻⁶ mol of metal content of this solid was used for the catalytic test.

2.4. Catalytic test of hydrogenations of octene and cyclooctene

Hydrogenation of both octene and cyclooctene were performed at atmospheric pressure at 30 °C in a closed 250 ml glass vessel equipped with a magnetic stirrer in a thermostated water bath. Exactly 5.3 ml solution of colloidal Pt catalyst (3.3×10^{-6} mol) was diluted with methanol (44.7 ml) and fed into the reactor. Hydrogen gas was flowed several times to eliminate air and then the catalyst was activated for 60 min with vigorous stirring. The reaction was started after the injection of 0.5 ml of octene (3.1×10^{-3} mol). The hydrogen consumption was monitored with a graduated gas burette. The reaction mixtures were sampled at different intervals. The sample was distilled at 80 °C or precipitated out using NaOH–methanol solution to separate the catalyst from the product. The samples were analyzed using GC (Hitachi G-3000) with a carbowax capillary column 20 m (HP-20 M); with column temperature set at 50–120 °C, ramping at 5 °C/min for octene and the column temperature for cyclooctene analysis was 80 °C.

3. Result and discussion

Chitosan could stabilize Pt and Pd colloidal nanoparticles (1–2 nm) even at low molar ratio (chitosan–metal, 2:1–5:1). As comparison, PVP-stabilized Pt and Pd with PVP:M molar ratio of 40:1 were previously reported [22,23]. Chitosan could not stabilize platinum and palladium colloid when chitosan:M molar ratio <5 for Pt and <2 for Pd, and palladium salt coagulated chitosan at molar ratio of chitosan:Pd >20.

Process of stabilizing and dispersing Pt and Pd nanoparticles could be explained with formations of coordination bonds between the metal ions and amino and/or hydroxyl

groups of chitosan, by which the metal ions were dispersed in the chitosan matrix, prior to the metal reduction. The theory and experimental data on formation of coordination bonds between metal ions and chitosan have been reported [24,25]. It is suggested that the metal particles were preferably enclosed in the chitosan matrix with random configuration rather than folded around by the chitosan chains since the chitosan chains might not freely dangle and were relatively large compared with Pt and Pd nanoparticles (1–2 nm).

Unlike platinum, interaction of palladium with chitosan shows unique properties. The common method of palladium solution preparation was by suspending PdCl₂ in ethanol. However, this method could not be applied because the palladium salt precipitated out the chitosan. Instead, PdCl₂ crystal was dissolved in concentrated HCl, and the excess HCl was evaporated off at 70 °C in a water bath. PdCl₂ in HCl changed to [PdCl₄]²⁻ [26].

3.1. Spectrophotometry studies

UV–VIS spectra of Pt-me, Pt-nb, Pd-me and Pd-nb show monotony without a sharp peak but shoulders at 300 nm for Pd-me, 325 nm for Pd-nb. Hydrazine gave no absorbance at 275–700 nm, whereas Pt-hz gave large peaks at 300, 350, 425 nm and around 375 and 435 nm for Pd-hz as shown by the representative UV–VIS spectra in Fig. 1. Pt-hz and Pd-hz were aggregated, while Pt-me, Pt-nb, Pd-me, Pd-nb consist of fine dispersed particles. The Pd-me spectrum was comparable with palladium colloidal solution that was previously reported using PVP as the stabilizer [27]. The correlation of metal colloidal particle size with UV–VIS spectrum shape has been proposed in previous publication and it was suggested that colloidal metal solution containing large particles tended to give a sharper peak of the UV–VIS spectrum [27,28].

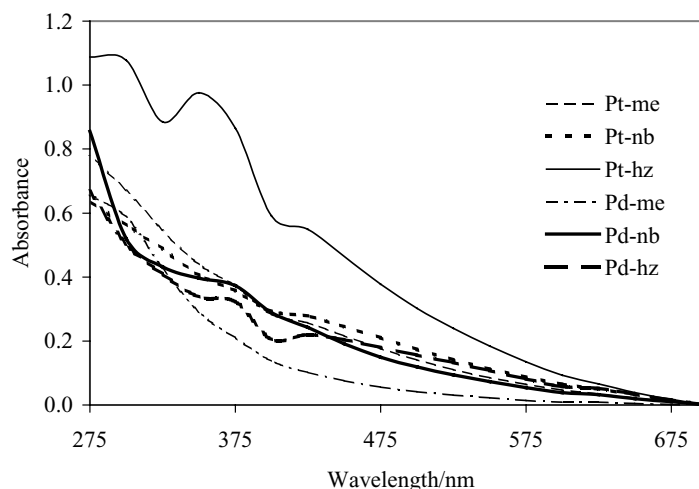


Fig. 1. UV–VIS spectra of chitosan-stabilized platinum and palladium colloidal nanoparticles in aqueous acetic acid-methanol giving a large peak at 200–300 nm.

The optimum condition for preparation of chitosan-stabilized Pt or Pd colloidal nanoparticles with metal concentration of $6.22 \times 10^{-7} \text{ mol ml}^{-1}$ was deduced from UV–VIS absorbance. The maximum intensity of the UV–VIS absorbance of platinum reduced by methanol reached faster at 33 min compared with palladium which required 180 min. It was also observed that Pd needed 4 times more NaBH_4 and 1.8 times more N_2H_4 than Pt to attain the maximum intensities, although the concentrations of Pd and Pt were equal. This disparity occurred because Pd-nb was not stable in the aqueous acetic acid–methanol solution (pH 3–4) as shown by the continuous decrease with time of the absorbance of the colloid after the Pd-nb was formed. In addition, the reduction of Pd ion with hydrazine was relatively slow.

Difference of reduction rate between Pt and Pd can be explained on the basis of the reduction potentials.

Reduction potential of Pt and Pd in acidic solution were $[\text{PdCl}_4]^{2-}/\text{Pd} = 0.600 \text{ V}$ and $[\text{PtCl}_4]^{2-}/\text{Pt} = 0.758 \text{ V}$, with the same reducing agent, ΔG° for Pt is more negative than for Pd. From transition state theory, the relation between Gibbs free energy with rate constant, k , is given by $\ln k = \ln[(k_B T)/h] - \Delta G^\ddagger/RT$. Assuming $\Delta G^\circ \cong \Delta G^\ddagger$ then, at relatively low temperature (303 K) the more negative ΔG^\ddagger gives the larger k , hence Pt was reduced faster than Pd.

3.2. Particle size distribution

Samples of chitosan-stabilized platinum and palladium prepared were characterized by TEM. Representative micrographs and the size distribution histograms are presented for Pt-me, Pt-nb and Pt-hz in Fig. 2(a). TEM and size distribution histograms of Pd-me, Pd-nb and Pd-hz were given in Fig. 2(b). The colloidal metal particle size distribution with

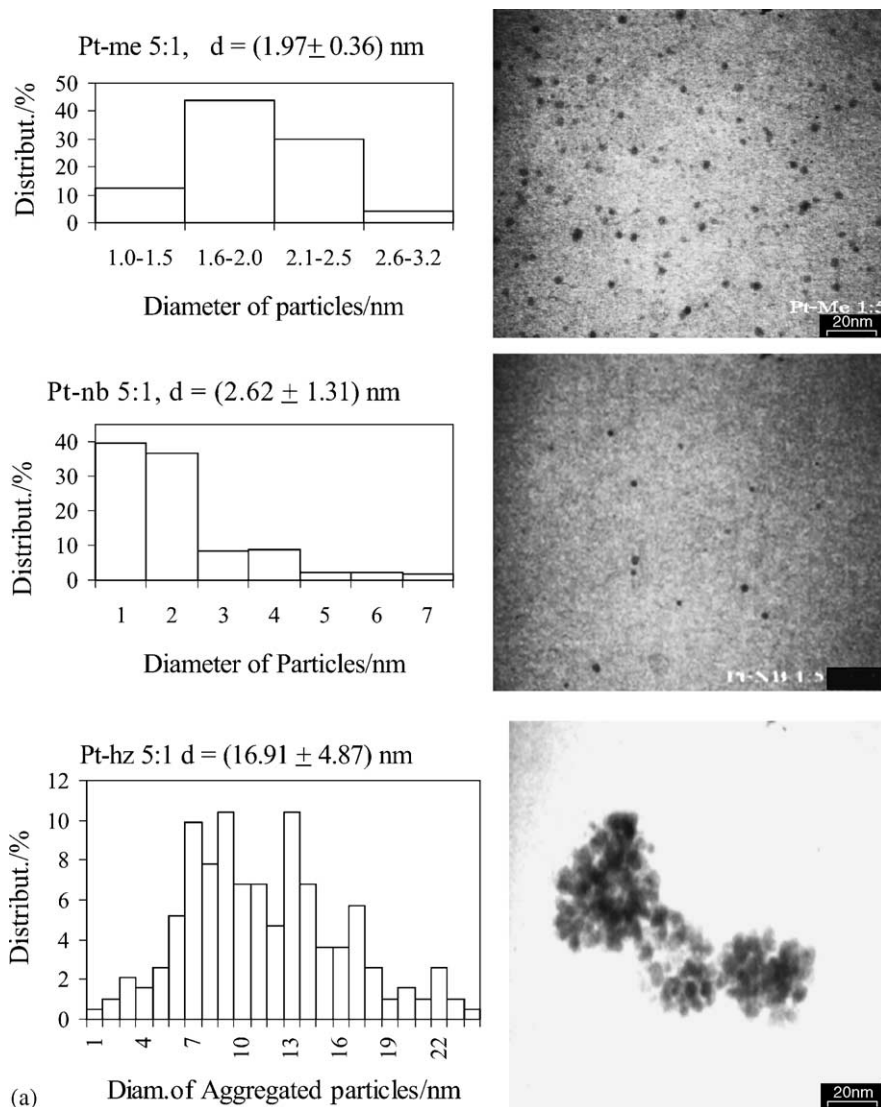


Fig. 2. Representative size distribution histograms of (a) Pt-me, Pt-nb and Pt-hz and a representative TEM images; the scale bar inside TEM image is 20 nm. (b) Pd-me, Pd-nb and Pd-hz and a representative TEM images.

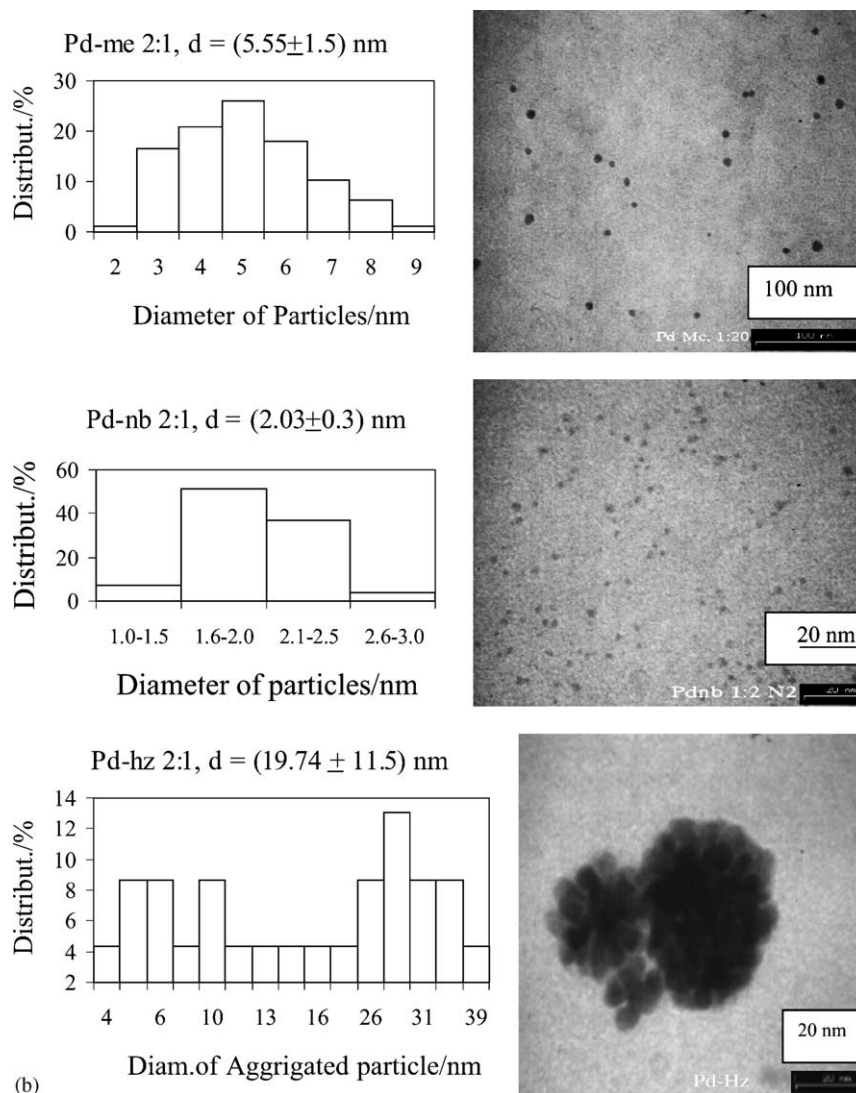


Fig. 2. (Continued)

various chitosan–metal molar ratio and reducing agents was summarized in Table 1.

Chitosan-stabilized Pt colloid prepared by using methanol–water as the reducing agent (reflux), Pt-me, gave the best system for catalyst preparation. As shown in Fig. 2(a), dispersed and fine particle of Pt colloid was observed consistently in all concentrations of chitosan (Pt-me and Pt-nb). The average size was 1.97–2.03 with very narrow size distribution and relative standard deviation of 0.2. In addition, the average particle diameters were much smaller than that previously reported for Pt–chitosan which was 6.8 nm [4]. This suggested that chitosan could control the particle size of platinum from 1 to 2 nm if Pt is refluxed with methanol or it could be controlled to <3 nm if reduced by NaBH_4 as summarized in Table 1.

NaBH_4 seems to be a good reducing agent for palladium since particle size and particle size distribution was smaller and narrower as shown in Fig. 2(b) compared with that

when MeOH–water and hydrazine were the reducing agents (Table 1). Consistently, for all molar ratios, chitosan could stabilize and control the particle size of Pd when NaBH_4 was the reducing agent. The average Pd size was 2 nm with very narrow size distribution ($\sigma_{\text{average}} = 0.3$). As shown in Fig. 2(a) chitosan-stabilized Pt colloid reduced by NaBH_4 also afforded dispersed and nanosize particles in the range of 2.00–2.71 nm, but the size distribution was relatively broader with relative standard deviation of 2.0–0.5 (Table 1).

Preparation of chitosan-stabilized Pt or Pd colloid reduced with hydrazine (Pt-hz or Pd-hz) gave aggregated particles in all concentrations of chitosan as shown Fig. 2(a and b). The aggregation size of Pt-hz was 16.91–27.96 nm with the relative standard deviation was 0.3–0.4 and Pd-hz gave even larger and more aggregated particles (Table 1).

In addition, Table 1 shows that increasing chitosan concentration did not affect the particle size of Pt-me, Pt-nb, Pt-me, and Pd-nb, but let to slightly increased aggregation

Table 1
Size and distribution of chitosan-stabilized Pt and Pd nanoparticles

Metals/reductants	Sample codes	$\bar{d} \pm \sigma$ (nm)	R.S.D. σ/\bar{d}	Dispersion of metal particles
Pt/CH ₃ OH–H ₂ O refluxed	Pt-me 5:1	1.97 ± 0.4	0.2	Dispersed
	Pt-me 7:1	2.01 ± 0.4	0.2	Dispersed
	Pt-me 10:1	2.03 ± 0.4	0.2	Dispersed
	Pt-me 15:1	1.93 ± 0.4	0.2	Dispersed
Pt/NaBH ₄	Pt-nb 5:1	2.62 ± 0.4	0.5	Dispersed
	Pt-nb 7:1	2.00 ± 0.4	0.2	Dispersed
	Pt-nb 10:1	2.71 ± 0.7	0.3	Dispersed
	Pt-nb 15:1	2.06 ± 0.4	0.2	Dispersed
Pt/N ₂ H ₄	Pt-hz 5:1	16.91 ± 4.9 ^a	0.3	Aggregated
	Pt-hz 7:1	Not measurable	–	Highly aggregated
	Pt-hz 10:1	22.31 ± 8.0 ^a	0.4	Aggregated
	Pt-hz 15:1	27.96 ± 11.0 ^a	0.4	Aggregated
Pd/CH ₃ OH–H ₂ O refluxed	Pd-me 2:1	5.55 ± 1.5	0.3	Dispersed
	Pd-me 5:1	3.80 ± 1.2	0.3	Dispersed
	Pd-me 7:1	2.59 ± 0.5	0.2	Dispersed
	Pd-me 10:1	2.26 ± 0.4	0.2	Aggregated
Pd/NaBH ₄	Pd-nb 2:1	2.03 ± 0.3	0.2	Dispersed
	Pd-nb 5:1	2.02 ± 0.3	0.1	Dispersed
	Pd-nb 7:1	2.15 ± 0.3	0.1	Dispersed
	Pd-nb 10:1	1.93 ± 0.3	0.5	Dispersed
Pd/N ₂ H ₄	Pd-hz 2:1	19.74 ± 11.5 ^a	0.6	Highly aggregated
	Pd-hz 5:1	22.45 ± 11.3 ^a	0.5	Highly aggregated
	Pd-hz 7:1	33.74 ± 18.4 ^a	0.5	Highly aggregated
	Pd-hz 10:1	36.56 ± 5.8 ^a	0.2	Highly aggregated

^a Aggregation size.

size of Pt-hz and Pt-hz. However, the particle size of Pd-me decreased with increasing chitosan concentration.

As the molar ratio of chitosan was increased, the decrease in particle size could be explained since the presence of larger amount of the stabilizer shall lead to a higher dispersion of the metal ions on the polymer matrix hence the metal atoms formed, the unchanging particle size may be because the smaller amount of stabilizing polymer is already sufficient for the stabilization. The increase in aggregated size in the hydrazine reduced sample was very likely due to chemical interaction between the polymer and the reducing agent since hydrazine is slightly reactive to hydroxyl and carbonyl groups especially in a cyclic ring [29].

3.3. Catalytic test on hydrogenation of octene and cyclooctene

Chitosan-stabilized Pt or Pd catalysts prepared with various molar ratios and reducing agents symbolized as chi-Pt and chi-Pd were tested on hydrogenation of octene and cyclooctene. The reaction product of octene hydrogenation catalyzed by platinum was solely octane but with palladium catalysis, the reaction products were not only octane but also its isomers: 2-octene and 3-octene. The reaction product of cyclooctene hydrogenation catalyzed by either platinum or palladium was cyclooctane.

The catalytic activities in terms of the turn over frequency (TOFs, mol product/(mol metal h)) was given in Table 2. Generally, the catalytic activities of platinum on octene hydrogenation decreased with increasing chitosan–metal molar ratios and the reducing agent used in catalyst preparation influenced significantly their catalytic activities in the order of Pt-me \gg Pt-nb > Pt-hz at the same molar ratios. The TOFs of Pt and Pd for these preparations were relatively higher than those previously reported as shown in Table 3. Among the catalysts, Pt-me 5:1 has the highest activity with maximum conversion of octene to octane (99.99%) which is consistent with the hydrogen uptake and the very fine Pt particles with very narrow size distribution (Fig. 2(a)). Pt-nb was expected to have better catalytic properties than Pt-hz since Pt-nb has more dispersed particles and higher hydrogen uptake than Pt-hz, however, TOF of Pt-nb was almost equal to that of Pt-hz.

A list of palladium catalytic activities with various molar ratios and reducing agents for octene hydrogenation after 50 min of reaction was tabulated in Table 4. The activity of Pd in terms of octane concentration, decreased with increasing chitosan concentration. In addition, the isomerization activity also decreased generally with increased chitosan concentration. The highest selectivity for octane was only 36.72% and the rest was isomerized to 2-octene and 3-octene.

Table 2
TOFs for chitosan-stabilized Pt and Pd catalysts

Substrates	Catalysts (chi-M ratios)	TOFs (mol product/(mol metal h))					
		Pt-me	Pt-nb	Pt-hz	Pd-me	Pd-nb	Pd-hz
Octene	5:1	93808	82291	86396	–	–	–
	10:1	47035	70032	15848	–	–	–
	15:1	25500	37068	10737	–	–	–
	2:1	–	–	–	94296	100090	54628
	5:1	–	–	–	12490	68640	44854
	7:1	–	–	–	4160	74208	46816
	10:1	–	–	–	1488	95672	37888
	TiO ₂ -chi-	–	–	–	64176	73047	19614
Cyclooctene	5:1	4486	3213	2705	–	–	–
	2:1	–	–	–	1906	2053	1596

Having known that the best molar ratio of chi-Pd was 2:1, we then focused the study on the catalytic activity of chi-Pd (2:1) prepared with various reducing agents and time intervals as presented in Fig. 3(a–c). We could see from these figures that octane increased rapidly with time initially and much slower after 30 min of the reaction and the isomer, 2-octene and 3-octene also decreased after half hours of reaction.

Colloidal platinum and palladium have similar catalytic properties for hydrogenation of cyclooctene which both gave cyclooctane but they show different properties on hydrogenation of octene in which Pd isomerized octene. The catalytic activity of both metals were higher for octene hydrogenation than for cyclooctene for which only 5% conversion was obtained after 1 h (Table 2). This is consistent with the hydrogen uptake which is very low <10 ml in one hour. The activity of platinum for cyclooctene hydrogenation was slightly higher than that of palladium with the order of activity Pt-me > Pt-nb > Pt-hz and Pd-nb > Pd-me > Pd-hz respectively.

A plot of octane and cyclooctane concentrations versus time for Pt and Pd catalysis on hydrogenation of both octene and 1-cyclooctene gave straight lines at the beginning of the reaction indicating a zero order reaction, since initial reactions were not much affected by changing the substrate concentration. The rate constants for both octene and cyclooctene hydrogenation with various catalysts are given in

Table 3
TOFs of Pt and Pd catalysts previously reported

Catalysts/substrates	TOFs (mol product/(mol metal h))	References
PVP-Pd-ethanol/1-octene	334.6	[30]
PVP-Pd-NaBH ₄ /1-octene	335.6	[30]
Al ₂ O ₃ -Pt/ethyl pyruvate	84000	[31]
Al ₂ O ₃ -Pt/isopropyl-4,4,4-trifluoroacetate	810	[32]
Chi-PAA-SiO ₂ -Pd/nitrobenzene	3500–2333	[6]
SiO ₂ -Pd/hexene	38250	[33]
5%Pd/C/isoprene	17760	[34]
PVP-Pd-me/1,3-cyclooctadiene	2100	[35]

Table 5. For both the reactions, Pt catalysts were much more active than Pd.

Catalytic activity of palladium is higher in Pd-nb compared to Pd-me and Pd-hz. This result corresponded to the particle size and dispersion of Pd-nb which is smaller and more dispersed than those Pd-me and Pd-hz. Even though Pd-me has nanosize and were dispersed, the activity of Pd-me at the initial rate of octene hydrogenation was almost equal to that of Pd-hz which is large and aggregated. The rate constants of Pd-me and Pd-hz was 2.60×10^{-5} and 2.40×10^{-5} mol min⁻¹ respectively. In chi-Pd 2:1 catalysis, Pd-me was slightly more active than Pd-hz especially by the end of octene hydrogenation. However, at higher molar ratio of chi-Pd, the activity of Pd-hz was higher than Pd-me.

Table 4
Product distribution in octene hydrogenation catalyzed by Palladium prepared with various methods

Type of catalysts	Chi:M	Reaction composition	Product distribution (%)		
			Pd-me	Pd-nb	Pd-hz
TiO ₂ -chi-Pd	2:1	1-Octene	43.07	35.20	82.6
		Octane	30.09	41.03	6.50
		2-Octene	13.15	12.53	7.52
		3-Octene	13.69	11.24	3.38
Colloidal Pd	2:1	1-Octene	16.35	11.21	51.54
		Octane	34.34	36.72	24.05
		2-Octene	35.65	40.00	16.94
		3-Octene	13.66	12.07	7.47
	5:1	1-Octene	88.92	39.11	60.21
		Octane	4.02	32.86	20.33
		2-Octene	5.20	12.31	13.60
		3-Octene	1.86	15.72	5.86
	7:1	1-Octene	96.31	34.17	58.47
		Octane	1.92	34.86	19.25
		2-Octene	1.23	26.28	15.88
		3-Octene	0.54	4.69	6.40
10:1	1-Octene	98.68	15.13	66.39	
	Octane	1.29	33.09	13.99	
	2-Octene	0.03	43.36	13.98	
	3-Octene	0.00	8.42	5.64	

The reaction condition; solvent: methanol at 30 °C, 1 atm, [Pd] = 3.3×10^{-6} mol, [octene] = 3.1×10^{-3} mol, reaction time: 50 min.

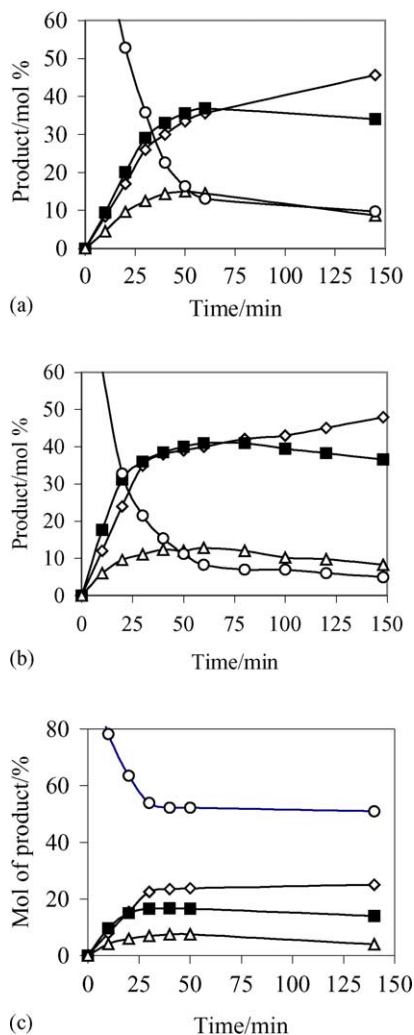


Fig. 3. Composition of reactions in octene hydrogenation catalyzed by chitosan-stabilized palladium (2:1) prepared with various reducing agents; (a) Pd-me, Pd-nb, (c) Pd-hz, with Reaction composition of (O): octene, (◇): octane, (■): 2-octene, (△): 3-octene. The reaction condition; solvent: methanol at 30°C, 1 atm, [Pd] = 3.3×10^{-6} mol, [octene] = 3.1×10^{-3} mol.

The activity of the catalyst prepared with hydrazine could have been caused by the excess hydrazine which could also act as a source of hydrogen for the hydrogenation [35]. The excess of hydrazine has also been neutralized with addition of HCl in the catalytic preparation as reported previously [36], but the catalytic activity was not much changed. The purpose of neutralizing hydrazine with HCl was to precipitate out the excess hydrazine as $N_2H_4 \cdot HCl$. However, since the solvent used was polar, the $N_2H_4 \cdot HCl$ was dissolved and it is still likely as hydrogen donor. As a comparison, hydrazinium monoformate ($N_2H_4 \cdot HCOOH$) was reported as hydrogen donor for Raney nickel catalysis in a facile reduction of nitro and nitrile moieties [35].

To further investigate, the effect of excess hydrazine, we prepared solid catalysts by immobilizing chitosan on

Table 5

Rate constants of octene and cyclooctene hydrogenation catalyzed by chitosan-stabilized Pt and Pd colloidal catalysts prepared with various methods

Substrates	Catalysts (chi-M ratios)	k_o ($\times 10^{-5}$ mol/min)					
		Pt-me	Pt-nb	Pt-hz	Pd-me	Pd-nb	Pd-hz
Octene	5:1	9.99	3.82	4.37	–	–	–
	10:1	2.36	3.42	0.84	–	–	–
	15:1	1.16	2.09	0.58	–	–	–
	2:1	–	–	–	2.60	3.68	2.40
	5:1	–	–	–	0.31	0.22	1.68
	7:1	–	–	–	0.25	2.56	1.46
	10:1	–	–	–	0.01	2.66	1.04
		k_o ($\times 10^{-7}$ mol/min)					
Cyclooctene	5:1	20.91	17.95	14.61	–	–	–
	2:1	–	–	–	10.35	13.73	7.71

The reaction condition; solvent: methanol at 30°C, 1 atm, [Pt] or [Pd] = 3.3×10^{-6} mol, [octene] = [cyclooctene] = 3.1×10^{-3} mol.

TiO₂. Metal ions were absorbed by chitosan immobilized on TiO₂ and the ions were reduced by reducing agents (methanol, NaBH₄ or N₂H₄) by which the excessive NaBH₄ or N₂H₄ were easily eliminated by filtration and washing. The particles were dispersed except for TiO₂-chi-Pd(hz) which is aggregated. The particle sizes were large which were: 7.38 ± 2.7 , 7.57 ± 2.0 , and 10.91 ± 5.0 nm for TiO₂-chi-Pd(me), TiO₂-chi-Pd(nb), and TiO₂-chi-Pd(hz) respectively. The catalytic activities were much lower than the colloidal catalysts and the order of activity slightly changed to be Pd-me \cong Pd-nb \gg Pd-hz. We could see from this trend change that when there was no longer excessive hydrazine in the solution the catalytic activity of Pd-hz decreased and when the solvent was no longer acidic, the activity of Pd-me increased. The catalytic activity of Pd-nb and Pt-nb especially in the colloidal solution might also be influenced by traces of boron as reported for ruthenium catalyst preparation [37,38].

4. Conclusions

Chitosan could control the particle size of Pt and Pd within 1.93–2.03 and 1.93–2.15 nm respectively with narrow size distribution if they were prepared by using methanol or NaBH₄ as the reducing agent. Chitosan-stabilized Pt or Pd prepared by using hydrazine as the reducing agent gave aggregated particles. The activity of the catalyst decreased with increasing concentration of chitosan. Chitosan-stabilized Pt or Pd catalyzed hydrogenation of cyclooctene gave cyclooctane only but in octene hydrogenation, Pt gave octane with 99.99% selectivity, while Pd gave octane and isomerized products of 2-octene and 3-octene. The catalytic activity of Pt was higher than Pd.

Acknowledgements

This work is supported by a USM IRPA short term and FRGS grants number: 304/P.KIMIA/634009 and 304/P.KIMIA/670007 respectively. M. Adlim acknowledges Universitas Syiah Kuala for a OECF-Unsyiah scholarship and a leave of absence to undertake this work.

References

- [1] M.N.V.R. Kumar, *React. Funct. Polym.* 47 (2000) 1.
- [2] T. Tan, F. Wang, H. Zhang, *J. Mol. Catal. B: Enzym.* 18 (2002) 325.
- [3] N. Ishizuki, K. Torigoe, K. Esumi, K. Meguro, *Colloids Surf.* 55 (1991) 15.
- [4] H. Lu, H. Wang, H. Liu, *Acta Polymer. Sin.* 1 (1993) 100 (Chinese).
- [5] M.Y. Yin, G.L. Yuan, Y.Q. Wu, M.Y. Huang, Y.Y. Jiang, *J. Mol. Catal. A: Chem.* 147 (1999) 93.
- [6] J.J. Jin, G.C. Chen, M.Y. Huang, Y.Y. Jiang, *React. Polym.* 23 (1994) 95.
- [7] F. Quignard, A. Choplin, A. Domard, *Langmuir* 16 (2000) 9106.
- [8] B.D. Summ, N.I. Ivanova, *Russian Chem. Rev.* 69 (2000) 911.
- [9] T.S. Ahmadi, Z.L. Wang, T.C. Green, A. Henglein, M.A. El-Sayed, *Science* 272 (1996) 1924.
- [10] S. Chen, R.W. Murray, *J. Phys. Chem. B* 103 (1999) 9996.
- [11] L.N. Lewis, *Chem. Rev.* 93 (1993) 2693.
- [12] G. Schmidt, *Chem. Rev.* 92 (1992) 1709.
- [13] H. Weller, *Angew. Chem. Int. Ed. Engl.* 32 (1993) 41.
- [14] X. Yan, H. Liu, K.Y. Liew, *J. Mater. Chem.* 11 (2001) 3387.
- [15] H. Hirai, N. Thosima, in: Y. Iwasawa (Ed.), *Tailored Metal Catalysis*, Raidel, Dordrecht, 1986, p. 99.
- [16] A. Duteil, R. Queau, B. Chaudret, R. Mazel, C. Roucau, J.S. Bradley, *Chem. Mater.* 5 (1993) 341.
- [17] H. Bönemann, W. Brijoux, R. Fretzen, T. Jousen, R. Koppler, B. Korall, P. Neiteler, J. Richter, *J. Mol. Catal.* 86 (1994) 129.
- [18] T. Teranishi, M. House, T. Tanaka, M. Miyake, *J. Phy. Chem. B* 103 (1999) 3818.
- [19] T. Teranishi, M. Miyake, *Chem. Mater.* 10 (1998) 594.
- [20] C.D. Sanguesa, R. Urbina, M. Figlarz, *Solid State Ion.* 63–65 (1993) 25.
- [21] A.B.R. Meyer, J.E. Mark, *Colloid Polym. Sci.* 275 (1997) 333.
- [22] H.P. Choo, K.Y. Liew, W.A.K. Mahmood, H. Liu, *J. Mater. Chem.* 11 (2001) 934.
- [23] H.P. Choo, K.Y. Liew, H.F. Liu, C.E. Seng, *J. Mol. Catal. A: Chem.* 165 (2001) 127.
- [24] G. Micera, S.D.A. Dessi, P.D.B. Dubois, H. Kozłowski, *Inorg. Chim. Acta* 107 (1985) 45.
- [25] E. Guibal, N.V.O. Sweeney, M.C. Zikan, T. Vincent, J.M. Tobin, *Inter. J. Biol. Macromol.* 28 (2001) 401.
- [26] F.A. Cotton, G. Wilkinson, P.L. Gaus, *Basic Inorganic Chemistry*, second edition, Wiley, Singapore, 1987, p. 536.
- [27] N. Toshima, T. Yonezawa, K. Kushihashi, *J. Chem. Soc. Faraday Trans.* 89 (1993) 2537.
- [28] C. Petit, P. Lixon, M.P. Pileni, *J. Phys. Chem.* 97 (1993) 12974.
- [29] J.K. Stille, R. Ertz, *J. Am. Chem. Soc.* 86 (1964) 66.
- [30] C. Liu, Y. Xu, S. Liao, D. Yu, *J. Mol. Catal. A: Chem.* 149 (1999) 119.
- [31] N. Künzle, J.-W. Solèr, A. Baiker, *Catal. Today* 79/80 (2003) 503.
- [32] N. Künzle, T. Mallat, A. Baiker, *Appl. Catal. A: Gen.* 238 (2003) 251.
- [33] G.C. Bond, A.F. Rawle, *J. Mol. Catal. A: Chem.* 109 (1996) 261.
- [34] H. Hirai, H. Chawanya, N. Toshima, *Macromol. Chem. Rapid Commun.* 2 (1981) 99.
- [35] S. Gowda, D.C. Gowda, *Tetrahedron* 58 (2002) 2211.
- [36] S. Mossmer, J.P. Spatz, M. Moller, *Macromology* 33 (2000) 4791.
- [37] M. Liu, W. Yu, K. Liew, *J. Mol. Catal. A: Chem.* 138 (1999) 295.
- [38] X. Yan, M. Liu, H. Liu, K.Y. Liew, *J. Mol. Catal. A: Chem.* 169 (2001) 223.