Preparation of Palladium Nanoparticles Stabilized by Cyclodextrins in Aqueous Solution and Their Activity for Hydrogenation of Palm Oil

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Abstract. Palladium (Pd) nanoparticles were prepared in aqueous solution with different cyclodextrins (CDs) as stabilizer and alcohols as reducing agent. An optimum condition for the preparation of Pd nanoparticles was found to involve the use of 2-propanol as reducing agent at 30^{o}C (room temperature). UV-visible and FT-IR spectra of the products indicated the presence of interaction between CD and metallic Pd. The TEM micrographs showed that the nanoparticles were less than 30 nm in diameter. It was observed that the nanoparticles were stable as colloid solution for weeks. The CD stabilized Pd nanoparticles shows high catalytic activity towards hydrogenation reaction of palm oil at room temperature. The C18:2 in palm oil were totally hydrogenated within 20 min of reaction, while γ-CD-Pd was observed to show highest hydrogenation activity.

Introduction

Noble metal collids of the palladium with nano size have high activity and selectivity for the hydrogenation of various substracts,however it is difficult to use in the homogeneous reaction system because of difficulties in separation of products from catalysts. Recently, nanoparticles prepared in water and aqueous solvent have received much attention[1],which appeared an enviromentally friendly method to produce organic compounds, thus the catalysts can be easily recovered and reused with simple methods at the end of the reaction. However,CD-Pd used for catalysts for hydrogenation of palm oil were seldom reported.

As one memember of sacharide ,cyclodextrins (CDs) are toroids compounds made up of glucose monomers[2], they are with suitable water-soluablity and have been widely used for host-guest interaction, molecular recognition, drug delivery, catalysis, foods, cosmetics and so on[3]. With the development of nano science and technology, CDs have drawn extensive attention for the preparation of nanoparticles, in the latest research, CDs [5-7] and Chemical modified-CDs [8, 9] were started to be used as stabilizer for the preparation of nanoparticles.

In this paper, the cyclodextrins stabilized Pd (CD-Pd) nanoparticles were prepared in aqueous solution. Condition experiments were designed to select a proper method, finally 2-propanol was used as reducing agent for the preparation of nanoparticles at room temperature. The structures of the Pa nanoparticles were characterized by UV, FT-IR and TEM. The nanoparticles were used for the hydrogenation of palm oil, the activities and selectivities were studied.

Experimental

Materials and equipments

All the materials were purchased and used directly. KOH (AR), $H_2PtCl_6 \cdot 6H_2O$ (≥37.5%Pt from Sigma-Aldrich), $PdCl_2$(59%Pd from Merk), α-CD(99% from Sigma), β-CD(98% from Sigma), γ-CD(>99% from sigma), Methanol(AR from Merk), 2-Propanol(AR from Merk), Glycol (AR from Merk), HCl (38% from Fisher Chemicals).

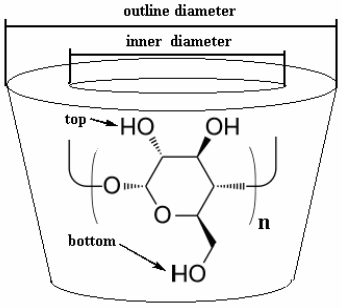
UV-Vis spectra were recorded with a Hitachi U-1800 UV-Vis Spectrophotometer, the original colloid solutions were analyzed after three times dilution. FT-IR was acquired with a Ge detector using a Thermo Nicolet Avatar 370 DTGS Infrared Spectrometer, the IR spectra in the range from 500 to 4000 cm^{-1} was collected. Transmission electron microscopy (TEM) images were obtained with a LIBRA 120 transmission electron microscope for determination of particle sizes and size distributions, about 10–20 of the particle images were taken randomly, the average particle size (*d*) and standard deviation (σ) were obtained from at least 150 of particles. Agilent-6890 gas chromatograph (GC) equipped with FID detector and *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 ℃ at 2 ℃·min^{-1}, after held for 2 min then raised to 230 ℃ at 3 ℃·min^{-1} and held for 3 min with helium as carrier gas.

Preparation of the CD stabilized Pd nanoparticles and the hydrogenation of palm oil

The solution of H_2PdCl_4 was prepared as below: 0177 g (0.1mmol) $PdCl_2$ was shake together with 1mL concentrated HCl until all the particles dissolved, then the concentrated HCl was evaporated, the dark brown residue was dissolved in deionized water and used for further reaction.

Pd nanoparticles were prepared by the reduction of metallic solution with 2-propanol at room temperature (rt).In brief, the mixtured solution of 0.25 mmol of CD and 0.05 mmol metallic ions in 25 mL deionized water was stirred at room temperature for over night, then 10 mL 2-propanol was added immediately to the mixture under vigorous stirring. The residue solution was stirred at room temperature until the colour change into dark brown. The mixture was kept in frozen for further usage. The molar ratio of CD with metallic ion was kept as five while different reducing agents were used.

CD-Pd was prepared with β-CD,α-CD and γ-CD while other conditions remained the same. The structure and diameters for the different CDs were show as in *scheme 1*.



CD	n	Inner diameter/Å	Outline diameter/Å
α-CD	6	4.6-6.0	14.5
β-CD	7	6.0-8.0	15.4
γ-CD	8	8.0-10.0	17.5

Scheme 1. The structures and diameters of different CDs

Hydrogenation of palm oil was performed at room temperature and atmospheric pressure in a bubbling reactor, hydrogen was supplied continuously by hydrogen steel bottle. In a Glass vessel (100 mL) nano particles was firstly equipped with a magnetic stirrer and charged several times with hydrogen to replace air, the total volume of the solution was 12.5mL containing 0.0125mmol of metallic nano catalyst and 5 mL of 1-propanol used as a co-solvent for palm oil. The catalyst was activated for 60 min with vigorous stirring, after activation, palm oil (2.5 mmol) was injected and the reaction was started. The product was extracted with hexane and analyzed with GC after the sample was converted into methyl esters upon treatment with a 1mol·L^{-1} NaOH solution in methanol.

Result and discussion

During preparation, the colloide solutions were prepared under different conditions, the parameters were cited as in *Table 1*.

Table 1. Different conditions for the preparation of CD-Pd nanoparticles

Items	conditions
1	β -CD:Pd:KOH=5:1:0(molar ratio),2-propanol as reducing agent,water as solution,60℃
2	β -CD:Pd:KOH=5:1:0(molar ratio),methanol as reducing agent,water as solution,60℃
3	β -CD:Pd:KOH=5:1:0(molar ratio), glycol as reducing agent,water as solution,60℃
4	β -CD:Pd:KOH=5:1:2(molar ratio),2-propanol as reducing agent,water as solution,60℃
5	β -CD:Pd:KOH=5:1:1(molar ratio),2-propanol as reducing agent,water as solution,60℃
6	β -CD:Pd:KOH=5:1:0(molar ratio),2-propanol as reducing agent,water as solution,30℃
7	β -CD:Pd:KOH=5:1:0(molar ratio),methanol as reducing agent,water as solution,30℃
8	β -CD:Pd:KOH=5:1:0(molar ratio), glycol as reducing agent,water as solution,30℃
9	α -CD:Pd:KOH=5:1:0(molar ratio),2-propanol as reducing agent,water as solution,30℃
10	γ -CD:Pd:KOH=5:1:0(molar ratio),2-propanol as reducing agent,water as solution,30℃

KOH was selected as a catalytical additive for the reduction of Pd ion base on the previous work[10], 2-propanol was used as a reducing agent. The reductive reaction was performed at 60 ℃ under atmospheric pressure as shown from item 3 to item 5 in *Table 1*. It had been proven that KOH was not the primary effect for the preparation of nanoparticles but negative for stability, so KOH was abscised for the following study. Methanol, 2-propanol and glycol were chosen as reducing agent both at 60℃ and 30℃, β-CD-Pd formed under the conditions from item 1 to item 8. As shown during the experiments, glycol and 2-propnaol could reduce Pd ions both at 60 ℃and 30℃. Nano colloid solution formed more slowly and more stable at 30℃ compared with 60℃. The formation rate, stability ,activities and selectivites(trans) for the hydrogenation of palm oil were concluded as in *Table 2*.

Table 2. Physical characters of CD-Pd and their catlytical properties for hydrogenation of palm oil

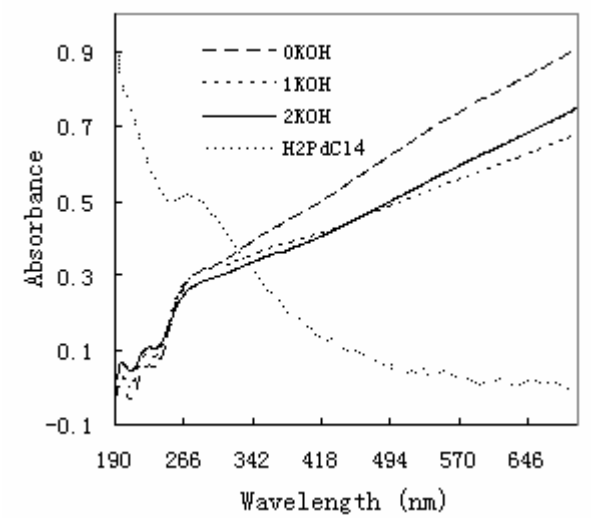
Item [a]	Formation rate [min]	Stability [day]	Activity [%][b]	Selectivity [%] [c]
1	≈ 30	>7	63.7	6.2
2	>120	3	97.2	12.7
3	≈ 60	>7	94.4	11.3
4	<10	2	71.1	6.9
5	<10	3	70.2	6.9
6	≈ 60	>14	100	14.4
7	---	---	31.0	2.4
8	≈ 60	>14	90.7	12.1
9	≈ 60	>14	100	18.8
10	≈ 60	>20	100	16.2

[a] different nanoparticles prepared under the conditions as in *Table 1*

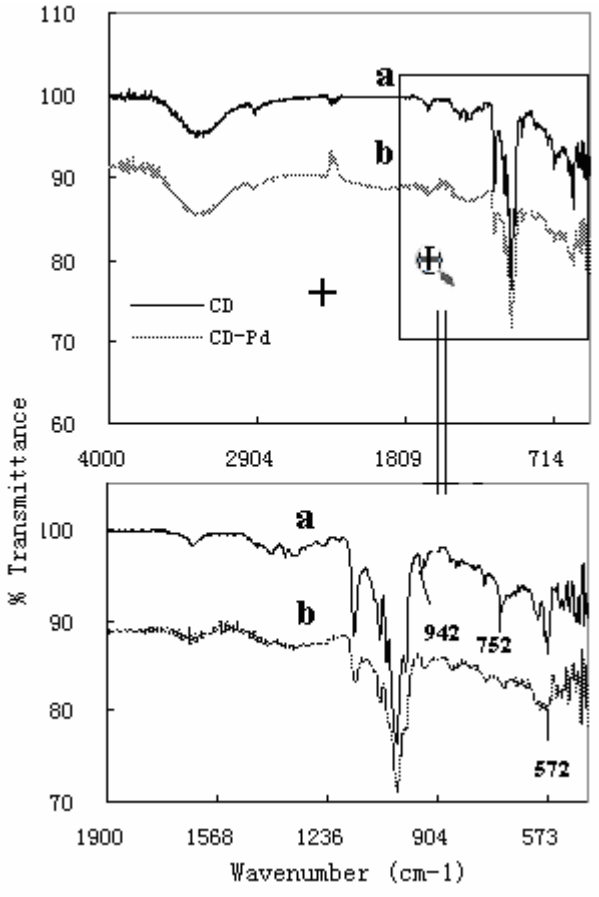
[b] the consumption percentage of C18:2 sampled at 10 min

[c] the formation of trans-C18:1 sampled at 10 min, percentage in palm oil

UV–Vis spectra (prepared under different amount of KOH) and FT-IR of β-CD-Pd were measured and shown as in *Fig.1*. According to the UV–Vis spectra, sharp peak appeared at 197 nm and 222 nm while a broad absorption peak generated in visible light region. The order of absorbency in ultraviolet region was 2KOH>1KOH>0KOH, which was concordant with the decreasing of reducing power by the decreasing addition of KOH. Nanoparticles prepared without KOH (0 KOH) has both highest intensity band in visible light region and lowest absorbency in ultraviolet region which was due to the small aggregates [9]. The absorption of CD-Pd in ultraviolet showed blue shift compared with the original H_2PdCl_4 solution (271nm), which was an indicator for the formation of interaction force between CD and Pd.



UV-Vis spectra of β-CD-Pd prepared with different amount of KOH

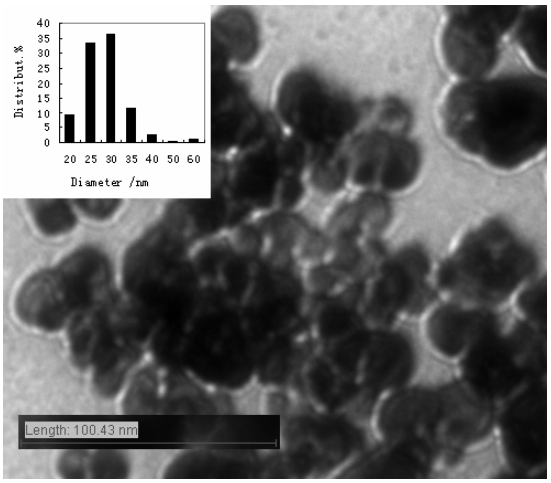


FT-IR of CD and CD-Pd

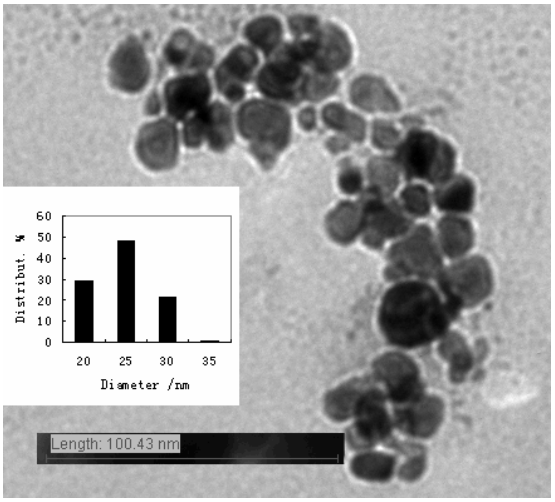
Fig 1. Characterization of CD and CD-Pd with UV-Vis and FT-IR

Another evidence was present by FT-IR spectra, the relative intensity of the transmittance band at 942 cm^{-1} (skeletal vibration involving α-1, 4 linkage), 753 cm^{-1} (ring'breathing' vibration), and 572 cm^{-1} (pyranose ring vibration) of free CD (see Fig.1, a) decreased in Fig. 1 b, which was interpreted as the interaction force with CD that prevented the skeletal and pyranose ring vibration [9].

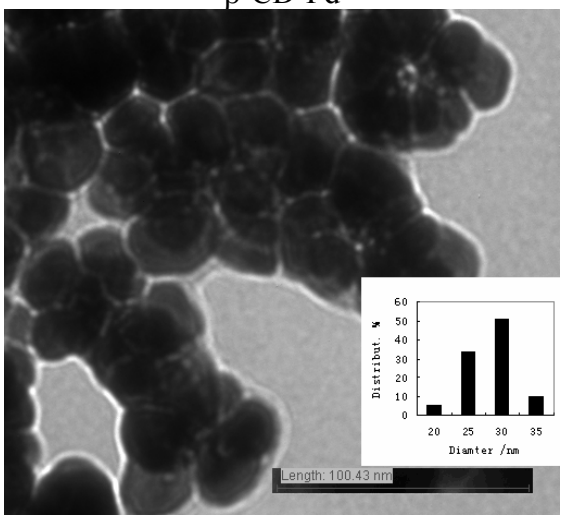
The size measurements were performed using TEM, the results for size and size distribution were summarized in *Fig.2* and the average particle size (d) and standard deviation (σ) were calculated.



α-CD-Pd



β-CD-Pd



γ-CD-Pd

	α-CD-Pd	β-CD-Pd	γ-CD-Pd
d /nm	27.20	24.67	28.30
σ	5.96	3.66	3.62

Fig 2.TEM images of CD-Pd and their average particle size (*d*) and standard deviation (*σ*)

TEM measurements were recorded on the precipitates collected from centrifuge; particles with spherical shape were obtained. The average diameters for α-CD-Pd, β-CD-Pd and γ-CD-Pd were 27.2±5.96 nm, 24.67±3.66 nm and 28.30±3.62 nm respectively. It can be concluded that the structure of CD also affect the particle size, compared with α-CD-Pd and γ-CD-Pd, β-CD-Pd show smaller size

and narrow size distribution. All the size for nanoparticles was much larger than the CD cavities which indicated that the nanoparticles were not formed by including inside the CD cavity [9] but with surface-attached.

The aqueous colloid solution could be used as catalysts for the hydrogenation of palm oil, they were with good activities as shown in Table 2, the activity of CD-Pd was much higher than the report before[11]. Nano catalysts with different stabilizers showed different activities and selectivities, the active order was as γ-CD-Pd> β-CD-Pd>α-CD-Pd, which was concordant with the deceasing order of the inner diameters of CD. For γ-CD-Pd and β-CD-Pd ,the selectivities for trans were lower compared with α-CD-Pd.

Conclusion

CD had been proved to be the stabilizer for the preparation of Pd nanoparticles, 2-propanol was an efficient reducing agent for the reduction of Pd ions with and without the assistant of alkali. Good separated metallic colloids were prepared based on the conditional research. The nanoparticles can be stable for several weeks in aqueous and used for the hydrogenation of palm oil with good activities, this should provide a future momentum for‘green’chemistry.

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