

Phenanthroline-stabilized palladium nanoparticles in polyethylene glycol—an active and recyclable catalyst system for the selective hydrogenation of olefins using molecular hydrogen

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Abstract

1,10-Phenanthroline-stabilized palladium nanoparticles dispersed in a polyethylene glycol (PEG) matrix is synthesized which is found to be a stable and active catalyst for the selective hydrogenation of olefins using molecular hydrogen under mild reaction conditions. A variety of olefins are hydrogenated to their corresponding alkanes with good to excellent yield at room temperature. The catalyst is easily separable and recyclable.

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1. Introduction

The development of novel nano-structured materials has attracted great attention recently due to their unique characteristics that differ from individual atoms and bulk materials [1]. Nanoparticles have different physical (heat capacity, vapor pressure, melting point), chemical, optical and electronic properties [1–3]. Their increased number of edges, corners and faces give them a high surface-to-volume ratio and therefore are highly useful as catalysts with a higher activity and selectivity during catalytic reactions [4,5].

Transition metal nanoparticles have wide ranging applications in catalysis. However, due to their large surface area and surface energy, they tend to agglomerate during the reactions and therefore need to be stabilized for effective utilization. Polyoxoanions and tetrabutyl ammonium have been used as

stabilizing ligands for transition metal nanoparticles and used as catalysts for the hydrogenation of arenes [6–11]. Dispersion or supporting these stabilized nanoparticles on to some matrix is very important to ensure its maximum effectiveness. Different types of ligand-stabilized metal nanoparticles have been synthesized and used as catalysts after being anchored on to some solid supports [12–18]. Reduction and capping of metal nanoparticles by multifunctional molecules such as hexadecyl aniline which in turn may be dispersed in an organic solvent for the effective hydrogenation of arenes is also described [19]. Dendrimer-encapsulated metal nanoparticles are also synthesized in which metal ions are sorbed into the interior of dendrimers and then chemically reduced to yield nano-sized metal particles [20].

A method of enhancing the catalytic activity of these nanoparticle catalysts is to mobilize them using some liquid polymeric matrices thereby achieving the advantages of both homogeneous and heterogeneous catalysis. Recently, phenanthroline ligand-stabilized palladium nanoparticles dispersed in ionic liquid has been reported to be very active for the hydrogenation of olefins [21]. However, ionic

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liquid is not only very expensive but also not yet accepted as an environmentally friendly medium and there are reports of it being toxic in nature in spite of several studies in this medium [22].

The search for an alternative environmentally friendly reaction medium in place of the volatile and toxic organic solvents is an important goal of green chemistry research with significant environmental consequence. Therefore, it is desirable to develop nano-structured catalytic systems supported or dispersed on a suitable mobile phase that are very active, selective, stable, non hazardous and recyclable. Polyethylene glycol (PEG) has been emerging as a very convenient support for the synthesis of a variety of catalysts, ligands and organic compounds [23]. It is relatively inexpensive, environmentally benign and can readily be functionalized. It is soluble in many organic solvents but insoluble in some others such as diethyl ether. These properties render it very attractive as a mobile support wherein a reaction catalyzed by the PEG supported catalyst can be carried out under homogeneous condition while the PEG-catalyst system can be easily recovered after extracting the reaction mixture with diethyl ether.

Herein, we report such a catalyst system where phenanthroline-stabilized palladium nanoparticles are dispersed in a PEG matrix for the selective hydrogenation of olefins using molecular hydrogen. There have been numerous studies on the synthesis of metal nanoparticles in PEG (polyol method) where PEG functions as a reducing agent [24–27]. However, in this study, PEG is used not only as a reducing agent but also as a dispersing medium for the ligand-stabilized metal nanoparticles. The catalyst is easy to prepare, easy to recover and reusable. Hydrogenation of olefins continues to be of great interest among catalytic processes due to the increasing industrial demand for low-aromatic diesel fuels and in the synthesis of intermediates for several pharmaceuticals and chemicals [28–30].

2. Experimental

2.1. Catalyst preparation

Phenanthroline-stabilized palladium nanoparticles in PEG was synthesized by the following procedure. Approximately 5 mg palladium acetate was mixed with 1.5 g of 1,10-phenanthroline in 4 g PEG in a 25 mL round-bottomed flask. The mixture is stirred under an atmosphere of hydrogen at room temperature for about 15 min when the palladium nanoparticles are formed indicated by a dark color of the mixture. Polyvinylpyrrolidone (PVP) and 1-hexadecylaniline (HAD) stabilized palladium nanoparticles in PEG are also prepared in a similar fashion.

2.2. Catalyst characterization

The synthesized catalyst was characterized by UV–vis spectroscopy using a HP UV-vis spectrophotometer (Model

8453) and also by transmission electron microscopy (Philips 320 TEM).

2.3. Hydrogenation

Hydrogenation of olefins was conducted in liquid phase in a 25 mL round-bottomed flask equipped with a reflux condenser and a magnetic stirrer. In a typical reaction procedure, 10 mmol of the substrate was added to the above catalyst mixture and was purged with oxygen. The mixture was then vigorously stirred in the presence of hydrogen at atmospheric pressure for the desired time period at the desired temperature. After the reaction, the mixture was extracted with diethyl ether and analyzed by a Hewlett-Packard 6890 Gas Chromatograph using a HP-55% phenyl methyl siloxane capillary column (30 m × 320 μm × 0.25 μm) and a quadrupole mass filter equipped HP 5973 mass selective detector. All the products are known compounds. Identification of the compounds was carried out by comparing the retention time of the standard and also by GC-MS. Quantification of the products was obtained by a peak area ratio method.

In the catalyst recycling experiments, the mixture after the reaction was cooled to room temperature and the organic products were extracted into diethyl ether and removed by simple decantation. The ether-immiscible PEG layer containing the metal nanoparticle catalyst was recovered followed by warming up in a rotavapor to remove any organics. The catalyst thus recovered was used for the next reaction cycle.

3. Results and discussion

Phenanthroline-stabilized palladium nanoparticles in PEG are synthesized using a procedure similar to that reported by Han and co-workers for preparing the same system in ionic liquid [21]. The conversion of cyclohexene hydrogenation using the above catalyst system under different conditions is shown in Table 1. It is apparent that phenanthroline-stabilized palladium nanoparticles are highly active for the hydrogenation of cyclohexene using molecular hydrogen under mild conditions. Cyclohexene conversion of up to 84% is obtained at 35 °C (entry 3) by using palladium acetate and phenanthroline in PEG. Studies on the effect of temperature show that increasing temperature increases the conversion (entries 4–6), however, tends to precipitate out palladium from the colloidal state over 70 °C. The effects of varying the amounts of palladium, phenanthroline and PEG are also given. Of the three palladium precursors studied, using the palladium acetate has resulted in the most effective catalyst for the hydrogenation of cyclohexene. The molecular weight of PEG does not seem to be very influential in determining the catalyst activity (not shown in Table 1). However, the higher the molecular weight of PEG, the greater is the boiling point (lower vapor pressure), which reduces the evaporation loss and also facilitates its separation after the reaction for recycling. Other metallic systems are also tested for the reaction (entries 14–17);

Table 1
Phenanthroline-stabilized metal nanoparticles in PEG for the hydrogenation of cyclohexene using molecular hydrogen^a

Entry	Metal Salt	Pd acetate (mg)	Phenan-throline (mg)	Solvent (g)	Temperature (°C)	Conversion (%)
1	Pd acetate	2	1	4	35	10
2	Pd acetate	5	1.5	4	35	74
3	Pd acetate	10	2.5	4	35	84
4	Pd acetate	10	5	4	35	53
5	Pd acetate	10	5	4	50	45
6	Pd acetate	10	5	4	70	59
7	Pd acetate	5	1.5	1	35	20
8	Pd acetate	5	1.5	2	35	31
9	Pd acetate	5	1.5	3	35	50
10	Pd acetate	5	1.5	6	35	72
11	Pd acetate	5	0	4	35	36
12	Pd chloride	5	1.5	4	35	54
13	Pd acetyl acetonate	5	1.5	4	35	10
14	Cu acetate	10	3	4	35	46
15	Ni acetate	10	3	4	35	30
16	Co acetate	10	3	4	35	35
17	Zn acetate	10	3	4	35	10

^a Reaction conditions: 10 mmol cyclohexene, stir, H₂ balloon, 4 h.

however, under the reaction conditions used, catalysts prepared with palladium are found to be the most active for the reaction.

The application of the catalyst system is further verified by extending the reaction to a series of aliphatic, alicyclic and aromatic olefins as illustrated in Table 2. The catalyst system is found to be active and selective for the hydrogenation of a variety of olefins with good to excellent conversion under mild reaction conditions. For example, acyclic, aliphatic, and aromatic olefins are easily converted to their corresponding alkanes within 8 h reaction period at 30–50 °C. Hydrogenation of 1,5-cyclooctadiene affords the mono hydrogenated product selectively (entries 15 and 16) at 30–40 °C and 8 h reaction time. The selectivity of the di-hydrogenated product increases with increase in the reaction time (entry 16). Similarly, hydrogenation of unsaturated ketones, such

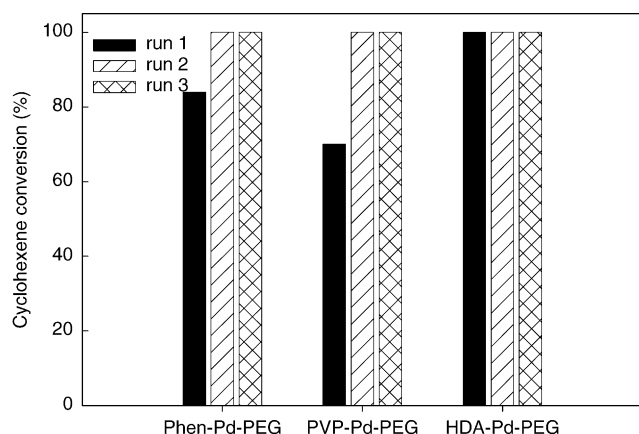


Fig. 1. Comparison of conversion and reusability of phenanthroline–Pd–PEG, polyvinyl pyrrolidone–Pd–PEG and hexadecylaniline–Pd–PEG system for cyclohexene hydrogenation using hydrogen at 35 °C (reaction conditions: 10 mmol substrate, 5 mg Pd acetate, 1.5–3.0 mg 1,10-phenanthroline/PVP/HDA, 4 g PEG (400), stir, 4 h, H₂ balloon).

as cinnamyl alcohol (entries 22 and 23) and citral (entries 24 and 25) form the C=C hydrogenated product selectively without affecting the C=O group. Only one C=C bond is selectively hydrogenated at short reaction times. However, the selectivity of the di-hydrogenated product increases with reaction time (20 h, entry 25). The selectivity of the catalyst system is ascribed to the nanoparticle size and the nature of the metal. The calculated turn over numbers (TON, the number of moles of product formed per mol of palladium) for this catalyst system are relatively higher than some of the other systems.

The catalyst system is also examined for its recyclability and the results are shown in Table 3. The phenanthroline–stabilized palladium nanoparticles–PEG catalyst system is easily separable from the reaction mixture by extraction of the products with diethyl ether and can be reused several times without any loss of activity or selectivity. The activity of the non-stabilized Pd particles in PEG is much lower than the phenanthroline-stabilized Pd in PEG. The phenanthroline ligand stabilizes the nanoparticles of palladium by preventing their agglomeration during the reaction. This is verified by comparing the activity and recyclability of phenanthroline-stabilized palladium and non-stabilized

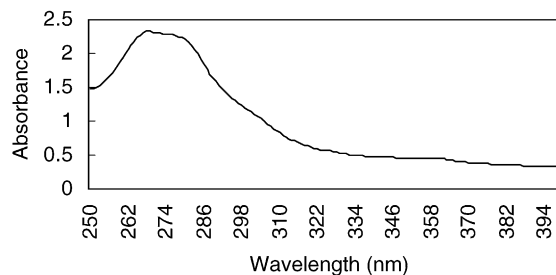


Fig. 2. UV–vis absorption spectra of phenanthroline-stabilized palladium nanoparticles in polyethylene glycol.

Table 2
Phenanthroline-stabilized palladium nanoparticles in PEG for the hydrogenation of olefins using molecular hydrogen^a

Entry	Substrate (g)	Product	Temp (°C)	Time (h)	Conversion (%)	Selectivity (%)	TON
1	Cyclopentene	Cyclopentane	30	8	50	100	242
				20	100	100	448
2	1-Hexene	<i>n</i> -Hexane	30	8	44	100	197
				20	100	100	448
3	1-Hexene	<i>n</i> -Hexane	50	4	61	100	274
				8	100	100	448
4	Cyclohexene	Cyclohexane	30	4	74	100	332
				8	100	100	448
5	1-Methyl cyclohexene	Methyl cyclohexane	40	8	5	100	22
				20	18	100	81
6	1-Methyl cyclohexene	Methyl cyclohexane	50	8	22	100	99
				20	54	100	242
7	1-Phenyl cyclohexene	Phenyl cyclohexane	40	8	13	62 ^b	58
				20	38	87 ^b	170
8	1-Phenyl cyclohexene	Phenyl cyclohexane	50	8	89	95 ^b	399
				20	100	94 ^b	448
9	1-Octene	<i>n</i> -Octane	40	8	64	100	287
				20	100	100	448
10	1-Octene	<i>n</i> -Octane	50	4	69	100	309
				8	100	100	448
11	2-Octene	<i>n</i> -Octane	40	8	38	100	170
				20	78	100	350
12	2-Octene	<i>n</i> -Octane	50	8	65	100	291
				20	100	100	448
13	Cyclooctene	Cyclooctane	40	8	24	100	108
				20	50	100	224
14	Cyclooctene	Cyclooctane	50	4	46	100	206
				8	100	100	448
15	1,5-Cyclooctadiene	Cyclooctene	30	8	32	62 ^c	143
				20	54	70 ^c	242
16	1,5-Cyclooctadiene	Cyclooctene	40	8	83	89 ^c	372
				20	100	38 ^c	448
17	Styrene	Ethyl benzene	30	8	61	100	274
				20	100	100	448
18	Styrene	Ethyl benzene	50	4	100	100	448
19	Stilbene	Dibenzyl	40	8	43	100	193
				20	90	100	404
20	Stilbene	Dibenzyl	50	4	100	100	448
21	Norbornylene	Norborane	40	4	100	100	448
22	Cinnamyl alcohol	3-Phenyl propanol	40	8	36	100	161
				20	100	100	448
23	Cinnamyl alcohol	3-Phenyl propanol	50	4	71	97 ^d	318
				8	100	94 ^d	448
24	Citral	Citronellal	40	8	12	100	54
				20	23	100	103
25	Citral	Citronellal	50	8	85	82 ^e	381
				20	100	15 ^e	448
26	3-Methyl-2-butenal	3-Methyl butenal	40	8	92	100	413
27	Mesityl oxide	4-Methyl-2-pentanone	40	8	94	100	422
28	Cyclohexenone	Cyclohexanone	40	8	94	100	422
29	3-Methyl cyclohexene-1-ol	3-Methyl cyclohexanol	40	8	51	100	229
				20	100	100	448

^aReaction conditions: 10 mmol substrate, 5 mg Pd acetate, 1.5–3.0 mg 1,10-phenanthroline, 4 g PEG (400), stir, H₂ balloon. ^bremaining biphenyl, ^cremaining cyclooctane, ^dremaining cinnamaldehyde, ^eremaining hydrocitronellal, TON: turn over number, calculated as the number of moles of product formed per mol of palladium.

palladium in PEG. Pd-PEG without the ligand showed a much lower initial activity (Table 3). However, the recyclability was not affected due to the absence of the ligand even though the activity was much lower than the ligand-stabilized palladium in PEG. Control experiments in the absence of pal-

ladium did not show any activity. These results suggest that phenanthroline can stabilize the palladium nanoparticles in PEG which can act as a mobile supporting phase thereby achieving high stability and high activity for the catalyst system.

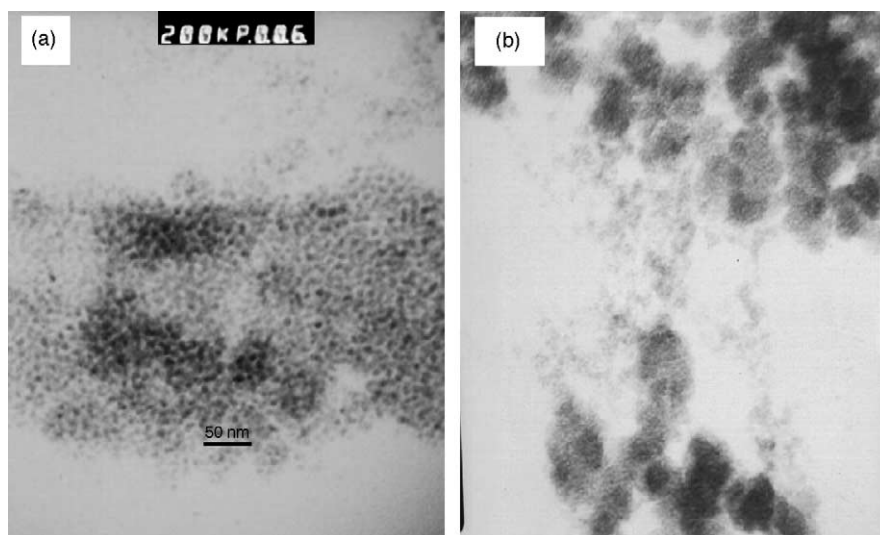


Fig. 3. TEM picture of (a) phenanthroline-stabilized palladium nanoparticles in PEG and (b) palladium particles in PEG with no phenanthroline (200 kV, Philips 320 CM).

The phenanthroline–Pd–PEG catalyst system has also been compared with other active ligand-stabilized palladium nanoparticles reported earlier for hydrogenation viz., polyvinyl pyrrolidone and 1-hexadecylaniline-stabilized palladium nanoparticles dispersed in PEG as shown in Fig. 1 [6,8]. The results reveal that the phenanthroline–Pd–PEG has comparable hydrogenation activity with that of the other two systems (polyvinylpyrrolidone–Pd–PEG and 1-hexadecylaniline–Pd–PEG) under identical reaction conditions. An increase in the activity is observed for the second run when compared to the first run which may be ascribed to the palladium precatalyst not being fully converted to nanoclusters in the first run. Similar observation has been made earlier [1].

The phenanthroline-stabilized palladium nanoparticles in PEG has been characterized by both UV–vis spectroscopy and by TEM analysis. The UV–vis spectrum of phenanthroline-stabilized palladium shows absorption maximum at around 265 nm, which is characteristic of nanoparticles (Fig. 2). The peak at 275 nm also appeared after the reduction, which may be due to the formation of some intermediate species formed during the reduction of Pd²⁺. The UV–vis spectrum of gray colloid showed broad absorption

continua extending throughout the visible–near-ultraviolet region. This suggests the formation of palladium colloid having particle size less than 10 nm. A TEM image (Philips CM 20) of the freshly prepared sample after reduction for 15 min shows the formation of well-defined, discrete palladium nanoparticles of 2–6 nm size (Fig. 3a). On the other hand, the particle sizes were in 500–1000 nm range in the case of palladium particles dispersed in PEG in the absence of phenanthroline (Fig. 3b).

The reduction of palladium acetate in polyethylene glycol in the presence of phenanthroline ligand may proceed in two steps: (i) ligand exchange around Pd²⁺ and (ii) reduction of Pd²⁺ to Pd metal. PEG can also act as a reducing agent similar to ethylene glycol in the polyol method.

4. Conclusions

In summary, this study demonstrates that phenanthroline-stabilized palladium nanoclusters in PEG is a stable, active and recyclable catalyst for the hydrogenation of olefins using molecular hydrogen under mild reaction conditions. The phenanthroline–Pd–PEG catalyst system has comparable hydrogenation activity like other reported ligand-stabilized metal nanoparticles such as polyvinyl pyrrolidone and 1-hexadecylaniline-stabilized metal nanoparticles.

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Table 3

Recyclability of phenanthroline-stabilized Pd nanoparticles in PEG for the hydrogenation of cyclohexene^a

Cycle number	Conversion in phenanthroline–Pd–PEG (%)	Conversion in Pd–PEG ^b (%)
1	84	54
2	100	49
3	100	43
4	100	46
5	100	42
6	100	43

^a Reaction conditions same as that given for Table 2.

^b Pd acetate in PEG (no phenanthroline).

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