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Synthesis of Palladium Nanoparticle by Bio-reduction Method and Its Effectiveness as Heterogeneous Catalyst Towards Selective Oxidation of Benzyl Alcohols in Aqueous Media

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Abstract Monodispersed palladium nanoparticles (PdNp) have been synthesized by a green rapid bio-reduction method under room temperature and pressure. The reducing agents mainly involved in these processes are the various water soluble plant metabolites, polyphenols as well as co-enzymes present in the leaf extract of Tulsi (*Ocimum sanctum*). An active and stable montmorillonite K-10 supported heterogeneous catalyst was prepared using these PdNp for oxidation of alcohols to their corresponding carbonyl compounds with efficient yield and having good reusability. These are characterized by TEM, XRD, BET surface area and UV–Vis absorption spectroscopy.

Graphical Abstract

Keywords Palladium nanoparticles (PdNp) · Mont K-10 · Green synthesis · Alcohol oxidation · Heterogeneous catalysis

1 Introduction

The area of metal nanoparticle synthesis has received tremendous boost during last two decades because of their wide applications and unique characters. Among the various metal nanostructures, those obtained from transition metals are getting wide attention due to their unique physicochemical properties as well as their practical utility in catalysis and biochemistry [1], of which Pd based nanostructures are well known for their excellent catalytic activity and selectivity [2]. There are various methods available for synthesis of nanoparticles, but most of these involve toxic chemicals and harsh conditions. Efforts are now being directed to develop new green protocols for synthesis of Pd-nanoparticles (PdNp). Use of biomaterials in this area has emerged as a very promising green synthetic protocol. There are a few such reported methods of preparing PdNps using plant extracts of tea, coffee, *C. Camphora* etc. [3, 4].

The alcohol oxidation is one of the most frequently used reactions in various organic syntheses involving manufacture of drugs, agro-chemicals and fragrances. Traditionally, alcohols are oxidized using oxidizing agents such as oxides of manganese and chromium in presence of acid and harmful organic solvents which produces toxic metal salts [5]. The alcohol oxidation by catalysts involving nanomaterials is also found to be very effective for their high performance and easy controllability. Several synthetic methodologies have also been developed for alcohol oxidation involving the use of silver nanoparticles supported on hydrotalcites, gold nanoparticles supported on metal oxides and PdNp supported on hydroxyapatite, mesoporous carbon, silica–alumina, clay etc. [6–11]. But most of these methods involve the use of large amount of additives as oxidant and organic solvents contrary to green chemistry protocols.

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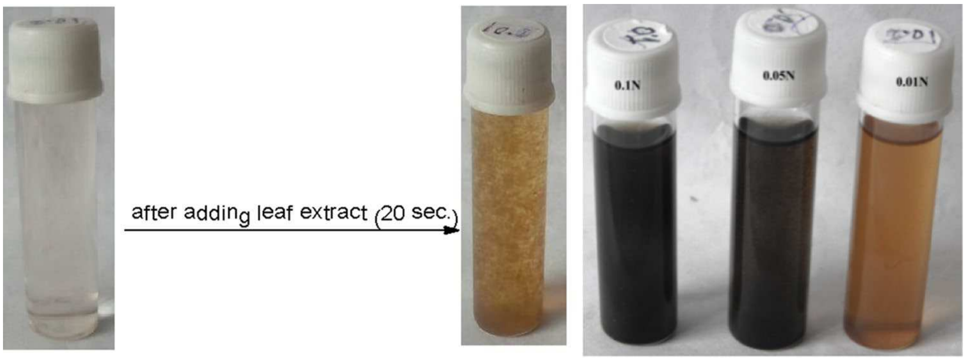
In the present work, we report the development of an efficient, reusable heterogeneous catalytic system involving mont K-10 supported PdNp, synthesized by using leaf extracts of Tulsi (*Ocimum sanctum*) at room temperature under aerobic condition in aqueous medium with excellent results. This catalytic system was found to be very effective for usually unreactive alcohol such as heteroatom containing alcohol, cinnamyl alcohol in aqueous media.

2 Results and Discussion

When the leaf extract of 2 ml of Tulsi (*O. sanctum*) was mixed in the 0.05 N (0.177 g $PdCl_2$ in 20 ml ethanol) alcoholic solution of palladium chloride, it started to change colour (within 30 min) from light brown to black (Fig. 1b) indicating the generation of PdNp. The various water soluble plant metabolites, polyphenols as well as co-enzymes present in the leaf extract act as reducing agent and thus reduces Pd^{2+} ions. The formation of PdNp was characterized by TEM, BET surface area measurement, UV–Vis spectroscopy, XRD and inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis.

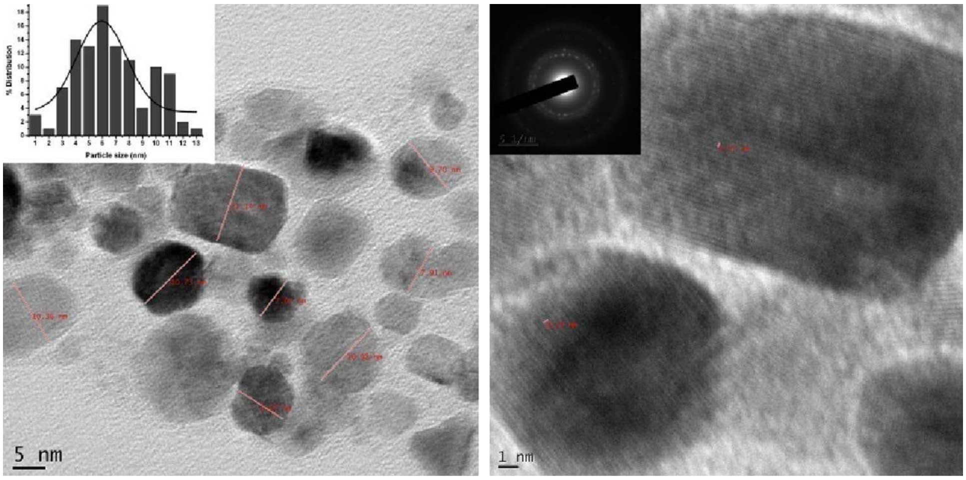
2.1 TEM Study

The morphology, size and size distribution pattern of the PdNps in colloidal solutions were investigated by TEM (Fig. 2a) which indicate homogeneous particle size distribution in the range of 1–13 nm with majority of particles being in the range of 3–6 nm (Fig. 2a inset histogram). The selective area electron diffraction (SAED) pattern indicates the highly crystalline nature of PdNps (Fig. 2b, inset). The spacing between two crystal planes is found to be about 0.19 nm, which corresponds to the (200) plane of the metal nanocrystals (Fig. 2b) [12]. The Fig. 3 depicts the TEM image of PdNp@mont K-10 catalyst. Comparing Figs. 2 and 3, it can be concluded that after using of montmorillonite K-10 clay as supporting material, the particle size of PdNps were not changed and led to the uniform deposition on the clay without any surface modification or agglomeration.



(a) (b)

Fig. 1 **a** change of colour after adding leaf extract of tulsi (20 s.). **b** Change of colour with change of $PdCl_2$ concentration



(a) (b)

Fig. 2 **a** TEM image of PdNp, **b** SAED pattern of PdNp

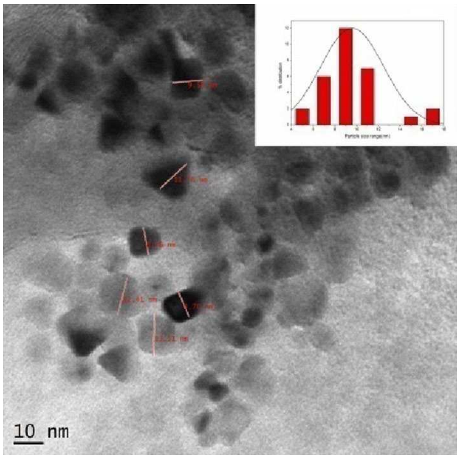


Fig. 3 TEM image of PdNp@mont K-10

2.2 UV–Vis Spectroscopy and ICP-AES Analysis

The formation of PdNps was monitored by recording the electronic spectrum (200–600 nm) of the colloidal PdNp solution. Figure 4b shows the absorption spectrum of colloidal suspensions of PdNps after 48 h of bio-reduction while Fig. 4a shows the absorption spectrum of $PdCl_2$ solution. The weak bands appearing around 290 and 340 nm for $PdCl_2$ solution could be due to the ligand to metal charge transfer transition of the Pd(II) ions [13]. The non appearance of any absorption peaks above 300 nm (Fig. 4b) is indicative of the complete reduction of the Pd(II) ions. From ICP-AES analysis the Pd content in PdNp@mont K-10 was found to be 0.004 mol% or 0.005 mg (0.21 ppm) per 20 mg of the solid catalyst (0.2625 mg Pd per gram of the catalyst, PdNp@mont K-10).

2.3 XRD

The XRD pattern of PdNp (Fig. 5a) exhibits diffraction peaks at 2θ value of 40.1°, 46.3° and 67.8° corresponding to (111), (200) and (220) planes of fcc structure of Pd(0) nanoparticles [14]. On incorporation of PdNps to mont K-10 reveals diffraction peaks with similar 2θ values with comparatively weak intensity which is due to very small amount of Pd(0) loading (0.21 ppm) in PdNp@mont K-10. The appearance of an intense peak at 2 θ = 26.08° is due to mont K-10 [15] (Fig. 5b).

2.4 BET Surface Area Analysis

According to BET surface measurement, the surface areas of the montmorillonite K-10 clay and PdNp@mont K-10 were found to be 446 and 333 $m^2\ g^{-1}$, respectively.

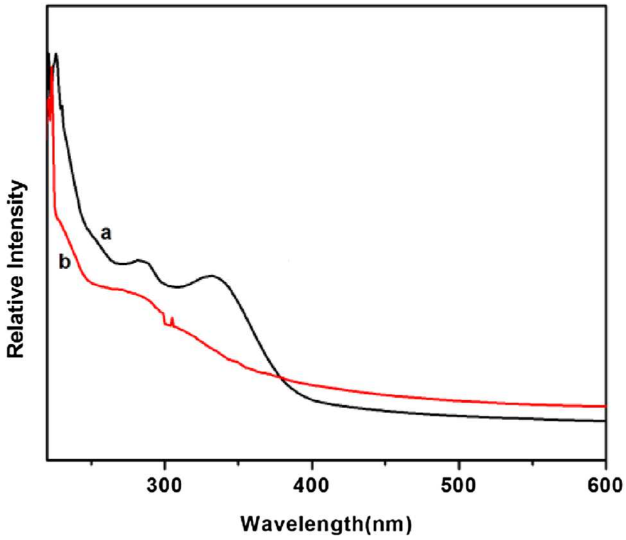


Fig. 4 UV–Visible spectra of **a** 0.1 N $PdCl_2$ solution and **b** 0.05 N PdNps

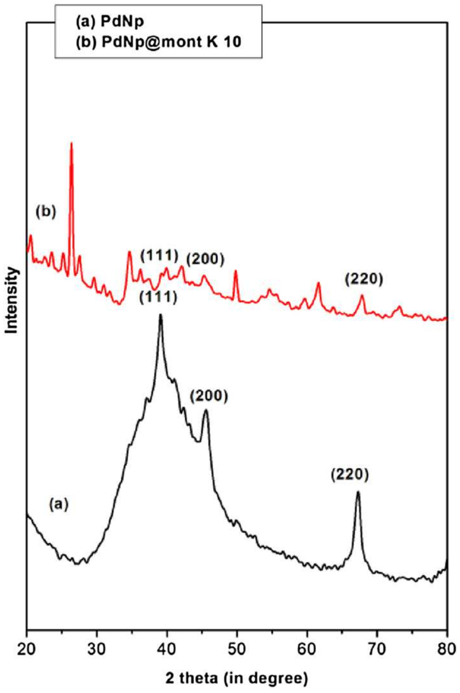


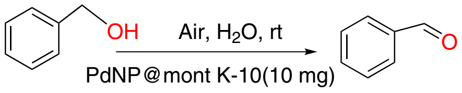
Fig. 5 XRD pattern of **a** PdNp and **b** PdNp@mont K-10

The decrease in surface area of the catalyst can be attributed to the incorporation of PdNp into the clay.

2.5 Use of PdNp@mont K-10 for Selective Alcohol Oxidation Reaction

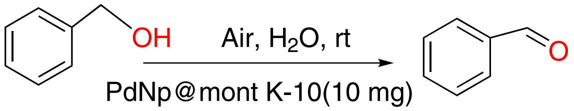
The prepared PdNp@mont K-10 catalyst was applied for the selective aerobic oxidation of benzyl alcohols. For this purpose, benzyl alcohol was chosen as model substrate and initially the reaction was carried out in water at room temperature as shown in Scheme 1.

The screening of different solvent, oxidant, amount of catalyst and temperature is illustrated in Table 1. It is noteworthy that the PdNp@mont K-10 catalyst shows excellent performance even at room temperature in water under aerobic condition (Table 1, entry 1). Solvent effect on the activity of PdNp@mont K-10 was surveyed with different polar and nonpolar solvents although significant variations in yields were noticed. The reaction was conducted in toluene, acetonitrile, DMSO, DMF, ^{i}PrOH and methanol (Table 1, entries 2–7) and best results was obtained when water was used as solvent (entry 1). Generally, the presence of water with high polarity index facilitates the solubility of the organic substrates, which in turn facilitates the adsorption of reactants on the active site of the catalyst and increases the effectiveness of the conversion and selectivity [16]. This may be the reason for low yield in toluene, acetonitrile, DMSO, DMF, ^{i}PrOH and methanol (entries 2–7). When mixture of solvents was used, excellent yield of products was obtained (entries 8–10). In solvent free condition, the yield of product was found to be of trace amount (entry 11).When the loading of PdNp@mont K-10 was decreased from 10 mg (0.002 mol%) to 5 mg (0.001 mol%), the yield of product was slightly decreased (entry 12).



Scheme 1 Oxidation of benzyl alcohol

Table 1 Optimization of reaction condition



Entry	Catalyst (mg)	Solvent	Time (h)	Yield^{a} (%)
1	PdNp@mont K-10	H_2O	5	98
2	PdNp@mont K-10	acetonitrile	6	88
3	PdNp@mont K-10	Toluene	5	85
4	PdNp@mont K-10	DMSO	5	86
5	PdNp@mont K-10	DMF	7	88
6	PdNp@mont K-10	^{i}PrOH	6	80
7	PdNp@mont K-10	Methanol	5	82
8	PdNp@mont K-10	H_2O:^{i}PrOH (1:1)	5	92
9	PdNp@mont K-10	H_2O:acetonitrile (1:1)	5	95
10	PdNp@mont K-10	H_2O:DMF (1:1)	5	90
11	PdNp@mont K-10	–	5	Trace amount
12	PdNp@mont K-10	H_2O	5	94^{b}
13	PdNp@mont K-10	H_2O	5	98^{c}
14	Mont K-10 clay	H_2O	5	Trace amount
15	PdNp	H_2O	5	97
16	–	H_2O	5	Trace amount
17	PdNp@mont K-10	H_2O	5	98^{d}

Reaction condition: benzyl alcohol (1 mmol), PdNp@mont K-10 (10 mg), 3 ml H_2O under aerobic condition at room temperature

[a] Isolated yield

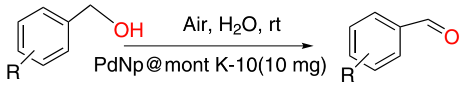
[b] Amount of catalyst(5 mg)

[c] Amount of catalyst (15 mg)

[d] 50 °C temperature used

Similarly, increase of catalyst loading (15 mg, 0.003 mol%) does not effect the product yield (entry 13). The reaction was also performed in the presence of neat mont K-10 clay and PdNp (entries 14, 15). But no significant increase in product yield was observed in presence of neat mont K-10, while in presence of only 10 mg of PdNp, yield was 97%, indicating the prime role of PdNps in this reaction. Furthermore, when the reaction was performed in absence of catalyst no product was isolated (entry 16). Again, it was noticed that increase of temperature beyond ambient condition has no significant effect in this current protocol (entry 17).

Table 2 Aerobic oxidation of different substituted benzyl alcohol



Entry	Substrate (R)	Time (h)	Yield (%)[a]	TON	TOF (h^{-1})
1	4-OCH_3	5	95	47,500	9500
2	4-Cl	7	79	39,500	5642
3	4-CH_3	7	92	46,000	6571
4	4-NO_2	7	88	44,000	6285
5	H	5	98	49,000	9800

Reaction condition: alcohol (1 mmol), PdNp@mont K-10 (10 mg), H_2O (3 ml) in air at room temperature

[a] Isolated yield

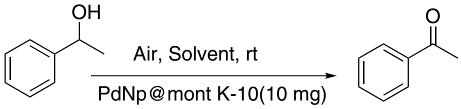
TON = Mole of product/Pd mole; TOF = TON/time in h

After investigating the effect of different parameter, we next examined the catalytic activity of PdNp@mont K-10 catalyst in different substituted benzyl alcohol (Table 2). Primary benzyl alcohols with electron donating and withdrawing groups such as *p*-Cl, *p*-NO_2, *p*-MeO, *p*-Me in the benzene ring gave the desired products in 79–98% yield (Table 2, entries 1–5). Primary benzyl alcohols bearing halogen group as substituent was also successfully oxidized to benzaldehyde with satisfactory yields (entry 2).

In order to expand the scope of the use of our catalyst for secondary alcohol, initially we have conducted the screening reaction with 1-phenyl ethanol as model substrate using the same optimum condition used for benzyl alcohol. Our result suggests that air is not sufficient for complete conversion of secondary alcohol to their corresponding product. Therefore we have used hydrogen peroxide (H_2O_2) as external oxidant, which is considered as a stoichiometric and environmentally acceptable oxidant [17, 18] (Table 3).

However, search for an alternative reaction condition revealed that changing the solvent with toluene, acetonitrile and DMSO, increasing the temperature and increasing the catalyst loading to 20 mg does not affect in conversion

Table 3 Optimization of reaction condition for secondary alcohol



Entry	Catalyst (mg)	Solvent	Time (h)	Yield (%)[a]
1	PdNp@mont K-10	H_2O	5	82
2	PdNp@mont K-10	acetonitrile	6	72
3	PdNp@mont K-10	Toluene	5	75
4	PdNp@mont K-10	DMSO	5	70
5	PdNp@mont K-10	H_2O:acetonitrile(1:1)	5	75
6	PdNp@mont K-10	H_2O:DMF (1:1)	6	75
7	PdNp@mont K-10	H_2O	4	95[b]
8	PdNp@mont K-10	H_2O	4	95[c]
9	PdNp@mont K-10	H_2O	4	88[d]
10	PdNp@mont K-10	H_2O	4	95[e]
11	PdNp@mont K-10	H_2O	4	95[f]

Reaction condition: 1-phenyl ethanol (1 mmol), PdNp@mont K-10 (10 mg), solvent (3 ml) in air at room temperature

[a] Isolated yield

[b] 0.1 ml H_2O_2 used as oxidant

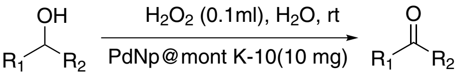
[c] 20 mg catalyst used

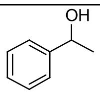
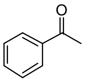
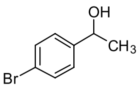
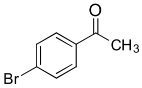
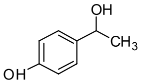
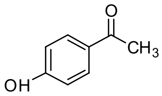
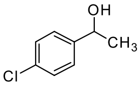
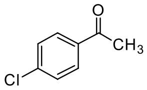
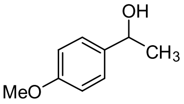
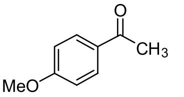
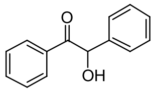
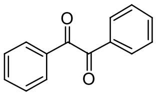
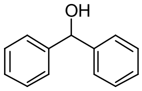
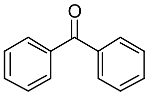
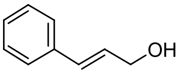
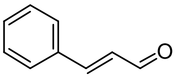
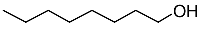
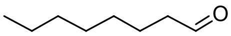
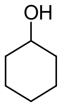
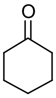
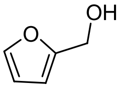
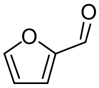
[d] 5 mg catalyst used

[e] 50 °C temperature used

[f] 0.2 ml H_2O_2 used

Table 4 Oxidation of different secondary alcohol[a]



Entry	Substrate	Product	Time (h)	Yield (%)[b]	TON	TOF (h^{-1})
1			5	95	47500	9500
2			6	92	46000	7666
3			5	92	46000	9200
4			6	90	45000	7500
5			7	94	47000	6714
6			5	90	45000	9000
7			5	89	44500	8900
8			9	78	39000	4333
9			9	70	35000	3888
10			8	81	40500	5062
11			9	70	35000	3888

[a] Reaction condition: alcohol (1 mmol), PdNp@mont K-10 (10 mg), H_2O (3 ml), H_2O_2 (0.1 ml) at room temperature

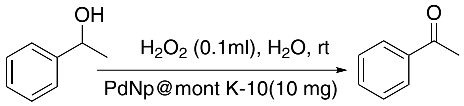
[b] Isolated yield

TON = Mole of product/Pd mole; TOF = TON/time in h

of alcohol to corresponding carbonyl compound (Table 3, entries 1–6).

After optimization of reaction conditions various alcohols were oxidized in the presence of 10 mg catalyst and H_2O_2 as an oxidant at room temperature in water (entry 7). The results are summarized in the Table 4. Alcohols with an aromatic substituent were found to be more reactive than aliphatic alcohols (Table 4, entry 9), which can be attributed to the presence of delocalization. Similarly, alcohols with electron donating substituent were found to slow down the oxidation process whereas in case of electron withdrawing substituent, it is accelerated. The PdNp@mont K-10 catalyst comfortably catalyzed the usually unreactive cinnamyl alcohol as well as cyclic alcohol (Table 4, entries 8, 10). Furfuryl alcohol

Table 5 Reusability of Pd catalyst on alcohol oxidation of 1-phenyl ethanol



No. of runs	1st run	2nd run	3rd run	4th run	5th run
Isolated yield (%)	95	95	95	94	94

containing the heteroatom and aliphatic octanol afforded the products in good yield (entries 9, 11) (Table 4).

To know the leaching of Pd metal in the solution, we have performed ICP-AES analysis of the filtrate after 5th run. Detection of negligible amount (below detection limit) of palladium in the solution suggests the robust nature of the catalyst. Thus it confirms the heterogeneity of the catalyst [16]. After completion of first cycle, catalyst can be separated from the reaction mixture by simple centrifugation process. Upon being isolated, 1-phenyl ethanol as model substrate, the catalyst is fully active upto fifth cycle giving excellent yield (Table 5). When the catalyst was removed from the reaction mixture by centrifugation after about 50% conversion of 1-phenyl ethanol, the reaction ceased completely, indicating heterogeneous nature of the catalyst.

3 Conclusion

Synthesis of PdNp was done by adopting green methodology. The active heterogeneous catalyst PdNp@mont K-10 catalyst was prepared with mont K-10 as support which was found to be an excellent catalyst for oxidation of both primary and secondary alcohols. This protocol was also effective for usually unreactive substrates such as cinnamyl alcohol, cyclohexanol, aliphatic alcohol as well as alcohol containing heteroatom like fufuryl alcohol. The advantageous features of the present catalytic system include the use of aqueous solvent, air as oxidant, no ligands and reusability of catalyst upto fifth cycle.

4 Experimental

4.1 Material

The chemicals were obtained commercially and used as received without further drying or purification. The solvents such as DMSO, acetonitrile, ethyl acetate, methanol and toluene and oxidant such as H_2O_2 were purchased from MERCK. Palladium(II) chloride was purchased from Arora Matthey Limited. Alcohol substrates were purchased from Sigma-Aldrich and Tokyo Chemical Industry and were used as received without further treatment.

4.2 Synthesis of PdNp [19]

To synthesize PdNp, 2 gm wet leaves of Tulsi (*O. sanctum*) were collected and washed thoroughly with distilled water and crushed in a mortar. The leaf extract obtained after boiling in 20 ml water for 5 min was centrifuged and the filtrate was collected for further experimental purpose. Two milliliters of leaf extract was added to 20 ml of 0.05 N alcoholic $PdCl_2$ (0.177 g $PdCl_2$ in 20 ml ethanol) solutions and kept for 5 min at room temperature followed by stirring for 5 h. The mixture so obtained was again centrifuged and the nanoparticles were collected for characterization.

4.3 Procedure for Preparation of PdNp@mont K-10 Catalyst [20]

Two grams of mont K-10 clay was added to a PdNp suspension and continuously stirred for 6 days. After that the mixture was filtered and washed several times with water and dried in air for 24 h to get the PdNp@mont K-10 catalyst.

4.4 Characterization of PdNp and PdNp@mont K-10 Catalyst

Prepared PdNp and PdNp@mont K-10 were characterized by high resolution TEM (HR-TEM), X-ray diffraction (XRD) and UV–Vis spectroscopy. TEM images were recorded on a JEOL/JEM- 2100 operating at 200 kV. XRD study was conducted on a Bruker AXS D8 advance diffractometer with Cu-Kα (λ = 1.541 A°) radiation. The surface area of the catalyst was determined using Brunauer–Emmett–Teller (BET) surface area analysis with nitrogen gas adsorption method (Quantachrome Instruments, Boynton Beach, FL). Amount of Pd on PdNp@mont K-10 catalyst was analyzed by ICP-AES on a thermo electron IRIS intrepid II XSP DUO. All products were characterized using ^{1}H NMR, ^{13}C NMR and mass spectroscopy. ^{1}H NMR and ^{13}C NMR spectra were recorded at room temperature with a Bruker Avance 400 MHz instrument.

4.5 General Procedure for Aerobic Alcohol Oxidation

The alcohol oxidation reaction was performed by taking 10 mg PdNp@mont K-10 catalyst, 1 mmol alcohol and 3 ml water in a 50 ml round bottom flask under aerobic condition. The mixture was stirred at room temperature up to the required time. The progress of the reaction was monitored by taking thin layer chromatography (TLC). After completion of the reaction, stirring was stopped and the catalyst was subjected to centrifugation and the residual solid after filtration was washed with water (4 ml) three times. To this filtrate 10 ml ether was added and extracted the product with ether. The resultant organic phases was dried over anhydrous Na_2SO_4, filtered and evaporated under reduced pressure. The residue was subjected to silica gel column chromatography (ethyl acetate–hexane, 2:8) to obtain the desired products.

4.6 Recycling Test

Catalyst was isolated from the reaction mixture by simple centrifugation process after complete conversion and washed with ethyl acetate and water to remove the organic contaminants. After getting the solid part of catalyst, it was drying at 110 °C in an oven for whole night. Then catalyst was used for fresh oxidation reaction of 1-phenyl ethanol. Reaction conditions were kept similar to the other oxidation reactions.

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