Catalytic reduction of 4-nitrophenol to 4-aminophenol using an efficient Pd nanoparticles

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Abstract. Highly stable catalytically active polyvinyl alcohol supported Pd nanoparticles (Pd NPs) are synthesized and used as catalysts in reduction of 4-nitrophenol in aqueous phase by sodium borohydride as reducing agent. The as–synthesized Pd NPs are characterized with the help of UV–vis. absorption spectroscopy, X–ray diffraction (XRD), transmission electron microscopy (TEM). The TEM and high resolution TEM images reveal that the synthesized Pd NPs are mostly global shaped with mean radius of c.a. 2.1 nm. The progress of the reaction is conveniently monitored by UV–vis. spectroscopy. The rate constant of the pseudo–first–order reaction increases with temperature up to 318 K. The rate constant and the activation energy for the reduction of 4-nitrophenol by using Pd nanoparticles were found as 0.013 s⁻¹ and 14.12 kJ mol⁻¹ respectively at 318 K. The as-prepared Pd NPs are stable, easy to prepare, cost effective and have significant efficiency for reduction of 4-nitrophenol in green protocol.

1. Introduction
Metallic nanoparticles (NPs) especially noble metal nanoparticles (MNPs) have recently attracted considerable attention in the fields of fuel cells, sensors, catalysis etc. due to their unique properties compare to bulk materials [1]. Scientists were highly interested for this reason to fabricate catalysts involving MNPs for catalytic and electrocatalytic applications, in the last few decades [2]. The catalytic efficiency of the MNPs in heterogeneous catalytic reactions depends on the particle shape, dimension, morphology etc. As a result a universal model reaction is necessary to investigate the efficacy of metal and metallic oxide NPs in a heterogeneous catalytic environment. Recently, the hydrogenation reaction of 4-nitrophenol (4-NP) by NaBH₄ in aqueous media to 4-aminophenol (4-AP) have been used as a model reaction to study the efficacy of various metal and metal oxide nanocatalysts [3]. NPs of a variety of metals like Ni, Ag, Pt, Au, Ru, and Pd can be employed as catalysts for this reaction. For the synthesis of a large number of pesticides, herbicides, and synthetic dyes etc. 4-NP and its derivatives are obtained as by–products. Moreover, these are common hazardous organic pollutants in agricultural wastewaters. 4-NP has harmful effects on human health, since it damages the central nervous system, liver, kidney etc. Hence its removal from the environment is a crucial task. In contrary, 4-AP is a significant chemical intermediate in the preparation of antipyretic drugs such as paracetamol, dye stuffs, corrosion inhibitors etc. The important method for the removal of hazardous 4-NP and preparation of 4-AP is the direct hydrogenation of 4-NP catalyzed by Pt, Pd, Au, Ni etc. Although, Raney Ni has been used successfully for catalytic hydrogenation of nitro group, but one of the major drawback of its use is that it catalyzes the hydrogenation of both the nitro group and aromatic ring of 4-NP. J. Chen et al. have reported the hydrogenation of 4-NP catalysed by nitroreductase in presence of nicotinamide adenine dinucleotide under green protocol [4].
Furthermore, J. Chen et al. reported that 4-AP and 4-hydroxylaminophenol were found as the reductive products. Moreover, the catalytic performance of metal nanocatalysts largely depends on the morphologies of nanoparticles because of their extremely high surface energy. So, there is possibility of self-aggregation to minimise the extremely high surface energy especially in absence of stabilizer causing decrease in the catalytic performance of such nanocatalysts. For this reason, polymer matrix, dendrimers, metal organic frame works and micelle encapsulated metal nanoparticles have demonstrated excellent catalytic efficacy towards the reduction of 4-NP to 4-AP [5]. He and co-workers synthesized immobilized silver nanoparticles on leaky bio–scaffolds like a membrane of natural egg shell, at room temperature. Procyandine, a polyphenol was used as a reductant and a stabilizer during synthesis [6]. C. Na et al. prepared multifunctional and reusable carbon nanotube ponytails by integrating CNT’s into micrometer-sized colloidal particles. These carbon nanotube ponytails act as catalysts for the hydrogenation of 4-nitrophenol [7]. Ramaraj groups synthesized gold nanoparticles at room temperature and reduced with sodium citrate and NaBH₄. They were then supported on original gel of phloroglucinol carboxylic acid-formaldehyde gel [8]. This Au nanocatalyst exhibits good catalytic activity towards the reduction of 4-NP. Zero-valent Pd is a well-known catalyst and widely used in several reactions like C-C coupling reactions, hydrogenation reactions etc. [1]. In the present work, we have investigated the catalytic activity of polyvinyl alcohol (PVA) stabilized Pd nanoparticle, for the reduction of 4-NP to 4-AP with NaBH₄ in aqueous medium. The catalytic capability in terms of the rate constants and different thermodynamics parameters which are still relatively rare in literature, are fully discussed. Our as-synthesized PVA embedded Pd nanocatalyst appear to exhibit remarkable performance towards the reduction of 4-NP in aqueous medium.

2. Experimental Section

2.1. Materials

Palladium chloride (PdCl₂) was supplied from Arora-Matthey Limited, Millipore water (Synergy) was used throughout the experiment. 4-nitrophenol, NaBH₄ were purchased from sigma Aldrich, potassium chloride and polyvinyl alcohol (number average relative molar mass: 150000) were purchased from Merck. The all other materials were supplied from Merck, India.

2.2. Instrumental characterization

UV–visible spectra were captured using UV–1800 spectrophotometer (Shimadzu) (source lamp: deuterium (D2); tungsten-halogen). X-ray diffraction pattern was obtained by a Bruker D8 Advance diffractometer using Ni−filtered CuKα source of radiation (λ = 1.5418 Å) operating at 40 kV and 40 mA, using a scan rate of 0.2° / second. TEM and HRTEM measurements were obtained by H-7600 transmission electron microscope (Hitachi, Japan) instrument.

2.3. Synthesis of PVA embedded Palladium nanoparticles

For the synthesis of PVA embedded Pd NPs, initially 0.5 mL 0.056 (M) aqueous K₂PdCl₄ (2.81 × 10⁻⁵ mol) solution was added drop-wise into the solution of 24.5 mL 1% (W/V) polyvinyl alcohol in a 100 mL beaker under stirring. Then 1.07 mg of NaBH₄ was added to this solution and stirred for 30 min at room temperature (30 °C) [3]. The yellow colour of K₂PdCl₄ solution changed to greyish black, manifesting the formation of Pd(0) NPs [scheme S1 in Supporting Information].

2.4. Reduction of 4-nitrophenol by using palladium nanocatalyst

The catalytic hydrogenation of 4-nitrophenol by using sodium borohydride as reductant was carried out in a standard quartz cuvette by using as-synthesized Pd NPs as catalyst. For catalytic reduction of 4-NP 0.03 M aqueous solution of NaBH₄ was prepared in ice-cold water 10 min before of each set of kinetic study. About 2.14 mL of water, 0.5 mL of 8.0 × 10⁻⁴ M solution of 4-NP, and 0.35 mL of 0.03 M NaBH₄ were mixed in a standard quartz cuvette (path length = 1 cm). That led to a colour change immediately from pale yellow to bright yellow. To this reaction mixture 11 μL 1.127×10⁻³ M Pd NPs solution was added and the time-dependent UV–vis. absorption spectra were recorded at a temperature of 318 K. The background correction was performed with Millipore water as reference. The rate constants of the reduction reaction were determined at an ambient temperature by measuring
the decrease of absorbance of 4-nitrophenolate ion (at 400 nm) as a function of time. For evaluation of the thermodynamic data, the temperature was varied from 298 K to 318 K.

2.5. Calculation of rate constant

The kinetic parameters were analyzed by using pseudo first order kinetic equations. The absorbance of electromagnetic radiation of wavelength 400 nm ($\lambda_{\text{max}}$ of 4-nitrophenolate ion in aqueous media) was utilized to determine the concentration of 4-NP. The natural logarithm of the absorbance of 4-nitrophenolate at 400 nm was plotted against time, and the steepest part of the curve was fit with a line, the negative slope of this line was taken as the apparent rate constant ($k_{\text{app}}$).

3. Results and Discussions

The as-synthesized Pd nanoparticles exhibited typical UV–visible spectra of Pd. Surface Plasmon resonance band was completely absent and the peak for Pd$^{\text{II}}$–PVA complex disappears indicating complete reduction of Pd$^{\text{II}}$ to Pd(0) (Figure S1a in Supplementary Information). The X-ray diffractogram is shown in Figure S1b which depicts diffraction peaks at 20 values of 40.01°, 79.80° corresponding to the lattice planes (111) and (311) of face-centred cubic Pd [JCPDS No. 87-0637]. Moreover, the XRD profile shows a peak at 20 = 44.52° marked by (101) plane of hexagonal primitive lattices of graphite carbon [JCPDS Card No. 89-8487]. Morphological studies were performed by using TEM analysis of as-synthesized Pd nanocatalysts. Figure 1a depicts the TEM image of Pd NPs and corresponding histogram is shown in Fig 1b. Figure 1b clearly reveals that the average diameter of as-prepared Pd NPs is 4.2 nm. Figure 1a clearly indicates that the as-synthesized Pd materials are predominantly globular shaped having nano-dot structure revealing unique three-dimensional quantum confinement of electron.

Figure 1. TEM image of as-prepared Pd NPs (a), and their corresponding histogram (b), HR-TEM image (c), and SAED pattern (d).

The HR-TEM micrograph and the selected area electron diffraction pattern of the Pd nanodots are shown in Figs. 1c and 1d, respectively. Figure 1c exhibits the lattice spacing is about 0.232 nm which correspond to the (111) plane of face-centred cubic Pd. The SAED pattern is also revealed the (111) plane of Pd with the spacing of 0.232 nm (Figure 1d). Therefore, HR-TEM image and SAED pattern further confirmed the XRD results. To test the efficacy of as-synthesized Pd nanodots for catalytic conversion of 4-NP to 4-AP, NaBH$_4$ was chosen as reducing agent. The main advantage is that the absorbance of 4-nitrophenolate ion obtained from 4-NP in presence of NaBH$_4$, can be easily monitored by UV–vis. spectrophotometrically. Fig. 2a shows the successive decrease of absorbance with time at 400 nm ($\lambda_{\text{max}}$ of 4-nitrophenolate ion) with the concomitant evolution of a peak at 300 nm ($\lambda_{\text{max}}$ of 4-AP) at 318 K, clearly revealing the catalytic reduction of 4-NP to 4-AP. In all the experiments we used excess NaBH$_4$ so that the reduction of 4-NP in presence of Pd NPs was zero order with respect to NaBH$_4$ and first-order with respect to 4-NP. To describe the reaction kinetics quantitatively typical plot of ln($A_t/A_0$) versus the reaction time is shown in Fig. 2b, where $A_t$ and $A_0$ are the absorbance of 4-nitrophenolate ion at any time $t$, and at the initial stage respectively at about 400 nm. The linear
relationship between the $\ln \left( \frac{A_t}{A_0} \right)$ versus the reaction time suggests that the reduction of 4-NP follows pseudo-first-order kinetics. The apparent rate constant of the reduction of 4-NP in presence of Pd NPs, as calculated from the slope of a linear fit of $\ln \left( \frac{A_t}{A_0} \right)$ versus reaction time, is $1.3 \times 10^{-2} \, \text{s}^{-1}$ at 318 K. It demonstrates that the catalytic efficiency of as–prepared Pd NPs is significantly higher than other synthesized Pd NPs found in the literature. The catalytic reduction of 4-NP in presence of as–prepared Pd NPs was studied at different temperatures of 298 K, 308 K, 313 K, and 318 K to evaluate the activation energy ($E_a$) of the catalyst (Fig. 3a). Table T1 (in Supplementary Information) shows the value of rate constants for reaction of 4-NP at different temperatures.

Figure 2. (a) UV–visible spectra that monitor the time-bound reduction of 4-nitrophenol to 4-aminophenol over Pd NPs at 318 K, and (b) the corresponding plot of $\ln \left( \frac{A_t}{A_0} \right)$ against the reaction time at $\lambda_{\text{max}} = 400 \, \text{nm}$.

$$\ln \left( \frac{A_t}{A_0} \right) = -k \times t \quad (1)$$

$$\ln k = \ln A - \frac{E_a}{RT} \quad (2)$$

As depicted in Fig. 3a, the catalytic reduction of 4-NP by using as–prepared Pd NPs increases with an increase of the temperature. The $E_a$ obtained by linear fitting of $\ln k$ against $1/T$, (Fig. 3b) and by using Arrhenius equation (Eq 2).

Figure 3. (a) Plots of $\ln \left( \frac{A_t}{A_0} \right)$ versus reaction time at $\lambda_{\text{max}} = 400 \, \text{nm}$ at different temperatures, (b) plot of $\ln k$ versus $1/T$, and (c) plot of $\ln (k/T)$ versus $1/T$ for the hydrogenation of 4-NP by NaBH$_4$ with Pd NPs as catalyst.

Moreover, the calculated activation energy was 14.12 kJ mol$^{-1}$ which was much lower than that of several recently reported nanocatalysts. Table 1 depicts the comparison of the catalytic performance of as–synthesized Pd NPs in the reduction of 4-NP in aqueous medium with some catalysts presented in the literature. On the basis of above analysis, our synthesized Pd NPs exhibit excellent catalytic performance towards 4-nitrophenol reduction. The reusability of the Pd NPs was examined by catalyzing the reaction with the used catalyst for four times more. Figure S2 exhibits this recycling activity of the catalyst. It is found that the reaction is almost completed within 6 min for the 1st run but takes 10.4 min for the 4th run. In the study, the value the activation enthalpy ($\Delta H^\circ$) and activation entropy ($\Delta S^\circ$) for the reduction of 4-NP were determined by using Eyring equation. These are 11.6 kJ mol$^{-1}$ and $-0.25$ J mol$^{-1}$ respectively as obtained by Fig. 3c. The later supports the proposition that the adsorption of 4-nitrophenol is the rate determined step in Langmuir-Hinshelwood mechanism [9]. Initially, 4-NPs and the borohydride ions (BH$_4^-$) are adsorbed on the surface of Pd NPs, then by the
transfer of electron from the borohydride ions to the 4-NP via the metal surface converted it 4-AP, which then desorbed from the surface of Pd NPs. The slim size distribution of spherical Pd NPs with smaller dimensions, elevated surface region, and unique three-dimensional quantum confinement increase the diffusion of the reactant molecules and thus exhibit excellent catalytic activity towards 4-NP reduction reaction.

Table 1. Comparison of catalytic performances of various nanocatalysts for reduction of 4-NP in aqueous media.

| Entry | Catalysts | Average diameter (nm) | Rate constant (s⁻¹) at 25 °C | Activation energy (kJ mol⁻¹) | Ref. |
|-------|-----------|-----------------------|-------------------------------|-------------------------------|-----|
| 1     | Pd        | 4.2                   | 8.7×10⁻³                     | 14.12                         | This work |
| 2     | Au@[C4C16Im]Br | 10                   | 1.1×10⁻⁴                     | 99.4                          | [9] |
| 3     | Pt@Ag NPs | 185.47                | 5.9×10⁻³                     | –                             | [10] |
| 4     | Pd13-DENs | 1.33 ± 0.15           | –                             | 30.6                          | [5] |

4. Conclusions
In summary, PVA embedded stable Pd NPs with average diameter of 4.2 nm are easily prepared. The particles exhibit remarkable catalytic capability for catalytic conversion of 4-nitrophenol by NaBH₄ in aqueous media. It might be applicable in wastewater treatment. The low poly-disperse characteristic and large adsorbent area make the Pd NPs an efficient catalyst for the reduction of 4-nitrophenol. Our catalyst exhibits greater rate constant and lower activation energy than Au, Pt and Ag catalysts available in the literature.

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Supplementary Information

Catalytic reduction of 4-nitrophenol to 4-aminophenol using an efficient Pd nanoparticles

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Scheme S1. A schematic illustration of the synthesis of PVA embedded Pd NPs.

Supplementary Figures

Figure S1. (a) UV–visible absorption spectrum of ten times diluted aqueous solution Pd NPs. (b) the XRD pattern of Pd NPs (in presence of activated charcoal).
Figure S2. Reusability of Pd nanocatalysts for the hydrogenation of 4-NP at 45 °C in aqueous media.

Supplementary Table

Table T1. Influence of temperature in rate constants for catalytic reduction of 4-NP.

| Temperature (K) | $10^3 \times$ Rate constant (s$^{-1}$) |
|----------------|--------------------------------------|
| 298            | 8.7                                  |
| 308            | 10.6                                 |
| 313            | 11.8                                 |
| 318            | 12.5                                 |