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p(AA)-Pd nanoreactor as a green catalyst for selective aerobic oxidation of primary alcohols and reduction of nitrophenol

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ABSTRACT

Hydrogels are attracting increasing attention recently and are used as carrier systems for the in-situ synthesis of metal nanoparticles. The present study aims to createnanoreactor systems through the preparation of hydrogels based on poly (acrylic acid). Poly (acrylic acid), p(AA), hydrogels have been synthesized by radical polymerization in solution of AA as monomer, N,N′-Methylene bis acryl amide, (MBA), as cross linking agents and ammonium per-sulfate (APS) as initiator and N,N,N′,N′-tetramethylmethylenediamine (TEMED) as accelerator. The investigated hydrogels were characterized by Fourier transform infrared (FT-IR) spectroscopy and the porosity of hydrogels was determined by Scanning Electron Microscope (SEM). As the polymeric hydrogel matrices are inherently negatively charged, the metal salt of $PdCl_2$ was loaded into hydrogel matrices from the corresponding metal salt solution in ethanol. Pd nanoparticles are generated in situ inside related hydrogels by chemical reduction of the absorbed metal ions with a reducing agent such as sodium boron hydride ($NaBH_4$). P(AA)-Pd nanocomposites were characterized by transmission electron microscopy (TEM), thermal gravimetric analysis (TGA), X-Ray photo electron spectroscopy (XPS) and inductively coupled plasma atomic emission spectrometer (ICP). The catalytic activity of p(AA)-Pd catalyst was investigated in the aerobic oxidation of primary alcohols and reduction of nitro compounds by emphasizing the effect of different parameters such as temperature, catalyst amount, substituent effect, *etc*. The catalyst was easily recovered from the reaction media and it could be re-used for other three runs without significant loss of activity.

Keywords: Hydrogel; Green catalyst; O_2; H_2O

1. Introduction

Selective oxidation of primary alcohols to aldehydes and restricting their over oxidation to acids is an important problem in organic synthesis [1,2]. Many researchers have been recently focused on the development of new and efficient heterogeneous and recyclable catalysts to achieve the efficient oxidation of alcohols in green solvent, such as water, with molecular oxygen as an oxidant [3,4]. Recently, noble metal nanocatalysts, such as Au [5], Pd [6], Pt [7] and Rh [8], have stimulated great interest because they avoid using toxic oxidizing reagent and no by-product other than water is produced. Of all the noble metal nanocatalysts, palladium nanoparticles are favorable owing to their high catalytic efficiency [9]. However, palladium nanoparticles, similarly to other nanoparticles, have a tendency to aggregate and lose their important properties. To overcome this problem, metal nanoparticles are usually loaded or dispersed in a solid matrix, such as polymeric matrices like hydrogels [10], poly electrolyte brushes [11] and dendrimers [12], or inorganic oxides like silica [13], alumina [14], titania [15] and zeolite [16]. Amongst these, hydrogels are attracting increasing attention recently and are used as carrier systems for the in-situ synthesis of metal nanoparticles [17]. In fact, the swol-

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len hydrogels provide free space for nucleation and growth of noble metal nanoparticles [18]. In addition, among all the stabilizing systems, hydrogels are the most effective ones, particularly when stabilized metal nanoparticles are used as catalysts. For instance, the surface of the embedded metal nanoparticles within hydrogels, is not covered and for this reason catalytic activity is not affected by stabilization. Also, the swelling ability allows an easy and fast diffusion of reactants into the hydrogels and the speed of catalytic reaction can be tuned by controlling the cross linking density of polymeric networks.

Nitrophenol and its derivatives are important by-products produced from pesticides, herbicides and synthetic dyes [19–20]. 4-Nitrophenol (4-Np) can damage the kidney, central nervous system and liver. Thus its removal from the environment is a crucial task. The reduction of 4-Np is also necessary for the manufacture of analgesic, antipyretic and other drugs, in pharmaceutical industries [21]. In addition this reaction has been widely exploited for confirming the synthesis of efficient nanoparticle catalysts by the study of catalytic activities of nanoparticles [22].

In these regards, synthesis of Pd nanocatalyst embedded within the p(AA) hydrogel matrix's for aerobic alcohol oxidation and reduction of nitrophenol was studied. Synthesis of Pd nanoparticle within the p(AA) hydrogels was easily achieved just by adjusting reducing agents. The effects of various parameters on the oxidation/reduction reactions were studied. The high efficiency of encapsulated Pd nanoparticles for aerobic alcohol oxidation can be attributed to the highly-concentrated reactants and Pd nanocatalyst within the hydrogels and activated alcohol through strong hydrogen bonding between alcohol and the acrylic acid segment [23]. Finally, the reusability of the catalyst was also investigated for several times. The hydrogel/Pd composite catalyst systems were easily recovered and reused.

According to the best of our knowledge this is for the very first time that Pd is fabricated in p(AA) hydrogel. Also, no report exists in literature regarding the investigation of reduction of nitrophenol and oxidation of alcohols in the presence of O_2 as an oxidant in aqueous medium by poly (AA)-Pd composite.

2. Experimental

2.1. Materials and equipment

The monomer, acrylic acid (AA) (99%, Sigma Aldrich), the cross linker, N,N′-methylenebisacrylamide (MBA) (99%, Across), the initiator, ammonium persulfate (APS) (99%, Sigma Aldrich), and the accelerator N,N,N′,N′-tetramethylmethylenediamine (TEMED) (98% Across) were used in hydrogel preparation. Palladium (II) chloride (65% Merck) was used as metal ion source. Sodium borohydride ($NaBH_4$, 98%, Merck) was used in the reduction of metal ions to prepare metal nanoparticles. All the chemicals were used as received without further purification. FT-IR spectra of samples pelletized with KBr were recorded in KBr disks with a Bruker FT–IR spectrophotometer. The exact amount of the palladium in the composites was determined by ICP-AES, Spectro Genesis. The morphology of swollen p(AA), hydrogel was investigated with Scanning Electron Microscopy (SEM) via MIRA3 FEG SEM (Tescan, Czech Republic) and an accelerating voltage of 10 keV. The sample was swollen and quickly frozen in liquid nitrogen. The hydrogel was freeze-dried at –50ºC for 3 days to preserve its porous structure without any collapse. After that, the dried samples were deposited onto an aluminum stub and sputter-coated with gold for 60 s to enhance conductivity. Transmission electron micro copy (TEM, HITACHI S-4800) was used to determine the size of metal nanoparticles inside the hydrogel nanocomposites. To image the palladium nanoparticles, TEM analysis was performed on a JEM-2100 (JEOL). The swollen hydrogel was finely grounded with the help of a soft ball and the resulted hydrogel nanocomposite samples were dispersed in 1 mL of ethanol and dropped on collodion film coated copper grid for TEM analysis. The X-ray photo electron spectrum (XPS) was collected in a 1600E Perkin Elmer using Mg-Kα excitation sources. All the binding energy (BE) values were referenced to the C 1s line at 284.5 eV. The reaction products of oxidation were determined and analyzed using an HP Agilent 6890 gas chromatograph equipped with a HP-5 capillary column (phenyl methyl siloxane 30 m × 320 μm × 0.25 μm).

2.2. Preparation of hydrogels

Polymeric hydrogels were synthesized from AA via free radical polymerization reaction techniques in mild condition (40°C), as shown in Fig. 1, [24,25]. In the synthesis of p(AA) hydrogels, 5 mL AA (0.0725 mol), 0.055 g MBA (0.5%), and 10 μL TEMED were mixed with 4 mL pure water and to this solution a separately prepared APS solution of 0.165 g APS in 1 mL water (1 mol% of AA) was added and vortexed homogeneously. The mixture was placed into plastic straws (~4 mm in diameter), and these plastic straws were immersed in a 40°C water bath controlled by a thermostat for 4 h to complete polymerization and cross linking. Finally, the obtained 3-D hydrogels were cut in equal shapes and washed with approximately of 2000 mL of water for 24 h. The wash water replenished every 2 h to remove un-reacted species (monomer, cross linker, accelerator, and initiator). After the cleaning procedure, hydrogels were dried in an oven to a constant weight at 40°C and kept in sealed containers for further use.

Selected FT-IR (KBr, cm^{-1}): (p(AA)): 3530 (br, strong), 2935 m), 2865 (w), 1739 (vs), 1558 (m), 1462 (s), 1419 (m), 1257 (m), 1172 (s), 1118 (w), 937 (w), 805 (m), 642 (w), 491 (w).

2.3. In situ synthesis of metal nanoparticles within p(AA) hydrogel

For in situ fabrication of metal nanoparticles within p(AA) hydrogel, first palladium ions were loaded into hydrogel networks by dispersing 0.1 g of the dried p(AA) hydrogel into 500 ppm aqueous solution of $PdCl_2$ (50 mL) for 24 h at room temperature under continuous stirring. Pd(II) ions loaded on hydrogels were washed with DI to remove unbound metal ions. Then, to reduce metal ions within hydrogel networks, metal ions loaded on hydrogels were treated with 0.1 M $NaBH_4$ (50 mL). Finally, the prepared p(AA)–Pd hydrogel composites were filtered, washed with DI water and used for characterization and as catalyst. The amounts of metal nanoparticles entrapped in p(AA) hydrogels were calculated by ICP measurements after dissolution of metal nanoparti-

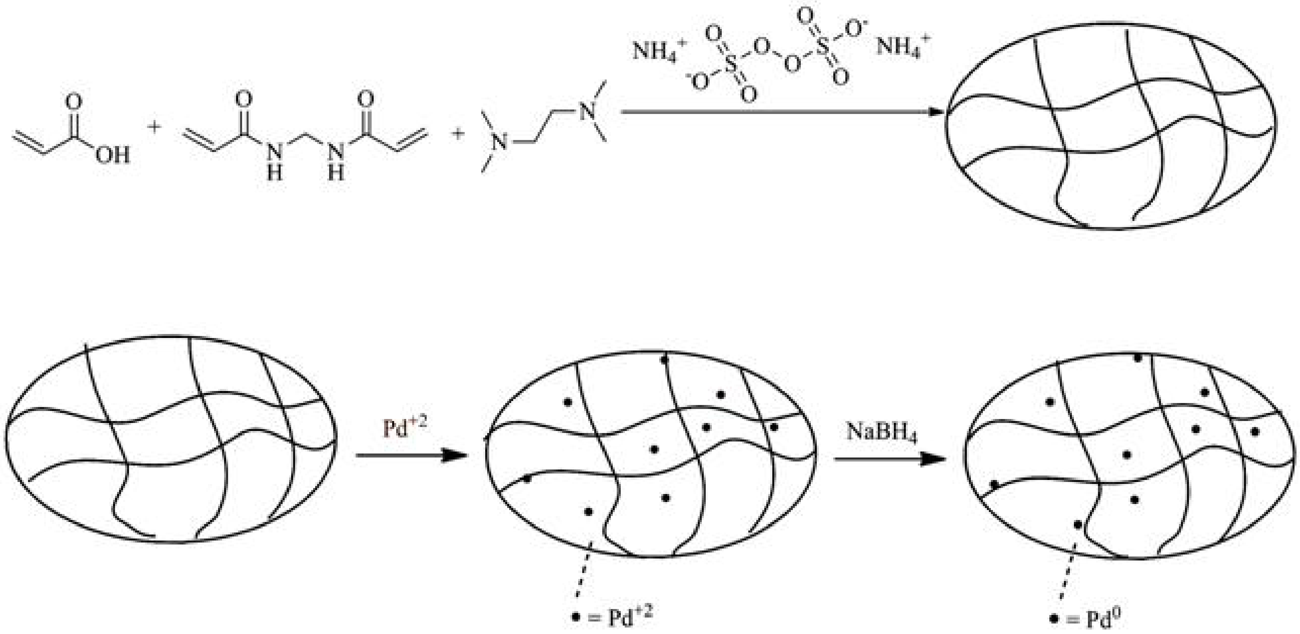


Fig. 1. Schematic presentation of p(AA) synthesis and preparation of metal nanoparticle within p(AA) hydrogel.

cles embedded within p(AA) hydrogel by treating with 5 M HCl aqueous solution.

2.4. Determination of the amount of metal nanoparticle within p(AA)-Pd composites

The amount of metal nanoparticle within p(AA) was determined by inductively coupled plasma atomic emission spectrometer (ICP) (Spectro Genesis) using the metal ion solution obtained by treating p(AA)-Pd composites with 5 M 30 mL HCl three times for 8 h to dissolve the metal nanoparticle in the p(AA)-Pd composites.

2.5. General oxidation procedure

A mixture of p(AA)-Pd hydrogel-composites in water (3.0 mL) was placed into a two-necked flask equipped with a magnetic stirrer. The flask was evacuated and refilled with pure oxygen (balloon filled). Then the benzyl alcohol (0.108 g, 1.0 mmol) was added into the solution with a syringe. The mixture was heated to reach the set temperature under O_2 atmosphere for 24 h. Then the solution was introduced to continue the reaction in the stable temperature. The resulting mixture was vigorously stirred at 60°C under O_2 atmosphere for 24 h. After the reaction, the catalyst was de-swelled in MeOH (2.0 mL) for 24 h. Then the organic phase was combined and removed the solvent and analyzed immediately by GC. The oxidation products were identified by comparing the retention times with the literature data. For the blank test with the bare hydrogel without Pd, the oxidation reaction of benzyl alcohol was accomplished with p(AA).

To test the reusability of the p(AA)-Pd composites, after every usage, the catalyst systems were separated from reaction mixture by filtration, washed with DI water and reused in the same reaction conditions again.

2.6. General reduction procedure

Catalytic activity of p(AA)-Pd composites was studied for the catalytic reduction of 4-NP. 0.01 M solution of 4-NP was prepared and into 50 mL of this solution 0.35 M of $NaBH_4$ was added and stirred at 250 rpm. Certain amount of hydrogel composite was added as a catalyst into this mixture. About 0.3 mL sample was taken out from reaction mixture at different time intervals and diluted up to 15 times. Then the progress of the reduction reaction was observed by measuring the absorption maxima at 400 nm by UV-Visible spectrophotometer (Shimadzu 1601). Reduction rate constant was calculated by measuring the decrease in intensity of absorption peak at 400 nm. To study the effect of temperature on the rate of reduction of 4-NP, the reduction was carried out at three different temperatures; 30°C, 50°C and 70°C keeping the amount of reactants and catalyst constant. Also the effect of amount of catalyst was investigated on the reduction of 4-NP. For this, different amounts of catalysts were used and other reaction conditions were kept constant. To evaluate the reusability of catalysts, after first cycle the catalysts were separated from reaction medium by filtration, washed with DI water and used again for the reduction of 4-NP under the same conditions till fourth cycle.

3. Results and discussion

3.1. Synthesis and characterization

The FT-IR spectra of AA and p(AA) hydrogels are presented in Figs. 2a and b, respectively. Fig. 2a indicates the O–H stretching band in 3530 cm^{-1} region and the C–H stretching at 2935 and 2865 cm^{-1} regions, respectively [26]. Also the bands at 1739 and 1462 cm^{-1} are assigned to C=O and COO$^-$ stretching band of acrylic acid, respectively [27]. In addition, the NH band of MBA is overlapped by OH band at about 3200 cm^{-1} [28] so the related band is disordered.

Scanning electron microscopy technique was used to analyze the morphology of hydrogel. The SEM image of p(AA), shown in Fig. 3, indicates the formation of homogeneous and highly porous material.

To determine the thermal properties and the amount of metal nanoparticles entrapped inside the hydrogel networks, thermal gravimetric analysis (TGA) was performed for pure and composite hydrogels. Fig. 4 shows TGA curves of bare p(AA) (Fig. 4a), and p(AA)–Pd composites (Fig. 4b). It could be seen clearly that there were two processes of weight loss for all samples when heating up the temperature. The first stage at less than 250°C was due to the release of the physically absorbed water. The second as a major weight loss in the range of 250–800°C was obtained from the decomposition of p(AA). p(AA) was thermally decomposed completely with a negligible carbon residue at 800°C. These results indicate that the amount of metallic palladium nanoparticles in the synthesized p(AA)–Pd was found to be 17.6 wt%. The amount of metal ion within the hydrogel was determined, also, by using ICP after dissolution by HCl treatment and it was to be 1.45 mmol Pd/g hydrogel.

To investigate the nanostructure of the sample, TEM measurement was carried out. The TEM images of metal nanoparticles-containing p(AA) hydrogels are given in Fig. 5. As can be seen, metal nanoparticles with a uniform spherical shape, about <50 nm, are distributed within p(AA) hydrogel matrices.

To gain further insight into the ionic state of the nanoparticles, XPS measurements were performed. A high-resolution Pd 3d X-ray photo electron spectrum of the palladium nanoparticles is shown in Fig. 6. The XPS data of p(AA)-Pd shows a dominating Pd^0 due to two significant binding energies of the Pd 3d$_{5/2}$ and 3d$_{3/2}$electrons at 336.3 and 341.6 eV [29–31].

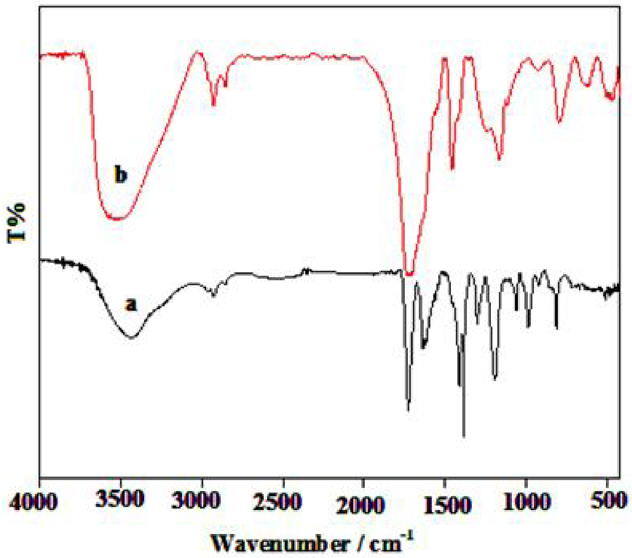


Fig. 2. FTIR spectra of a) acrylic acid, b) p(acrylic acid) hydrogel.

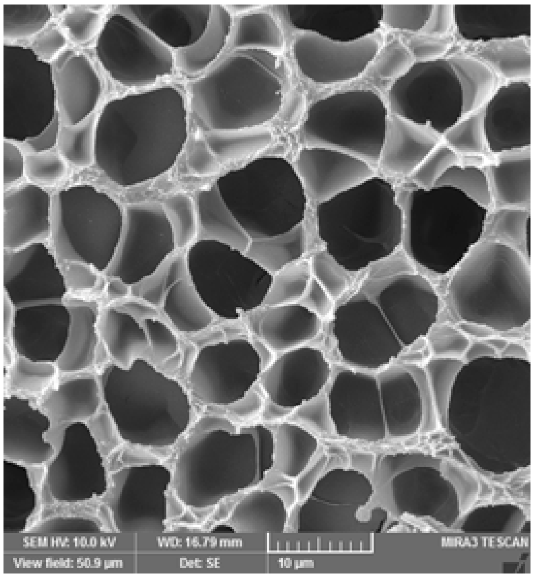


Fig. 3. SEM images of p(AA) hydrogel.

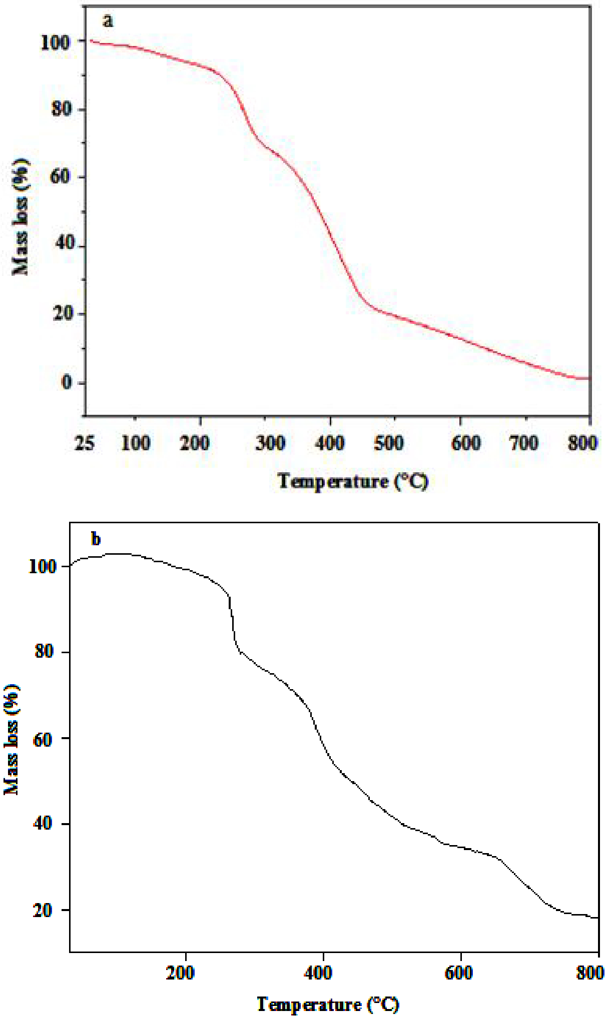


Fig. 4. TGA thermogrames of a) bare p(AA) hydrogel, b) p(AA)-Pd composite.

Fig. 5. TEM images of metal nanoparticles from p(AA)-Pd (white spots can be considered as Pd nanoparticles).

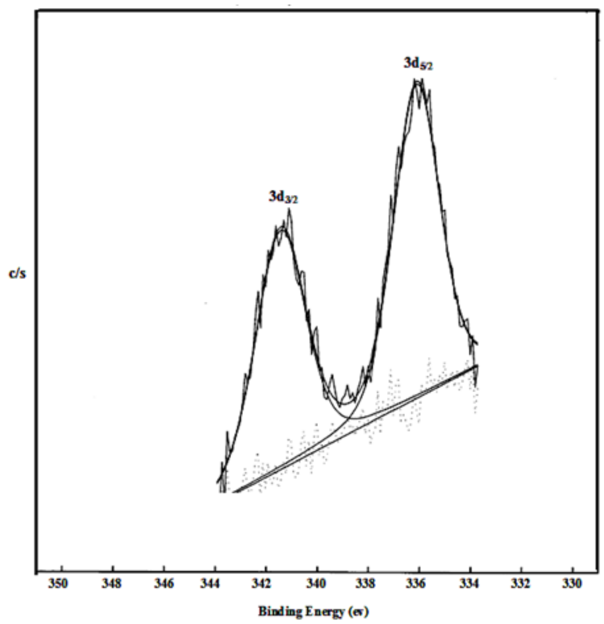


Fig. 6. Palladium 3d XPS spectrum of the palladium–polymer composite.

3.2. The catalytic activity of p(AA)-Pd toward the oxidation reaction of alcohols

The selective oxidation of alcohols, especially employing oxygen as the terminal oxidant, is one of the most important reactions in organic synthesis [32].

With the p(AA)-Pd catalysts in hand, we evaluated their catalytic activity for the aerobic oxidation of alcohols by using water as a green solvent at 60°C, and some results are summarized in Table 1. Initially, the oxidation reaction of the benzyl alcohol as the model substrate was selected, and was carried out in water at 60°C. The blank experiment without Pd loading exhibits a negligible benzyl alcohol conversion (<5% at 60°C and 24 h reaction time). However, in the presence of the Pd catalyst, benzyl alcohol conversion increases. Within 24 h and with 0.011 mmol Pd, 18% isolated yield of the benzaldehyde was obtained and the selectivity was more than 99 % (Table 1, entry 1). In another reaction, 0.022 mmol Pd was used with increased yield to 86% (Table 1, entry 2). Therefore, the optimized amount of catalyst was determined to be 0.022 mmol Pd for model reaction.

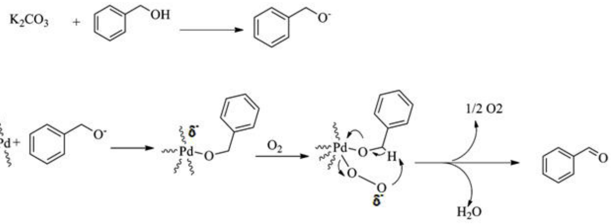


Fig. 7. Plausible pathways for the oxidation of alcohols in the presence of p(AA)-Pd.

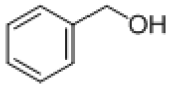
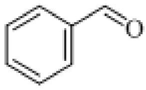
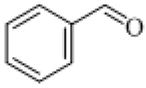
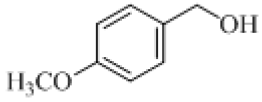
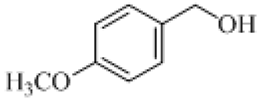
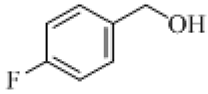
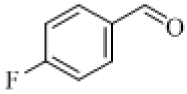
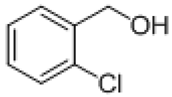
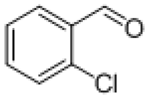
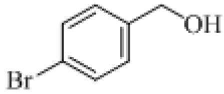
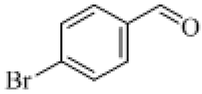
To establish the scope for the activity of p(AA)-Pd, this study was further extended to the catalytic oxidation of other primary benzyl alcohols with substituent such as 4-MeO, 4-F, 4-Br and 2-Cl groups (Table 1, entries 3–6). No carboxylic acids or esters were observed for all substrates investigated. The substitution effect on aromatic substrates was studied as shown in Table 1.

Primary benzylic alcohols with electron-donating substituent, such as *p*-methoxybenzyl alcohol, were converted to *p*-anisaldehyde in excellent yield. The conversion of alcohols, increased in the presence of electron-donating substituent, such as –OMe at the *para* position of benzyl alcohol, (Table 1, entry 3), but in contrary, withdrawing groups, such as –F, Cl and –Br, (Table 1, entries 4, 5 and 6) decreased the conversion [33]. This trend is in agreement with Hammett plot results [34]. In addition, the oxidation of 2-substitute benzyl alcohol was obtained in a moderate yield (Table 1, entry 5), which may be attributed to the steric hindrance by the surface of the palladium sites [35].

A hypothesis of the possible mechanism of catalytic oxidation of alcohols by p(AA)-Pd is presented in Fig. 2. Deprotonation of alcohol was promoted by K_2CO_3 to from alkoxide on the Pd surfaces. Pd catalyzes the β-hydride elimination to produce corresponding aldehyde along with the formation of O_2 and H_2O.

The reusability of p(AA)–Pd catalyst systems was studied by using the same catalyst in benzyl alcohol oxidation repeatedly up to three times. After every use, the catalysts were filtered and washed with DI water, and used again for the same reaction under the same reaction conditions. The results for benzyl alcohol oxidation by p(AA)–Pd are illustrated in Table 2.

Table 1
Catalytic activity of p(AA)-Pd on benzyl alcohol oxidation[a]

Entry	Substrate	Catalyst amount (mmol Pd)	Conversion [b] (%)	Product	Benzaldehyde Selectivity (%)
1		0.011	18		>99
2		0.022	86		>99
3		0.022	93.5		>99
4		0.022	70		>99
5		0.022	19.4		>99
6		0.022	75		>99

[a] Catalyst (p(AA)-Pd), substrate (1.0 mmol), H_2O, (3 mL) as solvent, K_2CO_3 1.2 mmol, temperature 60ºC, Time = 24 h under O_2 atmosphere
[b] Conversions are based on the starting substrate.

Table 2
Effect of catalyst recycling on benzyl alcohol oxidation [a]

Number of cycle	Conversion (%)	Benzaldehyde selectivity (%)
Fresh	86	>99
1	84	>99
2	87	>99
3	85	>99

[a] Catalyst (p(AA)-Pd), substrate (1.0 mmol), H_2O, (3 mL) as solvent, K_2CO_3 1.2 mmol, temperature 60ºC, Time = 24 h under O_2 atmosphere.

3.3. The catalytic activity of p(AA)-Pd toward the reduction reaction of nitro phenol

Catalytic activity of the prepared p(AA)–Pd composites was investigated for reduction of 4-NP.

Nitro compound reduction reactions were selected because of their importance in the environments, and in the number of manufacturing of various pharmacology products, dye and pigment industries [36]. According to thermodynamic studies, the reduction of nitro compounds is possible in the presence of excess amounts of aqueous solution of $NaBH_4$, as reducing agent, with large kinetic barrier [37]. Fortunately, the presence of a catalyst helps to overcome this energy barrier and makes these reactions feasible under mild conditions such as room temperature.

In all the catalytic reduction of nitro aromatic compounds, 0.022 mmol of hydrogel–Pd composites were used as catalyst.

Reduction of nitro compounds was tracked by measuring the decrease in their absorbance peak in UV-Vis spectra taken at various intervals of times. Only a small amount of 4-NP was reduced in the absence of catalyst even after 3 h as shown in Fig. 8. But after the addition of catalyst almost all of the 4-NP present in the reaction mixture was reduced within 8 min as demonstrated in Fig. 9.

In order to evaluate the effect of temperature on the catalytic activity of p(AA)–Pd composites, the reduction of 4-NP was investigated at three different temperatures; 30°C, 50°C, 70°C keeping the amount of reactant and catalyst constant.

Since the reduction was performed in the excess amount of $NaBH_4$, as reducing agent, the reactions supposed as pseudo first order and values of k_{app} were calculated by plotting $ln(C_t/C_0)$ *vs*. time as shown in Fig. 10. Where C_0 is the initial concentration of 4-NP and C_t is the concentration of 4-NP at different time intervals during the reduction reaction. As presented in Fig. 10, a good linear pattern of plots of $ln(C_t/C_0)$ *vs* time for the reduction of 4-NP catalyzed by p(AA)–Pd composites was observed. Such a linear correlation not only confirms that these reactions follow pseudo first order kinetics but also demonstrates the homogeneous distribution of Pd MNPs within p(AA) hydrogels. The reduction rates were increased linearly as temperature rise. Because at higher temperature, rate of diffusion of reactant molecules into hydrogel composites and collision

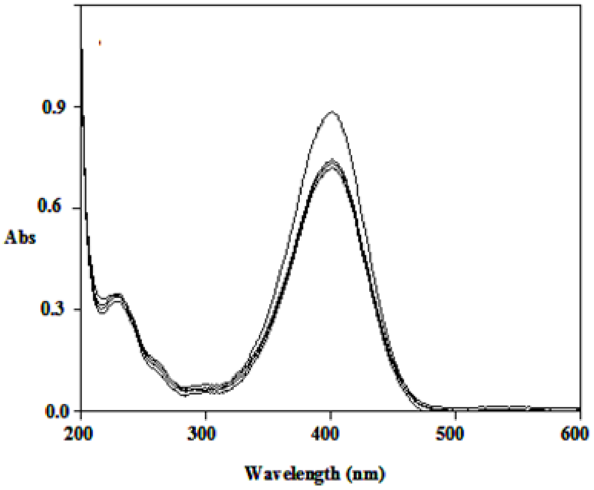


Fig. 8. UV-Visible spectra of 4-NP in the absence of catalyst and presence of $NaBH_4$. Reaction conditions; 0.01 M 4-NP 50 mL, $NaBH_4$ = 0.35 M, catalyst = non, 30°C.

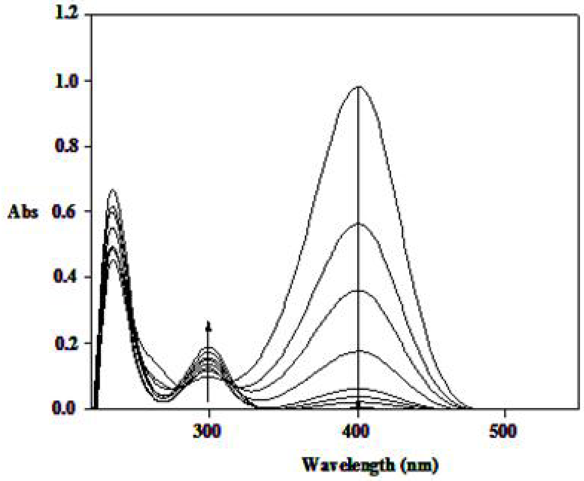


Fig. 9. UV-Visible spectra for the reduction of 4-NP catalyzed by p(AA)-Pd composite and $NaBH_4$. Reaction conditions; 0.01 M 4-NP 50 mL, $NaBH_4$ = 0.35 M, catalyst = 0.022 mmol, 30°C.

frequency of reactant and catalyst increase due to enhance in the average kinetic energy of molecules.

Activation parameters can be calculated from the data obtained by the reduction reactions carried out at different temperatures catalyzed by p(AA)-Pd composite. Energy of activation (E_a) was calculated from Arrhenius equation which is given below

$$\ln k = \ln A - (E_a / RT) \tag{1}$$

According the Arrhenius equation, ln k_{app} was plotted against *1/T*, as shown in Fig. 11, E_a was calculated from the slope of this plot and found to be 17.50 kJ mol^{-1}. The activation enthalpy ($\Delta H_{\#}$) and entropy ($\Delta S_{\#}$) were calculated by using Eyring equations [Eq. (2)].

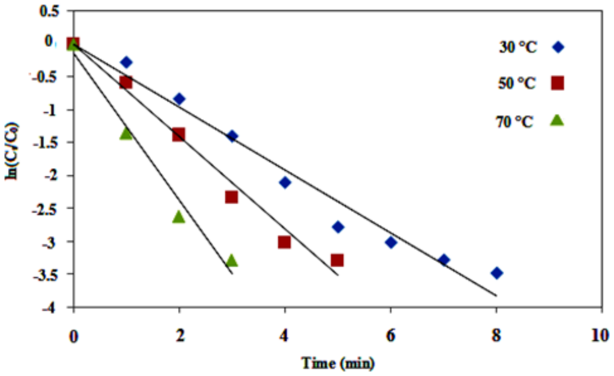


Fig. 10. The determination of apparent rate constants (k_{app}) for the reduction 4-NP catalyzed by p(AA)–Pd composites with temperature.

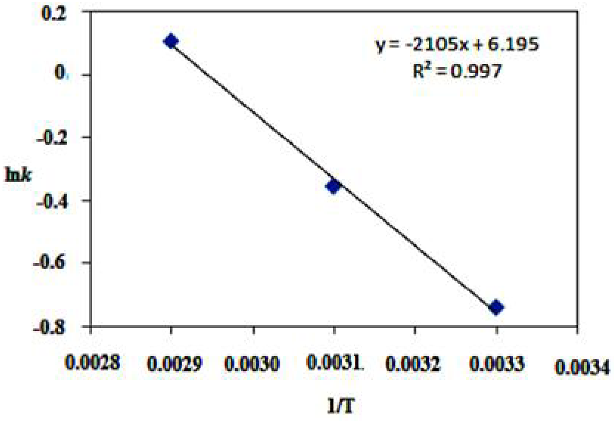


Fig. 11. The determination of apparent rate constants (k_{app}) for the reduction 4-NP catalyzed by p(AA)–Pd with temperature.

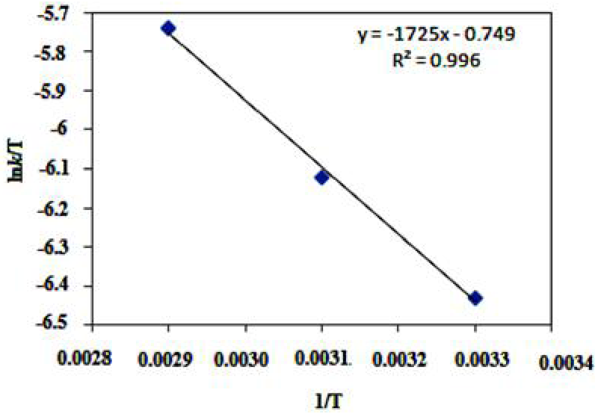


Fig. 12. Plot of ln(k_{app} /T) vs. 1/T for the reduction 4-NP catalyzed by p(AA)–Pd with temperature.

$$\ln k / T = \ln(kB / h) + \Delta S^{\#} / R - \Delta H^{\#} / R(1 / T) \tag{2}$$

According to Eyring equation, ln k_{app}/T was plotted against *1/T*, as shown in Fig. 12. The value of $\Delta H_{\#}$ was calculated from the slope of this plot and was found to be 14.34 kJ mol^{-1}. The positive value of $\Delta H_{\#}$ shows that the formation of an activated complex in the reduction of 4-NP is an endothermic process [39]. The value of $\Delta S_{\#}$ was calculated from the intercept of plot of $\ln(k_{app}/T)$ *vs.* $1/T$ and was found as –203.75 J mol^{-1} K^{-1}.The negative value of $\Delta S_{\#}$ shows that the reduction of 4-NP is entropically unfavorable which can be made favorable by adding catalyst [38].

The effect of catalyst amount on the reduction rate of 4-NP was also investigated. The reaction was studied at three different amounts of catalyst *viz*. 0.011, 0.022, 0.044 mmol. As shown in Fig. 13, with an increase in catalyst amount, the increase in rate of reaction was observed, as expected. As with the increase in amount of catalysts, the available catalytic sites are also increased. The presence of larger catalytic sites in the reaction mixture increases the effective collision frequency, and hence the rate of reaction is also increased.

The recyclability of p(AA)-Pd was investigated in several runs of the reduction reaction of 4-NP. At the end of the reaction, the p(AA)-Pd catalyst systems were separated and their activity in the next runs was investigated. The catalytic activity of p(AA)-Pd is preserved even after 4 runs. After every use, the catalysts were filtered and washed with DI, and used again for the same reaction under the same reaction conditions. The percent activity and conversion for 4-NP reduction by p(AA)–Pd are illustrated in Fig. 14. Activity was calculated by taking ratio of reduction rate of every successive reaction to the initial reduction rate, and as illustrated from Fig. 11, 100% conversion of 4-NP was observed after 4th use of Pdnanocatalyst system. However, 4% loss in the activity of p(AA)–Pd catalyst was observed at the end of four consecutive use.

4. Conclusions

It was demonstrated here that a facile preparation of p(AA) hydrogels via radical polymerization was accomplished. The p(AA) hydrogels were then used as templates for *in situ* synthesis of Pd nanoparticles to prepare p(AA)-Pd composites. The prepared composites were found to be very effective catalysts toward oxidation reaction of benzyl alcohols and reduction of nitrophenol under green conditions such as easy separation of the catalyst, using water as solvent and relatively low temperature. These organic inorganic hybrid hydrogels were found to be efficient and reusable catalysts in oxidation reactions of primary benzyl alcohols in good to excellent yields.

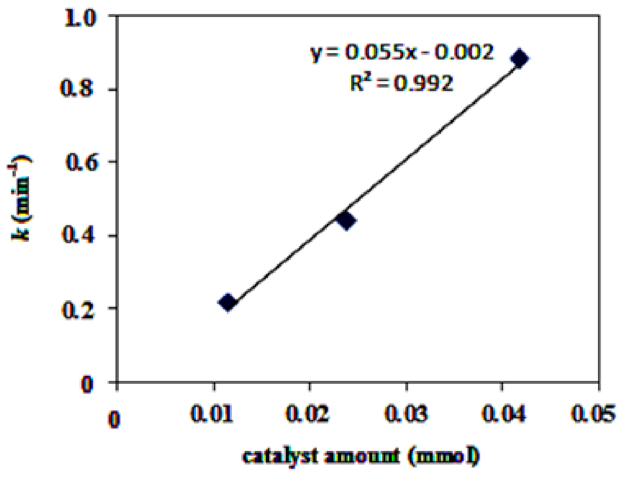


Fig. 13. The change in reduction rate constant of 4-NP with the amount of Pd catalyst inside p(AA)–Pd composites.

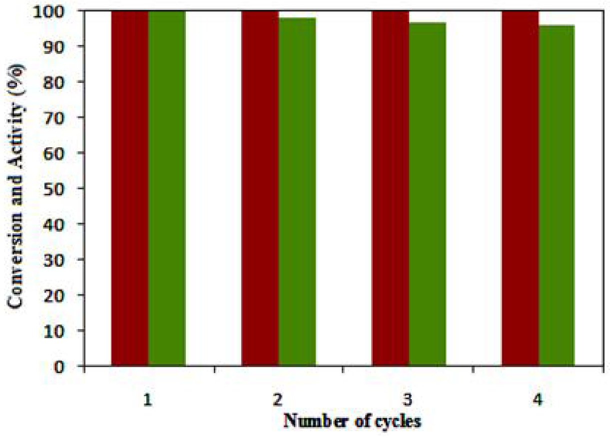


Fig. 14. The change in conversion (red column) and activity (green column) of p(AA)–Pd catalyst systems with repetitive usage in 4-NP reduction. [30 °C, 0.01 M 4-NP = 50 mL, [NaBH$_4$] = 0.35 M, catalyst = 0.022 mmol].

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