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#### WILEY Applied Organometallic Chemistry

# Ag-nanoparticle embedded p(AA) hydrogel as an efficient green heterogeneous Nano-catalyst for oxidation and reduction of organic compounds

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Massomeh Ghorbanloo, Department of Chemistry, Faculty of Science, University of Zanjan, 45371-38791 Zanjan, Iran. Email: m\_ghorbanloo@yahoo.com P(AA)-Ag heterogeneous catalyst system comprised of Ag nanoparticles embedded within hydrogel matrices has been described for the selective aerobic oxidation of alcohols and reduction of nitro phenols in water. P(AA)-Ag nanocomposite was characterized by Fourier transform infrared (FT-IR), scanning electron microscopy (SEM), transmission electron microscopy (TEM), thermal gravimetric analysis (TGA), X-Ray photoelectron spectroscopy (XPS) and inductively coupled plasma atomic emission spectrometer (ICP). Catalytic activity of p(AA)-Ag 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 medium and it could be re-used for other three runs without significant loss of activity.

#### KEYWORDS

green nano- catalyst, nitro phenols, oxidation, primary alcohols, reduction

# **1 | INTRODUCTION**

Silver nanoparticles, NPs, are versatile building blocks with strong surface plasmon resonance, high electrical, optical and high surface-to-volume ratio<sup>[1,2]</sup> that makes them an interesting subject in electronics,<sup>[3]</sup> surface enhanced Raman spectroscopy,<sup>[4]</sup> sensing,<sup>[5]</sup> and catalysis.<sup>[6]</sup> However, the aggregation of these nanoparticles due to their high surface charge and surface to volume ratio, decreases their surface area,<sup>[7]</sup> which results in a decrease in their catalytic activity.<sup>[8]</sup> To overcome this problem, silver NPs are usually loaded or dispersed in a solid matrix, such as polymeric matrices e.g. hydrogels,<sup>[9]</sup> polyelectrolyte brushes,<sup>[10]</sup> and dendrimers,<sup>[11]</sup> or inorganic oxides e.g. silica,<sup>[12]</sup> alumina,<sup>[13]</sup> titania<sup>[14]</sup> and zeolite.<sup>[15]</sup> The catalytic activity of silver nanoparticles is shown to be dependent on their size, content and the interaction between the Ag NPs and the matrix.<sup>[16]</sup> For example, the catalytic activity of Ag NPs dispersed in zeolite matrix is lower compared to the other media, because of the ineffective interaction between Ag NPs and zeolite, which prevents efficient disperse and stabilization of Ag NPs in the matrix. In contrast to the zeloits, the polymer matrixes have the ability to tune the guest-host interaction in order to provide welldefined spatial distribution. The well-defined spatial distribution provides kinetic stability for metal nanoparticles, as well as excellent mechanical properties for the composites. 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 metal nanoparticles is not covered and for this reason catalytic activity is not affected by stabilization. Or the speed of catalytic reaction can be tuned by controlling the crosslinking density of polymeric network. These composites were further used as catalysts for oxidation of alcohols and reduction of nitrophenols.

Nitrophenol and its derivatives are important by-products produced from pesticides, herbicides and synthetic dyes.<sup>[17,18]</sup> 4-Nitrophenol (4-NP) can damage the kidney,

central nervous system and liver. Thus removal of NP from the environment is important reaction. The reduction of 4-NP is also necessary for the manufacture of analgesic, antipyretic and other drugs, in pharmaceutical industries.<sup>[19]</sup> In addition this reaction has been widely exploited for confirming the synthesis of efficient nanoparticle catalyst by the study of catalytic activities of nanoparticles.<sup>[20]</sup>

The selective oxidation of alcohols to the corresponding carbonyl compounds has been comprehensively studied, due to their importance in production of fine chemicals and intermediates.<sup>[21,22]</sup> As a result of the ever-growing concerns over green chemistry and chemical processes, many efforts have been made to develop new catalytic protocols for the oxidation of alcohols, especially with O<sub>2</sub> as oxidant, in water as green solvent.<sup>[23]</sup>

In these regards, we prepared poly(acrylic acid) (p(AA)) hydrogel and used it as reactor as well as stabilizers for the synthesis of silver metal nanoparticles. The catalytic activity of the prepared p(AA)-Ag composite was investigated for the reduction of 4-NP and oxidation of alcohols. The effect of different parameters on the reduction and oxidation reactions were studied. In addition, the reusability of the catalyst was also investigated for four consecutive cycles. According to the best of our knowledge this is for the very first time that Ag is fabricated in p(AA) hydrogel. Also, no report exists in literature regarding the investigation of oxidation of alcohols in the presence of  $O_2$  as an oxidant and reduction of nitrophenol in the presence of NaBH<sub>4</sub> as reducing agent in aqueous medium by poly(AA)-Ag composite.

### 2 | EXPERIMENTAL

### 2.1 | General considerations

The monomer, acrylic acid (AA) (99%, Sigma Aldrich), the crosslinker, N,N'-methylenebisacrylamide (MBA) (99%, Across), the initiators, ammonium persulfate (APS) (99%, Sigma Aldrich) and the accelerator N,N,N',N'-tetramethylmethylenediamine (TEMED) (98% Across) were used in hydrogel preparation. Ag(CH<sub>3</sub>COO) (Merck) was used as metal ion source. Sodium borohydride (NaBH<sub>4</sub>, 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 were recorded in KBr disks with a Bruker FT-IR spectrophotometer. The exact amount of the silver in the composites was determined by ICP-AES, Spectro Genesis. 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 -50 °C for 3 days to preserve their 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 microcopy (TEM, HITACHI S-4800) was used to find out the size of metal nanoparticles inside the hydrogel nanocomposites. To image the silver nano particles, 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. Thermogravimetric analysis (TGA) was performed on an STA409PC Netzsch thermal analyzer and BÄHR-Thermoanalse GmbH-Type TAS03, Germany in flowing N<sub>2</sub> (60 mL min<sup>-1</sup>) at a heating rate of 10 °C min<sup>-1</sup>. The X-ray photoelectron spectrum (XPS) was collected in a 1600E Perkin Elmer using Mg-Ka excitation sources. All the binding energy (BE) values were referenced to the C 1 s 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  $\times$  320 µm  $\times$  0.25 µm).

### 2.2 | Preparation of hydrogels

Polymeric hydrogel was synthesized from AA via free radical polymerization reaction techniques in mild condition (40 °C), as shown in Scheme 1.<sup>[24,25]</sup> 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 vortexes 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 crosslinking. Finally, the obtained 3-D hydrogels were cut in equal shapes, washed with approximately of 2000 ml of water for 24 h. The wash water replenished every 2 h to remove un-reacted species (monomer, crosslinker, 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<sup>-1</sup>): (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 silver ions were loaded into hydrogel



SCHEME 1 Schematic presentation of p(AA) synthesis and preparation of metal nanoparticle within p(AA) hydrogels

network by dispersing 0.1 g of the dried p(AA) hydrogel in 50 ml, 500 ppm aqueous solution of silver acetate for 24 h at room temperature under continuous stirring. Ag(I) ions loaded hydrogels were washed with DI to remove unbound metal ions. Then, to reduced metal ions within hydrogel network, metal ions loaded hydrogels were treated with 50 ml, 0.1 M NaBH<sub>4</sub>. Finally, the prepared p(AA)–Ag hydrogel composites were filtered, washed with DI and used for characterization, as shown in Scheme 1 and Figure 1-a,b and c. The amounts of metal nanoparticles entrapped in hydrogels were calculated by ICP measurements after dissolution of metal nanoparticles embedded within p(AA) hydrogel by treating with 5 M HCl aqueous solution.

#### 2.4 | General oxidation procedure

A mixture of p(AA)-Ag (0.036 mmol Ag) in water (5.0 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) and K<sub>2</sub>CO<sub>3</sub> (0.166 g, 1.2 mmol) was added into the solution with a syringe. The mixture was heated to reach the set temperature under O2 atmosphere for 24 h. Then the solution was introduced to continue the reaction in the stable temperature. The resulting mixture was vigorously stirred at 80 °C under O<sub>2</sub> 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, the oxidation reaction of benzyl alcohol was accomplished with bare p(AA).

To test the reusability of the p(AA)-Ag composite, after every usage, the catalyst was separated from reaction mixture by filtration, washed with DI and reused in the same reaction conditions again. All the experiments were repeated at least three times and there average values are given with standard deviations.

#### 2.5 | General reduction procedure

Catalytic activity of p(AA)-Ag 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<sub>4</sub> 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; 25 °C, 40 °C and 60 °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. All the experiments were repeated at least three times and there average values are given with standard deviations.



**FIGURE 1** The digital camera images of a) bare p(AA), b) p(AA)-Ag<sup>+</sup>, c) p(AA)-Ag<sup>0</sup>, d) FTIR spectra of acrylic acid, e) FTIR spectra of p(acrylic acid) hydrogel, f) SEM images of p(AA) hydrogel

## **3** | **RESULTS AND DISCUSSION**

#### **3.1** | Synthesis and characterization

The FT-IR spectra of AA and p(AA) hydrogel are presented in Figure 1-d and e, respectively. Figure 2-a indicates the O–H stretching band in 3530 cm<sup>-1</sup> region and the C–H stretching at 2935 and 2865 cm<sup>-1</sup> regions, respectively.<sup>[26]</sup> Also the bands at 1739 and 1462 cm<sup>-1</sup> are assigned to C = O and COO<sup>-</sup> stretching band of acrylic acid, respectively.<sup>[27]</sup> In addition, the NH band of MBA is overlapped by OH peak at about 3200 cm<sup>-1[28]</sup> so the related peak is disordered.

Scanning electron microscopy technique was used to analyze the morphology of hydrogels. The SEM image of p(AA), shown in Figure 1-f, indicates the formation of homogeneous and highly porous material.

To determine the thermal properties and the amount of silver nanoparticles entrapped inside the gels network, thermal gravimetric analysis (TGA) were performed for pure and composite hydrogels. About 3 mg hydrogel was put in the pan of the TGA analyzer and heated from 30 to 800 °C with a heating rate of 10 °C/min under 60 mL/min N<sub>2</sub> flow. Figure 2 shows TGA curves of bare p(AA) (Figure 2-a), and p(AA)-Ag composite (Figure 2-b). 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 no carbon residue at 800 °C, which is similar to other previous reports. Upon their comparison and reduction of bare p(AA) hydrogel from p(AA)-Ag composite hydrogels, it was found that the metal content of the composite was 19.7 wt.% Ag compounds. Increased in thermal stability of p(AA)-Ag composite in comparison with bare p(AA)



**FIGURE 2** TGA thermogrames of a) bare p(AA) hydrogel, b) p(AA)-Ag composite

hydrogel, can be attributed to the coordination of silver nanoparticle with functional groups of poly acrylic acid hydrogels, because the TGA experiments were performed under  $N_2$ atmosphere, there is no possibility of presence of  $O_2$ . So, the formation of oxide compounds in the TGA experiment can be negligible.

The amount of metal ion within the hydrogel was determined, also, by using ICP after dissolution by 5 M 100 ml HCl treatment and according to the ICP measurement results, 0.1 g p(AA) hydrogel absorbed 194 mg Ag.

To investigate the nanostructure, the sample was examined with TEM observations. The TEM images of metal nanoparticles-containing p(AA) hydrogels are given in Figure 3. As can be seen, metal nanoparticles with a uniform spherical shape, about 20–40 nm, are distributed within p(AA) hydrogel matrices.

To obtain further information on the Ag-NPs in the hydrogel matrix and in order to gain further insight into the ionic state of the nanoparticles, we performed XPS measurements on the sample p(AA)-Ag. A high-resolution Ag 3d X-ray photoelectron spectrum of the silver nanoparticles is shown in Figure 4. Ag 3d<sub>5/2</sub> and 3d<sub>3/2</sub> spin-orbit coupled core levels are observed at 369.95 eV and 375.97 eV respectively. This confirms the presence of Ag in metallic state.<sup>[29]</sup> In addition, the energy splitting value of 6.0 eV for the 3d doublet of Ag indicates formation of metallic silver nanoparticles.<sup>[30,31]</sup>

# **3.2** | The catalytic activity of p(AA)-Ag toward the oxidation reaction of alcohols

The selective oxidation of alcohols, especially employing oxygen as the terminal oxidant, has been believed one of the most important reactions in organic synthesis.<sup>[32]</sup> With the p(AA)-Ag catalyst in hand, we effort to evaluate its catalytic activity for the aerobic oxidation of alcohols, and some examples 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 80 °C. The blank experiments without Ag loading exhibits a negligible benzyl alcohol conversion (<7% at 80 °C and 24 h reaction time). However, in the presence of the Ag catalyst, benzyl alcohol conversion increases. Within 24 h and with 0.018 mmol Ag, 15% isolated yield of the benzoic acid was obtained. Within 24 h and with 0.036 mmol Ag, 79% isolated yield of the benzoic acid and 1.96% yield of the benzaldehyde were obtained (Table 1, entry 1). B. Zahed *et al.* has been reported oxidation of benzyl alcohol in the presence of AgNPs.<sup>[33]</sup> In comparison with their results, p(AA)-Ag could act as better catalytic system with high selectivity to benzoic acid.

To establish the scope for the activity of p(AA)-Ag, this study was further extended to the catalytic oxidation of other







**FIGURE 3** TEM images of metal nanoparticles from p(AA)-Ag (white spots can be considered as Ag nanoparticles)





**FIGURE 4** Silver 3d XPS spectrum of the silver–polymer composite. The peaks at binding energies of 368.17 eV for  $3d_{5/2}$  and 374.23 eV for  $3d_{3/2}$  are indicative of metallic silver

primary benzyl alcohols with substituent such as 4-MeO, 2-Br and 3-NO<sub>2</sub> groups (Table 1, entries 2–4). Carboxylic acids (as major product) and aldehyde (as minor product) were observed for all substrates investigated. The substitution effect on aromatic substrates was studied. As shown in Table 1, 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 2), but in contrary, withdrawing group, such as NO<sub>2</sub> (Table 1, entry 3) decreased the conversion.<sup>[34]</sup> This trend is in agreement with Hammett plot results<sup>[35,36]</sup> and suggesting that the formation of the transition state with a carbocationic character on the benzylic carbon during the discharge of hydrogen in the rate-determining step is involved in the oxidation pathway over the present catalysts.<sup>[37]</sup> In addition, the oxidation of 2-substitute benzyl alcohol was obtained in a low yield (Table 1, entry 4), which may be attributed to the steric hindrance by the surface of the silver sites.<sup>[38]</sup>

A hypothesis of the possible mechanism of catalytic oxidation of alcohols by p(AA)-Ag was presented in Scheme 2. Deprotonation of alcohol was promoted by  $K_2CO_3$  to from alkoxide on the Ag surfaces. Ag catalyzes the  $\beta$ -hydride elimination to produce corresponding aldehyde along with the formation of  $O_2$  and  $H_2O$ . As shown in Scheme 2, alcohol converted to aldehyde then  $H_2O$  and  $O_2$  are released. Aldehyde is the first product of this process whereas carboxylic acids can generally be obtained in two steps in an aqueous medium, via the *in situ* generation of geminal diol through hydration of aldehyde followed by oxidation into the corresponding carboxylic acid (Scheme 2). The reusability of p(AA)–Ag catalyst system was studied by using the same catalyst in benzyl alcohol oxidation repeatedly up to three times. After every use, the catalyst was filtered and washed with DI, and used again for the same reaction under the same reaction conditions. The conversion for benzyl alcohol oxidation by p(AA)–Ag are illustrated in Table 2.

# **3.3** | The catalytic activity of p(AA)-Ag toward the reduction reaction of nitrophenol

Catalytic activity of the prepared p(AA)–Ag composite was investigated for reduction of 4-NP (Figure 5-a).

Nitro compound reduction reactions were elected because of their importance in the environments, and in the number of manufacturing of various pharmacology products, dye and pigment industries.<sup>[39]</sup> According to thermodynamic studies, the reduction of nitro compounds is possible in the presence of excess amounts of aqueous solution of NaBH<sub>4</sub>, as reducing agent, with large kinetic barrier.<sup>[40]</sup> 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 0.036 mmol of hydrogel–Ag composites were used as catalyst.

Reduction of nitro compound 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 hours as shown in Figure 5-b. But after the addition of catalyst almost all of the 4-NP present in the reaction mixture was reduced within 40 minutes as demonstrated in Figure 5-c.

As degradation of NP was carried out in large excess of NaBH<sub>4</sub> so this reaction was supposed as pseudo first order and values of  $k_{app}$  were calculated by plotting  $\ln(C_t/C_0)$  vs. time as shown in Figure 6. From the linear relations of  $\ln(C_t/C_0)$  (Figure 6), we found that therate constant was  $0.134(\pm 0.0042)$  min<sup>-1</sup>. In order to evaluate the effect of temperature on the catalytic activity of p(AA)-Ag composite the reduction of 4-NP was investigated three different temperatures; 25 °C, 40 °C, 60 °C keeping the amount of reactant and catalyst constant. Dependence of reaction rate on temperature is displayed in Figure 6,  $(\ln(C_t/C_0))$  versus time at different temperatures). The reduction rates were increased linearly as temperature rise. Because at higher temperature, rate of diffusion of reactant molecules into hydrogel composites and collision 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)-Ag composite. Energy of

-WILEY-Organometallic 7 of 11 Chemistry

TABLE 1 Catalytic activity of p(AA)-Ag on the oxidation of benzyl alcohol<sup>a</sup>

Entry	Substrate	Catalyst amount (mmol Ag)	Conversion $^{b}$ (%) ( $\sigma$ ) <sup>c</sup>	Product	Selectivity (%)
1	ОН	0.036	80.96 (1.12)	0	1.96
				ОН	79
4	Н3СО ОН	0.036	84.6 (0.92)	H <sub>3</sub> CO	0.08
				Н3СО	84.52
2	NO <sub>2</sub> OH	0.036	75.8 (1.36)	NO <sub>2</sub>	4.34
				OH NO <sub>2</sub>	89
3	OH Br	0.036	36.5 (0.52)	O Br	6.24
				ОН	90

<sup>a</sup>Catalyst (p(AA)-Ag), substrate (1.0 mmol), H<sub>2</sub>O, (5 ml) as solvent, K<sub>2</sub>CO<sub>3</sub> 1.2 mmol, temperature 80 °C, Time = 24 h under O<sub>2</sub> atmosphere <sup>b</sup>Conversions are based on the starting substrate;;

 $^{c}\sigma$  = Standard deviation;

activation  $(E_a)$  was calculated from Arrhenius equation which is given below

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

According the Arrhenius equation  $\ln k_{app}$  was plotted against 1/T as shown in Figure 7-a,  $E_a$  was calculated from the slope of this plot and found to be 22.11 kJ mol<sup>-1</sup>.

The activation enthalpy  $(\Delta H^{\#})$  and entropy  $(\Delta S^{\#})$  were calculated by using Eyring equations (Equation (2)).

$$\ln k/T = \ln(k_{\rm B}/h) + \Delta S^{\#}/R - \Delta H^{\#}/R(l/T)$$
(2)

According to Eyring equation  $\ln k_{app}/T$  was plotted against l/T as shown in Figure 7-b. The value of  $\Delta H^{\#}$  was calculated from the slope of this plot and was found to be 19.47 kJ mol<sup>-1</sup>. The positive value of  $\Delta H^{\#}$  shows that the formation of an activated complex in the reduction of 4-NP is an endothermic process.<sup>[41]</sup> The value of  $\Delta S^{\#}$  was calculated from the intercept of plot of  $\ln(k_{app}/T)$  vs. 1/T and was found as -196.17 J mol<sup>-1</sup> K<sup>-1</sup>. The negative value of  $\Delta S^{\#}$  shows that the reduction of 4-NP is entropically unfavorable which can be made favorable by adding catalyst.<sup>[40]</sup> The value of  $\Delta G^{\#}$  was calculated from the following equation,

$$\Delta G^{\#} = \Delta H^{\#} - T \Delta S^{\#}$$

The values of  $\Delta G^{\#}$  at 298 K, 313 K, 333 K were calculated as 77.92 kJ mol<sup>-1</sup>, 80.87 kJ mol<sup>-1</sup>, 84.79 kJ mol<sup>-1</sup>, respectively. The positive values of  $\Delta G^{\#}$  shows that reduction of 4-NP is a non-spontaneous process<sup>[7]</sup> and it needs an input energy to proceed which is provided by the addition of the catalyst.

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*. 0.018, 0.036, 0.072 mmol. As shown in Figure 8-a, with an increase in catalyst amount, the increase in rate of reaction was observed, as expected. As  $\begin{array}{c} \underline{\mathsf{B} \text{ of } 11} \\ WILEY - \underbrace{\mathsf{Organometallic}}_{\mathsf{Chemistry}} \\ K_2CO_3 + \underbrace{\mathsf{O}}^{\mathsf{O}} \\ \underbrace{\mathsf{O}}^{\mathsf{A}}_{\mathsf{A}} + \underbrace{\mathsf{O}}^{\mathsf{O}} \\ \underbrace{\mathsf{O}}^{\mathsf{A}}_{\mathsf{A}} \underbrace{\mathsf{O}}^{\mathsf{$ 

SCHEME 2 Plausible pathways for the oxidation of alcohols in the presence of p(AA)-Ag nano composite

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.

In order to investigate the effect of amount of reducing agent on the reduction rate, different amounts of NaBH<sub>4</sub> were used by assuming all other parameters constants. To assess the effect of NaBH<sub>4</sub> on the reduction rate, different amounts of NaBH<sub>4</sub> (0.1–0.5 M) were used in reduction of 4-NP. As can be seen from Figure 8-b, there is a linear increase in the reduction rate of 4-NP with the increase in the amount of NaBH4 at 25 °C. The same trend has been reported in several literatures.<sup>[42]</sup>

The reusability of p(AA)–Ag catalyst system was studied by using the same catalyst in 4-NP reduction repeatedly up to four times. 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)–Ag is illustrated in Figure 9. Activity was calculated by taking ratio of reduction rate of every successive reaction to the initial reduction rate, and as illustrated from Figure 9, 100% conversion of 4-NP was observed after 4th use of Ag nano catalyst system. However, 3.5% loss in the activity of p(AA)–Ag catalyst was observed at the end of four consecutive use.

 TABLE 2
 Effect of catalyst recycling on the oxidation of benzyl alcohol<sup>a</sup>

	Conversion (%) $(\sigma)^{c}$	Benzoic acid
Number of cycle		selectivity (%)
Fresh	80.96 (0.92)	79
1	81.5 (1.20)	78
2	80 (1.15)	80
3	81 (0.95)	79

<sup>a</sup>Catalyst (p(AA)-Ag), Benzyl alcohol (1.0 mmol), H<sub>2</sub>O, (5 ml) as solvent,  $K_2CO_3$ 1.2 mmol, temperature 80 °C, Time = 24 h under O<sub>2</sub> atmosphere;

<sup>b</sup>Conversions are based on the starting substrate;

 $^{c}\sigma$  = Standard deviation;



**FIGURE 5** (a) representation of the reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) by the p(AA)-Ag nanoparticle, (b) UV-visible spectra of 4-NP in the absence of catalyst and presence of NaBH<sub>4</sub>, (c) UV-visible spectra for the reduction of 4-NP catalyzed by p(AA)-Ag composite and NaBH<sub>4</sub>. Reaction conditions; 0.01 M 4-NP 50 mL, NaBH<sub>4</sub> = 0.35 M, catalyst = 0.036 mmol, 25 °C



**FIGURE 6** The determination of apparent rate constants  $(k_{app})$  for the reduction 4-NP catalyzed by p(AA)–Ag composites with temperature



**FIGURE 7** The determination of apparent rate constants  $(k_{app})$  for the reduction 4-NP catalyzed by p(AA)–Ag with temperature, a) plot of  $\ln(k_{app})$  vs. 1/T b) plot of  $\ln(k_{app}$  /T) vs. 1/T for the reduction 4-NP catalyzed by p(AA)–Ag with temperature

# **3.4** | Comparison with other reported catalytic system

Table 3 provides a comparison of the NP reduction results obtained ( $k_{app}$  and  $E_a$ ) for our present catalytic system with those reported in the literatures.<sup>[43–51]</sup> Also, oxidation of benzyl alcohol under heterogeneous conditions over a variety of catalysts has been studied<sup>[52–57]</sup> (Table 4). From Table 3 and



**FIGURE 8** a) the change in reduction rate constant of 4-NP with the amount of Ag catalyst inside p(AA)–Ag composites b) change in values of  $k_{app}$  with the change in of concentration of NaBH<sub>4</sub> during the reduction of NP



**FIGURE 9** The change in conversion and activity of p(AA)–Ag catalyst systems with repetitive usage in 4-NP reduction. [25 °C, 0.01 M 4-NP = 50 mL, [NaBH<sub>4</sub>] = 0.35 M, catalyst = 0.036 [mmol]

4, it is seen that p(AA)-Ag showed higher catalytic activity over reported catalysts. Although CPL-Ag NCs and AgNPs@MWCNTs-polymer showed high reaction rate in NP reduction and Ag@IPN, PdNPs@P2VP-Fe<sub>3</sub>O<sub>4</sub> showed high catalytic activity in oxidation of benzyl alcohol. A comparison between the system represented here, and the previously reported systems indicates higher catalytic activities for our system. One reason for the high catalytic activities in our system could be the softness, flexibility, and hydrophilic nature of the hydrogels, carriers, and stabilizers, which were used for the preparation of the metal nanoparticles. The other reason could be the hydrophilicity and types of 10 of 11 WILEY-Organometallic Chemistry

TABLE 3 Comparison of the rate constant and activation energy calculated in the present work with reported literature

GHORB	ANLOO	ΕT	AL

Catalyst	$K_{app}$ (min <sup>-1</sup> )	Eact	Reference
PS-NIPA-Ag composite	0.00216	Not reported	[43]
p(AMPS)-cu hydrogel composite	0.1032	28.2	[44]
PS-PVImAgNPs	0.03072	Not reported	[45]
Poly-(acrylamide glycolic acid)/Ag composites	0.0923	33.8	[46]
P(AMPS)-Ni composite	0.0563	25.7	[47]
p(AMPS)-co	0.12	27.8	[48]
PVA/PS-PEGMA/Ag	0.00468	Not reported	[49]
CPL-Ag NCs	0.9	Not reported	[50]
AgNPs@MWCNTs-polymer	0.472	Not reported	[51]
P(AA)-Ag	0.134	22.11	This work

TABLE 4 Comparison of the benzyl alcohol oxidation in this work with reported literature

Entry	Catalyst	Conversion (%)	Reaction conditions	Reference
1	AgNPs	33	CH <sub>3</sub> CN, NHPI, 24 h, 80 °C	[52]
2	Pd@U-B20	43	H <sub>2</sub> O, K <sub>2</sub> CO <sub>3</sub> , 24 h, 90 °C	[53]
3	Pd/Fe@C	63	H <sub>2</sub> O, K <sub>2</sub> CO <sub>3</sub> , 25 h, 80 °C,	[54]
4	Ag@IPN	98	p-xylene, 130 °C, 12 h	[55]
5	PdNPs@P2VP-Fe <sub>3</sub> O <sub>4</sub>	96	H <sub>2</sub> O, K <sub>2</sub> CO <sub>3</sub> , 4 h, 80 °C, O <sub>2</sub>	[56]
6	Au NPs@CLIL	90	H <sub>2</sub> O, K <sub>2</sub> CO <sub>3</sub> , 4 h, 90 °C, O <sub>2</sub>	[57]
7	P(AA)-Ag	80.96	H <sub>2</sub> O, K <sub>2</sub> CO <sub>3</sub> , 24 h, 80 °C, O <sub>2</sub>	This work

functional groups in the polymeric network, which promotes the overall catalytic process in the system.

### **4** | **CONCLUSION**

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 Ag nanoparticles to prepare p(AA)-Ag 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. This organic inorganic hybrid hydrogel was found to be efficient and reusable catalysts in oxidation reactions of primary alcohols in short reaction time and good to excellent yields.

#### ACKNOWLEDGMENTS

Authors are thankful to University of Zanjan for financial support of this study.

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Applied

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11 of 11

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How to cite this article: Ghorbanloo M, Heydari A, Yahiro H. Ag-nanoparticle embedded p(AA) hydrogel as an efficient green heterogeneous Nano-catalyst for oxidation and reduction of organic compounds. *Appl Organometal Chem.* 2017;e3917. <u>https://doi.org/</u> 10.1002/aoc.3917