NaOH Modified P(acrylamide) Hydrogel Matrices for *In Situ* Metal Nanoparticles Preparation and Their Use in H₂ Generation from Hydrolysis of NaBH₄

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ABSTRACT: Crosslinked poly(acrylamide) (p(AAm)) as neutral hydrogel is synthesized via photo polymerization technique, and the amide groups within p(AAm) matrices are converted to strongly ionizable carboxylic acids groups via facile modification route by simple treatment of NaOH to obtained NaOH-p(AAm) hydrogels. Because of the highly ionizable nature of carboxylate groups within mod-p(AAm), the swelling and metal ion absorbing capacities are increased tremendously, almost 40 and 7.5 folds, respectively. The Co(II) and Ni(II) metal ions are loaded into NaOH-p(AAm) hydrogels, and are treated with NaBH₄ to form corresponding metal nanoparticles *in situ* within mod-p(AAm) matrices, and used in H₂ generation production from hydrolysis of NaBH₄. Various parameters such as functionality of polymeric matrices, the kinds and the amount of metal nanoparticles, and the temperature effecting the H₂ generation are investigated. Comparable low E_a with the similar researches in the literature, $E_a = 20.07 \pm 0.05$ kJ mol^{-1} is obtained in NaBH₄ hydrolysis catalyzed by NaOH-p(AAM)-Co composite system. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 41106.

INTRODUCTION

The use of hydrogen (H₂) as environmentally friendly and clean energy from different source has been the foremost significance in many investigations. It is a great desire in near future to use H₂ as energy carrier in a usable form for wide range of consumers.[1–4] Scientists expected to utilize H₂ as a potential fuel for power generating system such as on-board auxiliary power, stationary power generation, and as an energy storage medium for many purposes.[5–7] However, molecular H₂ does not instinctively exist in nature; nonetheless, it can be generated from numerous methods such as hydrolysis of chemical hydrides, steam reforming hydrocarbons, and some H₂ compounds, water electrolysis or by other methods.[8–10] The chemical hydrides such as NaBH₄, NH₃BH₃, LiAlH₄, and others are very well known as high hydrogen containing materials.[11–13] Especially, NaBH₄ has a number of discernible benefits such as the evolving H₂ can be measured readily during the reaction, no toxic waste product and side-reaction, chemically stable, non toxic nature and high H₂ content.[14–18] H₂ can be liberated, only by mixing NaBH₄ and H₂O in the presence of a suitable metal catalyst systems at ambient temperature according to following reaction.[19,20]

$$NaBH_4 + 2H_2O \xrightarrow{\text{M:catalysts}} NaBO_2 + 4H_2 + \text{heat} \uparrow \quad (1)$$

This reaction approaches a remarkable 10.8 wt % gravimetric efficiency when calculated in relation to the weight of the NaBH₄ alone, and in the presence of excess amounts of water this ratio decrease to 2.9 wt % when calculated in relation to both water and NaBH₄.[21,22] Noticeable H₂ generation has not occurred when NaBH₄ dissolves in water without catalyst. The reactivity of heterogeneous catalysts or nanomaterial-based catalysts generally occurs at the surface atoms. Therefore, great effort has been exerted to maximize the surface area of a catalyst by distributing it over the support.[23,24] In addition, the support may be inertly participate or contribute to the catalytic reactions. Carbon, alumina, silica and hydrogels are the most commonly used supports for various catalytic reactions.[25–27] Hydrogels are versatile polymeric materials with three-dimensional hydrophilic networks that swell by absorbing large amounts of water from aqueous medium without dissolving.[28,29] Generally, strongly ionizable acidic or basic functionality groups on hydrogels networks are responsible for metal nanoparticles preparation, and make them useful in hydrogen generation reactions from hydrolysis of various chemical

hydrides.[30,31] In this article, a different approach was used by employing neutral poly(Acrylamide) (p(AAm)) network to make charged network for *in situ* metal nanoparticles preparation after modification by NaOH treatment. The composites were obtained by situ metal nanoparticle preparation such as Co, and Ni within NaOH-p(AAm) networks, and used in hydrolysis reaction of NaBH$_4$ for H$_2$ generation. The modification induced higher water swelling and metal absorbing capability for NaOH-p(AAm). Up till now, various kinds of methods such as the functional hydrophilic co-monomer addition to the network, irradiation in the presence of different chemicals, and the use of different chemical functional crosslinkers etc were used to improve swelling and metal ion absorbing properties of p(AAm) networks.[32–34] Here, we used a simple and effective novel modification method to convert neutral amide groups that are exist in the p(AAM) network to strongly ionizable carboxylate via NaOH treatment. This novel approach enables to prepare Co, Ni metal particle preparation *in situ* better and great catalytic performance in H$_2$ generation from the hydrolysis of NaBH$_4$.

EXPERIMENTAL

Materials

The monomer, acrylamide (AAm) (98%, Merck), the crosslinker, *N,N'*-methylenebisacrylamide (MBA) (99%, Acros) and the UV-initiator, 2,2 azobis(2-methylpropion amidine) dihydrochloride (99%, Sigma-Aldrich) were used in hydrogel preparation. Sodium hydroxide (NaOH) (97%, Sigma-Aldrich) was used in modification reactions of hydrogels. Cobalt (II) chloride hexahydrate (CoCl$_2$.6H$_2$O) (99%, Sigma-Aldrich) and nickel (II) chloride hexahydrate (NiCl$_2$.6H$_2$O) (97%, Sigma-Aldrich) were used as metal ion sources. Sodium borohydride (NaBH$_4$, 98%, Merck) was used as reduction agent and H$_2$ source for preparation of metal nanoparticles and hydrolysis reactions. DI water (18.2 MΩ cm) was used for all experimental studies.

Synthesis and Modification of p(AAm) Hydrogels

The synthesis of p(AAm) hydrogel via photo polymerization method was performed by exposing initiator and 50% w/w water-monomer mixtures to UV light in a photoreactor. In brief, 10 g (0.137 mole) monomer was dissolved in 20 mL water that contained 0.05 mol % crosslinker, MBA (based on the total amount of monomer). Then, 0.02 mol % initiator (based on the total monomer amount) was added and the mixture was rapidly stirred to completely dissolve all the solid. The mixture was put into plastic pipettes, and placed in a photo reactor (LUZCHEM, 420 nm, Canada), and the samples were irradiated with UV irradiation for 30 min to prepare polymeric hydrogels. The obtained p(AAm) hydrogels were cut to approximately equal shapes and size (∼0.8 mm in diameter and 0.5 cm thickness), and they were washed with plenty of water during two day. Finally, swollen hydrogels were dried in an oven at 40°C, and stored in the closed zip-lock for the experimental studies.

Modification reaction of p(AAm) hydrogels was performed by using sodium hydroxide as modification agents: 0.1 g p(AAm) hydrogels were placed in 100 mL 10*M* sodium hydroxide solution at 60°C under constant mixing at 500 rpm for 32 h for chemical modification reaction to take place. After modification, NaOH-p(AAm)

hydrogels were washed with excess amount of water for 2 days by changing the wash water every 8 h, and dried in an oven at 40°C, and they were used for *in situ* metal nanoparticles preparation, and then in H$_2$ generation reactions from hydrolysis of NaBH$_4$.

The Preparation of Metal Nanoparticles Within p(AAm) and NaOH-p(AAm) Networks and Their Use in H$_2$ Production from Hydrolysis Reaction of NaBH$_4$

To prepare metal nanoparticles within hydrogel networks, 0.1 g samples of p(AAm) and NaOH-p(AAm) hydrogels were immersed into 100 mL 500 ppm Co (II) and Ni (II) metal ion solutions for 24 h at room temperature to load these metal ions into hydrogel networks. Upon loading metal ions into hydrogel, the unbound metal ions were removed from polymeric hydrogel networks by washing the metal ion loaded hydrogels with DI water for 1 h, and the metal ions within hydrogels were reduced to their corresponding nanoparticles via *in situ* reduction method by treating them with 50 mL 0.3*M* NaBH$_4$ solution for 3 h. Finally, p(AAm)-M and NaOH-p(AAm)-M metal composites (M:Co, and Ni) were washed with plenty of water, and polymer-M composites were used in H$_2$ generation from hydrolysis reaction of NaBH$_4$ at the determined certain reaction conditions, e.g., 50 mL 50 m*M* NaBH$_4$, containing 5 wt % NaOH under 1000 rpm mixing rate at 30°C unless otherwise stated.

RESULTS AND DISCUSSION

Characterization of Neutral and NaOH-p(AAm) Networks

Various techniques were employed in the characterization studies to determine the changes in the inherit properties such as swelling, porosity, metal ion absorbing amounts, thermal behaviors of p(AAm) based hydrogels and their metal composites before and after the post modifications. The neutral p(AAm) hydrogels were chemically modified by using NaOH as modifying agent to obtain newly formed acidic groups that are strongly ionizable on the p(AAm) backbones (NaOH-p(AAm)). The modification reaction mechanism of p(AAm) hydrogel was given in Figure 1(a). The swelling characteristics in both DI (distilled) water, and at different pH solutions of p(AAm) based were determined gravimetrically and illustrated in Figure 1(b,c). The swelling behaviors of p(AAm) hydrogels changed significantly, after the modification with sodium hydroxide, due to formation of strongly ionizable carboxylic acid groups. The swelling studies of neutral p(AAm) and NaOH-p(AAm) were carried out by placing about 100 mg were hydrogels within 100 ml DI water, and the increases in their weights were determined according to following equation.

$$\%S = [(m_t - m_d)/m_d] \times 100 \qquad (2)$$

where m_t is the weight at time t, and m_d is the dried weight of p(AAm) based hydrogels. As illustrated in Figure 1(b), the percent maximum swelling ratio of pristine p(AAm) is about 1060%, whereas the percent maximum swelling ratios of NaOH-p(AAm) hydrogels reached about 40,100%, which is about 37.8-fold increase in swelling. To corroborate that the new functional group on the p(AAm) polymer backbone is pH sensitive after modification, pH swelling studies of both modified and unmodified p(AAm) was carried out, and their $\%S_{max}$ is given as seen in Figure 1(c). It is clear that the modified
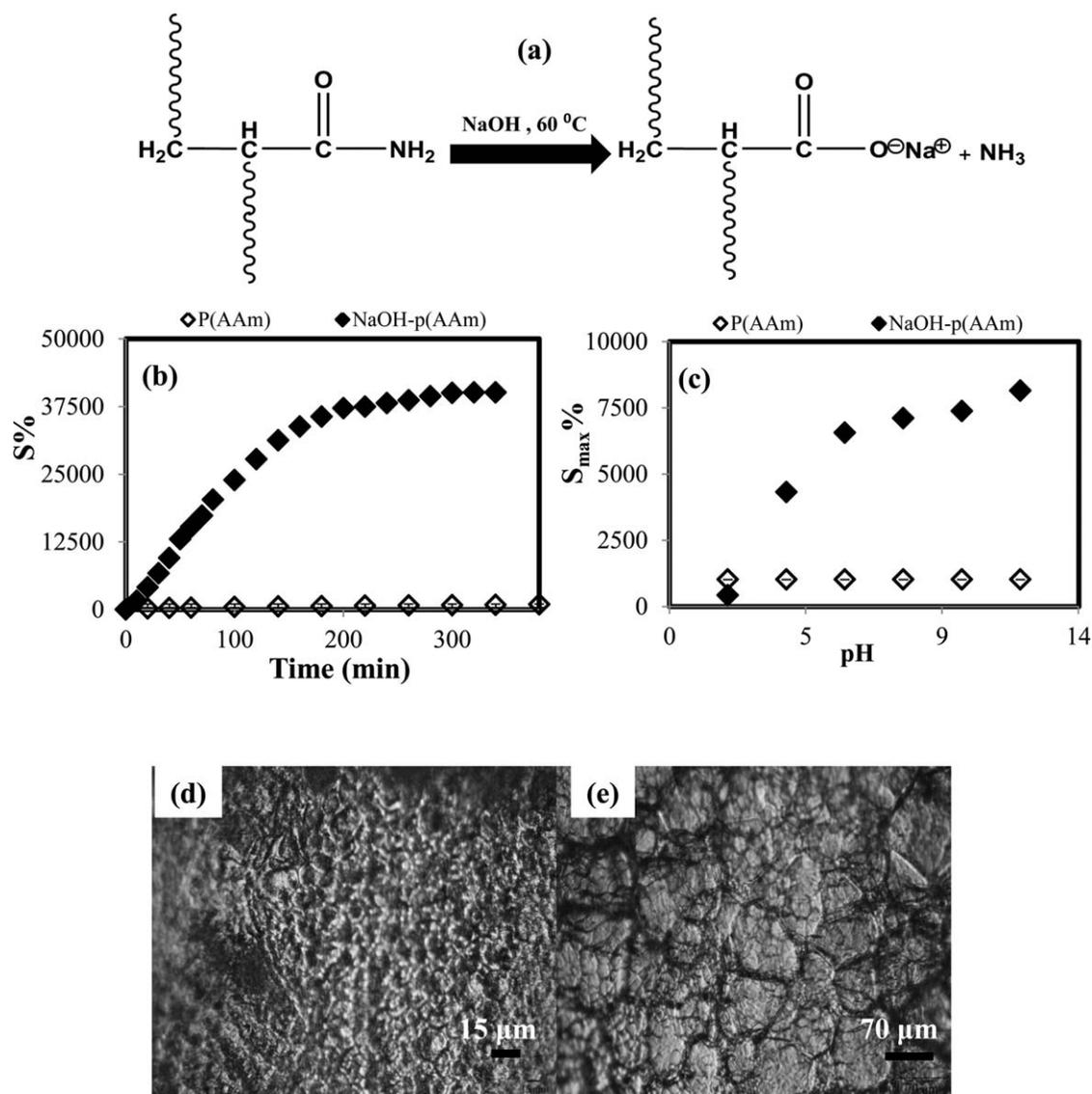
Figure 1. (a) Modification reaction mechanism of p(AAm) with NaOH, and the swelling studies of modified and unmodified p(AAm) (b) in water, and (c) at different pH solutions. The optical microscope images of (d) p(AAm) and (e) NaOH-p(AAm) under the 10× magnification.

p(AAm) hydrogel swelling values increased with the increase in the pH of the medium, whereas there was no significant change in the swelling properties of pristine p(AAm) with increased in the pHs of the medium was observed. Due to presence of strongly ionizable carboxylic acid groups on NaOH-p(AAm) networks, their swelling ratio was increased up to 7110% about pH 8, and stay almost stable with little changes. At pH 12, the NaOH-p(AAm) hydrogels swelled to about 8150%, whereas p(AAm) hydrogels swelled to maximum of 1200%. Due to the presence of neutral amide groups that are insensitive to pHs within p(AAm) hydrogel, high swelling values can not be obtained in both acidic and basic mediums.

The optical microscopy images of the freeze-dried normal p(AAm) and NaOH-p(AAm) hydrogels were demonstrated in Figure 1(c). As can be clearly seen, there is tremendous increase in the porosity of hydrogels matrices in accordance with swel-

ling experiments that upon modification NaOH-p(AAm) hydrogels absorbed great amounts of water. Another confirmation in relation to the formation of new functionality of modified p(AAm) hydrogel could be the determination of pK_a value of the NaOH-p(AAm) hydrogels. To determine the pK_a value of the modified hydrogel, it was titrated with hydrochloric acid solution. For this purpose, about 50 mg dried hydrogel was placed into 100 mL 0.1M NaCl solution. The pH of this solution was fixed to 2 by the addition of 0.1M HCl. After that, 0.1M NaOH was added drop wise and the change in pH of the medium was determined via a pH-meter. All the pH swelling and titration studies were carried out via pH-meter (Sartorius pH-/mV meters). The obtained titration curves and their derivative *versus* volume of added NaOH curves for NaOH-p(AAm) hydrogels is given in Figure 2(a). The pK_a value of NaOH-p(AAm) were determined as 4.9 from derivative of the titration curves. Upon titration of the pristine p(AAm) hydrogel, no
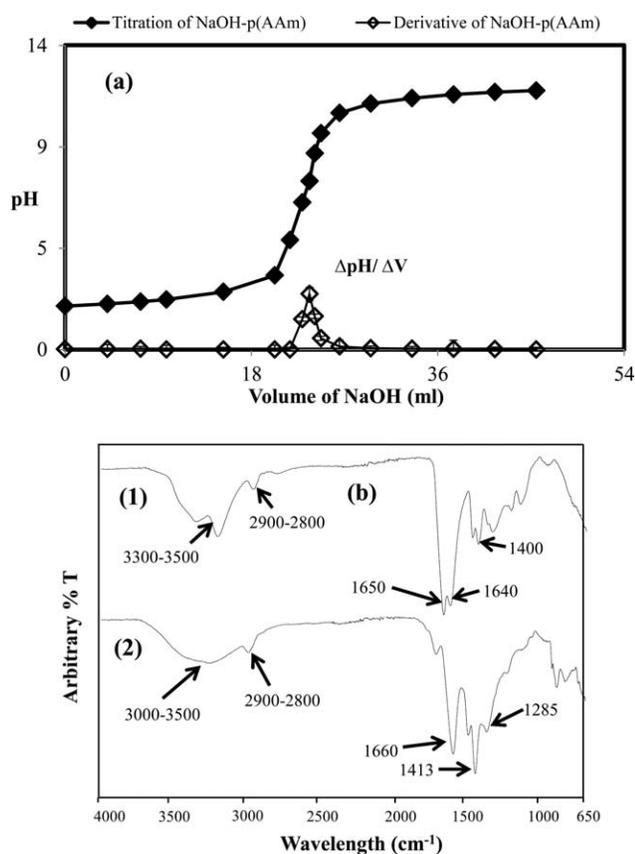
Figure 2. (a) Titration and derivative curves of NaOH-p(AAm) hydrogels, (b) FT-IR spectra of (a) pristine p(AAm) and NaOH-p(AAm).

change in titration curve is observed except the neutralization reaction of the initially added HCl. Therefore, it is obvious that NaOH modification resulted in highly ionizable acidic functional groups creation on the p(AAm) hydrogel networks.

The change in the structural of p(AAm) hydrogels after NaOH treatment was also determined via Fourier Transform Infrared Spectroscopy (FT-IR, Perkin Elmer Spectrum 100) as demonstrated in Figure 2(b). As can be seen, the N-H stretching band of primary amide, N-H bending vibration, aliphatic C-H stretching peak, and C=O and C-N stretching peaks belonging to p(AAm) hydrogels were observed at 3300 to 3500, 1650, 2900 to 2800, 1640 and 1400 cm^{-1}, respectively, and shown in Figure 2(b) as (1). The change in the characteristic peak of p(AAm) were illustrated in Figure 2(b) as (2). Due to presence of carboxylic acids generated in structures of p(AAm) hydrogels after modification with NaOH, almost all of the N-H stretching band of primary amid overlapped with this very broad O-H stretching band due to carboxylic acid peaks at about 3300 to 3500 cm^{-1}. Aliphatic C-H stretching band was again observed for NaOH-p(AAm) at 2900 to 2800 cm^{-1}, and the C=O stretching vibration band of NaOH-p(AAm) hydrogels was observed at 1660 cm^{-1}, and N-H bending vibrations of primary amid disappeared due to chemical conversion to carboxylic acid groups. The peaks at 1413 and 1285 cm^{-1} belong to C-OH and C-O stretching vibration, respectively for NaOH-p(AAm) hydrogels were also clearly seen.

Additionally, the metal ion binding ability of p(AAm) hydrogels were determined via Atomic Absorption Spectroscopy (AAS, Thermo, ICA 3500 AA SPECTRO). To check the modification time of p(AAm) hydrogels by metal ion absorption capacity, the amounts of absorbed metal ions by NaOH-p(AAm) hydrogel networks that were exposed to different modification reaction times with NaOH were used in Co(II) ion absorption from aqueous medium. At different modification time course NaOH-p(AAm) hydrogel were removed from the medium and washed with DI water for 6 h, and immersed into 100 mL 500 ppm Co(II) metal ion solution. As shown in Figure 3(a), the amount of metal ion absorption capacity of NaOH-p(AAm) hydrogel network increased with modification reaction time of up to 24 h and then stayed unchanged. Therefore, in this investigation 32 h NaOH modifications reaction of p(AAm) hydrogels were used for *in situ* metal nanoparticle preparation and for catalytic applications. The shrunken, swollen and metal ion absorption and metal nanoparticles formation schema with their corresponding digital camera images were also given in Figure 3(b,c), respectively. As shown, Co(II) ion loading and their reduction *in situ* to metal nanoparticles was given in Figure 3(c). It is obvious that after modification, the sizes of hydrogels changed to 3.5 cm from 1 cm. From the figure, while bare NaOH-p(AAm) hydrogel is transparent, the Co(II) metal ions loaded NaOH-p(AAm) hydrogel is colored (red) assuming the color of Co(II), and then upon reduction by NaBH$_4$ treatment within NaOH-p(AAm) matrices, the color changed to black as an indication of corresponding Co metal nanoparticle formation. The size of metal nanoparticles inside NaOH-p(AAm) based metal composites were determined through high contrast TEM (Transmission Electron Microscopy FEI Tecnai G^2 Spirit Bio-Twin), and given in Figure 3(d,e). From the analysis of TEM images, NaOH-p(AAm) matrices contain Co metal nanoparticles that are in range of 50 to 100 nm. The exact amounts of metal nanoparticles within the NaOH-p(AAm) hydrogels were determined by AAS measurements after treatment of composites with 50 mL 5M HCl solution. The amount of cobalt nanoparticles inside per gram of p(AAm) and NaOH-p(AAm) hydrogels were determined as 29.49 ± 0.5 mg/g and 218.52 ± 0.27 mg/g. About 7.5-fold increase in Co(II) ion absorption capacity is another verification, and the advantages of this simple chemical modification method for p(AAm). We also study the Ni(II) absorption and Ni metal nanoparticle formation within p(AAm) and NaOH-p(AAm) hydrogel and found that the amount of nickel nanoparticles per gram of NaOH-p(AAm) hydrogels were determined as 199.95 ± 0.25 mg/g. As Co nanoparticle are known for better catalytic performances in H$_2$ generation from the hydrolysis of NaBH$_4$,[35] NaOH-p(AAm)-Co composite hydrogel networks were used in H$_2$ production reaction in this investigation. The thermal behaviors and the change in metal absorption capacity of hydrogels before and after NaOH modifications were also confirmed via Thermogravimetric Analysis (TGA/DTA-SII, 6300). The TGA curves of normal p(AAm)-Co and NaOH-p(AAm)-Co are given in Figure 4. About 2 mg dry powdered samples were heated up to 1000°C from 50° and their mass losses were recorded against temperature. As clearly seen from Figure 4, the thermal resistances of the cobalt nanoparticle-containing p(AAm)-Co and
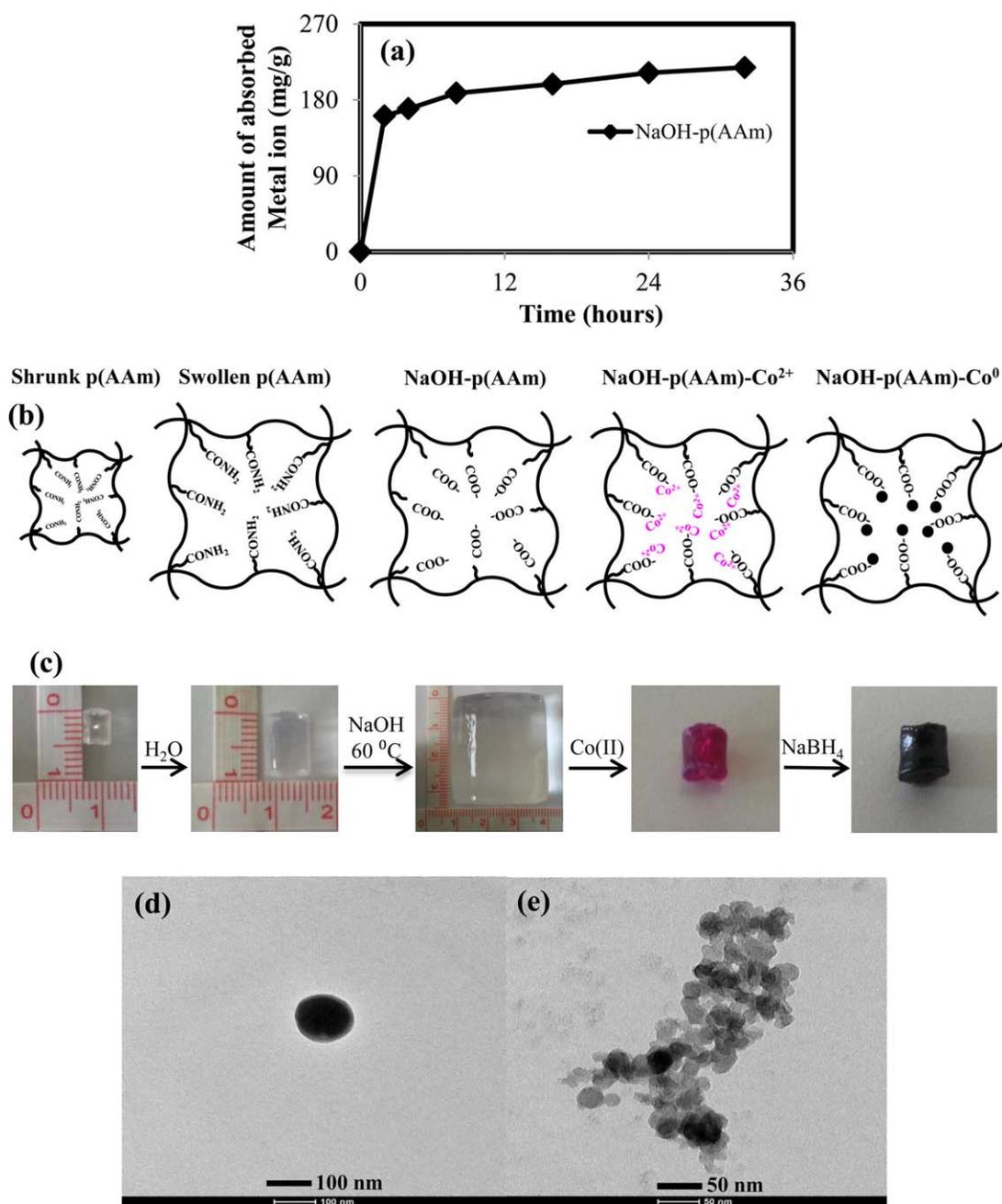
Figure 3. (a) The metal ion absorption capacity of NaOH-p(AAm) hydrogel exposed to different reaction times, (b) and schematic representation of their Co(II) absorption, and (c) their corresponding digital camera images of dry, and swollen p(AAm) hydrogels, NaOH-p(AAm) swollen, metal ion loaded, and metal nanoparticles contain NaOH-p(AAm) hydrogels, and (d) the TEM images of Co metal nanoparticles inside NaOH-p(AAm) hydrogels under different magnification, the scale bars are at (c) 100 nm and (d) 50 nm. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

NaOH-p(AAm)-Co metal composites were found as 3.84%, and 40.44% at 950°C. Additionally, even though both hydrogel composites show similar degradation characteristics, the p(AAm)-Co composites major degradation started at about 300°C, whereas NaOH-p(AAm)-Co major degradation started at about 400°C, and after these both composites continued to degrade up to 1000°C. Therefore, it can be inferred that chemical modification can also provide some thermal stability of metal ion loaded hydrogel matrices.

The Effect of Functionality of p(AAm) Polymeric Networks and the Effect of Metal Types Inside NaOH-p(AAm) Networks on Hydrolysis Reactions of NaBH₄

As the swelling, metal ion absorption capacity are highly increased due to change in the functionality by new acidic functional group within NaOH-p(AAm), NaOH-p(AAm)-Co composites were used for catalytic applications. To compare the catalytic performances, equal amounts (about 0.1 g) of pristine p(AAm) and NaOH-p(AAm) that contain highly different
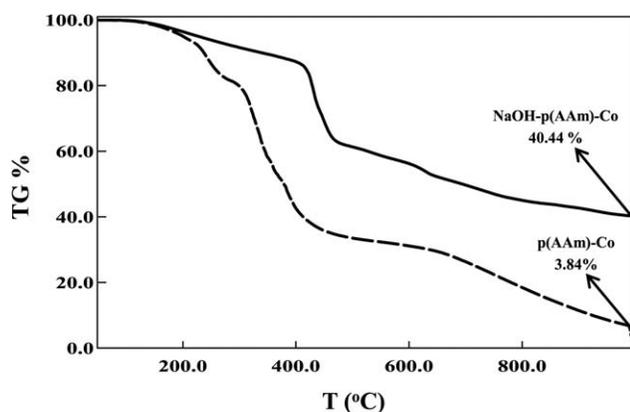
Figure 4. TGA thermogram of p(AAm)-Co and NaOH-p(AAm)-Co metal composites.

amount of metal nanoparticles such as 2.94 and 21.85 mg Co nanoparticles, respectively, were used in hydrolysis reaction of $NaBH_4$ under the same reaction conditions: 50 mL 50 mM $NaBH_4$, containing 5 wt % NaOH under 1000 rpm mixing rate at 30°C. As illustrated in Figure 5(a), both p(AAm)-Co and NaOH-p(AAm)-Co hydrogel composites generated equal amount of H_2 (about 248 mL), except their hydrolysis reactions were completed at different times. The H_2 hydrogen generation
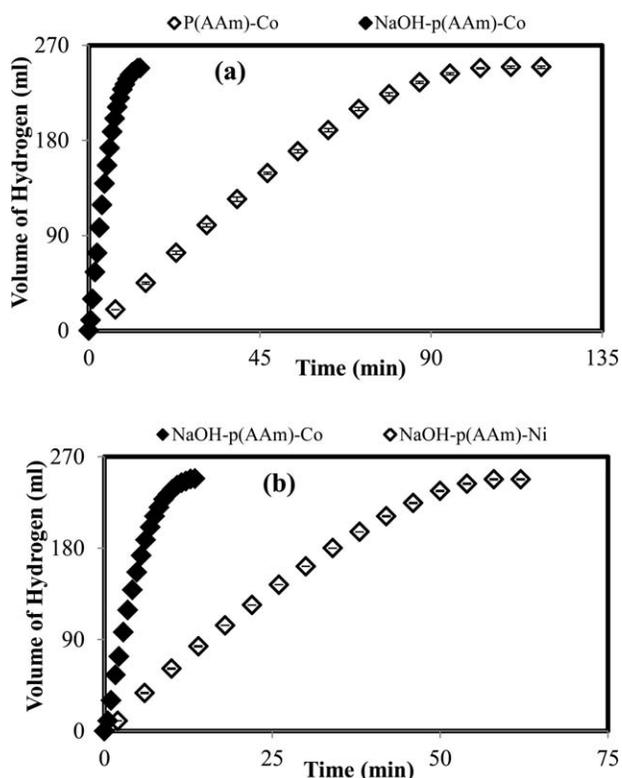
Figure 5. (a) Hydrogen generation from hydrolysis of $NaBH_4$ by using unmodified 0.1 g p(AAm)-Co (containing 2.94 mg nanoparticles) and 0.1 g NaOH-p(AAm)-Co (containing 21.85 mg nanoparticles). (b) Hydrolysis reactions of $NaBH_4$ by using 0.1 g NaOH-p(AAm)-Co (contains 21.85 mg Co nanoparticles), and 0.1g NaOH-p(AAm)-Ni (contains 19.99 mg Ni nanoparticles) [Reaction conditions: 50 mL 50 mM $NaBH_4$, 5 wt % NaOH, 30°C, 1000 rpm].
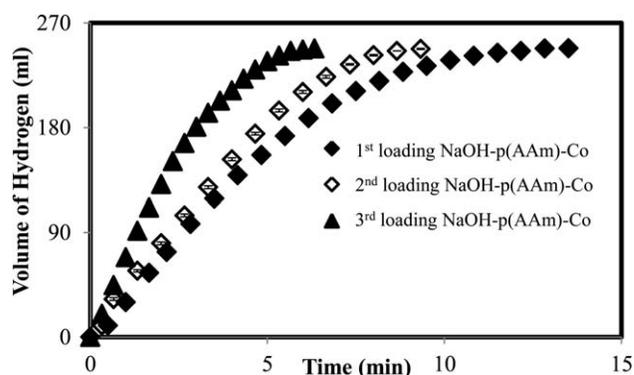
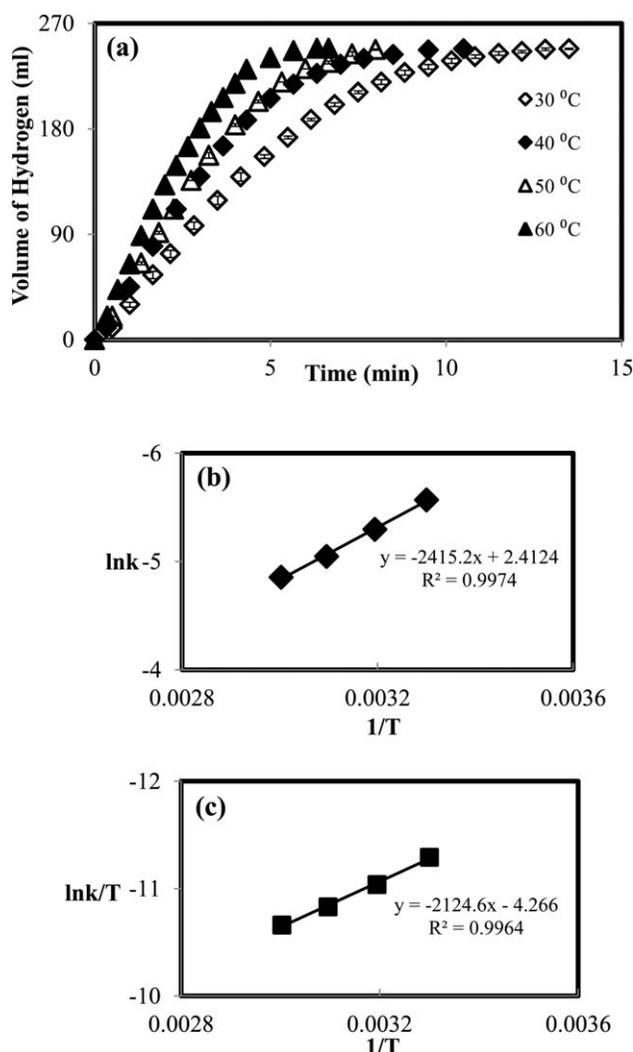**Figure 6.** Hydrogen generation from hydrolysis reactions of $NaBH_4$ with reloading and reduction cycles of Co(II) ions into 0.1 g NaOH-p(AAm)-Co composites. The amounts of Co nanoparticles are 218.5, 299.8 and 385.9 mg Co for first, second, and third loading and reduction cycle. [Reaction conditions: 50 mL 50 mM $NaBH_4$, 5 wt % NaOH, 30°C, 1000 rpm].

reaction catalyzed by pristine p(AAm)-Co was completed within 119 min, whereas the same reaction was completed within 13 min by NaOH-p(AAm)-Co catalysts as seen in the Figure 5(a).

To determine the effect of the types of metal nanoparticles, Co and Ni metal nanoparticles prepared *in situ* within NaOH-p(AAm) networks, and were used in H_2 generation reactions from hydrolysis of $NaBH_4$, and their results were compared as illustrated in Figure 5(b). Both hydrogels amounts were the same, 0.1 g NaOH-p(AAm)-M (M:Co, Ni) that contain 21.85 mg Co and 19.99 mg Ni metal nanoparticles were used in hydrolysis reaction of $NaBH_4$ at the same reaction conditions (50 mL 50 mM $NaBH_4$, 5 wt % NaOH, 1000 rpm mixing rate, 30°C), and the time to complete the reactions were compared. As can be seen from Figure 5(b), Co metal nanocatalyst containing system completed the same hydrolysis reaction in about 13 min, whereas the same reaction was completed at about 58 min by Ni metal nanocatalyst containing composite system. Consequently, cobalt metal nanoparticles showed faster H_2 generation kinetics in comparison to nickel metal nanoparticles that is in accordance with the literature.[3,19,27,35]

The Effect of Metal Ion Reloading Cycles to be Used in the Catalytic Hydrolysis Reaction of $NaBH_4$

To increase the metal nanoparticles content of NaOH-p(AAm) hydrogels, repetitively up to three times Co(II) ion loading and reduction cycles were carried out. After first loading-reduction cycles of Co(II) ions, 21.85 mg cobalt nanoparticles containing 0.1 g NaOH-p(AAm)-Co metal composites were washed with plenty of water, and again immersed within 100 mL 500 ppm Co(II) metal ion solution for 24 h at 500 rpm mixing rate. After than metal loaded NaOH-p(AAm)-Co composites again reduced to Co metal nanoparticles by treatment of 50 mL 0.3M $NaBH_4$ for 3 h to obtain second time Co loaded metal nanoparticles, and the same processes were carried out to obtain third time Co loaded composites by using second time metal ion loaded-reduced composites. As seen in Figure 6, due to the increase in metal content of NaOH-p(AAm)-Co metal composites, the catalytic activity or the H_2 generation rate is also

Figure 7. (a) Hydrogen generation rates from hydrolysis reaction of NaBH$_4$ at different temperatures by using 0.1 g NaOH-p(AAm)-Co (containing 218.5 mg Co nanoparticles) (b) ln k versus 1/T (Arrhenius eq.), and (c) ln (k/T) versus 1/T (Eyring eq.). [Reaction conditions: 50 mL 50 mM NaBH$_4$, 5 wt % NaOH, 1000 rpm].

increased. For all catalytic systems, the same amounts of H$_2$ gas (approximately 248 mL) were produced at different times. The hydrolysis reaction of NaBH$_4$ was completed within 13 min via

first time Co(II) loaded-reduced NaOH-p(AAm)-Co (contain 218.5 mg metal nanoparticles/g hydrogel) whereas hydrolysis reactions were completed within about 9 and 6 min with second, and third time Co(II) ion loaded-reduced composites systems that contain 299.8 and 385.9 mg Co particles per gram dried modified hydrogel, respectively. Therefore, to obtain fast H$_2$ production, the catalyst amounts can be increased by these NaOH-p(AAm) hydrogels by repetitive use of metal ion loading and reduction cycles. This is also another proof and the versatility of this modified p(AAm) hydrogel matrices that can be used in metal nanoparticle preparations and catalysis media even for different reactions.[35]

The Effect of Temperature on Hydrolysis Reactions of NaBH$_4$ Catalyzed by NaOH-p(AAm)-Co

The effect of temperature on the hydrolysis reaction of NaBH$_4$ were investigated by using 0.1 g NaOH-p(AAm)-Co metal composites that contains 21.85 mg Co particles in the temperatures range of 30 to 60°C with 10°C increments under the same reaction conditions (50 mL 50 mM NaBH$_4$, containing 5 wt % NaOH, 1000 rpm mixing rate). As shown in Figure 7(a), H$_2$ generation rate is increased with the increase in hydrolysis temperatures that realized by shorter completion of reaction time by the increase in the reaction temperature. For example, the H$_2$ generation reaction was completed within 13 min at 30°C, whereas the same reaction was completed within about 6 min at 60°C. The kinetic parameters of the hydrolysis reaction of NaBH$_4$ were also calculated by using very well known Arrhenius [eq. (3)] and Eyring [eq. (4)] equations by constructing the graphs ln k versus 1/T, and ln(k/T) versus 1/T graphs[36,37] were given in Figure 7(b,c), respectively.

$$\ln k = \ln A - [E_a/RT] \tag{3}$$

$$\ln [k/T] = \ln [k_B/h] + [\Delta S/R] - [\Delta H/R] [1/T] \tag{4}$$

Here, k is the reaction rate constant and was calculated according to a zero-order kinetic expression, E_a is the activation energy, T is the absolute temperature, k_B is Boltzmann constant (1.381 $\times$ 10^{-23} J K^{-1}), h is Planck's constant (6.626 $\times$ 10^{-34} J s), ΔH is activation enthalpy, ΔS is the entropy and R the gas is constant (8.314 J K^{-1} mol^{-1}). Kinetic parameters such as energy, enthalpy, and entropy of NaOH-p(AAm)-Co composite system were also determined as E_a = 20.07 $\pm$ 0.05 kJ mol^{-1}, ΔH = 17.66 $\pm$ 0.33 kJ mol^{-1} and ΔS = −162.12 $\pm$ 0.07 J mol^{-1} K^{-1}, respectively. The other kinetic parameters such as reaction rate constants were given in Table I. As can be seen, the k values

Table I. The Amounts of Metal Nanocatalyst, Rate Constants, Hydrogen Generation Rates and Kinetic Parameters for Hydrolysis Reactions of NaBH$_4$ at Different Temperatures for NaOH Modified-p(AAm)-Co Catalyst Systems

Metal composites	Amount of metal nanoparticles (mg)*	T(K)	k x10^{-3} (mol/min)	TOF mol H$_2$ (mol catalyst.min)$^{-1}$	Ea (kJmol^{-1})	ΔH (kJmol^{-1})	ΔS (Jmol^{-1}K^{-1})
NaOH-p(AAm)-Co	21.85 $\pm$0.22	303$\pm$0.5	3.7$\pm$0.1	2.10$\pm$0.02			
		313$\pm$0.5	4.91$\pm$0.2	2.64$\pm$0.03	20.36$\pm$0.05	17.72$\pm$0.33	−162.26$\pm$0.07
		323$\pm$0.5	6.46$\pm$0.3	3.20$\pm$0.04			
		333$\pm$0.5	7.80$\pm$0.1	4.135$\pm$0.06			

*The amount of metal nanoparticles inside 0.1 g dried NaOH-p(AAm)hydrogel (mg)

Table II. Reusability, and the Change in Catalytic Activity of 0.1 g NaOH-p(AAm)-Co Metal Composites in NaBH$_4$ Hydrolysis [Reaction Conditions: 50 mL 50 mM, 30°C, 1000 rpm and Contain 21.85 mg Co nanoparticles]

Number of reuse	1	2	3	4	5
% Conversion	100	100	100	100	100
% Activty	100±0.7	95.79±1.3	88.05±0.6	84.30±1.5	80.05±1

for the hydrolysis reaction increased to 7.8 × 10^3 from 3.7 × 10^3 (mol min^{-1}) by increasing the reaction temperature from 30 to 60°C. The kinetic parameters of modified NaOH-p(AAm)-Co composite systems are interestingly lower in comparison to the other catalyst systems in the literature such as p(SPM)-Co, p(AMPS)-Co and p(VI)-Co.[27,30,31] In addition, Total Turnover Frequency (TOF) values of modified p(AAm)-Co composite catalyst systems were determined for all temperatures and given in Table I. The TOF value is defined as the moles of produced H$_2$ per unit time per moles of catalyst. From Table I, the TOF values of NaOH-p(AAm)-Co composite system was calculated as 4.135 ± 0.06 mol H$_2$ (mol catalyst min)$^{-1}$ for 60°C, while the TOF value of same catalyst was found as 2.10 ± 0.02 mol H$_2$ (mol catalyst min)$^{-1}$ for 30°C.

The Reusability of Modified p(AAm)-Co Composite Systems in NaBH$_4$ Hydrolysis

The repetitively use of NaOH-p(AAm)-Co metal catalyst systems were carried out in the hydrolysis reactions of NaBH$_4$ to determine the reuse feasibility of the composites catalyst system. The losses in the catalytic activities were determined by taking initial hydrolysis reaction rate to the next hydrolysis reactions carried out at the same reaction condition as described earlier. The H$_2$ generation reactions carried out for the first time by using 0.1 g NaOH-p(AAm)-Co metal composite, then this NaOH-p(AAm)-Co metal composites were removed from reaction medium and washed with plenty of water, and again immersed in the same reaction hydrolysis reaction condition for second time, and this procedure repeated 5 times successively. As the results were given in Table II, the conversions of NaBH$_4$ by NaOH-p(AAm) catalyst systems is 100% every time, but the catalytic activity decreased to 80% from 100% at the end of the fifth use. The catalytic activity is calculated by taking the first hydrolysis rate (or H$_2$ generation rate) to the rate of every use. The metal nanoparticles content of NaOH-p(AAm) hydrogels did not change after each use as we determined by AAS measurements, however, it was reported the accumulation and formation of sodium metaborate (NaBO$_2$) on the surface area of metal catalyst cause a decrease in the catalytic performances of common catalysts.[3,19,27,30,31,35] It is also possible that the oxidation of metal nanoparticle can occur due to their contact with air, water, and the carboxylic acid on modified NaOH-p(AAm)-Co hydrogel causing a decrease in catalytic performances.

CONCLUSIONS

Here, we demonstrated a simple modification of p(AAm) hydrogel by NaOH treatment, and the use of this NaOH-p(AAm) hydrogel for *in situ* metal nanoparticle such as Co and Ni preparation. In addition to the easily synthesis and simple chemical modification, NaOH-p(AAm) hydrogels showed higher

swelling ratio, and higher metal ions capability properties owing to the newly formed carboxylic acid groups enabling this material as soft template in the preparation of metal nanoparticles from the absorbed metal ion by treatment of NaBH$_4$ with metal ion laden modified hydrogel network. Then this NaOH-p(AAm)-M (M:Co, Ni) composites were shown to be highly effective in H$_2$ generation from the hydrolysis of NaBH$_4$. Furthermore, NaOH-p(AAm)-Co catalyst systems showed superior catalytic performance in H$_2$ generation from NaBH$_4$ hydrolysis. Due to numerous advantages of this novel catalyst support, following deduction were made by this investigation:

- This facile modification technique provided chemical conversion of neutral amine groups to highly ionizable carboxylic acid groups resulting in highly swelling and metal ion absorption capabilities that also lead *in situ* metal nanoparticle preparation with high metal content for catalytic application.
- Novel NaOH-p(AAm)-Co catalyst systems have comparably low activation energy and enthalpy such as 20.07 ± 0.05 kJ mol^{-1} and ΔH=17.66 ± 0.33 kJ mol^{-1} in comparison to many catalyst systems which have been reported earlier in the literature.[19,27,30,31,35]
- Highly active NaOH-p(AAm)-Co catalyst systems have shown reusability in repetitive use experiments of up to five times without significant loss in their catalytic activity with 100% conversion in every use.

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