# Controllable hydrogen generation by use smart hydrogel reactor containing Ru nano catalyst and magnetic iron nanoparticles

Nurettin Sahiner [a,b,*], Ozgur Ozay [a], Erk Inger [c], Nahit Aktas [d]

[a] Canakkale Onsekiz Mart University, Faculty of Sciences and Arts, Chemistry Department, Terzioglu Campus, 17020, Canakkale, Turkey
[b] Nanoscience and Technology Research and Application Center (NTRAC), Terzioglu Campus, 17020, Canakkale, Turkey
[c] Gazi University, Institute of Science and Technology, Mechanical Engineering Department, 06500, Ankara, Turkey
[d] Yuzuncu Yil University, Faculty of Engineering, Chemical Engineering Department, 65080, Van, Turkey

## ARTICLE INFO

## ABSTRACT

In this study, p(AMPS) hydrogels are synthesized from 2-acrylamido-2-methyl-1-propansulfonic acid (AMPS) via a photo polymerization technique. The hydrogels are used as template for metal nanoparticles and magnetic ferrite nanoparticles, and also as a catalysis vessel in the generation of hydrogen from the hydrolysis of NaBH$_4$. Approximately 5 nm Ru (0) and 20–30 nm magnetic ferrite particles are generated *in situ* inside this p(AMPS) hydrogel network and then used as a catalysis medium in hydrogen production by hydrolysis of sodium boron hydride in a basic medium. With an applied external magnetic field, the hydrogel reactor, containing Ru and ferrite magnetic particles, can be removed from the catalysis medium; providing on-demand generation of hydrogen. The effect of various parameters such as the initial concentration of NaBH$_4$, the amount of catalyst and temperature on the hydrolysis reaction is evaluated. The activation energy for hydrogen production by Ru (0) nanoparticles is found to be 27.5 kJ mol$^{-1}$; while the activation enthalpy is 30.4 kJ mol$^{-1}$. The hydrogen generation rate in presence of 5 wt% NaOH and 50 mg p(AMPS)-Ru catalyst is 8.2 L H$_2$ min$^{-1}$ g Ru.

## 1. Introduction

Hydrogels, referred to as intelligent materials (smart materials) due to their responsiveness to small changes in their environment, are crosslinked polymeric networks. They can imbibe large amounts of water and swell owing to hydrophilic groups (–SO$_3$H, –COOH, –NH$_2$) in their polymeric chains [1–3]. Due to these features, hydrogels have a wide range of applications in various areas including medical fields, environmental fields, sensors, separation and purification processes [1–9]. In addition to these applications, hydrogels have been used as supporting materials in order to prepare metal nanoparticles [3–9]. Metal nanoparticles are used in various applications ranging from antimicrobial materials and sensors to catalysts [4–6]. In their utilization as catalyst the most important problem is aggregation, which causes a reduction in catalytic activation of metal particles [8,9]. In order to overcome this problem, metal particles can be prepared by using support materials such as zeolite [10–12], carbon [13,14], graphite [15], resin [16], polymer [17], clay [18] and hydrogels [3–9].

Hydrogen is assumed to be environmentally friendly, renewable and a clean energy carrier due to its high efficiency and power density, and zero emission of pollutants [9,19,20]. Many researchers have focused their attention on hydrogen production from chemical hydrides such as CaH$_2$, LiH, NaBH$_4$, MgH$_2$, LiAlH$_4$ and NH$_3$BH$_3$ [8–11,21–23]. Among these hydrogen storage materials NaBH$_4$ is the most widely used owing to its advantages, such as nontoxic properties, high hydrogen storage capacity (10.8%), nonflammability of the basic aqueous solution, stability in air, easily controlled hydrogen generation rate [24–27]. In the presence of a catalyst, the hydrolysis of basic aqueous sodium borohydride solution is exothermic and yields two fold more hydrogen than its content according to the following equation [8,9]:

$$(1) \quad NaBH_4 + 2H_2O \xrightarrow{catalyst} NaBO_2 + 4H_2$$

Recently, numerous metal catalyst systems such as Co nanoparticles [8,10,13,26], Ni nanoparticles [9,19,28], Co–B [18,27,29], Ru nanoparticles [12,15,17,30,31], Pt particles [14], Ni–Ru nanocomposite [16], Co–Fe–B [20], Co–P–B [24], Co–Ni–P–B [25], ruthenium (III) acetylacetonate [32], and Fe–Co–B/Ni foam catalyst [33] have been reported for use in the hydrolysis reaction of sodium borohydride.

Previously we reported *in situ* metal particle preparation in 2-methyl-1-acrylamido-2-propansulfonic acid (AMPS) hydrogels and usage of *in situ* iron, nickel and cobalt nanoparticles in p(AMPS)

---

hydrogel networks as catalyst for the hydrolysis of sodium boro-hydride and the catalytic reduction of aromatic nitro compounds [3,5–9]. In this study, p(AMPS) hydrogels were loaded with ruthenium (III) via electrostatic interactions between $-SO_3^-$ groups of p(AMPS) and Ru (III) ions in solution, and then these ions, held in position inside the hydrogels, were reduced with $NaBH_4$ to produce Ru (0) nanoparticles at room temperature. The obtained hydrogel nanoparticle composite systems were employed in the hydrolysis of sodium borohydride in a basic medium for the production of hydrogen. It was found that the hydrogel-Ru composites are very effective catalysts and provide a novel reactor. Additionally, Ru (0) nanoparticles were also prepared in magnetically functionalized hydrogel networks for the first time and it is reported that the reaction can be stopped or restarted on demand by use of an externally applied magnetic field to remove the catalyst system (hydrogel-metal nanoparticles) from the reaction media. Various parameters, such as NaOH concentration, the amount of catalyst, $NaBH_4$ concentration, and temperature, effects on the reaction rate and the conversions were investigated.

## 2. Experimental

### 2.1. Materials

For hydrogel synthesis, 2-acrylamido-2-methyl-1-propansulfonic acid as monomer, N,N′-methylenebisacrylamide (MBA) as crosslinker, 2,2′-azobis(2-methylpropionamidine) dihydrochloride as UV initiator were purchased from Aldrich and Acros Chemical Companies. $RuCl_3$ (Merck) was used as metal ion source and $NaBH_4$ (98%) (Aldrich) as reducing agent was used for *in situ* metal nanoparticle preparation. All the reagents were of analytical grade or highest purity available, and used without further purification. The 18.2 M ohm cm (Millipore Direct-Q3 UV) distilled water was used for preparation and washing of hydrogels and in all reactions.

### 2.2. Synthesis of hydrogels and composite hydrogels

The crosslinked p(AMPS) hydrogel was prepared as reported earlier [2,3,8,9]. In brief, 0.5 mol% MBA was dissolved in 50 wt% aqueous AMPS and 0.5 mol% (with respect to monomer) UV-initiator was added to this mixture and the mixture placed in plastic straws. The straws were irradiated in a photoreactor (LUZCHEM, 420 nm, Canada) for 2 h. The obtained hydrogels were placed in DI water and washed for 24 h to remove unreacted species and dried in an oven. They were stored for use in metal particle preparation and the catalysis reactions.

The magnetic ferrite particles were prepared by modifying the reported procedure in the literature, employing 50 mg p(AMPS) hydrogels [1,2]. The obtained magnetic hydrogels were cleaned by washing with DI water for another 12 h and dried in a vacuum oven at 40 °C.

Ru (0) nanoparticles inside the hydrogel were also prepared in a similar way to that reported earlier, by the reduction of ruthenium (III) ions with $NaBH_4$ [3–9]. In brief, the cleaned and dried 50 mg p(AMPS) and magnetic p(AMPS) hydrogels were placed in 25 ml of 0.05 M Ru (III) solution. The hydrogels were kept in the metal ion solution for 24 h in a water shaker bath for the loading procedure. The amount of Ru (III) absorbed was determined from the metal ion solution using ICP-AES (Inductive Coupled Plasma-Atomic Spectrometry (Varian Liberty II AX Sequential). Again, after metal ion loading, the hydrogels were transferred to DI water for cleaning for another 24 h. Then, the metal ions inside the hydrogels were reduced by transferring these metal ion-loaded hydrogels into 50 ml 0.5 M $NaBH_4$ solution. The reduction period continued for 5 h

in a water shaker bath followed by washing procedure in DI water for 12 h. The black-colored hydrogel-metal nanoparticle composites were broken into smaller pieces and used as catalyst media on the same day. Additionally, to determine the exact amount of metal ions inside the hydrogel matrices, the metal nanoparticles were dissolved with concentrated acid (three times with 5 M HCl) and their quantification was done with ICP-AES. To get information about the metal nanoparticles embedded inside p(AMPS) matrices, Transmission Electron Microscopy (JEOL 2010) was employed. The p(AMPS)-Ru and magnetic p(AMPS)-Ru composites were ground with mortar and pestle to form powder, a drop of this powder suspended in ethanol was placed on a formvar-coated TEM grid and visualized under vacuum at an operating voltage of 200 kV.

### 2.3. Catalytic hydrolysis and kinetic studies of sodium borohydride

The catalytic activity of *in situ* prepared Ru (0) nanoparticles inside p(AMPS) hydrogels in the hydrolysis of sodium borohydride was determined by measuring the hydrogen generation rate. In all the experiments, the generated amount of hydrogen was determined by passing the generated hydrogen through 100 ml of concentrated $H_2SO_4$ to remove water vapor from the gas washing bottle via the inverted volumetric cylinder, based on the principle of substitution (filled water was replaced by produced $H_2$ gas). All the experiments were conducted three times and the constructed graphs are presented with standard deviation.

In order to determine the effect of NaOH concentration on the hydrolysis reaction of $NaBH_4$ at 30 °C and 1500 rpm mixing rate, 3.47 mg Ru nanoparticle-containing hydrogels were placed into 50 mM 50 ml $NaBH_4$ solution containing various amounts of NaOH 2.5–10 wt%.

To observe the effect of the amount of catalyst at 30 °C, different amounts of Ru (0) nanoparticle-containing hydrogels were placed into basic 50 mM 50 ml $NaBH_4$ solution (containing 5 wt% NaOH). The weights of the hydrogels were 25, 50, 75, 100, and 150 mg.

To determine the effect of initial concentration of $NaBH_4$ on the reaction rate and to assess the degree of reaction, four different concentrations of $NaBH_4$ (25, 50, 100 and 200 mM) were used, each containing 50 mg hydrogel-Ru catalyst in the presence of 5 wt% NaOH at 30 °C and 1500 rpm mixing rate.

For the kinetic studies, 50 mg hydrogel-Ru composite was used in hydrolysis of 50 mM 50 ml $NaBH_4$ solution in the presence of 5 wt% NaOH at five different temperatures with an increment of 10 °C in the range from 30–70 °C and 1500 rpm mixing rate.

To evaluate the activity and the conversion, two experiments were performed. Firstly, hydrogel-Ru catalyst weighing 50 mg was used 5 times sequentially in the reduction reaction at the standard reaction conditions (each time: 50 ml 50 mM $NaBH_4$ with 5 wt% NaOH at 30 °C and 1500 rpm mixing rate). Secondly, to determine the shelf life of the prepared composite catalyst systems, after their synthesis they were stored in DI water for 1, 5, 10 and 15 days and tested for their catalytic performances four times sequentially.

## 3. Result and discussion

### 3.1. Synthesis, characterization and determination of the amount of ruthenium particles inside p(AMPS) network

The schematic representation of magnetic ferrite and Ru nanoparticles *in situ* preparation in p(AMPS) hydrogel network is shown in Fig. 1. As can clearly be seen before and after *in situ* magnetic particle preparation inside p(AMPS) hydrogels, Ru(III)
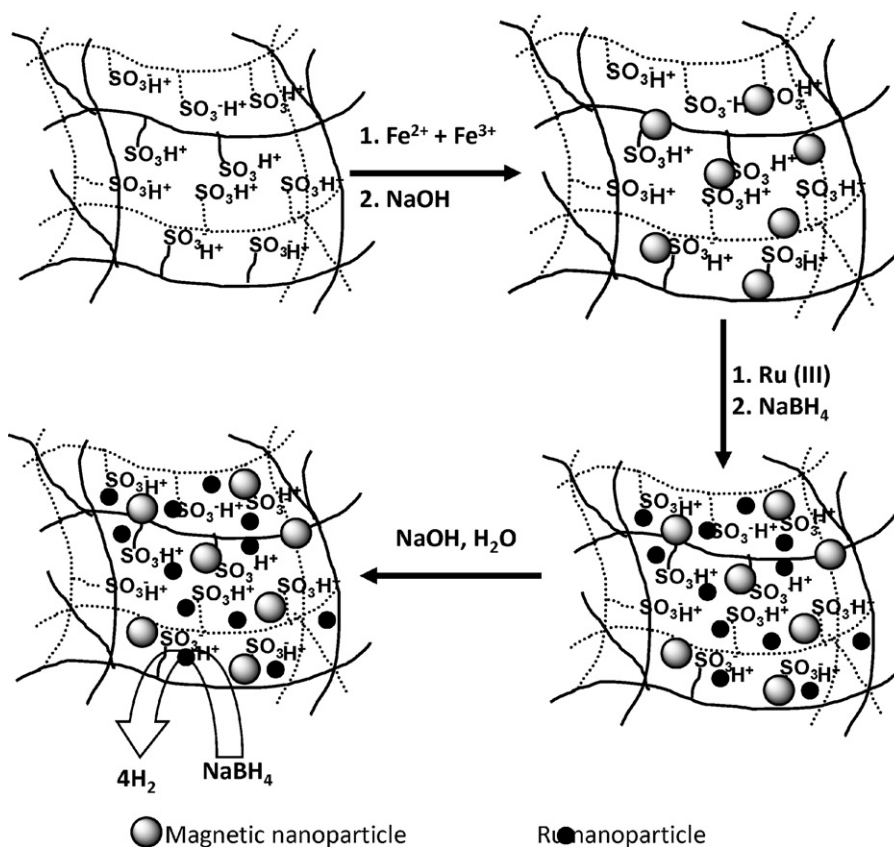
**Fig. 1.** Schematic presentation of magnetic p(AMPS) hydrogel composite and magnetic p(AMPS)-Ru composite catalyst synthesis and their use in hydrolysis reaction.

ions were loaded and reduced in the hydrogel network via the electrostatic interaction with the functional groups of the hydrogel (–SO$_3$H) and the metal ions, and then reduced with NaBH$_4$. To determine the amount of metal nanoparticles inside p(AMPS) e.g., Ru, p(AMPS)-Ru composite systems were treated with 5 M 100 ml HCl three times to elute Ru (III) and the concentration was 69.4 mg g$^{-1}$ dry gel determined by ICP-AES.

To visualize the Ru particles in p(AMPS)-Ru magnetic p(AMPS)-Ru composites TEM images are illustrated in Fig. 2. It is evident that the obtained Ru nanoparticles are much smaller (about 5 nm) than that of magnetic particles which are 20–30 nm in size, in accordance with the literature. The hydrophilic polymer network with Ru metal particles embedded in p(AMPS) hydrogel and magnetic

ferrite particles did not elute from the hydrogel matrices due to polymeric chain stabilization of the metal nanparticles [8–12]. As the EDX analysis confirms (see supporting info Fig. 1), the obtained Ru particles are amorphous whereas the magnetic ferrite particles are in crystalline form.

The control of hydrogen generation, or on-demand generation of hydrogen, is one of the main obstacles in the use of hydrogen-powered devices in real applications. Therefore, we introduced magnetic responsive behavior to metal nanoparticle catalyst-containing p(AMPS) system for the first time by the *in situ* preparation of ferrites. The iron ions (Fe (II):Fe (III) in 1:2 molar ratio) were loaded into the hydrogel and precipitated with ammonia as reported earlier [1,2]. The Ru (III) were also absorbed into
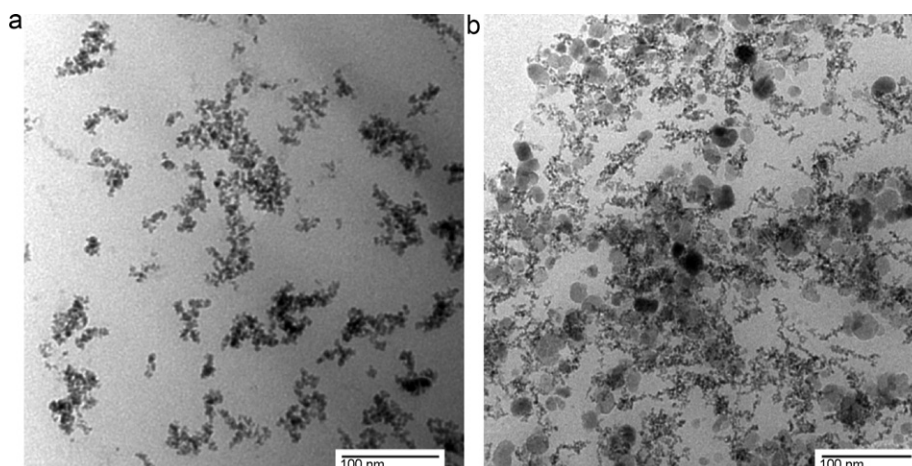


**Fig. 2.** TEM images of (a) Ru metal nanoparticles, (b) Ru and magnetic ferrites inside p(AMPS) hydrogel networks.
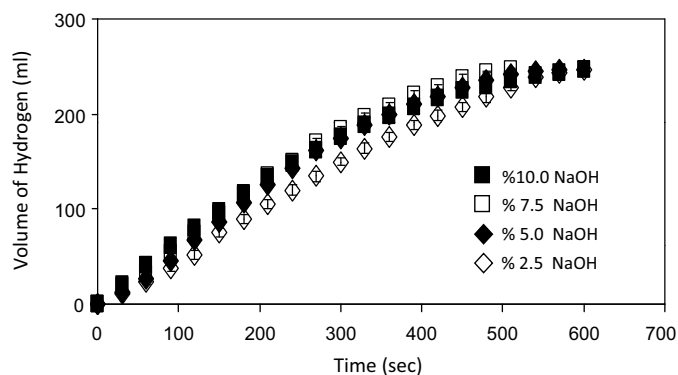
**Fig. 3.** The effect of NaOH on the hydrolysis of NaBH$_4$ [50 mg p(AMPS)-Ru composite. (containing 3.47 mg Ru nanoparticles); 50 mM 50 ml NaBH$_4$; 30 °C; 1500 rpm].

magnetic-p(AMPS) and reduced with NaBH$_4$ to generate magnetic-responsive hydrogel composites embedded in a catalyst.

### 3.2. The effect of NaOH concentration on the hydrogen generation rate

The hydrolysis of NaBH$_4$ is generally performed in a basic medium in the presence of various catalysts. To determine the optimum conditions for NaBH$_4$ hydrolysis with p(AMPS)-Ru catalyst system, NaOH concentrations were varied from 2.5 to 10 wt% at ambient temperature. Fig. 3 shows the plot of hydrogen generation versus time for different concentrations of NaOH. As illustrated in the figure in hydrolysis of NaBH$_4$ with p(AMPS)-Ru catalyst, beyond a certain amount of NaOH the production rate of H$_2$ and conversion do not change significantly and are almost the same for 5 and 10 wt% NaOH. In the hydrolysis of NaBH$_4$ (50 ml 50 mM) with 5 wt% NaOH in presence of 50 mg p(AMPS)-Ru catalyst (containing 3.47 mg Ru nanoparticles, at 30 °C and 1500 rpm mixing rate), 246 ml H$_2$(g) was generated and the yield was 99%. The hydrogen generation rate in the presence of 5 wt% NaOH and 50 mg p(AMPS)-Ru catalyst system is 8.2 L H$_2$) min$^{-1}$ g of Ru$^{-1}$.

### 3.3. The effect of catalyst amount on the hydrogen generation rate

To determine whether the amount of catalyst affected the hydrolysis rate or not, different amounts of Ru nanoparticle-containing (1.74–10.41 mg) p(AMPS)-Ru composites weighing 25–150 mg were used in the hydrolysis of 50 mM 50 ml NaBH$_4$ in presence of 5 wt% NaOH at 30 °C and 1500 rpm mixing rate. As illustrated in Fig. 4, all the reactions produced the same amount of hydrogen (246 ml) in different reaction times; as the amount of catalyst increased the reaction rate also increased. It is apparent
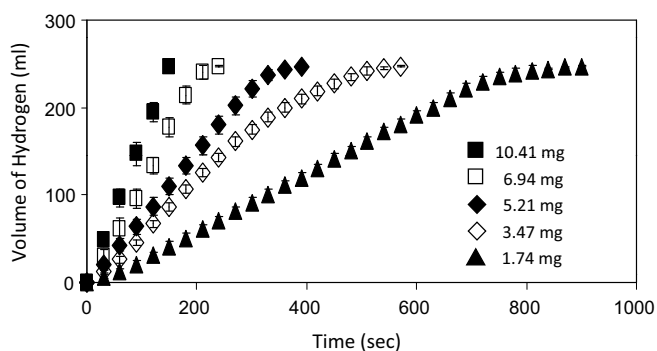


**Fig. 4.** The effect of catalyst amount on the hydrolysis of NaBH$_4$ [5 wt% NaOH; 50 mM 50 ml NaBH$_4$; 30 °C; 1500 rpm].
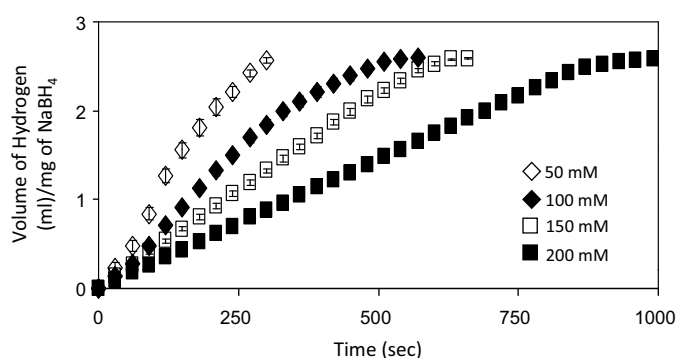


**Fig. 5.** The normalized H$_2$ production with respect to the amount NaBH$_4$ versus time [(volume 50 ml, 50 mg p(AMPS)-Ru composite (containing 3.47 mg Ru), 5 wt% NaOH; 30 °C; 1500 rpm].

from the figure, 246 ml hydrogen with 25 mg p(AMPS)-Ru (containing 1.74 mg Ru) was produced in 900 s; on the other hand, the same reaction took 150 s with 150 mg p(AMPS)-Ru composite (containing 10.41 mg Ru). An almost six fold increase in the amount of catalyst speeded the reaction six fold. Therefore, the increase in amount of catalyst increases the rate of hydrogen production almost linearly for all the reactions performed under the same conditions. The reaction is first order with respect to the amount of catalyst.

### 3.4. The effect of NaBH$_4$ concentration on the hydrogen generation rate

In order to determine the effect of NaBH$_4$ concentration on hydrolysis rate, a series of experiments at four different sodium borohydride concentrations (25 mM, 50 mM, 100 mM, and 200 mM; each 50 ml) were carried out while keeping the catalyst amount constant at 50 mg p(AMPS)-Ru composite (3. 47 mg Ru) in the presence of 5 wt% NaOH at 30 °C and 1500 rpm mixing rate. The normalized H$_2$ production with respect to the amount NaBH$_4$ versus time graph was shown in Fig. 5. As the hydrolysis reaction is zero order with respect to the initial concentration of NaBH$_4$, upon increase in the concentration of NaBH$_4$, the amount of the produced hydrogen gas is also increased. As 25 mM (47.5 mg NaBH$_4$ in 50 ml H$_2$O) NaBH$_4$ was used, 122 ml H$_2$ was produced in 300 s, and when 200 mM (380 mg NaBH$_4$ in 50 ml H$_2$O) NaBH$_4$ was used 982 ml H$_2$ gas was produced that is little less than 8 fold in 990 s. Almost there is a linear relation between the amounts of used NaBH$_4$ and the produced amounts of hydrogen as shown in supporting info Fig. 2. This figure was constructed with use of 75% of initial data with time.

### 3.5. The effect of temperature on the hydrogen generation rate

To examine the effect of temperature on the hydrolysis reaction, the catalytic hydrolysis of sodium borohydride (50 ml 50 mM) in the presence of 50 mg p(AMPS)-Ru catalyst and 5 wt% NaOH was carried out at five different temperatures in the range of 30–70 °C and an average of 246 ml H$_2$ gas was generated. At 30 °C the reaction was completed in 570 s, whereas at 70 °C the hydrolysis reaction was completed in about 180 s, almost 3 times faster than the reaction at 30 °C, shown in Fig. 6. The rate constants were determined from the linear portions of generated hydrogen volume versus time plots at five different temperatures (Fig. 6). To calculate the activation parameters for the hydrolysis reaction these rate constants at different temperatures were used and the activation energy ($E_a$), activation enthalpy ($\Delta H^{\#}$) and activation entropy ($\Delta S^{\#}$) were calculated by using the Arrhenius
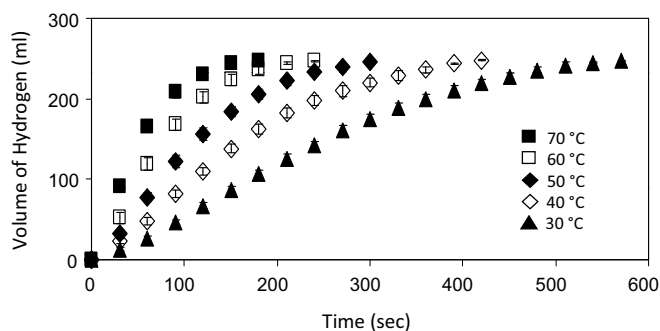
**Fig. 6.** The effect of temperature on the hydrolysis of $NaBH_4$. [(50 mM 50 ml $NaBH_4$; 50 mg p(AMPS)-Ru (containing 3.47 mg Ru); 5 wt% NaOH;1500 rpm)].



**Fig. 7.** The catalytic activities of p(AMPS)-Ru and their conversion during five consecutive runs, and their catalytic capabilities after different storage times (the inset). [50 mg hydrogel-Ru (containing 3.47 mg Ru); 50 mM 50 ml $NaBH_4$; 5 wt% NaOH; 30 °C; 1500 rpm].

and Eyring equations and were 27.5 kJ mol$^{-1}$, 30.4 kJ mol$^{-1}$, and −196.9 J mol$^{-1}$ K$^{-1}$, respectively. (see supporting information Fig. 3.)

The total turnover frequency (TOF) values calculated [12] for 30 and 70 °C were 1920 mol $NaBH_4$/mol catalyst min and 6920 mol $NaBH_4$/mol catalyst min, respectively. As can be seen the TOF values depend on the temperature, as the temperature increased the TOF values increase significantly, as reported in the literature.

The comparison of other catalyst systems with this investigation in terms of activation energies for the hydrolysis reaction of
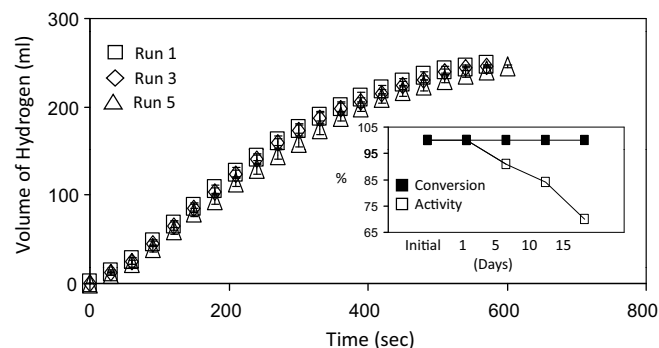
$NaBH_4$ solution is listed in supporting Table 1. As shown in the table, p(AMPS)-Ru composite catalyst provide the lowest activation energy in the catalytic hydrolysis of $NaBH_4$ solution with additional characteristics. The activation energy for the hydrolysis of $NaBH_4$ by Ru (0) nanoparticle catalyst was 27.5 kJ mol$^{-1}$. This value is in accordance with our previous studies which found values of 42.28 kJ mol$^{-1}$ for Ni (0) and 38.14 kJ mol$^{-1}$ for Co (0) [8,9]. Therefore, for the metal nanoparticles prepared in the same p(AMPS) matrix the catalytic activity is in the order Ni < Co < Ru.
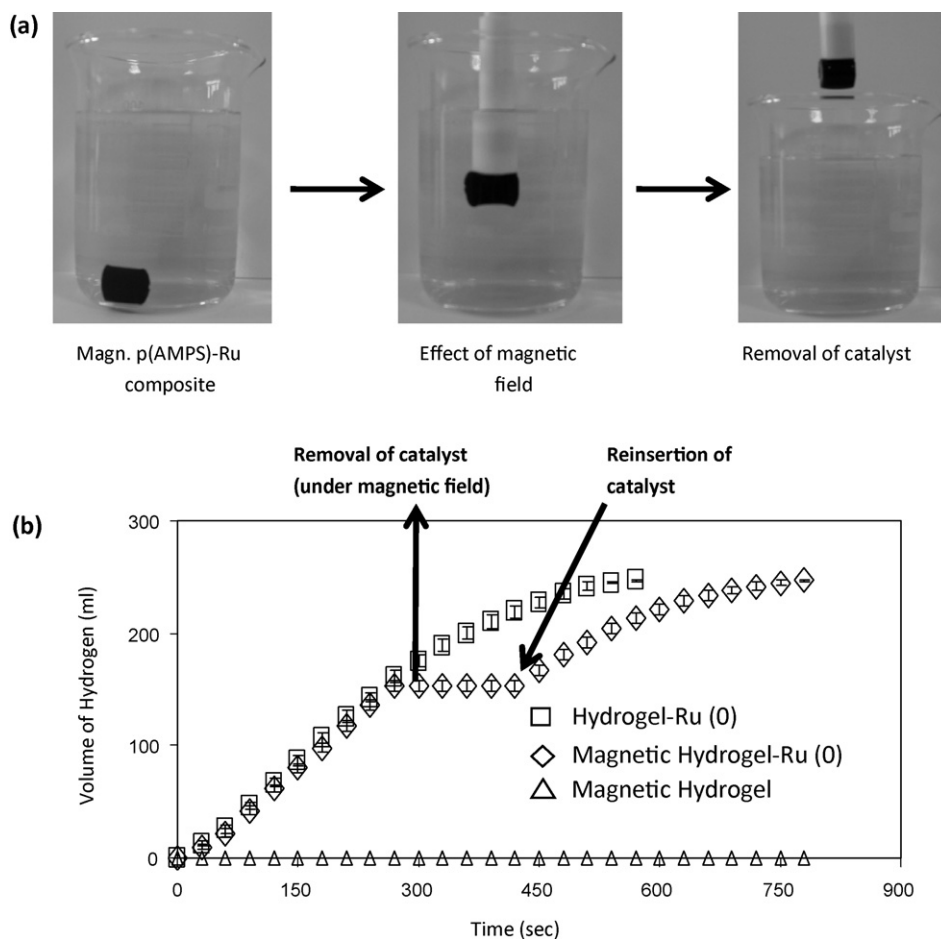


**Fig. 8.** (a) The removal of hydrogel–catalyst system during hydrolysis reaction by an externally applied magnetic field, and (b) The control of $H_2$ generation by an externally applied magnetic field on the hydrolysis of $NaBH_4$. [50 mg hydrogel-Ru (containing 3.47 mg Ru), 5 wt% NaOH; 50 mM 50 ml $NaBH_4$; 30 °C; 1500 rpm].

### 3.6. Catalytic activity test

In addition to the higher catalytic activity, readily prepared and inexpensive nature of catalyst materials, reusability is another very important characteristic of catalyst materials in industrial applications. Therefore, we investigated the reusability of p(AMPS)-Ru composite catalyst by performing 5 consecutive experiments in the same day after catalyst material synthesis. Although each time 100% conversion was obtained, the catalytic activity was reduced to 89% at the end of the 5th use as illustrated in Fig. 7. The activity was determined by taking the ratio of initial hydrogen production rate to the hydrogen production rate of every use. The values of hydrogen generation volume vs time for 1st, 3rd and 5th use of the same p(AMPS)-Ru catalysts in the hydrolysis of $NaBH_4$ is shown in Fig. 7. As can be seen every time almost same amount of $H_2$ was produced (∼246 ml). Additionally, to determine the storage capacity of the catalyst system, the prepared p(AMPS)-Ru catalyst was stored in $N_2$ bubbled DI water for up to 15 days and their conversion and activities were calculated, as illustrated in the inset of Fig. 8. It was found that the conversion and activity were 100% and 70%, respectively with 3.47 mg Ru(0) catalyst-containing hydrogel system. These materials retained a significant portion of their catalytic performance even after 15 days storage.

One other important outcome of this result is that p(AMPS)-Ru composite hydrogels can be treated with 5 M HCl and can be reused for Ru (0) nanoparticle preparation. These reloaded Ru (0) nanoparticles showed 100% catalytic activity and 100% conversion in the first use and similar characteristics in the following usages. So, the present investigation also provides a very simple and economically feasible method for renewing expensive catalyst systems after they have lost their catalytic activity; by dissolving and reloading the nanocatalysts in the template and regaining the catalytic activity from the same matrices. It could be possible to use a catalyst many times with multiple dissolution and reloading procedures and this provides significant reduction of cost for the catalyst system.

### 3.7. Effect of magnetic field on the hydrolysis of $NaBH_4$

The inclusion of magnetic ferrite particles to control the hydrogen generation from the hydrolysis of $NaBH_4$ on demand by an externally applied magnetic field is a novel concept and here, to best of our knowledge, is the first report of the use of magnetic particle-embedded hydrogel catalyst systems to control the hydrogen generation by an externally applied magnetic field. For example, the hydrogen production can be stopped by removing the hydrogel–catalyst system with a magnet from the hydrolysis medium as visually illustrated in Fig. 8(a). At 300 s in the progress of the reaction, the catalyst system was removed from the reaction mixture by an externally applied magnetic field and the $H_2$ generation was stopped. And after 150 s (450 s after initiation of the reaction), the catalyst system was reinserted in the reaction mixture, and $H_2$ production was restarted with no loss in total amounts of produced $H_2$ in comparison to continues production as shown in the figure. The magnetic particle-containing p(AMPS) cannot catalyze the hydrolysis reaction and the presence of magnetic ferrite particles do not hinder or prevent the hydrolysis of $NaBH_4$ as shown in Fig. 8(b). As illustrated in the figure, after removing the magnetic-p(AMPS)-Ru catalyst system with a magnet and reinserting back into the reaction medium the same amount of $H_2$ gas was obtained. This outcome is vital as a manifestation of the control of a magnetic catalyst system that can have other potential applications in industry and in the design of novel catalyst systems.

## 4. Conclusions

In this investigation, we report Ru and magnetic ferrite particle preparation in situ in p(AMPS) hydrogel and their utilization in the hydrolysis of $NaBH_4$. The template is a pH-responsive hydrophilic polymer network that absorbs metal ions such as Fe (II), Fe (III), and Ru (III) readily, and upon precipitation and reduction with suitable agents such as NaOH and $NaBH_4$, magnetic ferrites and metal nanoparticles/nanoclusters were obtained respectively. The introduction of magnetic particles inside the hydrogel provides a control on hydrogen production from the hydrolysis of $NaBH_4$ catalyzed by the Ru metal nanoparticle/clusters in the same hydrogel matrices. The hydrophilic hydrogel network provided stabilization for the metal nanoparticle and/or clusters. An external magnetic field was applied to the catalyst system to remove from the reaction mixture to stop hydrogen production, and then reinserted back into the reaction medium with no loss in the performance of the catalyst, even with ferrites inside the hydrogel matrices. This important outcome can also be applicable to other catalyst systems for various applications. Furthermore, it was also demonstrated that after repetitive use of p(AMPS)-metal catalyst system the metal catalyst can be dissolved by treatment with acid and reloaded into the same hydrogel matrices to supply 100% of the original catalytic performance. In conclusion, the hydrolysis reaction is zero order with respect to $NaBH_4$ amount and first order with respect to catalyst amount. The parameters that affect the hydrolysis of p(AMPS)-Ru catalyst system were the amount of catalyst (Ru), the amount of $NaBH_4$, and the pH of the medium and the temperature.

## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jpowsour.2011.08.068.

## References

[1] O. Ozay, S. Ekici, Y. Baran, S. Kubilay, N. Aktas, N. Sahiner, Desalination 260 (2010) 57–64.
[2] O. Ozay, S. Ekici, Y. Baran, N. Aktas, N. Sahiner, Water Res. 43 (2009) 4403–4411.
[3] N. Sahiner, Colloid Polym. Sci. 285 (2006) 283–292.
[4] O. Ozay, A. Akcali, M.T. Otkun, C. Silan, N. Aktas, N. Sahiner, Colloids Surf. B 79 (2010) 460–466.
[5] N. Sahiner, H. Ozay, O. Ozay, N. Aktas, Appl. Catal. B 101 (2010) 7–143.
[6] N. Sahiner, H. Ozay, O. Ozay, N. Aktas, Appl. Catal. A 385 (2010) 201–207.
[7] H. Özay, S. Kubilay, N. Aktas, N. Sahiner, Int. J. Polym. Mater. 60 (2011) 163–173.
[8] N. Sahiner, O. Ozay, E. Inger, N. Aktas, Appl. Catal., B 102 (2011) 201–206.
[9] O. Ozay, N. Aktas, E. Inger, N. Sahiner, Int. J. Hydrogen Energy 36 (2011) 1998–2006.
[10] M. Rakap, S. Özkar, Appl. Catal., B 91 (2009) 21–29.
[11] M. Zahmakiran, S. Özkar, Appl. Catal., B 89 (2009) 104–110.
[12] M. Zahmakiran, S. Özkar, Langmuir 25 (2009) 2667–2678.
[13] D. Xu, P. Dai, X. Liu, C. Cao, Q. Guo, J. Power Sources 182 (2008) 6–620.
[14] Y. Bai, C. Wu, F. Wu, B. Yi, Mater. Lett. 60 (2006) 2236–2239.
[15] Y. Liang, H.B. Dai, L.P. Ma, P. Wang, H.M. Cheng, Int. J. Hydrogen Energy 35 (2010) 3023–3028.
[16] C.H. Liu, B.H. Chen, C.H. Hsueh, J.R. Ku, M.S. Jeng, F. Tsau, Int. J. Hydrogen Energy 34 (2009) 2153–2163.
[17] C.W. Chen, C.Y. Chen, Y.H. Huang, Int. J. Hydrogen Energy 34 (2009) 2164–2173.
[18] H. Tian, Q. Guo, D. Xu, J. Power Sources 195 (2010) 2136–2142.
[19] Ö. Metin, V.S. Mazumder, S. Özkar, J. Am. Chem. Soc. 132 (2010) 1468–1469.
[20] Y.P. Wang, Y.J. Wang, Q.L. Ren, L. Li, L.F. Jiao, D.W. Song, G. Liu, Y. Han, H.T. Yuan, Ultrafine amorphous Co–Fe–B catalysts for the hydrolysis of NaBH4 solution to generate hydrogen for PEMFC, Fuel Cells 10 (2010) 132–138.
[21] F. Durap, M. Zahmakiran, S. Özkar, Int. J. Hydrogen Energy 34 (2009) 7223–7230.

[22] F. Durap, M. Zahmakıran, S. Özkar, Appl. Catal. A 369 (2009) 53–59.
[23] Ö. Metin, Int. J. Hydrogen Energy 34 (2009) 6304–6313.
[24] N. Patel, R. Fernandes, N. Bazzanella, A. Miotello, Thin Solid Films 518 (2010) 4779–4785.
[25] R. Fernandes, N. Patel, A. Miotello, Int. J. Hydrogen Energy 34 (2009) 2893–2900.
[26] Ö. Metin, S. Özkar, Energy Fuels 23 (2009) 3517–3526.
[27] J. Lee, K.Y. Kong, C.R. Jung, E. Cho, S.P. Yoon, J. Han, T.G. Lee, S.W. Nam, Catal. Today 120 (2007) 305–310.
[28] Ö. Metin, S. Özkar, Int. J. Hydrogen Energy 32 (2007) 1707–1715.
[29] N. Patel, R. Fernandes, A. Miotello, J. Catal. 271 (2010) 315–324.
[30] U.B. Demirci, F. Garin, J. Mol. Catal. A: Chem. 279 (2008) 57–62.
[31] M. Zahmakıran, S. Özkar, J. Mol. Catal. A: Chem. 258 (2006) 95–103.
[32] E. Keçeli, S. Özkar, J. Mol. Catal. A: Chem. 286 (2008) 87–91.
[33] Y. Liang, P. Wang, H.B. Dai, J. Alloys Compd. 491 (2010) 359–365.