

Metal-Ion-Containing Ionic Liquid Hydrogels and Their Application to Hydrogen Production

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ABSTRACT: A cationic hydrogel synthesized from (3-acrylamidopropyl) trimethyl ammonium chloride as poly[(3-acrylamidopropyl) trimethyl ammonium chloride] [p(APTMACl)] was put into contact with the chloride salts of metals such as CoCl₂, NiCl₂, and CuCl₂ in ethanol. The metal-loaded p(APTMACl) hydrogels were used as catalyst systems in hydrogen generation from the hydrolysis of sodium borohydride (NaBH₄) and ammonia borane. The activation energy values for the hydrolysis reaction were calculated for all of the catalyst systems and were found to be 53.43 and 26.74 kJ/mol for p(APTMACl)-[CoCl₄]²⁻ and p(APTMACl)-[NiCl₄]²⁻, respectively. These activation parameters were better than values reported in the literature for the ionic liquid metal complexes of smaller molecules used for the same purpose. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40183.

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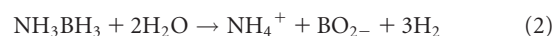
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INTRODUCTION

In recent years, in direct correlation with the increase in the world's population, an increase in fuel demand has occurred. Global warming has begun to affect the climate. These events have increased the need for new and renewable energy sources. For this reason, scientists have focused on hydrogen energy. Hydrogen is assumed to be an environmentally friendly, renewable, and clean energy carrier.¹⁻⁴ Because of the main obstacles of the storage and transport of hydrogen, chemical hydrides, such as CaH₂, LiH, MgH₂, KBH₄, LiAlH₄, sodium borohydride (NaBH₄), NH₃BH₄, and ammonia borane (AB), are generally used as hydrogen carriers and storage materials to safely obtain hydrogen on demand from their hydrolysis by aid of metal catalysts.^{1-3,5,6} NaBH₄ and AB are among the favorites and are most widely used as they are environmentally benign, nontoxic, readily obtainable, and economically feasible. NaBH₄ is exclusively attractive because of its high hydrogen storage capacity (10.8%), nonflammability, and its exothermic reaction, which allows hydrolysis even at 0°C. Most importantly, NaBH₄ yields twofold more hydrogen than its content according to the hydrolysis reaction shown as follows. The 2 mol of additional hydrogen is provided from water in the hydrolysis reaction, which is a great advantage:



Even though AB has a low molecular weight (30.7 g mol) with a high hydrogen capacity (19.6%), high water solubility (833.6 g/100 g of water), and nontoxicity with an exothermic hydrolysis reaction (the reaction enthalpy (ΔH) = -155.96 kJ/mol), it can produce at maximum the content of its hydrogen; that is 3 mol, as shown in eq. (2):^{2,7}



Although there have been many catalyst systems developed on the basis of Ru, Rh, Pt, Pd, and other transition metals in various formulations, the use of the most inexpensive ones such as Co, Ni, and Cu with similar performances in place of expensive counterparts are the most attractive because of their high reactivity, low cost, ready availability, and their ease of handling in the development of diverse formulations.⁶⁻⁹

Salts with low melting points and containing only ions in liquid form at room temperature are called *ionic liquids* (ILs). ILs have their own unique features, such as a high dissolution capacity, high conductivity, low melting point, good thermal stability, nonvolatility, and chemical stability; this makes them unique materials for many applications.¹⁰⁻¹⁵ In addition, they are generally nontoxic and, in some cases, are low-cost materials that can be obtained by simple processes. There are many applications of ILs, including catalytic media.^{10,11} Also, hydrogels, with

their highly water-swollen nature and various formulations, sizes, and morphology, can be used for the preparation of metal nanoparticles and catalysts for various reactions.^{16,17}

In the last 15 years, ILs have attracted tremendous attention because of their green chemical nature, low vapor pressure, high ionic conductivity, and low-melting-point characteristics in organic synthesis.^{11,15,18} The IL structure has many uses because of its unique physical and chemical properties. The use of ILs include solvent and catalyst support,^{11,17–23} CO₂ capture in environmental applications,²⁴ fuels,^{24,25} electrolytes for solar cells,^{24–29} and support materials for enzyme technology.^{20,23,26} In addition, ILs have been used as solvents for extraction processes,^{24,27} lubricant agents,^{16,18,24,28} supercritical fluids,²⁹ colloidal systems and colloidal crystals,^{30–34} surfactants,³⁵ and in chromatography for different purposes, for example, fixed-phase components^{18,24,35} gas chromatography and mobile-phase components in liquid chromatography,^{18,24,36} and electrolytes for capillary electrophoresis.^{24,37} ILs are also extensively used as media for a variety of organic and inorganic reactions³⁸ as dispersing agents; they are even used in chromate and uranium extraction from aqueous solutions^{39,40} and as antimicrobial and embalming agents.⁴¹

In this study, a novel polymeric ionic crystal hydrogel was prepared from a cationic hydrogel [poly[(3-acrylamidopropyl) trimethyl ammonium chloride] [p(APTMACl)]] containing metal ions such as Co(II), Ni(II), and Cu(II) that were loaded from alcoholic media. The corresponding metal salts were dissolved in ethyl alcohol, put into contact with the cationic hydrogel, and then used directly in the catalysis of NaBH₄ and NH₃BH₃ hydrolysis to generate hydrogen. The prepared metal-ion-loaded ILs of the p(APTMACl) hydrogel demonstrated better catalytic performance in terms of turnover frequency (TOF) values, reuses, and activation energies (E_a 's) compared to molecular liquids.

EXPERIMENTAL

Materials

A hydrogel based on (3-acrylamidopropyl) trimethyl ammonium chloride (APTMACl) monomer was prepared with *N,N'*-methylene bisacrylamide as a crosslinker and *N,N,N',N'*-tetramethyl ethylene diamine as an accelerator, which were used as received and purchased from Sigma-Aldrich and Acros Chemical Co. NiCl₂·6H₂O (Riedel de Haen), CoCl₂·6H₂O (Aldrich), and CuCl₂·2H₂O (Aldrich) as metal-ion sources and NaBH₄ (Aldrich) as a reducing agent were used for *in situ* metal nanoparticle preparation within the cationic p(APTMACl) hydrogel. NaBH₄ was used as a hydrogen source in the hydrolysis reaction. All of the reagents were analytical grade or of the highest purity available and were used without further purification.

Cationic p(APTMACl) Hydrogel Synthesis and *In Situ* Metal Particle Preparation

p(APTMACl) cationic hydrogels were synthesized according to a procedure in the literature with some modifications.^{42–44} The cationic p(APTMACl) hydrogels were synthesized via a redox polymerization technique. In brief, in a certain amount of APTMACl solution, 0.25 mol % *N,N'*-methylene bisacrylamide with

respect to the total monomer amount as the crosslinking agent was dissolved through thorough mixing with a vortex mixer. Then, to this solution, 5 μL of *N,N,N',N'*-tetramethyl ethylene diamine was added, and finally, the initiator solution ammonium persulfate (APS) (1 mol % with respect to the monomer) in 100 μL of water was included. When mixing was complete, the solution was injected into plastic straws with a 5 mm diameter and allowed to polymerize and crosslink at ambient temperature for 12 h. The formed cationic p(APTMACl) hydrogels were removed from the plastic straws, cut into 6 mm long cylinders, and cleaned by placement in deionized (DI) water for 72 h. We washed the cationic p(APTMACl) hydrogels by placing them in excess amounts of water and replenishing the wash water every 8 h to remove unreacted species (monomer, polymer, crosslinker, accelerator, and initiator). After the cleaning procedure, the p(APTMACl) hydrogels were dried in an oven at 40°C to a constant weight and kept in sealed containers for absorption experiments and swelling studies. The synthesis of metal nanoparticles inside the cationic p(APTMACl) hydrogel network was carried out with 100 mg of dried p(APTMACl) hydrogel according to a procedure in the literature.^{39–42,45} The amounts of the metals were 4.041, 4.044, and 2.029 g for NiCl₂·6H₂O, CoCl₂·6H₂O, and CuCl₂·2H₂O, respectively, and they were dissolved in 50 mL of ethanol (EtOH) and stirred at room temperature for 24 days. When the metal was loaded in the EtOH solution into the hydrogel, the metal-loaded hydrogels were separated by decantation. The hydrogel composite was then washed with DI water several times and dried in oven at 40°C for 4 h.¹⁰

Characterization and Swelling Behavior of the Cationic p(APTMACl) Hydrogel

The swelling studies of the cationic p(APTMACl) hydrogels were carried out in triplicate at room temperature with DI water. The mass increase was periodically measured by the removal of the cationic p(APTMACl) hydrogels from DI water and weighing after blot drying with filter paper to remove the surficial water. Then, the hydrogels were returned to the same swelling media. Cationic p(APTMACl) hydrogels were kept in the swelling medium for 24 h to determine the swelling percentage values (% *S*). The % *S* values were calculated with eq. (3). About 0.01 g of the dried cationic p(APTMACl) hydrogel was placed in 50 mL of DI water, and the mass increase with time was calculated. The % *S* was calculated as follows:

$$\%S = [(M_t - M_0) / M_0] \times 100 \quad (3)$$

where M_0 and M_t are the initial mass and the mass at time t , respectively. All of the experiments were carried out in triplicate, and the average values are reported in the data.

To investigate the thermal behavior of the cationic p(APTMACl) hydrogels, samples of approximately 4–6 mg were placed in a ceramic crucible of a thermogravimetric analyzer (SII TG/DTA 6300) and heated up to 1000°C from 50°C under N₂ with a 100 mL/min flow rate at a 10°C/min heating rate, and the weight loss against temperature was recorded.

To investigate the magnetic susceptibility of the cationic bare p(APTMACl) and metal-salt-loaded hydrogels, approximately 0.5–1-g samples were placed in the glass tubes of a magnetic

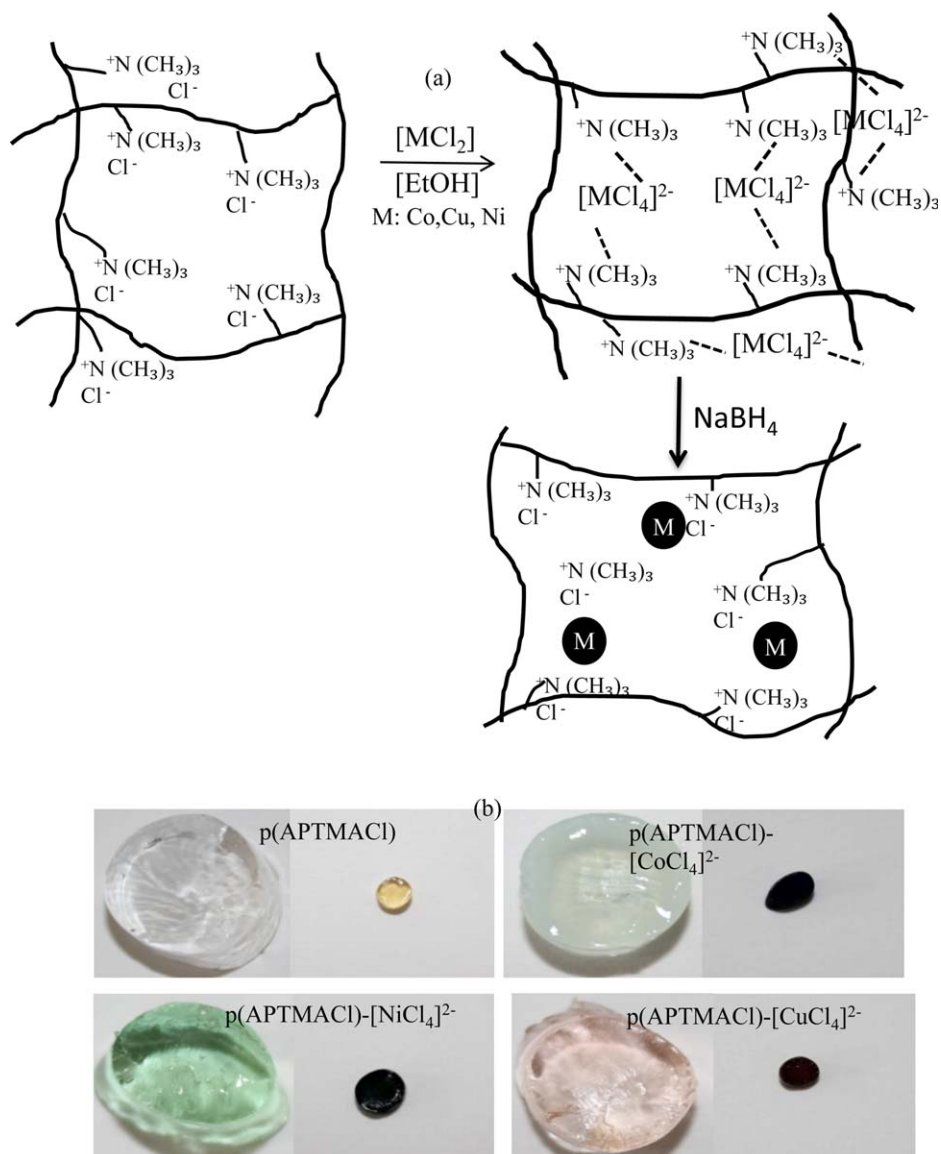


Figure 1. (a) Schematic representation of the re-preparation of metal nanoparticles in a hydrogel network and $[MCl_2]$ is metal chloride. (b) corresponding digital camera images of the $p(\text{APTMACl})\text{-}[\text{CoCl}_4]^{2-}$, $p(\text{APTMACl})\text{-}[\text{NiCl}_4]^{2-}$, and $p(\text{APTMACl})\text{-}[\text{CuCl}_4]^{2-}$ hydrogels (water-swollen and dry). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

susceptibility balance (MSB; MSB mk1, Alfa Aesar) for measurement:

$$X_g = \left\{ \frac{NE [\text{Length of tube filled (cm)}]}{\text{Mass of sample in tube (g)} \times C \times (R - R_0)} \right\} \quad (4)$$

where X_g is the mass susceptibility; R and R_0 are the empty tube and sample masses in the tube, respectively; and C is a constant with a value of 1×10^{-9} .

Catalytic Performances of $[\text{CoCl}_2]$ -, $[\text{NiCl}_2]$ -, and $[\text{CuCl}_2]$ -Loaded Cationic $p(\text{APTMACl})$ Hydrogel Networks for Hydrogen Production

The cationic $p(\text{APTMACl})$ hydrogels loaded with $[\text{CoCl}_2]$, $[\text{NiCl}_2]$, and $[\text{CuCl}_2]$ in EtOH were used in hydrogen production from the hydrolysis of NaBH_4 and NH_3BH_3 . The amounts

of metal ions within $p(\text{APTMACl})$ were determined by the treatment of the metal-salt-loaded hydrogel with 50 mL of 5M HCl for 24 h, and the amount of dissolved metal ions was calculated via atomic absorption spectroscopy (AAS; Thermo, ICA 3500 AA SPECTRO).

To determine the catalytic performances of the $p(\text{APTMACl})\text{-}M$ hydrogel composite system (where M is $[\text{CoCl}_4]^{2-}$, $[\text{NiCl}_4]^{2-}$, or $[\text{CuCl}_4]^{2-}$), a certain amount of the hydrogel composite catalyst (100 mg) was placed in 50 mL (0.097 g) of a 50 mM NaBH_4 solution at a 1000 rpm mixing rate. The same reaction conditions were also fixed for the hydrolysis of NH_3BH_3 (0.077 g in 50 mL of water) with $p(\text{APTMACl})\text{-}[\text{CuCl}_4]^{2-}$. In all of the hydrogen generation experiments, we measured the amount of produced hydrogen by passing the generated hydrogen through 100 mL of concentrated H_2SO_4 to remove the water

vapor as the reactions were run in an aqueous solution of NaBH_4 via a gas washing setup from an inverted volumetric cylinder. All of the experiments were repeated three times, and the constructed graphs are presented with standard deviations. To determine the effect of the NaOH amount, the hydrolysis reaction was carried out in the presence of different amounts of NaOH-containing (1–10 wt %) solutions.

To evaluate the temperature effect of the hydrolysis reaction on the hydrogen-production kinetics, the hydrolysis of NaBH_4 catalyzed by p(APTMACI)-M and NH_3BH_3 hydrolysis catalyzed by $\text{p(APTMACI)-[CoCl}_4\text{]}^{2-}$ were carried out at different temperatures (30, 40, 50, and 60°C). In the hydrolysis experiments, 0.1 g of the p(APTMACI)-M composite was crushed and placed in 50 mL of a 50 mM aqueous NaBH_4 solution for p(APTMACI)-M and 50 mL of a 50 mM aqueous NH_3BH_3 solution for $\text{p(APTMACI)-[CuCl}_4\text{]}^{2-}$ under constant stirring rate of 1000 rpm. The hydrogen gas produced with time was recorded at different temperatures. Additionally, the hydrolysis of NaBH_4 catalyzed by $\text{p(APTMACI)-[CoCl}_4\text{]}^{2-}$ was even carried out at 0°C.

We tested the repeated use of the $\text{p(APTMACI)[CoCl}_4\text{]}^{2-}$ composite system by reuse experiments in the hydrolysis of NaBH_4 by washing the catalyst system with DI water before every use.

RESULTS AND DISCUSSION

Characterization of the p(APTMACI) , $\text{p(APTMACI)-[CoCl}_4\text{]}^{2-}$, $\text{p(APTMACI)-[NiCl}_4\text{]}^{2-}$, and $\text{p(APTMACI)-[CuCl}_4\text{]}^{2-}$ Hydrogels

The schematic representation of the cobalt, nickel, and copper loadings into the cationic p(APTMACI) hydrogel network is shown in Figure 1(a), and their corresponding digital camera images are given in Figure 1(b). As shown in the figure, the color of the p(APTMACI) changed according to the color of the metal solution.

The DI water swelling of the p(APTMACI) , $\text{p(APTMACI)-[CoCl}_4\text{]}^{2-}$, $\text{p(APTMACI)-[NiCl}_4\text{]}^{2-}$, and $\text{p(APTMACI)-[CuCl}_4\text{]}^{2-}$ hydrogels were carried out in terms of increases in mass with time. As illustrated in Figure 2, the % S curves of the bare p(APTMACI) hydrogel was much greater than those of the metal-loaded hydrogels. The maximum or equilibrium swelling percentage (% S_{max}) is the value at which no more mass increase is observed, and it was found that the equilibrium swelling values were about 10,440, 8390, 6890, and 5960 for p(APTMACI) , $\text{p(APTMACI)-[CuCl}_4\text{]}^{2-}$, $\text{p(APTMACI)-[CoCl}_4\text{]}^{2-}$, and $\text{p(APTMACI)-[NiCl}_4\text{]}^{2-}$, respectively. The greater swelling of the bare p(APTMACI) confirmed that the metal salts were loaded in anionic forms; this led to a lesser degree of swelling for $\text{p(APTMACI)-[MCl}_4\text{]}^{2-}$. % S_{max} was also studied as a function of pH for p(APTMACI) , as shown in Figure 2(a), the % S_{max} values varied between 2254 and 5059% for p(APTMACI) as function of pH (pH 2–12) and the swelling behavior was in accordance with the inherited behavior from functional groups (quaternary ammonium salts) in the literature.⁴⁵

The thermal behavior of p(APTMACI) , $\text{p(APTMACI)-[CoCl}_4\text{]}^{2-}$, $\text{p(APTMACI)-[NiCl}_4\text{]}^{2-}$, and $\text{p(APTMACI)-[CuCl}_4\text{]}^{2-}$ was investigated with thermogravimetric analysis (TGA) under a nitrogen atmosphere up to 700°C, and the corresponding thermograms are given in Figure 3(a). As shown in the thermogram,

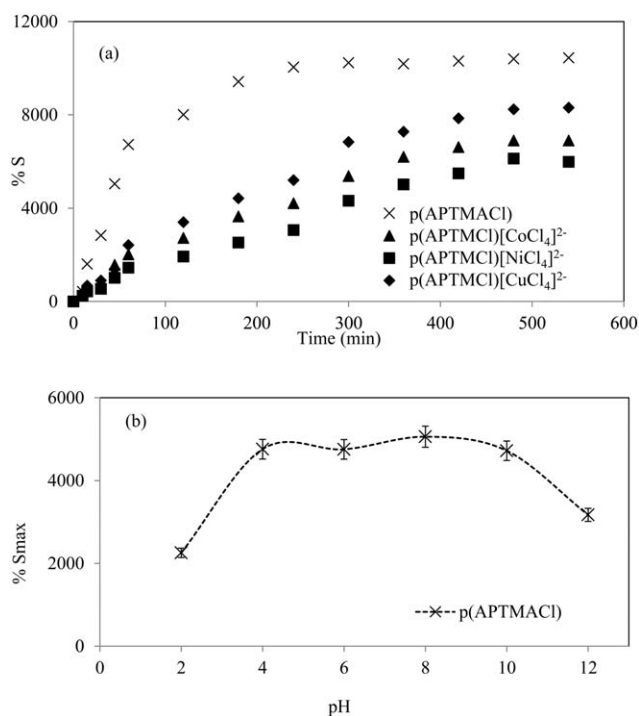


Figure 2. (a) Swelling degree (% S) of the $\text{p(APTMACI)-[CoCl}_4\text{]}^{2-}$, $\text{p(APTMACI)-[NiCl}_4\text{]}^{2-}$, and $\text{p(APTMACI)-[CuCl}_4\text{]}^{2-}$ hydrogels with time in DI water and (b) swelling degree of the $\text{p(APTMACI)-[CoCl}_4\text{]}^{2-}$, $\text{p(APTMACI)-[NiCl}_4\text{]}^{2-}$, and $\text{p(APTMACI)-[CuCl}_4\text{]}^{2-}$ hydrogels as a function of the pH (the pH was adjusted with the addition of 0.1M HCl and 0.1M NaOH).

p(APTMACI) had multiple degradation temperatures, which started at 155°C with 3 wt %, which could have been due to bound water, and the second degradation started at about 309°C and continued to 321°C with a weight loss of about 50 wt %. The third degradation continued up to 413°C with a weight loss of 84 wt %. The metal-chloride-loaded p(APTMACI) hydrogels degraded very little up to 300°C, and after that, they all had sharp degradations up to 400°C. With heating up to 700°C, the amounts of Co, Ni, and Cu were 21, 11, and 35 wt % in comparison to that of bare p(APTMACI) . As an example, the $\text{p(APTMACI)-[CoCl}_4\text{]}^{2-}$ weight loss demonstrated four-step degradations starting at about 310, 354, 472, and 559°C; these were similar to those of the $\text{p(APTMACI)-[NiCl}_4\text{]}^{2-}$ hydrogel, which also had four degradation temperatures starting at about 173, 324, 378, and 465°C. The temperature-dependent weight loss of $\text{p(APTMACI)[CuCl}_4\text{]}^{2-}$ demonstrated five-step degradations beginning at about 238, 267, 280, 363, and 379°C.

The metal-salt absorption capacity of the cationic p(APTMACI) hydrogels were determined with time. A certain amount of p(APTMACI) hydrogel was removed from the absorption medium, the metal ion solution in EtOH, and treated with 50 mL of a 5M HCl solution to dissolve the metal ions. Then, the Co(II), Cu(II), and Ni(II) ion concentrations were determined with AAS.

According to the AAS measurement results, 0.1 g of the p(APTMACI) cationic p(APTMACI) hydrogel was found to absorb 650

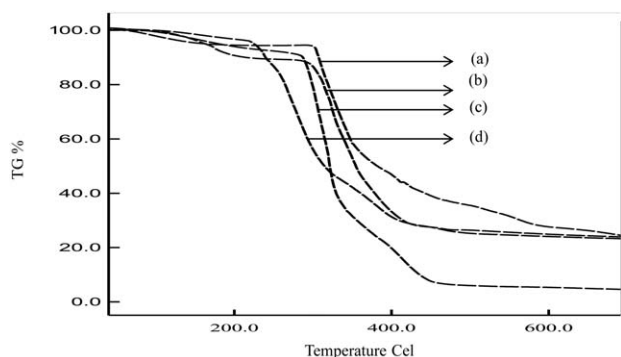


Figure 3. TGA of the (a) p(APTMACI)-[CoCl₄]²⁻ liquid hydrogel, (b) the p(APTMACI)-[NiCl₄]²⁻ liquid hydrogel, (c) the p(APTMACI)-[CuCl₄]²⁻ IL hydrogel, and (d) p(APTMACI). TG is Thermo Gravimetric.

± 5 mg/g [CoCl₄]²⁻, 87.10 ± 2 mg/g [CuCl₄]²⁻, and 391.20 ± 3 mg/g [NiCl₄]²⁻. The measurements were done five times. The constructed absorption amounts of metal ions per gram of dry p(APTMACI) with time are given in Figure 4. As shown, the absorption capacity of p(APTMACI) was much greater for the Co salt than for the other metal salts.

To determine whether the metal-loaded particles had magnetic properties, the MSB measurements were done on bare and metal-loaded p(APTMACI) hydrogels.^{46,47} As illustrated in Table I, the Co-loaded hydrogel showed an increased amount of magnetic behavior. The X_g values were found to be -5.56×10^{-7} , -1.4×10^{-6} , 7.4×10^{-7} , and -1.5×10^{-7} cgs for p(APTMACI), p(APTMACI)-[CoCl₄]²⁻, p(APTMACI)-[NiCl₄]²⁻, and p(APTMACI)-[CuCl₄]²⁻, respectively. This also confirmed the magnetic behavior of the Co materials, as reported in the literature.⁴⁷

Effects of the NaOH Concentration on the Hydrolysis Reaction

In hydrogen-production reactions from the hydrolysis of NaBH₄, the reactions are generally performed in basic media in the presence of various catalysts.^{1-3,6,8} Therefore, p(APTMACI)-[CoCl₄]²⁻-catalyzed NaBH₄ (50 mM at 30°C and with a 1000-rpm mixing rate) hydrolysis reactions containing different amounts of NaOH, namely, 1, 5, and 10 wt %, were performed with 0.1 g of p(APTMACI)-[CoCl₄]²⁻ (65 mg of Co/g of

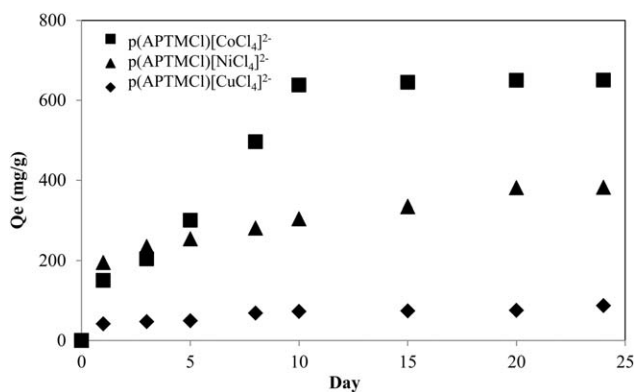


Figure 4. [CoCl₄]²⁻, [NiCl₄]²⁻, and [CuCl₄]²⁻ absorption of the p(APTMACI) hydrogels. Q_e is "Absorbed amounts".

Table I. X_g Properties of the p(APTMACI), p(APTMACI)-[CoCl₄]²⁻, p(APTMACI)-[NiCl₄]²⁻, and p(APTMACI)-[CuCl₄]²⁻ Hydrogels

	X_g (cgs)
p(APTMACI)	-5.56×10^{-7}
p(APTMACI)-[CoCl ₄] ²⁻	-1.4×10^{-6}
p(APTMACI)-[NiCl ₄] ²⁻	-7.4×10^{-7}
p(APTMACI)-[CuCl ₄] ²⁻	-1.5×10^{-7}

hydrogel). The produced amount of hydrogen versus time for each base concentration is given in Figure 5. As revealed from the figure, there was a significant relationship between the hydrolysis rate of NaBH₄ and the amounts of used NaOH. The lower the amount of NaOH used was, the faster the hydrolysis reaction rate was. This was unexpected as it is contrary to results reported earlier for other catalyst systems.⁷ The reaction rate was inversely exponentially proportional to the amount of used NaOH, as shown clearly by the hydrogen-production rates, and the hydrogen-production rate increased from 0.62 to 4.82 mL/min with the change in NaOH from 10 to 0 wt %, as shown in Figure 5(b). As the used amount of NaOH slowed down the hydrogen-production rate, the hydrolysis reactions carried out with p(APTMACI)-[NiCl₄]²⁻ and p(APTMACI)-[CuCl₄]²⁻ were performed without NaOH solution throughout

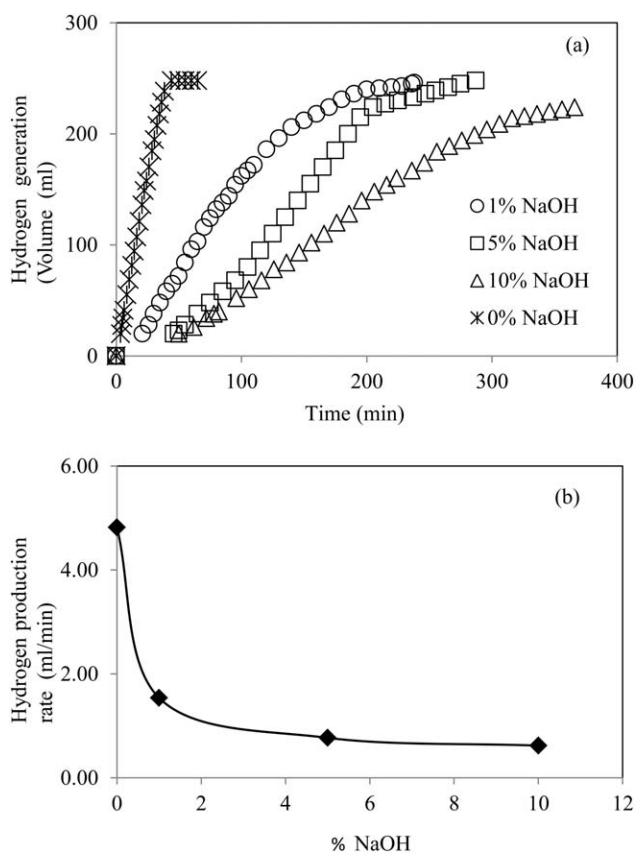


Figure 5. (a) Effect of the amount of NaOH on the hydrolysis of NaBH₄ [0.1 g of the p(APTMACI)-[CoCl₄]²⁻ composite containing 65 mg, 50 mL of 50 mM NaBH₄, 30°C, and 1000 rpm] and (b) hydrogen-production rate versus the amount of NaOH.

Table II. pH Values of the Solutions Containing p(APTMACI)-Hydrogel-Based Composite Catalyst Systems (0.1 g hydrogel, 50 mL of the 50 mM NaBH₄ at 30°C)

Hydrogel	pH	
	Hydrogel + NaBH ₄	Hydrogel + NaBH ₄ + NaOH
p(APTMACI)	9 ± 0.4	12 ± 0.4
p(APTMACI)-[CoCl ₄] ²⁻	9 ± 0.5	11 ± 0.2
p(APTMACI)-[NiCl ₄] ²⁻	8 ± 0.5	11 ± 0.2
Hydrogel	Hydrogel + AB	Hydrogel + AB + NaOH
p(APTMACI)-[CuCl ₄] ²⁻	7 ± 0.4	11 ± 0.2

the experiments. The pH values of the solution containing the p(APTMACI)-hydrogel-based composite catalyst systems (0.1 g of hydrogel, 50 mL of the 50 mM hydrogen source at 30°C) are given in Table II. It was clear that the p(APTMACI) hydrogel was inherently basic in character and showed a change in the solution properties. The reason for the increase in the effect on the reaction rate of NaBH₄ hydrolysis by NaOH addition maybe due to the reduction in activity of aqueous solutions. In general, the hydrolysis reactions catalyzed by metal nanoparticles for hydrogen generations are carried in the presence of NaOH; however, in this study, the metal salts were directly loaded into the hydrogels where they were in their ionic forms. The used NaOH could have caused the metal hydroxide precipitation within hydrogel matrices and caused a reduction in the amount of catalyst that was effective in hydrogen generation.^{48–53} Therefore, the higher the amount of NaOH was used, the lower hydrogen-

production rates were. Hence, the presence of NaOH in the hydrolysis reaction slowed the reaction rate and promoted the deactivation of metal catalysts embedded within the hydrogel network. The zero-base catalyst (NaOH) hydrolysis of NaBH₄ was a very important outcome of these IL hydrogel catalyst systems and may offer great advantages for real applications.

Effects of the Temperature on the Hydrolysis Reaction

The hydrolysis reaction in 50 mL of 50 mM NaBH₄ was carried out at 30°C and was catalyzed by p(APTMACI)-[CoCl₄]²⁻ and p(APTMACI)-[NiCl₄]²⁻. As it is very well known, Cu particles generally catalyze NH₃BH₃ hydrolysis faster than Co and Ni particles. The hydrolysis of the 50 mL of 50 mM NH₃BH₃ was done with p(APTMACI)[CuCl₄]²⁻ at 30°C under the same reaction conditions. As illustrated in Figure 6(a), the hydrolysis reaction rates of NaBH₄ catalyzed by p(APTMACI)-[CoCl₄]²⁻

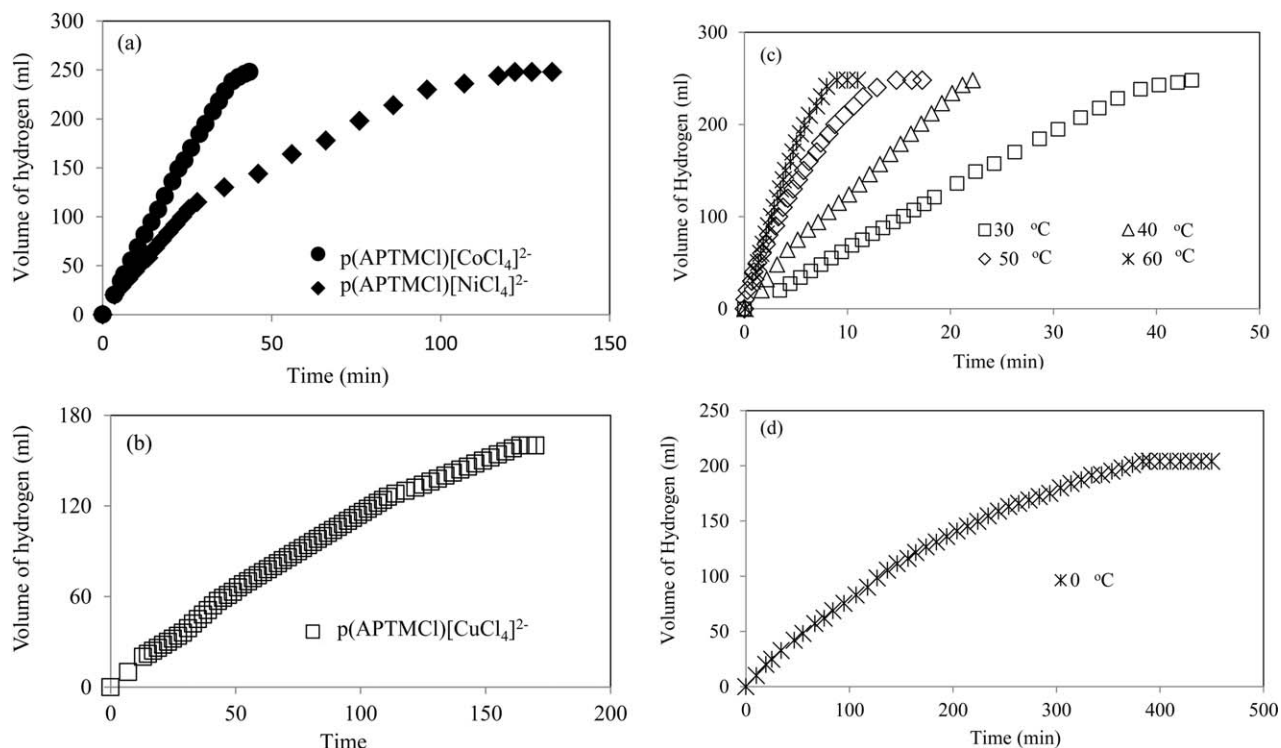


Figure 6. (a) Hydrolysis of NaBH₄ at 30°C by p(APTMACI)-[CoCl₄]²⁻, p(APTMACI)-[NiCl₄]²⁻, and (b) p(APTMACI)-[CuCl₄]²⁻ for NH₃BH₃ hydrolysis, and the effect of the temperature on NaBH₄ hydrolysis (c) between 30 and 60°C and (d) 0°C p(APTMACI)-[CoCl₄]²⁻, 0.1 g of composite containing 65 mg of Co nanoparticles (50 mM, 50 mL, aqueous solutions) at 1000 rpm].

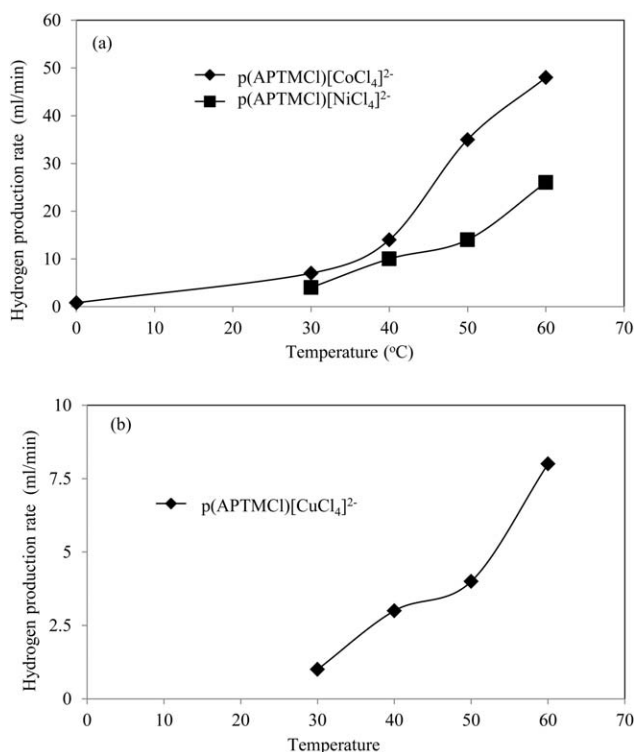


Figure 7. (a) Hydrogen-production rate versus the temperature for the hydrolysis of NaBH₄ catalyzed by p(APTMACl)-[CoCl₄]²⁻ and p(APTMACl)-[NiCl₄]²⁻ and (b) hydrolysis of NH₃BH₃ catalyzed by p(APTMACl)-[CuCl₄]²⁻.

and p(APTMACl)-[NiCl₄]²⁻ were similar, and they all produced about 248 mL of hydrogen at 30°C in about 30 and 40 min, respectively. The NH₃BH₃ hydrolysis catalyzed by p(APTMACl)-[CuCl₄]²⁻ was much slower than those of the other two catalyst composite systems, as given in Figure 6(b), and 162 mL of H₂ was produced in about 164 min.

One of the most important parameters that affect the hydrolysis rate of NaBH₄ is the reaction temperature. Therefore, NaBH₄ hydrolysis was carried out at different temperatures ranging between 30 and 60°C at 10°C increments with 0.1 mg of p(APTMACl)-[CoCl₄]²⁻ and p(APTMACl)-[NiCl₄]²⁻ compos-

ite for 50 mL of the 50 mM aqueous NaBH₄ solution. The hydrogen-production rate versus time for the hydrolysis of NaBH₄ at different temperatures catalyzed by p(APTMACl)-[CoCl₄]²⁻ is given in Figure 6(c). It was obvious that the hydrogen-production rate was directly proportional to the temperature; for example, 248 mL of H₂ was produced in about 10 min at 60°C, whereas the same amount of H₂ was produced in 44 min. It was of paramount significance that the hydrolysis of the NaBH₄ reaction could even be carried out at 0°C, as the corresponding reaction hydrogen-production rate is illustrated in Figure 6(d). Although the reaction media was full of ice crystals without mixing, the hydrogen evolution was observed to continue up to 162 mL, which was supposed to be 248 mL theoretically. The difference could have been due to the entrapment of H₂ molecules within some ice crystals. As illustrated in Figure 7(a), there was very little increase between 30 and 50°C for the hydrogen production by the Ni-loaded p(APTMACl) and a sharp increase after 50°C for both metal salts in NaBH₄ hydrolysis. The hydrogen-production rate of amine borane hydrolysis by p(APTMACl)-[CuCl₄]²⁻ is given in Figure 7(b), and it also showed similar behavior. As illustrated in Table III, the hydrogen-production rate for p(APTMACl)-[CoCl₄]²⁻ for 0 and 60°C were found to be 0.823 and 47.304 mL of H₂ min⁻¹ (g of catalyst)⁻¹. The hydrogen-production rate values were 8.571 and 45.305 for p(APTMACl)-[NiCl₄]²⁻, and 11.342 and 84.552 mL of H₂ min⁻¹ (g of catalyst)⁻¹ for p(APTMACl)-[CuCl₄]²⁻ for the amine borane hydrolysis.

As illustrated in Figure 8, the total TOF values were graphed against the temperature for all of the prepared p(APTMACl)-[MCl₄]²⁻ materials. As shown, they all obeyed natural logarithmic exponential functions for $ae^{-0.051}$ mol of H₂ (mol of catalyst × min)⁻¹ for p(APTMACl)-[CoCl₄]²⁻ and p(APTMACl)-[NiCl₄]²⁻, whereas p(APTMACl)-[CuCl₄]²⁻ in the hydrolysis of NH₃BH₃ was represented by $ae^{-0.063}$ mol of H₂ (mol of catalyst × min)⁻¹; *a* *e* was a constant that did not change very much.

To calculate the *E_a*'s for each catalyst system, the reaction rate constants were determined for all of the studied temperatures, and their values are given in Table IV. From the constructed ln *k* versus 1/*T* graphs for the p(APTMACl) composite catalyst

Table III. Hydrogen Generation Rates and TOF Values for the p(APTMACl)-Based Hydrogel Composite Catalysts

Temperature (°C)	Hydrogen generation rate		
	p(APTMACl)-[CoCl ₄] ²⁻	p(APTMACl)-[NiCl ₄] ²⁻	p(APTMACl)-[CuCl ₄] ²⁻
0	0.823		
30	8.671	5.335	11.342
40	16.589	13.561	26.959
50	22.443	21.697	46.504
60	47.692	46.494	84.552
Catalyst	$f(T) = \text{TOF mol of H}_2 \text{ (mol of catalyst} \times \text{min)}^{-1}$	Temperature (°C)	<i>R</i> ²
p(APTMACl)-[CoCl ₄] ²⁻	$y = 0.0451e^{0.51x}$	30–60	0.974
p(APTMACl)-[NiCl ₄] ²⁻	$y = 0.0181e^{0.66x}$	30–60	0.9842
p(APTMACl)-[CuCl ₄] ²⁻	$y = 0.0048e^{0.63x}$	30–60	0.9876

f(T): Turnover frequency function.

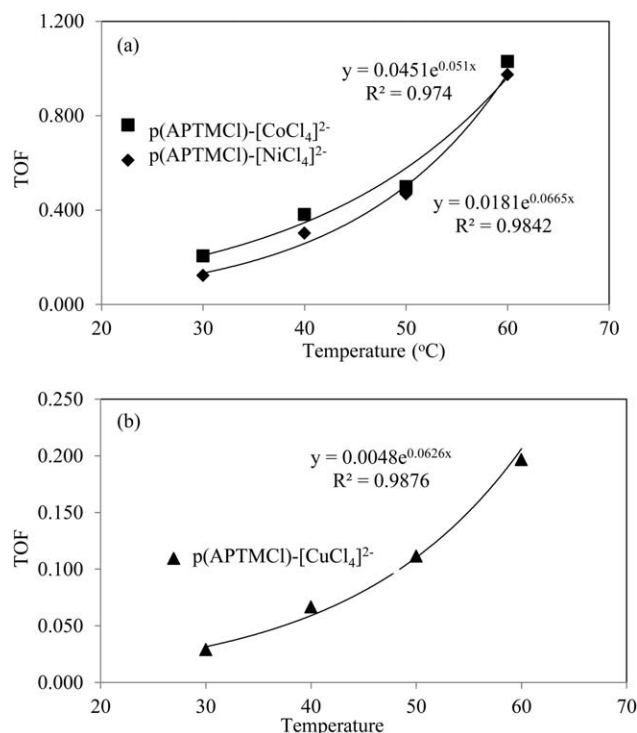


Figure 8. Effect of the temperature on TOF for the hydrolysis of NaBH₄ between 30 and 60°C catalyzed by (a) p(APTMACI)-[CoCl₄]²⁻ and p(APTMACI)-[NiCl₄]²⁻ and for the hydrolysis of NH₃BH₃ catalyzed by (b) p(APTMACI)-[CuCl₄]²⁻.

systems, the E_a values were determined and found to be 52.2 and 30.9 kJ/mol for the p(APTMACI)-[CoCl₄]²⁻ and p(APTMACI)-[NiCl₄]²⁻ composite catalyst systems. This was also very interesting: as illustrated in Table V, in the literature, the particle forms of the same metal were different from the IL forms. The E_a values for all of the Co nanoparticles were lower than those of the Ni particles but, upon the loading of the metal salts in ionic forms as in these experiments, the nickel tetrachlorate E_a values were lower than those of the cobalt tetrachlorates.¹⁰ Also, in the literature, dicationic ILs were complexed with metal chloride salts and used as catalysts in the hydrolysis of NaBH₄ and had higher E_a 's than the IL hydrogels reported here.^{10,50} The E_a value for the NH₃BH₃ hydrolysis catalyzed by the p(APTMACI)-[CuCl₄]²⁻ composite was done for the first time and was calculated to be $E_a = 61.9$ k/mol.

Table V. Comparison of the E_a Values with Similar Structures for the Hydrolysis of Chemical Hydrides

Catalyst	E_a (kJ/mol)	Reduction agent	Material structure	Reference
IL hydrogel [CoCl ₄] ²⁻	52.2	NaBH ₄	p(APTMACI)	This study
IL hydrogel [NiCl ₄] ²⁻	39.9	NaBH ₄	p(APTMACI)	This study
IL [CoCl ₄] ²⁻	75.00	NaBH ₄	C ₆ (mpy) ₂	Chinnapan A. et al. ¹⁰
IL [NiCl ₄] ²⁻	71.00	NaBH ₄	C ₆ (mpy) ₂	Chinnapan A. et al. ¹⁰
IL Ru	56.00	NaBH ₄	C ₆ (mpy) ₂	Chinnapan A. et al. ¹⁰
IL hydrogel [CuCl ₄] ²⁻	63.5	AB	p(APTMACI)	This study

C₆(mpy)₂ = 1,1'-Hexane-1,6-diylbis (3-methylpyridinium)

Table IV. Activation Parameters for the p(APTMACI)-Based Hydrogel Composite Catalyst Systems

Catalyst	E_a (kJ/mol)	ΔH (kJ/mol)	ΔS (J mol ⁻¹ k ⁻¹)
p(APTMACI)-[CoCl ₄] ²⁻	52.2	48.6	-138
p(APTMACI)-[NiCl ₄] ²⁻	39.9	36.5	-181
p(APTMACI)-[CuCl ₄] ²⁻	63.5	59.6	-117

ΔS is "the entropy"

Reusability of the p(APTMACI)-[CoCl₄]²⁻ Composite Catalyst in the Hydrolysis Reaction

The reusability of a catalyst system is very important. Therefore, the p(APTMACI)-[CoCl₄]²⁻ composite catalyst system was tested 10 times in the hydrolysis of the NaBH₄ reaction in the same day, and the percentage conversion and activity of the catalyst system was calculated. The corresponding graph is given in Figure 9. The conversion was calculated on the basis of the theoretical amount that half of the produced hydrogen came from 50 mL of 50 mM NaBH₄ and the other half came from the water in the medium. We calculated the activity by taking the ratio of the initial hydrogen-production rate to the following hydrogen-production rate in repetitive use. As illustrated in Figure 9, the conversion was 100% in every use up to 10 times, and the catalytic activity was 100% even after the third use, decreased to 97% at the fourth use, and was 94% at the 5th use. This was very important in comparison to the other studies carried out with metal nanoparticles.^{6,8-10} Even after up to 10 repeated uses, a 65% activity was still attainable. These kinds of reductions in the catalytic activities were also observed in similar studies.^{6,8-10} The reduction in the catalytic activity of the catalyst system was due to the formation of sodium metaborate (NaBO₂), which accumulated on the surface of the metal catalyst in every use and reduced the catalytic activity. However, the obtained results in this investigation were noteworthy in terms of the reusability of the p(APTMACI)-[CoCl₄]²⁻ composite catalyst system in real applications without any significant loss in the catalytic performance.

CONCLUSIONS

Here, for the first time, cationic hydrogels containing metal salts were reported as IL soft materials and were illustrated to be very effective in hydrogen generation from the hydrolysis of

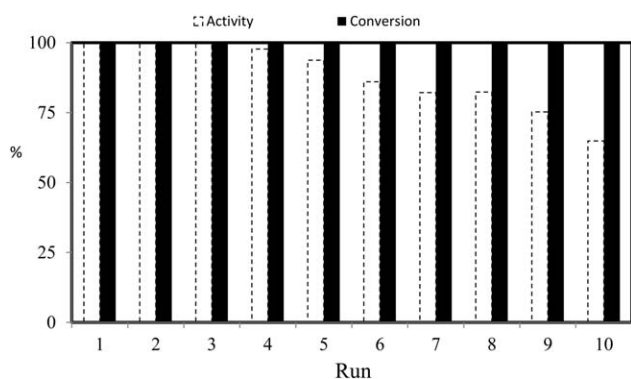


Figure 9. Change in the conversion and activity of the p(APTMACl)-[CoCl₄]²⁻ composite catalyst system over 10 consecutive uses for the hydrolysis of NaBH₄.

NaBH₄ and amine boranes. It is very important to note that metal ions are generally loaded from aquatic environments into functional materials that have functional groups such as —NH₂, —COOH, —SO₃H, and —PO₃H₂. In this study, on the other hand, quaternary ammonium salt functionality containing hydrogels [—N⁺(CH₃)₃Cl⁻] were used successfully to load metal salts in a molecular form and then used in hydrogen production from the catalysis of hydrides.

In summary, in this investigation, we came to the following conclusions:

- The cationic p(APTMACl) hydrogel provided a novel template matrix for metal-ion loadings from alcoholic environments and could be used in the hydrolysis of AB and NaBH₄ without NaOH at room temperature.
- The E_a 's for the hydrolysis reactions of NaBH₄ with p(APTMACl)-[CoCl₄]²⁻ and p(APTMACl)-[NiCl₄]²⁻ catalysis were found to be 52.2 and 30.9 kJ/mol. The E_a 's for the hydrolysis reactions of AB with p(APTMACl)-[CuCl₄]²⁻ catalysis was found to be 61.9 kJ/mol.
- Almost all of the hydrolysis of the NaBH₄ reaction was carried out in a basic medium (in the presence of NaOH), and it was also demonstrated that there was no need to use NaOH, as an increase in the amount of NaOH reduced the hydrogen-production rate.

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