



A facile synthesis route to improve the catalytic activity of inherently cationic and magnetic catalyst systems for hydrogen generation from sodium borohydride hydrolysis

Nurettin Sahiner^{a,b,*}, Fahriye Seven^a

^a Canakkale Onsekiz Mart University, Faculty of Sciences and Arts, Chemistry Department, Terzioğlu Campus, 17100 Canakkale, Turkey

^b Nanoscience and Technology Research and Application Center (NANORAC), Terzioğlu Campus, 17100 Canakkale, Turkey

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ABSTRACT

Inherently cationic poly(3-acrylamidopropyl)trimethylammonium chloride (p(APTMACI)) as hydrogel and cryogel as nonporous and superporous structures to use as template for cobalt and Nickel metal nanoparticle preparation and then H₂ production from NaBH₄ hydrolysis. Use of p(APTMACI) hydrogels in H₂ generation reactions from hydrolysis is an advantage due to their inherently cationic nature and no requirement for any modification/quaternization steps to load metal salts for in situ metal nanoparticle preparation. However, it is very well known that the metal loading processes of p(APTMACI) hydrogels are very slow. Therefore, the superporous cryogels prepared from p(APTMACI) offered great advantages in terms of swelling, metal absorption for in situ metal nanoparticle preparation, and then higher catalytic activity in hydrolysis of NaBH₄. The p(APTMACI) cryogels and their metal composites provide 32, 3600, 1.5, 5.5 and 3.5 fold faster swelling degree, swelling time, metal absorption capacity, metal absorption time and H₂ generation rate, respectively than hydrogels and metal composites. In addition, p(APTMACI)-Co metal composites are shown to have highly useful characteristics in H₂ generation reaction from hydrolysis of NaBH₄, due to their innate magnetic character, which allows control by an externally applied magnetic field, and reusability, with almost 80% at the end of 5th use.

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1. Introduction

High purity molecular H₂ is considered one of the most useful and well-known energy carriers with its cumbersome nature in storage, transportation, and production as well as distribution for on-board and off-board applications [1,2]. Until now, a number of materials were investigated as H₂ sources, such as water, natural gas, coal, plant and chemical hydrides [3–7]. Chemisorbed materials, as reversible hydrogen storage media containing chemically bound hydrogen which can be in situ released through suitable chemical reactions and conditions, may be useful in H₂ powered devices in the future. Chemical and metal hydrides exhibit an impressive volumetric H₂ storage density on material basis and therefore, they are considered one of the most promising H₂ storage resources for portable applications. Chemical hydrides are considered the most viable H₂ storage and delivery materials [8–10]. In general, NaBH₄ is investigated as the representation of

chemical hydrides as H₂ can be readily stored, and delivered through simple chemical reactions as illustrated below [11–13].



H₂ generation from the hydrolysis reaction of NaBH₄ necessitates the use of a suitable potent metal nanocatalyst. Various metal nanoparticles such as Co, Ni, Cu, Ru, Pt, and Pd are employed for H₂ generation [14,15]. Novel supports are designed and developed with varying sizes, porosity, and functionality, such as polymeric micro and nanogel, porous silica nanocomposites, core-shell structures, macro hydrogels, and highly porous cryogels, to obtain the best catalytic activity for H₂ generation from NaBH₄ hydrolysis [16–18]. Recently, much attention has focused on the polymerization of superporous cryogels that were developed to overcome the inferior characteristics of conventional hydrogels. Cryogels can be defined as materials that have 3-D networks containing connected micrometer-sized pores [19,20]. Generally, the synthesis method of cryogels includes low concentration monomer, high concentration water, and appropriate amounts of initiator and catalyst with high degree of crosslinker in subzero-reaction temperatures [21,22].

* Corresponding author at: Canakkale Onsekiz Mart University, Faculty of Sciences and Arts, Chemistry Department, Terzioğlu Campus, 17100 Canakkale, Turkey. Tel.: +90 2862180018 2041; fax: +90 2862181948.

E-mail address: sahiner71@gmail.com (N. Sahiner).

Cryopolymerization and crosslinking reactions can be accomplished by providing the reaction conditions in which ice-crystals are generated below the crystallization temperature of the solvent, and the cryogenic networks progress within the non-frozen liquid microphase known as the reaction medium where bound water, and the solute such as initiator, crosslinking agent, catalyst and monomer molecules accumulate with relatively higher concentration around ice-crystals in comparison to non-frozen conditions. Cryogels are formed in the non-frozen liquid microphase around the ice crystals that act as porogens and macroporosity occurs upon the melting of ice-crystals at room temperature, in other words macropores are constituted by melting ice-crystals [23–25]. The sizes of interconnected macro-pores of cryogels varies between about 1–100 μm according to shape, size and the formation history of the ice-crystals. In addition, specific properties such as pore size, pore wall thickness, elasticity, and mechanical strength of cryogels are highly variable depending on the preparation conditions and composition of solutions such as amounts of water, organic co-solvents, cooling rate, gradients of temperature, solute concentrations, etc. [26, 27]. Superporous cryogels can respond faster to external stimuli such as pH, solvent, and ionic strength with smaller changes than conventional hydrogels [28,29]. Superior properties of cryogels such as frost-free construction, highly porous, broad and connected pores, short diffusion pathways, absorbing water faster and releasing when mechanical strength is applied, and faster swelling/deswelling ability make them ideal materials as polymeric templates and catalyst support for metal ion absorption and in situ reduction of catalyst for use in the catalytic hydrolysis of chemical hydrides for H_2 production [28,30–32].

Various functional groups in the hydrogel networks such as $-\text{SO}_3\text{H}$, $-\text{PO}_3\text{H}$, $-\text{OH}$, $-\text{COOH}$, $-\text{NH}_2$, and $-\text{CONH}_2$ were reported for metal catalyst preparation in H_2 generation studies [15,16,32–34]. However, here cationic poly(3-(acrylamidopropyl)-trimethylammonium chloride) p(APTMAcI) cryogel that has inherently positive charge on polymer chains was used for metal nanoparticle preparation in situ to be used in the hydrolysis of NaBH_4 . The inherent cationic nature provided high metal absorption character to p(APTMAcI) cryogels without any chemical modification from corresponding metal salt solution in alcohol. Due to large and interconnected pores, fast swelling ability allowed rapid hydrolysis of NaBH_4 catalyzed by superporous p(APTMAcI)-Co cryogel-M composites in comparison to the same conventional hydrogel metal composites. Also, with inherently magnetic properties without needing magnetic ferrite preparation within cryogel networks and with fast reloading-reduction cycles of metal salts to increase metal catalyst amounts, the superporous p(APTMAcI) cryogel networks are indispensable materials for fast H_2 generation from NaBH_4 hydrolysis with versatile characteristics.

2. Materials and methods

2.1. Materials

The monomer, (3-acrylamidopropyl) trimethylammonium chloride (APTMAcI) (75 wt.%, Sigma-Aldrich), the crosslinker, N,N'-Methylenebisacrylamide (MBA) (99%, Acros), the initiator systems ammonium persulfate (APS, 99%, Sigma-Aldrich) or potassium persulfate (KPS) (99%, Sigma-Aldrich) and the accelerator N,N,N',N'-tetramethylethylenediamine (TEMED) (98% Acros) were used in preparation of cryogels and hydrogels. Cobalt(II) chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$) (99%, Sigma-Aldrich) and nickel(II) chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$) (97%, Sigma-Aldrich) were used as metal ion sources. Ethanol ($\text{C}_2\text{H}_5\text{OH}$) (99.5%, Sigma-Aldrich) was used for preparation of metal ion solutions and washing processes. Sodium borohydride (NaBH_4 , 98%, Merck) was used for preparation of metal nanoparticles and hydrolysis reactions as strong reducing agent, and as H_2 source. Sodium hydroxide (NaOH) (97%, Sigma-Aldrich) was used in H_2 generation reactions from hydrolysis of NaBH_4 . Distilled (DI) water (18.2 M Ω cm) was used for all experimental studies.

2.2. Preparation of p(APTMAcI) hydrogels and cryogels

Poly((3-acrylamidopropyl) trimethylammonium chloride) p(APTMAcI) hydrogels were synthesized by free radical polymerization with some modification of the reported technique [34–38]. The monomer, APTMAcI, 5 ml (0.0132 mol) and 0.01 g crosslinker (0.5% based on the mole of monomer) were mixed in 1 ml pure water. Separately, 0.03 g APS (1% according to total mole of monomer) was dissolved in 1 ml DI water and this solution was transferred into the monomer-crosslinker mixture. The mixture was stirred rapidly and placed within plastic pipettes (~4 mm diameter). The reaction completed in 1 h, and the obtained hydrogels were cut to about equal size, washed with water for 2 days, and dried in an oven at 40 $^\circ\text{C}$. On the other hand, the p(APTMAcI) cryogels were synthesized according to cryopolymerization technique under freezing conditions. Firstly, 0.832 g monomer (8 wt.%), 0.0842 g MBA (18%) and 50 μl TEMED were mixed in 6.168 ml DI water, and separately, 0.0083 g KPS (1%) was dissolved within 1 ml pure water. These two solutions were placed in an ice-bath for about 5 min to cool. Finally, an initiator was quickly added into monomer-solute mixture and after quick stirring, it was transferred to plastic straws (~8 mm diameter) and placed in a deep freezer at -18 $^\circ\text{C}$ for 24 h for cryopolymerization and crosslink. After the cryopolymerization reaction, the obtained cryogels were cut into equal shape/size and dried in an oven at 40 $^\circ\text{C}$.

3. Result and discussion

3.1. Characterization of super-porous p(APTMAcI) hydrogels, cryogels and their metal composites

Highly porous p(APTMAcI) hydrogels and cryogels and their metal composites were characterized by using swelling studies and visualization techniques, SEM and TEM images, and AAS and TGA analysis.

The maximum percent swelling degree of p(APTMAcI) hydrogel and cryogels was calculated as about 14,090% and 440% according to Eqs. (3) and (4). Interestingly, the swelling degree of 0.5% crosslinked p(APTMAcI) hydrogels swelled about 32 fold more than 18% crosslinked p(AMPS) cryogels.

$$\%S = \left[\frac{(m_{\text{wet hydrogel}} - m_{\text{dry hydrogel}})}{m_{\text{dry hydrogel}}} \right] \times 100 \quad (3)$$

$$\%S = \left[\frac{(m_{\text{squeezed cryogel}} - m_{\text{dry cryogel}})}{m_{\text{dry cryogel}}} \right] \times 100 \quad (4)$$

The digital camera images of swollen p(APTMAcI) hydrogels and cryogels are given in Fig. 1a and b. It took the conventional nonporous p(APTMAcI) hydrogels about 8 h to reach %S equilibrium swelling, whereas the super-porous p(APTMAcI) cryogels reached their %S equilibrium swelling in only 8 s. So, the cryogel response time, e.g., to reach maximum %Seq, is 3600 times shorter than conventional hydrogels. Even though cryogels have higher crosslinking degree (36 fold more than p(APTMAcI) hydrogels), they possess a larger connected porosity enabling them to reach swelling equilibrium within only a few seconds by absorbing lesser amounts of water inside porous networks. The highly large and interconnected pore structures of p(APTMAcI) cryogels were visualized with SEM images as illustrated in Fig. 1c and d. The structure and size of pores in thin sections of freeze-dried p(APTMAcI) cryogels were determined via Scanning Electron Microscope (SEM, JEOL). The pore sizes of p(APTMAcI) cryogels were 100–10 μm under different magnifications as seen in Fig. 1c and d. Moreover, % porosity of cryogels was calculated by using the Eq. (5), and almost 70% porosity was found.

$$\% \text{ porosity} = \left[\frac{(m_{\text{wet cryogel}} - m_{\text{squeezed cryogel}})}{m_{\text{wet cryogel}}} \right] \times 100 \quad (5)$$

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