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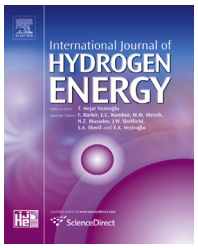

Metal nanoparticle-embedded super porous poly(3-sulfopropyl methacrylate) cryogel for H_2 production from chemical hydride hydrolysis

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ARTICLE INFO

Article history:
Received 19 May 2014
Received in revised form
30 June 2014
Accepted 8 July 2014
Available online 4 August 2014

Keywords:
p(SPM) hydrogel/cryogel
Super macroporous p(SPM)-M composite catalyst
Cryogenic hydrogel
H_2 production
Chemical hydride hydrolysis

ABSTRACT

Poly(3-sulfopropyl methacrylate) (p(SPM)) cryogel was prepared under cryogenic conditions ($T = -18$ °C) and used as template for in situ metal nanoparticle preparation of Co, Ni and Cu. These metal nanoparticle-containing super macroporous cryogel composites were tested for H_2 production from hydrolysis of sodium borohydride ($NaBH_4$) and ammonia borane (AB). It was found that amongst p(SPM)-M (M: Co, Ni, and Cu) composite catalyst systems, the catalytic performances of Co- and Ni-containing p(SPM) cryogel composite catalyst systems were the same, however in hydrolysis of NH_3BH_3, the order of performance of the catalysts was Co > Ni > Cu. Interestingly, p(SPM)-Co cryogel composite demonstrated better catalytic performances in salt environments e.g., faster H_2 production rate in sea and tap water compared to DI water, and almost no effect of ionic strength of the solution medium was observed, but the salt types were found to affect the H_2 generation rate. Other parameters that affect H_2 production rate such as metal type, temperature, water source, salt concentration, amount of metal nanocatalyst and reusability were investigated. It was found that the hydrogen generation rate (HGR) was increased to 2836 ± 90 from 1000 ± 53 (ml H_2)(g of Co min)$^{-1}$ by multiple loading and reduction cycles of Co catalyst. Also, it was found that TOF values are highly temperature dependent, and increased to 15.1 ± 0.8 from 2.4 ± 0.1 (mol H_2)(mol catalyst min)$^{-1}$ by increasing the temperature from 30 to 70 °C. The activation energy, activation enthalpy and activation entropy were determined as 40.8 kJ (mol)$^{-1}$, 37.23 kJ (mol K)$^{-1}$, and −170.87 J (mol K)$^{-1}$, respectively, for the hydrolysis reaction of $NaBH_4$ with p(SPM)-Co catalyst system, and 25.03 kJ (mol)$^{-1}$, 22.41 kJ (mol K)$^{-1}$, and −182.8 J (mol K)$^{-1}$, respectively, for AB hydrolysis catalyzed by p(SPM)-Co composite system.

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http://dx.doi.org/10.1016/j.ijhydene.2014.07.035

Introduction

Hydrogels are diverse functional group-containing materials with many applications such as template metal nanoparticle preparation and catalysis [1]. As the size of the hydrogel can be tuned from bulk to micro and/or nanometer, the pore size can also be designed as microporous (2 nm and below), mesoporous (between 50 and 2 nm) and super porous up to a few micrometer [1]. Additionally, hydrogels can be chemically modified to allow new functional groups for specific tasks e.g., metal ion absorption, etc. Interestingly hydrogels with binding ability to diverse metal ions can also be utilized for the in situ synthesis of different metal nanoparticles separately or simultaneously [1,2].

Cryogels are, on the other hand, macroporous hydrophilic materials prepared by cryo-polymerization of monomers in the presence of ice crystals under frozen conditions [3,4]. Macroporous cryogels are prepared at temperatures below the melting point of the solvent, which is generally water [5], and upon thawing; the solid crystals of solvent generate large and interconnected super macropores [6]. The crystalline structure of solvent molecules are responsible for the pores occurring in a super-macroporous and sponge-like polymeric interconnected network [7,8]. High porosity, super macropore structures up to sizes of few hundreds of microns, high mechanical strength, and elasticity provide cryogels with great advantages over hydrogels [9–11]. Cryogels can be used instead of hydrogel in many places where these sponge-like materials also have great potential applications as template for inorganic material preparation, biotechnology, tissue engineering [12], energy applications [13,14], and as drug delivery devices in pharmaceuticals [15,16].

H_2 is one of the most abundant elements on the earth, and the use of hydrogen as a clean energy carrier is attracting great attention recently as a promising alternative energy to conventional fossil fuels [17,18]. The consideration of H_2 as energy material is unavoidable due to the increasing energy demands of the world, as H_2 can also be generated from sustainable and renewable sources such as water, plants and biomass [19].

Recently, chemical H_2 storage materials such as $NaBH_4$, and AB, etc. with high hydrogen contents have been regarded as promising hydrogen sources for fuel cells [20]. $NaBH_4$ is the most commonly studied borohydride compound because of its high hydrogen storage capacity (as high as 10.8 wt%) and the great stability of its solution even in high pH range [21,22]. $NaBH_4$ generates hydrogen from a hydrolysis reaction occurring according to the following reaction (Eq. (1)) [23–25].

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

In the above reaction, various metals such as Co, Ni, Cu, Ru, Pd, Pt and their alloys can be utilized as catalysts [26,27]. The reaction byproduct sodium metaborate ($NaBO_2$) can be recycled to produce $NaBH_4$. Among the various reproduction methods such as mechanical, electrical and thermochemical processes, and H_2 production even at low temperatures can be possible with exothermic hydrolysis reactions [28–30]. The thermochemical reaction is represented as follows (Eq. (2)):

$$NaBO_2\left(s\right) + 2H_2\left(g\right) + xRe \xrightarrow{\text{Catalyst}} NaBH_4 + Re_xO_2\left(l\right) \quad (2)$$

In this reaction, Re indicates the reducing agent such as active metals (Mg, Al, Ca, etc.) and metal hydrides (MgH_2, etc) [28].

Anhydrous liquid NH_3 and BH_3 were reacted under pressure to obtain NH_3BH_3 as resource for fuel cell applications and it has high solubility in water [31]. NH_3BH_3 is stable in aqueous solution at room temperature [32]. The hydrolysis reaction of ammonia borane occurs according to Eq (3) [33]:

$$NH_3BH_3 + 2H_2O \xrightarrow{\text{Catalyst}} NH_4^+ + BO_2^- + 3H_2 \quad (3)$$

This reaction is also catalyzed with many metal-based catalysts, such as Co, Ni, Cu and their nanoparticles. Currently the catalytic hydrolysis of AB with different formulations of metal catalysts is being investigated [33–35].

Herein, p(SPM) cryogels with highly ionizable character were prepared under cryogenic conditions, and used as template in Co, Ni, and Cu nanoparticle preparation, then in the catalysis of $NaBH_4$, and AB for H_2 generation. Various parameters affecting H_2 production performance and different reaction media were tested to improve H_2 generation.

Experimental

Materials

The monomer, 3-sulfopropyl methacrylate potassium salt, (SPM, 98%, Aldrich), 1,4-dibromobutane (98%, Merck) and 1-vinylimidazole (VI, 99%, Aldrich) as cross-linker, potassium persulfate (KPS, 99%, Sigma–Aldrich) as initiator; and N,N,N′,N′-tetramethylethylenediamine (TEMED, 99%, Merck) as accelerator were used in p(SPM) cryogen preparation. Cobalt (II) sulfate heptahydrate ($CoSO_4.7H_2O$, 99%, Merck), nickel (II) sulfate heptahydrate ($NiSO_4.7H_2O$, 99%, Sigma–Aldrich), and copper (II) sulfate pentahydrate ($CuSO_4.5H_2O$, 99%, Sigma–Aldrich) were used as metal sources, and sodium borohydride ($NaBH_4$, 98%, Merck) was used as reducing agent and hydrogen (H_2) source. Also, ammonia borane (NH_3BH_3, 97%, Aldrich) was used as chemical hydride for hydrolysis reactions. Hydrogen chloride (HCl, 37%, Merck), methanol (99.9%, Sigma–Aldrich) and acetone (99.8%, Sigma–Aldrich) were used as received. NaOH (97%) was used to form the basic reaction medium for reactions and 18.2 MΩ cm DI water was used in all experiments.

Synthesis of p(SPM) cryogels

The synthesis of p(SPM) cryogels were carried out by a cryogellation technique via free radical polymerization under freezing conditions. In brief, 0.2 g (0.8119 mmol) SPM and 0.0443 g crosslinker (13.5 mol% with respect to monomer) were dissolved in 3 ml DI water and 50 μl TEMED as accelerator was added, vortex mixed then cooled in an ice bath for five min. The initiator, 0.8 ml of aqueous KPS solution (1 mol% with respect to monomer), was mixed with hydrogel precursors until a homogenous solution was obtained. Then, this solution was placed into plastic straws of 8 mm in diameter, and put in a freezer at −18 °C. The cryogellation reaction proceeded for 24 h. The obtained cryogels were cut into 1 cm