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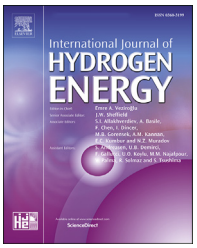

The first catalytic hydrolysis of ethylenediamine bisborane with hydrogel-supported metallic nanoparticles

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ABSTRACT

Ethylene diamine bisborane (EDB) was synthesized in a single step as the hydrogen storage material. The synthesized compound was firstly used in the literature for the production of hydrogen gas by catalytic hydrolysis reaction. Cu, Co and Ni nanoparticles with average sizes of 75–150 nm formed in p(acrylicacid-co-vinylimidazole) hydrogel network structures were used as catalysts for the hydrolysis reaction. The effect of the parameters such as catalyst type, EDB concentration, catalyst concentration, temperature and solvent environment on the catalytic hydrolysis reaction of EDB was investigated. In the activity tests for the catalyst, it was determined that the catalyst had a loss of only 15% in activity even at the end of 5 cycles. The activation energies of hydrolysis reaction were calculated as 39.42 kJmol^{-1}, 44.77 kJmol^{-1} and 47.48 kJmol^{-1} for Cu, Co and Ni hydrogel composite catalyst, respectively.

Introduction

Increasing energy demands worldwide and a reduction in fossil fuel resources are often cause energy crises. In addition, environmental pollution and greenhouse gas emissions caused by fossil fuels in recent years have led scientists to research clean and renewable energy sources [1–4]. One of the alternative energy sources that will help solve all these problems related to energy consumption is hydrogen energy. Hydrogen is traditionally produced from coal, natural gas, and petroleum derivatives and is used in vehicles as fuel for proton exchange membranes (PEM) [5–7]. The main advantages of hydrogen are high energy density (142 Mj/kg), low toxicity, low cost, being renewable and not causing environmental pollution as a result of combustion [8,9]. However, the most important disadvantage of using hydrogen energy is the difficulty of storing because of the flammability of hydrogen gas. With the overcoming of storage and security issues, hydrogen

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will be a renewable energy source that will play a key role in the energy industry in the future [10–13]. Hydrogen can be stored at low temperatures as liquid, under high pressure, with organic compounds, by adsorption/absorption methods and in metal/complex hydrides [14–16]. In recent years, hydrogen storage systems at cryogenic temperatures in insulated pressure vessels have been developed to facilitate the use of hydrogen in fuel cells. The volumetric efficiency of liquefied hydrogen in the automotive sector has improved thanks to this method developed by Aceves et al. [17,18]. Another storage method that is vital for the future of energy storage is the electrochemical hydrogen storage. In this method, hydrogen storage material is an anode of alkali fuel cells. In general, it can be said that the electrochemical hydrogen storage method plays an important role in the electrochemical power sources besides hydrogen storage [19]. However, chemical hydrides and amine borane compounds as solid hydrogen storage materials are very popular. Recently, researchers have been working on the thermolysis, hydrolysis and methanolysis of chemical hydrides such as LiH, MgH_2, CaH_2, KBH_4, $NaBH_4$, $LiBH_4$, and NH_3BH_3 [20–22].

The hydrolysis reactions of the chemical hydrides can be carried out in the presence of a catalyst such as Co (0), Pd (0), Rh (0), Pt (0), Co–B, Au–Co, Ni–Ru, and Co– or in the presence of a heterogeneous catalyst such as Cu, Fe–B, Ni–PB, Cu–Co, Co–Ni–P, and Co–Co_3O_4 [22–28]. The most important problem encountered in hydrolysis reactions is the agglomeration of metal nanoparticles and as a result, the activity of the catalyst is lost and the catalyst cannot be homogeneously distributed in the reaction medium [29–31]. In order to overcome these problems, a number of metals or alloys to be used as catalysts have been prepared in the presence of a suitable support material in the literature. For this purpose, support materials such as nanosheets, metal-organic framework, metal core-metal shell structures [26–28], various clay types, thin films, water soluble polymers, carbon, resin and recently hydrogels have been used for the preparation of the catalyst [32–34].

Hydrogels are cross-linked network polymers that swell in water due to their functional groups. In addition to their ability to hold water up to thousands of times their mass, hydrogels have the ability to respond to changes in the environment, such as electric field, temperature, pH, or solvent, by swelling or shrinking. Because of these properties, hydrogels can be used in a wide variety of fields, such as environmental technologies, controlled drug release systems, antimicrobial materials, pharmaceuticals, sensors, agriculture, tissue engineering and catalyst support materials [35–37]. Hydrogels, called intelligent materials due to their ability to respond to changes in the environment, can be designed as anionic, cationic and neutral. In particular, hydrogels synthesized using anionic monomers can electrostatically interact with positively-charged metal ions. Both these properties and their ability to swell in water make the hydrogels a unique catalyst support material for aqueous media reactions [33,38].

EDB is an important hydrogen storage material with stable structure in atmosphere and 16.3% hydrogen content. It can release some of the hydrogen present in the structure at high temperatures as hydrogen gas. In addition, it can be used as a high performance hydrogen carrier compound with a yield of 11.4% by weight hydrogen [39–41]. EDB, which is hydrolysable in aqueous media and in the presence of catalyst, has recently attracted the attention of researchers. However, the number of studies on hydrogen production from EDB is very limited in the literature. This study was planned in order to gain the first hydrolysis reaction of EDB to literature and to give direction to new studies to be carried out after this. Recently, researchers have focuse on the fuel cell applications and thermal dehydrogenation of EDB compound, one of the hydrogen carrier compounds. However, there is no literature on the catalytic hydrolysis of the EDB compound [39–41]. For this reason, EDB, an amine borane derivative compound, was synthesized as a hydrogen storage material in this study. Then, the catalytic hydrolysis of EDB was carried out in the presence of this heterogeneous catalyst. The, for use as the catalyst support material in the hydrolysis reaction, poly (acrylic acid-co-vinylimidazole) (p (AAc-c-VI)) hydrogels were synthesized by redox polymerization. Cu, Co and Ni metal nanoparticles were formed in the network structures of the synthesized polymer. In the study, the effects of variables such as the type of metal used as the catalyst, EDB concentration, and amount of catalyst, reaction medium, and temperature were investigated on the catalytic hydrolysis reaction.

Experimental section

Materials

Acrylic acid (AAc) and 1-vinylimidazole used as monomers were obtained from Sigma-Aldrich. N,N′-methylenebisacryamide (MBA) used as crosslinker, ammonium persulfate used as an initiator, and N,N,N′,N′-tetramethylenediamine (TEMED) used as accelerator in the polymerization reaction were purchased from Sigma-Aldrich and Acros Organics chemical company and used without purification. $CuCl_2.2H_2O$ (Sigma-Aldrich), $NiCl_2.6H_2O$ (Riedel-de Haen) and $CoCl_2.6H_2O$ (Fluka) were used as metal ion sources. HCl (Sigma-Aldrich) and NaOH (Merck) used in swelling tests for hydrogels, ethylenediamine dihydrochloride salt (Sigma-Aldrich), THF (Sigma-Aldrich) and methanol (Aldrich) used for the synthesis of EDB, and $NaBH_4$ (Merck) used as a reducing agent were purchased from various chemical companies. All solutions and calibration standards were prepared with distilled water.

SEM (JEOL SEM-7100-EDX), TEM (JEOL TEM-1400-EDX) and XRD (PANalytical Empyrean) devices were used for the characterization of hydrogels and hydrogel-metal composites.

Synthesis of ethylenediamine bisborane

The synthesis of EDB was carried out according to the literature [42]. For the synthesis, ethylenediamine dihydrochloride salt (36.61 mmol) and $NaBH_4$ (76.66 mmol) were suspended in 300 mL of dry THF. The reaction mixture was stirred at 1000 rpm in an argon atmosphere at room temperature for 24 h. At the end of this time, the mixture was filtered, and then the solvent was removed from the filtrate with an rotary evaporator to obtain white crystalline EDB (2.73 g, 86%).

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