Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he

Fabrication of electrospun nanofiber catalysts and ammonia borane hydrogen release efficiency

*Bilge Coşkuner Filiz, Aysel Kantürk Figen**

Department of Chemical Engineering, Yildiz Technical University, İstanbul, Turkey

ARTICLE INFO

Article history:
Received 16 December 2015
Received in revised form
28 March 2016
Accepted 28 March 2016
Available online 18 April 2016

Keywords:
Hydrogen
Ammonia borane
Electrospun
Nanofiber catalysts

ABSTRACT

In the present study, Electrospun nanofibers (Co-NF, Ni-NF, and Cu-NF) were used as efficient catalysts for hydrogen release through ammonia borane (NH_3BH_3) hydrolysis. Poly(-vinyl alcohol) solutions containing metal acetates provided sol–gel materials for electrospinning. The electrospun fibers were fabricated by a low cost and facile technique. The effects of different process parameters such as solution preparation and electrospinning conditions that directly influence the texture, crystalline phase, and chemical properties of electrospun nanofibers fibers were studied. The nanofibers were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), Brunauer–Emmett–Teller surface area (BET), and scanning electron microscope (SEM). The metal oxide-loaded nanofibers with average diameters from approximately 187 to 452 nm showed catalytic activity toward increasing NH_3BH_3 hydrogen release efficacy, with activation energies as low as 41.59 kJ mol^{-1} (Co-NF), 35.54 kJ mol^{-1} (Ni-NF), and 36.70 kJ mol^{-1} (Cu-NF). Based on recyclability tests, Co-NF metal oxide nanofiber catalysts showed unaltered catalytic activity toward hydrogen release and good chemical stability after ten successive cycles.

Introduction

The electrospinning sol–gel method is a convenient technique for fabricating fibers with unique properties such as controlled diameter, very large surface area, flexibility in surface functionalities, and superior mechanical properties [1]. Electrospinning is an unequaled approach that uses electrostatic forces to produce fine fibers from polymer solutions/melts ranging in diameter from nanometers to micrometers. Synthetic and natural polymers such as polyglycolide (polyglycolic acid, PGA), polyvinyl alcohol (PVA), silk fibroin, gelatin, and cellulose are used to form fine nanofibers for use in a wide of applications, for example in nanocatalysis, tissue engineering scaffolds, protective clothing, optical electronics, filtration, defense and security, and environmental engineering, as well as those important to applications in biomedical, pharmaceutical, healthcare, and biotechnology fields [2].

Electrospinning is finding increasing importance in the hydrogen energy system. Electrospun fiber catalysts, having smaller pores and higher surface area than regular catalysts, have been successfully applied in hydrolysis reactions of metal hydrides to supply pure hydrogen gas to a fuel cell. Hydrogen release from ammonia borane (NH_3BH_3, AB), an amminetrihydroboron, is one of the future strategies for energy applications due to its high hydrogen content (19.6 wt%)

* *Corresponding author*. Department of Chemical Engineering, Yildiz Technical University, Istanbul, 34210, Turkey. Tel.: +90 2123834774; fax: +90 2123834725.
E-mail addresses: akanturk@yildiz.edu.tr, ayselkanturk@gmail.com (A. Kantürk Figen).
http://dx.doi.org/10.1016/j.ijhydene.2016.03.182

and a low molecular weight (30.9 g mol^{-1}) [3,4]. The hydrolysis reaction has received considerable attention since 2006, with special focus on catalytic materials [5]. Noble and non-noble metals [6], metal oxides [7], bimetallic nanoparticles [8], and porous powders [9] have been produced by several techniques, including chemical reduction, wet impregnation [10], sol–gel [11], and precipitation [12] due to their high catalytic activities and large surface areas; these catalytic materials are of special interest for hydrogen applications [13]. Also, oxide forms of metals are more stable against atmospheric degradation and humidity compared with metallic forms. To obtain high catalytic activity, the recommendation is to use metals in oxide forms, or doped on various supports, or embedded in polymeric mediums [14]. It is also possible to use metal oxides in combination with elemental boron to increase their activity [15].

Beyond that, the conventional catalyst preparation techniques are utilized by electrospinning to control the surface area, size, and morphology of catalysts to obtain the required acceleration of hydrogen release. Cu^0/S-doped TiO_2 nanoparticles decorated with carbon nanofibers as a photo catalyst for the hydrolysis of AB under visible light were produced by electrospinning; reportedly, the nanofiber catalyst exhibited good photo catalytic activity [16]. Co-B nano flake-like structures supported over nanoporous TiO_2 was synthesized in two steps using electrospinning along with chemical reduction and was tested in AB hydrolysis. The synthesized nanocatalyst showed a low effective activation energy and high maximum rate [17]. A new system of ionic liquid with metal complex, chemically crosslinked, electrospun nanofibers based on polyvinylidene fluoride (PVDF) was developed for hydrogen generation by hydrolysis of $NaBH_4$. The cross-linked nanofibers retained their morphology even after thermal treatment and have potential as a catalyst in energy-related applications [18]. Cerium-nickel–loaded titanium nanofibers have been fabricated for use in catalytic applications for hydrogen production; it has been shown that addition of cerium along with nickel significantly enhanced the catalytic activity, but that excessive cerium-loading had a negative effect on the $NaBH_4$ hydrolysis [7]. A synchronous etching-epitaxial growth approach has been developed for the fabrication of facet-coupling $NaTaO_3/Ta_2O_5$ hetero-structured nanofibers for use as a photo catalyst for hydrogen production from pure water and 20 vol% methanol aqueous solutions. In the absence of any catalysts this system can exhibit a photocatalytic activity for hydrogen production as high as 1579 μmol h^{-1} g^{-1} [19]. A silica-supported palladium (Pd/SiO_2) nanofiber catalyst with an average diameter of 500 nm has shown 93.48% efficiency in a hydrogenation reaction for acrylic acid; this could be promising for a wide range of applications in the catalyst industry [20]. It has been reported that chemically stable bimetallic NiCu nanorods incorporated with carbon nanofibers show superior catalytic activity toward hydrogen release from AB, with a low activation energy of about 28.9 kJ mol^{-1} [21]. Bimetallic Pd-doped Co nanofibers have been successfully prepared by electrospinning to improve the stoichiometric hydrogen release performance from AB via hydrolysis and photo hydrolysis, the same efficiency over several successive test [22].

To best of our knowledge, there are only limited reports of nanofiber catalysts for NH_3BH_3 hydrogen release; fabrication of the effective metal-loaded nanofiber might be a successful strategy to obtain rapid hydrogen release with low activation energy. The present study investigates that approach by fabrication of electrospun nanofiber catalysts (Co-NF, Ni-NF, Cu-NF); their NH_3BH_3 hydrogen-release efficiency is demonstrated and opens a new perspective on a different class of catalysts.

Experimental

Materials

Poly(vinyl alcohol) (PVA, MW 85,000–124,000, 99% hydrolyzed) was purchased from Aldrich. Cobalt(II)acetate tetrahydrate ($Co(C_2H_3O_2)_2{\cdot}4H_2O$), nickel(II)acetate tetrahydrate ($Ni(C_2H_3O_2)_2{\cdot}4H_2O$), and copper(II)acetate tetrahydrate ($Cu(C_2H_3O_2)_2{\cdot}4H_2O$) from Aldrich were used as received. Homemade NH_3BH_3 was used as a hydrogen storage carrier for hydrogen release prepared by the one-pot chemical reaction described in our previous work [23].

Fabrication of electrospun nanofiber catalysts

PVA fibers and electrospun fiber catalysts were prepared by electrospinning by forcing the polymer solution through a spinneret by an electrical field. The fibers were subsequently dried and then calcinated, resulting in nanometer-sized fibers.

In the present study, we first prepared PVA solutions for fabrication of PVA fibers with different process parameters such as solution concentration, preparation conditions, electrospinning conditions, collection distance, polymer flow rates (see Table 1). PVA solutions with different concentrations of 5–15 wt% were prepared by dissolving a weighted amount of polymer in deionized water at 80 °C–90 °C and gently stirring for 5 h. To obtain completely homogeneous and spinnable solutions, the PVA solutions underwent magnetic stirring for another 24 h at room temperature before being used in the electrospinning process. The electrospinning of the as-prepared PVA solutions was carried out by loading the solutions in a 10-ml plastic syringe. A single-nozzle basic-level electrospinning machine, (Inovenso Co.) was used to charge the solution across the needle and to supply the variable high voltage for electrospinning. A flat metal plate covered with aluminum foil was used to collect the fibers. After electrospinning under different conditions, the resulting PVA fibers were characterized; the results are shown in Table 1. After electrospinning, the fiber mats were kept in an oven at 110 °C to remove any residual water.

To fabricate electrospun fiber catalysts, PVA-metal acetate solutions were prepared by dissolving the metal acetate (Co, Ni, Cu) in PVA solution, following by stirring at 90 °C for 2 h. The resulting metal acetate-containing polymer solutions were used for electrospinning; 20, 25, or 30 kV volts were applied between the spinneret and the drum collector. The flow rate of the polymer solution was adjusted to 1 ml h^{-1} using a pump; the tip-to-collector distance varied from 7.5 cm to 15 cm to determine its effect of nanofiber formation. The nanomats were dried for 110 °C for 6 h; the Co, Ni, Cu composite nanomats were then subjected to heat treatment to