



Effect of Ni-alloys on thermal decomposition of ammonia borane



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ARTICLE INFO

Article history:

Available online 17 January 2015

Keywords:

Ammonia borane
Thermolysis
Ni alloys
Hydrogen storage

ABSTRACT

The principal disadvantage of thermal decomposition of ammonia borane is release of borazine during generation of hydrogen gas. In the current work, ZrNi, FeNi and CuNi alloys have been synthesized and used as additives to decrease the amount of borazine release. It was observed that ZrNi was most efficient resulting in ~22% decrease in the borazine release. The effect of the additives in decreasing the borazine release was observed to be in the order of ZrNi > FeNi > CuNi.

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1. Introduction

The declining fossil fuel reserve, emission of green house gases has prompted the need to find an alternative pollution free energy source [1]. Hydrogen, owing to its high calorific value, cleaner by-product is a favorable choice as a replacement of fossil fuel. However, owing to the low density and high inflammability of hydrogen gas, storage of hydrogen is one of the major issue for developing hydrogen economy. Storage of hydrogen in liquid or compressed gaseous state are not suited for widespread application due to energy intensive processes, safety issues and low volumetric storage capacity [2]. Physical absorption of hydrogen in different high surface area materials, like carbon, MOFs and mesoporous silica overcome the safety issues but do not show significant hydrogen storage capacity [2]. On the other hand, chemical hydrides (ammonia borane, borohydrides, alanates, etc.) show better hydrogen storage capacity due to their low molecular weight and high hydrogen content.

Among various complex hydrides, ammonia borane is noteworthy because unlike other borohydrides, it undergoes thermolytic decomposition reaction producing hydrogen at considerably lower temperature [3]. Decomposition of ammonia borane proceeds as Eqs. (1)–(3).



The first exothermic decomposition step, liberating one mol equivalent of H₂, takes place in between the temperature range 107–117 °C (Eq. (1)). The first step of ammonia borane decomposition proceeds with formation of polymeric aminoborane (PAB), [(NH₂BH₂)_n] as by product. Consecutively, the PAB species also undergoes decomposition, releasing total two mole equivalent of H₂ and leading to the formation of polyiminoborane (PIB), [(NHBH)_n] (Eq. (2)). The second step of decomposition takes place within a temperature frame of 125–180 °C. Up to 180 °C ammonia borane releases almost 2.2 mol of H₂ per mol of AB. Isothermal heating influences AB to gradually release H₂ at temperatures well below 107 °C. Although exhibiting poor kinetic behavior, thermolysis of ammonia borane provides highest recorded gravimetric hydrogen storage capacity of 7–11% below 120 °C [4].

However, the thermal decomposition of ammonia borane, although achieved at comparably lower temperature than other borohydrides is not devoid of limitations. Following a highly exothermic reaction pathway, ammonia borane also decomposes to form other unwanted gaseous by-products. It has been observed that during thermolysis, gaseous by products such as ammonia (NH₃), diborane (B₂H₆) and borazine (B₃N₃H₆) form, which possess serious damaging threats toward the polymeric membrane of PEM fuel cell [5].

Several materials have been employed as catalyst or additive to ammonia borane in order to eliminate the threat of these noxious by products. Benzouaa et al. used iron, cobalt and aluminum chloride (FeCl₃, CoCl₂, AlCl₃) with ammonia borane in 1:10 ratio. The onset decomposition temperature of ammonia borane were observed to be 52, 65, 85 °C in presence of CoCl₂, FeCl₃ and AlCl₃ respectively against that of pristine AB (99 °C). Substantial decrease in the borazine release was observed, although not completely eliminated [6]. Ionic liquids and carbon cryogel has also been effectively applied to minimize the borazine release [7,8].

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Co–P–B coated Ni foam was observed to drastically decrease the peak decomposition temperature by 30 °C, although the effect was not similarly reverberated in suppression of borazine release [9]. Ammonium chloride also was observed to successfully decrease the induction period (by ~450 min) when subjected toward isothermal heating at 80 °C [10]. In another work, NiCl₂ and CuCl₂ were employed to facilitate the AB decomposition reaction by Kalidindi et al. and yielded almost 9 wt% H₂ after 6.5 h, when isothermally heated at 80 °C. Since CuCl₂ actively participated in reaction with AB, the reaction proceeded through a separate intermediate [NH₄]⁺[BCl₄]⁻, minimizing the release of borazine and hence, decreasing the chances of regenerability [11]. The principal disadvantage of these catalysts are their tendency to chemically interact with the ammonia borane molecules. Such association compromises the pristinity of the reactants which may pose a challenge during regeneration of the reactant species.

In the current work the selection of the additive was primarily governed by the inactivity of the additive toward the reactants, in order to facilitate the regeneration of ammonia borane from the thermolyzed end product. Transition metal nickel alloys, such as, iron nickel (FeNi), zirconium nickel (ZrNi) and copper nickel (CuNi) alloys were synthesized, characterized and employed as additives in order to achieve insight on their influence in facilitating the decomposition reaction of AB.

2. Experimental

2.1. Synthesis of FeNi and CuNi alloys

Iron nickel (FeNi) and copper nickel (CuNi) alloys were prepared by co-precipitation of hydroxide followed by reduction. In a typical synthesis procedure, 198.91 mg of Ferrous chloride (FeCl₂, Merck India) and 237.66 mg of Nickel(II) chloride hexahydrate (NiCl₂·6H₂O; Merck India) were solvated in 50 ml of 0.05 N HCl solution separately and mixed together after complete dissolution. NaOH solution (0.5 N) was added dropwise to the mixed solution until the pH of the solution becomes >10. The appeared brownish green precipitate was filtered through vacuum filtration followed by washing with DI water repeatedly and drying in hot air oven at 85 °C for 24 h. Upon evaporation the hydroxides of transition elements release water vapor in order to form more stable oxides. The brown mixed oxide residue as obtained was powdered with mortar and pestle. Reduction of the oxide was performed using activated charcoal as reducing agent. The reactant mixture was kept in a muffle furnace and was annealed at 600 °C under inert atmosphere to obtain the brown magnetic powder (FeNi).

For synthesis of CuNi, 170.48 mg of Copper(II) chloride dihydrate (CuCl₂·2H₂O, Merck India), and 237.66 mg of Nickel(II) chloride hexahydrate (NiCl₂·6H₂O, Merck India) were solvated in 50 ml of 0.05 N HCl solution separately. Rest of the preparation process through hydroxide precipitation and reduction were similar as of FeNi synthesis.

2.2. Synthesis of ZrNi alloy

Zirconium nickel alloy was synthesized from metallic zirconium (Sigma Aldrich) and nickel (Sigma Aldrich). Zirconium was mixed with nickel and ball milled in 1:1 M ratio in a Fritsch Pulverisette 6 ball miller at 300 rpm for 5 min. The mixture was then heated at 400 °C in a muffle furnace under inert atmosphere. The obtained product was kept away and used for characterization and thermal analysis.

2.3. Preparation of AB + MNI

Ammonia borane (NH₃BH₃, 97%, Sigma Aldrich) and the Ni alloy (MNI, where M = Fe, Cu and Zr) additives were homogeneously mixed in a 5:1 (wt/wt) ratio in mortar pestle. All sample operations involving ammonia borane were carried out in a glove box (MBraun) maintained under argon atmosphere.

2.4. Characterization

The synthesized catalysts were characterized by X-ray diffraction (XRD) with Philips X-ray Diffractometer using Cu K α radiation having wavelength 1.54 Å within the 2 θ range of 10–90°. XRD studied were also performed for all the pre- and post-heated AB + MNI samples. EDS study of these catalysts was done by Jeol JSM-7600F field emission gun scanning electron microscopy (FEG-SEM). PHILIPS CM200 field emission gun transmission electron microscopy (FEG-TEM) was used to analyze the particle size. In case of FEG-TEM, operating voltage and resolution were

maintained at 20–200 kV and 2.4 Å respectively. The pre- and post-heated AB + Ni samples were characterized by Fourier Transform IR (FTIR) spectroscopy to observe the change in bond vibrations of the samples due to thermolysis. FTIR studies were performed with JASCO 6000 spectrometer using KBr pellet of the samples over the range of 350–4000 cm⁻¹.

2.5. Thermal analysis

Thermo gravimetric analysis (TGA) measurements were performed with Mettler Toledo TGA/SDTA 851^e using 70 μ l alumina crucible and nitrogen as purge flow gas (60 ml/min). For analysis, the total sample mass was confined within 2–3 mg and heating range of 25–225 °C was used with a heating rate of 10 °C min⁻¹. Sample mass loss and associated thermal effects were obtained by TGA/SDTA. Both instruments were calibrated in the studied range of temperature, i.e., 25–225 °C min⁻¹. Concerning the TGA, the melting points of two elements (aluminum and indium) obtained from the DTA signals were used for the sample temperature calibration. The calibration gave a straight line with a regression coefficient of 1. The MS analyses were performed by using a Netzsch Aeolos QMS 403D mass spectrometer. The evolved gases with nitrogen as purge gas (flow rate 60 ml/min) were introduced to the MS through a quartz glass capillary of diameter 75 μ m maintained at 300 °C temperature. The MS uses an Y₂O₃ coated iridium cathode and faraday and SEV (channeltron) detector. Channels corresponding to *m/e* = 2 (hydrogen) and *m/e* = 80 (borazine) were used to analyze the evolved gases. The MS data were normalized with respect to the sample mass in order to demonstrate a direct comparison for the hydrogen and borazine release from pure AB and AB + MNI samples. All experiments were repeated at least three times to ensure the reproducibility of the reaction.

3. Results and discussion

3.1. Characterization

Fig. 1 demonstrates the XRD patterns of the synthesized MNI alloys (where M = Fe, Cu and Zr). The peak pattern exhibited similarity with both intermetallic intermediate compositional alloys of ZrNi, ZrNi (70/30) and ZrNi (30/70) respectively as reported by Escobar et al. [12]. The XRD pattern of synthesized FeNi alloy directly corresponds to (110), (111), (210) and (220) planes of FeNi crystal lattice [13]. Alongside representing the characteristic peaks, the XRD pattern of synthesized FeNi alloy also bears additional peaks which may indicate toward the formation of iron oxide [14]. Similarly presence of crystalline nickel and copper oxides were observed in the XRD pattern of CuNi alloy [15–17]. Formation of these oxides may be interpreted as surface oxidation of the Ni alloys, as a result of surface passivation.

The XRD pattern of all AB + Ni samples bear a prominent resemblance with the JCPDS reference code 00-013-0292 of ammonia borane (Fig. S1 in supplementary information). From Fig. S1, it may be observed that the peaks corresponding to Ni alloy additives are perceivable, although overshadowed by the sharp peaks of ammonia borane. After decomposition, ammonia borane produces

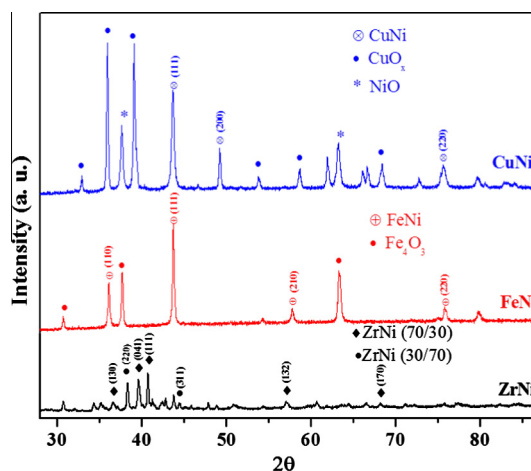


Fig. 1. XRD pattern of synthesized CuNi, FeNi, and ZrNi.

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