



Kinetics of hydrogen release from dissolutions of ammonia borane in different ionic liquids



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ABSTRACT

Ammonia borane is a promising hydrogen storage material that liberates hydrogen by thermolysis at moderate temperatures, but it also presents major limitations for practical applications including a long induction time before the initiation of hydrogen release and a difficult regeneration. Previous works have demonstrated that by dissolution of ammonia borane into several ionic liquids, and particularly in 1-butyl-3-methylimidazolium chloride bmimCl, the induction period at the beginning of the thermolysis is eliminated, but some problems persist, including foaming and the formation of a residue after thermolysis that is insoluble in the ionic liquid. In this work, the release of hydrogen from ammonia borane dissolved in different ionic liquids has been analyzed, measuring the kinetics of hydrogen release, visually following the evolution of the sample during the process using pressure glass tube reactors, and analyzing the residue by spectroscopic techniques. While dissolutions of ammonia borane in most ionic liquids analyzed show similar properties as dissolutions in bmimCl, using ionic liquids with bis(trifluoromethylsulfanyl)imide Tf₂N anion the foaming problem is reduced, and in some cases the residue remains dissolved in the ionic liquid, while with ionic liquids with choline anion higher hydrogen yields are achieved that indicate that the decomposition of ammonia borane proceeds through a different path.

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1. Introduction

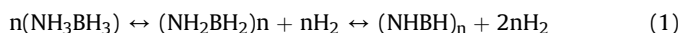
In the near future, renewable energies will have to be adopted as the main source of energy due to the depletion of fossil resources. Establishing a new energy system based on renewable resources is a challenging task for several reasons, including the fluctuating nature of many renewable energy sources such as wind and sun. The direct use of renewable energies in vehicles and other mobile applications is also problematic.

A possible solution for some of these problems could be to use hydrogen as an energy carrier [1,2]. Hydrogen is a very attractive fuel because it combusts very cleanly, producing only water. Hydrogen can be produced by the electrolysis of water using renewable resources. It can then be stored for use during periods lacking in direct generation of energy in renewable power plants, or transported and used in vehicles or other mobile applications. To make this new paradigm a feasible reality, several technical issues

must be solved, including the efficient production of hydrogen by electrolysis of water or from renewable biological sources, the conversion of hydrogen into electricity using improved fuel cells, and the storage of hydrogen [3–5].

In particular, storing hydrogen in small mobile applications or in vehicles presents significant challenges, as some of the obvious solutions such as compressed gas or cryogenic liquid are limited with respect to the storage capacities or energy consumptions. For these reasons, in recent years a considerable effort has been made to develop new hydrogen storage systems by different approaches, including metallic and chemical hydrides, carbon nanotubes, hydrates or metal-organic frameworks [6–9].

Among the different hydrogen storage materials, chemical and metallic hydrides are some of the most promising alternatives [10,11]. One of the most extensively studied hydrides is AB (ammonia borane), which is relatively stable, safer and easier to handle than other more reactive hydrides, and can release up to 13 wt% of hydrogen at temperatures below 180 °C according to the following global reaction [12]:



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Nevertheless, the application of hydrides as hydrogen storage materials still faces some important limitations, which can be classified into two categories: thermodynamic limitations, because in general, hydrides proposed for hydrogen storage are very stable and high temperatures are required in order to decompose these materials and to release the stored hydrogen, and kinetic limitations, because hydrogen uptake and release from hydrides can be very slow. Different approaches have been proposed to overcome these limitations, such as the modification of the chemical composition of hydrides adding destabilizing compounds [13], the use of catalysts [14] or the manufacture of nano-structured or nano-confined materials [15].

Since several of these limitations are related to the solid–gas nature of hydride decomposition reactions, a possible strategy to avoid them is to employ a dissolution instead of the solid compound. However, conventional volatile solvents cannot be used for this purpose, because the solvent would evaporate during the heating process required to decompose the hydrides, causing a contamination of the gaseous hydrogen that could damage fuel cells. In order to circumvent this problem, Bluhm et al. proposed to use ionic liquids as solvents [16]. Ionic liquids are substances entirely composed of ions, which are liquid at near ambient temperature. As one of their most remarkable properties is their negligible vapor pressure [17], using ionic liquids the problem of hydrogen contamination by evaporation of the solvent would be avoided.

In their seminal work, Bluhm et al. observed a considerable enhancement of the kinetics of hydrogen release from ammonia borane dissolved in the ionic liquid 1-butyl-3-methylimidazolium chloride bmimCl with respect to solid ammonia borane [16]. In particular, the long induction period characteristic of hydrogen release from solid ammonia borane was not observed in the ionic liquid solutions. Based on this observation and on NMR (neutron magnetic resonance) analyses of reaction products, authors hypothesized that the ionic liquid participated in the decomposition reaction inducing the formation of diammoniate of diborane ($[(\text{NH}_3)_2\text{BH}_2^+][\text{BH}_4^-]$) and BH_4^- ionic species. On a subsequent work, Himmelberger et al. [18] observed that the dehydrogenation rate enhancement was still produced in mixtures of ammonia borane and bmimCl when the concentration of ionic liquid was reduced down to a 80:20 wt% AB:ionic liquid ratio, and determined a decomposition mechanism based on the conversion of ammonia borane into the more reactive diammoniate of diborane ion, that was converted into polyaminoborane polymers and, finally, into polyborazylene, a mechanism that was not observed in the decomposition of AB from solutions in organic solvents such as tetraglyme. In this work, Himmelberger et al. [18] also tested other ionic liquids beside bmimCl, observing that the release of hydrogen was accelerated by dissolution in a variety of ionic liquids, especially during the release of the first hydrogen equivalent from ammonia borane. However, important differences were observed during the release of the second equivalent according to reaction (1): while some ionic liquids such as bmimCl or 1-butyl-3-methylimidazolium tetrafluoroborate bmimBF₄ yielded over two hydrogen equivalents at 85 °C with accelerated rates, only one hydrogen equivalent was released from AB solutions in 1-propyl-2,3-dimethylimidazolium trifluoromethylsulfonate pmmimTf₃C at the same temperature. Basu et al. [19] also investigated the decomposition of ammonia borane in bmimCl and proved that the dissolution of the hydride in the ionic liquid not only increased the hydrogen release rate, but also the gravimetric yield, which was higher in 80:20 wt% mixtures of AB and ionic liquid than in neat AB when temperature was above 107 °C. They also observed that foaming, a problem in the utilization of ammonia borane for hydrogen storage, was partially suppressed by the addition of the ionic liquid. Wright

et al. [20] added ruthenium catalysts to AB solutions in bmimCl and 1-ethyl-3-methylimidazolium ethyl sulfate emimESO₄, observing that this approach gave enhanced initial hydrogen release rates at low temperatures.

These previous studies have demonstrated the advantages of employing ammonia borane – ionic liquid mixtures, having tested a small range of different ionic liquids. The objective of this work is to explore the possibilities for using alternative ionic liquids as solvents for ammonia borane. With this purpose, the hydrogen release from ammonia borane dissolved in 13 ionic liquids has been systematically investigated. Results of hydrogen release rate and yield are reported, together with a characterization of the foaming and solubilization behavior of the solutions observed during hydrogen release experiments in high pressure glass tubes, and with a characterization of the reaction mixtures by FT-IR spectroscopy.

2. Materials and methods

Table 1 displays information of the ionic liquids tested in this work. All these ionic liquids were purchased from Iolitec Ionic Liquids Technologies GmbH (Germany). Ammonia borane (purity: 97%wt) was purchased from Sigma–Aldrich (Spain).

Fig. 1 shows a scheme and a photograph of the glass pressure reactor used in hydrogen release experiments. Prior to every experiment, ionic liquids were dried at 90 °C in a vacuum oven (J.P. SELECTA VACIOTEM-T9, Spain) for at least 24 h. Working inside a glove box inertized with nitrogen, a solution of ammonia borane in the ionic liquid of known composition was then prepared by weighing, and a weighed amount of this solution was loaded inside the glass pressure reactor (model Q-Tube, manufactured by Q Labtech, United States). The glass reactor was sealed and subjected to vacuum down to an absolute pressure of 10 mbar using a vacuum pump (model FB6545, manufactured by ILMVAC GmbH, Germany). The reactor was then introduced in an oven (J.P. SELECTA DIGITRONIC, Spain) thermostated at 85 °C (uncertainty: ± 1 °C). All experiments were conducted at the fixed temperature of 85 °C because this is a typical operational temperature of PEM (polymer electrolyte membrane) fuel cells [21]. Therefore at this temperature it could be possible to use excess heat from the fuel cell to decompose the hydride. Moreover, all experiments have been performed with a fixed concentration of AB in the solution of 10% wt, in order to facilitate the preparation of dissolutions and to allow a clear comparison of the results obtained with the solutions in different ionic liquids. The evolution of pressure inside the reactor during heating, due to the release of hydrogen, was measured during a period of at least 8 h with a certified pressure gauge (model DRUCK DPI 104, manufactured by General Electric Measurement & Control, United States, uncertainty: ± 1 mbar), connected to a computer with the SiCal Pro data acquisition software. The evolution of the sample along the experiment was also video recorded with a digital camcorder. At the end of the experiment, the glass reactor was cooled down to ambient temperature, hydrogen inside the reactor was purged, and in selected experiments a sample of the solution was retrieved from the reactor working inside the glove box and analyzed by FT-IR (fourier transform infrared) spectroscopy (spectrometer Bruker ALPHA, sampling module Platinum ATR, Bruker, Spain). After the experiment, the amount of hydrogen released was calculated from pressure recordings and fixed conditions of temperature and glass reactor volume (calculated from the difference of weight between the empty reactor and the reactor filled with water), employing the Hydrogen Reference Equation of State [22] implemented in the REFPROP (Reference Fluid Thermodynamic and Transport Properties Database) software developed by the NIST (National Institute of

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