



Enhancement of hydrogen release kinetics from ethane 1,2 diamineborane (EDAB) by micronization using Supercritical Antisolvent (SAS) precipitation

Miriam Rueda^a, Luis Miguel Sanz-Moral^a, José Juan Segovia^b, Ángel Martín^{a,*}

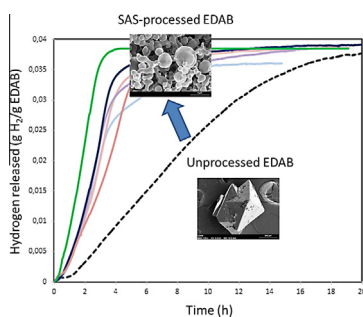
^a Department of Chemical Engineering and Environmental Technology, University of Valladolid, c/ Doctor Mergelina s/n, 47011 Valladolid, Spain

^b TERMOCAL Research Group, University of Valladolid, c/ Paseo del Cauce 59, 47011 Valladolid, Spain

HIGHLIGHTS

- Supercritical Antisolvent solution applied to micronize 1,2 ethane diamineborane.
- The influence of parameters on the final properties of the compound is studied.
- Prismatic particles of 400 μm converted into microspheres smaller than 2 μm .
- H_2 release time reduced by factor of 6 due to reduction of particle and grain size.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 12 May 2016

Received in revised form 12 July 2016

Accepted 13 July 2016

Available online 15 July 2016

Keywords:

Hydrogen storage

Ethane diamineborane

Micronization

Kinetics

Supercritical carbon dioxide

Supercritical Antisolvent

ABSTRACT

Ethane 1,2 diamineborane (EDAB) was micronized from THF solutions using Supercritical Antisolvent (SAS) process. The influence of temperature, solute concentration and carbon dioxide fraction on the final properties of EDAB particles was studied. By SAS micronization, the original prismatic EDAB particles of about 400 μm with a crystallite size of 100 nm were converted into microspheres of less than 2 μm with a crystallite size of 50 nm. This reduction in the particle and grain sizes resulted in an improvement in thermal properties. The kinetics of release of hydrogen by thermolysis at 100 °C was also significantly enhanced due to the reduction in the diffusion length, reducing the time needed for the decomposition of the hydride by a factor of six. Moreover, a suppression of induction time was obtained by destabilization of the hydride after treatment. XRD and FTIR analyses showed that no chemical decomposition and no variation of the crystalline structure took place by SAS processing.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

In recent years, important efforts have been made in order to find renewable energy sources that can satisfy the current necessities. This is promoted by the depletion of fossil fuels and the climate change due to the release of greenhouse gases [1]. However, an important limitation of the main renewable energy

resources is the unpredictability of fluctuations in their output. In this context, hydrogen could be a solution to these problems using it as an energy vector, in an approach known as ‘hydrogen economy’ or ‘hydrogen society’ [2].

In the case of onboard applications, the simplest idea would be to use hydrogen as gas or a liquid. However, in the case of gas, high pressures tanks would be necessary in order to have the required high density of hydrogen and this would mean high volumes of tanks and, therefore, high costs of material. Using hydrogen at cryogenic conditions, a considerable energy input (estimated

* Corresponding author.

E-mail address: mamaan@iq.uva.es (Á. Martín).

around 30% of the total energy stored in hydrogen) would be required in order to maintain the desired temperature [3]. For these reasons, solid state hydrogen storage appears as a compelling alternative.

Different solid hydrogen storage materials have been tested, such as metal hydrides, complex hydrides [4], metal organic frameworks (MOF) [5], adsorbents, polymer composites or clathrate hydrates [6], among others [7,8]. However, till now, no material satisfies all the latest targets set for onboard applications by the US Department of Energy (DoE) for 2017 for a practical automotive application (5.5 wt% hydrogen content, release temperature at 85 °C, 100% reversibility, good cyclability) [9].

Many recent research works have been focused in boron-nitrogen-hydrogen systems, especially in ammonia borane (AB). AB has been widely investigated due to its high content of hydrogen (19.6 wt%) which is released at moderate temperatures. Moreover, it is non-toxic and stable at room temperature. However, the most important limitations related to this compound are the regeneration and cyclability of the compound and the emission of some volatile byproducts as borazine, diborane or ammonia during the release of hydrogen which could be poisonous for the fuel cell [10].

Carbon derivatives of AB, such as ethane 1,2 diamineborane ($\text{BH}_3\text{NH}_2\text{CH}_2$)₂, known as EDAB, are promising alternatives. EDAB has a high content in hydrogen (10 wt%), which is released below 473 K in a two-step reaction. Moreover, it is also very stable under ambient conditions (particularly, against ambient oxygen and humidity), even more than AB, which facilitates the manipulation of this material. However, only a few works can be found related to this compound [11–13]. Among other results, it has been observed that the modification of AB to obtain EDAB produces a chemical structure with a stronger B-H bond and a more thermal stable B-N bond due to the existence of C-N and C-C bonds, resulting in the production of less non-desirable volatile gases in the hydrogen outstream [11]. However, more investigation is necessary in order to destabilize the compound during thermal decomposition process at moderate temperatures, in order to improve the kinetics of release of hydrogen.

Nanoengineering could be a solution to reduce the crystallite size and improve the decomposition rate by increasing the diffusion rate and therefore, reduce the hydrogen release temperature [7]. Different methods can be used in order to reduce the size of the metal hydride such as laser ablation, vapor condensation, sputtering or ball milling [14]. One of the most used methods is ball milling [4,15]. With this method, hydrogen release kinetics are enhanced due to the reduction of the diffusion lengths without any cost of a catalyst or a reduction of storage capacity. Milling can also induce other material changes, such as an increase in the number of defects [16], create more disorder and strain into the material [17], and therefore improve surface properties.

The problem of this method is the inhomogeneity of the product after milling [18]. Because of this disadvantage, Supercritical Antisolvent Solution is proposed as a promising alternative method in order to micronize the hydride controlling the reduction of the particle size by changing the conditions and the supersaturation driving forces. In this way, the advantages of milling are present in this method, while obtaining a much more homogeneous product. This technique has been used to micronize a wide range of compounds such as polymers, pharmaceutical compounds [19] or catalysts. For its application, the only requirement is that the compound which is going to be micronized needs to be soluble in an organic solvent and stable in CO₂ atmosphere [20].

In this work, the micronization of EDAB from THF solutions using Supercritical Antisolvent (SAS) process is reported. The influence of the concentration of the solution, the temperature and the carbon dioxide molar fraction on the properties of the micronized

product has been studied. Scanning electron microscopy, FT-IR spectroscopy, X-ray diffraction, DSC analyses and the measurement of hydrogen release kinetics by thermal decomposition at 100 °C have been done in order to characterize and compare the final products obtained at different conditions in contrast to the bulk EDAB.

2. Experimental methods

2.1. Materials

Ethane 1,2 diamineborane (EDAB, purity: 96 wt%) was supplied by Sigma-Aldrich. As shown in the SEM micrograph presented in Fig. 1, the material was constituted by prismatic particles of around 400 μm.

Dry tetrahydrofuran (with maximum water of 0.0075 wt%) was purchased from Panreac (Spain). Carbon dioxide (purity: 99.95 wt %) was supplied from Carbueros Metálicos S.A. (Spain).

2.2. Micronization of EDAB by Supercritical Antisolvent (SAS) process

Supercritical Antisolvent technique is the process used to micronize EDAB in this work. It takes place in the same semi continuous equipment reported in a previous work [18], and schematically represented in Fig. 2.

A cylindrical vessel of 1.5 L was used as precipitator. First, preheated carbon dioxide was pumped at a flowrate of 2 kg/h with a diaphragm pump (Dosapro Milton Roy, Spain) until stable conditions of temperature and pressure were reached. The pressure was maintained in all the experiments at 100 bar in order to have a single phase in the system [21]. Pressure was controlled with a back pressure valve (model BP66, GO, USA).

Then, pure THF was flowed to the precipitator in order to obtain steady composition conditions of the fluid phase. After this, 0.5 g of EDAB dissolved in different volumes (0.02–0.15 L) of THF, depending on the concentration studied in each experiment, were pumped to the precipitator using a HPLC pump Jasco model PU-2080, maximum flow rate: 10 mL/min (flow rate control with an accuracy of 1%). Both solutions were pumped continuously through a coaxial nozzle which was located in the upper zone of the vessel in which the solution flowed through the inner tube, with an inner diameter of 100 μm, and CO₂ flowed through the coaxial annulus. At this point of the vessel, the mixture produces the super saturation of the dispersed phase and the particles are formed [22]. The particles thus formed were collected in a stainless steel frit covered with a polymeric membrane filter (pore size of 0.1 μm) which was located at the bottom of the precipitator. Once the solution was pumped, CO₂ was flowed for 1 h to assure the total elimination of the solvent and after this time, the system was depressurized till ambient conditions.

The influence of the concentration of EDAB in THF in the range 3–25 g/L, which is within the solubility limit of EDAB in THF (46–47 g/L at 25 °C) [23], the temperature (308–318 K) and the molar fraction of CO₂ in the CO₂-THF fluid mixture (0.96–0.98) were studied.

2.3. Product characterization

Particle morphology was observed by Scanning Electron Microscopy (SEM) using Jeol JSM 820 equipment. A gold sputter was used to cover the samples with a thin layer of gold to allow the electron reflection for particle evaluation. To determine particle size from SEM micrographs, around 100 individual particles were counted from SEM photos using Image J software. The mean particle size was calculated as number average diameter [24].

Download English Version:

<https://daneshyari.com/en/article/145279>

Download Persian Version:

<https://daneshyari.com/article/145279>

[Daneshyari.com](https://daneshyari.com)