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

Miriam Rueda[1], Luis Miguel Sanz-Moral[1], José Juan Segovia[2], Ángel Martín[1]*

[1]Department of Chemical Engineering and Environmental Technology - University of Valladolid

c/ Doctor Mergelina s/n 47011 Valladolid (Spain)

[2]TERMOCAL Research Group – University of Valladolid, c/ Paseo del Cauce 59 47011

Valladolid (Spain)

Tel: +34 983423174, e-mail: mamaan@iq.uva.es (Á. Martín)

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 100ºC 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.

Keywords: Hydrogen storage; Ethane diamineborane; micronization; kinetics; supercritical carbon dioxide; supercritical anti solvent

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 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 $(BH_3NH_2CH_2)_2$, 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 [11,12,13]. 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 CO_2 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 ºC 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 Figure 1, the material was constituted by prismatic particles of around 400 μm.

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

(FIGURE 1)

2.2 Micronization of EDAB by Supercritical Anti Solvent (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 Figure 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 CO_2 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, CO_2 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

(308-318K) and the molar fraction of CO_2 in the CO_2-THF fluid mixture (0.96-0.98) were studied.

(FIGURE 2)

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].

Crystallinity of the different samples obtained after micronization was examined using an X-ray powder diffractometer (model Bruker Discover D8). The measuring conditions were CuKα radiation, λ=1.5418 Å, 2θ angle ranging from 5º to 70º with a scan rate of 4 s/step and a step size of 0.020º. Also, Fourier Transform Infrared Spectroscopy (FT-IR) assays were performed using a BRUKER ALPHA spectrometer with a Platinum-ATR single diffraction sampling module.

Regarding the thermal characterization of products, differential scanning calorimetry (DSC) analyses were carried out in a Mettler Toledo model 822e with a ceramic sensor of high sensitivity. Nitrogen gas flowed at 60 mL/min, with a heating rate of 5ºC/min from 0 to 250ºC (273.15 to 523.15K) using less than 1 mg of sample in each analysis.

Hydrogen release kinetics were measured by a volumetric method employing a stainless steel cell of 4.7 mL. The cell was loaded with around 30 mg of EDAB, weighed using a balance with ±0.1 mg of uncertainty. Air was then removed from inside the cell with a vacuum pump, down to an absolute pressure of less than 0.02 bar. After that, the sample was heated to 100ºC (373.15K), introducing the cell in a chromatographic oven. The

release rate of hydrogen from the sample was determined by measuring the increasing gas pressure inside the cell, which was recorded with a certified pressure transducer model DPI-104 (GE Druck from Germany) with an accuracy of 0.001 MPa, connected to a data acquisition computer that recorded the pressure measurement every 10 seconds. The amount of hydrogen released was calculated from pressure recordings assuming that the gas phase formed was entirely constituted by hydrogen according to [12], using the Hydrogen Reference Equation of State [25] implemented in the Reference Fluid Thermodynamic and Transport Properties Database (REFPROP) software developed by the National Institute of Standards and Technology (NIST) [26].

3. Results and discussion

Table 1 shows a summary of the conditions for the different SAS experiments performed, together with the particle size obtained by image analysis of SEM micrographs. As previously described, different experiments were carried out varying the concentration of EDAB in the solution (runs 1-7), the temperature (runs 7-9) and the molar fraction of CO_2 (runs 7, 10 and 11).

(TABLE 1)

3.1 Structural properties of micronized EDAB

Regarding the crystallinity, Figure 3 shows the diffractogram of unprocessed EDAB which agrees well with those previously reported [27]. As it can be observed in Figure 3, the diffractogram of micronized samples corresponds to that of unprocessed material, indicating that the crystalline structure of the material was preserved. While Figure 3 only presents the results corresponding to the micronized sample obtained in experimental run 9, similar spectra were obtained in all SAS experiments.

(FIGURE 3)

8

The average crystallize size was calculated using the Scherrer equation [28] which is shown in equation 1.

$$D = \frac{K\lambda}{\beta \cos\theta} \quad \text{eq[1]}$$

Where K is a Scherrer constant (0.9 for spherical particles), λ is the wavelength of the incident x-rays (1.5418Å), β is the full width at half maximum (FWHM) and θ is the Bragg angle. The final diameter is the mean of the diameter obtained for the peaks at $2\theta = 16.4°, 19.7°, 23.4°, 24.4°$ and $25.6°$. Table 2 shows the crystallite size obtained for unprocessed EDAB and micronized SAS in experiments 1, 7, 8 and 9.

(TABLE 2)

As table 2 shows, crystallite size was reduced by SAS micronization, but a big difference is not observed between the different experiments carried out using SAS technique.

(FIGURE 4)

Regarding the results of FTIR analyses, the peaks identified correspond with those reported for EDAB in [11,29]. Figure 4 shows no variation in the FTIR spectra of EDAB after SAS process (for all the conditions tested). This result indicates that no chemical decomposition took place during recrystallization process at supercritical conditions. B-H stretching and N-H bands appeared at the same wavenumber value without any shift that could indicate a weakening in the bond. This is due to the strong C-N and C-C bond that makes this compound much more thermal stable compared to other compounds from the family of Ammine Boranes [11].

Regarding the results obtained from microscopy (figures 5, 6 and 7), a considerable reduction in the particle size was observed after SAS micronization (table 1). The mean

particle size was reduced from 400 μm (unprocessed EDAB) to around 2 μm. The particle morphology also changed: the prismatic structure of unprocessed EDAB was converted into microspheres interconnected between them due to the droplet and particle coalescence phenomena during SAS process.

With respect to the influence of the conditions tested in the different SAS experiments, the mean particle size and particle size distribution (PSD) did not change significantly. First, particle size distribution is shifted to the right when the concentration increases till c=10g/L. At higher concentration than 10g/L, the opposite behavior is observed. This means that till this concentration, the coagulation and condensation mechanisms allow the growth of the particles inside the droplets and limit SAS process [30]. However, at higher concentration of the solution than 10g/L, higher supersaturations were achieved, and therefore the rate of formation of new particles by nucleation increased exponentially obtaining particles with lower mean size [31].

(FIGURE 5)

In the case of the temperature, figure 6 shows that when temperature in SAS process is increased, more agglomeration is observed but a similar mean particle size is obtained for the range of temperature studied 35-45°C (308.15-318-15K).

Similarly, only small differences were observed in the experiments carried out at different CO_2 molar fractions by varying the flow of CO_2 or the flow of the inlet solution, as it can be seen in figure 7.

(FIGURE 6)

(FIGURE 7)

3.2 Thermal properties of micronized EDAB

Figure 8 shows the Differential Scanning Calorimetry (DSC) of the different samples treated in SAS process in contrast to unprocessed EDAB. As shown in this figure, the

first exothermic peak related to the decomposition of EDAB has been shifted from 141 ºC (414.15K) in unprocessed EDAB to 134 °C (407.15K) for the best SAS micronized sample (run 9). This improvement is due to the lower particle and grain size obtained in treated samples in contrast to unprocessed EDAB. Similar results have been reported in the case of milled MgH_2 [15], getting a reduction of the hydrogen desorption temperature which indicates faster hydrogen desorption kinetics and lower activation energy or the production of nanoparticles of AB through a solvent-free method [32] which showed superior dehydrogenation behaviour.

Regarding the influence of the concentration in the inlet solution (figure 8A), a higher shift to lower temperatures is observed when the concentration increases till c=10g/L. This could be due to the lower grain size and thinner bridges between the particles. At higher concentration (12.5-25.0 g/L), the same tendency is followed obtaining almost the same peak temperature.

In the case of the temperature of SAS process (figure 8B), the variation of the peak temperature in DSC assays follows the same tendency that the grain size calculated with Scherrer equation and the PSD obtained from SEM images. Lower exothermic temperature peak is observed in samples processed by SAS at higher temperatures.

Varying the molar fractions of carbon dioxide (figure 8C), a significant difference is not observed.

(FIGURE 8)

Regarding the second step of hydrogen release, similar results were obtained for all the micronized samples with a peak temperature in the range 187°C-190°C (460-463K). It is observed in figure 9 that samples obtained at different conditions in SAS process show the same tendency than in the first peak.

11

Comparing with previous results [12], both decomposition peak temperatures are higher than previously reported. This can be explained by the difference in gradient temperature in the analyses (5 K/min instead of 1K/min) or due to the different stability of bulk EDAB due to the different source of the chemical compound.

(FIGURE 9)

The variations in particle morphology and decomposition temperature reported in the previous section result in important variations in the hydrogen release kinetics. Figure 10 shows the kinetic of hydrogen released by thermolysis at 100 ℃ (373.15K) for unprocessed EDAB in contrast to micronized EDAB in SAS process.

As presented in this figure, the kinetic has been considerably improved after micronization due to the reduction of the particle and grain size. Moreover, it induces the increase of surface area and surface energy, reducing the diffusion lengths and therefore improving the decomposition rate [33]. Almost 1 day is taken to release 1 mol of H_2 in unprocessed EDAB, whereas less than 4 hours are taken for sample 9 after SAS process, which means a reduction by a factor of 6.

Comparing the different SAS samples obtained after treatment at different conditions, they follow the same tendency that was reported in the previous analyses, without any significant difference among them.

In the case of unprocessed EDAB, in this work different kinetic properties have been observed with respect to the results reported in previous works [12]. In our case, neat EDAB seems to be more stable than in previous works due to the slower kinetic that has been measured at the same temperature and the induction time of more than 1 hour. This fact was also seen in DSC analyses. This difference can be attributed to the different

12

starting material. In our work, EDAB was supplied by Sigma-Aldrich whereas Neiner et al. prepared it according to Moore and Kelly [34].

On the other hand and following the mechanism proposed by Neiner et al. [12] and corroborated by Leardini et al. [11], this difference could be explained by the higher stability of unprocessed EDAB from this work to initiate the isomerization in order to form the borohydride. Neiner et al. [12] reported the appearance of this isomer at 98°C (371.15K) after 15min by NMR whereas kinetic measurements from this work indicate that a longer induction time is required to form this intermediate compound.

In SAS samples, not only an improvement in the kinetic of H_2 release is observed, but also the elimination of induction time can be seen in micronized samples. This indicates that the reduction of particle size achieved by SAS process is accompanied by a destabilization of the molecule, leading to a faster dimerization and the consequent reduction of induction time.

Regarding the amount of H_2 released, an amount of 3.9 wt% H_2 is obtained with respect to unprocessed EDAB or 3.7 wt% regarding pure EDAB, taking into account that the purity is 96%, whose value is similar to those reported in the literature at the same temperature [12].

(FIGURE 10)

In order to clarify the compounds that are formed after thermal decomposition at 100 °C (373.15K) and the mechanism that is followed, FTIR analyses were performed and shown in figure 11. The same spectrum is obtained for unprocessed EDAB and SAS samples, but only one is shown for simplicity.

These spectra are similar to those reported by Leardini et al. [11]. Lattice mode at 435cm^{-1} disappears but a new one at around 420cm^{-1} is detected. On the other hand, B-

N stretching peak at 706cm^{-1} is attenuated after thermal decomposition accompanied by the formation of a broader peak around 805cm^{-1} related to a new B-N stretching mode. Regarding B-H and N-H bands, they are broadened but they are still present after releasing almost 4 wt% H_2. This is due to the proposed polymerization mechanism, similar to those reported in AB [35]. In this case, chains of molecules of EDAB are formed with new B-N bonds resulting in a polyaminoborane with still more solid hydrogen stored which can be released at higher temperature. The bands corresponding to C-H groups remain after thermal decomposition due to the stability of these bonds at this temperature.

(FIGURE 11)

4. Conclusions

1, 2 diamineborane (EDAB) was successfully micronized using Supercritical Antisolvent (SAS) Process. Therefore, SAS process could be suitable for the micronization of other hydrides compounds, especially boron-nitrogen-hydrogen compounds, in the case that the compound dissolved in an organic solvent is stable in CO_2 atmosphere. The influence of the concentration of THF solutions, the temperature of the process and the fraction of carbon dioxide in the fluid phase on the final structural and thermal properties of EDAB was studied. Similar results were obtained for all the studied conditions regarding particle size, calorimetry and kinetic results.

After micronization process of EDAB, the particle size of about 400 μm with a crystallite size of 100 nm were drastically reduced to 2 μm with a crystal size of 50 nm. Also, the shape suffered variations after SAS process: prismatic structure from unprocessed EDAB changed into microspheres showing agglomeration. XRD and FTIR

analyses showed that no chemical decomposition and no variation of the crystalline structure was produced by SAS processing.

Thermal analyses showed a reduction in decomposition temperatures after SAS process. DSC showed a reduction of 7 K in the decomposition peak temperature after micronization process, releasing hydrogen in a 2 step pathway whose peak temperatures were 134.1 °C (407.25K) and 187.1 °C (460.25K) respectively. In the case of the kinetics of release of hydrogen at 100 ºC (373.15K), the reduction of the particle and grain size resulted in a considerable acceleration of kinetics, reducing by a factor of 6 the time required to release 3.9%wt H_2, comparing to unprocessed EDAB. Moreover, a suppression of induction time was observed due to the destabilization of the hydride after SAS treatment.

5. Acknowledgement

6. References

[1] M.Balat, Potential importance of hydrogen as a future solution to environmental and transportation problems, Int. J. Hydrogen Energ. 33 (2008) 4013-4029.

[2] F.H.Sobrino, C.R.Monroy, J.L.H.Pérez., Critical analysis on hydrogen as an alternative to fossil fuels and biofuels for vehicles in Europe, Renew. Sust. Energ. Rev., 14 (2010) 772-780.

[3]V.Strubel. StorHY. Available at http://www.storhy.net/pdf/StorHy_FourthActivityReport_PES.pdf. (Accessed on October 15th, 2015)

[4] B.Sakintuna, F.Lamari-Darkrim, M.Hirschet, Metal hydride materials for solid hydrogen storage:A review, Int. J. Hydrogen Energ. 32 (2007) 1121-1140.

[5] M.P.Suh, H.J.Park, T.K.Prasad, D.Lim, Hydrogen storage in Metal Organic framework, Chem. Rev. 112 (2012) 782-835.

[6]. Y.H.Hu, E.Ruckenstein, Clathrate hydrogen hydrate- A promising material for hydrogen storage, Angew. Chem. Int. Ed. 45 (2006) 2011-2013

[7] M.Niemann, S.S.Srinivasan, A.R.Phani, A.Kumar, D.Y.Goswami, E.K.Stefanakos, Nanomaterials for Hydrogen Storage Applications: A review, J. Nanomater. (2008) 1-9.

[8] A.Züttel, Materials for hydrogen storage, Mater. Today 6 (2003) 24-33.

[9] Office of Energy Efficiency and Renewable Energy. DoE targets. Available at http://www1.eere.energy.gov/hydrogenandfuelcells/storage/pdfs/targets_onboard_hydro _storage.pdf. (accessed on October 14th, 2015.]

[10] S.D.Rassat, C.L.Aardahl, T.Autrey, R.S.Smith, Thermal stability of ammonia borane: A case study for exothermic hydrogen materials, Energ. Fuel. 24 (2010) 2596-2606.

[11] F.Leardini, M.J.Valero-Pedraza, E.Perez-Mayoral, R.Cantelli, M.A.Bañares, Thermolytic decomposition of ethane 1,2 -diamineborane investigated by thermoanalytical methods and in situ vibrational spectroscopy, J. Phys. Chem. C. 118 (2014) 17221-17230.

[12]D.Neiner, A.Karkamkar, M.Bowden, Y.J.Choi, A.Luedtke, J.Holladay, A.Fisher, N.Szymezak, T.Autrey, Kinetic and thermodynamic investigation of hydrogen release from ethane 1,2-di-amineborane, Energ. Environ. Sci. 4 (2011) 4187-4193.

[13] S.Sahler, H.Konnerth, N.Knoblauch, M.H.G.Prechtl, Hydrogen Storage in Amine Boranes: Ionic Liquid supported thermal dehydrogenation of Ethylene Diamine Bisborane, Int. J. Hydrogen Energ 38 (2013) 3283-3290.

[14] V.Bewrubé, G.Radtke, M.Dresselhaus, G.Chen, Size effects on the hydrogen storage properties of nanostuctured metal hydrides: A review, Int. J. Energ. Res. 31 (2007) 637-663.

[15]J.Huot, G.Liang, S.Boily, A.Van Neste, R.Schulz, Structural study and hydrogen sorption kinetics of ball-milled magneisum hydride, J. Alloy. Compd. 293-295 (1999) 495-500.

[16] P.E. de Jongh, P. Adelhelm, Nanosizing and Nanoconfinement: New Strategies towards Meeting Hydrogen Storage Goals, ChemSusChem 3 (2010) 1332-1348.

[17] L.Zaluski, A.J, Nanocrystaliine metal hydrides, J. Alloy. Compd.253-254 (1997) 70-79

[18] M.Rueda, L.M.Sanz-Moral, A.Martín, Micronization of Magnesium Acetate by the Supercritical Antisolvent Process as a Precursor for the Production of Magnesium Oxide and Magnesium Hydride, Cryst. Growth Des. 14 (2014) 4768-4776.

[19]A.Martín, K.Xcholle, F.Mattea, D.Meterc, M.J.Cocero, Production of Polymorphs of Ibuprofen Sodium by Supercritical Antisolvent (SAS) Precipitation, Cryst. Growth Des. 9 (2009) 2504-2511.

[20] E.Reverchon, Supercritical antisolvent precipitation of micro and nano particles, J. Supercrit. Fluids 15 (1999) 1-21.

[21] J.Li, M.Rodrigues, A.Paiva, H.A.Matos, E.Gomes, Vapor–liquid equilibria and volume expansion of the tetrahydrofuran/CO2 system: Application to a SAS-atomization process, J. Supercrit. Fluids 41 (2007) 343-351.

[22] F.Mattea, A.Martín, A.Matías-Gago, M.J.Cocero, Supercritical antisolvent precipitation from an emulsion: beta-Carotene nanoparticle formation, J. Supercrit. Fluids 51 (2009) 238-247.

[23] H.C.Kelly, J.O.Edwards, Evidence for the Open Chain Structure of Ethane 1,2-Diamineborane, Inorg. Chem. 2 (1963) 226-227.

[24] C.Amorim, M.A.Keane, Palladium supported on structured and nonstructured carbon: A consideration of Pd particle size and the nature of reactive hydrogen, J. Colloid Interf. Sci. 322 (2008)196-208.

[25] J.W.Leachman, R.T.Jacobsen, S.G.Penoncello, E.W.Lemmon, Fundamental Equations of State for Parahydrogen, Normal Hydrogen and Orthohydrogen, J. Chem. Eng. Data, 38 (2009) 721-748.

[26] E.W.Lemmon, M.L.Huber, M.O.McLinden. NIST Standard Reference Database 23: Reference Fluid Thermodynamic and Transport Properties-REFPROP, Version 9.1. National Institute of Standards and Technology, Standard Reference Data Program. Gaithersburd : s.n., 2013.

[27] H.Ting, W.H.Watson, C.Kelly, The molecular and crystal structure of Ethylendiamine-Bisborane, Inorg. Chem.11 (1972) 374-376.

[28] L.Alexander, H.P.Klug, Determination of crystallite size with the XRay Spectrometer, J. Appl. Phys. 21 (1950) 137-142.

[29] J.Goubeau, H.Schneider, Borin-Anlagerungsverbindungen des Äthylendiamins, Chem. Ber. 94 (1961) 816-821.

[30] I. de Marco, E.Reverchon, Influence of pressure, temperature and concentration on the mechanisms of particle precipitation in supercritical antisolvent micronization, J. Supercrit. Fluids 58, (2011) 295-302.

[31] A.Martín, M.J.Cocero, Numerical modeling of jet hydrodynamics, mass transfer and crystallization kinetics in the supercritical antisolvent (SAS) process, J. Supercrit. Fluids 32 (2001) 203-219.

[32] Y.Song, N.Ma, X.Ma, F.Fang, X.Chen, Y.Guo, Syntehsis of Ammonia Borane Nanoparticles and the Diammoniate of Diborane by direct combination of Diborane and Ammonia, Chem. Eur. J. 22 (2016) 6228-6233.

[33] Bérubé V; Radked G; Dresselhaus M; Chen G, Size effects on the hydrogen storage properties of nanostuctured metal hydrides: A review. Int. J. Energ. Res. 31 (2007) 637–663

[34] R.C.W.Moore, S.S.Kelly. Inorganic Syntheses. s.l.: Mc-Graw Hill Book Company, (1970) 109-115.

[35] S.Frueh, R.Kellett, C.Mallery et al, Pirolytic decomposition of ammonia borane to boron nitride, Inorg. Chem. 50 (2011) 783-792.

Figure Captions

Figure 1. SEM image (magnification ratio: 25x/120x, size bar: 900 μm/200 μm) of unprocessed EDAB.

Figure 2. Schematic diagram of the Supercritical Anti Solvent apparatus.

Figure 3. XRD spectra of unprocessed and SAS EDAB samples. Curves are vertically displaced for clarity.

Figure 4. FTIR spectra of unprocessed and SAS-micronized EDAB samples. Curves are vertically displaced for clarity.

Figure 5. a) SEM for micronized EDAB samples at different concentration of the solution. A) c=3.3g/L; B) c=8.1g/L; C) c=10.0g/L; D) c=12.5g/L; E) c=16.7g/L; F) c=25.0g/L (magnification ratio: 5000X; size bar: 5 μm). b) Particle size distribution of the samples obtained from SEM micrographs.

Figure 6. a) SEM for micronized EDAB samples at different temperature and c=25g/L. G) T=35 °C (308.15K); H) T= 40 °C (313.15K); I) T= 45 °C (318.15K) (Magnification ratio: 5000X; size bar: 5 μm). b) Particle size distribution of the samples obtained from SEM micrographs.

Figure 7. a) SEM for micronized EDAB samples at different molar fraction of CO_2 at 40 °C (313.15K) and c=25g/L. J) x=0.964; K) x=0.975; L) x=0.981 (Magnification ratio: 5000X; size bar: 5 μm). b) Particle size distribution of the samples obtained from SEM micrographs.

Figure 8. DSC curves of unprocessed EDAB and micronized SAS samples at different conditions. A) Influence of the concentration of the inlet solution B) Influence of the temperature of the SAS process C) Influence of the molar fraction of CO_2.

Figure 9. DSC curves of micronized SAS samples at different conditions in the range 170-200 ℃ (443.15-473.15K). A) Influence of the concentration of the inlet solution B) Influence of the temperature of the SAS process C) Influence of the molar fraction of CO_2.

Figure 10. Isothermal kinetics of hydrogen release from unprocessed and SAS processed EDAB samples at 100ºC.

Figure 11. FTIR spectra of EDAB before and after thermal kinetic at 100 °C (373.15K). Curves are vertically displaced for clarity.

Tables

Run	T (°C)	c EDAB (g/L)	x CO_2 (mol frac)	D_p (μm)
0		unprocessed		400
1	40	3.3	0.964	2.3
2	40	6.1	0.964	2.3
3	40	8.1	0.964	2.2
4	40	10.0	0.964	2.7
5	40	12.5	0.964	1.7
6	40	16.7	0.964	2.1
7	40	25.0	0.964	2.3
8	35	25.0	0.959	2.0
9	45	25.0	0.971	2.2
10	40	25.2	0.975	2.3
11	40	24.8	0.981	2.0

Table 1. Experimental conditions of different experiments carried out to micronize

EDAB using Supercritical Antisolvent (SAS) process.

Run	Crystallite size (nm)
unprocessed	93.1±10.7
SAS 1	59.6±4.1
SAS 7	52.6±3.1
SAS 8	57.4±6.0
SAS 9	52.6±3.0

Table 2. Crystallite size obtained by Scherer equation for unprocessed and SAS micronized EDAB samples.