



Borane compounds for chemical hydrogen storage and carbon dioxide capture

Carlos Castilla Martinez

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THESE POUR OBTENIR LE GRADE DE DOCTEUR DE L'ECOLE NATIONALE SUPERIEURE DE CHIMIE DE MONTPELLIER

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Institut Européen des Membranes (IEM)

Borane compounds for chemical hydrogen storage and carbon dioxide capture

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le 19 Février 2021

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"It's the questions we can't answer that teach us the most.

They teach us how to think.

If you give a man an answer, all he gains is a little fact.

But give him a question and he'll look for his own answers"

-Patrick Rothfuss

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Abstract

In the last decade, boron- and nitrogen- based compounds have been considered as potential materials for chemical hydrogen storage due to their unique properties. Ammonia borane (NH_3BH_3 , AB, 19.5 wt. % H) and hydrazine borane ($\text{N}_2\text{H}_4\text{BH}_3$, HB, 15.4 wt. % H) are two of the most representative examples. However, these materials cannot be used in the pristine state due to different drawbacks (i.e. release of unwanted byproducts during thermolysis, high dehydrogenation temperature...). To overcome these problems, different approaches have been studied. The chemical modification of AB and HB is one of these options, where a protic hydrogen atom of the molecule is substituted by a metal cation. Thereby, the derivatives of AB and HB (amidoboranes and hydrazinidoboranes) have emerged with improved dehydrogenation properties.

In this work, the last two members of the alkali derivatives of hydrazine borane are presented. Rubidium hydrazinidoborane ($\text{RbN}_2\text{H}_3\text{BH}_3$, RbHB, 4.6 wt. % H) and cesium hydrazinidoborane ($\text{CsN}_2\text{H}_3\text{BH}_3$, CsHB, 3.4 wt. % H) were obtained by a wet synthesis between hydrazine borane and the respective alkali metal. Two new crystalline solids were obtained. The full characterization of RbHB and CsHB was performed in the context of hydrogen storage materials. The successful introduction of the alkali metal cation and the destabilization of the molecule were confirmed. With the family of alkali derivatives of HB complete, we have a better overview of these materials and the findings are discussed.

This thesis also pretends to open new perspectives for amidoboranes. Computational works have shown that boron nitride (BN) can uptake hydrogen or carbon dioxide (CO_2) at room conditions. In this way, we selected the lithium and sodium amidoboranes to be studied as precursors of boron nitride-like structures in order to test their gas sorption properties. The formation of hexagonal BN has been observed when the materials were treated at 800°C . The capacity of CO_2 capture of these materials was investigated. The results are presented for the first time in this work.

Résumé

Au cours de la dernière décennie, les composés à base de bore et d'azote ont été considérés comme des matériaux potentiels pour le stockage chimique de l'hydrogène grâce à ses propriétés uniques. L'ammonia-borane (NH_3BH_3 , AB, 19.5 wt. % H) et l'hydrazine borane ($\text{N}_2\text{H}_4\text{BH}_3$, HB, 15.4 wt. % H) sont deux des exemples les plus représentatifs. Malheureusement, ces matériaux ne peuvent pas être utilisés à l'état vierge en raison de différents inconvénients associés à leur déshydrogénation. Pour surmonter ces problèmes, plusieurs stratégies ont été considérées. L'une d'elles est la modification chimique de l'AB et de l'HB, où un des atomes d'hydrogène protique de la molécule est substitué par un cation métallique. Ainsi, les dérivés de l'AB et de l'HB (amidoboranes et hydrazinidoboranes) ont émergé avec des propriétés de déshydrogénation améliorées.

Dans ce travail, les deux derniers membres des dérivés alcalins de l'hydrazine borane sont présentés. L'hydrazinidoborane de rubidium ($\text{RbN}_2\text{H}_3\text{BH}_3$, RbHB, 4.6 m % H) et l'hydrazinidoborane de césium ($\text{CsN}_2\text{H}_3\text{BH}_3$, CsHB, 3.4 m % H) ont été obtenus par une synthèse par voie humide entre l'HB et le métal alcalin respectif. Deux nouveaux solides cristallins ont été obtenus. La caractérisation complète du RbHB et du CsHB a été réalisée dans le contexte des matériaux par le stockage de l'hydrogène. L'introduction réussie du cation alcalin et la déstabilisation de la molécule ont été confirmées par rapport au précurseur HB. La famille des dérivés alcalins de HB étant complète, nous avons une meilleure vue d'ensemble de ces matériaux et de nouvelles perspectives sont abordées.

Cette thèse a également pour objectif d'ouvrir des nouvelles perspectives pour les amidoboranes. Des études théoriques ont montré que le nitrure de bore (BN) peut absorber l'hydrogène ou le dioxyde de carbone (CO_2) à l'ambiante. Des lors, les amidoboranes de lithium et de sodium ont été étudiés en tant que précurseurs de structures similaires au BN afin d'évaluer leurs propriétés de sorption de gaz. La formation de BN hexagonal a été observée lorsque les matériaux étaient traités à 800°C . La capacité de captage de CO_2 de ces matériaux a été estimée. Des résultats intéressants ont été obtenus et ils sont présentés dans ce manuscrit.

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Chapter 1

GENERAL INTRODUCTION

1 General introduction

1. The problem of energy and global warming

Energy is essential for humanity. All the economic, technological and social progresses that we have accomplished are mainly thanks to the use of energy. However, as the population increases, the necessity for energy does it too. Only in 2018 the increase on the energy demand was of 2.3%, which represents twice the 2010-2017 average.¹ At this rate, the energy consumption will rise up more than 25% in 2040 in comparison with this year.² At present, the energy is mainly obtained from fossil fuels (oil, gas, coal) and secondarily from alternative sources like solar, wind and nuclear energy (Figure 1).³

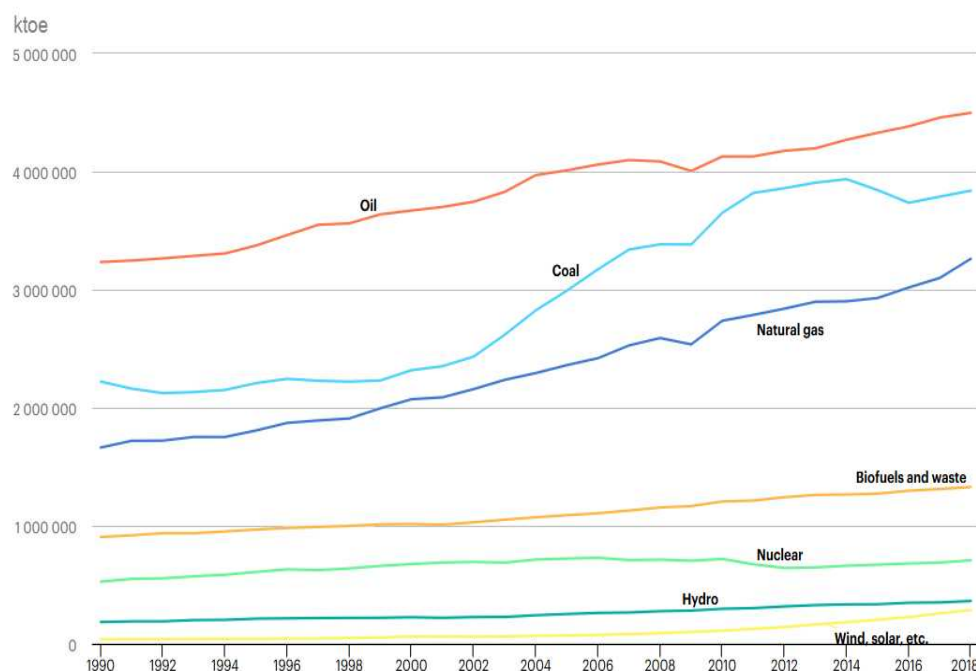


Figure 1. Total energy supply by sources in the 1990-2018 period.³

Fossil fuels are limited non-renewable resources that are being depleted. The difficulty to extract such fuels is increasing and it is becoming harder. In addition, the burning of fossil fuels is the main source of the greenhouse gases (carbon dioxide CO_2 , methane CH_4 , nitrous oxide N_2O , chlorofluorocarbons and hydrofluorocarbons). The release of greenhouse gases into the atmosphere, especially CO_2 , is the main contributor to anthropogenic climate change and global warming.⁴⁻⁷ The emissions of CO_2 has reached a peak in 2019 (**Figure 2**) and has surpassed by far the highest concentration of this gas in previous years.

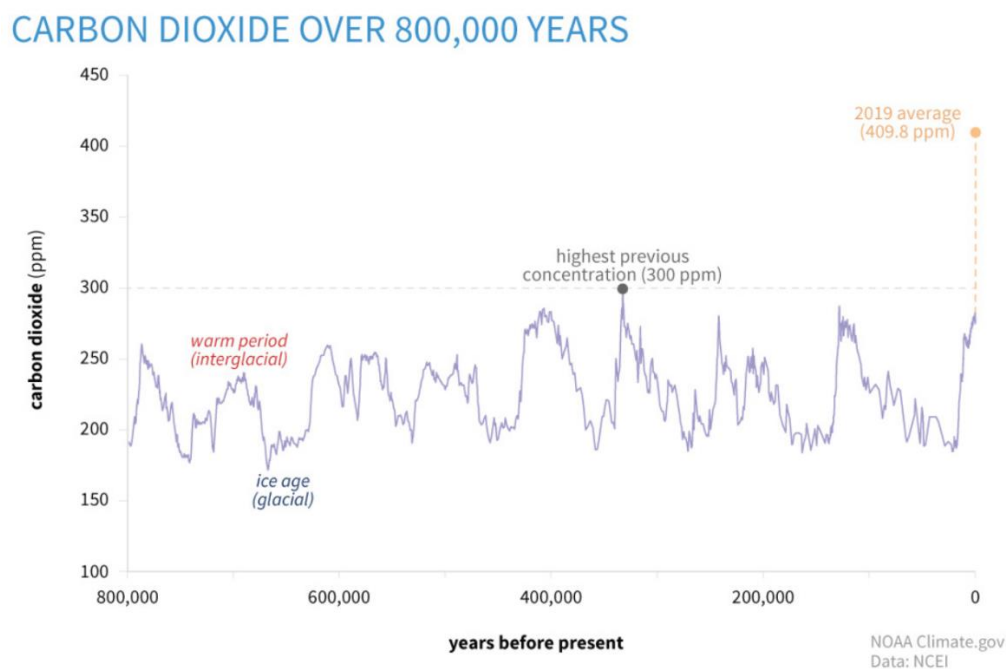


Figure 2. Global atmospheric CO_2 concentrations in ppm for the past 800 000 years.⁷

Global warming has caused negative effects that affect both humanity and the environment: the acidification of the oceans, more intense and frequently droughts and hurricanes, modifications in ecosystems and melting of glaciers.⁸⁻¹⁰ All of these phenomena have a negative impact on society and the economy. For these reasons, efforts have been made to alleviate climate change. Over 100 countries have adopted actions to mitigate global warming to prevent a rise on 2°C in temperature to 2050.¹¹ But despite the efforts, the global average temperature has increased by 0.8°C . It is

evident that the energy consumption has a direct impact on the generation of greenhouse gases and thus in global warming. That is why decreasing the pollutant emissions while supplying and/or reducing the need for energy has become an urgent matter. Different efforts have been done in order to reduce the energy demand, but it is a challenging task that has not had fruitful results up to now.¹² The only option is to find new ways to provide the required energy with sources that produce zero or near zero noxious emissions.

Hydrogen arises as the best option to substitute fossil fuels due to its high energy density and because it produces zero emission during its combustion. In addition, it can overcome the disadvantages of other renewable sources, like the intermittency of solar and wind energy. Thanks to this potential, the concept of a hydrogen economy was created: it is an alternative economic model where the basic energy needs are supplied by hydrogen. Several reports show that hydrogen can participate in almost every part of the energy system (**Figure 3**), including electricity generation and heat power.¹³ This will lead to the decarbonization of the energy chain supply. But different efforts must still be done to achieve a feasible hydrogen economy. There are different challenges that have to be addressed simultaneously which include the production, storage, transportation and distribution of hydrogen. However, hydrogen storage is one of the biggest challenges regarding the hydrogen economy.

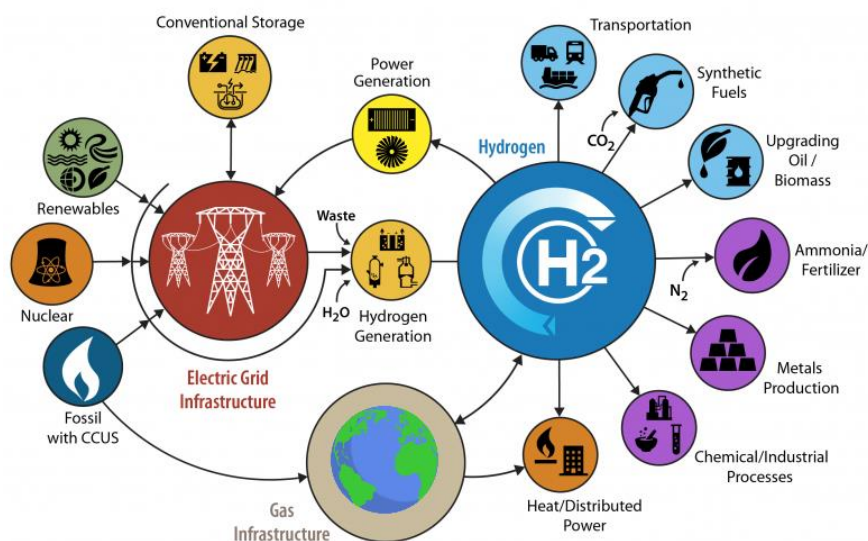


Figure 3. Potential of hydrogen to participate in the energy system. Modified from ¹⁴.

On the other hand, the reduction of the CO₂ emissions to the atmosphere is also important. The carbon capture and storage (CCS) technologies can contribute to achieve this. With the implementation of this technologies, the rise in the global average temperature can be avoided in up to 2°C.¹⁵ Some of the CCS technologies are based on the use of a suitable adsorbent to capture CO₂. Research works are being focused in the development of materials able to capture CO₂ in an efficient way.

The present work intends to contribute and widen the knowledge about boron- and nitrogen-based materials. This thesis presents the results of new materials evaluated in the context of hydrogen storage, and it opens new perspectives regarding CO₂ capture.

The rest of the thesis is organized as follows:

Chapter 2 follows the literature review by describing hydrogen and summarizing the processes of production and conversion to obtain it. The emphasis of this chapter is on materials for hydrogen storage, especially the boron- and nitrogen-based compounds.

Chapter 3 presents rubidium hydrazinidoborane, a new alkaline derivative of hydrazine borane and its evaluation in the context of hydrogen storage.

Chapter 4 introduces cesium hydrazinidoborane, the last alkali derivative of hydrazine borane. The characterization as potential hydrogen storage material is described.

Chapter 5 features the synthesis of boron nitride derived from ammonia borane and two of its alkali derivatives, lithium and sodium amidoboranes. In addition, the CO₂ sorption properties of these materials were briefly studied.

Chapter 6 gives the general conclusion of this work and open new perspectives to boron- and nitrogen-based materials.

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Chapter 2

LITERATURE REVIEW

2 Literature review

1. Hydrogen as energy carrier

1.1 Properties of hydrogen

Hydrogen is the lightest element ($1.0079 \text{ g mol}^{-1}$) and is the most abundant in the universe. As an element, it is the third most abundant on Earth, present mainly in water and organic compounds. As a molecule, the concentration of H_2 is lower than 1 ppm in the atmosphere. H_2 is a non-toxic, colorless and odorless gas. H_2 has a density of 0.08 g L^{-1} at room temperature and it has melting and boiling points of -259.3 and -252.9 °C, respectively (Figure 1).

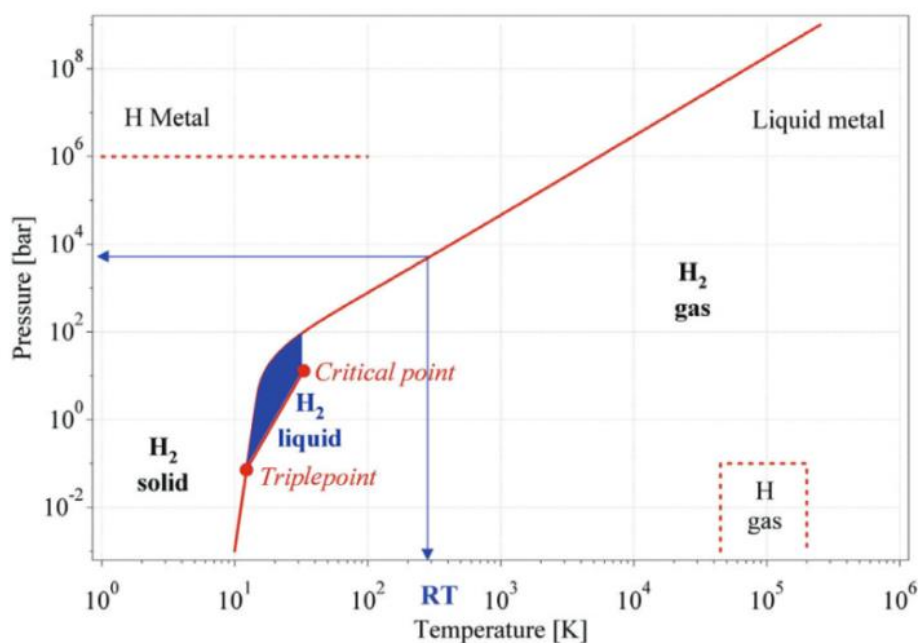


Figure 1. Phase diagram of H_2 .¹

H₂ presents two isomeric forms (spin isomers): ortho-hydrogen, when the proton nuclear spins have a parallel alignment; and para-hydrogen, when the proton nuclear spins are aligned antiparallel. At standard conditions, H₂ gas consists of both ortho-hydrogen (75%) and para-hydrogen (25%). H₂ possesses three isotopes: protium (99.985%), deuterium (0.0156%) and tritium (<1 in 10¹⁷ atoms). H₂ can react with different elements. Depending on the element with which it reacts, the H atom can have a partial positive charge H^{δ+} (with more electronegative elements) or a partial negative charge H^{δ-} (with more electropositive elements). H₂ is a highly flammable gas and it can burn in air. The combustion of H₂ (Equation 1) has an enthalpy of combustion of -286 kJ mol⁻¹. The energy released by this reaction allows H₂ to act as a fuel.

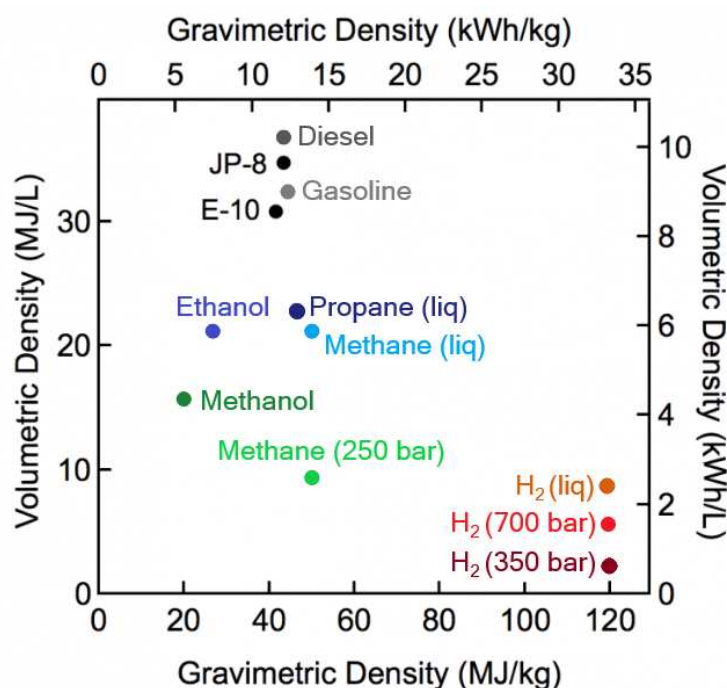


Figure 2. Specific energy and energy density for different fuels based on heating values.²

H₂ has a high gravimetric energy density in comparison with other fuels (Figure 2). It has an energy density between 120 and 142 MJ kg⁻¹. The lowest value is the lower heating value, and it

assumes that the latent heat of vaporization of water after H_2 combustion is not recovered. The highest value is known as the higher lower heating value and it considers that water is condensed after the combustion of H_2 . This range of energy density is about three times more than fossil fuels. But opposite to fossil fuels, H_2 is a clean and non-toxic fuel, and it has a long-term viability.³⁻⁵ In the concept of an economy based on hydrogen, the fossil fuels will be replaced by H_2 .⁶⁻⁸ But to reach this goal, some technical issues should be solved: the production, the distribution, the infrastructure, the storage and the conversion technologies.^{9,10}

1.2 Production of hydrogen

Besides being considered as a fuel, H_2 is also useful for different applications and chemical processes. For example, H_2 is used in the hydrocracking and hydro-processing of hydrocarbons; in the production of organic compounds; in the production of ammonia (NH_3) and nitrogen-based fertilizers; in metal refining; as a rocket fuel; and in food preparation.¹¹⁻¹³ In order to obtain H_2 , different chemical processes have been developed. The main processes are presented in Figure 3. The next section briefly describes each one of them.

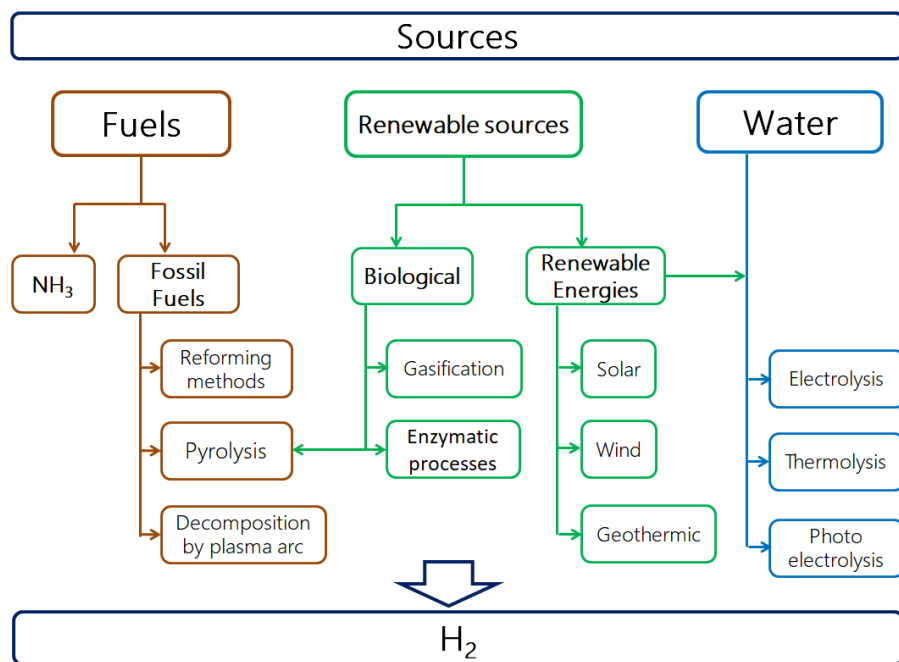


Figure 3. Main H_2 production methods.

1.2.1 Hydrogen from fuels

Up to 48% of H₂ is obtained from natural gas, 30% from heavy oils and 18% from coal.¹⁴ Less than 5% is obtained from non-pollutant sources. For a sustainable future, it is indispensable to increase the use of cleaner processes that release less harmful emissions. Nowadays, H₂ is mostly obtained from fossil fuels.

1.2.1.1 Hydrocarbon reforming methods

The hydrocarbon reforming is a process in which the hydrocarbon fuel is transformed into H₂ through reforming techniques. The most used reforming technologies are the steam methane reforming (SMR), partial oxidation (POX) and auto-thermal reforming (ATR) processes.¹⁵ SMR is the most used process to produce H₂,¹³ where natural gas or methane reacts with steam (Equation 2) in the presence of a catalyst (usually nickel-based), producing H₂ and carbon oxides. In a further step, additional H₂ is obtained through the reaction of carbon monoxide (CO) and steam (Equation 3). This process requires temperatures between 700-1100°C, pressures up to 3.5 MPa and a ratio steam/carbon of about 3.5. This is a well-known H₂ production process in the industry, but it is the one with the highest emissions of CO₂ to the atmosphere.

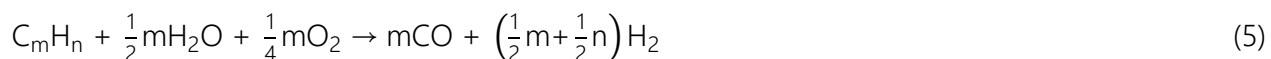


The partial oxidation process is used to convert hydrocarbons into H₂ through the partial oxidation of the hydrocarbon with oxygen (Equation 4). This process can work with any kind of liquid/gaseous fuel and without a catalyst. The main disadvantages of this process are the high temperatures required (1150-1320°C) and that CO is produced.



Finally, the auto-thermal reforming process involves the mixture of the steam methane reforming and the partial oxidation. The principle is to carry out the reforming and oxidation reactions simultaneously, introducing oxygen and steam into the reactor (Equation 5). The advantage of

this method is that it requires lower working temperatures ($\sim 700^\circ\text{C}$). However, it produces CO this process is industrially limited.¹⁵



1.2.1.2 Hydrocarbon pyrolysis

The pyrolysis is a process where the hydrocarbon is thermally decomposed in the absence of air and water, obtaining carbon and H_2 (Equation 6). The nature of the pyrolysis products (gas, liquid and/or solid) can be adjusted modifying variables such as the temperature, heating rate and residence time in the reactor.¹⁶ The advantages of this process include its simplicity, fuel flexibility, the reduction of carbon oxides emissions. However, if oxygen and/or water are present during the pyrolysis, the release of such carbon compounds is not avoided.

In comparison with other processes, the pyrolysis is more energetically efficient. For example, 1 mol of H_2 obtained from the pyrolysis of methane will require only 37.8 kJ mol^{-1} while in the steam reforming process, 63.3 kJ mol^{-1} are required.¹⁷



1.2.1.3 Methane decomposition by plasma arc

Plasma is the state of matter that consists of a gas of ions and electrons in an excited state. Thanks to the presence of the electrically charged particles, it can release high voltage electric current. For example, CH_4 can be decomposed by the thermal activity of plasma (Equation 7):¹⁸



The working temperature of this process is of about $1700\text{--}1800^\circ\text{C}$. Conversion of 100% has been achieved with this method, and with zero emissions of carbon oxides.¹⁹ The main challenge for this technology is to reduce the cost of the energy required to produce the plasma.

1.2.1.4 Ammonia cracking

Ammonia has a higher energy density (8.9 kWh kg^{-1}) than ethanol and methanol, but lower than diesel or gasoline (Figure 2). It is used in the production of fertilizers, but it also has been considered as a fuel for solid oxide fuel cells (SOFC).²⁰ The industrial synthesis of ammonia (Haber-Bosch process) comprises the reaction between N_2 and H_2 in the presence of a metal catalyst that will determine the temperature of the process.²¹ Normally, the reaction takes place at 15-25 MPa and between 400 and 500°C. The most used catalysts in the Haber-Bosch process are based on iron oxide, ruthenium, nickel and molybdenum.¹⁵ H_2 can be obtained by the inverse synthesis reaction, called ammonia cracking (Equation 8), that is an endothermic process (383 kJ mol^{-1}) which requires operating temperatures between 850 and 950°C.



1.2.2 Hydrogen from water

Water is one of the most abundant compounds on Earth and it can be used in the production of H_2 . The commercial use of this process started at the end of the XIX century,¹⁵ but an intense research on an efficient splitting of water into H_2 and O_2 started in recent decades. This research has focused in three main splitting processes: water electrolysis, water thermolysis and water photo-electrolysis.

1.2.2.1 Water electrolysis

Among the water splitting methods, water electrolysis is the most basic industrial process and it produces highly pure H_2 (>99.999%).²² Water electrolysis is an electrochemical reaction that splits water into H_2 and O_2 with the help of an electrolyzer. This device consists on a cathode and an anode immersed in an electrolyte. When an electrical current with a potential of 1.23 V is applied in the system, water is separated into its components (Equation 9).



Different types of electrolytes can be used. For example, soluble salts based on Na or Li, acid electrolytes or solid polymer electrolyte in proton-exchange membrane fuel cells. The use of a catalyst can also be considered to increase the rate of the reaction and current density. Platinum-based catalysts are the most used for water splitting.¹⁸ Despite the extremely pure H₂ that can be obtained with this method, the high costs related to the electricity has prevented a feasible implementation at large-scale yet.²³

1.2.2.2 Water thermolysis

Water thermolysis is the decomposition of water into H₂ and oxygen by action of the temperature. However, this reaction has a thermodynamic limitation: the Gibbs free energy of the reaction needs to be near zero and for this, temperatures above 2500°C are required.²⁴ The difficulties that represent to work at such conditions have complicated the implementation of this technology. In order to overcome this limitation, different thermochemical processes (i.e. Ispra Mark 9 or Shell process) have been proposed to increase the global efficiency of the reaction.²⁵

1.2.2.3 Water photo-electrolysis

In water photo-electrolysis, visible light is used to decompose the water into H₂ and oxygen. In principle, it is similar to electrolysis but this technology uses a semiconductor and photo-electrodes to split H₂O. Different materials with photoelectrocatalytic effect have been tested as electrodes, such as Sb₂S₃, ZnS, p-SiC/Pt or TiO₂.^{26–29} The materials used as electrodes and semiconductors determine the efficiency of the system. This technology is still in an early stage, so the H₂ production cost is estimated on 10.36 \$ kg⁻¹, which is high in comparison with fossil fuel reforming (0.75 \$ kg⁻¹) and plasma arc decomposition (0.85 \$ kg⁻¹).¹⁸ The expected price for H₂ obtained by photo-electrolysis is 2.3 \$ kg⁻¹ for 2020.³⁰

1.2.3 Hydrogen from renewable sources

The production of H₂ from fossil fuels has reached the maturity in the industry, but the main problem with those processes is the release of hazardous gases to the atmosphere. In addition, the extraction of fossil fuels represents an environmental risk. The only alternative is the

development and implementation of H₂ production technologies from cleaner sources, such as the renewables ones. The following are examples of technologies that can produce H₂ with a lower environmental impact.

1.2.3.1 Hydrogen from biological sources

The biological production of H₂ can be performed at room conditions, which represents a big advantage over other processes. Other advantage is that different waste materials can be used to produce H₂, contributing to the recycling of waste products from other industries. For example, biomass is the most viable organic substitute to petroleum, and it can be obtained from different sources like agricultural/livestock waste, municipal solid wastes, and aquatic plants.¹⁵ Thermochemical processes are widely used in the conversion of biomass into H₂. For example, biomass gasification uses oxygen, steam or air (or a mixture of all of them) in a temperature range of 700-1200°C to produce a gas consisting mainly of H₂, CO, CO₂ and CH₄.^{31,32} From a typical biomass, the stoichiometric yield of H₂ expected is 14.3 wt. % (Equation 10). In real processes, this yield tends to be lower as by-products like char, tar and CO₂ are formed.²² The gasification process depends on different parameters such as the type of biomass used, the reactor design and the gasification medium. Other important aspect of the process is the catalyst, since it has a key role on the reaction: the correct selection of an appropriate catalyst will lead to an increase on the gas production and its quality while lowering the costs. Different catalysts such as ZnO₂, Ca(OH)₂, clay or cement kiln can be used.³³



Pyrolysis of biomass is another attractive thermochemical conversion process for H₂ production. After the biomass pyrolysis, a catalytic steam reforming process can be done in order to obtain bio-oil. These two steps can be carried out at two different places, which benefit small-scale applications and benefits the economic efficiency of the process. The potential yield of H₂ from pyrolysis is 13 wt. %.²²

A third option are the enzymatic processes. Enzymatic processes for H₂ production are classified as follows: (i) biophotolysis of water using algae and cyanobacteria, (ii) photodecomposition of

organic compounds by photosynthetic bacteria, (iii) fermentation from organic compounds; and (iv) hybrid systems.³⁴ The processes are controlled by H_2 -producing enzymes (hydrogenase, nitrogenase).³⁵ However, these methods have not been proved at large-scale yet.

1.2.3.2 Hydrogen from renewable energy

The use of renewable energies for H_2 production is one of the most sustainable options. The energy required to perform some of the processes aforementioned can be supplied from renewable sources. For example, solar energy has been used to perform water electrolysis by two different ways: (i) photo-electrochemical water splitting, which uses the sunlight to convert water into oxygen and H_2 and (ii) photovoltaic electrolysis, which consists of photovoltaic modules that use electrolyzer units.³⁶ Wind energy can also be used to provide the required energy for the water electrolysis. Another option is the harness of the thermal and electric energy obtained by geothermal sources that can be used in thermal cycles or electrolysis, to produce H_2 .³⁷

As discussed before, fossil fuels are still the main source for H_2 but, there are other options with the potential to produce H_2 without releasing hazardous emissions to the atmosphere. However, to have a feasible and competitive sustainable technology, different factors have to be considered and evaluated, such as the life cycle, costs, impact on the environment and sustainability of each one of the processes.³⁸

1.3 Energy from hydrogen

1.3.1 Fuel cells

One of the most promising technologies that can provide energy and even compete with internal combustion engines and batteries are fuel cells.³⁹ A fuel cell is an electrochemical device that converts chemical energy directly into electrical energy, using a fuel and an oxidant.⁴⁰ Fuel cells consist of an electrolyte between two porous electrodes (anode and cathode) containing a catalyst. The electrolyte allows the ions to move between the electrodes. The chemical reactions take place at the surface of the electrodes: H_2 and O_2 are feed to the fuel cell and they react to produce electricity. Ethanol, methanol, ammonia and hydrazine are examples of fuels that can be

used.⁴¹ The overall reaction in fuel cells is the inverse of the water electrolysis (Equation 11). Fuel cells have the potential to be used in both portable or stationary applications.



Different types of fuel cells exist (Figure 4), but the most common are the polymer electrolyte membrane fuel cells (PEMFCs), alkaline fuel cells (AFCs), phosphoric acid fuel cells (PAFCs), molten carbonate fuel cells (MCFCs) and solid oxide fuel cells (SOFCs).^{40,42} The classification is based on the type of electrolyte of each fuel cell. Depending on the chosen electrolyte, other parameters change, like the type of fuel, the catalyst or the operating temperature.

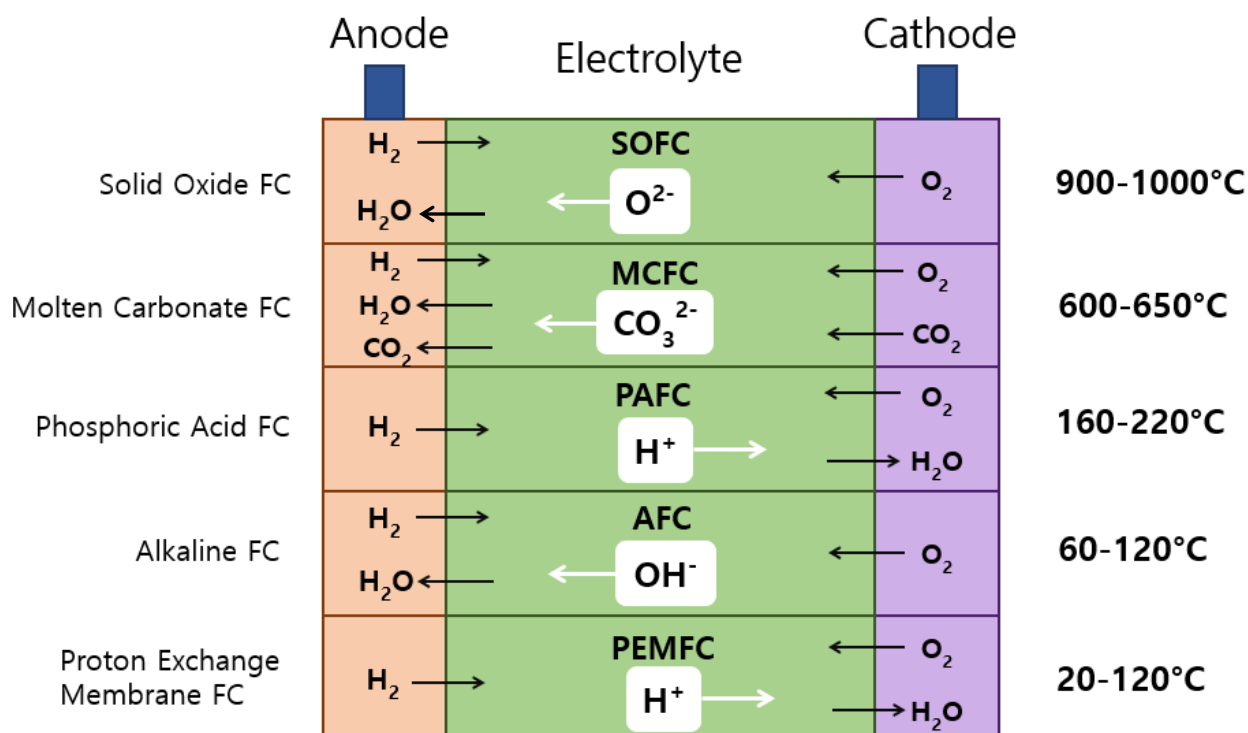


Figure 4. Summary of main types of fuel cells describing the feedstock, products, range of working temperature and ions exchanged through the electrolyte. Adapted and modified from ⁴².

However, there are other types of fuel cells in development. In recent years, the anionic alkaline exchange membrane fuel cells (AAEMFCs) have bloomed.⁴³⁻⁴⁵ In the case of the AAEMFCs the ion

(OH⁻) is transported from the cathode to the anode. At difference of the PEMFCs, the AAEMFCs create an alkaline pH environment in the cell which have some advantages:⁴⁶ (i) the use of Pt-free or precious group metal free catalysts is possible; (ii) different fuels, like nitrogen-based fuels such as hydrazine or ammonia, can be used as feedstock; and (iii) the materials for these fuel cells are cheaper. However, AAEMFCs still have some challenges ahead, like the compatibility of the polyhydrocarbon-based membranes with the electrodes, the stability of the hydroxide ion and the scale-up of the cell.⁴⁷

As mentioned before, fuel cells can provide energy for portable applications. In the last years, portable electronic devices have received attention and market demand, due to its simplicity and convenience for our lives. However, these applications demand compact and long-life power sources, low weight and a long operation.⁴⁸ Some fuel cells have been adapted to fulfill these requirements. One example is the direct borohydride fuel cell (DBFC), which uses the chemical energy stored in the borohydride ion (BH₄⁻) as fuel and O₂ as oxidant, according to the reactions at the anode (Equation 12) and the cathode (Equation 13).⁴⁹ Usually, a DBFC uses an alkaline solution of sodium borohydride NaBH₄.



The DBFC presents some advantageous features. For example, NaBH₄ solutions are safely to handle: they are stable under air and they are nonflammable; besides, the products of the reaction in the fuel cell are environmentally safe and can be recycled back to NaBH₄.⁵⁰ However, DBFC also present drawbacks: the fuel undergo through side reactions, the poisoning of the catalyst at the electrodes, the durability, and the cost and operation at long term.⁵¹

1.3.2 Batteries

Even if the metal ion batteries dominate the energy storage field, there have been some attempts to develop batteries that operate with H₂. Dargily *et al.*⁵² worked on a device that has a Pt-electrocatalyst supported on carbon as anode and a benzoquinone-based cathode, separated by

an H^+ ion conducting membrane. In their configuration, the electrons generated from the oxidation of H_2 migrate from the anode to the cathode through the membrane, prompting the conversion of benzoquinone to hydroquinone. This mechanism allows a rechargeable system. Hsu *et al.*⁵³ and Boddien *et al.*⁵⁴ worked in a rechargeable H_2 battery based on the hydrogenation of CO_2 to formic acid (charging process) and the decomposition of formic acid to CO_2 (discharging process), mediated by a ruthenium catalyst. At difference from normal electron-based batteries, in these devices H_2 is used as the energy carrier. This system has a limitation of 4.4 wt. % H_2 content, but is fully reversible. Such devices were able to perform five cycles of charging-discharging without loses in storage capacity. However, these batteries still have some technical issues like the necessity of solid CO_2 .

2. Hydrogen storage

Even if some of the H_2 -based technologies are already available in the market, there is still a big issue in order to supply H_2 : its storage. The U.S. Department of Energy (DOE) recognized H_2 storage as the most challenging problem for the hydrogen economy.⁵⁵ The targets established by the DOE for 2025 for light-duty vehicles include: specific energy of $1.8 \text{ kg H}_2 \text{ kg}^{-1}$, energy density of $1.3 \text{ kg H}_2 \text{ L}^{-1}$, cost of $9 \text{ \$ kg}^{-1}$ and an operating temperature between -40 and 85°C .⁵⁶ Unfortunately, no existing systems meet these conditions. The remaining challenges for H_2 storage technologies comprise the weight, volume, efficiency, safety and cost of the system. At present, H_2 storage technologies consist of high-pressure tanks, liquefaction at cryogenic conditions and the storage into a host material.

2.1 Compressed hydrogen

H_2 can be stored in suitable tanks, cylinders or containers at high pressure, up to 700 bar. Three main applications for high pressure vessels can be identified: stationary, vehicular and bulk transportation.⁵⁷ The stationary storage is used in H_2 refueling stations because of the low cost. Storage in vehicles should meet three characteristics: high density, light weight of the vessel and

low cost. The bulk transportation of H_2 is used to deliver it from its production to the end user, and it requires of a high capacity and a lightweight to optimize the costs.

H_2 storage at high pressure presents advantages: the concept of the technology is simple, the fast release rate of the gas and the reversibility of the process. However, this technology also possesses disadvantages:⁵⁸ for transportation and for portable applications, the constraints are the high weight of the vessels, the volume savings and the cost. For stationary applications, the main restriction is the pressure cycle life of the tank. In any case, the safety requirements must be considered. Another problem includes the compatibility of the tank materials and the gas. Finally, there is an additional issue regarding the thermodynamic aspect of the compression: as the process is adiabatic and isentropic, the vessel heats in the inside leading to a loss of exergy. When the vessel cools down to normal storage temperature, there is a loss of pressure and thus of the total H_2 stored.⁵⁹ Despite the simplicity and the convenience of the technology for some applications, different storage options with better characteristics are required.

2.2 Liquid hydrogen

H_2 is a liquid at -253°C and atmospheric pressure. It is an attractive option due to the potential to store a large amount of hydrogen that can be easily transported.⁶⁰ The vessels to store gases at cryogenic conditions have been used for more than 40 years, and they are composed of an inner pressure vessel with an external jacket to protect it, with an insulator between them.⁶¹ These tanks can store up to 70 g L^{-1} of liquid H_2 , which is a higher value compared to the capacity of high pressure tanks (30 g L^{-1}).⁶²

The conventional process to liquefy H_2 follows three steps:⁵⁹

- 1) Compression. Pure and dry H_2 is compressed above its critical point.
- 2) Cooling. This is a double-step process: first, H_2 is cooled down to $-193 \pm 15^\circ\text{C}$; after, the gas is cooled down between -251 and -228°C . Heat is removed from the system in each step.
- 3) Expansion. H_2 is depressurized and partially liquefied. Liquid hydrogen is collected in a vessel and the remaining gaseous H_2 is then reinjected to the first compression step.

The storage of liquid H_2 is a good alternative in terms of mass and volume, but it presents some disadvantages. First, the necessary energy to liquefy H_2 represents 30% of the total stored energy of the system.⁶³ Second, the insulation of the tank is not highly efficient: each day 2-3% of the stored H_2 is lost due to the heating of the vessel.⁶⁴ Third, the cost of the tank. Although this technology is very promising, the problems must be overcome in order to assure the feasibility of liquid H_2 .

2.3 Hydrogen stored in materials

H_2 stored in a material might be the most promising technology of storage, due to the high H_2 density of different materials. The ultimate targets established by the DOE for H_2 storage materials are a gravimetric density of $0.065 \text{ kg-}H_2 \text{ kg}^{-1}$, a volumetric density of $50 \text{ g } H_2 \text{ L}^{-1}$, a cost of $266 \$ \text{ kg}^{-1} H_2$ and a performance near ambient conditions.⁶⁵ H_2 can be stored by physical or chemical interactions into a material, and this allows a higher storage capacity compared with the other technologies (Figure 5). In the next section, some of the materials used for chemical or physical H_2 storage in the solid state are described.

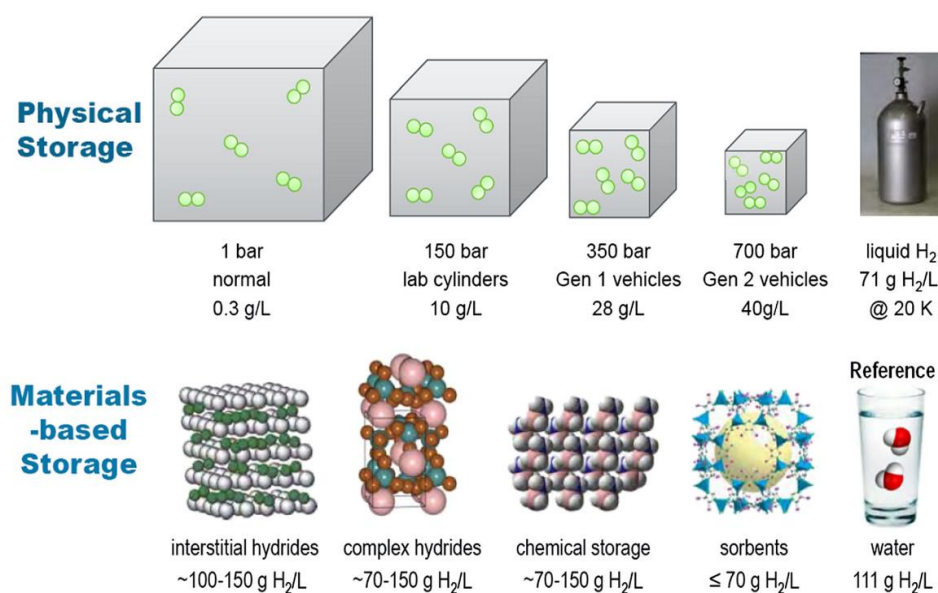


Figure 5. Materials-based H_2 storage versus compressed and cryogenic storage systems.⁶⁶

2.3.1 Physisorption of hydrogen

H₂ can be stored as a molecule by physical adsorption on the surface of a porous solid material. According to the IUPAC, there are three types of porous materials: macroporous (pore size >50 nm), mesoporous (pore size between 2 and 50 nm), and microporous materials (pore size <2 nm). The physisorption of a gas is a cyclic reversible process of adsorption/desorption in the surface of a porous solid, where the involved species do not experiment any change or decomposition. The physical adsorption of H₂ on an adsorbent surface is caused by weak interactions (van der Waals or London dispersion forces). This relatively low binding energy allows an 'easy' release of H₂ from the material. For example, for metal organic frameworks, low binding enthalpies in the range of 4-10 kJ mol⁻¹ are insufficient to hold H₂ molecules on the surface of the material, causing a low storage capacity at room temperature. Some reports have suggested that the ideal heat of adsorption for a determined material is 20-30 kJ mol⁻¹ to operate at room temperature.⁶⁷ In contrast, high enthalpies in the range of 40-100 kJ mol⁻¹ will favor the chemisorption of H₂, leading to a 'harder' release of the molecule, poor reversibility and slow kinetics.

A good candidate to store H₂ by physisorption should consider different parameters like the binding energy between H₂ and the selected material, the pore size, the bulky density of the solid and especially, the specific surface area.^{68,69} The advantages of physisorption over chemisorption are fast kinetics, reversibility of the process and low heat produced while refueling; while the main disadvantage is that high storage capacities are obtained at low temperatures (-196°C).⁷⁰ Different porous materials have been studied as hosts for H₂. Some of them are briefly discussed in the following section.

2.3.1.1 Carbon materials

Different structures based on carbon exist due to the partially filled sp² orbitals of the carbon atom. Each atom can bind with up to seven neighboring carbon atoms, leading to the formation of different structures such as activated carbon, diamond, fullerenes, graphene, and nanotubes. These compounds have pores of different sizes which are good places for gas physisorption.

Carbon atoms also have the propensity to bind to other atoms or molecules, making it suitable as a H₂ storage material. It has been reported that these materials can adsorb up to 5.5 wt. % H₂.⁷¹ However, carbon-based materials adsorb H₂ at high pressure or cryogenic temperatures (or both).

Activated carbons are materials with specific surface areas up to 3000 m² g⁻¹. They have been widely studied as H₂ storage materials. However, the adsorption of H₂ must be done at cryogenic conditions and at high pressure: it has been reported that only 1 wt. % H₂ is adsorbed by activated carbons at room temperature and at 100 bar.⁷² There are some approaches to increase the uptake of H₂ in activated carbons. One is to control the pore size of the material. Zhao *et al.*⁷³ found that uptakes higher than 3 wt. % H₂ are due to the presence of pores with a diameter above 0.7 nm. Another approach is to dope the carbon atoms with other elements. Wang *et al.*⁷⁴ worked with activated carbon doped with nitrogen atoms with different pore widths. They obtained an uptake of 2.96 wt. % H₂ at 1 bar and -196°C. Sethia and Sayari⁷⁵ achieved an uptake between 4.23-6.77 wt. % H₂ at -196°C and 20 bar from an activated carbon doped with nitrogen; the content of H₂ differs in relation with the surface area of the carbon.

Carbon nanotubes are other of the most investigated materials for H₂ storage based on carbon. The nanotubes are obtained in two different types: single-walled carbon nanotubes (SWCNT) and multi-walled carbon nanotubes (MWCNT). Basically, SWCNT consist of a graphene sheet rolled up into a cylinder with nanometer diameter and microns length. Dillon *et al.*⁷⁶ were the first to report experimental data of H₂ adsorption in SWCNT, and estimated a gravimetric storage density from 5 to 10%. More recently, the surface of carbon nanotubes has been modified to enhance H₂ sorption. Rajaura *et al.*⁷⁷ worked on the functionalization of carbon nanotubes with an acidic treatment. They increased the gravimetric H₂ storage capacity from 0.65 wt. % to 0.89 wt. % with the functionalized nanotubes at room temperature and high pressure. Other approach to improve the uptake of H₂ is to incorporate precious metals, such as palladium, to the surface of the carbon nanotubes.^{78,79} Pd allows a high adsorption of H₂ at room conditions. This is because at the surface of the Pd, the dissociative adsorption of H₂ molecules presents a negligible activation energy barrier.⁸⁰

Graphene is a 2D carbon material which theoretically can store up to 8.3 wt. % H_2 .⁸¹ Klechikov *et al.*⁸² reported a high H_2 uptake of ~5 wt. %, at -196°C and 10 bar working with a bulk graphene with a surface area of 2300 m² g⁻¹. Nevertheless, they conclude that bulk-graphene materials do not exhibit superior H_2 storage parameters in comparison with other carbon-based materials, as experimentally they present a similar uptake as activated carbon, carbon nanotubes or nanofibers. As determined for other carbon materials, the functionalization of graphene with different atoms can enhance H_2 adsorption.⁸³ A comparison between different H_2 storage systems including graphene systems is showed in Figure 6.

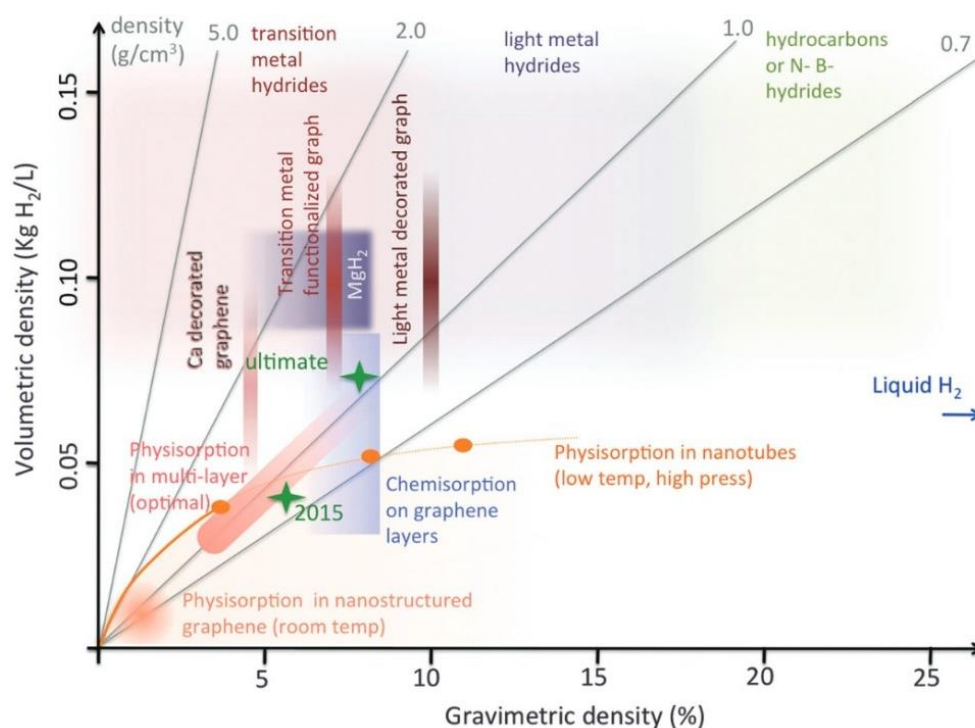


Figure 6. Gravimetric vs. volumetric density for different H_2 storage systems.⁸¹

2.3.1.2 Zeolites

Zeolites are materials with the general formula $M_{n/x}(Al_nSi_mO_{2(n+m)}) \cdot yH_2O$ where M is the counterbalancing cation. Zeolites are usually used as molecular sieves, ion exchangers or catalysts.⁸⁴ These materials have a regular open pore microstructure with different frameworks

and have been tested as H₂ storage materials, due to some advantageous characteristics: they are inexpensive, environmentally friendly, thermally stable and their ion-exchange property can be easily exploited.⁸⁵ It has been reported that the H₂ uptake in these materials depends on factors such as the framework structure and the radius and density of the cation.^{86,87} Several types of zeolites have been tested, reaching a H₂ uptake between 0.08-2 wt. %.⁸⁸ In a recent computational work, Martin-Calvo *et al.*⁸⁹ analyzed 219 zeolites and evaluated parameters like the saturation capacity, the pore size distribution and the curves of H₂ adsorption. They determined that at extreme conditions (100 MPa and -248°C) only six of the analyzed zeolites have the potential of store 7 wt. % H₂.

Like for other porous materials, computational studies have suggested that doping a zeolite with metal atoms can improve the uptake of H₂. Ozturk found that dispersed lithium in a pure silica zeolite (CHA-type) can increase the H₂ storage capacity between 3 and 6 times in comparison with the pristine zeolite.⁹⁰ Sun *et al.*⁹¹ also analyzed a zeolite (FAU type) by computational methods, finding that the adsorption of H₂ can be enhanced with the introduction of silver atoms in the framework. At -196°C and 5 bar of pressure, the zeolites can store 16.4 g L⁻¹ of H₂, in comparison with the 9.2 g L⁻¹ of the pure zeolite.

2.3.1.3 Metal organic frameworks

Metal organic frameworks (MOFs) are structures composed of inorganic and organic units linked by strong bonds. MOFs have a high crystallinity and their surface area range between 1000 and 10 000 m² g⁻¹, surpassing those of other porous materials like zeolites and carbon-based materials.⁹² These microporous structures have been considered as H₂ storage materials due to their high crystallinity, purity and porosity, in addition to their controllable structural characteristics. The first work that reported H₂ storage in a MOF was done by the group of Yaghi,⁹³ where they achieved a H₂ uptake of 4.5 wt. % at -195°C and 1 wt. % at room temperature and 20 bar, in the MOF-5. In a further work, the same research group concluded that the interaction between H₂ and the framework of the MOFs can be improved by changing the chemical nature of the organic linker.⁹⁴ After these works, it was reported that the adsorption of a gas into a MOF is also strongly dependent on the metal atom.⁹⁵ Other relevant approach to

improve the adsorption of H_2 on the MOFs is to dope them with electropositive metals, such as lithium, sodium or magnesium.^{96–99}

Due to the huge number of MOFs that can be used for H_2 storage applications, it is difficult to determine the right material with the optimal characteristics. Ahmed *et al.*^{100,101} did a systematic assessment of 500 000 MOFs to evaluate their storage capacity. Three of them were selected: SNU-70 (Metal: Zn; linker: 4-(2-carboxyvinyl)-benzoic acid), UMCM-9 (Metal: Zn; linker: H_2 BDC and H_2 NDC) and PCN-610/NU-100 (Metal: Cu; linker: hexatopic carboxylate LH_6), having a usable gravimetric capacity between 10.6 and 13.9 wt. %. This group also established a volumetric ceiling of 40 g H_2 L^{-1} as H_2 adsorbents. However, on a recent study Chen *et al.*¹⁰² reported the synthesis of two highly porous materials, NU-1501-M (Metal: Al or Fe; linker: triptycene-based). The aluminum-based material has a H_2 storage capacity of 14.5 wt. % (47.9 g L^{-1}) at 100 bar and $-196^\circ C$ while the iron-based showed 13.2 wt. % (45.4 g L^{-1}) under the same conditions. Based on these results, it is evident that MOFs are good candidates for H_2 storage, but further work is still required to achieve a high H_2 uptake at near ambient conditions.

2.3.1.4 Clathrate hydrates

A clathrate hydrate is a crystalline compound formed by solid water, which resembles ice, in which a gas molecule is trapped inside. These H_2 -bonded water frameworks can build cages around H_2 molecules. During its formation, the gaseous molecules are hosted in the solid cavities, which increase the density of the guest gas.¹⁰³ Two common structures for clathrate hydrates have been identified: (i) hydrates with structure I (sI), consisting of two pentagonal dodecahedron (5^{12}) and six tetrakaidecahedron ($5^{12}6^2$) cages per unit cell; and (ii) hydrates with structure II (sII), consisting of sixteen 5^{12} and eight $5^{12}6^4$ cages per unit cell (Figure 7).

In 2004,¹⁰⁴ Mao and Mao reported a sII clathrate synthesized (5.3 wt. % H_2) at 200–300 MPa and between -33 and $-24^\circ C$ that could release H_2 at ambient pressure and $-133^\circ C$. The same year, Florusse *et al.*¹⁰⁵ suggested the use of a promoter, like THF, to improve the storage of H_2 in the clathrate. In this way, the THF molecules would fill the bigger cavities of the clathrate, leaving the smaller cavities for H_2 . They estimated a theoretical value of 4 wt. % H_2 .

In fact, Lee *et al.*¹⁰⁶ achieved the 4 wt. % H₂ in a clathrate synthesized at 12 MPa and 4°C, adding 0.15 mol % of THF. However, they realized that the H₂ occupied both larger and smaller cavities of the clathrate. Clathrate hydrates are safe and environmentally friendly materials. Nevertheless, they present important disadvantages: (i) to synthesize them, high pressures are needed, (ii) slow kinetics of formation and (iii) they are stable only under cold conditions.¹⁰⁷

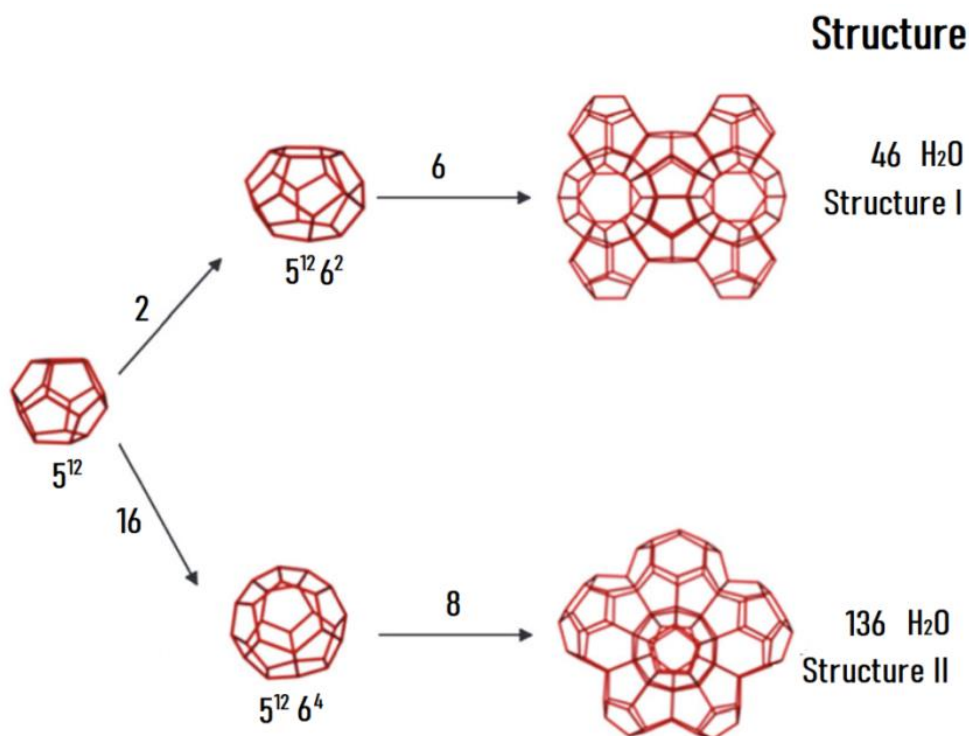


Figure 7. Structure I and II of clathrate hydrates.¹⁰⁸

2.3.2 Chemisorption of hydrogen

In the chemical H₂ storage, a H₂ atom is chemically bonded or complexed into a material. This means that the H₂ uptake/release process implicate the formation and rupture of chemical bonds. The stability of these materials depends on the pressure and temperature. H₂ is released from the compound when it is subjected to thermal or catalytic decomposition. The principal challenges of chemical adsorption are the reversibility of the process, the storage capacity and the stability of

the material.⁷⁰ Table 1 presents the most investigated compounds considered for H₂ storage with their respective H₂ storage capacity, the starting decomposition temperature and other properties. Binary, intermetallic and complex hydrides are typical examples of materials that chemically store H₂.

Table 1. Hydrides considered for H₂ storage. Adapted from references ^{109–111}.

Hydride	Molecular weight (g mol ⁻¹)	Density (g cm ⁻³)	H ₂ content		T _{dec} (°C)
			wt. %	g L ⁻¹	
LiH	7.95	0.77	12.70	102	720
NaH	24.00	1.36	4.20	58	420
MgH ₂	26.32	1.45	7.70	109	330
CaH ₂	42.10	1.7	4.80	81	600
LiBH ₄	21.78	0.67	18.40	122.5	400
NaBH ₄	37.83	1.07	10.80	115.6	505
KBH ₄	53.94	1.17	7.42	87.1	585
Mg(BH ₄) ₂	53.99	0.78	7.20	100	320
Ca(BH ₄) ₂	69.76	1.07	5.60	97	260
Al(BH ₄) ₃	71.51	0.78	16.78	132	480
LiAlH ₄	37.95	0.92	10.6	9750	190
Li ₃ AlH ₆	53.85	1.02	11.2	114.20	200
NaAlH ₄	54.00	1.28	7.30	93.40	230
Na ₃ AlH ₆	102.00	1.45	5.90	85.60	275
KAlH ₄	70.11	-	5.71	53.20	-
Mg(AlH ₄) ₂	86.33	-	9.27	72.30	-
Ca(AlH ₄) ₂	102.10	-	7.84	70.4	230
LiNH ₂	22.96	1.18	8.8	104	200
NaNH ₂	39.01	1.39	5.2	72	280
KNH ₂	55.12	1.62	3.66	59.3	338
Mg(NH ₂) ₂	56.37	1.39	7.15	99.4	360
Ca(NH ₂) ₂	72.13	1.74	5.59	97.3	-

2.3.2.1 Metal hydrides

Back at the 1960s, it was observed that some intermetallic compounds such as LaNi_5 , Mg_2Ni and TiFe could reversibly adsorb and desorb H_2 at reasonable conditions (between -23 and 377°C), which started different research works on metal hydrides for energy applications.¹¹² Since then, an extensive investigation on different hydrides has been performed. Metal hydrides are usually classified in three groups:¹¹³ (i) binary hydrides MH_x (such as MgH_2 , NaH , AlH_3 , $\text{PdH}_{0.6}$); (ii) intermetallic hydrides $\text{A}_x\text{B}_y\text{H}_z$ (where A is the hydriding metal and B the non-hydriding metal, like CeNi_3H_4 , $\text{ZrV}_2\text{H}_{5.5}$ or Mg_2NiH_4); and (iii) complex metal hydrides MEH_x , where E is a boron atom in borohydrides, a nitrogen atom in amides, or an aluminum atom in alanates (e.g. NaBH_4 , LiNH_2 , $\text{Mg}(\text{AlH}_4)_2$ respectively). Interestingly, H_2 exists as the negative hydride ion H^- in binary hydrides, as dissolved atoms in intermetallic hydrides, and with δ^+ or δ^- polarity in complex hydrides. This is due to the different types of bonding that H_2 can present: metallic, ionic or covalent bonding, depending on the nature of the hydride.¹¹¹

2.3.2.1.1 Binary metal hydrides

Most of the elements can form stable binary metal hydrides, but just a few have been considered as H_2 storage materials. Despite a considerable H_2 storage capacity of the lightest metal hydrides such as LiH (12.5 wt. %), NaH (4.2 wt. %) and CaH_2 (4.7 wt. %), they present a high temperature of decomposition (~ 700 , ~ 400 and $\sim 600^\circ\text{C}$, respectively),¹¹⁴ which exceeds the desired working conditions expected by the DOE. Other applications can be envisaged for this type of hydrides, like as thermal energy storage materials.^{115,116}

On the other side, MgH_2 is a widely investigated material for H_2 storage because it has the highest energy density (9 MJ kg^{-1}) of all reversible hydrides, it has a high gravimetric and volumetric H_2 storage capacities (7.6 wt. % and $109 \text{ g H}_2 \text{ L}^{-1}$), and Mg is an abundant metal.¹¹⁷ However, MgH_2 presents a high decomposition temperature ($\sim 300^\circ\text{C}$), shows slow kinetics and high reactivity in the presence of oxygen. Different approaches to enhance the kinetics and/or thermodynamics of the dehydrogenation of MgH_2 have been proposed. The nanosizing of MgH_2 is one of them, where it has been observed that kinetic enhancement occurs even at particle size up to 50 nm,

but the thermodynamic improvements only occur for particle sizes <10 nm.¹¹³ Other approaches include the confinement of the hydride, the use of catalysts, to dope with transition metals or form composites with Mg-based alloys.¹¹⁸

2.3.2.1.2 Intermetallic hydrides

Ideally, an intermetallic hydride $A_xB_yH_z$ is formed from an A_xB_y compound that will absorb H_2 while releasing heat (Equation 14).



Metal A can form stable binary hydrides (alkaline/alkaline-earth metals, transition metals, and rare-earth metals). Metal B does not form a stable hydride (like Ni, Co, Fe, Mn, Al) but it takes part in the dissociation of H_2 .¹¹² The properties of these hydrides are largely dependent on their crystalline structure.¹¹⁹ There are different metal hydride families, but the A_2B , AB_2 and AB_5 alloys have showed better H_2 storage properties.¹²⁰ Intermetallic hydrides have been used not only for H_2 storage, but also as battery electrodes, catalysts, H_2 purification and cooling systems.¹²¹

One example is the alloy $LaNi_5$, that can absorb up to ~ 1.5 wt. % H_2 . This compound can form hydrides at a low H_2 pressure and ambient temperature and it can be easily activated.¹²² However, one of the disadvantages presented by $LaNi_5$ is the long-term hydrogen absorption/desorption cycling and the limited hydrogen storage capacity. Research has been done in order to introduce other elements into the alloy (such as Al, Cu or Mg) to reduce the H_2 capacity loss because of the cycling.^{123–125} Another example of intermetallic compounds is the iron titanium hydride (storage capacity ~ 1.9 wt. % H_2). The reversible absorption and release of hydrogen of the TiFe alloy at near ambient temperature and low pressures (10–20 bar) was reported for the first time in 1974.¹²⁶ In addition, the TiFe hydride is non-toxic, cheap and the abundance of the raw elements is high. Most of the research focused on this compound is about enhancing its activation kinetics and the nanosizing of the material.¹²⁷

However, one of the major drawbacks of intermetallic hydrides is that in the practice it is not possible to obtain more than 2 wt. % H_2 from these materials, due to their high stability.^{128,129} For this reason, different efforts have been done in order to improve the storage capacity of

intermetallic hydrides, like to optimize the composition and morphology of the hydrides or the nanoconfinement.^{130,131} However, the use of intermetallic hydrides is still limited for on-board applications due to the low storage capacity, slow kinetics and complicated activation procedure.¹¹⁹

2.3.2.1.3 Complex hydrides

Complex hydrides are composed of light metal cations (such as Na, Li, Mg, Ca) and complex anions in which the hydrogen atoms are covalently bonded to the central atom (like B, Al or N). These hydrides have received attention for solid-state H₂ storage due to their high gravimetric and volumetric H₂ contents.¹¹⁰ Among the drawbacks of complex hydrides, we can mention a highly endothermic dehydrogenation process and the lack of reversibility.¹¹³

Borohydrides are compounds that fall in this category. For example, LiBH₄ has a high gravimetric H₂ capacity (18.3 wt. %). It starts to decompose above 320°C, but the major decomposition step takes place between 400 and 600°C.¹³² Zuttel *et al.*¹³³ found that if SiO₂ is added as a catalyst, LiBH₄ can release up to 9 wt. % H₂ below 400°C. However, this is still a high dehydrogenation temperature for on-board applications. Another example is NaBH₄ (10.6 wt. % H₂), that suffers the same problem: it presents sluggish kinetics and it starts to release H₂ above 500°C.¹³⁴ However, NaBH₄ can be hydrolyzed at ambient conditions, due to the spontaneous reaction between the hydridic hydrogens H^{δ-} of the BH₄⁻ anion and the protic hydrogens H^{δ+} of water (Equation 15).¹³⁵ In this way, NaBH₄ can release up to 4 equivalents of H₂.



A last interesting case is Mg(BH₄)₂ (14.9 wt. %). It has different crystalline phases, but the polymorph γ-Mg(BH₄)₂ presents a 3D net of channels with a pore size of ~8.8 Å and it is the first metal hydride reported to reversibly adsorb H₂.¹³⁶ This compound opened the research for new metal borohydride frameworks materials.

The alumino-hydrides, or alanates, refer to a family of complex hydrides where a central Al atom is ionically bonded to metal cation and covalently bonded to four hydrogens. After the work

published by Bogdanovic and Schwickardi in 1997, alanates started to receive attention.¹³⁷ The main disadvantages of these complex hydrides are their poor kinetics and multistep decomposition.¹¹⁷ One example is NaAlH₄ (5.5 wt. % H₂), a widely studied material with a high theoretical H₂ capacity. However, experimentally only a 5 wt. % H₂ has been released. The dehydrogenation takes place in two steps, releasing 3.7 wt. % H₂ in the first step, and 1.8 wt. % H₂ in the second (Equations 16 and 17). However, it has been evidenced that NaAlH₄ is not suitable for on-board applications, but rather it can be used in portable applications as the source of H₂.¹³⁸



A last example is LiAlH₄ (10.5 wt. % H₂), which dehydrogenates in three steps. In the first two steps, it can release 7.9 wt. % H₂, but the onset dehydrogenation temperature and the kinetics are not practical. Different options have been presented to improve the dehydrogenation properties of LiAlH₄ like the using Ti-based catalysts or the destabilization of the hydride with metal halides.^{139,140}

Metal amides and metal imides are another type of complex hydrides. Alkali metal amides have been used in the synthesis of organic compounds, but also they have been tested for H₂ storage applications. One example is the LiNH₂+LiH system, that has been widely investigated.¹⁴¹ When mixed with LiH, LiNH₂ presents a reversible hydrogen storage capacity of 6.5 wt. % H₂ and with an onset dehydrogenation temperature of 285°C. The mechanism of dehydrogenation has been described in the literature: H₂ is produced in a first step due to the interaction between the H^{δ+} of the LiNH₂ and the H^{δ-} of LiH, with the release of NH₃.^{142,143} A second desorbing mechanism takes place after (Equations 18 and 19).



The main problem with this system is the production of NH₃, because it poisons the catalysts in a fuel cell. Besides, Ikeda *et al.*¹⁴⁴ determined that the decay in H₂ capacity of the system is

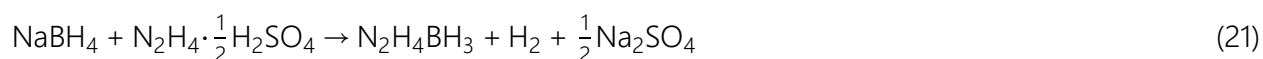
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3. Boron- and nitrogen-based materials

Reports on the first boron-, nitrogen- and hydrogen-based compounds (BNH) started to be published in the 1950s; but there was no greater interest on these compounds, and the research stopped for 50 years. After this, in the 2000s, BNH materials regained attention due to their potential use as H₂ storage materials.^{146–154} BNH compounds have two main advantages over other materials for H₂ storage: (i) both B and N are lightweight elements capable of bonding with multiple hydrogens; and (ii) the interaction between the hydridic hydrogens H^{δ-} from the B atom and the protic hydrogens H^{δ+} from the N atom results in an easier release of H₂.¹⁴⁶ Several BNH materials meet the requirements established by the DOE. The next section will describe in detail two of the most investigated materials, and their derivatives, considered for H₂ storage: ammonia borane and hydrazine borane.

3.1 Ammonia borane and hydrazine borane

Ammonia borane NH₃BH₃ (AB; tetragonal, s.g. *I4mm*) and hydrazine borane N₂H₄BH₃ (HB; orthorhombic, s.g. *Pbcn*) have several features in common. First, they are synthesized in a similar way (metathesis followed by dehydrogenation) using NaBH₄ and an ammonium/hydrazine salt in an organic solvent like THF at 30–40°C (Equation 20 and Equation 21).^{155,156} Second, AB and HB are solid at ambient conditions. And third, they show comparable stability under argon atmosphere, under air and in an organic/protic solution.^{146,157–159}



AB is isoelectronic with ethane C₂H₆, and carries 6 hydrogen atoms, giving it a gravimetric H₂ density of 19.6 wt. %.¹⁶⁰ It carries three protic hydrogens H^{δ+} in the NH₃ moiety and three hydridic hydrogens H^{δ-} in the BH₃ group. The presence of these two types of H atoms implies intermolecular dihydrogen interactions H^{δ+}...H^{δ-} which allow the solid state of the compound and the possibility of start the dehydrogenation under heating at ca. 100°C.^{157,161,162} In fact, the thermolysis of AB has been widely investigated,¹⁵⁸ but unfortunately AB does not only release H₂:

it decomposes into gaseous species (ammonia NH_3 , diborane B_2H_6 and borazine $\text{B}_3\text{N}_3\text{H}_6$) and into a solid residue of complex composition. H_2 release by AB hydrolysis also has been investigated, despite the drawbacks associated with the NH_3 group (like the pollution of the H_2 stream by evolution of some NH_3 , and impossible dehydrogenation of NH_3 in hydrolysis conditions).^{163,164}

HB (15.4 wt. % H_2), a derivative of AB where the N_2H_4 moiety replaces NH_3 , also has been studied as potential candidate for H_2 storage.¹⁶⁵ The hydrolysis of HB is more attractive than AB due to the possibility to dehydrogenate not only the BH_3 moiety, but also the N_2H_4 group (Equation 22).^{166,167} For example, in the presence of a selective nickel-based catalyst, a total dehydrogenation of aqueous HB (with the formation of N_2 and $\text{B}(\text{OH})_3$) is achieved.¹⁶⁸



HB also has been investigated for dehydrocoupling in thermolytic conditions,¹⁶⁵ even though it is not suitable: it decomposes mainly into the unwanted N_2H_4 and generates a shock-sensitive solid when the temperature exceeds 300°C . A schematic representation of the thermal decomposition of AB and HB is presented in **Figure 9**.

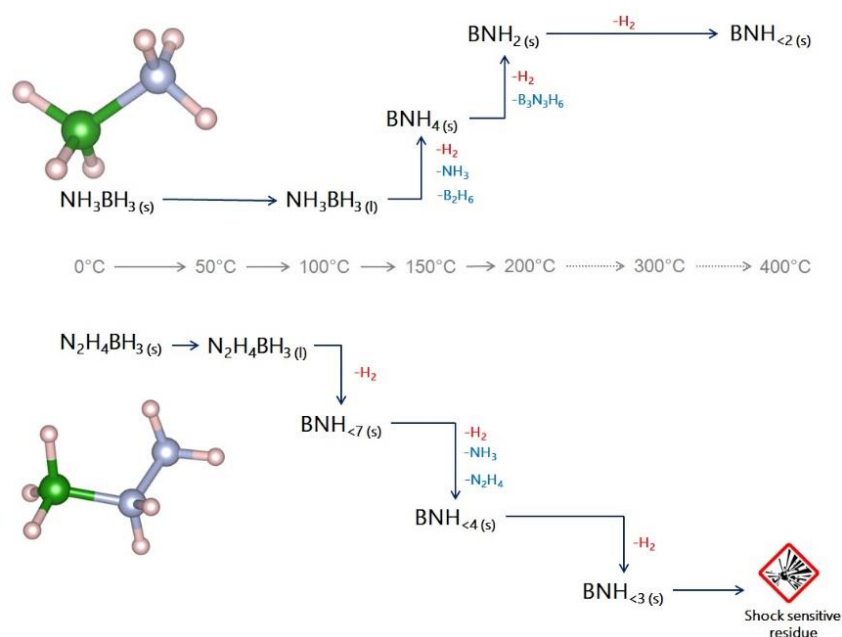


Figure 9. Representation of the thermolytic decomposition of AB and HB up to 400°C . The thermolytic residues are of complex composition and they are represented by BNH_x ($x \leq 7$).

3.1.1 Destabilization strategies of AB

AB and HB are unsuitable for solid-state H₂ storage in pristine state because of inappropriate thermolytic dehydrogenation properties. This drawback promoted strategies to destabilize these molecules to obtain a purer H₂.¹⁴⁶ For example, there have been several approaches to destabilize AB: the use of catalysts, the nanoconfinement, the nanosizing or the chemical modification.

The kinetics of AB can be enhanced using a catalyst. Different homogeneous catalysts have been tested for the dehydrogenation of AB in solution. It was reported that in the presence of an iridium-based catalyst ($[\eta^3\text{-}1,3\text{-(OP}^t\text{Bu}_2)_2\text{C}_6\text{H}_3]\text{Ir(H)}_2$), a THF solution of AB can liberate 1 equiv H₂ in 14 min.¹⁶⁹ Ruthenium-based catalysts have also been tested in the dehydrogenation of AB. For example, different derivatives of the Shvo catalyst (organoruthenium compound) were developed in order to suppress the formation of borazine, to enhance H₂ release from AB and to avoid the deactivation of the catalyst by hydroboration.¹⁷⁰ The use of heterogeneous catalysts for the dehydrogenation of AB also has been widely reported in the literature based on different metals:¹⁷¹ Rh/CNT, Pt/CNT, Pd/CeO₂, AuCo/CNT, PtAuNi are some examples. The use of catalysts with a low content of noble metals is also of interest. Other materials like metal ruthenate perovskites (CaRuO₃, Ca₂CoRuO₆, SrRuO₃, Sr₂LaRuO₆) work as an active and durable catalysts for the dehydrogenation of AB.¹⁷² These compounds achieve a comparable H₂ release rate than other metal noble-based heterogeneous catalysts.

Nanoconfinement of AB has been suggested as a strategy to improve the kinetics and the thermodynamics of the dehydrogenation of AB, as well to reduce undesired by-products.¹⁷³ Different materials have been proposed to host ammonia borane: carbon,^{174–176} metal organic frameworks,^{177–179} or porous silica supports.^{180–182} The results indicate the success in destabilizing AB: the dehydrogenation takes places at lower temperatures, the thermodynamics and kinetic parameters were improved and the emission of gaseous by-products was reduced or even suppressed. However, there are many challenges ahead for nanoconfined AB: to find suitable scaffolds with smaller pores and higher pore volume, and to understand the mechanism of decomposition of confined AB.¹⁷³ Recently, the encapsulation of AB in halloysite nanotubes embedded with Pd was reported.¹⁸³ H₂ evolution started from 60°C and the activation energy of

AB@Pd/HNTs was estimated as 46 kJ mol⁻¹ (vs 183 kJ mol⁻¹ for neat AB). But the nanosizing of ammonia borane is possible even without a scaffold.¹⁸⁴ AB nanospheres were obtained in an aqueous solution using a surfactant. The nanostructures showed a lower dehydrogenation temperature and reduced by-product emissions. Such nanostructures open new opportunities in the development of H₂ storage materials.

A last option for destabilizing AB and HB is the chemical modification to obtain derivatives via substitution of one of the H^{δ+} by a metal cation. This approach improves the dehydrogenation properties of the compounds. The derivatives, namely amidoboranes (MAB) and hydrazinidoboranes (MHB), have shown better dehydrogenation properties than the parent boranes. MAB and MHB will be further discussed in the next sections.

3.2 Background on amidoboranes

The first report of an amidoborane dates from the 1940s: sodium amidoborane NaNH₂BH₃ (NaAB), synthesized through a two-step process.^{185,186} About 60 years later, the lithium amidoborane LiNH₂BH₃ (LiAB) was reported.¹⁸⁷ LiAB was found to be a highly nucleophilic reducing agent for transformation of tertiary amides into primary alcohols.

Ten years later, the amidoboranes began to flourish. The first amidoborane to be presented as a potential H₂ storage material is calcium amidoborane Ca(NH₂BH₃)₂ (CaAB). It was synthesized according to a two-step process.¹⁸⁸ Like the parent AB, CaAB dehydrogenates above 100°C, but it offers some advantages. The amidoborane releases cleaner H₂ (polluted by less than 0.1 wt. % of NH₃ and B₃N₃H₆); it does not show an induction period in isothermal conditions; it does not foam; its dehydrogenation extent is higher than 2 equiv H₂; and the dehydrogenation process is less exothermic.^{188,189}

The potential of amidoboranes for H₂ storage was primarily confirmed with the re-discovery of both LiAB and NaAB,¹⁹⁰ and this gave new opportunities towards new amidoboranes: amidoboranes with heavy cations like Y³⁺ or Al³⁺,^{191,192} mixed-cation amidoboranes like LiAl(NH₂BH₃)₄, NaLi(NH₂BH₃)₂, NaMg(NH₂BH₃)₃, KMg(NH₂BH₃)₃ and RbMg(NH₂BH₃)₃,^{193–199} methyl-substituted amidoboranes like LiN(CH₃)₂BH₃,²⁰⁰ and organometallic-complexed amidoboranes.²⁰¹

3.3 Alkali amidoboranes and hydrazinidoboranes

Alkali and alkaline-earth derivatives of AB and HB have emerged due to the dehydrogenation at temperatures above 100°C, the emissions of unwanted by-products over the temperature range 100-200°C and the formation of polymeric residues of complex composition by the parent boranes.^{202–204}

3.3.1 Synthesis

The substitution of one of the H^{δ+} of NH₃ or N₂H₄ by M⁺ is relatively easy. In HB, the substituted H^{δ+} is one on the central N atom, giving then the formula NH₂NH(M)BH₃; the middle N retains a tetrahedral sp³ hybridization. Two main routes have been developed for the syntheses of MAB and MHB (Table 2 and Table 3).^{190,205,214–222,206–213}

Syntheses of MAB and MHB must be performed under inert atmosphere (He, Ar, N₂). The reactants (MH, M, AB or HB) as well as the products (MAB and MHB) are not stable under air, especially when it is humid, due to the spontaneous hydrolysis of these compounds. For instance, NaAB evolves under air (mass increase of 48.7%) towards the formation of e.g. sodium carbonate Na₂CO₃,²¹¹ and generates H₂ by solvolysis when put into contact with water or methanol.²¹³ Two other examples are RbAB and CsAB that decompose in air within minutes and are moisture sensitive.^{215,216}

The light MAB and MHB compounds (M=Li, Na) are principally prepared by ball- or disc-milling AB or HB with the alkali hydride MH (Equation 23 and Equation 24).



The milling conditions for LiAB and LiHB are mild, because harsh conditions (e.g. >200 rpm or > 1 h) leads to the decomposition into other phases.²⁰⁶ With respect to NaAB, the milling conditions are softer because NaH is more reactive than LiH.²²³ Mixing an equimolar quantity of NaH and AB with a spatula in a mortar under argon atmosphere for 15 min are enough to obtain pure

NaAB.²¹³ The trend is similar for MHB. Because LiH is relatively inert towards HB (enthalpy of reaction $<0.1 \text{ kJ mol}^{-1}$),²²⁴ LiHB is formed by ball milling only.^{217,218,221} NaHB has to be synthesized at -30°C ,²²⁰ otherwise the reactivity is too high (enthalpy of reaction $-27.8 \text{ kJ mol}^{-1}$),²²⁴ leading to an explosive reaction. Other approaches to synthesize LiAB, NaAB and NaHB includes using LiNH_2 , NaNH_2 and Li_3N as source of the metal cation,^{207–209} or using a wet method with THF as anhydrous solvent.^{208,212,221} However, the reaction of NaNH_2 and AB in THF is less efficient than the synthesis with NaH, because it presents slow kinetics.²¹²

Table 2. Syntheses of alkali MAB. Details about the nature of the source of M^+ (Prec.), molar ratio AB:M+, synthesis method, conditions, temperature of reaction and atmosphere are given.

Prec.	AB:M ⁺	Method	Conditions	Temp.	Atm.	Ref.
LiH	1:1	Ball milling	250 rpm / 3 h / Graphite	Room	Ar	190,205
LiH	1:1	Ball milling	250 rpm / 1 h	Room	He	206
LiH	1:1	Disc milling	3 min milling + 5 min break ^a	Room	Ar	207
LiH	1:1.5	Wet chemistry	THF / Stirring 75 min	Room	-	208
LiNH_2	1:1	Disc milling	3 min milling + 5 min break ^a	Room	Ar	206
Li_3N	4.2:1	Wet chemistry	THF / Stirring 60 min	30°C	Ar	209
NaH	1:1	Ball milling	250 rpm / 3 h / Graphite	Room	Ar	190
NaH	1:1	Ball milling	1 h	Room	H_2 (10 bar)	210
NaH	1:1	Disc milling	3 min milling + 5 min break ^a	Room	Ar	207
NaH	1:1	Disc milling		Room	-	211
NaH	1:1.2	Wet chemistry	THF / Stirring 10 min	Room	-	208
NaH	1:1	Wet chemistry	THF / Stirring 10 min	-3°C	-	212
NaH	1:1	Simple mixing	15 min	Room	Ar	213
NaNH_2	1:1	Wet chemistry	THF / Stirring 20 min	25°C	-	208
KH	1:1	Wet chemistry	THF / 4 h	Room	N_2/Ar	214
KH	1:1	Wet chemistry	Benzene / 48 h	Room	N_2/Ar	214
Rb	1:0.93	Wet chemistry	THF / Overnight	0°C	Ar	215
Rb	1:1	Wet chemistry	THF / 24 h	Room	Ar	216
Cs	1:1.03	Wet chemistry	THF / Overnight	0°C	Ar	215
Cs	1:1	Wet chemistry	THF	Room	Ar	216

^a The number of cycles has not been mentioned.

Table 3. Syntheses of alkali MHB. Details about the nature of the source of M⁺ (Prec.), molar ratio AB:M⁺, synthesis method, conditions, temperature of reaction and atmosphere are given.

Prec.	HB:M ⁺	Method	Conditions	Temp.	Atm.	Ref.
LiH	1:1	Ball milling	200 rpm / 1-3 h	Room	He (1 bar)	217
LiH	1:1	Ball milling	200 rpm / 10 min + 20 min ^a	Room	Ar	218
LiH	1:1	Ball milling	150 rpm / 16 h ^b	Room	He	221
LiH	1:1	Ball milling	300 rpm / 6 h	Room	Ar	219
NaH	1:1	Wet chemistry	THF / 300 rpm	0°C	Ar	221
NaH	1:1	Ball milling	250 rpm / 10 min	−30°C	Ar	220
KH	1:1	Wet chemistry	THF / 300 rpm	25°C	Ar	221
Rb	1.15:1	Wet chemistry	THF / 30 h	Room	Ar	222
Cs	1.15:1	Wet chemistry	THF / 6 h	−20°C	Ar	225

^a 10 min milling followed by 20 min break, 18 times
^b 1 min milling in one direction + 15 s break + 1 min in the other direction, for 16 h

Wet chemistry is the preferred method for the heavier MAB and MHB compounds (M=K, Rb, Cs). Both KAB and KHB can be prepared from KH in anhydrous THF (Equation 23 and Equation 24).^{214,221} The use of an autoclave reactor is recommended in the case of KHB; solid-solid mixtures have to be avoided due to the high reactivity of KH towards the borane (shock-sensitive mixture leading to explosive reaction).²²¹ KH has a stronger basicity than NaH and LiH and, for example, the enthalpy of reaction between KH and HB is thrice (−70.3 kJ mol^{−1}) than the one between NaH and HB.²²⁴

With respect to the Rb and Cs compounds, syntheses are carried out using the metallic alkali elements in anhydrous THF (Equation 25 and Equation 26), because RbH and CsH are not commercially available and the reactivity of Rb and Cs is lower, which is better from a safety point of view.^{215,216,222} As amidoborane and hydrazinidoborane compounds are not soluble in THF, they can be isolated by filtration.



3.3.2 Crystalline solids

MAB and MHB are crystalline (Table 4). LiAB has two allotropes: α -LiAB and β -LiAB.^{190,205,206} The α phase forms first, and it transforms to the β phase as the reaction progresses. Both allotropes crystallize in the orthorhombic space group $Pbca$. The unit cell of the β phase is twice that of the α phase. The β phase is seen as a metastable phase arising from energetic milling. The β -LiAB has two coordination environments for Li^+ : one is tetra-coordinated (with a distorted environment), and the other is penta-coordinated. The α -LiAB only displays a tetrahedral coordination. (Figure 10). The penta-coordination of β -LiAB makes this phase less stable in comparison with α -LiAB.

Table 4. Summary of crystallographic properties of MAB and MHB compounds.

Comp.	Unit cell ^a	s.g.	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	β (°)	Z	Ref.
AB	Tetrag.	<i>I4mm</i>	5.263	5.263	5.050	90	2	226
α -LiAB	Orthor.	<i>Pbca</i>	7.113	13.949	5.150	90	8	190
α -LiAB	Orthor.	<i>Pbca</i>	7.105	13.930	5.148	90	8	206
β -LiAB	Orthor.	<i>Pbca</i>	15.146	7.721	9.268	90	16	205
NaAB	Orthor.	<i>Pbca</i>	7.469	14.655	5.653	90	8	190
NaAB	Orthor.	<i>Pbca</i>	7.464	14.635	5.648	90	8	212
NaAB	Orthor.	<i>Pbca</i>	7.474	14.645	5.674	90	8	212
KAB	Orthor.	<i>Pbca</i>	9.430	8.261	17.340	90	16	214
α -RbAB	Monocl.	<i>P2₁/c</i>	6.931	5.015	11.074	101.688	4	216
β -RbAB	Cubic	<i>Fm$\bar{3}$m</i>	7.328	7.328	7.328	90	4	216
α -CsAB	Orthor.	<i>Pnam</i>	9.119	7.345	5.969	90	4	216
β -CsAB	Cubic	<i>Fm$\bar{3}$m</i>	7.596	7.596	7.596	90	4	216
HB	Orthor.	<i>Pbca</i>	13.123	5.100	9.581	90	8	217
α -LiHB	Monocl.	<i>P2₁/c</i>	5.852	7.466	8.897	122.381	4	217
β -LiAB	Orthor.	<i>Pbca</i>	10.252	8.479	7.469	90	4	218
NaHB	Monocl.	<i>P2₁/n</i>	4.974	7.958	9.292	93.814	4	220
KHB	Monocl.	<i>P2₁</i>	6.709	5.882	5.767	108.268	2	221
RbHB	Monocl.	<i>P2₁</i>	5.813	6.701	5.814	108.915	2	222
CsHB	Monocl.	<i>P2₁</i>	5.916	7.009	6.002	108.389	2	

^a Tetrag. for tetragonal; Orthor. for orthorhombic; Monocl. for monoclinic.

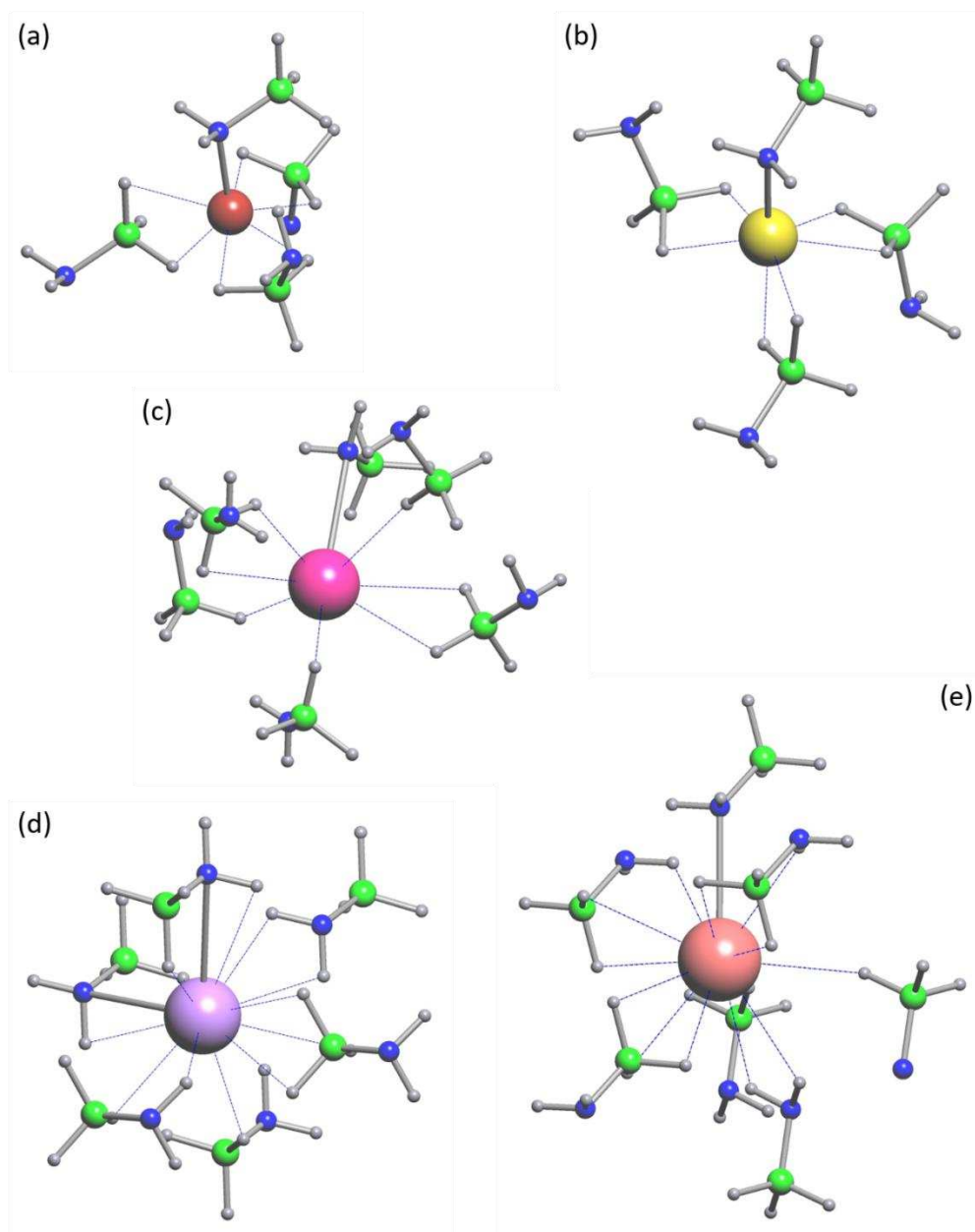


Figure 10. Coordination sphere of: (a) LiAB, (b) NaAB, (c) KAB, (d) RbAB, (e) CsAB. The green, blue and grey spheres represent the B, N and H atoms respectively. The other colored spheres show the alkali elements.

LiHB also has two phases, crystallizing, however, in different space groups. The β phase is the low-temperature phase (orthorhombic, s.g. *Pbca*) and is isostructural with LiAB. The high-

temperature phase is α -LiHB (monoclinic, s.g. $P2_1/c$).^{217–219,221,227} The phase transition β -LiHB \rightarrow α -LiHB occurs when the β phase is heated at 95°C for 2 h or at 90°C while heated at 5°C min⁻¹ from room temperature. β -LiHB is more stable, as evidenced by a longer distance between two Li⁺ (3.49 Å vs 3.31 Å for α -LiHB). For each phase, the Li⁺ cation has a tetrahedral environment, interacting with four [N₂H₃BH₃]⁻ anions (**Figure 11**).

NaAB and KAB are isostructural to LiAB.^{190,212,214} The Na⁺ has a tetrahedral coordination, as Li⁺, via one Na–N bond and three Na \cdots H–BH₂ interactions. The K⁺ cation is larger and more diffuse: it is octahedrally coordinated with six [NH₂BH₃]⁻ anions involving three K–N bonds and three K \cdots H–BH₂ interactions (**Figure 10**). Unlike the aforementioned amidoboranes, β -LiHB, NaHB and KHB crystallize in different monoclinic cells ($P2_1/c$, $P2_1/n$, $P2_1$ respectively).^{217,220,221} NaHB is surrounded by five [N₂H₃BH₃]⁻ anions, suggesting a trigonal bipyramid coordination sphere. For KHB, the number of surrounding anions is four. It interacts more intimately with the surrounding anions than Na⁺ does (**Figure 11**). The amidoboranes of heavier alkali elements, RbAB and CsAB are not isostructural to the previous MAB.^{215,216} RbAB crystallizes in a monoclinic system (s.g. $P2_1/c$) where each Rb⁺ coordinates with six [NH₂BH₃]⁻ anions according to a pseudo-octahedron. CsAB has a primitive orthorhombic structure (s.g. $Pnam$). Each Cs⁺ is surrounded by seven [NH₂BH₃]⁻ anions (**Figure 10**). Both amidoboranes undergo, under heating, a reversible phase transition. These β phases have a cubic $Fm\bar{3}m$ unit cell. RbHB and CsHB are isostructural to KHB, crystallizing in a monoclinic $P2_1$ unit cell.²²² The cations Rb⁺ and Cs⁺ have an octahedral coordination, with six surrounding [N₂H₃BH₃]⁻ anions (**Figure 11**).

With MAB, the volume of the unit cell per formula unit increases with the size of the metal cation. However, for MHB the volume of the unit cell per formula unit does not follow a constant evolution. It decreases from LiHB to NaHB, increases from NaHB to KHB, decreases from KHB to RbHB, and increases from RbHB to CsHB. Two factors can explain this behavior. The first one may be the non-linear evolution of the number of coordinating [N₂H₃BH₃]⁻ anions, since it is 4 for Li⁺, 5 for Na⁺, 4 for K⁺, and 6 for Rb⁺ and Cs⁺. The second might be related to the presence of two N atoms which may enhance the number of interactions resulting in compacter coordination spheres.

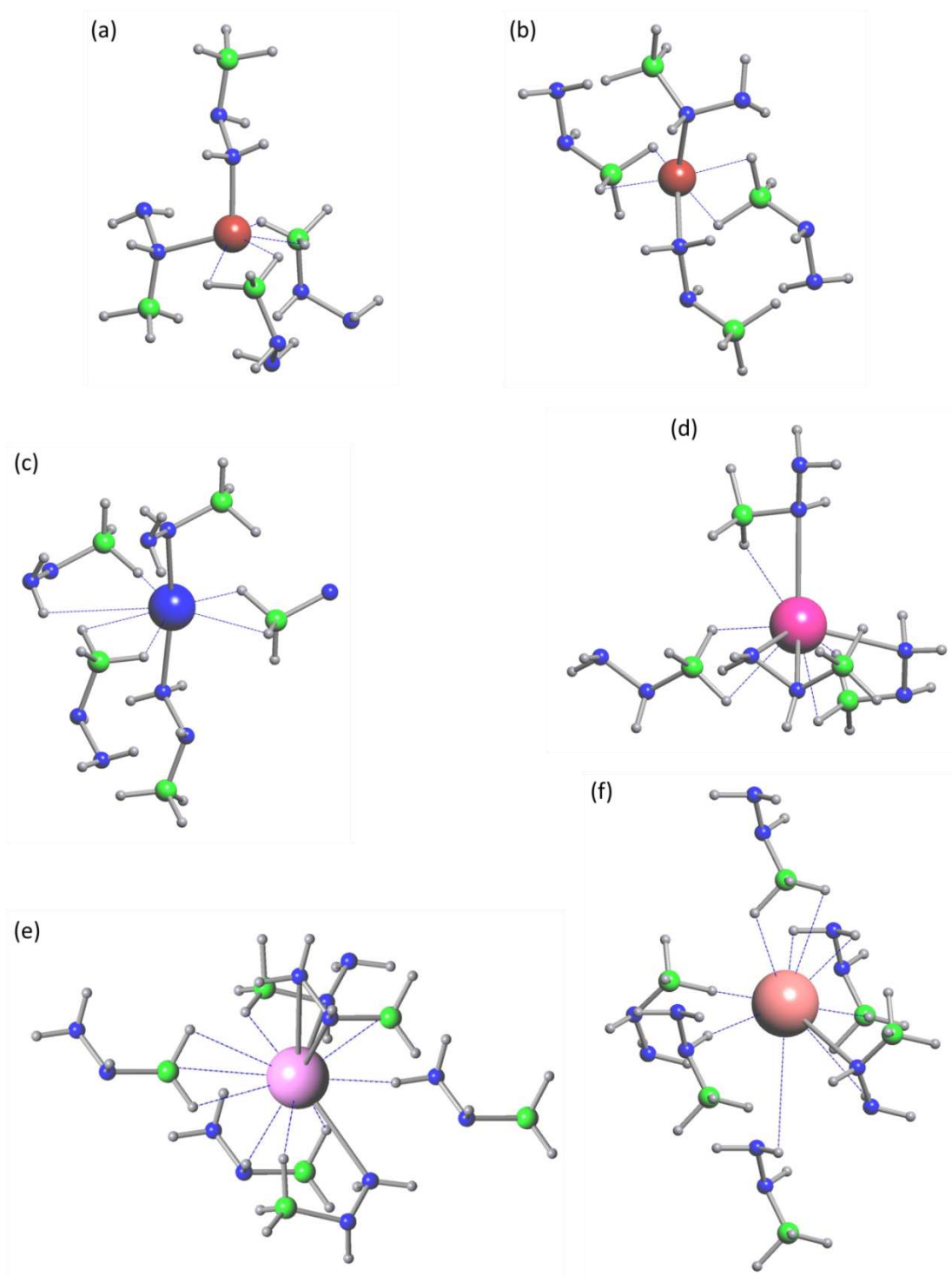


Figure 11. Coordination sphere of: (a) α -LiHB, (b) β -LiHB, (c) NaHB, (d) KHB, (e) RbHB, (f) CsHB. The green, blue and grey spheres represent the B, N and H atoms respectively. The other colored spheres show the alkali elements.

3.3.3 Dihydrogen bonding

One of the features of fundamental interest with BNH compounds is the existence of an intermolecular dihydrogen network owing to $H^{\delta+}\cdots H^{\delta-}$ interactions. With AB, the intermolecular $H^{\delta+}\cdots H^{\delta-}$ distance is 2.02 Å.²²⁸ With HB, it is 2.01 Å.¹⁵⁶ These distances are shorter than the sum of the van der Waals radii for two H atoms (2.4 Å). This is the characteristic of dihydrogen bonding. Weaker intermolecular dihydrogen bonding characterize MAB and MHB.²¹⁴ The $H^{\delta+}\cdots H^{\delta-}$ is longer than that determined for AB or HB, but it remains lower than the van der Waals distance. For example, the $H^{\delta+}\cdots H^{\delta-}$ distance is 2.25 Å in the case of α -LiAB and of β -LiHB.^{206,221} Dihydrogen $H^{\delta+}\cdots H^{\delta-}$ interactions are also present within each $[NH_2BH_3]^-$ or $[N_2H_3BH_3]^-$ anion. They have distances of 2.00-2.10 Å in $[N_2H_3BH_3]^-$ of α -LiHB for example.²¹⁷

Head-to-tail $H^{\delta+}\cdots H^{\delta-}$ interactions take part in the stabilization of the solid state, but they are not the only interactions that play a role on this. Homopolar $H^{\delta+}\cdots H^{\delta+}$ and $H^{\delta-}\cdots H^{\delta-}$ interactions also contribute to the stability of MAB and MHB.²²⁹ However, the van der Waals interactions between M^+ and the anionic entities predominate: they replace the dihydrogen bonding and are of sufficient energy so that MAB and MHB are solid at ambient conditions.^{208,214}

3.3.4 Thermolytic dehydrogenation

In comparison to AB and HB, all of the MAB and MHB compounds have shown better dehydrogenation properties with lower temperatures of dehydrogenation and higher purity of the released H_2 .

LiAB dehydrogenates at temperatures below 100°C according to a near thermally neutral event (-3 kJ mol^{-1}).^{190,205} NaAB has slightly better dehydrogenation properties. For example, heated at ca. 80°C, NaAB releases 0.5 equiv H_2 in 92 s, versus 3017 s for LiAB.²⁰⁸ For both materials, the purity of the released H_2 is contradictory. On the one side, pure H_2 was reported,^{190,206,208,212} on the other side, H_2 was found to be polluted by NH_3 .^{207,211,230} KAB also has attractive dehydrogenation properties, but the discrepancies in the experimental conditions and devices used make difficult to compare it with LiAB or NaAB. KAB releases 1.5 equiv H_2 up to 100°C, without any pollutant.²¹⁴ Both RbAB and CsAB decompose from ca. 65 and 55°C respectively and below 100°C, releasing

H₂ and significant amounts of NH₃.^{215,216} According to theoretical calculations made on the molecular level, the least stable would be LiAB and the most stable would be CsAB.^{231,232} This is in contradiction with the experimental observations made on the material level, which suggest a stability ranking of LiAB>NaAB>KAB>RbAB>CsAB. The least stable is CsAB, where the metal cation has the lower electronegativity; the stability of MAB would be driven by the metal electronegativity.¹⁵²

The high-temperature phase α -LiHB is responsible for a two-step decomposition occurring above 90°C.^{217,218,227} Together with H₂, N₂ and NH₃ are released. The dehydrogenation properties of NaHB are more attractive.^{220,221} It releases H₂ from ca. 60°C a total of 2 equiv H₂ up to 100°C. The decomposition mechanism is, however, a bit complex as it is composed of three successive dehydrogenation and one denitrogenation processes. Some traces of N₂, N₂H₄ and NH₃ contaminate the H₂ stream. In contrast, when NaHB is “doped” with an excess of NaH, pure H₂ is generated.²³³ KHB starts to dehydrogenate at ca. 50°C, releasing small amounts of NH₃ and N₂.²²¹ RbHB and CsHB start to decompose at ca. 60 and 75°C, respectively, releasing NH₃ together with H₂.²²² Though CsHB seems to be slightly more stable than RbHB, there is a rough correlation between the MHB reactivity and the alkali element electronegativity: the lower the electronegativity is, the less stable the MHB is.¹⁵²

The identification of the thermolytic solid residue recovered upon dehydrogenation of MAB and MHB is challenging. A poorly crystalline thermolytic residue systematically forms, which renders powder X-ray diffraction of little assistance. The technique however allows seeing the formation, over 200°C, of crystalline by-products such as NaH, RbH and CsH.^{211,212,216} Dehydrogenated NaAB is supposed to transform into a small amount of NaH (detected by ²³Na NMR spectroscopy),^{210,211} and mainly into an amorphous solid being either a mixture of boron nitride and polyiminoborane-like structures or boron nitride (**Figure 12**).^{210,212} More broadly, the thermolytic residue forming from MAB is considered as being polyborazylene- and polyiminoborane-like compounds.^{190,205,214,230,206–213}

With respect to MHB, the nature of the thermolytic residue is as complex. Polymeric compounds having tetragonal boron environments (such as BH₄, NBH₃, N₂BH₂) as well as trigonal boron

environments (i.e. NBH_2 , N_2BH , BN_3) form. These environments are systematically discussed as polymeric B–N based compounds (**Figure 12**). Because the thermolytic residues of MAB and MHB have not been well identified yet, the dehydrogenation mechanisms are also not well known. However, there are some elements that may help in better understanding these mechanisms.

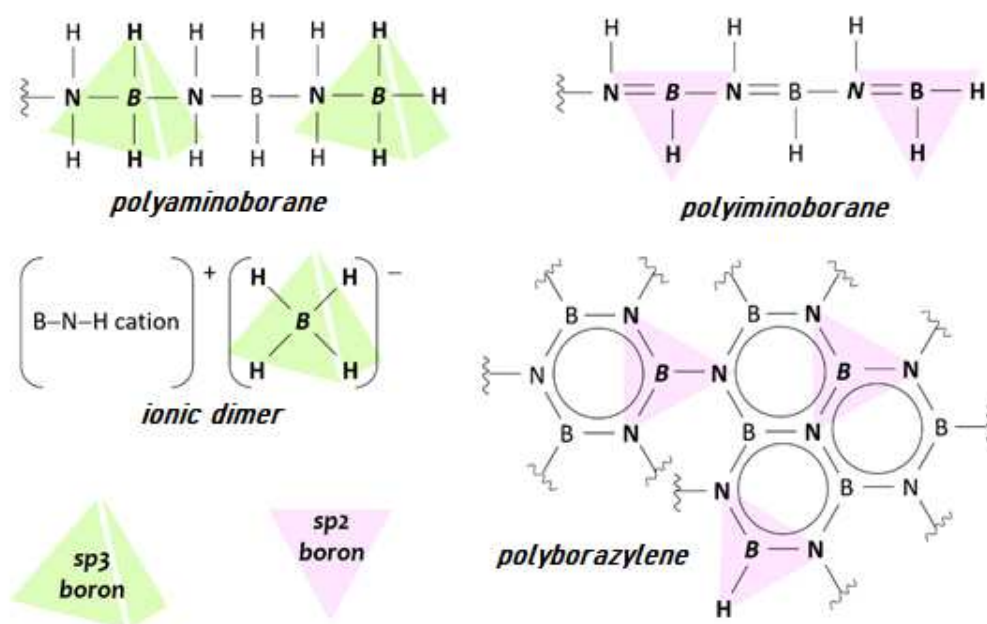


Figure 12. Examples of compounds having tetragonal boron environments and trigonal boron environments, present in the thermolytic residues of MAB and MHB.

With pristine AB, before the release of H_2 , the compound dimerizes into diammoniate of diborane $[(\text{NH}_3)_2\text{BH}_2]^+[\text{BH}_4]^-$.²³⁴ A comparable intermediate was predicted for LiAB:²³⁵ $[(\text{LiNH}_2)_2\text{BH}_2]^+[\text{BH}_4]^-$, considered also as a Li–H–Li complex. It would allow thermoneutral H_2 release via formation of a coiled polymeric product such as $\text{LiNH}_2\text{BH}_2\text{LiNHBH}_3$. Another predicted species is the dianion $[\text{NHBHNBH}_3]^{2-}$.²³⁶ For NaAB, the formation of an ionic dimer resembling those mentioned above is, on the one hand, discarded because ^{11}B NMR analyses did not show signals belonging to N_2BH_2 and BH_4 environments.²¹⁰ On the other hand, however, head-to-tail dimerization into the ionic salt $[\text{NH}_3\text{Na}]^+[\text{BH}_3(\text{NHNa})\text{BH}_3]^-$ would take place at ca. 55°C .^{207,210} This intermediate explains the formation and liberation of NH_3 at $>55^\circ\text{C}$ and that of NaH. The as-forming $\text{BH}_3(\text{NHNa})\text{BH}_2$

liberates H_2 above $55^\circ C$. This is a minor mechanism, estimated to have a contribution of 10%. The major mechanism is based on intramolecular dehydrogenation of NaAB. It is based on the key role of the in situ forming metal hydride $M-H$. In an initial step, it is believed to form by $H^{\delta-}$ transfer from e.g. $[NH_2BH_3]^-$ to M^+ . The mechanism is called metal ion assisted hydride transfer or metal cation driven hydride-transfer. It takes place involving one MAB compound and the $M-H$ formed induces low temperature dehydrogenation (Equation 27).^{237–241}



Regarding to the dehydrogenation of MHB, it is likely that ionic dimer species similar to diammoniate of diborane are involved as transient phases, such as $[(LiN_2H_3)_2BH_2]^+[BH_4]^-$ and $[(NaN_2H_3)_2BH_2]^+[BH_4]^-$.^{218,220} Other non-ionic dimer species are $NH_2NH(M)BH_2NHNH(M)BH_3$ and $NH_2NH(M)BHNNH(M)BH_3$ ($M=Li, Na, K$).²²¹ Theoretical studies have suggested that dimers of NaHB may play the major role in the dehydrogenation pathway.²⁴²

Dehydrogenation of BNH compounds also implies counterintuitive homopolar $H^{\delta+} \cdots H^{\delta+}$ and $H^{\delta-} \cdots H^{\delta-}$ reactions.^{243–245} For example, when heated, $LiND_2BH_3$ releases significant quantity of H_2 along with HD, and the formation of H_2 is explained by the existence of homopolar $H^{\delta-} \cdots H^{\delta-}$ interactions. On the other hand, $LiN_2H_3BD_3$ generates appreciable amounts of HD, H_2 and D_2 . More precisely, initial thermolytic dehydrocoupling at low temperature takes place through homopolar $H^{\delta+} \cdots H^{\delta+}$ interactions, and this step is followed by heteropolar $H^{\delta+} \cdots D^{\delta-}$ and homopolar $D^{\delta-} \cdots D^{\delta-}$ pathways.

3.3.5 Rehydrogenation of thermolytic residues of MAB and MHB

The dehydrogenation of MAB and MHB is exothermic, and the rehydrogenation of the thermolytic residues under H_2 is thermodynamically unfavorable. A few unsuccessful attempts were published. For $LiBNH_{1.32}$ (a by-product of Li AB heated up to $200^\circ C$), no hydrogenation took place at 50 bar H_2 and up to $250^\circ C$.²⁰⁶ Other example is the dehydrogenated form of NaAB, $[BN]_n$, which did not rehydrogenated at 120 bar H_2 .²¹²

Alternatively, MAB can be regenerated by chemical recycling/reduction of its thermolytic residue. Polyborazylene can be recycled back into AB by reduction using N_2H_4 in NH_3 medium.²⁴⁶ The

same path was applied to a thermolytic residue of LiAB identified as being made of cross-linked polyborazylene-based structures.²⁴⁷ The conversion back to LiAB was found to be 63%. The formation of boron nitride must be avoided because it is chemically stable, excluding then chemical recycling/reduction.²⁴⁸

Another regeneration approach was proposed,²⁴⁷ where a thermolytic residue (denoted MBNH, with M=Li, K) is first digested by methanol, and then, the forming product $B(OCH_3)_3$ is reduced by $LiAlH_4$ in the presence of a source of NH_3 . This regeneration approach results in the formation of AB, which finally can be reacted with MH to form MAB back. However, the energy efficiency of this process is not attractive (ca. 46%).

3.4 Alkaline-earth amidoboranes and hydrazinidoboranes

Beryllium is highly toxic and carcinogenic, and has not been considered as a possible cation for AB and HB derivatives. Magnesium amidoborane was first tried to be synthesized by ball milling 2 equivalents of AB with MgH_2 or Mg. However, both of them were apparently inert towards AB.^{206,249} This could be explained by the low Lewis basicity of MgH_2 compared with LiH, NaH or CaH_2 . However, a later work reported the slow evolution of $Mg(AB)_2$ from a mixture MgH_2 -2AB and Mg-2AB.²⁵⁰ Under argon atmosphere and room temperature, this evolution takes place between 45 days and 6 months. The process can be accelerated to 60-90 h by increasing the ageing temperature to 40°C.

The synthesis of $Mg(HB)_2$ have been tested in several occasions in our research team, but all of them have failed up to now.²²⁴ The attempts include the ball milling of HB with Mg or MgH_2 , or a wet route with di-n-butylmagnesium.

To synthesize a pure phase of $Ca(AB)_2$ is challenging. Intense milling is required to form mixtures where $Ca(AB)_2$ is the major phase; CaH_2 and AB are the minor phases.^{206,251} $Ca(AB)_2$ is less stable as $Mg(AB)_2$ as it is able to release H_2 from ca. 80°C, most of the H_2 being generated at 100 and 140°C. Within the range 80-250°C, $Ca(AB)_2$ generates ca. 3.8 equiv H_2 and transforms into an amorphous residue suggested to be $Ca_2B_2N_2H_{2.33}$.

As in the case for MgH_2 , CaH_2 does not react with HB when they are ball milled. The reaction can be however thermally activated.²⁵² At ca. 60°C , the temperature at which HB has melted, solid-state CaH_2 and liquid-state HB reacts and $\text{Ca}(\text{HB})_2$ forms. The conversion is not total, as it was crystalline CaH_2 was found together with crystalline $\text{Ca}(\text{HB})_2$ in relative amounts of 29 and 71 wt. %. Under heating, the $\text{Ca}(\text{HB})_2$ phase-rich solid decomposes from ca. 90°C . Up to 200°C , it releases 5.3 wt. % of gases composed mainly by H_2 and with traces of N_2 , NH_3 and N_2H_4 . The dehydrogenation extent of $\text{Ca}(\text{HB})_2$ was reported to be lower than any other MABs or MHBs, suggesting that the destabilization effect of Ca^{2+} is among the least important.

Strontium amidoborane $\text{Sr}(\text{AB})_2$ is prepared by the ball milling a mixture of strontium hydride and two equivalents of AB.²⁵³ The reactants have to be first milled at 0°C to avoid a partial decomposition of $\text{Sr}(\text{AB})_2$, and then the mixture is heated at 45°C for 2 h. The final product is not pure and it is composed of 55 wt. % of crystalline $\text{Sr}(\text{AB})_2$, 34 wt. % of an unidentified amorphous phase, 7 wt. % of SrH_2 and 4 wt. % of AB. This mixture dehydrogenates slowly from 60°C and violently at $80\text{--}90^\circ\text{C}$. $\text{Sr}(\text{AB})_2$ loses 9.9 wt. %, which ca. 3 wt. % higher than the gravimetric H_2 density, meaning the generation of volatile by-products.

$\text{Ba}(\text{AB})_2$ is synthesized by wet chemistry in THF, while using metallic Ba.²⁵⁴ The reaction is exothermic and it should be performed at low temperature (e.g. -10°C) to avoid the decomposition of $\text{Ba}(\text{AB})_2$. At this temperature, an amorphous white precipitate forms, confirmed to be pure $\text{Ba}(\text{AB})_2$ by FTIR and ^{11}B MAS NMR spectroscopy. This compound loses 5 wt. % H_2 between 81 and 161°C .

3.5 Boron Nitride

Boron nitride (BN) is likely to belong to the list of reversible H_2 storage materials. Almost twenty years ago, Wang *et al.*²⁵⁵ showed that milled hexagonal boron nitride (crystallites of about 3 nm) adsorbs up to 2.6 wt. % H_2 at 10 bar and room temperature. The uptake of H_2 is reversible though desorption takes place at high temperature (297°C), because of chemisorption. Ma *et al.*²⁵⁶ investigated bamboo-like BN nanotubes (BNNTs, $210\text{ m}^2\text{ g}^{-1}$) capable of adsorbing up to 2.6 wt. % H_2 under 100 bar and 20°C , with 0.8 wt. % H_2 being physisorbed. Desorption of the remaining 1.8

wt. % of chemisorbed requires heating up to 300°C. Such interesting H₂ uptake properties were explained in terms of defects in the nanostructured material, specific surface area, polarity and partial ionic character of the B–N bonds. However, boron nitride has been investigated more scarcely than any other material sorbing H₂ reversibly, which can be explained by a lack of easy approaches of boron nitride synthesis and by a preferential occurrence of H₂ chemisorption.²⁵⁷ Recently, computational calculations have identified strategies for improving the sorption properties of boron nitride, such as: higher specific surface area;²⁵⁸ substitution of some B and N atoms of boron nitride by C and/or O;²⁵⁹ surface functionalization (decoration) with e.g. Li or Na;^{260,261} 2D boron nitride layers with optimized interlayer spacing.²⁶² It is reasonable to affirm that boron nitride, boron nitride-based materials or their derivatives have the potential to be considered as a viable H₂ storage material.

Interestingly, besides H₂ sorption properties, boron nitride also has the potential to adsorb carbon dioxide. From computational calculations, strong adsorption of CO₂ was estimated on boron antisite in boron-rich boron nitride nanotubes, where the lone pair of electrons of CO₂ interact with the boron atoms.²⁶³ In another theoretical work, the interaction between pristine and doped boron nitride nanotubes was calculated.²⁶⁴ It was found that CO₂ molecules interact weakly with pristine BNNTs through van der Waals interactions. In the case of Co-doped BNNTs, the binding energy between the CO₂ and the nanotubes increased, showing stronger interaction in comparison with carbon nanotubes. The capture of CO₂ by BN structures also has been demonstrated experimentally. For example, BN nanosheets were functionalized with polyetherimide, increasing the CO₂ sorption capacity of the nanosheets (3.12 mmol g⁻¹ for BN functionalized vs. 0.29 mmol g⁻¹ for pristine BN at 75°).²⁶⁵ In another work, Cu-loaded porous BN nanofibers were tested for CO₂ capture. The results showed an enhance on the CO₂ sorption capacity of the Cu-doped BN nanofibers from 1.34 to 2.77 mmol g⁻¹ (at 1 bar and 0°C).²⁶⁶ As a last example, a work of a functionalized porous BN with a triblock copolymer surfactant (P123) was reported.²⁶⁷ The results showed that the BN-P123 had better adsorption properties than the pristine BN (2.69 mmol g⁻¹ vs. 2.00 mmol g⁻¹). Therefore, BN has the capacity of capture CO₂, and this can be improved by the functionalization of the structures, which offers new perspectives for BN.

4. Conclusion

The energy demand will rise in the years to come. The fossil fuels, which represent our main source of energy, are becoming scarce and the gases released by their combustion have a negative effect on the environment. The need of cleaner technologies is then imperative. H_2 emerges as the most attractive option to substitute fossil fuels and to reach a more sustainable future. However, to achieve a feasible hydrogen future some challenges need to be overcome, especially the ones regarding H_2 storage. As aforementioned, the current H_2 storage technologies are not efficient enough for most applications. The most promising alternative to attain a high H_2 storage capacity is to store the gas into a material.

Different materials have emerged as candidates for H_2 storage applications, each one with advantages and challenges to overcome. Among the possible choices, boron- and nitrogen-based materials represent a promising option as H_2 storage materials. Boron nitride, ammonia borane, hydrazine borane and their derivatives are good examples. However, fundamental research is still required to better understand the properties, behavior and chemistry of these compounds.

Amidoboranes and hydrazinidoboranes are new materials that have mostly been discovered in the last decade. Accordingly, these compounds have been investigated scarcely and there is a lack of knowledge on their chemistry. Further efforts are required to better understand the behavior and properties of amidoboranes and hydrazinidoboranes in the context of H_2 storage. This is important from a fundamental point of view, as new research will increase the knowledge of such materials in the fields of inorganic and material chemistry. The purpose of this work is to shed more light into the chemistry of alkali hydrazinidoboranes by the synthesis of the last two missing compounds. Besides, the exploration of new applications for amidoboranes is explored. A better overview over these materials is expected and new perspectives could be open.

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Chapter 3

RUBIDIUM

HYDRAZINIDOBORANE

3 Rubidium hydrazinidoborane

1. Introduction

Energy is one of the most critical issues for humanity, and it is expected that the energy demand will rise up to 30% by 2040.¹ The primary source of energy nowadays is based on fossil fuels, but the consumption in a large scale has led to the release of pollutants and greenhouse gases directly into the atmosphere contributing to global warming, with all the negative consequences that this implies.^{2,3} Besides, fossil fuels are limited resources that are being rapidly depleted. One of the alternatives to circumvent this problem is the use of hydrogen as an energy carrier because this fuel is clean and nontoxic. As an element, hydrogen is the most abundant in the universe and its molecular counterpart H_2 can be produced by a variety of methods (i.e. hydrocarbon and ammonia reforming, biomass gasification or water electrolysis).^{4–7} However, one of the major challenges to use hydrogen as a fuel is its storage. Currently, different approaches are under investigation: hydrogen can be stored by compression in high-pressure gas cylinders, as a liquid in cryogenic tanks, or stored in a host material. In addition, there are some requirements that a given technology must have to be considered for hydrogen storage such as high gravimetric/volumetric hydrogen storage capacity, reversibility of storage, stability, safety and its cycle life.^{7–9} On this basis, a series of materials have emerged due to high hydrogen storage capacities (e.g. metal hydrides, carbonaceous porous hosts, metal organic frameworks, and inorganic compounds).^{10–13}

Among the inorganic materials, boron and nitrogen-based compounds have received particular attention as chemical hydrogen storage materials.^{14–17} Ammonia borane NH_3BH_3 (AB) is a typical example. It is a crystalline solid at ambient conditions that was reported for the first time in 1955¹⁸, and since then it has been widely investigated for hydrogen storage.^{19,20} This material shows high

gravimetric hydrogen density (19.6 wt. % H) and is able to release, exothermically and thus irreversibly, 1 equiv. H_2 between 95-110°C; then, it liberates an additional 1.2-1.4 of hydrogen between 120-200°C, and the residual hydrogen above 500°C. However, there are some problems with AB: the thermolysis kinetics are slow; undesired by-products like borazine $B_3N_3H_6$, ammonia NH_3 , and diborane B_2H_6 are formed; and the solid polymeric residue product is of complex composition.²¹ In other words, pristine AB is not suitable for hydrogen storage in the solid state.

Hydrazine borane $N_2H_4BH_3$ (HB) is another boron and nitrogen-based compound that has been studied as hydrogen storage material.²² HB is a derivative of AB where the NH_3 moiety has been substituted by the hydrazine moiety N_2H_4 .²³ HB possesses a gravimetric hydrogen density of 15.4 wt. % H, but differently than AB, it has four protic hydrogens ($H^{\delta+}$) and three hydridic hydrogens ($H^{\delta-}$). The dehydrogenation of HB starts at about 60°C, and the borane loses 2 equivalents of H_2 up to 250°C, together with hazardous and toxic by-products (i.e. N_2H_4 , NH_3 and B_2H_6). Worse, it presents the formation of a shock-sensitive residue when heated above 300°C.²⁴ There have been attempts to avoid these problems. One method is the chemical modification of HB.

Alkali hydrazinidoboranes $MN_2H_3BH_3$ (MHB) are obtained by the substitution of one of the protic hydrogens $H^{\delta+}$ of the middle NH_2 of HB by an alkali cation M^+ , which results in an equivalent number of $H^{\delta+}$ and $H^{\delta-}$ in the as-formed ionic compound. Usually, MHB are synthesized by the reaction between HB and a metal hydride MH. The first hydrazinidoborane that was synthesized is lithium hydrazinidoborane $LiN_2H_3BH_3$ (LiHB, 11.7 wt. % H). Wu *et al.*²⁵ and Moury *et al.*²⁶ reported two different phases of LiHB obtained by ball milling, in different conditions, an equimolar mixture of HB and LiH. The former group obtained the high-temperature phase α -LiHB (monoclinic, s.g. $P2_1/c$), while the latter group obtained the low-temperature phase β -LiHB (orthorhombic, s.g. $Pbca$). The phase transition takes place at ca. 90°C and then α -LiHB dehydrogenates while liberating 2.6 equivalents of H_2 up to 150°C. Another derivative is sodium hydrazinidoborane $NaNH_3NH_3$ (NaHB, 8.9 wt. % H; monoclinic, s.g. $P2_1/n$). The synthesis of NaHB was carried out at -30°C due to the high reactivity of NaH towards HB at ambient conditions ($-27.7 \text{ kJ mol}^{-1}$).^{27,28} NaHB starts to release H_2 below 60°C, and it can release 2.6 equivalents of H_2 between 60 and 150°C. Despite this performance, NaHB also releases traces of N_2 and NH_3 . The last alkali derivative of HB reported is potassium hydrazinidoborane KNH_3NH_3 (KHB, 7.2 wt. % H;

monoclinic, s.g. $P2_1$).²⁹ It was prepared in a stainless steel vessel and in THF for safety reasons, as the reaction between KH and HB is highly exothermic (70.3 kJ mol^{-1}).²⁷ KHB shows slightly better dehydrogenation properties than NaHB and LiHB, with a first dehydrogenation step at 52°C .²⁹

Computational calculations have shared more light into the behavior of hydrazinidoboranes. The role of the metal cation M^+ was predicted to be crucial, as it is believed to drive the formation of the complex intermediate $M\text{-H}\cdots\text{H}_3\text{N}_2\text{BH}_2$.^{30,31} This is known as the “metal cation driven hydride-transfer” mechanism that was first reported for alkali amidoboranes MNH_2BH_3 (MAB), namely the alkali derivatives of AB.^{32,33} However the dehydrogenation mechanism is more complex, as for amidoboranes.^{34,35} While studying the isotopomer $\text{LiN}_2\text{H}_3\text{BD}_3$, Tan *et al.* brought to light the occurrence of counterintuitive homopolar $\text{H}^{\delta+}\cdots\text{H}^{\delta+}$ and $\text{D}^{\delta-}\cdots\text{D}^{\delta-}$ reactions resulting in the formation of H_2 and D_2 (together with heteropolar $\text{H}^{\delta+}\cdots\text{D}^{\delta-}$ reactions forming HD).³⁶

No other derivatives of HB have been reported so far. Efforts have been done to obtain $\text{Mg}(\text{N}_2\text{H}_3\text{BH}_3)_2$ (MgHB, 11.6 wt. % H) or $\text{Ca}(\text{N}_2\text{H}_3\text{BH}_3)_2$ (CaHB, 9.3 wt. % H) by ball milling MgH_2 or CaH_2 with HB, but all the attempts have failed.²⁷ It is evident that the chemical modification is an efficient strategy in getting derivatives of HB (as well as of AB) with improved dehydrogenation properties in terms of temperature, kinetics, and H_2 purity. We consider as crucial to obtain and study new derivatives, having 3 main reasons to do that. 1) It is important to increase our knowledge and fundamental understanding of boron and nitrogen-based materials through new compounds. 2) They may widen the prospects for hydrogen storage applications. 3) They might open up new opportunities. According to this, we present a new alkali derivative, namely rubidium hydrazinidoborane $\text{RbN}_2\text{H}_3\text{BH}_3$ (RbHB, 4.65 wt. % H) and the evaluation of its properties.

2. Experimental Section

2.1 Reagents

Hydrazine hemisulphate $\text{N}_2\text{H}_4\cdot\frac{1}{2}\text{H}_2\text{SO}_4$ ($\geq 98\%$), sodium borohydride NaBH_4 ($\geq 98\%$) and anhydrous 1,4-dioxane ($\geq 99.8\%$) were purchased from Sigma-Aldrich and used for the synthesis of hydrazine borane. Rubidium ingot (99.6%, Sigma-Aldrich) and THF (99.5%, extra dry, Acros

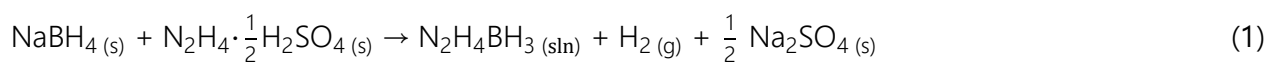
Organics) were used for the synthesis of RbHB. We preferred to use Rb over RbH for three reasons: i) RbH has not been found to be available commercially; ii) using RbH supposes its preparation and the subsequent reaction with HB, increasing the number of steps for the process; and iii) the use of RbH is not convenient for safety reasons, because of its high reactivity.

2.2 Synthesis

The boranes used in our works are sensitive to humidity and to oxygen. For this reason all the experiments were done in an argon-filled glovebox (MBraun M200B, $O_2 < 0.1$ ppm and $H_2O < 0.1$ ppm) or in a Schlenk line under an argon atmosphere.

2.2.1 Synthesis of hydrazine borane

The path to synthesize hydrazine borane was previously developed by our team.²⁴ For this work, HB was obtained by the same method: 10.1 g (0.267 mol) of $NaBH_4$ and 21.64 g (0.267 mol) of $N_2H_4 \cdot \frac{1}{2}H_2SO_4$ were weighted, grounded in a mortar and put into a Schlenk flask and a three-necked round-bottom flask, respectively. 150 mL of 1,4-dioxane was added to the $NaBH_4$, and the suspension was then poured into the $N_2H_4 \cdot \frac{1}{2}H_2SO_4$. A hydrogen evolution started immediately. The system was left under reflux and vigorous stirring for 48 h at 30°C. The reaction takes place as follows:

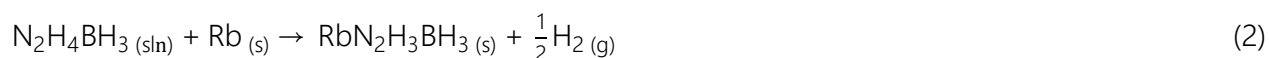


The obtained hydrazine borane was solved in the 1,4-dioxane, and the Na_2SO_4 was in suspension. The suspension is then filtered, the solution was recovered and the solvent was finally removed. The solid product was dried under vacuum for 48 h at room temperature. The obtained hydrazine borane was stored in the glovebox.

2.2.2 Synthesis of rubidium hydrazinidoborane

The synthesis of RbHB was carried out in the glovebox at room temperature. Hydrazine borane directly reacts with metallic rubidium, as ammonia borane does.^{37,38} HB (246 mg, 5.36 mmol) was solved in 20 mL of THF and poured into one flask that contained the metallic rubidium (400 mg,

4.68 mmol). The release of hydrogen started immediately. The reaction was left under stirring for 30 h. After, the remaining rubidium was collected (90 mg, 1.05 mmol). The solid precipitate was washed two times with THF and two times with 1,4 dioxane, dried under vacuum overnight and recovered. At most, it was possible to recover 393 mg of product (corresponding to a yield of 83% with respect to the reacted alkali metal). The reaction can be written as follows:



2.3 Characterization

2.3.1 Structural characterization

The obtained RbHB and the dehydrogenated solid products were analyzed by solid state ^{11}B magic angle spin – nuclear magnetic resonance MAS-NMR (Varian VNMR400, 128.31 MHz) and Fourier Transformed Infrared (FTIR) spectroscopy (NEXUS instrument, ThermoFisher Scientific; equipped with an attenuated total reflection accessory from 600 to 4000 cm^{-1} wavenumber). The samples analyzed by FTIR were prepared in closed vials inside the glovebox and the analyses were carried out in an air atmosphere. The samples were carried to the FTIR apparatus in the closed vials. The samples were taken out of the vials just before the FTIR analysis, in order to avoid a long time of exposition of the sample to the air atmosphere.

The samples for the MAS-NMR were prepared inside the glovebox, using zirconia rotors of 3.2 mm of diameter. Mr. Philippe Gaveau and Mr. Emmanuel Fernandez, from the Platform Balard of the University of Montpellier, did the sample preparation and the measurements.

The crystalline structure of RbHB was determined by power X-ray diffraction (PXRD) analysis. A PANalytical X'Pert Pro Multipurpose diffractometer equipped with an X'Celerator detector (Cu- $K_{\alpha 1/\alpha 2}$ radiation $\lambda=1.5418 \text{ \AA}$, 45 kV, 30 mA) equipped with fixed divergence slits was used for the measurements. The pattern was collected using Bragg-Brentano geometry on a spinning zero background sample holder that was prepared into the glovebox. The powder was protected using a Kapton film stuck onto the sample holder with Apiezon grease (H quality) to prevent any O_2 and H_2O contamination. The diffraction pattern was recorded in the 15-80° angle range in 2θ using a

step size of 0.017, and a scan step time of ~450 seconds. The crystallinity of the dehydrogenated solids was analyzed using a Debye-Scherrer configuration (Cu/K α_1 radiation $\lambda=1.5418$ Å). The samples were filled in glass capillary of 0.5 mm diameter in the glovebox, sealed and then analyzed in the equipment. Ms. Dominique Granier, from the Platform Balard of the University of Montpellier, performed all the manipulations of the XRD apparatus.

2.3.2 Thermal characterization

The thermal behavior of RbHB was preliminary analyzed by simultaneous thermogravimetric (TG) and differential scanning calorimetry (DSC) analysis (SDT Q600, TA Instruments). A further TG analysis was carried out in a Netzsch STA 449 F1 Jupiter equipment that was coupled to a mass spectrometer (MS; Netzsch QMS 403 D Aëolos Quadro) in order to analyze the gases released by RbHB. The sample preparation was done in the glovebox, where the powder was put into a Tzero hermetic pan to protect it from air. The pan is pierced right before the analysis to allow the produced gases to escape. The manipulation of the TGA-MS equipment was carried out by the technician of the apparatus Ms. Libeth Maldonado, from the Platform Balard of the University of Montpellier.

A gas chromatograph (GC; PerkinElmer Clarus 400 equipped to a ShinCarbon ST column) was used to analyze the purity of H₂ produced in the isothermal experiments. After the reaction finished and the reactor was cooled down to room temperature, a glass syringe was used to take a sample of the gas produced and it is injected in the GC.

2.4 Dehydrogenation experiments at isothermal conditions

The thermal behavior of rubidium hydrazinidoborane was analyzed at isothermal conditions (80, 100, 120 and 140°C) in a stainless steel reactor. Inside the glovebox, 100 mg of sample was weighted, placed into a glass vial inside the reactor and then closed tightly. Outside the glovebox, the reactor was connected to a pressure controller and immersed into an oil bath at the designated temperature. The evolution of the sample was followed by measuring the change of pressure inside the reactor. The data were converted into mol H₂ per mol of RbHB (i.e. equivalents of H₂, denoted equiv H₂) and were plotted as a function of time. The solid product was recovered for its characterization.

3. Results and discussion

3.1 Preliminary comments

The first attempt to synthesize rubidium hydrazinidoborane consisted in putting rubidium and hydrazine borane in a round flask and then add extra-dry THF. However, a violent reaction between both reactants occurred. After different attempts, we found that it is of extreme importance to dissolve HB in THF before putting it into contact with Rb. In this way, RbHB can be synthesized in safer conditions.

RbHB is a white powder. We looked for suitable (anhydrous) organic solvents for the compound. It is insoluble in THF, 1,4-dioxane and toluene. We also checked the behavior in the presence of protic solvents. RbHB reacts with water and ethanol (by solvolysis) and the reaction is accompanied by H_2 generation. These observations are consistent with those made for the other alkali hydrazinidoboranes and amidoboranes.^{16,25,26,28,39}

3.2 Molecular structure of RbHB

3.2.1 Fourier Transformed Infrared Spectroscopy (FTIR)

Rubidium hydrazinidoborane was analyzed by FTIR and the spectrum was compared to the one of HB (**Figure 1**). The N–H stretching region is different in comparison with HB. For RbHB, there are fewer bands of lower intensity. Less intense bands are also observed at the N–H bending region. This observation indicates differences between the $N_2H_4^-$ of HB and $N_2H_3(Rb)^-$ of RbHB in terms of electronic structure and binding strength. This is typical of derivatives where weaker interactions of $H^{\delta+}$ and $H^{\delta-}$ between molecules exist (because of longer distances due to the big Rb^+ cation)^{40,41}.

Regarding the B–H stretching region, RbHB presents the vibrational bands at lower wavenumbers than HB, suggesting a different chemical environment for the B–H bonds and the BH_3 groups. The band of N–N stretching shows a slight change; it is less intense for RbHB. In the B–N region, the peak at 906 cm^{-1} for HB has red-shifted to 838 cm^{-1} for RbHB, indicating a stronger B–N bond. Shorter B–N bonds are typical of hydrazinidoboranes and amidoboranes.^{16,25–28,37,38,42,43} All of the

changes in the spectrum are due to the displacement of one $\text{H}^{\delta+}$ by the Rb^+ into the network. Therefore, the modification of the chemical environment is caused by the alkaline cation Rb^+ .

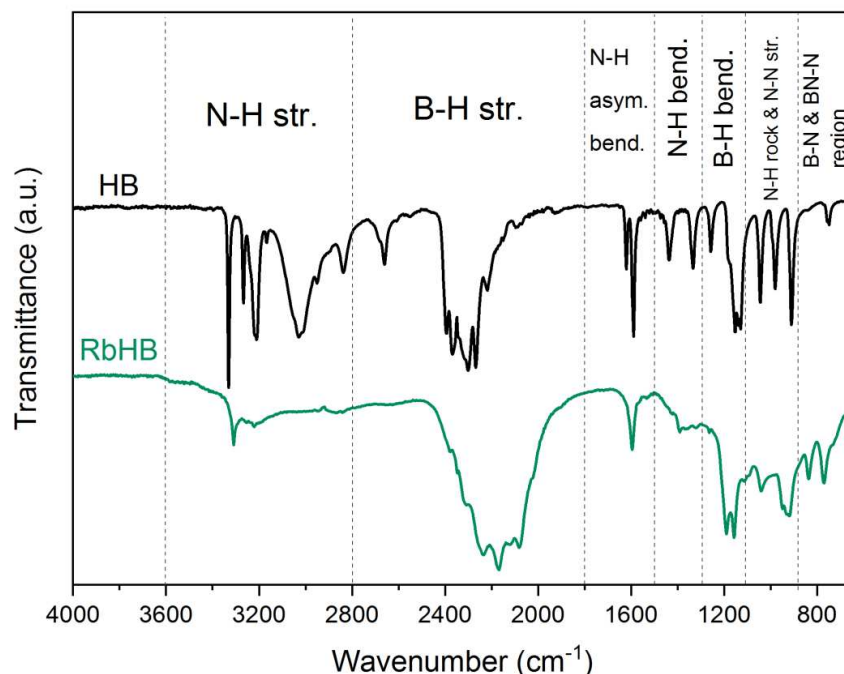


Figure 1. FTIR spectra of HB and RbHB. The bands have been assigned.

3.2.2 ^{11}B Magic Angle Spinning Nuclear Magnetic Resonance (MAS NMR)

Rubidium hydrazinidoborane was analyzed by solid state ^{11}B MAS NMR spectroscopy and the spectrum was compared to that of HB (**Figure 2**). The spectrum of HB shows a single signal centered at -24 ppm, with a split shape that is due to the quadrupolar coupling.^{44–47} The spectrum of RbHB shows a comparable split signal at lower chemical shift centered at -17.5 ppm, which is consistent with the substitution of one $\text{H}^{\delta+}$ of the hydrazine moiety by the rubidium cation. This thus indicates a different electronic arrangement in the NBH_3 environment of RbHB where $-\text{NH}(\text{Rb})-$ is a stronger donor complex with BH_3 .⁴³ This might also suggest shortening of the B–N bond of the anion $\text{N}_2\text{H}_3\text{BH}_3^-$, which agrees with the results of the FTIR analysis.¹⁶ It is interesting that the NBH_3 signal of RbHB is asymmetric and suggests the prevalence of anisotropy around the boron atom. In contrast, the other hydrazinidoborane and amidoborane compounds

presents a symmetric NBH_3 signal due to isotropy around the boron atom.^{16,25,26,28} We may suppose that the molecular degree of freedom is less pronounced for RbHB.

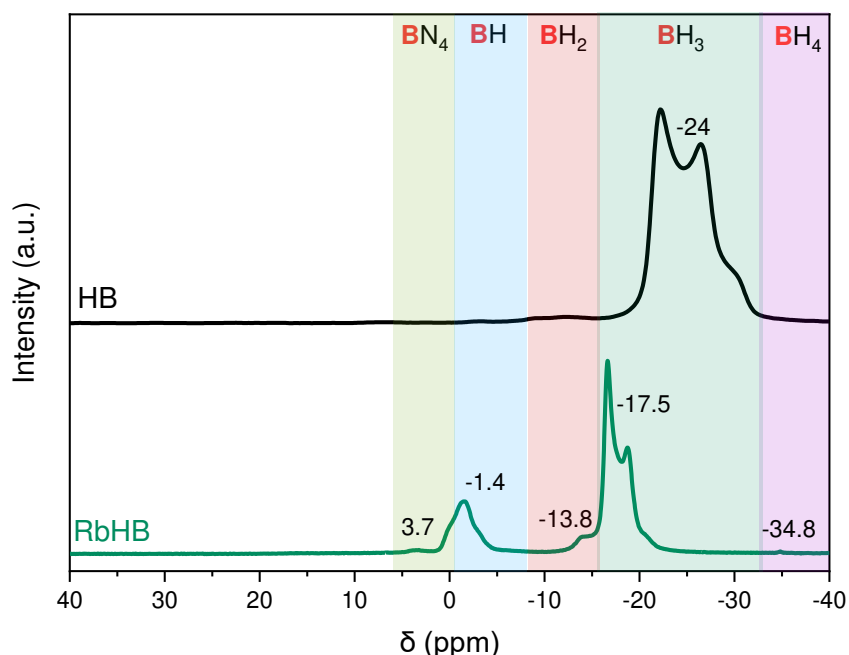


Figure 2. ^{11}B MAS NMR spectra of HB and RbHB. The chemical shifts in ppm and the assigned boron environments are indicated.

The ^{11}B MAS NMR spectrum of RbHB presents four other signals of different intensities at -34.8, -13.8, -1.4 and 3.7 ppm. The first two signals are ascribed to BH_4 and N_2BH_2 environments respectively.⁴⁸ They may occur due to the formation of some dehydrocoupling intermediates like the ionic dimer of formulae $[(\text{MN}_2\text{H}_3)_2\text{BH}_2]^+[\text{BH}_4]^-$.^{26,28} The N_2BH_2 environment could be assigned to the complex $\text{Rb}-\text{H}\cdots\text{H}_3\text{N}_2\text{BH}_2$ or the dimer $\text{N}_2\text{H}_3(\text{Rb})\text{BH}_2\text{N}_2\text{H}_2(\text{Rb})\text{BH}_3$.^{30,31,42} The signal at -1.4 ppm is attributed to an N_3BH environment, and that at 3.7 ppm to an BN_4 environment⁴⁹. The presence of such environments implies the formation of highly dehydrogenated polymeric residues of RbHB. Dehydrocoupling is likely to happen because of a slow evolution of RbHB at room temperature (the MAS NMR analyses are performed one day after the preparation of the sample), which could be aggravated due to the rotor rotation during the NMR analysis (slight decomposition of the sample during the analysis due to a possible increase of temperature).

3.2.3 Stability of rubidium hydrazinidoborane

The stability of RbHB in solid state was investigated by ^{11}B MAS NMR and FTIR spectroscopy. Two RbHB samples were stored in the argon-filled glovebox for one and seven months after synthesis. The FTIR analysis (Figure 3) indicates that the N–H stretching bands broaden with time. The broadening extends beyond 3400 cm^{-1} , which indicates the presence of polymeric compounds. Consistently, the B–H stretching bands become weaker in intensity.

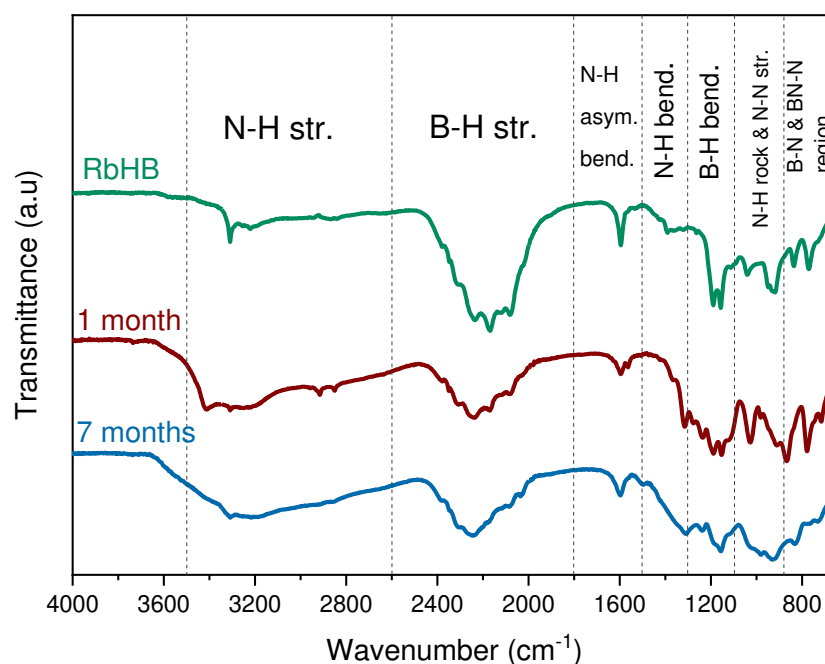


Figure 3. FTIR spectra of RbHB, RbHB after 1 and 7 months after synthesis (stored at room temperature and under argon atmosphere). The bands have been assigned.

The ^{11}B MAS NMR spectra show several changes (Figure 4). The most prominent one is the change of the signal at -17.5 ppm , attributed to the NBH_3 environment, which loses its initial asymmetric shape. It is symmetric, suggesting much higher isotropy around the boron atom. The intensity of the signal at around -35 ppm and that of the hump at around -15 ppm are higher. The former signal is characteristic of a BH_4 environment. The latter one may be ascribed to an N_2BH_2 environment⁴⁸. A broad signal of low intensity can be seen between 0 and -12 ppm and it

can be attributed to N_2BH and N_3BH environments. Another broad signal deconvoluted into 4-5 signals appeared at positive chemical shifts.

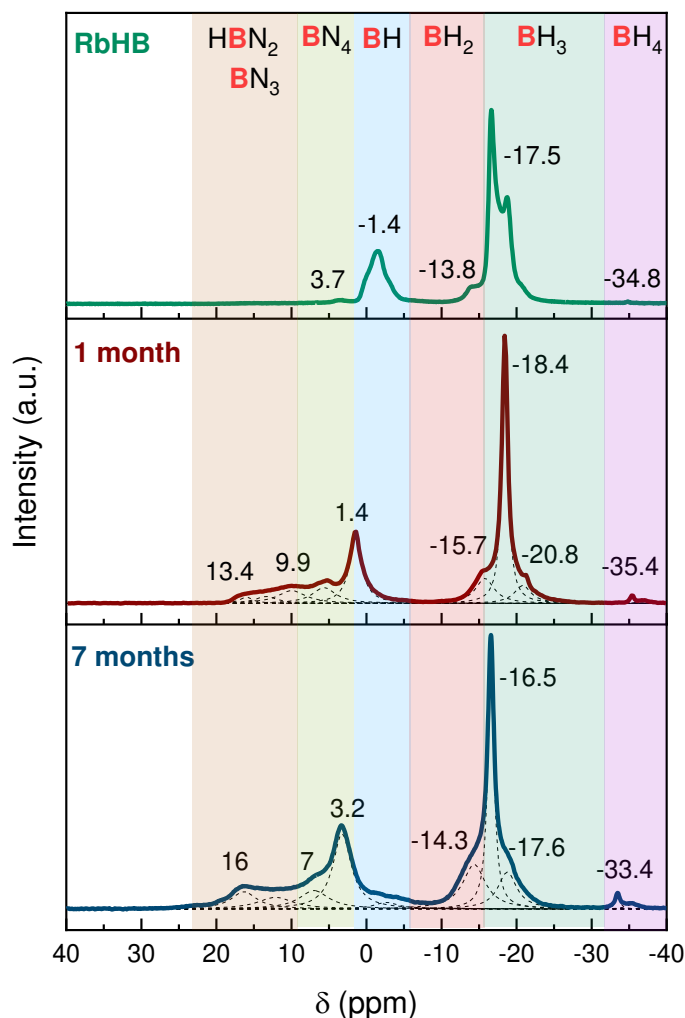


Figure 4. ^{11}B MAS NMR spectra of RbHB, RbHB after 1 month and after 7 months of synthesis (stored at room temperature and under an argon atmosphere). The signals for the aged samples were deconvoluted. The chemical shifts in ppm and the boron environments are indicated.

The signals at <10 ppm are typical of tetravalent BN_4 environments; the others are due to trivalent boron environments generally observed for borazine-linked polymeric species.^{48–54} Table 1 presents the chemical shifts of different compounds formed in the thermolysis of BNH compounds. The aged samples revealed that RbHB is not stable at room temperature. It evolves by dehydrocoupling and could form species such as polyiminoborane and/or polyborazylene-like

compounds. This behavior is similar to the one showed by the ammonia borane derivative, RbNH_2BH_3 , that also undergoes a slow decomposition at room temperature.^{37,38} The reason is the size of the Rb^+ cation that destabilizes the molecule.⁵⁵

Table 1. Typical chemical shifts assigned to different species formed during the thermal decomposition of BNH compounds.

δ (ppm)	Boron site	Assigned species	Reference
-38	BH_4	$[(\text{NH}_3)_2\text{BH}_2]^+[\text{BH}_4]^-$	48
-37	BH_4	DADB	49
-30	BNH_3	-	56
-24	BH_3	AB, HB, MAB, MHB	48
-22	BH_3N	MAB, MHB	48,49,52
-20	BH_2N_2	DADB	48,56
-13	BH_2	$[(\text{NH}_3)_2\text{BH}_2]^+[\text{BH}_4]^-$	48
-12	BH_2N_2	Linear and/or cyclic dimers	48,52
-10.9	BH_2	Transient species	48
-10	BH_2N_2	DADB	48,49
-6.1	BH	-	53
-4	BHN_3	-	49
-0.85	BH	-	53
1	BN_4	-	49
1.5	BN_4	-	53
27	B_3N_3	Polyborazylene	51,52,56,57
31	BN_3	Polyborazylene	51,52,57
35	BN_3	$\text{B}(\text{NBH})_2(\text{NB}_2)$	49
40	BHN_2	$\text{BH}(\text{NBH})_2$	49

3.2.4 Crystal structure

The PXRD pattern of RbHB was compared to that of HB (Figure 5). It does not exhibit any diffraction peaks of HB and can be considered as a pure phase. The broad amorphous-like peaks were identified from the Kapton film used to protect the sample. But as suggested by the ^{11}B MAS NMR results, the presence of some amorphous dehydrogenated products cannot be discarded.

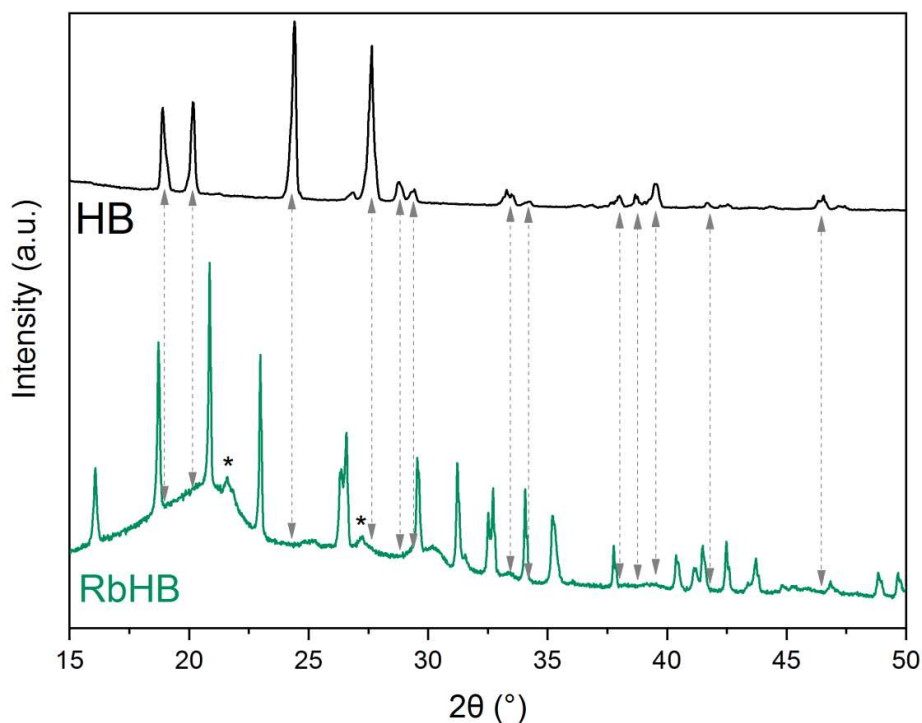


Figure 5. Comparison of the PXRD patterns of pure HB and RbHB. The stars indicate the peaks due to the Kapton foil used in the analysis.

The crystallographic data and the Rietveld refinement were obtained thanks to the collaboration with Mr. Pascal Yot (ICGM UMR5253 Montpellier), who performed these works. The PXRD pattern of RbHB was successfully indexed as a single phase using FOX.⁵⁸ JANA2006 package was used to refine the structure by the Rietveld method.⁵⁹ The position of Rb atoms was first determined by Charge Flipping algorithm 'SuperFlip' included into JANA2006 package, and then used into FOX to reach the position of the $\text{N}_2\text{H}_3\text{BH}_3^-$ anions.⁶⁰ The crystallographic data is presented in Table 2.

Table 2. Space group, unit cell parameters, goodness of fit and R values for the refined structure.

Space Group	P2 ₁ (No. 4)
Z	2
a (Å)	5.8128(5)
b (Å)	6.7010(5)
c (Å)	5.8143(5)
β (°)	108.915(4)
V (Å ³)	214.25(3)
Crystallographic density	1.7252
Temperature (°C)	20
GoF	2.44
R _p	1.23
wR _p	3.01
R _(obs) /wR _(obs)	7.85 / 7.91
R _(all) /wR _(all)	6.88 / 6.89

The Rietveld refinement of the pattern was carried out using a Lorentzian peak shape with a cut-off of 20. Considering the quality of the diffraction pattern, the atomic displacement parameters were taken equal and isotropic for all atoms of the unit cell. The peaks asymmetry was corrected using Howard model (Boole's rule) and preferred orientation using March-Dollase model following the (010) direction. As shown in Figure 6, the calculated pattern (red line) is comparable to the experimental one (black line). The B–H and N–H distances were constrained to 1.20 Å and 1.04 Å respectively, in accordance with the optimization realized by FoX program. The uncertainties of the atomic coordinates for hydrogen atoms are not reported here because they were not freely refined. The isotropic thermal parameters (U_{iso}) were constrained to be identical for all atom types (Table 3).

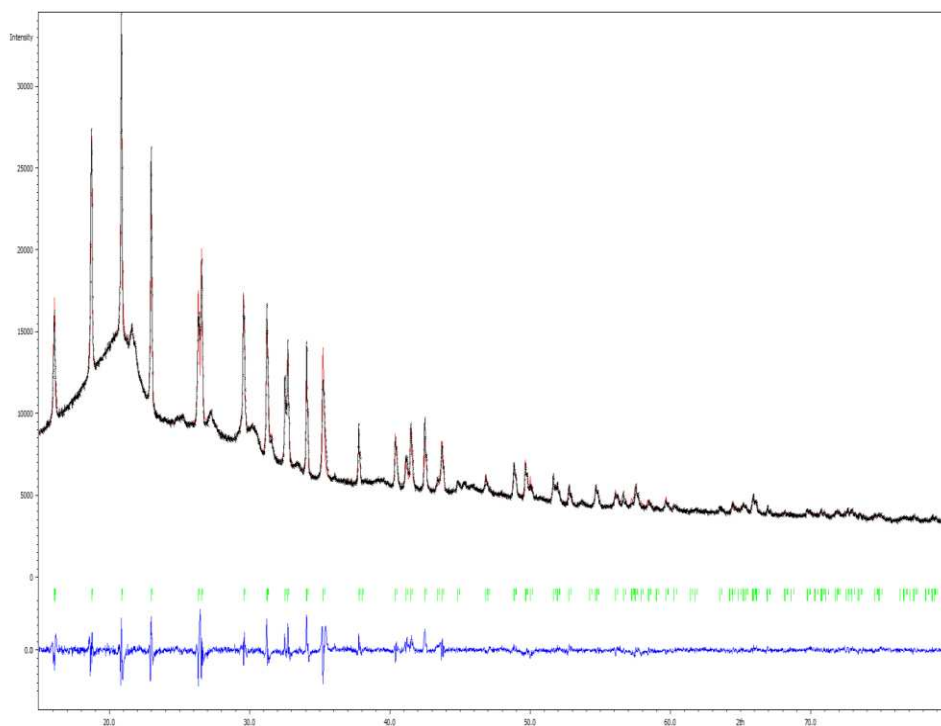


Figure 6. Observed (black line) and calculated (red line) powder XRD profile for the Rietveld refinement of RbHB, differences of the plots (blue line), and calculated angles for Bragg peaks in 2θ (green lines).

Table 3. Experimental structural parameters of RbHB (S.G. $P2_1$ No. 4) at room temperature

Atom	Site	Occupancy	x	y	z	U_{iso} (Å)
Rb			0.2315(5)	0.0029(4)	0.1235(5)	0.0359(10)
B1			0.379(5)	0.48(2)	0.196(5)	0.0359(10)
N1			0.116(5)	0.635(4)	0.410(4)	0.0359(10)
N2			0.2044(3)	0.447(4)	0.359(5)	0.0359(10)
H1	2a	1	0.27776	0.60148	0.03141	1.2
H2			0.56132	0.56955	0.31909	1.2
H3			0.42699	0.34464	0.11324	1.2
H4			0.02349	0.60979	0.48099	1.2
H5			0.25411	0.70648	0.55068	1.2
H6			0.30867	0.38206	0.52378	1.2

Another collaboration with Mr. Guillaume Maurin (ICGM UMR5253 Montpellier) was done, where he calculated the position of the H atoms of the molecule. The locations of the H atoms linked to the N and B atoms were determined by performing a geometry constrained optimization of the structure (Rb, B and N atoms fixed in their initial positions) at the force-field level. All atoms of the system were represented as Lennard-Jones charged sites with LJ parameters taken from the UFF force field while the charges were calculated using the QeQ method.^{61,62}

RbHB was indexed as a single phase in a monoclinic $P2_1$ (No. 4) unit cell (Figure 7); $Z=2$; $a=5.8128(2)$ Å, $b=6.7010(2)$ Å, $c=5.8143(2)$ Å and $\beta=108.915(2)^\circ$. RbHB is isostructural with KHB⁴², whereas α -LiHB and NaHB crystallize in different monoclinic cells ($P2_1/c$ and $P2_1/n$ respectively).^{25,28}

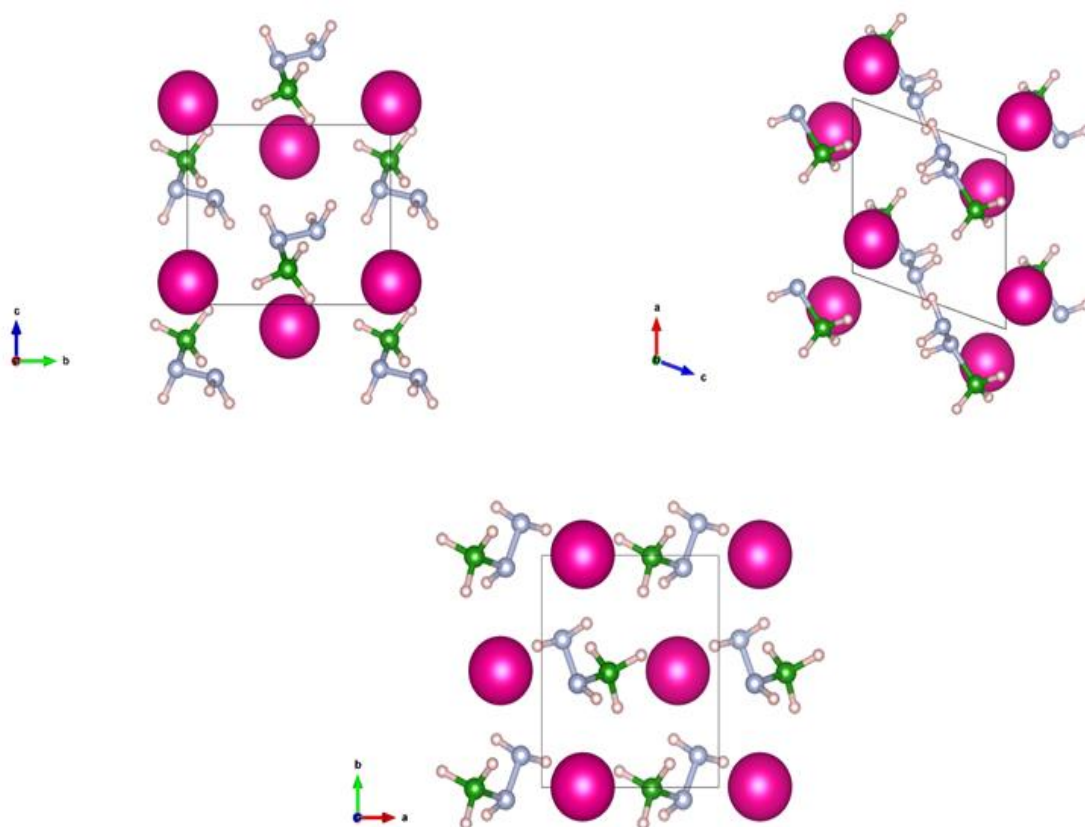


Figure 7. Crystal structure of $\text{RbN}_2\text{H}_3\text{BH}_3$ along the $[100]$, $[010]$, and $[001]$ directions. H, B, and N atoms are represented by pink, green, and blue spheres. Rb atoms are represented by fuchsia spheres.

As a derivative of AB, RbNH_2BH_3 shows a different monoclinic cell ($P2_1/c$) and a volume per formula unit of 94.24 \AA^3 ,^{37,38} which is slightly smaller than the volume per formula unit of 107.22 \AA^3 of RbHB ; this is consistent with the bigger size of the anion $[\text{N}_2\text{H}_3\text{BH}_3]^-$. The volume per formula unit of HB is also smaller with 80.154 \AA^3 ,²⁵ which is consistent with the presence of the bulkier cation Rb^+ . In RbHB , the cation Rb^+ is octahedrally coordinated with 6 $[\text{N}_2\text{H}_3\text{BH}_3]^-$ anions (Figure 8). This is consistent also with the bigger size of Rb^+ . The coordination number for Li^+ , Na^+ and K^+ in the corresponding hydrazinidoboranes were lower, being 4, 5 and 4, respectively.^{26,28,42} In RbNH_2BH_3 also, it was found a pseudo-octahedron around each Rb^+ cation.^{37,38}

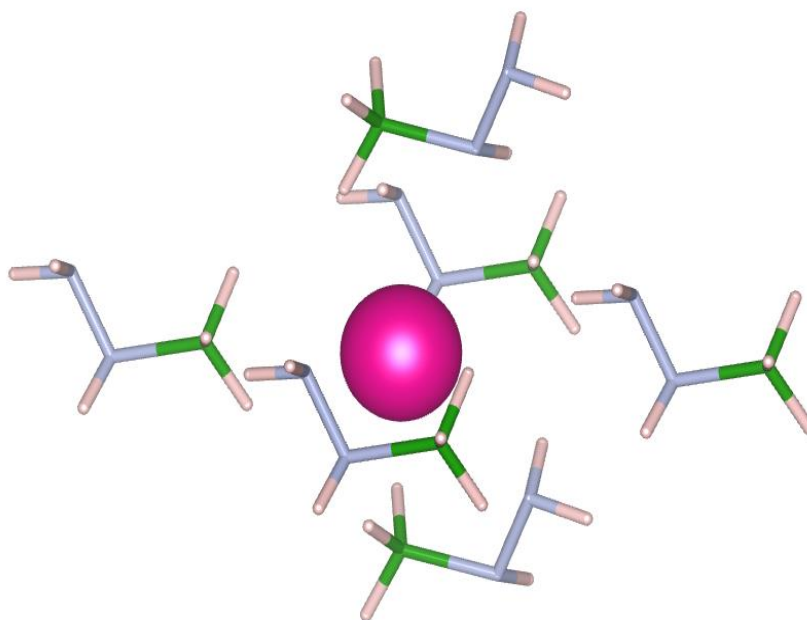


Figure 8. Coordination sphere of the cation Rb^+ surrounded by 6 $[\text{N}_2\text{H}_3\text{BH}_3]^-$ anions.

The locations of the H atoms linked to the N and B atoms were computationally determined, bringing out the interatomic distances (**Figure 9**). The shortest $\text{Rb}\cdots\text{Rb}$ distance is $4.246(2) \text{ \AA}$. This is slightly higher than the distance 4.025 \AA calculated for RbNH_2BH_3 , due to the bigger size of the anion $[\text{N}_2\text{H}_3\text{BH}_3]^-$. The shortest $\text{Rb}-\text{N}$ distance was determined as $3.132(3) \text{ \AA}$ (vs 3.06 \AA for RbNH_2BH_3). This is a longer distance than the shortest one in KHB (2.959 \AA) because of the bigger size of Rb^+ compared to K^+ .⁴² The B-N bond was determined as being of 1.55 \AA , which is

consistent with the values 1.54-1.55 Å found for LiHB, NaHB and KHB.^{26,28,42} This bond is besides shorter than the B-N bond of HB (1.59 Å).^{24,25} This is in good agreement with the aforementioned shortening of the B-N bond by Rb⁺ insertion as suggested by ¹¹B MAS NMR and FTIR spectroscopy. All of this is in favor of the formation of an ionic salt where the anion [N₂H₃BH₃]⁻ underwent strong electronic rearrangement due to the presence of Rb⁺.

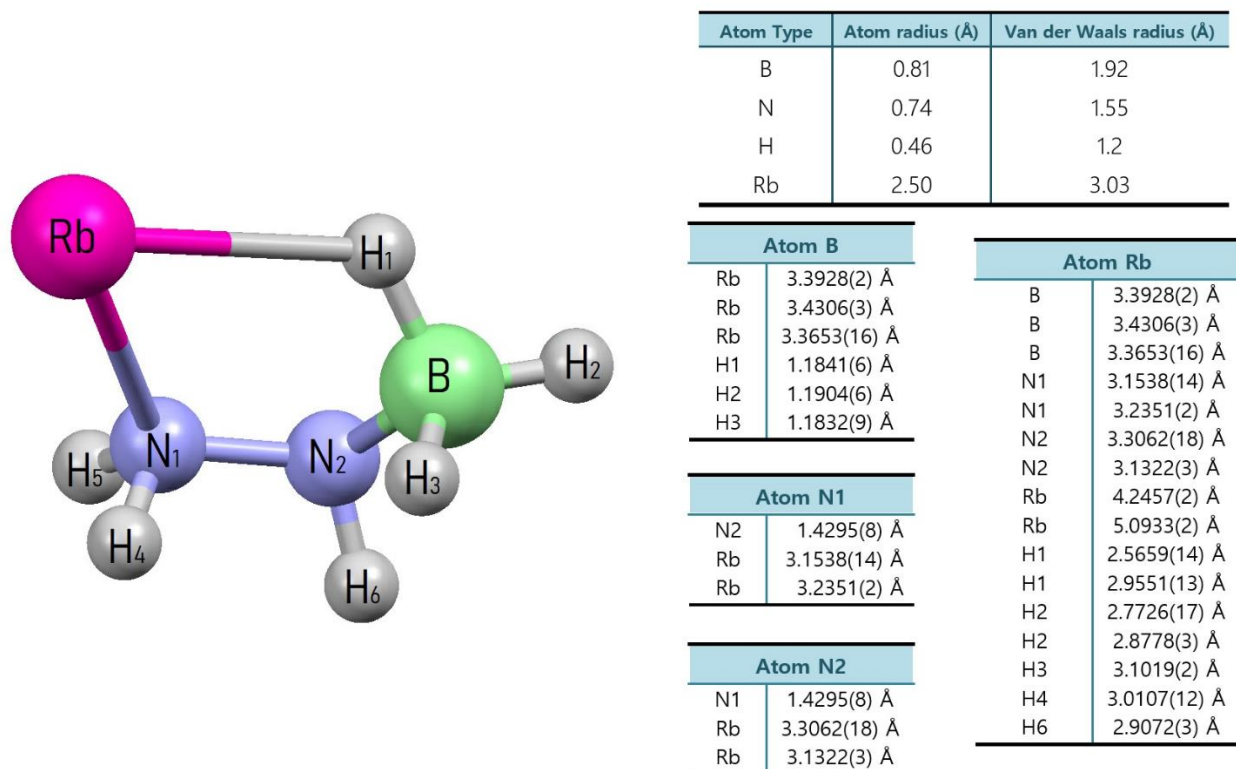


Figure 9. Calculated interatomic distances for rubidium hydrazinidoborane.

3.3 Thermal characterization

3.3.1 TG-MS and DSC analyses

Thermal decomposition of RbHB was studied by TG analysis (heating rate of 5°C min⁻¹) and the gases released were analyzed by MS. The material is stable up to ca. 60°C and then it starts to decompose (Figure 10). Over the range 60-100°C, RbHB loses ca. 5 wt. % of its initial weight, due

to the release of H_2 and NH_3 . The second decomposition step takes place in the range 115-145°C where the mass loss is 0.5 wt. %.

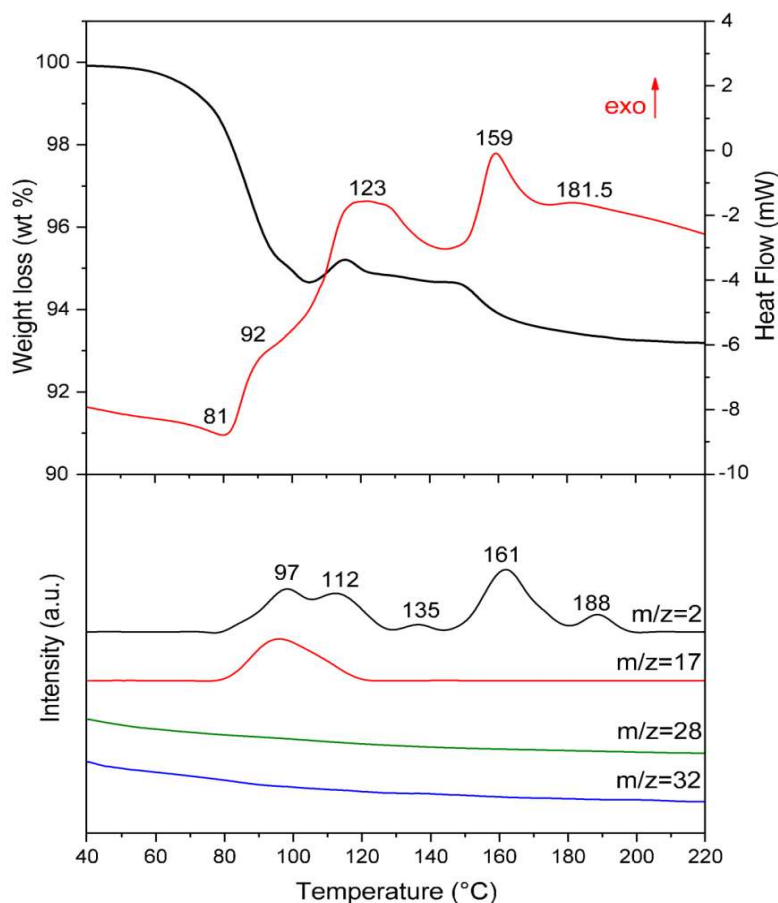


Figure 10. TGA-DSC (5°C min^{-1}) and MS results ($m/z = 2, 17, 28, 32$ for H_2 , NH_3 , B_2H_6 or N_2 , N_2H_4 respectively) of RbHB. The peak temperatures ($^\circ\text{C}$) observed by DSC and MS are given.

A third decomposition step occurs between 150-200°C, with a mass loss of 1.3 wt. %. For both of the last two steps, only H_2 was detected by MS. The overall weight loss in the range 60-200°C is 6.8 wt. %. This is higher than the 4.65 wt. % H carried by RbHB and such a difference may be explained by the loss of a significant amount of NH_3 . In our conditions, there was no detection of any other volatile by-products (like B_2H_6 , N_2H_4 or $\text{B}_3\text{N}_3\text{H}_6$). There is one slight gain of mass (hump) at around 110°C present in the TG analysis. A similar feature was reported for HB, NaHB and KHB. This is explained by a “buoyancy effect” that takes place when the melted borane solidifies while

releasing H_2 and it displaces the heavier argon gas inside the semi-closed crucible. The foaming of the sample generally intensifies the aforementioned hump (Figure 11). In terms of the onset temperature of dehydrogenation, RbHB shows better properties in comparison to HB, and is comparable to LiHB. In contrast, NaHB and KHB have better features. In terms of purity of the released H_2 , LiHB, NaHB and KHB are more attractive.^{26,28,42} It is noticeable that the amount of the unwanted volatile product NH_3 seems to increase with the size of the alkali cation M^+ down in the group.

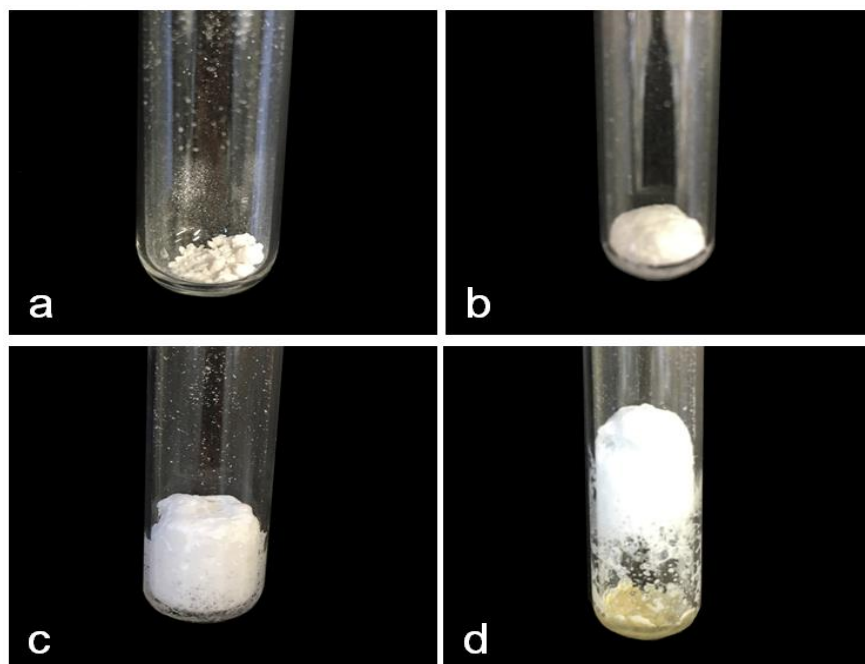


Figure 11. Pictures of the evolution of RbHB under heating: a) RbHB at room temperature; b) Foaming starting to occur at ca. 60 °C; c) Expansion of the foam due to the evolution of volatile products; d) Solidification of the foam resulting in a polymeric residue at ca. 100°C

RbHB was also analyzed by DSC (Figure 10). The DSC profile clearly suggests a complex decomposition path. A first endothermic event peaks at 80°C. As for HB, NaHB and KHB melting takes place and precedes the dehydrogenation of RbHB.^{24,28,42} Following, there are several exothermic events. The DSC and MS analyses suggest five successive steps. According to MS, these dehydrogenation steps peak at 97, 112, 135, 161 and 188°C. The first dehydrogenation step is concomitant with a deammoniation step peaking at 95°C. These results again confirm the

complicated dehydrogenation mechanism of RbHB. Due to the exothermicity of the dehydrogenation process, re-hydrogenation of the dehydrogenated samples is considered not possible under normal conditions.^{14–17} If the regeneration is considered, it should be done by other means, like the reduction of the spent fuel using hydrazine in NH_3 medium, or the digestion and ammoniation of the solid residue.^{63,64}

3.3.2 Calculation of the apparent activation energy by the Kissinger method

The activation energy and kinetics parameters of the thermolysis of RbHB were calculated using the Kissinger method (For more details, see Annex I).⁶⁵ **Figure 12** presents the superposition of the DSC analyses at different heating rates: 1, 3, 5, 7 and 10 $^{\circ}\text{C min}^{-1}$, and also the values obtained by the linear regression. We analyzed the two main exothermic signals indicated by the dashed lines.

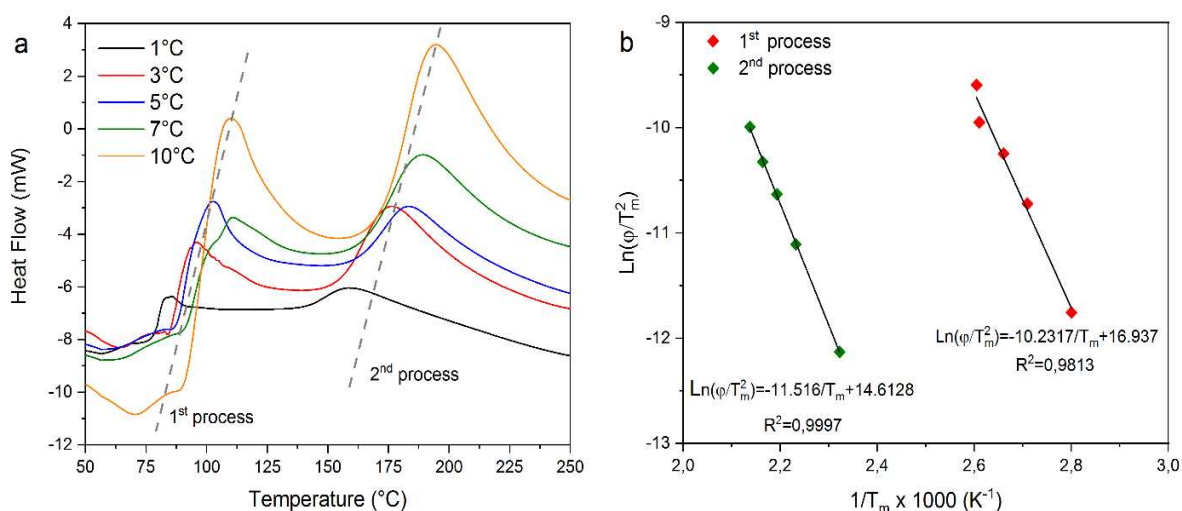


Figure 12. a) DSC curves for RbHB at different heating rates (1, 3, 5, 7, 10 $^{\circ}\text{C min}^{-1}$); b) Linear regression for the Kissinger method of the two exothermic events.

The first process corresponds to the dehydrogenation and deammoniation of the sample while the second corresponds only for dehydrogenation. The calculated activation energies of the first and second processes are $E_{a1}=85 \text{ kJ mol}^{-1}$ and $E_{a2}=94 \text{ kJ mol}^{-1}$ respectively. These values are close and indicate a similar energetic barrier for both processes. In comparison with another BNH materials considered for hydrogen storage, these values are lower. For example, hydrazine

bisborane HBB has a activation energy of $106.4 \text{ kJ mol}^{-1}$ for its first process of dehydrogenation and AB one activation energy of 160 kJ mol^{-1} .^{66,67}

Table 4 shows the kinetic parameters calculated with Kissinger method. From the activation energies, it is observed that the decomposition of RbHB is thermodynamically favorable due to the exothermicity of the processes. This means that we need to supply less energy to start the thermal decomposition of RbHB than for other BNH compounds. With these results, we confirm that the Rb^+ has a destabilization effect on the molecule. As it is evidenced by the TGA, RbHB starts its dehydrogenation at a lower temperature than HB but it releases a huge amount of ammonia that was detected by MS. RbHB presents a lower activation energy for the decomposition process in comparison with other BNH compounds that are used as potential hydrogen storage materials.^{66,67}

Table 4. Kinetics parameters of RbHB dehydrogenation process calculated by Kissinger method and Arrhenius equation.

Process	$E_a \text{ (kJ mol}^{-1}\text{)}$	$A \text{ (min}^{-1}\text{)}$	$k \text{ (min}^{-1}\text{)}$			
			80°C	100°C	120°C	140°C
1	84.91	2.3163×10^{11}	6.31×10^{-2}	2.98×10^{-1}	1.20	4.22
2	94.07	2.5118×10^{10}	3.02×10^{-4}	1.68×10^{-3}	7.88×10^{-3}	3.18×10^{-2}

3.3.3 Dehydrogenation experiments on RbHB

Experiments under isothermal conditions were carried out in a stainless reactor at 80, 100, 120 and 140°C to evaluate the dehydrogenation properties of RbHB. The dehydrogenation of RbHB is a two-step process (**Figure 13**). Similar profiles were reported for LiHB and NaHB, though for RbHB the break in the slope is more prominent.^{26,28} The first step takes place in the first 23, 20, 17 and 13 minutes for the sample heated at 80, 100, 120 and 140°C respectively. After a slow release of hydrogen, the second step takes place.

The H_2 evolution curves were exploited to determine the apparent activation energy E_a of the first step. The slope of the curves, denoted as a_0 , within the first minutes of the reaction was used as the hydrogen generation rate (equiv H_2 min $^{-1}$). The rate was plotted as a function of the inverse of the temperature (T in K $^{-1}$) using the “linearized” Arrhenius equation (Figure 13):

$$\ln a_0 = -\frac{E_a}{RT} + \ln A \quad (3)$$

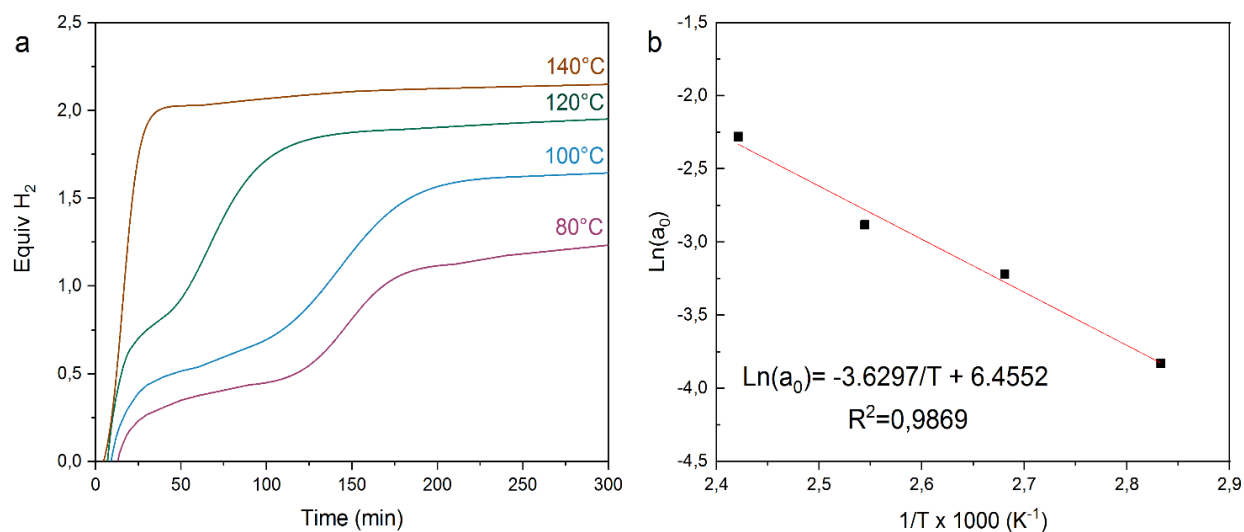


Figure 13. a) Time evolution of H_2 release from RbHB under heating at constant temperature (80, 100, 120 and 140°C); b) Arrhenius plot for the determination of the apparent activation energy.

An apparent activation energy of 30.1 kJ mol $^{-1}$ was calculated with the Arrhenius equation. This value is lower compared to other boron and nitrogen-based materials. Pure ammonia borane and LiH-doped ammonia borane have respective apparent activation energies of 183 and 75 kJ mol $^{-1}$, calculated by the same method.⁶⁸ Another example is lithium amidoborane $LiNH_2BH_3$ and the mixture $LiBH_4/LiNH_2BH_3$, with apparent activation energies of 71 and 61 kJ mol $^{-1}$, respectively.⁶⁹ In the case of the hydrazinidoboranes, the calculated apparent activation energy for LiHB is 58 kJ mol $^{-1}$, while NaH-doped NaHB possesses a lower activation energy of 14.4 kJ mol $^{-1}$.^{26,70}

The gases released by the sample in the isothermal experiments were analyzed by gas chromatography (Figure 14). There is only one signal that appeared after 0.46 min that corresponds to the retention time of hydrogen for our GC column. It can be observed also that

the higher the temperature, the more the amount of H_2 . This is in good agreement with the aforementioned discussion.

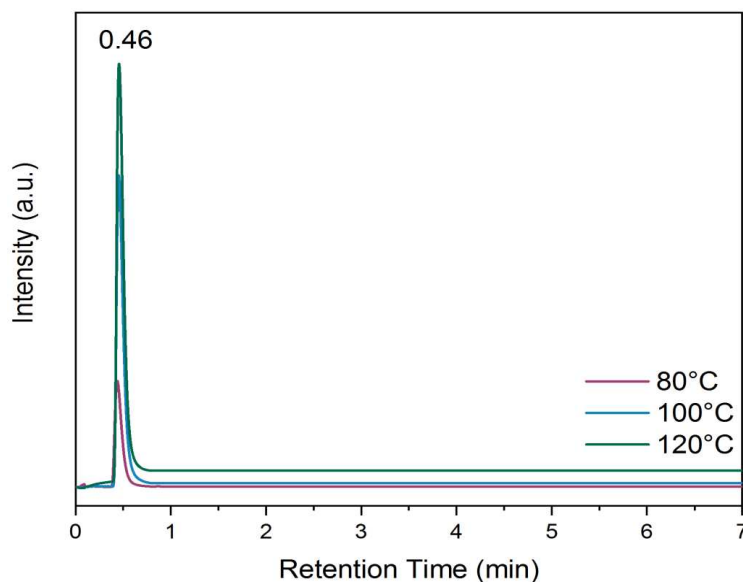


Figure 14. GC analyses of the gases liberated by RbHB in isothermal conditions (under heating at the constant temperature of 80, 100 and 120°C). The retention time for H_2 in min is indicated.

The equiv H_2 released by RbHB were compared to the available data reported for HB, LiHB and NaHB after 1 h of heat treatment at constant temperature.^{24,26,28} The data are shown in Table 5.

Table 5. Equivalents of H_2 liberated by different alkali hydrazinidoboranes after 1 h of heat treatment at constant temperature

Temperature	Compound			
	HB ²⁴	LiHB ²⁶	NaHB ²⁸	RbHB
80°C	0.4	-	0.62	0.38
100°C	0.65	0.6	2.6	0.55
120°C	-	-	-	1.1
140°C	1.1	2.2	-	2

Heated at 100°C, RbHB, HB and LiHB release a similar amount of H₂ in one hour (ca. 0.6 equiv H₂). This is less than the 2.6 equiv H₂ liberated by NaHB. Heated at 140°C for 1 h, RbHB releases 2 equiv H₂ vs 1.1 for HB. Slightly better performance was reported for LiHB with 2.2 equiv H₂. In resume, RbHB has improved dehydrogenation properties in comparison to those of pristine hydrazine borane, is comparable to LiHB, but is less attractive than NaHB. The destabilization effect of Rb⁺ is thus confirmed.

3.4 Analysis of the solid residues

The solid residues recovered upon the completion of the isothermal experiments were analyzed by FTIR (Figure 15). The intensity of the N–H and B–H stretching bands decays as the heating temperature increases. A similar behavior can be observed for the signal assigned to the N–H asymmetric bending. All of these bands almost disappeared for the solid heated at 140°C. This is consistent with the formation and release of H₂ from RbHB.

The solid residues were also analyzed by PXRD (Figure 16). No peaks can be founded in any of the patterns, which suggest a total composition of amorphous polymeric compounds.

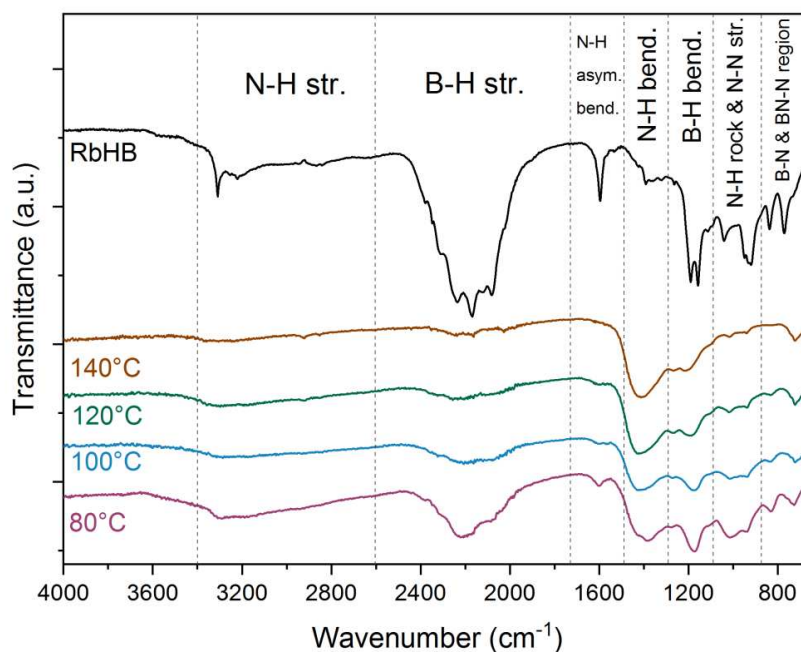


Figure 15. FTIR spectra of RbHB and of the solid residues recovered upon heating a sample of RbHB at 80, 100, 120 and 140°C. The bands have been assigned.

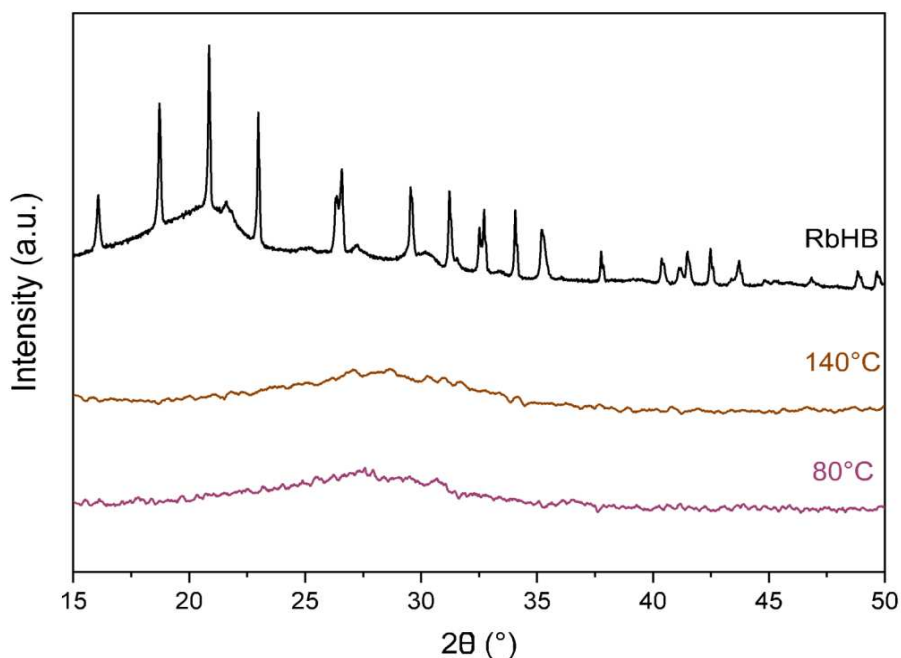


Figure 16. XRD patterns of RbHB and of the solid residues recovered upon heating a sample of RbHB at 80 and 140°C.

A better characterization was achieved by analyzing the solid residues by ^{11}B MAS NMR (Figure 17). A resonance centered at -34.4 ppm appeared in all heated samples. This signal is characteristic of a BH_4 environment. As discussed in section 3.2.2 for fresh RbHB, this boron environment may be explained by the formation of an ionic dimer like $[(\text{RbN}_2\text{H}_3)_2\text{BH}_2]^+ [\text{BH}_4]^-$.^{26,28} The existence of such dimer implies an additional resonance due to a N_2BH_2 environment that can be seen at -16 ppm. The intensity of this signal decreases as the temperature of the isothermal experiment increases.

For the sample heated at 80°C the asymmetric signal can be deconvoluted into two Gaussian signals centered at -14 and -17 ppm. The former is due the N_2BH_2 environment. The latter can be attributed to the NBH_3 environment, suggesting remaining RbHB and/or unreacted NH_3 groups. Referring to the literature dedicated to alkali derivatives of ammonia borane, several possible complex intermediates were tentatively identified via experimental analyses and theoretical calculations, and such intermediates (that are adapted to $\text{N}_2\text{H}_3\text{BH}_3^-$) might help in the association

of the aforementioned signals: for instance, $[\text{N}_2\text{H}_4\text{Rb}]^+ [\text{BH}_3(\text{N}_2\text{H}_2\text{Rb})\text{BH}_3]^-$, $\text{Rb}-\text{H}\cdots\text{H}_3\text{N}_2\text{BH}_2$, $\text{Rb}-\text{H}\cdots\text{RbN}_2\text{H}_3\text{BH}_2\text{N}_2\text{H}_3\text{BH}_3$, $[\text{RbN}_2\text{H}_3\text{BH}_2\text{RbN}_2\text{H}_3]^+ [\text{BH}_4]^-$.^{32,33,40,55,71,72}

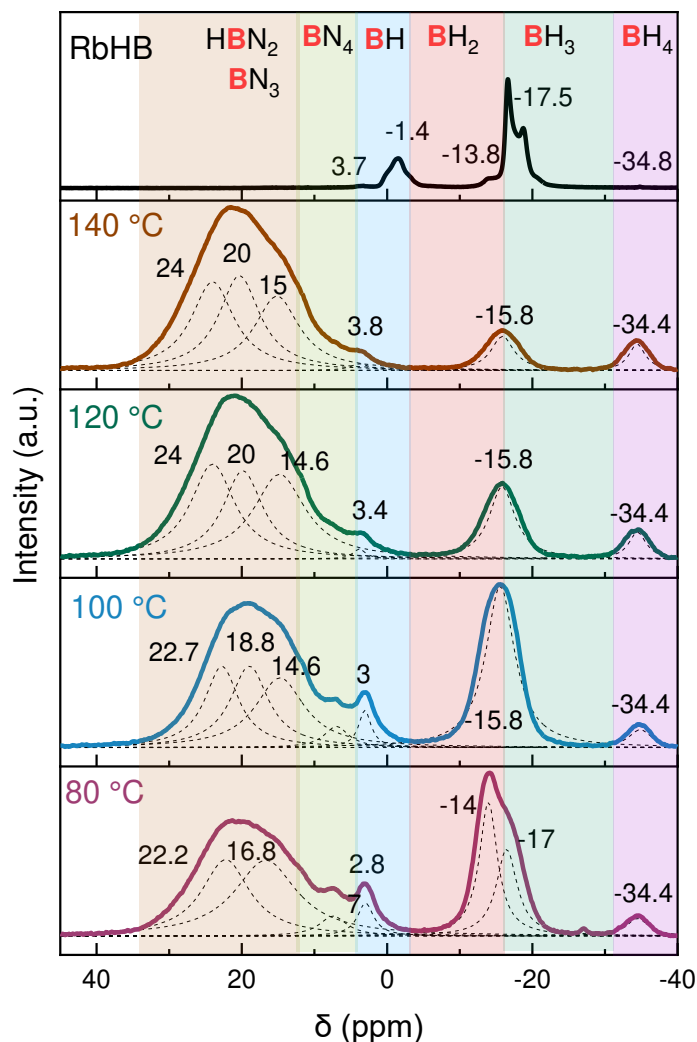


Figure 17. ^{11}B MAS NMR spectra of RbHB and of the solid residues recovered upon heating the sample at 80, 100, 120 and 140°C. The signals for the residues were deconvoluted. The chemical shifts in ppm are indicated.

The ^{11}B MAS NMR spectra also show a broad signal at positive chemical shifts and which contribution is larger as the temperature of the isothermal experiment increases. They are typical of trivalent boron environments.^{50–54} At lower temperatures (80 and 100°C), there are two signals centered around 3.8 and 7 ppm that could indicate the presence of a tetravalent BN_4 .⁴⁹ The broad

signal between 10 and 40 ppm is composed of mainly three signals centered on 14, 20 and 24 ppm. They are present due to the formation of borazine-linked polymeric species. The broadening of the signals is due to the quadrupolar effect of the trivalent boron, usually assigned to BN_2H and BN_3 . It seems that like in the case of AB, dehydrocoupling of RbHB results in the formation of polyborazylene-like compounds.

3.5 Decomposition mechanism of rubidium hydrazinidoborane

The analyses of thermal decomposition and the samples after isothermal experiments showed that the decomposition of RbHB follows a complex path. The TGA-MS analysis allowed us to identify NH_3 and H_2 . The ^{11}B MAS NMR and the XRD showed that after the isothermal experiments, the sample evolved to form a mixture of amorphous compounds, i.e. boron and nitrogen-based polymers with boron atoms with sp^2 and sp^3 hybridization. Based on the species identified by the MAS NMR analyses and previous computational works on LiHB,³⁰ we propose a tentative decomposition mechanism of RbHB. We should remind that the mechanism is speculative due to the difficulty to identify the intermediates that are formed in the decomposition path of BNH materials in the solid state. The proposed mechanism is presented in Figure 18.

We start from the molecules of RbHB in step ①. After the isothermal experiments we can observe two chemical shifts around -34 and -14 ppm. As discussed before, this was identified as an analogous compound to diammoniate of diborane DADB. Applied to our case, $[(\text{RbN}_2\text{H}_3)_2\text{BH}_2]^+[\text{BH}_4]^-$ (dirubidium dihydrazine of diborane) is formed in step ②. As proposed for LiHB,³⁰ the formation of NH_3 is explained by the migration of one atom of H across the N–N bond to break this bond after the process (step ③ and ④). Besides, it has been reported that the anion $[\text{BH}_4]^-$ participate in the dehydrogenation of ammonia borane,⁷³ resulting in the concomitant release of NH_3 and H_2 . Such a path is likely in our conditions. After this process, the species could lose more dihydrogen, or react with another molecule of RbHB followed by dehydrocoupling of the formed species (step ⑤). Either path leads to the formation of the polymeric species identified in the positive chemical shifts of the ^{11}B MAS NMR (step ⑥).

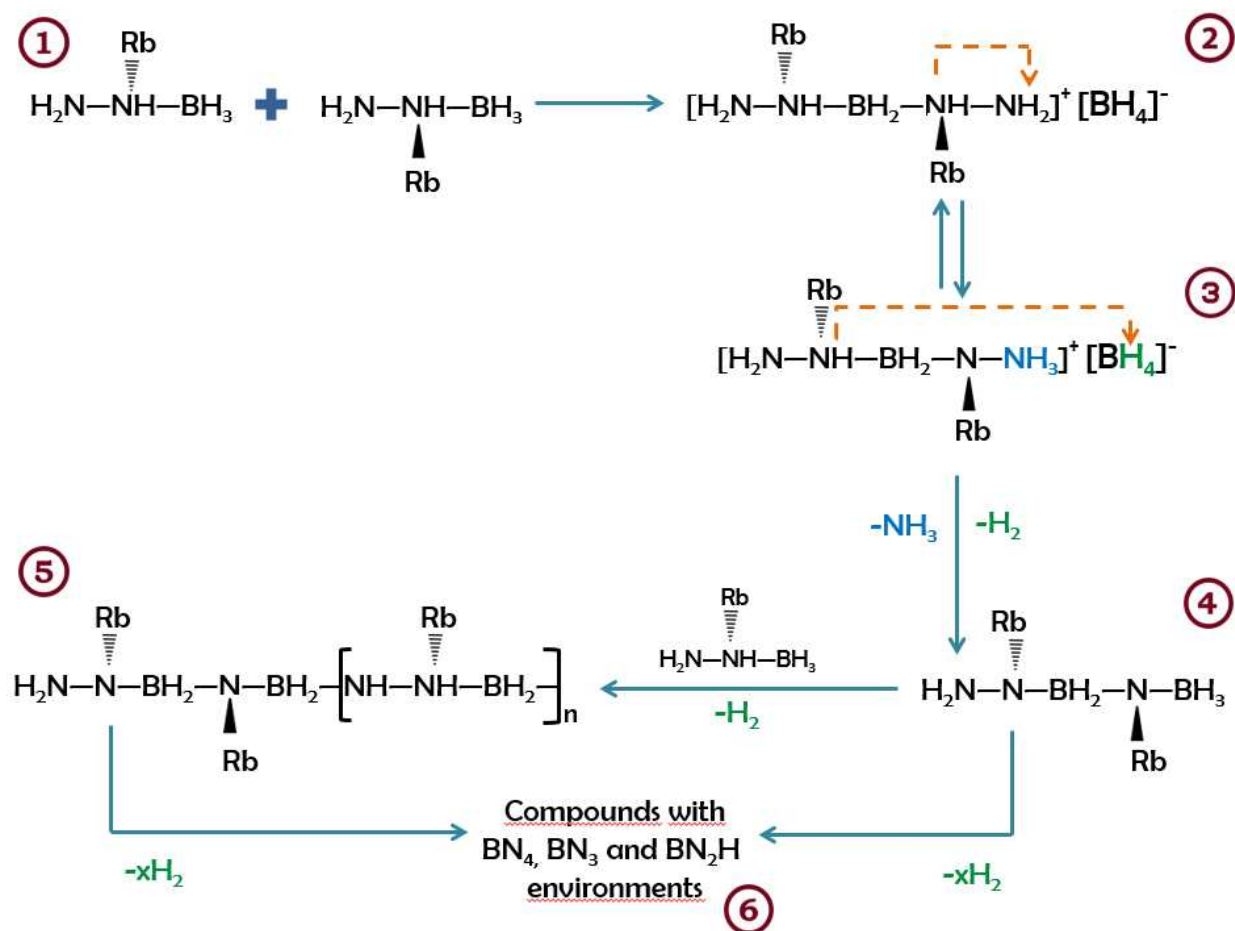


Figure 18. Proposed mechanism for the decomposition of RbHB. The proposed steps are indicated in circled numbers.

4. Conclusions

Rubidium hydrazinidoborane $\text{RbN}_2\text{H}_3\text{BH}_3$ (RbHB; 4.65 wt. % H) was synthesized and characterized for the first time. The substitution of one of the H^δ of the hydrazine moiety of $\text{N}_2\text{H}_4\text{BH}_3$ by Rb^+ was successful evidenced by ^{11}B MAS NMR and FTIR spectroscopy. RbHB is a crystalline material with a monoclinic unit cell, with a space group $P2_1$ (No.4) with cell parameters of $a = 5.8128(2) \text{ \AA}$, $b = 6.7010(2) \text{ \AA}$, $c = 5.8143(2) \text{ \AA}$, and $\beta = 108.915^\circ$, and it is isostructural with $\text{KN}_2\text{H}_3\text{BH}_3$.

The thermal characterization of RbHB was also carried out, under heating at a constant rate (5°C min^{-1}) and in isothermal conditions. RbHB shows improved dehydrogenation properties in

comparison to the parent HB. The presence of the Rb^+ has a destabilization effect on the molecule. The performance of RbHB is comparable to $\text{LiN}_2\text{H}_3\text{BH}_3$, but is less attractive than $\text{NaN}_2\text{H}_3\text{BH}_3$ in terms of onset temperature of dehydrogenation and H_2 release kinetics. RbHB releases H_2 and an important amount of NH_3 during the dehydrogenation. Upon the evolution of H_2 , an amorphous polymeric solid, mainly polyborazylene-like compound forms. A deeper investigation would be helpful in going further in the identification of this dehydrogenated solid, the reaction mechanisms, and the exact role that Rb^+ plays on it.

The synthesis and characterization of RbHB have provided results that first add knowledge about boron and nitrogen-based materials. Second, the results presented on this chapter have shown that the dehydrogenation properties of RbHB are interesting and better than those of HB, but for an application in the field of chemical hydrogen storage, rubidium hydrazinidoborane is not the best candidate. The behavior of RbHB is comparable to LiHB in terms of dehydrogenation properties whereas it carries less hydrogen (a theoretical amount of 4.65 wt. % H vs 11.7 wt. % H). Third, we now have one more HB derivative and future works could open new perspectives, such as exploring its potential as a precursor of boron nitride-based ceramics. The presence of the alkali cation might act as a possible crystallization promoter for the formation of hexagonal boron nitride at low temperature, or to obtain it with a crystalline structure different from the hexagonal one.⁷⁴ However, to start these investigations, it would be better to start with the more-known amidoboranes of Na and Li.

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Chapter 4

CESIUM

HYDRAZINIDOBORANE

4 Cesium Hydrazinidoborane

1. Introduction

Fossil fuels allowed the development of our society and technology. However, they are limited resources and their extraction is becoming more and more difficult. Besides, the burning of fossil fuels releases gases (mainly CO₂, but also CH₄, NO_x and fluorinated gases) to the atmosphere that have a negative impact on the society and the environment.^{1,2} Therefore, the transition to other sources of energy is necessary. One of the best options to obtain clean energy is hydrogen.

Molecular hydrogen (H₂) is a clean, non-toxic and renewable fuel that only releases water when it is burned.^{3,4} Hydrogen as an element is the most abundant in the universe. As molecular hydrogen, it possesses a high energy density (between 120 and 142 MJ kg⁻¹) that represents more than three times the energy density of gasoline or diesel. Nevertheless, one of the most challenging issues about hydrogen is its storage.⁴ To find a cost-effective and safe method to store hydrogen is still a major task. Currently, hydrogen can be stored in three ways: i) at high pressure, whose major drawbacks are the inefficiency in volumetric and gravimetric terms, the compatibility of the tank's material with the gas and the conditions of operation; ii) in cryogenic tanks at subzero temperatures, that is also not so efficient due to the cost of the tanks and the hydrogen losses; and iii) stored in a material.^{5,6} The most attractive method is the last one. Hydrogen can be stored reversibly in solid materials at different pressures and temperatures, and it can be liberated irreversibly by hydrolysis or thermolysis of different compounds. There are different materials capable to store hydrogen: carbon nanotubes, metal organic frameworks, covalent organic frameworks, metal hydrides, polymers, thin films, zeolites and other inorganic materials.⁷⁻¹⁴ In recent years, boron and nitrogen –based compounds have received attention because they are good candidates to store atomic hydrogen through B–H and N–H bonds.¹⁵⁻¹⁸

They possess some advantages over other materials: i) they have a high hydrogen content due to the lightness of the B and N atoms and their capacity of multiple bonding; ii) they present interactions between protic $H^{\delta+}$ and hydridic $H^{\delta-}$ hydrogens, which allow the destabilization of the molecule in solid state at lower temperatures in comparison with other materials; iii) many of these compounds are quite safe to handle.¹⁹ Examples of these materials are metal borohydrides, metal-N-H systems, ammonia and amine-/hydrazine-boranes.²⁰

For example, ammonia borane NH_3BH_3 (AB) is a widely investigated BNH material for hydrogen storage. Reported for the first time in 1955,²¹ it is a solid crystalline with high gravimetric hydrogen content (19.6 wt. % H). One of the most critical issues for a chemical storage material is the easiness and purity of the releasing H_2 . Despite its high hydrogen content, AB presents a high dehydrogenation temperature (it releases up to 2 equivalents H_2 at ca. 200°C) and it produces undesired and toxic by-products like ammonia NH_3 and borazine $B_3N_3H_6$.^{22,23} Different approaches have been investigated in order to overcome these drawbacks. The use of catalysts for the hydrolysis in protic and non protic solvents, and for the thermolysis of AB has been investigated.²⁴⁻²⁶ There has been a progress in this area, but there are some challenges to afford, like reducing the amount of NH_3 produced and the issues regarding the recyclability of the products of the reactions. Another approach is the infiltration of AB in a porous host material. Different works have been published in the recent years, showing faster kinetics and a cleaner hydrogen when AB is confined, for example, into a MOF.²⁷⁻³¹ A last approach is the chemical modification of ammonia borane. Amidoboranes (MAB) are compounds where one of the $H^{\delta+}$ of the molecule has been substituted by a metal cation, usually by the reaction of ammonia borane and a metal hydride. These compounds show improved dehydrogenation properties in comparison with AB. Different compounds have been synthesized during the last decade, including alkali, alkaline earth and mixed cation amidoboranes.³²⁻⁴⁰ Despite the efforts, the development of new materials is necessary to evaluate them and obtain suitable candidates for large-scale applications.

Hydrazine borane $N_2H_4BH_3$ (HB) is another material that has been investigated as a chemical hydrogen storage material.^{41,42} As well as AB, HB possesses high gravimetric hydrogen content

(15.4 wt. % H) and it is stable at room temperature under an inert atmosphere. But unlike AB, it has four $H^{\delta+}$ and three $H^{\delta-}$ hydrogens, which gives different properties to the molecule: for example, hydrazine borane can be dehydrogenated at a lower temperature than AB. However, HB also presents drawbacks: the dehydrogenation temperature is still considered high, it produces undesired by-products (NH_3 , B_2H_6 , N_2H_4 and $B_3N_3H_6$) and if the material is heated above $300^\circ C$, the formation of a shock-sensitive product is obtained.⁴² Due to this safety issue, it is difficult to think in a viable technology that could use pristine HB in the solid state. As in the case of AB, there are different approaches envisaged to improve the dehydrogenation properties of HB. Analogous to amidoboranes, hydrazinidoboranes (MHB) are obtained through the chemical modification of hydrazine borane. Hydrazinidoboranes are compounds where one of the $H^{\delta+}$ of the middle N atom of the molecule has been substituted by a metal cation. The first alkali hydrazinidoborane that was reported is lithium hydrazinidoborane $LiN_2H_3BH_3$ (LiHB, 11.7 wt. % H). This compound presents two crystalline phases: Wu *et al.*⁴³ obtained the high temperature phase α -LiHB (monoclinic, s.g. $P2_1/c$) and Moury *et al.*⁴⁴ the low temperature phase β -LiHB (orthorhombic, s.g. $Pbca$). This compound can release 2.6 equivalents of H_2 below $150^\circ C$. The gas liberated is free of B_2H_6 and $B_3N_3H_6$ but the presence of NH_3 was detected. Sodium hydrazinidoborane $NaN_2H_3BH_3$ (NaHB, 8.9 wt. % H) was synthesized by Moury *et al.* by mechanochemical synthesis.⁴⁵ As NaH is highly reactive towards HB ($-27.7 \text{ kJ mol}^{-1}$),⁴⁶ the synthesis has to be carried out in cold conditions (ca. $-30^\circ C$). The product obtained is a crystalline solid (monoclinic, s.g. $P2_1/n$) that starts the dehydrogenation process at ca. $60^\circ C$, releasing H_2 with traces of NH_3 and N_2 . Potassium hydrazinidoborane $KN_2H_3BH_3$ (KHB, 7.2 wt. % H; monoclinic, s.g. $P2_1$) was synthesized by Chua *et al.*⁴⁷ by wet synthesis in a stainless steel reactor because the reactivity of KH towards HB is even higher than for NaH (70.3 kJ mol^{-1}).⁴⁶ It shows better dehydrogenation properties than the previous alkali hydrazinidoboranes, as it starts to decompose at ca. $50^\circ C$. Rubidium hydrazinidoborane $RbN_2H_3BH_3$ (RbHB, 4.6 wt. % H; monoclinic, s.g. $P2_1$) was also synthesized by wet method by the reaction between metallic rubidium and hydrazine borane.⁴⁸ RbHB shows better dehydrogenation properties than HB and comparable to the ones of LiHB. Nevertheless, RbHB is not a stable compound: it evolves with time when stored under argon atmosphere, decomposing and favoring the formation of B- and N-based polymers,

and during its dehydrogenation, it releases a considerable amount of NH_3 . At present, those are all the alkali hydrazinidoboranes reported.

Cesium hydrazinidoborane $\text{CsN}_2\text{H}_3\text{BH}_3$ (CsHB, 3.4 wt. % H) is presented in this work. The synthesis and characterization of CsHB have provided of a better understanding on the chemistry and behavior of this kind of B- and N-based compounds. It also allowed completing the family of alkali derivatives of HB, providing us a more complete landscape on the knowledge of hydrazinidoboranes.

2. Experimental section

2.1 Reagents

Hydrazine borane was synthesized from commercial hydrazine hemisulphate $\text{N}_2\text{H}_4 \cdot \frac{1}{2}\text{H}_2\text{SO}_4$ ($\geq 98\%$, Sigma-Aldrich), sodium borohydride NaBH_4 ($\geq 98\%$, Sigma-Aldrich) and 1,4-dioxane (anhydrous, $\geq 99.8\%$, Sigma-Aldrich). In order to obtain cesium hydrazinidoborane, cesium (ingot, $\geq 99.95\%$, Sigma-Aldrich) and THF (99.5%, extra dry, Acros Organics) were used. Metallic cesium was used due to the commercial unavailability of CsH.

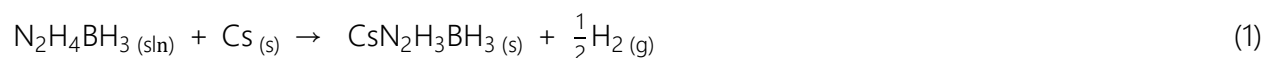
2.2 Synthesis

2.2.1 Synthesis of hydrazine borane

All the experiments were carried out under an inert atmosphere of argon, either in a glove box (MBraun M200B; $\text{O}_2 < 0.1$ ppm and $\text{H}_2\text{O} < 0.1$ ppm) or a Schlenk line. Hydrazine borane was synthesized at the laboratory with a route that was developed by our team before.⁴² Typically, 21.59 g of $\text{N}_2\text{H}_4 \cdot \frac{1}{2}\text{H}_2\text{SO}_4$ and 10.12 g of NaBH_4 are weighted in the glove box and then suspended under stirring in 150 mL of 1,4-dioxane in a round-bottom Schlenk at 30°C for 48 h. After this time, the suspension is filtered and a solution is obtained. The solvent is removed under vacuum and HB is obtained (A purity of 99.6% and a yield around 80% is achieved with this method).⁴²

2.2.2 Synthesis of cesium hydrazinidoborane

As ammonia borane, hydrazine borane also readily reacts with metallic cesium when they are put into contact.^{35,49} Under inert atmosphere, HB (120 mg, 2.59 mmol) was solved in 20 mL of THF; metallic cesium (300 mg, 2.25 mmol) was weighted and put into a round bottom flask. The HB solution was then poured into the flask that contained the Cs. The reaction was left under stirring for 6 h. After this time, the solid precipitate was washed two times with THF. The product was dried for 24 h under vacuum, the remaining cesium was removed and the solid product was recovered. The synthesis was carried out at -20°C and at room temperature in order to compare the effect of the temperature on the synthesis of the compound. The reaction can be written as follows:



At best, we recovered 340 mg of CsHB, which represents a yield of 85% with respect to Cs.

2.3 Characterization

2.3.1 Structural characterization

CsHB and the solid residues after decomposition experiments were analyzed by solid-state ¹¹B magic angle spinning nuclear magnetic resonance (MAS NMR; Varian VNMR4000, 128.31 MHz). Due to safety reasons, the dehydrogenated samples of CsHB were analyzed only by ¹¹B MAS NMR (Section 3.1). All the samples were prepared in the glovebox, in the corresponding rotors. The preparation of the samples and analyses were done by Mr. Emmanuel Fernandez and Mr. Philippe Gaveau, both from the Platform Balard from the University of Montpellier. CsHB was also analyzed by Fourier Transformed Infrared (FTIR) spectroscopy (NEXUS instrument, ThermoFisher Scientific, equipped with an attenuated total reflection accessory from 600 to 4000 cm⁻¹ wavelength). The samples were prepared in closed vials inside the glovebox, and were analyzed under an air atmosphere. The samples were maintained in the vial just before the analysis, and avoiding exposing the samples to the air for a long time.

Powder X-ray diffraction (PXRD) analysis was done in a PANalytical X'Pert Pro Multipurpose diffractometer equipped with an X'Celerator detector (Cu-K $_{\alpha 1/\alpha 2}$ radiation $\lambda=1.5418$ Å, 45 kV, 30 mA) equipped with fixed divergence slits. The pattern was collected using Bragg-Brentano geometry on a spinning glass sample holder loaded into the glovebox. The diffraction pattern was recorded in the 10-80° angle range in 2θ using a step size of 0.017, with a scan step time of ~450 seconds. The powder was protected using Parafilm® "M" to prevent any contact with O₂ and H₂O. It is important to remark that a Kapton foil was used in the first measurements, but we realized that CsHB reacted with the Kapton film during the analyses forming an orange powder, which made difficult the interpretation of the diffraction pattern. This phenomenon could not be deeply investigated due to a lack of time. The managing of the XRD equipment was done by Ms. Dominique Granier from the Platform Balard from the University of Montpellier.

2.3.2 Thermal characterization

For preliminary tests, CsHB was analyzed by simultaneous thermogravimetric (TG) and differential scanning calorimetry (DSC) analyses (SDT Q600, TA Instruments, N₂ atmosphere). Besides this, a TG analysis (Netzsch STA 449 F1 Jupiter, Ar atmosphere) coupled to a mass spectrometer (MS; Netzsch QMS 403 D Aëolos Quadro) was done to characterize the thermal behavior of the sample. Differential scanning calorimetry (DSC) was carried out at different heating rates to analyze the apparent activation energy of the decomposition of CsHB. The TG-MS analysis was carried out by Mr. Amine Geneste from the Platform Balard from the University of Montpellier. The preparation of the samples for thermal analyses was done inside the glovebox, where the powder was enclosed in a Tzero hermetic pan to protect it from air. This pan was pierced with a needle right before the analysis to allow the gases to escape.

The gases released by the decomposition reaction at isothermal conditions were analyzed by a gas chromatograph (GC; PerkinElmer Clarus 400 equipped with a ShinCarbon ST column) coupled to a mass spectrometer (MS; PerkinElmer Clarus 600 T). Typically, after the reaction had finished and the reactor was cooled down at room temperature, a sample of the gas was taken and injected into the GC with a glass syringe.

2.4 Decomposition experiments at isothermal conditions

The thermal behavior of CsHB was analyzed at isothermal conditions (90, 100, 110 and 120°C) in a stainless steel reactor. 100 mg of the sample was weighted and placed in a vial inside the reactor in the glovebox. Once outside, the reactor was connected to a pressure controller and immersed in an oil bath at the required temperature. The reaction of decomposition was monitored by the change of pressure inside the reactor. The equivalents of hydrogen liberated (i.e. equiv H₂) were calculated and plotted as a function of time, considering H₂ as an ideal gas.

3. Results and discussion

3.1 Synthesis conditions and security issues regarding CsHB

CsHB is a white fine powder. It is insoluble in anhydrous organic solvents like 1,4-dioxane, toluene, THF or dimethyl carbonate. CsHB reacts when it is solved in protic solvents like water, ethanol and methanol, releasing hydrogen. This is the same behavior reported for amidoboranes and the other hydrazinidoboranes.^{44,45,48,50}

It is important to highlight some security observations about the materials and synthesis used in this work:

- Cesium is highly reactive and presents a violent reaction in contact with water. Thus, all the works were carefully done in an inert atmosphere (glove box or Schlenk line). HB must be solved in THF before putting into contact with the metallic cesium.
- We also remark some issues about the handling of CsHB: at first, the compound was stored in a freezer in a closed vial under argon atmosphere and covered with Parafilm®. However, when the vial was recovered and the Parafilm® was removed, some of the powder inside exploded. We decided then to store the CsHB directly into the glovebox. The diffusion of some humidity inside the vial is much likely the reason of the explosive reaction.

- Some of the solid products obtained after the decomposition experiments at isothermal conditions showed spontaneous reactivity: when the sample heated at 100°C was being recovered, it suddenly exploded. Later, the same samples recovered after isothermal experiments were tried to be analyzed by FTIR but all of them ignited when they were put into contact with air. That is the reason why the solid residues were analyzed only by ^{11}B MAS NMR (at low temperature).

We emphasize that this compound should be treated with caution, due to its high reactivity and the probable formation of shock sensitive compounds after heating.

3.2 Molecular structure of CsHB

3.2.1 Fourier Transformed Infrared Spectroscopy (FTIR)

Cesium hydrazinidoborane was analyzed by FTIR and the resulting spectrum was compared to the one of hydrazine borane (Figure 1). CsHB presents a similar pattern as other hydrazinidoboranes. Particularly, it is close to the spectral fingerprint of RbHB.⁴⁸ The N–H stretching bands ($3500\text{--}2600\text{ cm}^{-1}$) are less complex in comparison to those for HB. This indicates a weaker interaction between the $\text{H}^{\delta+}$ of the CsN_2H_3 and the $\text{H}^{\delta-}$ of the BH_3 moiety and thus, a lesser stability in comparison to HB. As suggested for amidoborane and hydrazinidoborane compounds, this is the result of the insertion of the alkali cation in the molecule (in this case the Cs^+).^{44,45,51} The BN–N bond is also different for CsHB, being more intense in comparison to HB.

In the case of the B–H region, the hydrazinidoborane shows the bands at a lower wavelength than HB does. These observations are all due to the presence of the Cs^+ , which modifies the chemical environment and the electronic properties of the molecule. The B–N and BN–N bands are stronger for CsHB, which indicates a shorter bond between the boron and nitrogen atoms due to the size of the alkali cation. This is a well-known fact in several amidoboranes and hydrazinidoboranes and in all cases is due to the substitution of the metal cation for one of the $\text{H}^{\delta+}$ of the molecule.^{33–35,44,45,47,52}

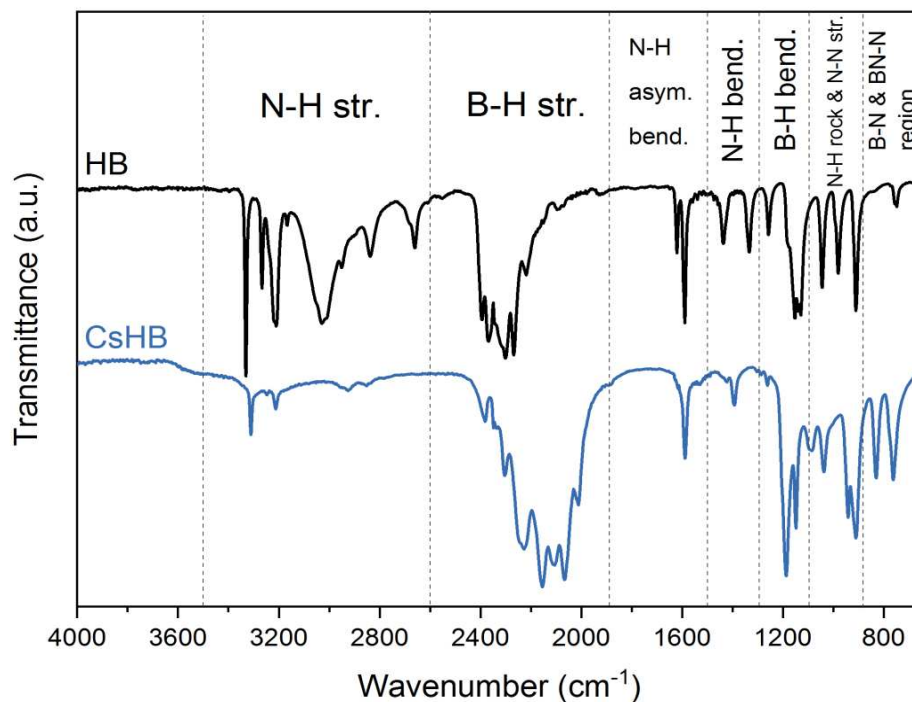


Figure 1. FTIR spectra of HB and CsHB with their respective bands.

3.2.2 ¹¹B Magic Angle Spinning Nuclear Magnetic Resonance (MAS NMR)

Figure 2 presents the comparison between the ¹¹B MAS NMR spectra of CsHB and HB. Hydrazine borane presents a single split shape at -24 ppm, due to the quadrupolar effect of the boron atom.^{53–55} On the other hand, CsHB presents the main signal at -16.3 ppm (for a NBH₃ environment). The displacement on the chemical shift indicates the presence of the Cs⁺ in the molecule. It is a symmetric signal that it has been observed in others alkali derivatives of AB and HB.^{44,45,49} The change from one split signal to a single signal indicates the disappearance of the quadrupolar effect of HB before mentioned, and shows that the Cs⁺ has a strong effect over the electronic array around the boron atom, presenting an isotropic environment.

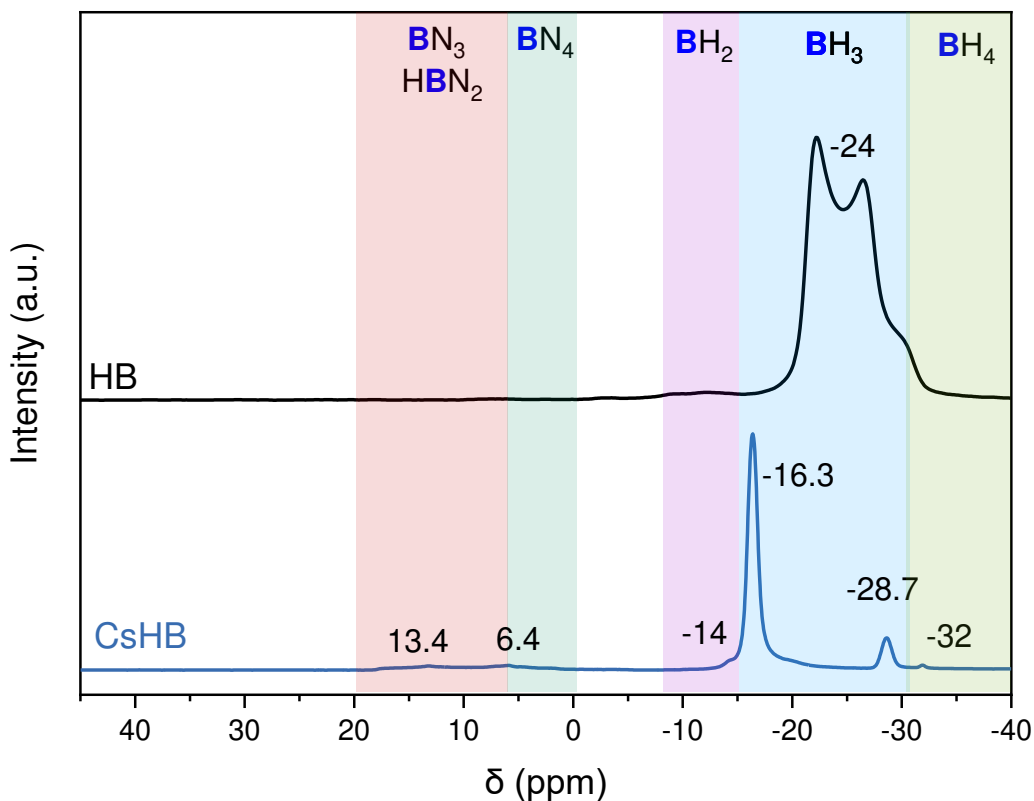


Figure 2. ^{11}B MAS NMR spectra of HB and CsHB. The chemical shifts in ppm and the assigned boron environments are indicated in the figure.

Other signals on the CsHB spectrum can be observed at -32, -28.7, -14, 6.4 and 13.4 ppm. The signals presented at -32 and -14 ppm can be assigned to an intermediate analogous to diammoniate diborane (DADB)⁵⁶ formed during the decomposition of AB, but in this case applied to CsHB that could have the formulae $[\text{CsN}_2\text{H}_3\text{BH}_2\text{CsN}_2\text{H}_3]^+[\text{BH}_4]^-$. The signal at -32 ppm would correspond to the BH_4 environment and the peak at -14 ppm to the BH_2 environment. The less intense signals at 6.4 and 13.4 ppm are attributed to the formation of BN_4 , BN_3 and BN_2H species, indicating the formation of amorphous boron and nitrogen-based polymeric species, typical in the decomposition of BNH compounds.^{57–62} The signal at -28.7 ppm suggests a BH_3 environment of an undesired by-product during the reaction. This signal could not be assigned to a known compound.

3.2.3 Stability of cesium hydrazinidoborane under inert atmosphere

CsHB was stored for two months inside the glovebox after its synthesis to be further analyzed by FTIR and ^{11}B MAS NMR. As it is observed in **Figure 3**, the FTIR analysis shows that the two compounds present almost identical bands. There is a slight broadening of the N–H stretching and bending region of the spectrum for the sample stored for 2 months. This could be explained due to the formation of the before mentioned polymeric species.

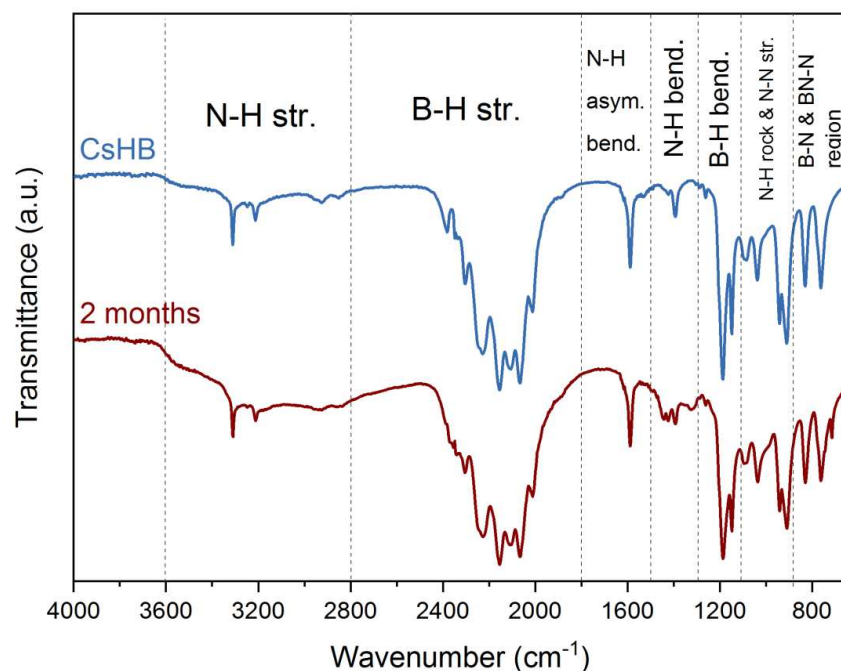


Figure 3. FTIR spectra of CsHB and CsHB after 2 months of its synthesis (stored at room temperature and under argon atmosphere). The bands have been assigned.

Regarding the ^{11}B MAS NMR spectra (**Figure 4**), the spectra do not present big changes between the two samples. The BH_3 environment at -16.3 ppm is the main peak in both spectra, showing the stability of the compound. The single peak neglects any changes on the isotropy of the molecule around the boron atom, contrary to the behavior of RbHB .⁴⁸

There are slight changes that are observed in the sample after two months: the signals at -32 and -14 ppm have disappeared. This indicates the evolution of the aforementioned intermediate

$[\text{CsN}_2\text{H}_3\text{BH}_2\text{CsN}_2\text{H}_3]^+[\text{BH}_4]^-$. In the positive chemical shifts, a peak appeared at 1.7 ppm. This implies the slow evolution of CsHB into boron and nitrogen-based polymers. Both ^{11}B MAS NMR and FTIR analyses confirm the formation of some polymeric species (e.g. polyaminoborane), but both spectra show that this decomposition is very slow and after two months, both samples present similar spectra. This is a different behavior than the one presented by rubidium hydrazinidoborane, where the decomposition of the compound is more pronounced after one month of its synthesis.⁴⁸ In other words, when stored under argon at room temperature, CsHB is more stable than RbHB.

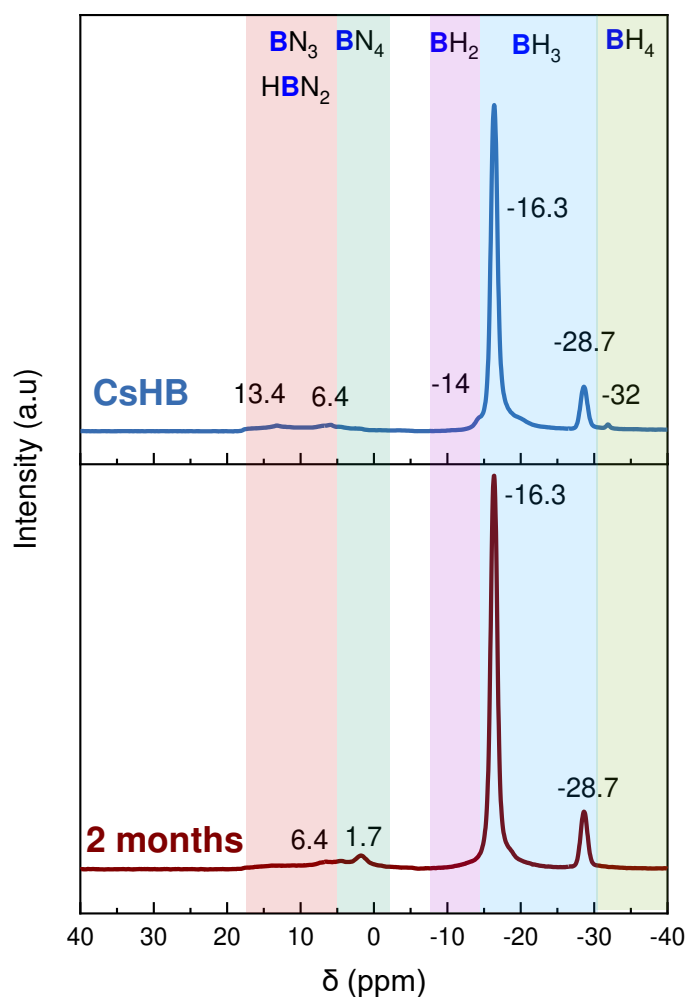


Figure 4. ^{11}B MAS NMR spectra of a fresh sample of CsHB and one stored for 2 months at room temperature and under argon atmosphere. The chemical shifts in ppm and the assigned boron environments are indicated.

3.2.4 Effect of the temperature on the synthesis of CsHB

Rubidium and cesium amidoboranes have been synthesized at 0°C to avoid the decomposition of these compounds and the side reactions due to the high reactivity of metal Rb and Cs towards AB.⁴⁹ The synthesis of CsHB was carried out at room temperature and at low temperature (-20°C), in order to evaluate the effect of the temperature on the synthesis of the compound. The products of both syntheses were characterized by FTIR, ¹¹B MAS NMR and PXRD. **Figure 5** shows the FTIR spectra of CsHB synthesized at -20°C and room temperature (R.T.). There are small changes between the two samples. In the sample synthesized at room temperature, the N-H stretching region presents a slight broadening of the signal, similar to the CsHB aged for two months in the glove box. The B-H stretching region has more defined bands in the case of the synthesis at -20°C.

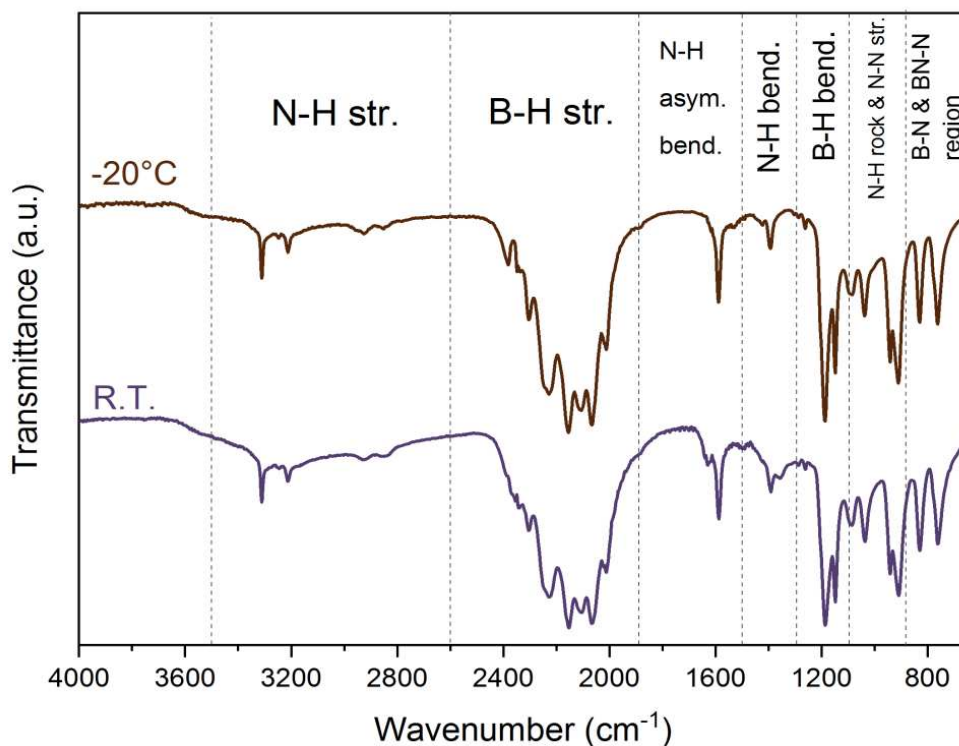


Figure 5. FTIR spectra of CsHB synthesized at -20°C and at room temperature.

Figure 6 shows the analysis performed by ^{11}B MAS NMR for CsHB at the two temperatures of synthesis. As observed, there is a noticeable difference: when the synthesis was carried out at -20°C , the signal at -28 ppm is more intense and the signals at positive chemical shifts are smaller. The opposite occurs when the compound was synthesized at room temperature: the before mentioned signals related to polymeric species due to the decomposition of CsHB increase, and the signal at -28 ppm decreases. The main signal at -16.3 ppm remains.

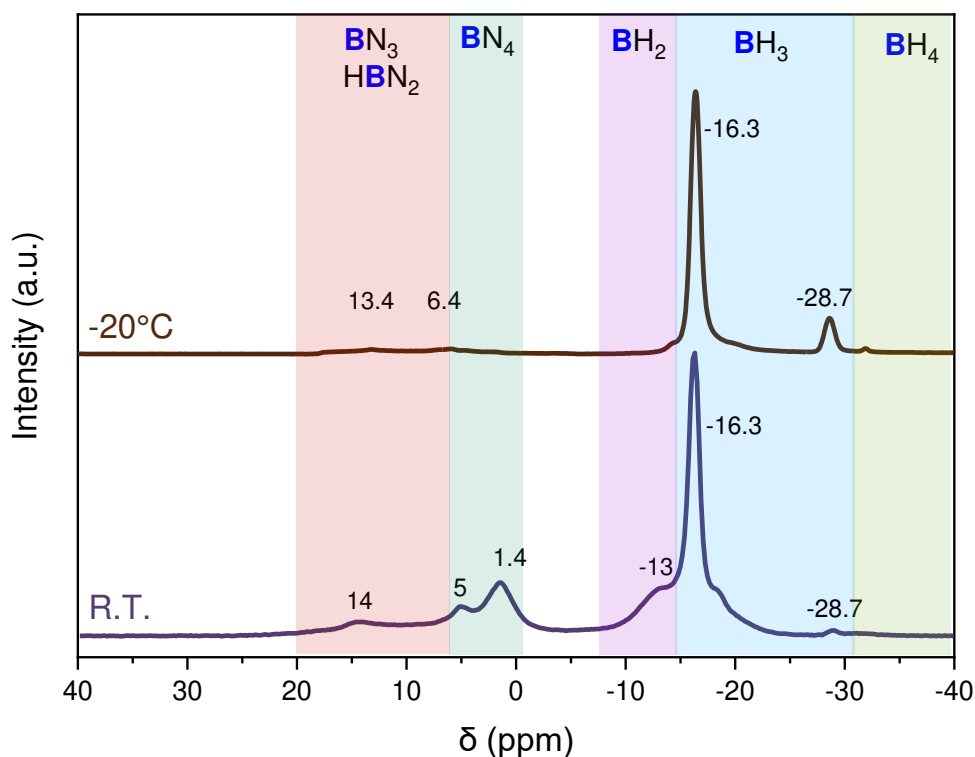


Figure 6. ^{11}B MAS NMR spectra of CsHB synthesized at -20°C and at room temperature. The chemical shifts in ppm and the assigned boron environments are indicated.

The analysis done by PXRD confirms the previous results. **Figure 7** shows that the pattern of the compound synthesized at -20°C has additional diffractions peaks of an unidentified phase that do not belong to CsHB. In contrast, the pattern of the synthesis at room temperature does not show these unassigned peaks. Unfortunately, it is evident that it is not possible to obtain a pure compound, nor at room temperature nor at subzero conditions. This highlights again the high

reactivity between metallic cesium and HB. It is likely that the undesired solid byproducts are formed during the synthesis reactions. In any case, the experiments were useful to obtain the crystal structure of CsHB.

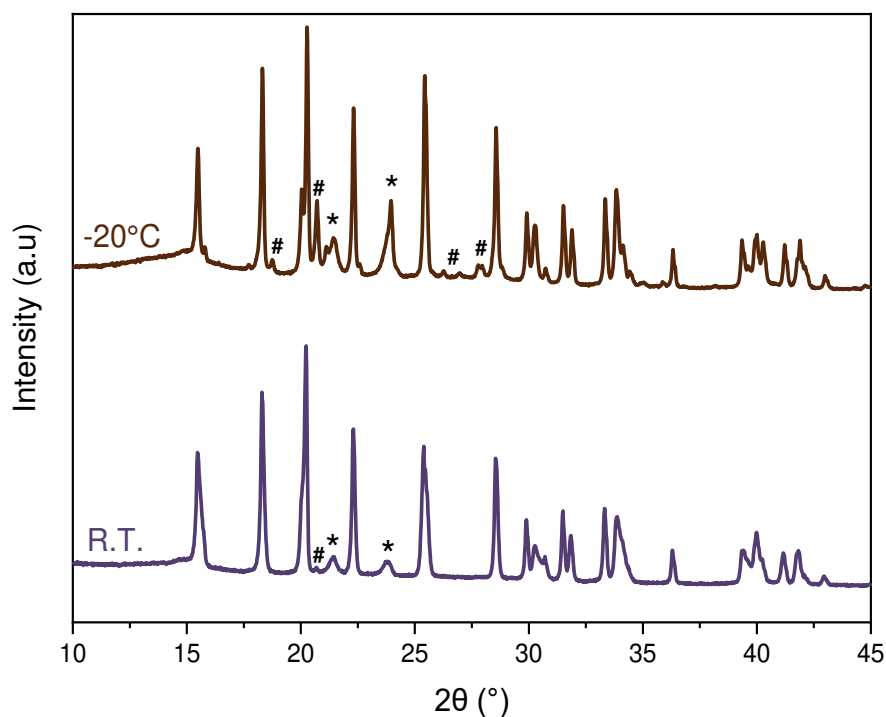


Figure 7. Comparison of PXRD patterns of CsHB synthesized at -20°C and at room temperature. The # indicate the diffraction peaks of an unidentified phase formed during the synthesis and the * symbol indicates the peaks belonging to the Parafilm[®] used to protect the sample from air.

3.2.5 Powder X-ray Diffraction (PXRD)

The patterns of HB and CsHB were compared (**Figure 8**). The peaks of the CsHB pattern are not comparable to those of HB, indicating a new phase. The three extra peaks (at 20.6 , 21.6 and 23° correspond to the unidentified phase and the Parafilm[®]) were excluded from the analysis to obtain the correct crystallographic parameters. To index the pattern of CsHB, the FoX software was used.⁶³ The Rietveld refinement was carried out in the JANA2006 package by Mr. Pascal Yot (ICGM UMR5253 Montpellier) and the determination of the position of the Cs atoms was done

with the 'SuperFlip' algorithm included in the software.⁶⁴ After this, FOX was used to reach the position of the $\text{N}_2\text{H}_3\text{BH}_3^-$ anions. The crystallographic parameters obtained are shown in Table 1.

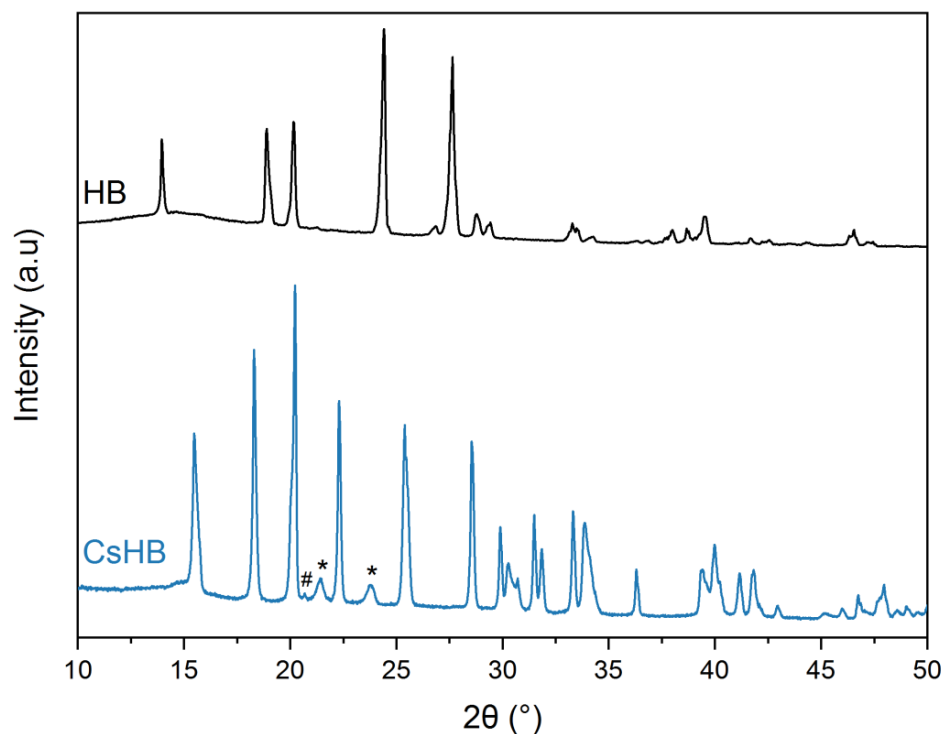


Figure 8. PXRD patterns of HB and CsHB. The # symbol indicates the diffraction peaks of an unidentified phase formed during the synthesis; the * indicates the diffraction peaks of Parafilm®.

Table 1. Crystallographic parameters of CsHB

CsHB							
Unit cell	S.G.	a (Å)	b (Å)	c (Å)	β (°)	Z	V (Å³)
Monoclinic	$P2_1$	5.9156(5)	7.0091(5)	6.0023(5)	108.389(4)	2	236.16(3)
Crystallographic density		2.5	Rp	6.66	R _(all) /wR _(all)	7.32/9.03	
Temperature (K)		293	wRp	10.17			
GoF		5.08	R _(obs) /wR _(obs)	7.32/9.03			

The Rietveld refinement of the pattern was carried out using a Pseudo-Voigt peak shape. The peaks asymmetry was corrected using Howard model (Boole's rule) and preferred orientation using March-Dollase model following the (010) direction. As it is shown in Figure 9, the calculated pattern (red line) is in good fit with the experimental one (black line). As discussed before, the peaks highlighted in gray were omitted in the analysis. The B–H and N–H distances were constrained to 1.20 Å and 1.04 Å respectively in accordance with the optimization realized by the FoX software. The uncertainties of the atomic coordinates for hydrogen atoms are not reported here because they were not freely refined. The isotropic thermal parameters (U_{iso}) were constrained to be identical for all atom types (Table 2).

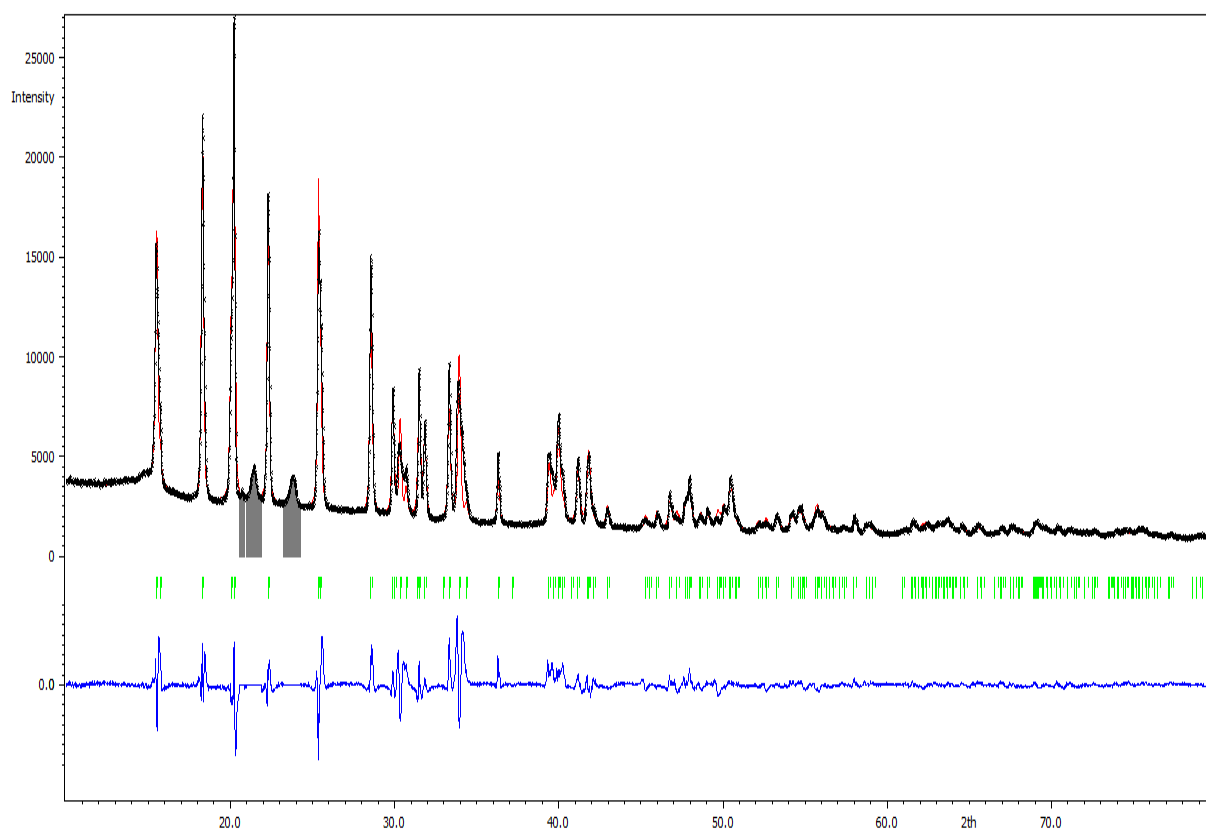


Figure 9. Observed (black line) and calculated (red line) PXRd profile for the Rietveld refinement of CsHB, differences of the plots (blue line), calculated angles for Bragg peaks in 2θ (green lines) and omitted peaks (gray peaks).

Table 2. Experimental structural parameters of CsHb (S.G. $P2_1$ No.4) at room temperature.

Atom	Site	Occupancy	x	y	z	U_{iso} (Å)
Cs			0.2208(5)	0.00019(12)	0.1133(5)	0.0477(9)
B1			0.658(6)	0.51(7)	0.805(6)	0.0477 (9)
N1			0.917(9)	0.067(11)	0.604(10)	0.0477 (9)
N2			0.723(9)	0.079(10)	0.660(10)	0.0477 (9)
H1	2a	1	0.03790	0.66835	0.29572	1.2
H2			0.00563	0.43052	0.35935	1.2
H3			0.41855	0.58430	0.49358	1.2
H4			0.17829	0.34395	0.11181	1.2
H5			0.52963	0.37079	0.28512	1.2
H6			0.33969	0.52748	0.02213	1.2

The locations of the hydrogen atoms linked to N and B atoms were determined by performing a constrained geometry optimization of the structure (Cs, B and N atoms fixed in their initial positions) at the force-field level. This work was done by Mr. Guillaume Maurin (ICGM UMR5253 Montpellier). The atoms of the system were represented as Lennard-Jones charged sites with LJ parameters taken from the UFF force field while the charges were calculated using the QeQ method.

Cesium hydrazinidoborane was successfully indexed as a single phase in a monoclinic $P2_1$ (No. 4) unit cell (Figure 10) with $Z=2$, $a=5.9156(5)$, $b=7.0091(5)$, $c=6.0023(5)$ and $\beta=108.389(4)^\circ$. Except for β -LiHB (orthorhombic, s.g. $Pbca$)⁴⁴, all the other hydrazinidoboranes crystallize in a monoclinic unit cell, though with different space groups (Table 3): α -LiHB does in a $P2_1/c$ group while NaHB does in a $P2_1/n$ group.^{43,45} CsHB is isostructural with KHB and with RbHB.^{47,48} In comparison with HB,⁴² CsHB has a bigger unit cell volume per formula V/Z (80.153 vs. 118.083 Å³). This is due to the effect of the big size of the Cs⁺ in the molecule. If we compare CsHB with the low temperature phase of its analogous amidoborane CsAB (orthorhombic, s.g. $Pnam$),^{35,49} we find

that CsHB has also a bigger unit cell volume per formula (99.42 vs 118.083 Å³). This is in good agreement with the smaller size of the [NH₂BH₃]⁻ anion of the amidoborane.

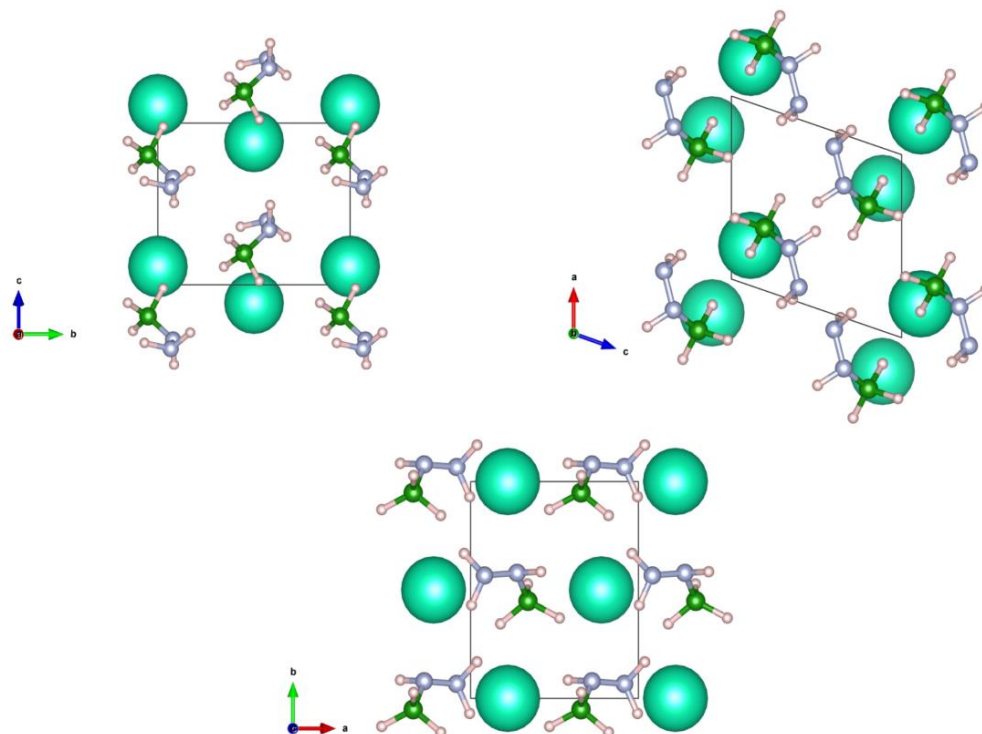


Figure 10. Crystal structure of CsHB along the [100], [010] and [001] directions. H, B and N atoms are represented by pink, green and blue spheres. Cs atoms are represented by turquoise spheres.

Table 3. Cell parameters of hydrazine borane and alkali hydrazinidoboranes.

MHB	Unit cell	S.G.	a (Å)	b (Å)	c (Å)	β (°)	Z	V/Z (Å ³)
HB	Orthorhombic	<i>Pbcn</i>	12.979(5)	5.062(2)	9.509(4)	90	8	78.081
α -LiHB ⁴³	Monoclinic	<i>P2₁/c</i>	5.850(11)	7.467(11)	8.893(15)	122.329(6)	4	82.068
β -LiHB ⁴⁴	Orthorhombic	<i>Pbca</i>	10.252(11)	8.479(10)	7.469(8)	90	4	162.313
NaHB ⁴⁵	Monoclinic	<i>P2₁/n</i>	4.974(11)	7.958(15)	9.292(19)	93.814(11)	4	91.747
KHB ⁴⁷	Monoclinic	<i>P2₁</i>	6.721(23)	5.892(20)	5.778(17)	108.279(13)	2	108.054
RbHB ⁴⁸	Monoclinic	<i>P2₁</i>	5.813(2)	6.701(2)	5.814(2)	108.915(2)	2	107.121
CsHB	Monoclinic	<i>P2₁</i>	5.916(5)	7.009(5)	6.002(5)	108.389(4)	2	118.083

Figure 11 shows the coordination sphere of the Cs^+ where the cation is surrounded by 6 $[\text{N}_2\text{H}_3\text{BH}_3]^-$ anions. The other hydrazinidoborane have coordination numbers of 4 (LiHB),⁴⁴ 5 (NaHB),⁴⁵ 4 (KHB)⁴⁷ and 6 (RbHB).⁴⁸ RbHB and CsHB can coordinate more anions due to the size of the cation. In comparison with the amidoboranes, CsAB is surrounded by 7 $[\text{NH}_2\text{BH}_3]^-$ anions.³⁵

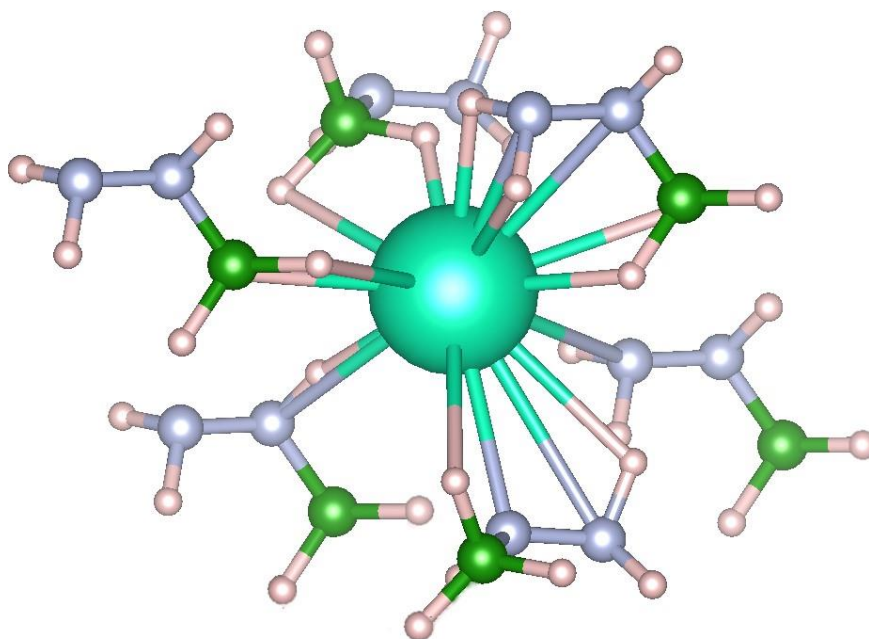
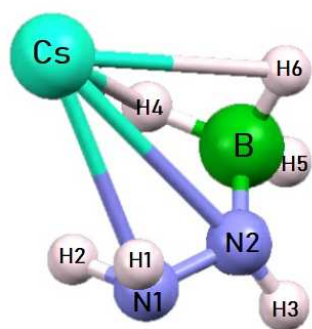


Figure 11. Coordination sphere of the Cs cation, surrounded by six $[\text{N}_2\text{H}_3\text{BH}_3]^-$ anions.

The positions of the hydrogen atoms of the molecule were obtained by computational methods, allowing us to determine the interatomic distances (**Figure 12**). The shortest interatomic distance between the metal ($\text{Cs}\cdots\text{Cs}$) is 4.32(4) Å and the shortest for the Cs–N bond of 3.22(7) Å. In comparison with the analogous amidoborane CsNH_2BH_3 , these values are shorter (4.60(6) and 3.28(13) Å respectively).³⁵ This can be explained because unlike CsHB , the Cs^+ in CsAB is surrounded by 7 $[\text{NH}_2\text{BH}_3]^-$ anions, which allows more interactions between the atoms and increasing the interatomic distances between them. In comparison with other alkali hydrazinidoboranes, the Cs–N distance decreases as the size of the alkali cation reduces: a value of 3.13 Å was found for RbHB ,⁴⁸ 2.96 Å for KHB ,⁴⁷ 2.41 Å for NaHB ⁴⁵ and 2.11 Å for LiHB .⁴⁴ This may indicate that the bond M–N has a higher ionicity for CsHB . The B–N bond is shorter for CsHB

(1.40(8) Å) in comparison with HB (1.59 Å),^{42,43} that is in good agreement with the changes observed in the ¹¹B MAS NMR and FTIR analyses.



Atom Type	Atom radius (Å)	Van der Waals radius (Å)
B	0.81	1.92
N	0.74	1.55
H	0.46	1.2
Cs	2.72	3.43

Atom B	
Cs	3.23(5) Å
Cs	3.28(4) Å
N2	1.40(8) Å
H4	1.19 Å
H5	1.20 Å
H6	1.17 Å

Atom N2	
Cs	3.22(7) Å
Cs	3.37(5) Å
Cs	3.71(5) Å
B	1.40(8) Å
N1	1.30(9) Å
H3	1.03 Å

Atom N1	
Cs	3.05(6) Å
Cs	3.69(8) Å
N2	1.30(9) Å

Atom Cs	
Cs	4.326(4) Å
B	3.23(5) Å
B	3.28(4) Å
N1	3.05(6) Å
N1	3.69(8) Å
N2	3.22(7) Å
N2	3.37(5) Å
N2	3.71(5) Å
H3	2.70 Å
H4	2.422 Å
H5	3.156 Å
H6	2.965 Å
H6	3.161 Å

Figure 12. Calculated interatomic distances for cesium hydrazinidoborane.

3.3 Thermal characterization

3.3.1 TGA-MS and DSC measurements

The thermal characterization of CsHB was done by TGA (heating rate of 5°C min⁻¹) coupled to a MS to analyze the produced gases (Figure 13). CsHB starts to decompose at ca. 75°C and in the range 75-160°C, it loses 3.5 wt % of the original weight releasing mainly hydrogen, but ammonia and diborane too. There is a second mass loss in the range of 160-190°C of ca. 1.4 wt % and a last loss after 190°C of ca. 2 wt %. The total weight loss between 75 and 250°C is of 6.9%. This is twice

the 3.4 wt % H carried by cesium hydrazinidoborane. As seen in the MS analysis, this is due to the release of NH_3 and the intermittent releasing of B_2H_6 . The other hydrazinidoborane compounds (Li, Na, K) release purer hydrogen and we see that as bigger is the metal alkali cation, the compound tends to release more ammonia and unwanted byproducts like B_2H_6 .^{44,45,47}

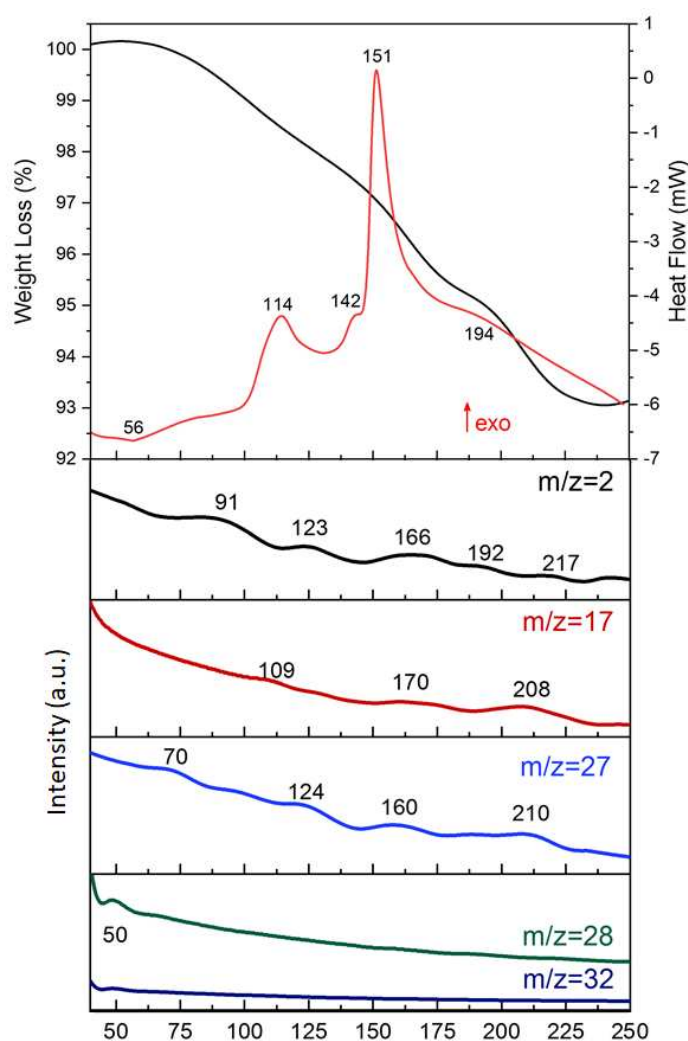


Figure 13. TGA-DSC (5°C min^{-1}) and MS results ($m/z=2, 17, 27, 28, 32$ for H_2 , NH_3 , B_2H_6 , N_2 , N_2H_4 or O_2 respectively) of CsHB. The peak temperatures ($^\circ\text{C}$) observed by DSC and MS are given.

The MS shows peaks for H_2 , NH_3 and B_2H_6 . There are two signals presented for $m/z=28$ and $m/z=32$ at 50°C . As at this temperature there is none important weight loss, and as both signals

appear at the same temperature, we assume that small quantities of air entered into the apparatus and the analysis indicate the presence of N_2 ($m/z=28$) and O_2 ($m/z=32$). In these conditions, the MS could not detect other possible volatile by-products of the decomposition of CsHB, such as hydrazine (N_2H_4) or borazine ($B_3N_3H_6$). It is also observed that the release of H_2 , NH_3 and B_2H_6 it is concomitant during all the heat treatment, suggesting a complicated path of decomposition.

Figure 13 also shows the results of the DSC analysis. The curve confirms the complex decomposition path. There is a first endothermic event at $56^\circ C$ related to the melting of the compound ($CsHB_{(s)} \rightarrow CsHB_{(l)}$), a behavior also presented by HB, NaHB, KHB and RbHB.^{42,45,47,48} After, there are four exothermic events that take place at 114, 142, 151 and $194^\circ C$ and some of them can be related to the emission of the byproducts identified by MS. For example, the exothermic peak at $114^\circ C$ is preceded by the release of some NH_3 and followed by the liberation of H_2 . The strongest signal presented at $151^\circ C$ is followed by the liberation of hydrogen. The last exothermic peak at $194^\circ C$ is preceded by the release of hydrogen. Because of the exothermicity of this process, the possibility of reusing or recycling the materials becomes difficult.

3.3.2 Calculation of apparent activation energy by the Kissinger method

The activation energy and kinetics parameters of the decomposition of a solid can be calculated using the Kissinger method, assuming a first order reaction (for further description of the method, see Annex I).⁶⁵ CsHB was analyzed by DSC at different heating rates of 1, 3, 5 and $7^\circ C \text{ min}^{-1}$. Figure 14 presents the superposition of the DSC curves and the linear regression analysis. We analyzed the three most important exothermic peaks of the process. These processes are related to the decomposition of CsHB. We decided to discard the first experimental point of the 3rd process, as the error was high. The apparent energies of activation of the processes 1, 2 and 3 are: $E_{a1}=226 \text{ kJ mol}^{-1}$, $E_{a2}=157 \text{ kJ mol}^{-1}$ and $E_{a3}=202.8 \text{ kJ mol}^{-1}$. These values are comparable with the values of others BNH materials used for hydrogen storage using the same method. For example, hydrazine bisborane possesses an $E_a=106.4 \text{ kJ mol}^{-1}$ and LiHB $E_a=156$ for the first decomposition step.^{44,66} Table 4 presents the kinetic data calculated for the selected exothermic events during the decomposition of CsHB. As expected, the value of k increases with the temperature.

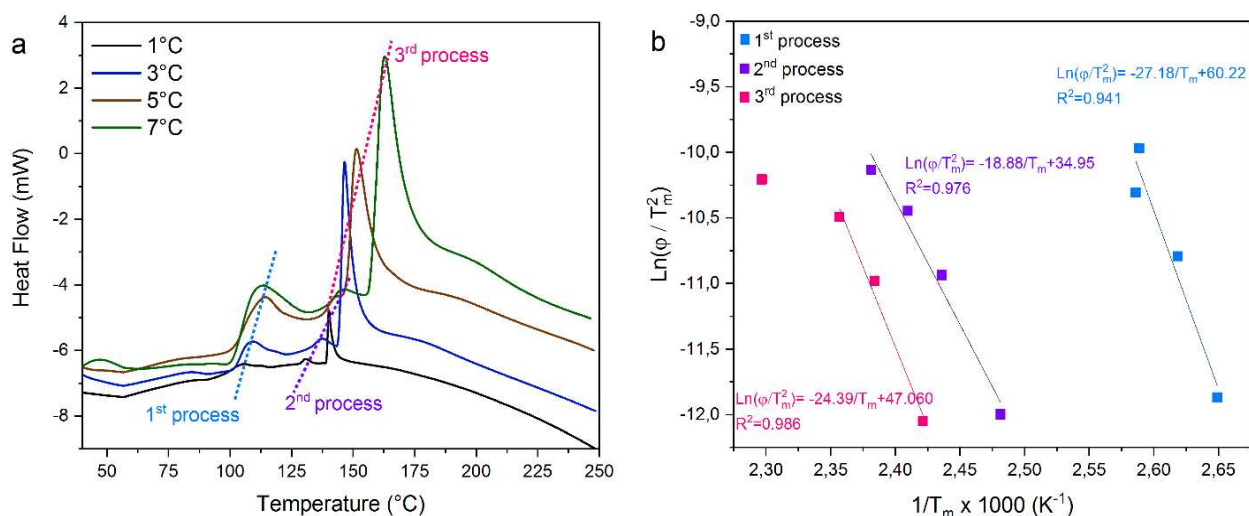


Figure 14. DSC curves for CsHB at different heating rates (1, 3, 5 and 7 °C min⁻¹); and linear regression for the Kissinger method of the three exothermic events.

Table 4. Kinetic parameters of the thermal decomposition of CsHB obtained by the Kissinger method and Arrhenius equation.

Process	E_a (kJ mol ⁻¹)	A (min ⁻¹)	k (min ⁻¹)			
			90°C	100°C	110°C	120°C
1	226	3.8682×10^{30}	1.163×10^{-2}	8.659×10^{-2}	5.805×10^{-1}	3.533
2	157	2.8489×10^{19}	7.278×10^{-4}	2.935×10^{-3}	1.101×10^{-2}	3.86×10^{-2}
3	202.8	6.6858×10^{24}	4.383×10^{-5}	2.655×10^{-4}	1.464×10^{-3}	7.405×10^{-3}

3.3.3 Decomposition experiments of CsHB

The evaluation of the decomposition behavior of CsHB was done by a heat treatment under isothermal conditions at 90, 100, 110 and 120°C. The decomposition of CsHB presents curves with a first short step where the hydrogen is slowly released and a second fast step (**Figure 15**). This same behavior is presented by the other alkali hydrazinidoboranes.^{44,45,48} Below 100°C, the slope of the second step of the decomposition of CsHB is the most pronounced in comparison with the

other hydrazinidoboranes. It is interesting how a smaller cation like Na^+ can destabilize the material in a better way than Cs^+ , as NaHB releases a higher amount of hydrogen at lower temperature and in a shorter time.⁴⁵ This phenomenon can be due to the formation of more stable by-products during the decomposition process, making more difficult the release of hydrogen. CsHB releases almost 2 equiv H_2 at 110°C and 2.5 equiv H_2 at 120°C in less than 20 min of treatment. This second fast step requires more time to occur at lower temperatures.

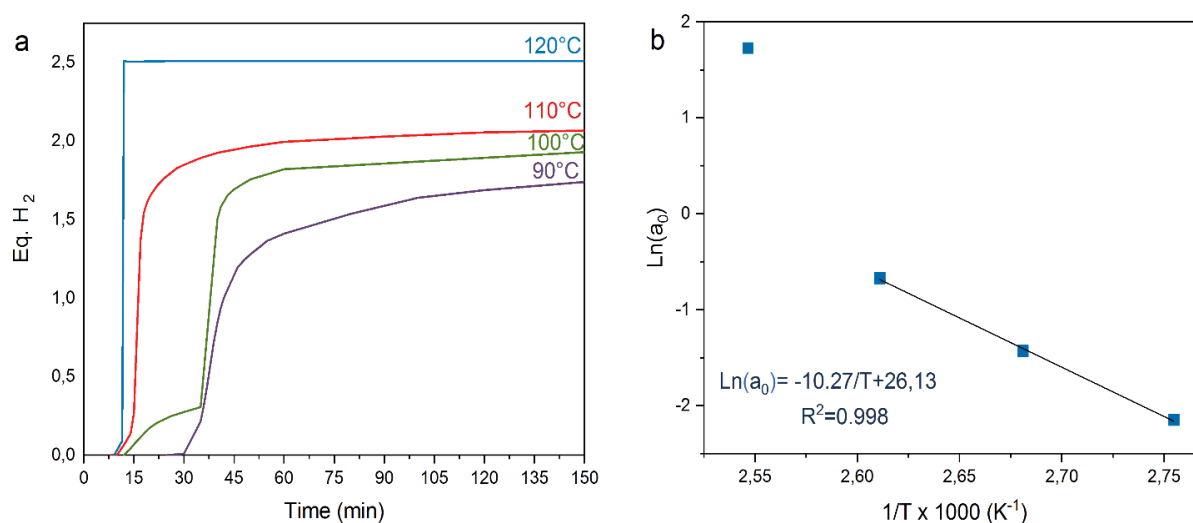


Figure 15. a) Time evolution of H_2 release from CsHB under heating at isothermal conditions (90, 100, 110 and 120°C); b) Arrhenius plot for the determination of the apparent activation energy.

The curves of **Figure 15** were used to determine the apparent activation energy of the decomposition process. As observed in **Figure 15b**, the first point was not taken into account for the calculations, due to a high error in the linear regression model. This point corresponds to $T=120^\circ\text{C}$, in which the decomposition is highly fast. This might occur due to the formation of shock sensitive products and because of the rapid decomposition of the sample at this temperature. The linear form of the Arrhenius equation was used with this purpose:

$$\ln a_0 = -\frac{E_a}{RT} + \ln A \quad (2)$$

Where a_0 is the hydrogen generation rate, E_a the apparent energy activation, T the temperature, R the universal gas constant and A the pre-exponential factor. The generation rate (the slope of the

curves in $\text{mol H}_2 \text{ min}^{-1}$) is plotted as function of the inverse of the temperature (in K) and E_a can be obtained. An apparent energy activation of $85.37 \text{ kJ mol}^{-1}$ was obtained. Table 5 presents the value of the apparent energy activation for different BNH compounds. The value for CsHB is higher than the values presented for other compounds such as LiH and LiBH_4 doped AB, LiAB and the other hydrazinidoboranes, but not as high as pure AB^{44,48,67–69}

Table 5. Apparent activation energy for different BNH compounds.

Compound	$E_a \text{ (kJ mol}^{-1}\text{)}$	Reference
Ammonia borane	183	67
LiH-doped ammonia borane	75	67
Lithium amidoborane	71	68
LiBH_4 -doped lithium amidoborane	61	68
α -Lithium amidoborane	157	70
β -Lithium amidoborane	272	70
Lithium hydrazinidoborane	58	44
NaH-doped sodium hydrazinidoborane	14.4	69
Rubidium hydrazinidoborane	30.1	48
Cesium hydrazinidoborane	85.37	-

The decomposition properties of CsHB were compared with those of hydrazine borane and the alkali derivatives (even if the experimental procedures are not the same for the case of HB, LiHB and NaHB). Table 6 presents the equivalents of H_2 released by these compounds after 1 h of isothermal treatment at different temperatures. At 100°C HB, LiHB and RbHB release a similar amount of hydrogen. CsHB releases a higher quantity of hydrogen (1.8 equivalents). However, we can observe that KHB releases a similar amount at just 88°C . The cesium cation has improved the dehydrogenation properties over HB and even from LiHB and RbHB. However, NaHB still has the best performance with 2.6 equivalents of hydrogen after 1 h of heat treatment at 100°C .

Table 6. Equivalents of H₂ liberated by the alkali hydrazinidoboranes and hydrazine borane after 1 h of heat treatment at isothermal conditions.

Temperature	Compound					
	HB ⁴⁵	LiHB ⁴⁴	NaHB ⁴⁵	KHB ⁴⁷	RbHB ⁴⁸	CsHB
80°C	0.4	-	0.62	-	0.38	-
88°C	0.46	-	-	1.75	-	-
90°C	0.63	-	1.15	-	-	1.4
100°C	0.65	0.6	2.6	-	0.55	1.8
110°C	-	0.9	2.7	-	-	1.9
120°C	-	-	-	-	1.1	2.5
140°C	1.1	2.2	-	-	2	-

The gases produced during the dehydrogenation experiments at isothermal conditions were analyzed by gas chromatography (GC). In the GC, the presence of hydrogen is confirmed by the single peak that appears at around 0.6 min for all temperatures, which represents the retention time for H₂ in the column used on the chromatograph (Figure 16).

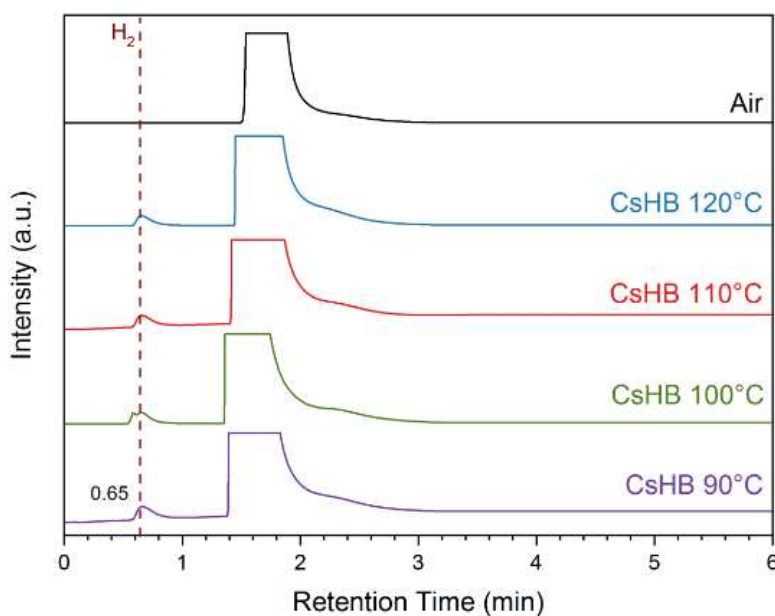


Figure 16. GC analyses of the gases liberated by CsHB at isothermal conditions (under heating at constant temperature of 90, 100, 110 and 120°C). The retention time in min is indicated.

A second signal can be observed after 1.3 min, corresponding to the retention time of air (introduced while injecting the sample). As a reference, air was injected in the GC and shown in the chromatogram.

The gases released by the samples treated at 100 and 120°C were analyzed by MS. The analysis showed that the gas produced is a mixture of different compounds. Besides H_2 we detected the presence of ammonia NH_3 , hydrazine N_2H_4 , diborane B_2H_6 and nitrogen N_2 at 120°C. In the case of the sample heated at 100°C, no hydrazine or diborane were found (Figure 17 and Figure 18).

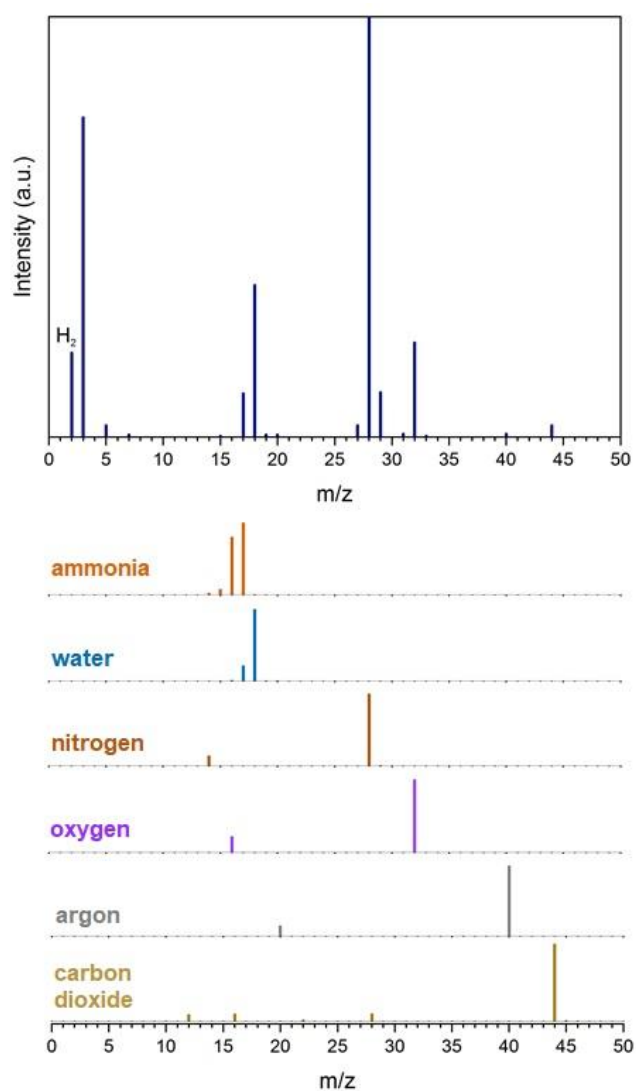


Figure 17. MS spectra of the gases released by the sample heated isothermally at 100°C. The m/z signals of the identified species are shown below.

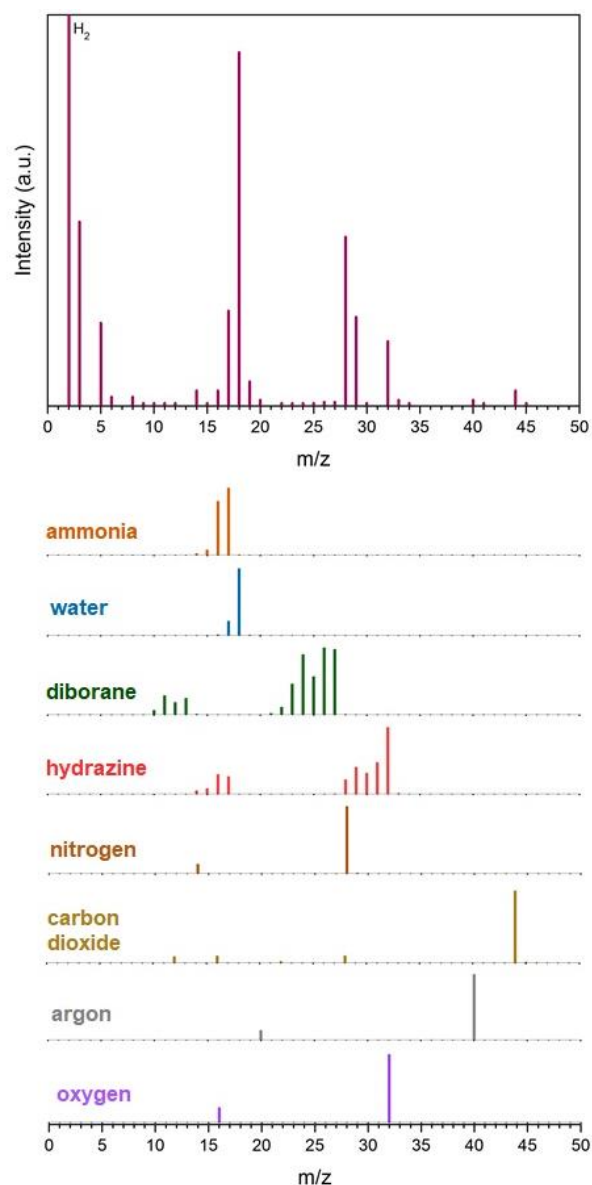


Figure 18. MS spectra of the gases released by the sample heated isothermally at 120°C. The m/z signals of the identified species are shown below.

The decomposition behavior presented by CsHB is different from other alkali hydrazinidoboranes.⁶⁹ This could be explained by any of the two following reasons (or both): (i) the by-products detected in the synthesis of CsHB by ¹¹B MAS NMR and PXRD are the responsible of the emission of these compounds or (ii) the big size of the Cs⁺ and the longer Cs–N bond distance means a higher degree of freedom on the molecule, which could result in the formation

of such compounds. As there is a lack of computational calculations to affirm exactly which compounds are formed, we propose possible mechanisms that are probably to take place during the thermolysis of CsHB, as shown in Figure 19 to Figure 21. We may recall that the presence of N_2 can be due to small quantities of air that enter when injecting the sample, because signals belonging to O_2 , H_2O and CO_2 were identified too. Other signals assigned as impurities from the carrier gas were also identified at $m/z=3$, 5 and 6.

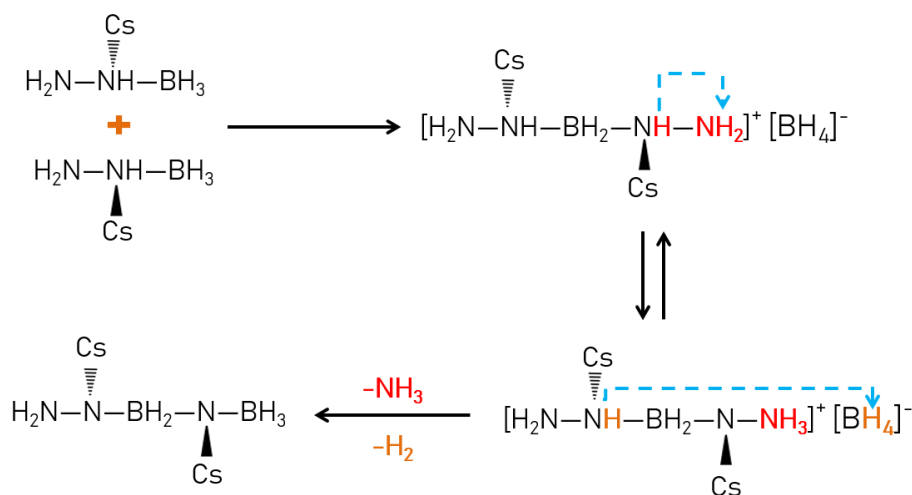


Figure 19. Formation of the dimer $[(CsN_2H_3)_2BH_2]^+[BH_4]^-$, which will release H_2 and NH_3 .

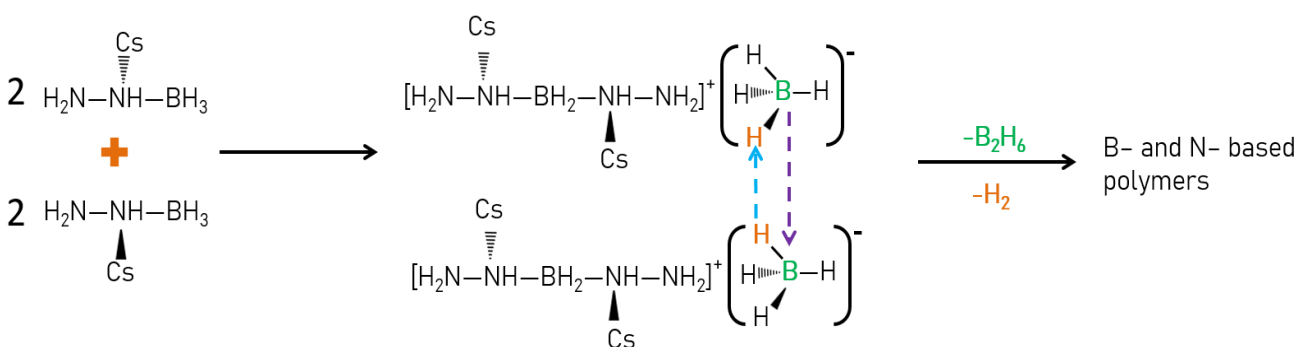


Figure 20. Formation of the dimer $[(CsN_2H_3)_2BH_2]^+[BH_4]^-$, which continues reacting to form B- and N-based polymers with the release of H_2 and B_2H_6 .

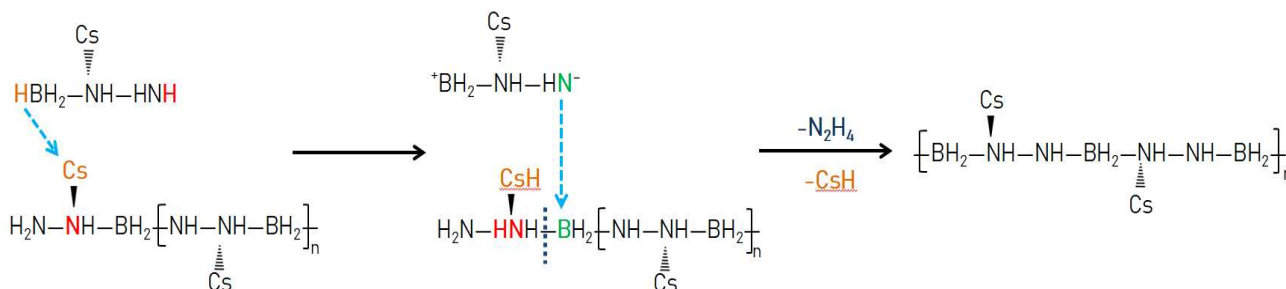


Figure 21. Reaction of a polymer chain product of the thermolysis of CsHB and a molecule of CsHB. This leads to a continued growth of the chain, forming CsH and releasing N₂H₄.

In any case, the release of these gaseous by-products is in good agreement with the TGA analysis, due to the high mass loss of CsHB during the decomposition (6.9 wt. % of mass loss, when the content of hydrogen is 3.4 wt. % H). A phenomenon present in the decomposition experiments of hydrazinidoboranes is the difference between the detected gases at different experimental conditions. This is explained because for example, in the TG-MS analysis the gases released by the sample are being carried away by the carrier gas of the apparatus. The isothermal experiments are carried out in a closed system, so the possible intermediates have the time to react and form these compounds, instead of being carried away.

3.4 Analyses of solid residues

As previously mentioned in section 3.1, the solid residues after isothermal experiments could only be analyzed by ¹¹B MAS NMR due to security issues. It is important to remind that the preparation of the rotors was carried out in a glove box and the analysis was performed at a low temperature to avoid any risk of explosion of the sample. Figure 22 shows the comparison of the spectra of the samples obtained after the heat treatment at isothermal conditions (90, 100, 110 and 120°C) and CsHB by ¹¹B MAS NMR.

As mentioned in section 3.2.2, the BH₄ environment is assigned to the presence of a ionic dimer [(CsN₂H₃)₂BH₂]⁺[BH₄]⁻. The signal centered at -13 ppm was deconvoluted in two signals. The one at -14.7 ppm suggests a NBH₃ group, which indicates some unreacted BH₃ groups; the one at

-12.7 ppm indicates a N_2BH_2 environment, suggesting the presence of the dimer $[\text{CsN}_2\text{H}_3\text{BH}_2\text{CsN}_2\text{H}_3]^+[\text{BH}_4]^-$, or the formation of some other compounds like $\text{Cs-H}\cdots\text{CsN}_2\text{H}_3\text{BH}_2\text{N}_2\text{H}_3\text{BH}_3$.^{57,58,61,62,71} At 120°C, these signals have disappeared, indicating an evolution of these compounds, and a new peak has appeared at -1.1 ppm suggesting the formation of N_3BH species.

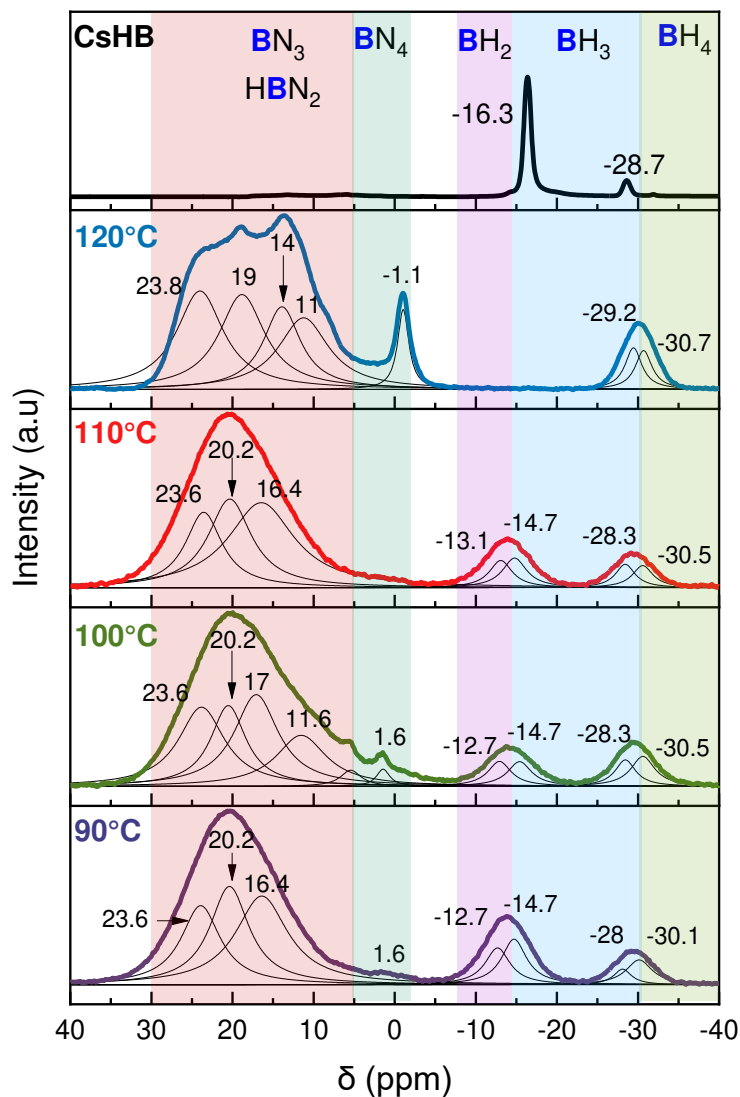


Figure 22. ^{11}B MAS NMR spectra of CsHB and the solid residues recovered after the isothermal treatment at 90, 100, 110 and 120°C. The signals for the residues were deconvoluted. The chemical shifts in ppm and the assigned boron environments are indicated.

The signal centered at -28.7 ppm broadens for all samples, and the intensity of this signal increases the temperature rises. At 120°C the BH_2 and BH_3 environments have disappeared, but the signal at -28.7 ppm is still present. This suggests a compound with a different **B** environment. One possibility is the presence of a cesium salt of B_3H_8^- . It has been reported that in the presence of a BH_3 environment, a pure alkali metal can react to form such salts:^{72,73}



Other work reported that environment for the B atom in CsB_3H_8 corresponds to a chemical shift of -29.8 ppm when analyzed in THF-d_8 .⁷⁴ The formation of this salt is likely due to the high reactivity of Cs, but is still speculative and it requires of a deeper investigation to confirm or discard such hypothesis. However, without computational analyses the identification of this compound is challenging by other characterization techniques due to safety reasons, as the heated samples ignite when they are put in contact with air.

For all the studied temperatures, a broad and intense signal appears at positive chemical shifts, typical from a sp^2 hybridized boron atom.^{58,59,61} At 90 and 100°C there is one signal that appears at lower positive chemical shifts (1.6 ppm), which can indicate the formation of a BN_4 environment.⁵⁷ The broad signal presented by all samples after 10 ppm was deconvoluted in mainly 3 signals centered around 16, 20 and 23 ppm. The environments are assigned to BN_3 and BN_2H . Typical compounds that can form in the decomposition of ammonia borane include polymeric species like polyborazilene and polyiminoborane.⁷⁵ Analogous species might form during the decomposition of CsHB .

4. Conclusions

The last of the alkali derivatives of hydrazine borane, cesium hydrazinidoborane $\text{CsN}_2\text{H}_3\text{BH}_3$ (CsHB ; 3.3 wt. % H) was synthesized and characterized in this work. The displacement of the $\text{H}^{\delta+}$ of the hydrazine moiety by Cs^+ was demonstrated by FTIR and ^{11}B MAS NMR techniques. The synthesis of a completely pure compound could not be obtained (neither at room or subzero temperature), but the experiments carried out allowed us to obtain the crystal structure of

$\text{CsN}_2\text{H}_3\text{BH}_3$. CsHB is a crystalline material isostructural to $\text{KN}_2\text{H}_3\text{BH}_3$ and $\text{RbN}_2\text{H}_3\text{BH}_3$, with a monoclinic unit cell and a $P2_1$ space group (No. 4) with cell parameters of $a=5.916 \text{ \AA}$, $b=7.009 \text{ \AA}$, $c=6.002 \text{ \AA}$ and $\beta=108.389^\circ$.

The behavior of CsHB under heating at constant rate (5°C min^{-1}) and at isothermal conditions was analyzed. The effect of the Cs^+ on the molecule was confirmed: CsHB starts to decompose at a lower temperature than HB does, confirming the destabilization that the cation has on the molecule. CsHB can release more equivalents of gas in 1 hour of heat treatment than LiHB and RbHB; however, the MS analyses showed that the composition of this gas is hydrogen accompanied by ammonia, hydrazine and diborane. This also explains the mass loss of CsHB during the TG analysis: while CsHB possesses 3.3 wt. % H, it loses more than 6 wt. % during its decomposition. However, it is not still clear if such gaseous by-products are emitted only by CsHB or if the other unidentified compounds formed in the synthesis reaction also have a contribution. The compounds obtained after the decomposition of CsHB presents a similar composition to dehydrogenated hydrazinidoboranes, which is a mixture of solid polymers composed mainly of polyborazylene-like compounds. The identification of such compounds still represents a challenge in the field, so deeper works should be performed in order to elucidate the intermediates and species that participate in the reaction and the exact products obtained.

Cesium hydrazinidoborane was obtained and its characteristics were evaluated in this work. This allowed us to complete the alkali family of hydrazine borane derivatives and let us to have a better landscape of these borane compounds. Although the thermal behavior of CsHB is improved in comparison to HB, the presence of undesired by-products in the released gas shows that it is not the best option as a chemical hydrogen storage material. Besides, the management of the thermolytic residues of CsHB represent a risk. Otherwise, this compound might be considered as an energetic material.

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Chapter 5

AMIDOBORANES-DERIVED BORON NITRIDE

5 Amidoborane-derived boron nitride

1. Introduction

At present, the primary source of energy is fossil fuels, but they are limited resources and the burning of such fuels releases pollutant emissions to the atmosphere, especially carbon dioxide (CO_2). Different sectors (transport, industrial, domestic) contribute to the enormous quantities of CO_2 released, which have a direct impact on global warming. Around 99 % of the CO_2 emissions are produced by the combustion of fossil fuels.¹ One approach to decrease these emissions, are the CO_2 capture and storage (CCS) technologies.^{2,3} For example, the physical and chemical sorption of CO_2 by materials; however, most of these technologies are not mature enough to be implemented in all kind of industrial processes.⁴

Different materials have been proposed to capture CO_2 : zeolites, ionic liquids, metal organic frameworks, porous carbons, amines, boron nitride, silica, among others.⁴⁻⁶ In the last years, boron nitride (BN) has received attention due to its unique properties and potential application in different fields, such as water treatment, photonics or coatings.⁷⁻¹² BN has also been considered for CO_2 capture. According to different studies, nitrogen atoms with a partial negative charge act as potential active sites for carbon dioxide chemisorption.^{13,14} Back in 1994, porous BN was already studied as a selective gas adsorbent for a mixture of CH_4/CO_2 .¹⁵ More recently, in 2010, a theoretical study predicted the strong CO_2 adsorption in boron-rich boron nitride nanotubes (BNNT).¹⁶ The work suggested that the BNNT could capture CO_2 at ambient conditions. Another work calculated the capture of CO_2 by different kind of structures. For example, CO_2 was weakly adsorbed by uncharged BN nanosheets and nanotubes; however, when extra electrons are introduced to the materials (negatively charged), CO_2 molecules are strongly adsorbed and the BN presents a selectivity for this gas.¹⁷ Other studies point to the possible ways to enhance the CO_2 capture by BN, like vacancies of

boron atoms or the doping of the BN structures.^{13,18} A few experimental works have reported the CO₂ capture by BN structures like porous nanofibers, nanosheets, foam or 3D structures.^{19–25} All of these studies have evidenced the uptake of CO₂ at near ambient conditions. For example, porous BN modified with P123 surfactant can capture 60.2 cm³ g⁻¹ (25°C, 1 bar), while BN nanosheets functionalized with polyethylenimine (PEI) can capture 69.9 cm³ g⁻¹ (120°C, 1 bar).^{20,21} In comparison, a CO₂ uptake of 10 cm³ g⁻¹ was reported for a mesostructured silica (SBA-15).²⁶

Beyond of being a potential material for CO₂ sorption applications, BN can be also considered for H₂ storage. Through ab-initio simulations, it has been estimated that BN could uptake 8.6 % wt. H₂ at room temperature.²⁷ Other computational studies have determined different approaches to improve the sorption properties of BN, like the surface functionalization with alkali atoms, the increase of the specific surface area, and/or the substitution of B atoms in the structure by C and/or O atoms.^{28–31}

Different boron- and nitrogen-containing precursors can be used to obtain BN. Ammonia borane (AB) is one of them.^{32,33} AB is a stable, crystalline solid at room temperature with a high hydrogen content (19.6 % wt.). During its thermolysis, AB undergoes a three step decomposition,³⁴ releasing one equivalent of H₂ in each stage. These steps take place at ca. 100, 150 and >400°C respectively. In this sense, metal amidoboranes (MAB) might also be precursors of boron nitride. MAB are derivatives of AB, formed when one of the protic hydrogens of the NH₃ moiety of AB is substituted by a metal cation. These derivatives have proved to improve the dehydrogenation properties of the former AB: they start to dehydrogenate at lower temperatures and they suppress some unwanted byproducts, releasing purer hydrogen.³⁵ Different amidoboranes have been synthesized up to now, starting with the alkali derivatives (Li, Na, K, Rb, Cs) followed by the alkaline-earth amidoboranes (Be, Mg, Ca, Sr, Ba), covering other metals such as yttrium, and the mixed cation amidoboranes.^{36–48}

Up to our knowledge, no work has reported the synthesis of BN using amidoboranes as precursors. MAB may offer some advantages over AB as precursors of BN:⁴⁹ i) a lower temperature to achieve the conversion due to the lower dehydrogenation temperature; ii) a higher ceramic yield due to lower emission of volatile byproducts; and iii) the role of the metal cation could favor a higher degree of crystallization of BN.⁵⁰ Accordingly, the present work selected the lithium (LiAB) and sodium (NaAB)

amidoboranes as a starting point to study them as precursors of BN. These materials were pyrolyzed at different temperatures and they were characterized.

Originally, the intention was to study these materials for both H₂ storage and CO₂ capture. However, due to the sanitary crisis of covid-19, this could not be done. A few preliminary tests for some of the samples showed that they were not able to uptake hydrogen at room temperature (1-100 bar, 25°C). The CO₂ capture was also intended to be analyzed more in depth, however due to technical delays related to the same crisis, we could only perform one set of measurements at 30°C and 1.5 bar. For this reason, this chapter is mostly focused on the characterization of the materials. The results are presented in the following sections.

2. Experimental section

2.1 Reagents

Commercial AB (NH₃BH₃) (Sigma Aldrich, 97%), lithium hydride (LiH) (Sigma Aldrich, 95%) and sodium hydride (NaH) (Sigma Aldrich, dry, 90%) were used as received. AB and the metal hydrides were used to obtain the respective alkali amidoboranes.

2.2 Synthesis

The reagents before synthesis were prepared in an argon-filled glovebox (MBraun M200B, H₂O ≤ 0.1 ppm; O₂ ≤ 0.1 ppm). A RETSCH PM100 planetary ball mill was used for the mechanochemical syntheses to obtain the alkali amidoboranes.

2.2.1 Synthesis of lithium amidoborane (LiAB)

LiAB was prepared by ball milling under an argon atmosphere. An equimolar mixture of AB (0.168 g) and LiH (0.043 g) was prepared in a stainless-steel reactor, containing 5 stainless-steel balls. The weight ratio of balls (R_{ball}) over reactants was set as 100. The reactor was taken outside the glovebox and the mixture was ball milled during 4 cycles consisting of 1 h of milling at 400 rpm and 15 min of

break. After the milling, the reactor was transferred into the glovebox and the sample was recovered. LiAB was then handled and stored into the glovebox. The overall reaction can be written as:



2.2.2 Synthesis of sodium amidoborane (NaAB)

NaAB was prepared in a similar way. An equimolar mixture of AB (0.117 g) and NaH (0.091 g) was prepared inside the stainless-steel reactor containing 5 stainless steel balls ($R_{\text{ball}}=100$), in the glovebox. The reactor was closed and transferred to the planetary ball mill, where the mixture was milled for 10 min at 250 rpm. The synthesis of NaAB is faster because NaH presents a higher reactivity towards AB than LiH does. Once the process was finished, the reactor was taken to the glovebox and the product was recovered. NaAB was handled and stored inside the glovebox. The reaction can be written as follows:



2.3 Heat treatment

AB, LiAB and NaAB were pyrolyzed at 200, 600, 800 and 1000°C. For the heat treatment at 200°C, the sample was put into a stainless-steel reactor, and transferred to the furnace. The temperature was increased in 20°C every 30 min. Once at 200°C, the temperature was kept for 20 h and then cooled down to room temperature. After, the solid products were recovered and stored in the glovebox

For AB and NaAB, the solid treated at 200°C was used to do the pyrolysis at 600, 800 and 1000°C. LiAB was directly pyrolyzed without a pre-treatment. To perform the pyrolysis, the sample was weighted and put into a ceramic crucible boat inside the glovebox, and then transferred into a closed glass cylinder. The sample was introduced into a tubular furnace and heated under N_2 atmosphere. The heating ramp was 1°C min^{-1} starting from room temperature up to the desired temperature. When the required temperature was reached, it was kept for 90 min, and then decreased to room temperature. The sample was recovered and stored in the glovebox for further analyses. Most of the heat treatment at high temperature (600, 800 and 1000°C) were performed by Ms. Rimeh Mighri, PhD

student at the University of Montpellier. It is important to recall that the samples could have entered in contact with air during the process, but efforts were done to avoid this at much as possible. The yield of the samples after heat treatment was calculated by a simple rule of three and is presented in Table 1. The resume of the heat treatment and the reference of each sample is presented in Table 2.

Table 1. Yield (wt. %) of the recovered samples after heat treatment.

Sample ↓	Yield			
	200°C	600°C	800°C	1000°C
AB	55 %	51 %	49 %	49 %
LiAB	96 %	83 %	82 %	76 %
NaAB	94 %	56 %	54 %	53 %

Table 2. Reference of the samples in function of the heat treatment.

Temperature ↓	Sample name		
	AB	LiAB	NaAB
Pristine	AB	LiAB	NaAB
200°C	AB200	LiAB200	NaAB200
600°C	AB600	LiAB600	NaAB600
800°C	AB800	LiAB800	NaAB800
1000°C	AB1000	LiAB1000	NaAB1000

2.4 Characterization

2.4.1 Structural characterization

All samples were analyzed by solid-state ^{11}B Magic Angle Spinning Nuclear Magnetic resonance (MAS NMR). LiAB, NaAB and the pyrolyzed samples were analyzed by ^7Li and ^{23}Na MAS NMR, respectively. The NMR spectra were obtained by a spectrometer Varian (VNMR400, 400 MHz) at 0°C. The

references for boron, lithium and sodium were NaBH_4 (at -42.1 ppm), LiCl (at 0 ppm) and NaCl (at 0 ppm) respectively. ZrO_2 rotors of 3.2 mm of diameter were used. Mr. Emmanuel Fernandez and Mr. Philippe Gaveau from the Platform Balard from the University of Montpellier prepared the samples and performed the NMR analyses.

All the samples were analyzed by Fourier Transformed Infrared (FTIR) spectroscopy by a NEXUS instrument (ThermoFisher) equipped with an attenuated total reflection accessory from 600 to 4000 cm^{-1} wavelength. To perform the analysis, the samples were put into a closed vial inside the glovebox, transferred to the equipment and then taken out of the vial right before the analysis. The exposure of the samples to air is kept at minimum as possible. The samples were analyzed by Raman Spectroscopy by a Horiba Yvon LabRAM apparatus, equipped with a laser quantum gem 660 nm of 100 mW and an Olympus BX40 microscope. Mr. Eddy Petit performed the analyses of Raman spectroscopy. Powder X-ray diffraction (PXRD) was used to characterize all the samples. A PANalytical X'pert Pro diffractometer in Bragg-Brentano geometry was used. The samples were analyzed over the 2θ range 20-60°. All the samples were prepared inside the glovebox and they were protected from air by a Kapton film. X-ray photoelectron spectroscopy (XPS) was performed using an ESCALAB 250 (ThermoElectron) equipped with an Al-K_α monochromatized source (1486.6 eV), and analyzing an area of 500 μm of diameter. Ms. Valérie Flaud from the Platform Balard from the University of Montpellier did the XPS analyses.

Some of the amidoboranes samples were analyzed by Scanning Electron Microscopy and Energy Dispersive X-ray analysis (SEM and EDX). The SEM analysis was done in a Hitachi S4800 microscope equipped with a secondary and backscattered electron detector. The samples were coated with platinum using an ion sputter coater. A Zeiss EVO HD15 equipped with an Oxford Instrument X-Max^N SDD detector was used for the EDX analysis. Mr. Didier Cot and Mr. Bertrand Rebiere did the SEM and EDX analyses respectively. Some of the pyrolyzed samples were analyzed by the Brunauer-Emmet-Teller (BET) method to analyze the possible porosity of the samples. A Micromeritics TriFlex equipment was used. The samples were degassed for 15 h at 200°C before the measurements. These analyses were done by Ms. Rimeh Mighri, PhD student at the University of Montpellier. The amidoborane-derived samples treated at 1000°C were analyzed by High Resolution Transmission

Electron Microscopy (HRTEM) using a JEOL 2200 FS microscope (200 kV). This analysis was performed by Mr. Erwan Oliviero from the Platform Balard from the University of Montpellier.

2.5 Sorption of CO₂

The CO₂ sorption measurements were performed in a Sieverts system made in our laboratory. The Sieverts method is useful to determine the uptake of a determined gas by a material. In a typical experiment, a calibrated reference volume is filled with the gas at a known pressure and then it is injected to the chamber where the sample is. The change of pressure in the chamber is measured as a function of time. The equilibrium is reached when the maximum quantity of gas is sorbed, and the quantity of gas taken by the material can be calculated through an equation of state.

The diagram of the system is shown in Figure 1. It is equipped with three pressure controllers (Keller PA-33X, range 0-3 bar, precision of ± 1.5 mbar) and a temperature sensor (PT100 with a precision of $\pm 0.15^\circ\text{C}$ at 30°C). All the valves and connections are from Swagelok. The system is contained in an incubation hood (Sartorius Certomat HK) which keeps a constant temperature during the measurements. Previous all experiments, the volumes of each part of the apparatus were carefully determined with He gas. For more accuracy during the measurements, the temperature and the pressure are followed at the sample chamber.

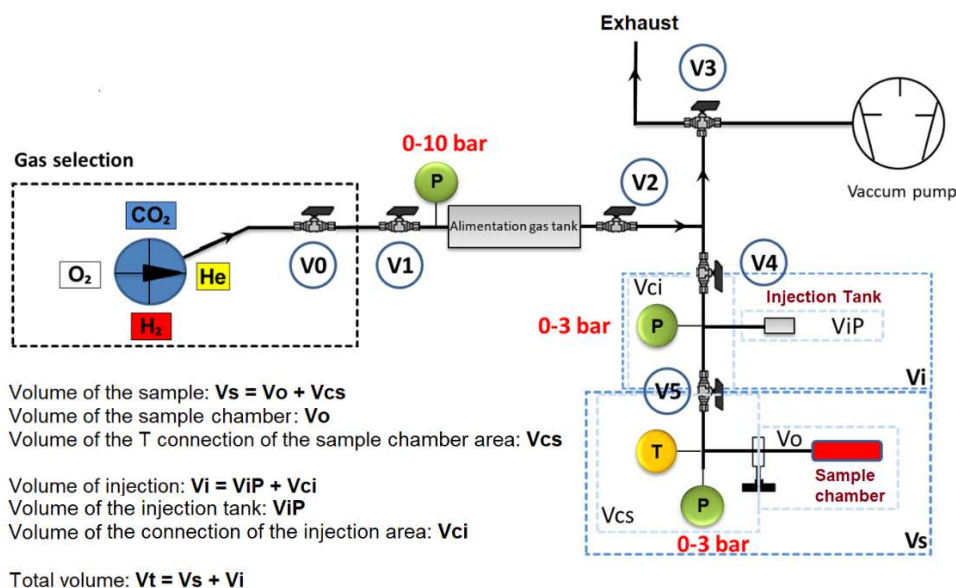


Figure 1. Diagram of the Sieverts system used for the CO₂ sorption experiments.

2.5.1 Sorption experiments

Before the first CO₂ sorption measurement, each material was outgassed overnight at 150°C at the Schlenk line. After this, the sample was put into the sample chamber inside the glovebox, and then the chamber was transferred and connected to the Sieverts apparatus. Once in the system, the samples were degassed under vacuum for 5 h at 50°C before each analysis. After this time, the system was cooled down to 30°C and the CO₂ was charged into the injection tank while the sample was kept under vacuum. Once all variables stabilized, the gas was allowed to enter the sample chamber. A software registered the change on the temperature and pressure. All measurements were performed at 30°C and at an initial CO₂ pressure of 1.5 bar. The samples were left under CO₂ atmosphere for a maximum equilibration time of 180 min. The experiments were repeated twice. CO₂ was considered as an ideal gas.

3. Results

3.1 Preliminary commentaries

As shown in Table 1, the yield obtained from AB at 200°C is 55 wt. %. This is explained by the loss of 2 equivalents of H₂ and the evolution of other gaseous species such as NH₃, B₃N₃H₆ and B₂H₆. At higher temperatures, we obtained a yield between 89-93 wt. % with respect to the sample heated at 200°C. This is in good agreement with the expected yield of boron nitride obtained from polyborazylene PB (93-84 wt. %).⁵¹ These yields are expected for PB with a high molecular weight ($M_w=3000-8000\text{ g mol}^{-1}$). In the case of the LiAB-derived samples, the yield is higher in comparison with AB. This is explained by the suppression of byproducts through the thermolysis and the release of purer H₂.⁵² However, the losses greater than the H₂ content (10.9 wt. %) of LiAB indicate the formation of some of the before mentioned gaseous byproducts, or by the decomposition products formed by parallel reactions. Regarding NaAB, the yields are lower than the ones of LiAB but higher than those of AB. This could be due to a considerable emission of NH₃ along with H₂.⁵³ In addition, the boiling point of Na is ~880°C, which can lead to a lower yield at high temperatures. As in the case of LiAB, additional products might form during pyrolysis, causing losses in the yield of this compound.

The density of all pyrolyzed samples were measured by a pycnometer (Micromeritics AccuPyc II 1340). The calibration was done with two metal balls of known volume. All the samples were degassed at 200°C overnight before the analysis.

As we wanted to test our samples for CO₂ sorption, we wanted to confirm the bulk state of the obtained materials. We performed BET analysis for the samples. For some of the samples treated between 200 and 600°C, the equipment could not measure the porosity (due to the lack of pores). For the materials obtained at 800°C, a low value was registered. We stopped the experiments after this pyrolysis temperature. The results of both density and BET measurements are shown in Table 3.

Table 3. Density and specific surface area of the pyrolyzed samples derived from AB, LiAB and NaAB.

Sample	ρ (g cm ⁻³)	S (m ² g ⁻¹)
AB200	1.3	– ^a
AB600	1.6	– ^a
AB800	1.8	– ^b
AB1000	1.4	– ^b
LiAB200	1.00	1
LiAB600	1.4	– ^a
LiAB800	1.6	4
LiAB1000	2.0	– ^b
NaAB200	1.5	2
NaAB600	1.8	– ^a
NaAB800	1.4	10
NaAB1000	1.7	– ^b

^a Not registered by the device. ^b Experiment not performed.

The LiAB- and NaAB-derived materials treated at 600, 800 and 1000°C were also analyzed by SEM analysis (**Figure 2**). The form of the materials in the bulk state was confirmed. As it shown, only

agglomeration of the materials is observed, and no signs of pores were detected. By the EDX analysis, we found a B/N atomic ratio around 1 on the surface of the materials (Annex I, Figures A1 to A8).

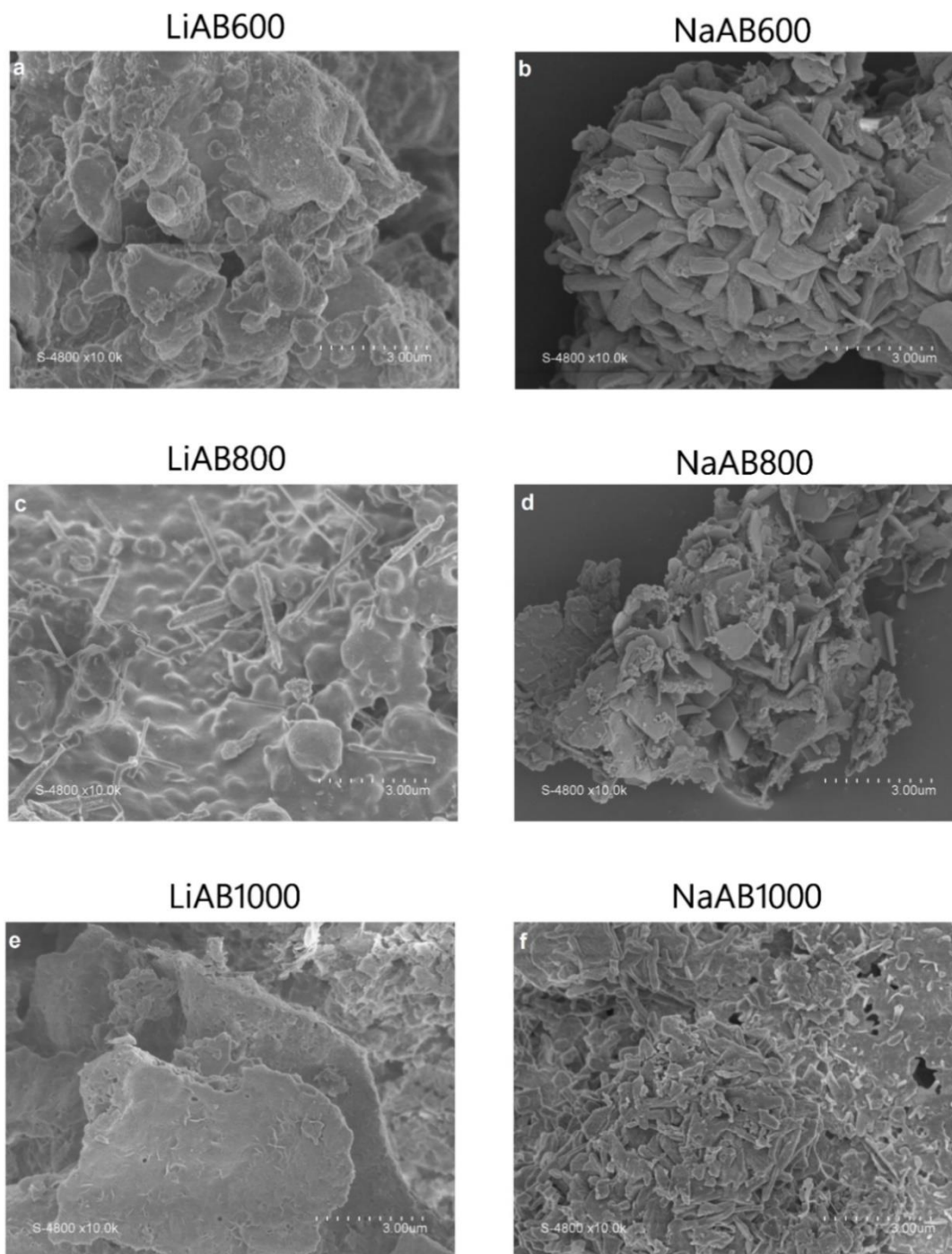


Figure 2. SEM images of pyrolyzed samples of LiAB and NaAB at 600, 800 and 1000°C at 10.0k.

3.2 Molecular characterization

3.2.1 Fourier Transformed Infrared Spectroscopy (FTIR)

Figure 3 presents the FTIR spectra of AB and the pyrolyzed solid products. The spectrum of our commercial AB matches well with the ones reported in the literature.⁵⁴

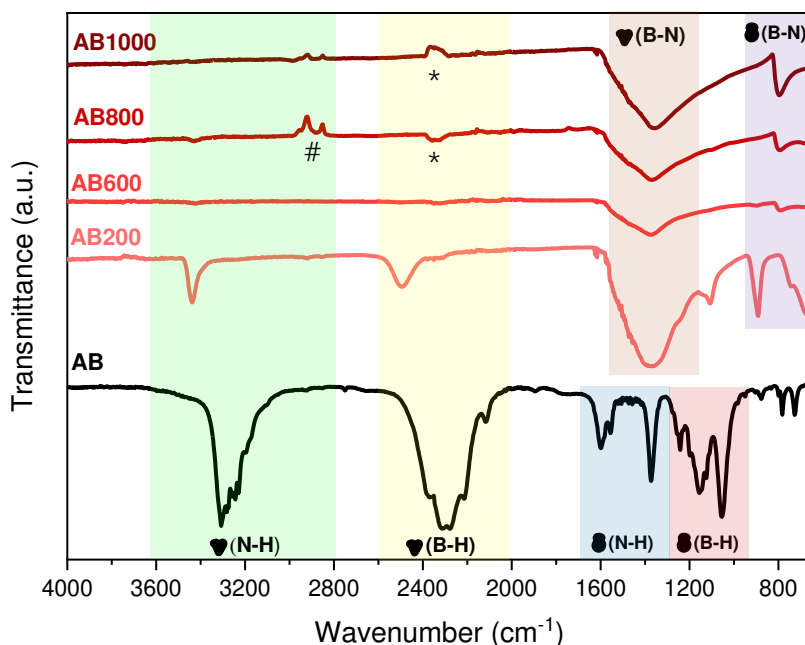


Figure 3. FTIR spectra of AB and the products after pyrolysis at 200, 600, 800 and 1000°C. The vibrational bands of interest have been assigned. The signals indicated by * point the presence of atmospheric CO₂ and by # the KBr film that protects the diamond of the apparatus.

The bands in the range 3100–3500 cm⁻¹ belong to the N–H stretching modes and the ones centered at 2000–2500 cm⁻¹ belong to the B–H stretching mode. Deformations of the NH₃ and BH₃ moieties can be seen at 1400–1600 and 1000–1300 cm⁻¹ respectively. The bands below 800 cm⁻¹ correspond to the B–N stretching modes. In the case of AB200, the main bands observed at 3500, 2400 and 1500 cm⁻¹ can be assigned to N–H, B–H and B–N stretching modes respectively, involving π bonded nitrogen and boron atoms.⁵⁵ The lower intensity in the N–H and B–H stretching regions, and the

strong band in the B–N region indicate the formation of N- and B-based polymers with formula BNH_x ($x \leq 2$).⁵⁶ The spectrum is also comparable to the one of polyaminoborane (PAB), polyborazylene (PB) or polyiminoborane (PIB).^{51,57,58} All of these products have been found in the thermolytic decomposition of AB (Figure 4).^{59–61} At 200°C, the product is likely to be PB and PIB.

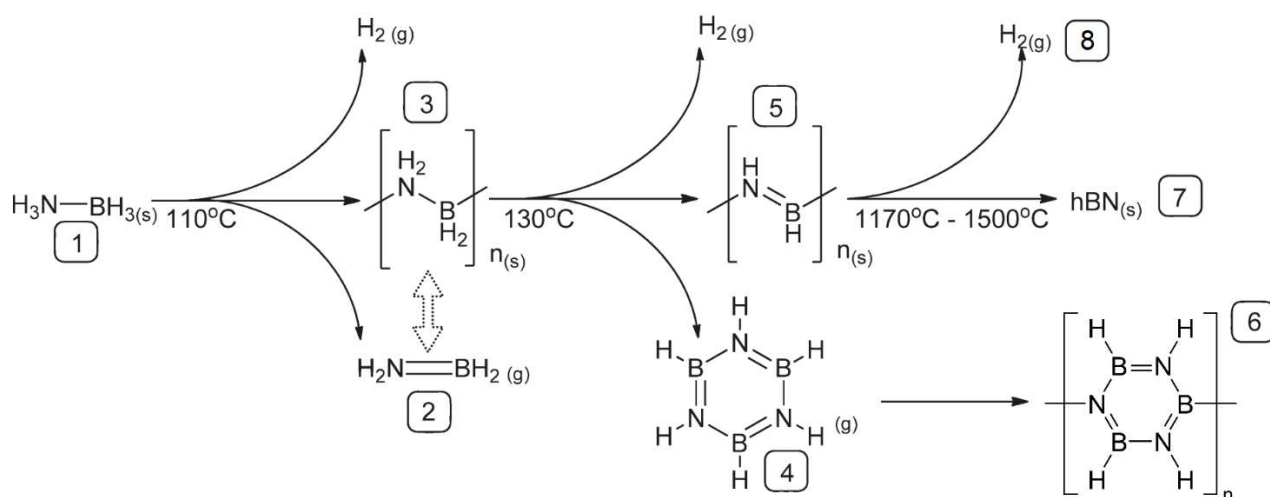


Figure 4. Species involved in AB thermal decomposition, adapted from reference ⁵⁵. (1) AB (2) molecular aminoborane; (3) Polyaminoborane (PAB); (4) Borazine; (5) Polyiminoborane (PIB); (6) Polyborazylene (PB); (7) semi-crystalline hexagonal boron nitride; (8) hydrogen evolution of molecular hydrogen at high temperature. The reversibility between (2) and (3) is inferred and likely to depend on temperature and chain length of PAB.

The spectra of AB600, AB800 and AB1000 are similar. The stretching bands of N–H and B–H have disappeared, indicating the almost-complete dehydrogenation of the sample. The intensity of the bands at ~ 1360 and $\sim 790\text{ cm}^{-1}$ increases with the increase on the temperature. The spectrum of AB1000 resembles to the one reported for hexagonal boron nitride (h-BN).^{62–64} Pure BN presents two characteristics bands: one strong broad band at 1373 cm^{-1} assigned to the B–N stretching vibrations and a second less intense band at 815 cm^{-1} attributed to B–N–B bending vibrations. The differences in the wavenumbers between the spectra of AB1000 and h-BN is associated to differences in the

crystallinity and anisotropy of pure h-BN, as lattice vibrations are expected to be more pronounced in a material with high crystallinity.⁵⁵

The spectra of LiAB and the pyrolyzed samples are shown in **Figure 5a**. LiAB presents a spectrum similar to those reported in the literature.^{46,65,66} LiAB shows two main bands assigned to N–H ($3000\text{--}3500\text{ cm}^{-1}$) and B–H ($1800\text{--}2500\text{ cm}^{-1}$) stretching vibrations. In comparison with AB, the N–H stretching region is different: the bands are less intense due to the different chemical environment caused by the substitution of one of the protic hydrogens ($\text{H}^{\delta+}$) of the NH_3 moiety by the Li^+ cation. The vibrational bending modes of N–H and B–H appear in the ranges $1400\text{--}1700$ and $1000\text{--}1300\text{ cm}^{-1}$ respectively. The bands observed at $\sim 800\text{ cm}^{-1}$ belong to BN–B vibration modes. For LiAB200, the stretching band of the N–H vibration has disappeared. The B–H stretching bands are present, but with a low intensity. The vibration related to B–N stretching starts to appear at $\sim 1300\text{ cm}^{-1}$. This spectrum is comparable to a dehydrogenated LiAB under similar conditions.⁵² LiAB600, LiAB800 and LiAB1000 present mainly 2 signals at ~ 1350 and 780 cm^{-1} similar to the spectrum of h-BN.

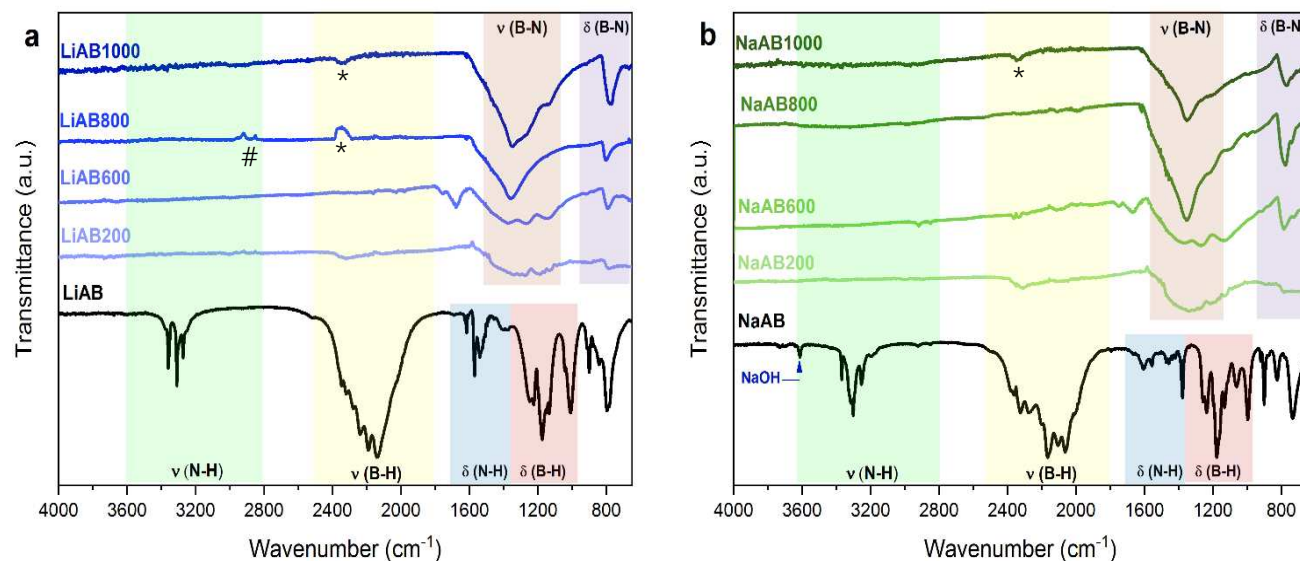


Figure 5. FTIR spectra of the alkali amidoboranes and the products after pyrolysis at 200, 600, 800 and 1000°C for a) LiAB and b) NaAB. The vibrational bands of interest have been assigned. The signals indicated by * point the presence of atmospheric CO_2 and by # the KBr film that protects the diamond of the apparatus.

Figure 5b presents the spectra of NaAB and the products after pyrolysis. The spectrum of NaAB matches with the ones reported in the literature.^{46,65,67} As AB and LiAB, NaAB presents strong bands for the N–H and B–H stretching vibrations in the range of 3100–3500 and 1900–2500 cm^{-1} . The small signal presented at 3600 cm^{-1} belongs to impurities of NaOH, formed when the sample is exposed to air during the FTIR measurements. The characteristic bending bands of the N–H and B–H bonds are also present. After the treatment at 200°C, the N–H bands have disappeared. However, the sample presents bands in both B–H stretching and bending regions. This is consistent with other works, where it has been reported the emission of H_2 and the evolution of NH_3 during the decomposition of NaAB, indicating an incomplete dehydrogenation of the BH_3 moiety.⁵³ As observed for LiAB, the samples treated above 600°C presents two main signals at ~ 1350 and 780 cm^{-1} , similar to h-BN spectrum.

A comparison between the spectra of the samples treated at the highest temperature and h-BN was made (Figure 6).⁶⁸ The samples treated at 1000°C show broader bands in both B–N stretching and bending regions, suggesting the presence of both crystalline and amorphous materials.

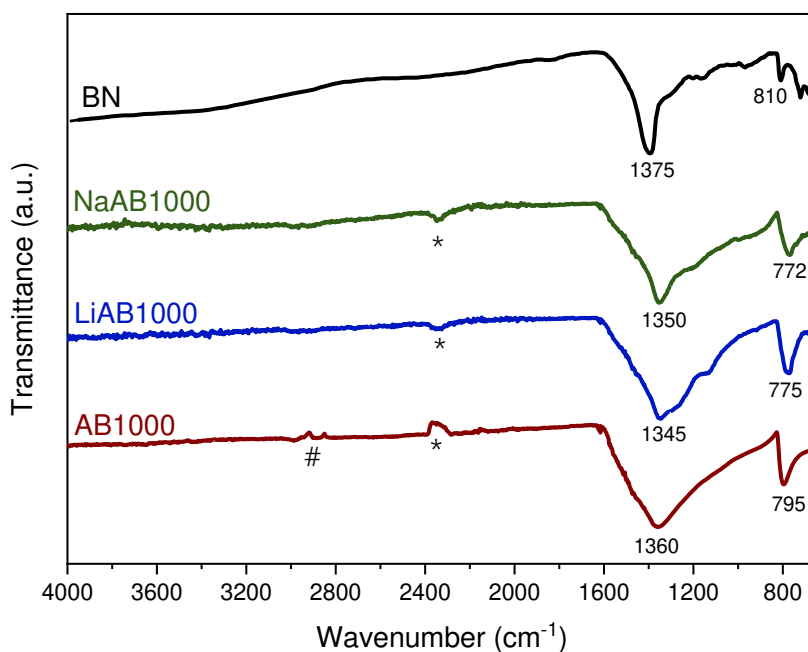


Figure 6. Comparison between the spectra of pure boron nitride and the samples pyrolyzed at 1000°C. The signals indicated by * point the presence of atmospheric CO_2 and by # the KBr film that protects the diamond of the apparatus.

3.2.2 Raman Spectroscopy

AB, LiAB, NaAB and their respective pyrolyzed samples were analyzed by Raman spectroscopy. The spectra of AB and the solid products obtained at different temperatures are shown in Figure 7. The characteristic vibrational modes of AB are indicated in Figure 7a. The spectrum matches well with the ones reported in the literature.^{69–71} The N–H stretches are located at high frequencies located at 3254 and 3316 cm^{-1} , corresponding to the symmetric and asymmetric modes. In the B–H stretching region, two peaks can be located at 2280 and 2381 cm^{-1} . The bending modes of the N–H bonds are located in 1376 (symmetric) and 1605 cm^{-1} (asymmetric). The bending vibrational modes of B–H can be seen at 1160 and 1190 cm^{-1} . Finally, the B–N stretching mode is observed at 780 (asymmetric bending) and 795 cm^{-1} (stretching).

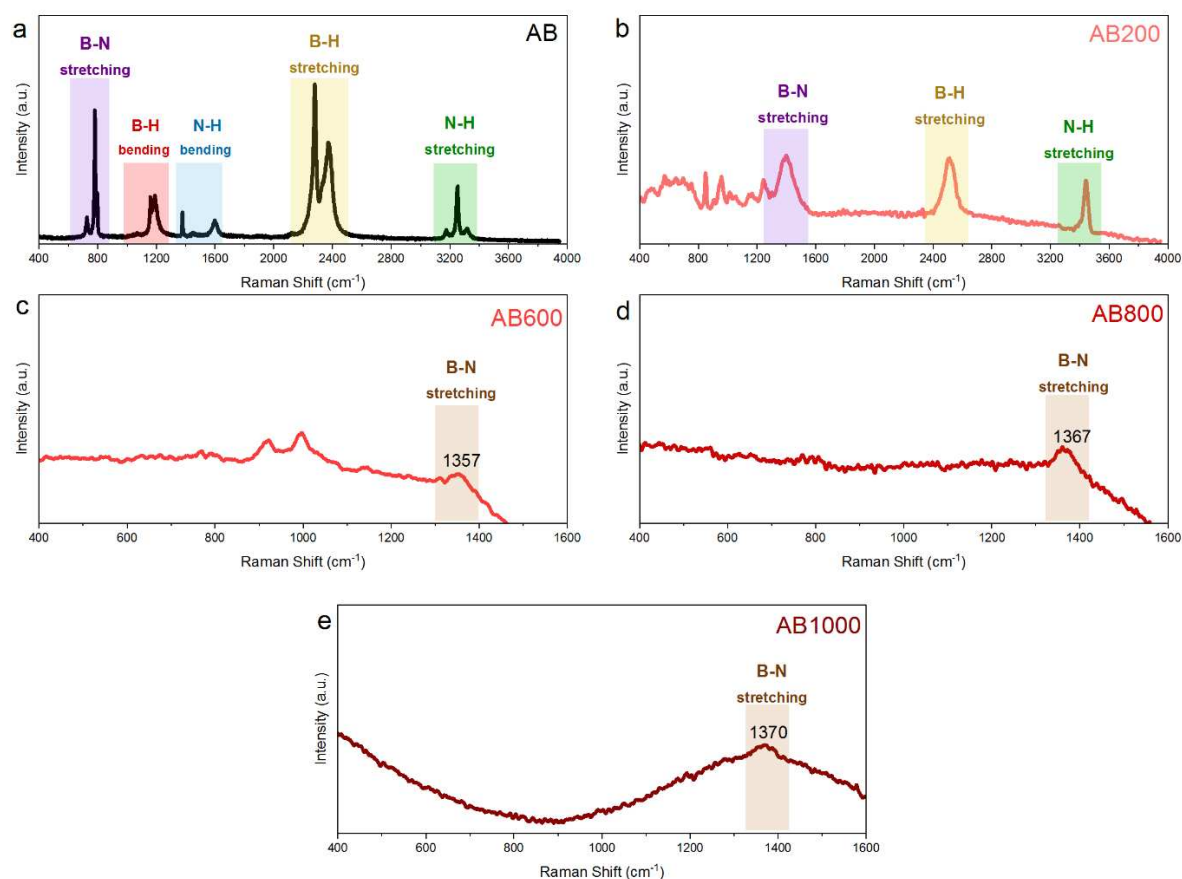


Figure 7. Raman spectra of AB at a) room temperature and pyrolyzed at b) 200°C; c) 600°C; 800°C and 1000°C.

Figure 7b shows the Raman spectrum of AB200. The sharp signal of the B–N bond below 800 cm^{-1} has disappeared. Other signals have appeared below 1000 cm^{-1} , but they do not belong to this vibrational mode. However, a new broad signal appeared at 1390 cm^{-1} , that coincides with the stretch of the B–N graphitic-layered in h-BN.⁷² Each B–H and N–H stretching bands have merged in a single broad signal, and they have shifted to higher frequencies. These bands are characteristic of NH and BH groups (bonded to a single H atom),⁷³ indicating the formation of mostly PB. Figure 7c shows two signals at below 1000 cm^{-1} that belong to B–H, due to an incomplete dehydrogenation. The B–H and N–H bands disappear in Figure 7d and Figure 7e and only a broad signal can be observed at $\sim 1360\text{ cm}^{-1}$, belonging to the stretching B–N bond in boron nitride.

The Raman spectra of LiAB, NaAB and their respective products pyrolysis are presented in Figure 8.

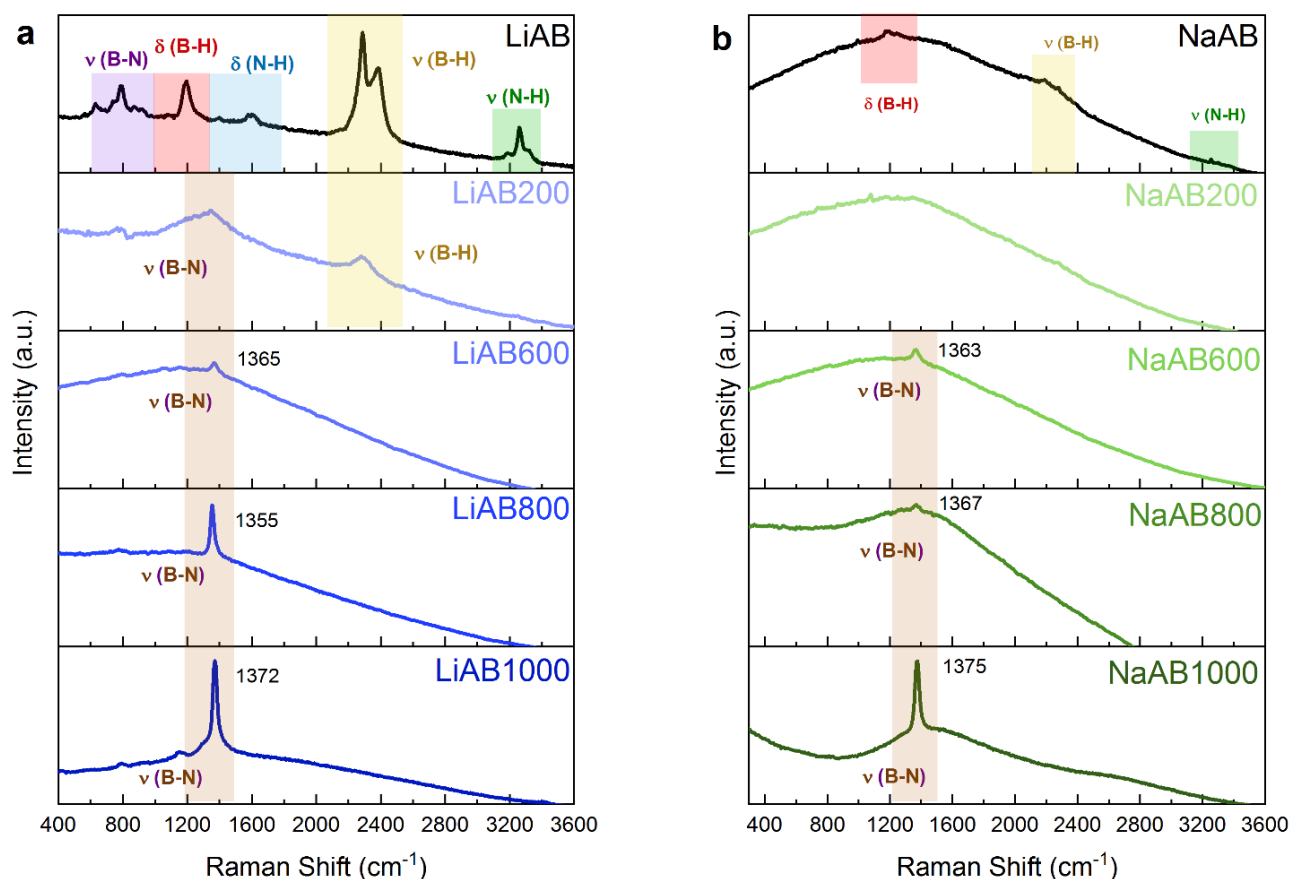
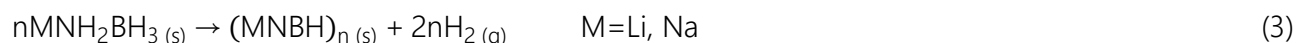


Figure 8. Raman spectra of the alkali amidoboranes and the products after pyrolysis at 200, 600, 800 and 1000°C for a) LiAB and b) NaAB. The vibrational bands of interest have been assigned.

The spectrum of LiAB at room temperature resembles the spectra that have been previously reported.⁶⁵ The spectrum of NaAB is not clearly seen, though poor intense bands can be observed. This phenomenon happens because the fluorescence of the synthesized NaAB could overlap the measured spectrum.

Regarding LiAB200, the B–H stretching band has merged and appears as one single band that has blueshifted (from 2270 to 2290 cm⁻¹). This indicates the evolution from BH₃ species to BH species. The N–H band has disappeared and a broad signal centered at 1300 cm⁻¹ appeared, like the stretching B–N vibrational mode in boron nitride. On the other hand, the poor intense signals have disappeared for NaAB200. It is likely that species such as (LiNBH)_n and (NaNBH)_n have formed, in agreement with the proposed mechanisms for the decomposition of both amidoboranes:⁴⁸



Like AB, the samples of amidoboranes treated at 600, 800 and 1000°C show a single peak in the B–N stretching region associated to h-BN. The peak becomes sharper as the temperature is increased. This characteristic signal (B–N) has been assigned to the E_{2g} vibrational mode within sheets of hexagonal boron nitride. Back in 1981, Nemanich reported that changes in the Raman spectra of BN is related to the crystals grain size of the sample.⁷⁴ There is a correlation between the width broadening (full width at half maximum FWHM) of the peak and the energy of this E_{2g} mode with the average crystal grain size of h-BN. In other words, when the E_{2g} mode shifts to higher frequency and the peak broadens, the average crystal grain size of BN nanoparticles decreases. This relationship has been observed in different BN nanostructures.^{63,75,76} For example, it has been reported that h-BN microcrystals present a signal at 1367 cm⁻¹ with a FWHM of 13 cm⁻¹ (estimated grain size of 33 nm by Equation 4).⁷⁷ In comparison, BN nanothorns and BN nanotubes present a shift to 1370 cm⁻¹ and a FWHM of 28 and 38 cm⁻¹, with a calculated grain size of 27 and 14 nm respectively.

In the case of AB, the E_{2g} vibrational mode is seen as a broad signal, probably because of the formation of amorphous BN. For AB600, this signal is centered at 1357 cm⁻¹ and then it shifts to 1367 cm⁻¹ for AB800 and 1370 cm⁻¹ for AB1000. However, in the case of the amidoboranes the E_{2g} mode starts to appear from 600°C as a sharp peak. In the case of LiAB, there is no clear trend (**Table 4**). The peak is

centered at 1365 cm^{-1} for LiAB600, it shifts to 1355 cm^{-1} for LiAB800 and finally it appears at 1372 cm^{-1} for LiAB1000. However, the FWHM decreases as the temperature increases. Concerning to NaAB, the trend is clear. As the temperature increases, the peak of the E_{2g} mode shifts towards higher frequencies and the FWHM decreases. The trend seen in the FWHM indicates that for both amidoboranes, when the temperature is increased, the crystallite size does too. The Raman analyses shows that a higher degree of crystallization is achieved at lower temperatures in comparison with AB, and that the alkali cation in the amidoborane plays a role in the crystallization of h-BN, as suggested elsewhere.^{76,78} To obtain the average crystallite size, the FWHM was obtained by fitting the E_{2g} peak with a Lorentzian function and using the relation given by Nemanich:⁷⁴

$$\Gamma_{1/2} = \frac{1417}{L_a} + 8.70 \quad (4)$$

Where $\Gamma_{1/2}$ is the full width at half maximum of the Lorentzian curve fitting the band and L_a is the equivalent grain size of the crystal in angstroms.

Table 4. Position of the E_{2g} vibrational mode in the materials, the calculated FWHM and average grain size.

Compound	Raman shift (cm^{-1})	FWHM (cm^{-1})	L_a (nm)
LiAB600	1365	26.9	7.7
LiAB800	1355	24.3	9.1
LiAB1000	1372	23.6	9.5
NaAB600	1363	34.9	5.4
NaAB800	1367	33.6	5.7
NaAB1000	1375	28.3	7.2

3.2.3 Powder X-Ray Diffraction (PXRD)

All samples were analyzed by PXRD. The PXRD patterns of AB and the solid products after heat treatment are presented in Figure 9a. The diffraction pattern of commercial AB matches with the one

reported in literature at ambient temperature.⁷⁹ The crystal structure of AB has been widely investigated,⁵⁴ and at room temperature it has a body-centered tetragonal structure, with a space group *I4mm*. AB200 does not present the peaks of neat AB and the formed species are amorphous, confirming the presence of polymeric compounds such as PB. Two broad signals start to appear at $\sim 26^\circ$ and $\sim 42^\circ$, with a low intensity. As it is observed from AB600 to AB1000, the intensity of these two broad bands starts to increase. h-BN presents diffraction peaks at 26.6° (002 peak), 41.5° , 43.8° , 50.1° , 54.9° and 59.3° . The sample AB1000 presents broad peaks centered at 26° and 42° , corresponding to the signals of h-BN (Figure 9b). This will be discussed later.

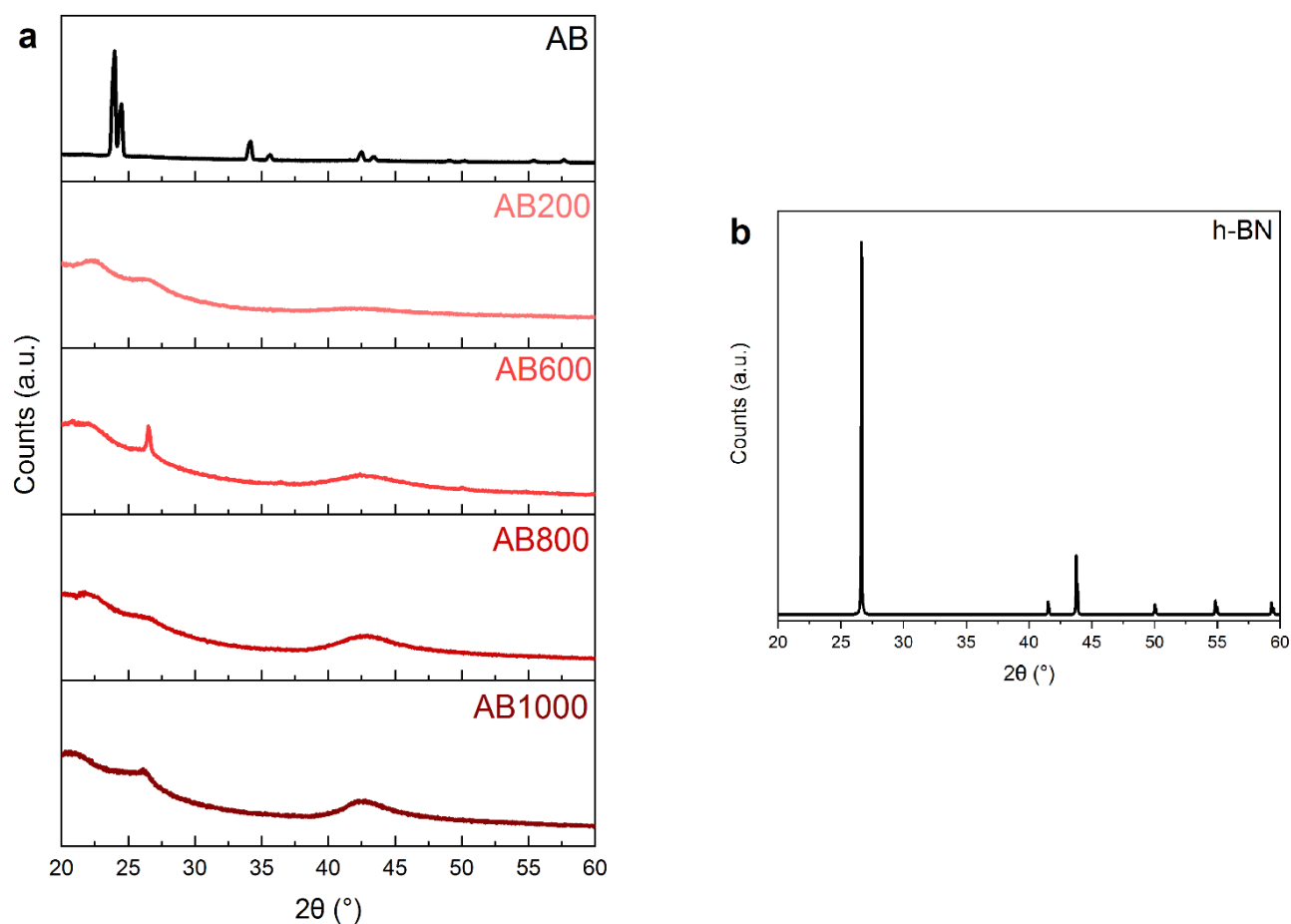


Figure 9. PXRD patterns of a) AB and the solid products after pyrolysis at 200, 600, 800 and 1000°C and b) hexagonal boron nitride.

The PXRD patterns of LiAB and the pyrolyzed samples are presented in Figure 10a. LiAB presents two allotropes: α -LiAB and β -LiAB.^{80–82} They present an orthorhombic unit cell with a *Pbca* space group, but the lattice parameters of β -LiAB are almost twice of α -LiAB. It was reported that the β phase is formed under energetic ball milling and can revert to the α phase after prolonged milling or by recrystallization.⁸¹ The pattern presented in Figure 10a corresponds to β -LiAB.

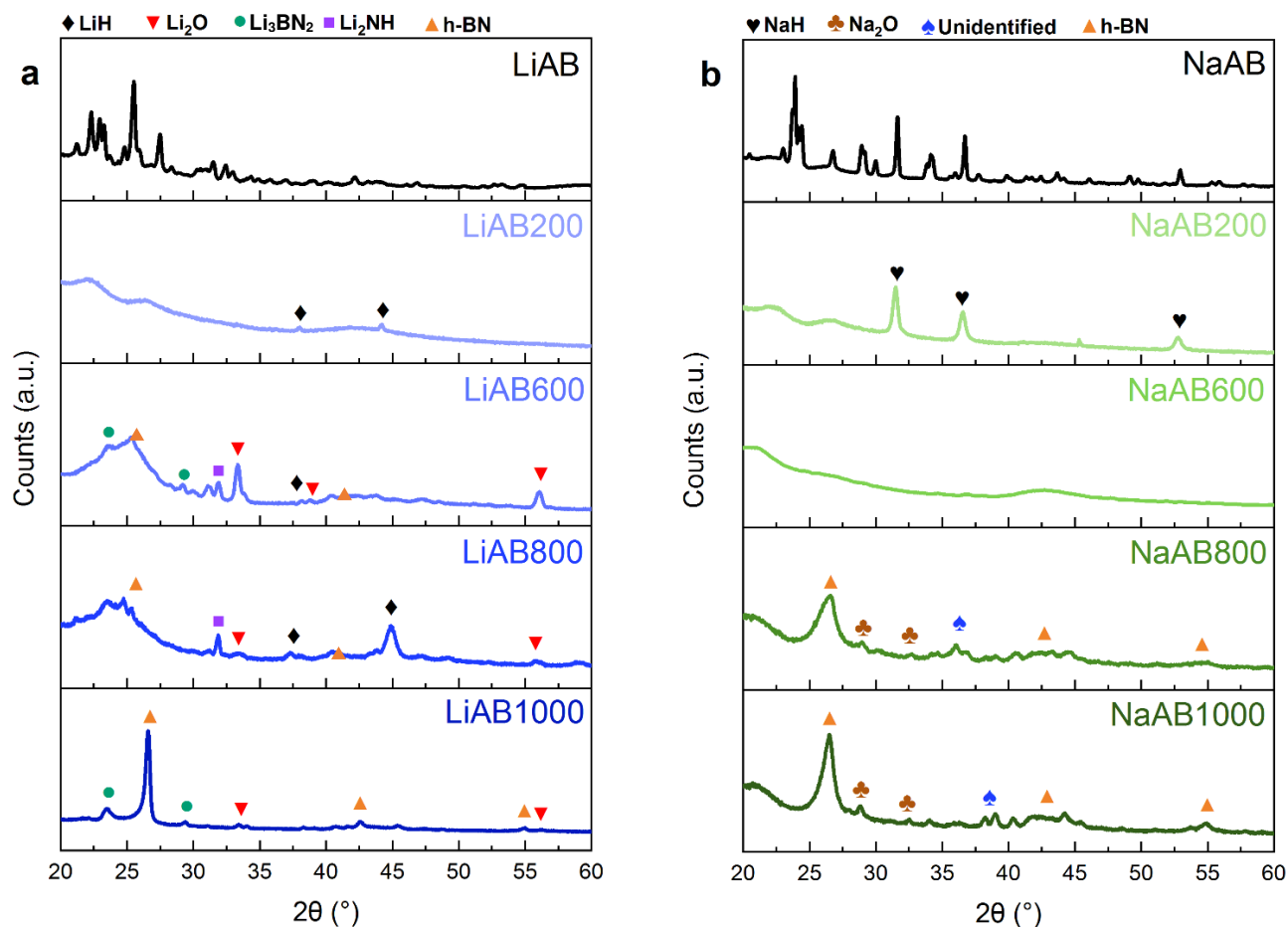


Figure 10. PXRD patterns of the alkali amidoboranes and the solids products treated at 200, 600, 800 and 1000°C for a) LiAB and b) NaAB. The possible byproducts are indicated by the colored figures.

LiAB200 does not present any peaks related to the former LiAB. There are two peaks at 38° and 44°, identified as diffraction peaks of LiH (stable up to ca. 720°C).⁸³ These two small signals can be still

detected for the samples LiAB600 and LiAB800, but they disappear as the other signals become stronger. For LiAB600, LiAB800 and in a minor extent for LiAB1000, other peaks are observed. They have been assigned to possible species that have formed during the pyrolysis of the samples. Li_2O is likely to form if some oxygen entered to the furnace when the sample was introduced, or by impurities in the gas stream. Li_2NH is likely to form between 300 and 450°C, and it is stable up to 750°C, when it can decompose following Equation 5.⁸⁴ Some of the metallic lithium could react to form Li_3N (Equation 6), and further interact with the BN-like structures to form Li_3BN_2 ,⁷⁸ identified by the peaks centered at ~25° and ~28°.



The diffraction pattern of NaAB and the treated samples at different temperatures are shown in Figure 10b. The NaAB patterns matches well with the ones reported in the literature.^{67,85} The presence of unreacted NaH is a recurrent problem in the synthesis of NaAB.^{67,85} NaAB200 is clearly amorphous, with the exception of the peaks of NaH that are clearly seen. Unlike LiAB600, NaAB600 does not show diffraction peaks. In fact, the pattern is more similar to the one of AB600. However, at 800°C, the sample starts to show some diffraction peaks. Finally, at 1000°C the characteristic diffraction peaks of h-BN at 26, 42 and 55° can be observed. The other peaks present in the pattern were assigned to Na_2O and to an unidentified phase. For the latter, it is possible that some intermediates can form before the complete evolution of the sample to BN. For example, when a mixture of NaNH_2 and NaBH_4 is heated at 220°C, Na_2BNH_6 is formed, which would dehydrogenate to form Na_3BN_2 at 600°C. Between 680 and 1100°C, Na_3BN_2 decomposes following the next reaction:⁸⁶



For a better comparison, the respective diffraction patterns of the samples treated at the highest temperature were analyzed (Annex I, Figure A 9). In the case of AB, the relatively low intensity and the broadening of the peaks centered at 26° and 42° implies the formation of thin BN layers and weaker stacking.⁸⁷ Besides, the shift of the 26° peak to lower angles, and the merge of the peaks centered at 42° indicate that the BN phase is poorly crystallized and might present a turbostratic phase,

characterized by graphitic layers stacked nearly parallel with a random orientation.^{44,88–90} Turbostratic boron nitride (t-BN) can be seen as an intermediate between h-BN and amorphous BN; in the past years has received attention due to its properties, such as polymer-like time-dependent deformation characteristics, a wide band gap of 6.0 eV and the incomplete crystallinity.^{91–93}

LiAB1000 and NaAB1000 present the peaks associated to h-BN at 26°, 42°, 55° and 75°.

Table 5 shows the interlayer lattice d , the FWHM and the crystallite size D calculated for the peak centered at 26° for LiAB1000 and NaAB1000, calculated by Equation 8 and by Equation 9 (Scherrer equation).

$$d = \frac{\lambda}{2\sin\theta} \quad (8)$$

$$D = \frac{0.9\lambda}{\beta\cos\theta} \quad (9)$$

Where d is the distance between adjacent layers (in nm), λ is the X-ray wavelength (0.154 nm), θ is the diffraction angle (radians), D is the crystallite size (nm) and β is the FWHM (radians).

Table 5. Diffractogram data for the (002) peak in LiAB1000 and NaAB1000.

Sample	Reflection	2 θ (°)	d (Å)	FWHM (°)	D (nm)
LiAB1000	(002)	26.54	0.335	0.3609	21.1
NaAB1000	(002)	26.48	0.336	0.8470	9.6

The interlayer layer distance for both samples has a close value to the theoretical one calculated for a well crystallized boron nitride (0.333 nm).^{78,94} LiAB1000 and NaAB1000 were also analyzed by HRTEM (Figure 11 and Figure 12). The results obtained are in good agreement with the PXRD results. The interlayer lattice (d) for LiAB1000 was estimated as an average value of 0.344 nm, while the average value for NaAB1000 is 0.343 nm. According to the Selected Area Electron Diffraction pattern, both samples are polycrystalline. NaAB1000 showed different size of crystals, ranging from small crystals of

~17 nm up to larger crystals of more of 30 nm. In concordance with the Raman spectroscopy analyses, this confirms that the alkali cations (Li^+ and Na^+) play a role in the crystallization of h-BN during the pyrolysis of the amidoboranes at lower temperatures than neat AB or PB.

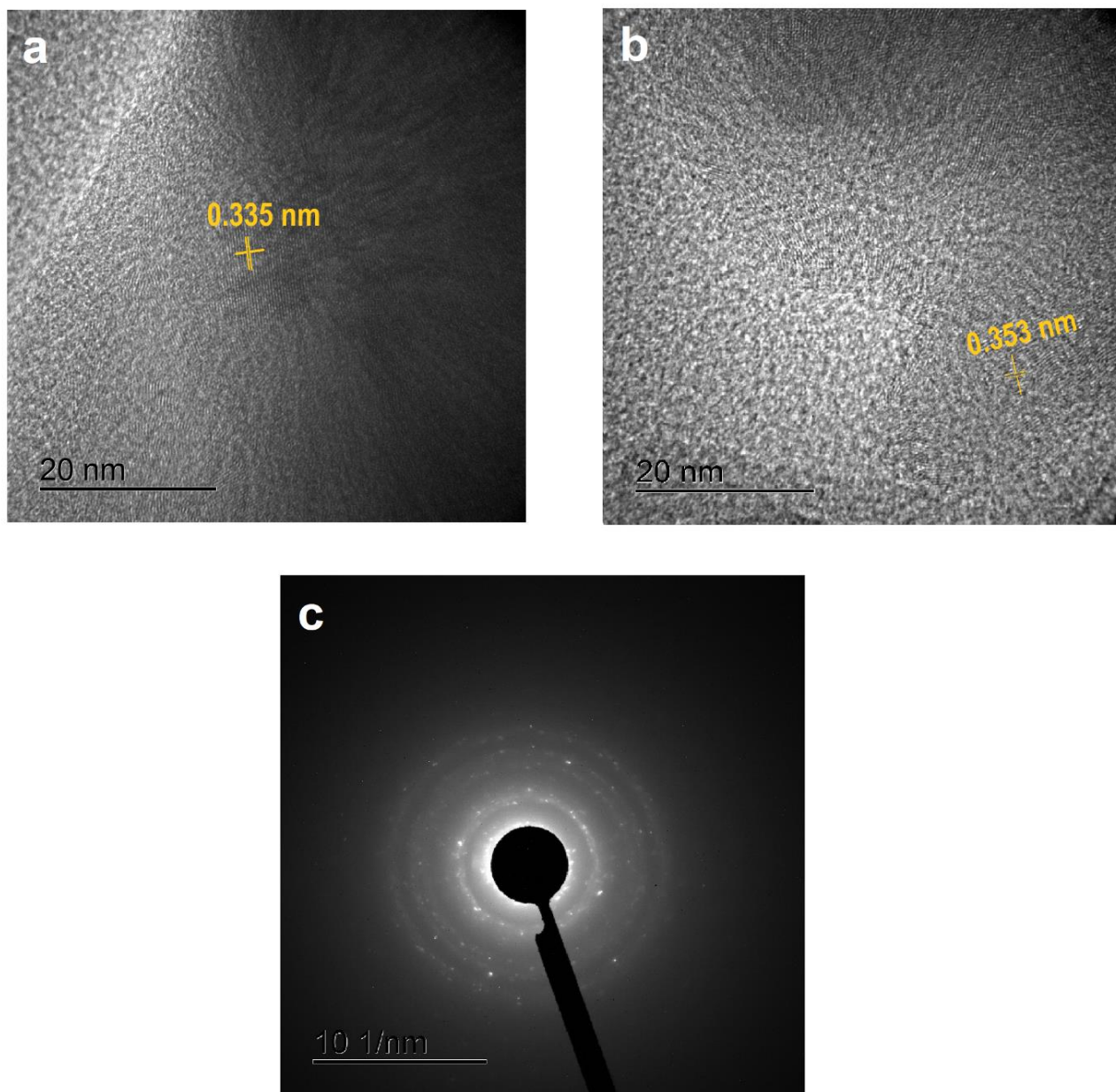


Figure 11. a,b) HRTEM images of LiAB1000 showing the interlayer distance and c) selected area electron diffraction showing a polycrystalline solid.

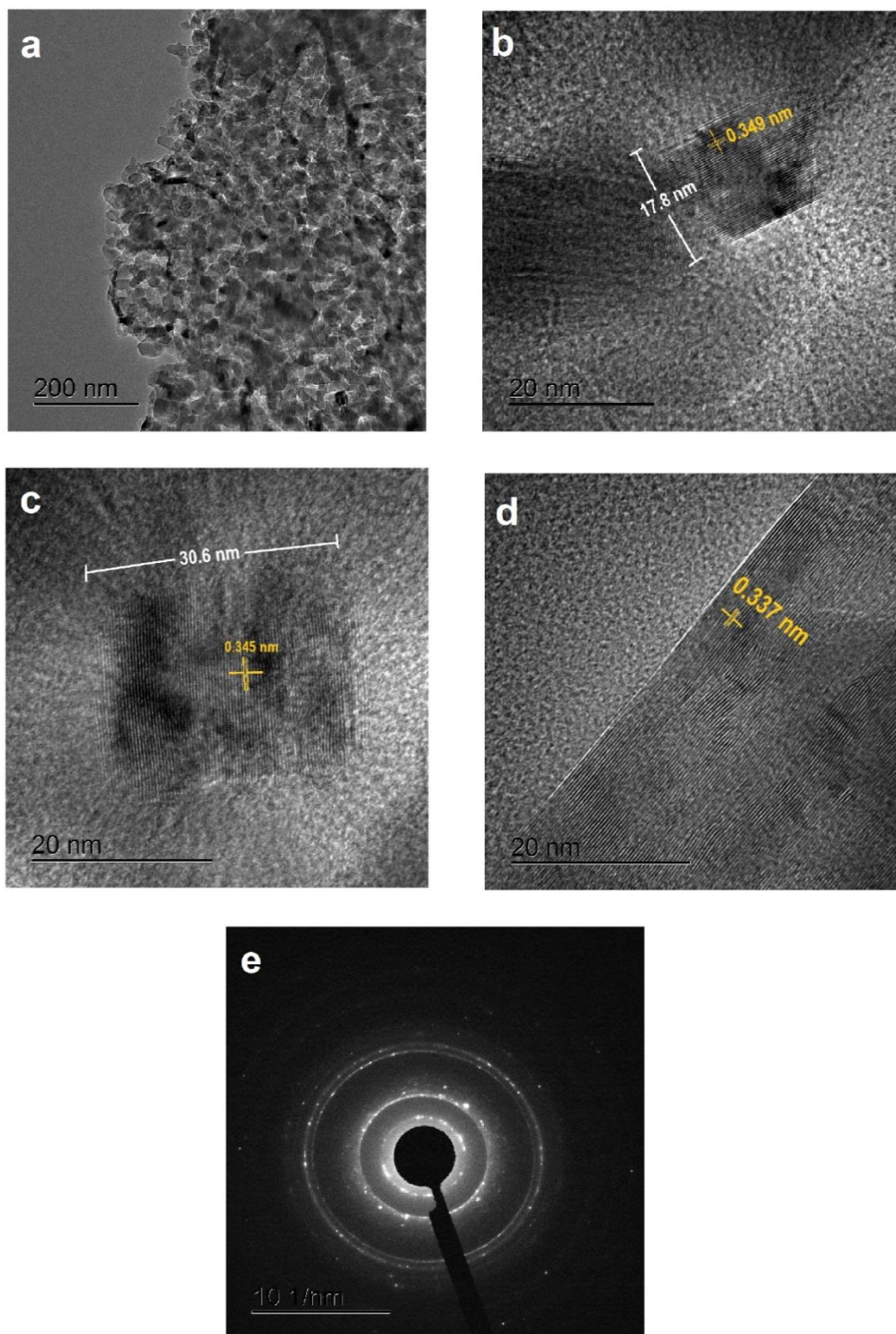


Figure 12. a) Multiple crystals in a particle of NaAB1000; b), c), d) crystals of different size and interlayer distances and e) selected area electron diffraction of NaAB1000 showing a polycrystalline composition.

3.2.4 Magic Angle Spinning Nuclear Magnetic Resonance (MAS NMR)

^{11}B MAS NMR analyses were performed on all samples. **Figure 13** presents the ^{11}B MAS NMR spectra of AB and the solid products after pyrolysis. AB shows a single split-shaped signal at -26 ppm due to the quadrupolar effect of the boron atom.^{95,96} The peak corresponds to a chemical environment NBH_3 .

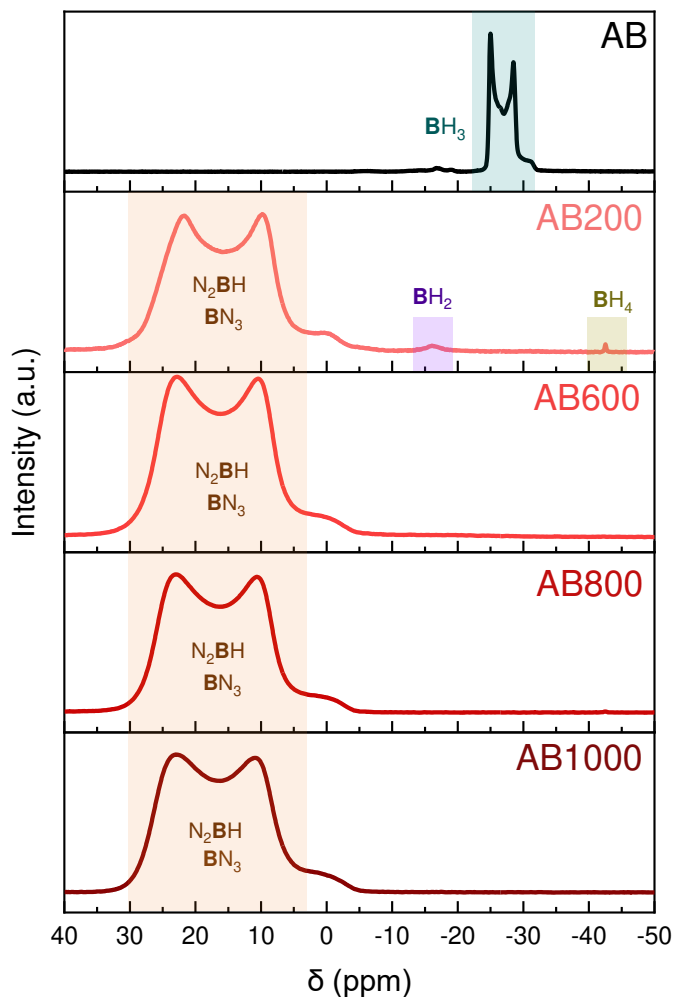


Figure 13. ^{11}B MAS NMR spectra of AB and the solid products heated at 200, 600, 800 and 1000°C.

The chemical environments have been assigned in the colored squares.

In the case of AB200, the environment belonging to NBH_3 has completely disappeared. Three new signals arise. In the negative chemical shifts (tetra-coordinated boron B^{IV}), two signals are present at

-42 and -16 ppm. These peaks are assigned to BH_4 and N_2BH_2 environments. The broad peak of the N_2BH_2 environment indicates that polymerization reactions took place at this temperature and suggests the presence of the ion pair diammoniate of diborane DADB ($[\text{H}_3\text{NBH}_2\text{NH}_3]^+[\text{BH}_4]^-$), DADB-ionic like species (i.e. $[\text{NH}_3\text{BH}_2\text{NH}_2\text{BH}_2\text{NH}_3]^+[\text{BH}_4]^-$) or PAB.^{97–101} In the positive chemical shifts (tri-coordinated boron B^{III}), a broad double shaped signal is observed. Several studies have reported the presence of such signal at above 200°C in the decomposition of AB of B- and N-based polymers,^{102–106} and it indicates BN_3 and N_2BH environments, such as PB. From AB600, all the B^{IV} environments have disappeared, and the signal at positive chemical shifts broadens, and it resembles to the pyrolyzed spectra of PB and boron nitride.¹⁰⁶ The chemical environments assigned for this signal are BN_3 and N_2BH . As the temperature of pyrolysis is high (>600°C), the major part of the hydrogen should have been released and we should expect a major presence of the BN_3 species.

The ^{11}B MAS NMR spectra of LiAB and the solid products at the different temperatures are presented in **Figure 14a**. The synthesized LiAB shows a single peak at -21 ppm, corresponding to a NBH_3 environment.^{48,107} A small signal at -9 ppm indicates the probable evolution of the sample during the MAS NMR analysis that we have observed systematically in our works. In the case of LiAB200, there are four main signals in the spectrum. The two signals at B^{IV} chemical shifts centered at -9 and -42 ppm belong to $\text{N}_2\text{BH}_2/\text{N}_3\text{BH}$ and BH_4 environments, respectively. The N_3BH environment might indicate the formation of a compound close to the formula $\text{LiNBH}_{1.4}$, reported elsewhere.¹⁰⁸ Regarding the N_2BH_2 and BH_4 species, structures analogues to DADB have been reported by computational studies in the case of amidoboranes.¹⁰⁹ LiDADB ($[\text{LiNH}_2\text{BH}_2\text{LiNH}_2]^+[\text{BH}_4]^-$) might explain the appearance of both signals. However, we do not discard the formation of LiBH_4 that can have a contribution for the peak centered at -42 ppm. On the other hand, the broadening of the NBH_3 peak (-22 ppm) indicates an amorphization of the species,¹¹⁰ in concordance with the PXRD pattern of LiAB200. Coiled polymers such as $\text{LiNH}_2\text{BH}_2\text{LiNHBH}_3$ may be the source of the signal.¹⁰⁹ In the B^{III} area, a characteristic quadrupolar line shape is seen and can be assigned to N_2BH and/or N_3B species.^{102,103} This peak is the only signal present in the spectra of LiAB600, LiAB800 and LiAB1000. However, one might notice that the shape of the signal evolves when the temperature is increased (is more symmetric at higher temperatures). In concordance with the previous analyses, this signal indicates the presence of BN.

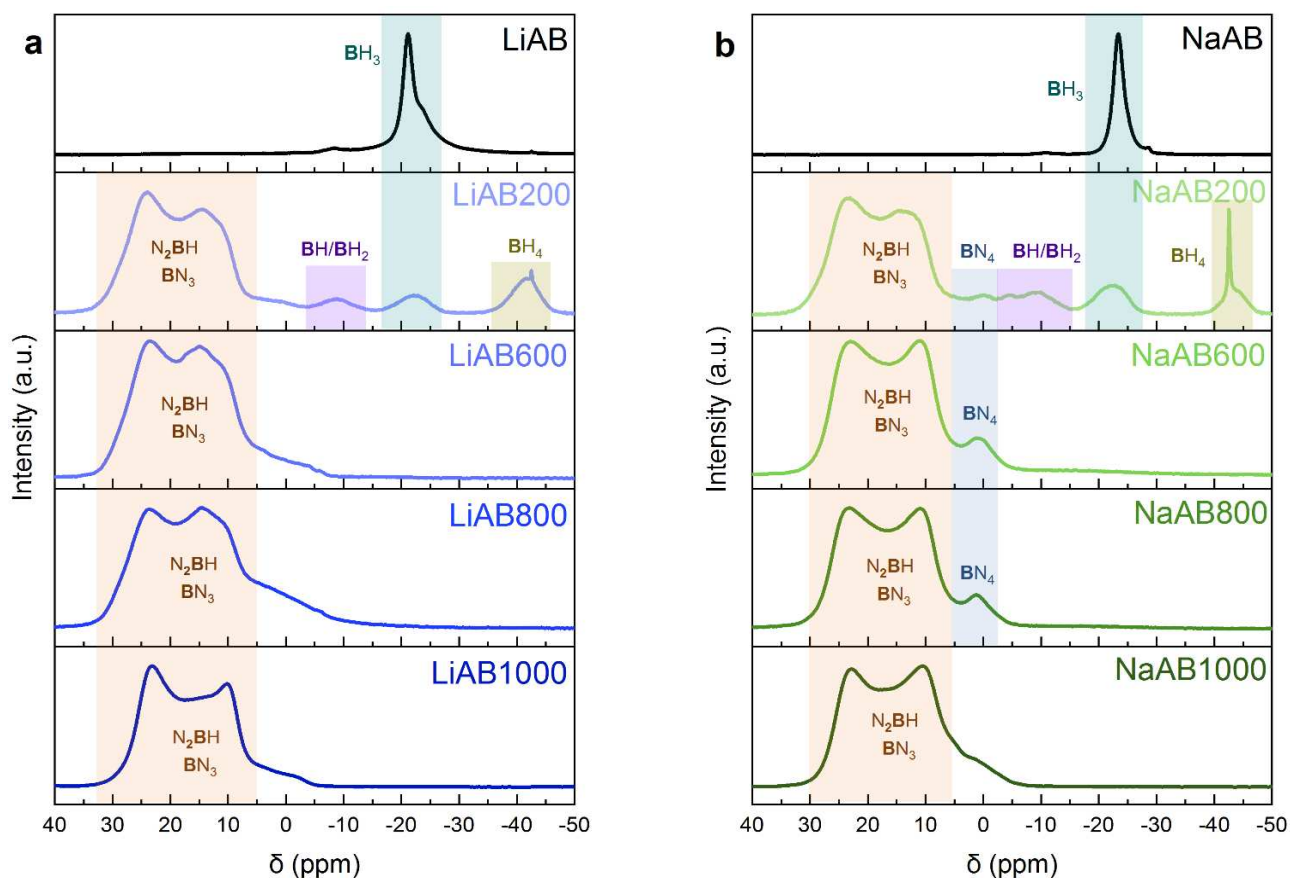


Figure 14. ^{11}B MAS NMR spectra of the alkali amidoboranes and the solid products pyrolyzed at 200, 600, 800 and 1000°C for a) LiAB and b) NaAB. The chemical environments have been assigned in the colored squares.

The spectra of NaAB and the solid products after pyrolysis is shown in **Figure 14b**. NaAB has a single peak centered at -23 ppm indicating the boron site NBH_3 of the amidoborane.^{46,48} The pyrolyzed samples of NaAB present a similar behavior than the ones of LiAB. The NBH_3 peak has broadened for NaAB200, indicating an amorphization of the compound.¹¹¹ Two new signals in the B^{III} area of the spectrum appears (from 0 to -12 ppm) and they belong to $\text{N}_2\text{BH}/\text{NBH}_2$. A BH_4 environment is also present with a peak at -43 ppm indicating the formation of a Na-containing DADB-like species, such as $[\text{NaNH}_2\text{BH}_2\text{NaNH}_2]^+[\text{BH}_4]^-$.¹⁰⁹ The signal at B^{III} sites belongs to $\text{BN}_3/\text{N}_2\text{BH}$ species. This signal is the principal at higher temperatures and the double shape characteristic of the quadrupolar effect in the boron atom is more defined from 600°C. For NaAB600 and NaAB800, the signal at 1 ppm indicates

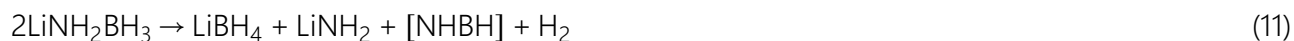
the presence of a BN_4 or BN_xO_y environment. It has been observed that the decomposition of alkali amidoboranes follows a similar path and a general formula was proposed:¹¹⁰



Where the amorphous MNBH phase is formed by the polymerization of $\text{M}^+[\text{NH}_2\text{BH}_3]^-$ molecules, that will finally form a composite of $\text{MH}+\text{BN}$ if the amidoborane is completely dehydrogenated.^{35,110–112}

A quantitative analysis of the ^{11}B MAS NMR was carried out, in order to observe the evolution of boron environments (Annex I, Figure A 10). For AB, almost all the NBH_3 environment (99 %) has been transformed into tri-coordinated boron at 200°C . Only a small fraction of BH_4 and N_2BH_2 is present (0.7 and 0.3 % respectively). This points again that the resulting compound is mostly PIB or PB. The B^{III} signal remains up to 1000°C , in agreement with the two-step dehydrogenation of AB.^{55,113}

Regarding LiAB, 86 % of the sample have transformed to B^{III} species at 200°C . The BH_4 species are present in an 8 %. As the N_2BH_2 is present in 2.1 %, the formation of a DADB-analogue species is confirmed. The higher proportion of BH_4 suggests the presence of amorphous LiBH_4 (as the PXRD pattern of LiAB200 did not show any peaks belonging to the borohydride). From 600°C , the only environment present is the B^{III} species. A tentative reaction is proposed and it can occur at high temperature (Equation 11).¹¹⁰ This would also explain the Li_2NH peaks identified in the PXRD analyses.



For NaAB200, 76 % of the species have converted to B^{III} species. The percentage of BH_4 species in NaAB (5.7 %) is lower in comparison with LiAB. However, the quantities of NBH_3 and $\text{N}_2\text{BH}_2/\text{N}_3\text{BH}$ are higher than for LiAB (7 and 11.3 % vs. 3.8 and 2.1 %). This might indicate the presence of more branched structures to compensate the NBH_3 species.¹¹⁰ There are some differences in the percentages obtained in this work and the ones reported in the literature.^{110,111} This suggests that the conditions of heat treatment have an impact in the final composition of the pyrolyzed products. In order to have a better overview in the possible formed species during the pyrolysis of AB, LiAB and NaAB, a recapitulative of proven and suggested compounds found in the literature is presented in **Figure 15**, according to the different chemical environments detected in the ^{11}B MAS NMR analyses.

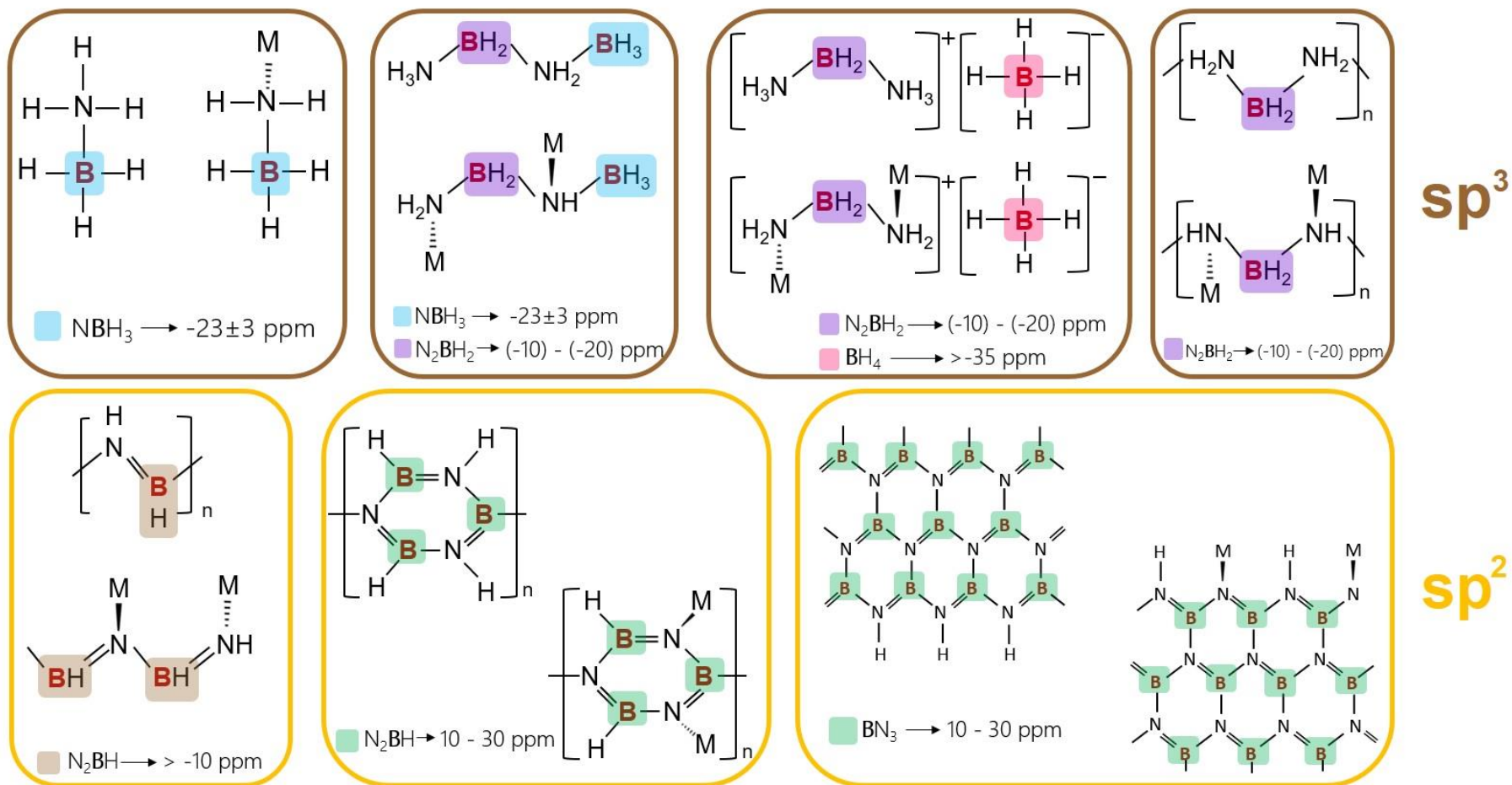


Figure 15. Possible compounds formed during the decomposition of AB, LiAB and NaAB ($M=Li, Na$) according to the ^{11}B MAS NMR spectra and reported in the literature.^{35,55,103,104,109,114–118} The brown squares indicate a sp^3 hybridization of the B atom (B^{IV}) and the yellow ones, a sp^2 hybridization (B^{III}). The boron environments are indicated in colored squares: blue for NBH_3 , purple for N_2BH_2 , red for BH_4 , brown for linear N_2BH and green for cyclic N_2BH or BN_3 .

3.2.5 X-Ray Photoelectron Spectroscopy (XPS)

The pyrolyzed samples of AB were analyzed by XPS and the spectra for B 1s and N 1s are shown in Figure 16. The B 1s spectra for every compound was deconvoluted in two signals (Figure 16a). The peak at 190.2 eV in AB200 is assigned to a B–N bonding in disordered BN,¹¹⁹ and the shift of this peak to higher energies is an evidence of the formation of h-BN,¹²⁰ in agreement with the PXRD analyses. The second peak is assigned to $B_xN_yO_z$ species.^{121–124} The peak related to $B_xN_yO_z$ has been reported before and is attributed to a substitutional oxygen in the place of a nitrogen atom. The shift of the binding energy might depend on the atoms bonded to boron (i.e. BNO_2 or BN_2O).^{124,125} However, we do not know if the oxygen comes from impurities during the pyrolysis or while performing the XPS analyses. The latter can happen because the samples are handed over 3 days before the analysis; besides, we are not aware if the samples were strictly handled under inert atmosphere all the time.

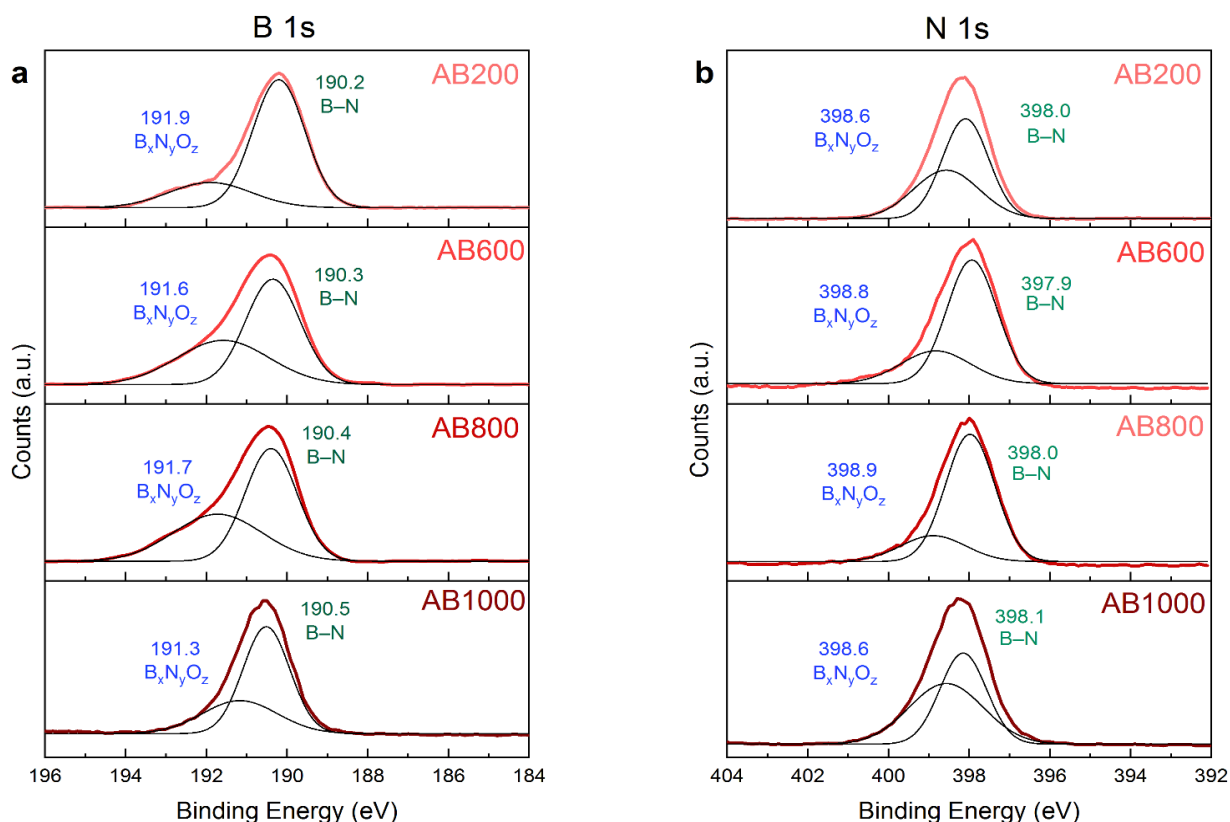


Figure 16. XPS spectra of AB and the solid products after pyrolysis at 200, 600, 800 and 1000°C for a) B 1s and b) N 1s. Component peaks were deconvoluted using a Gaussian fit.

Figure 16b shows the N 1s spectra of the pyrolyzed samples for AB. All curves were deconvoluted in two signals. The peak centered at 398.0 eV (± 0.1 eV) is assigned to the N–B bond that correspond for borazine-like species at 200°C, and for boron nitride at higher temperatures.^{119,126} The second deconvoluted signal, centered at 398.8 eV (± 0.3 eV) is assigned to the $B_xN_yO_z$ species.¹²²

The B 1s XPS spectra of LiAB, NaAB and the respective pyrolyzed samples are shown in Figure 17. Pristine LiAB and NaAB spectra show two deconvoluted signals. The peak at ~ 188.3 eV is assigned to B–H bonds.¹²⁷ The presence of the signal at ~ 191.4 eV assigned to $B_xN_yO_z$ might suggest the partial hydrolysis of the BH_3 moiety when the samples are exposed to air during the XPS analysis. Amidoborane salts are highly sensitive to moisture and humidity.⁶⁵

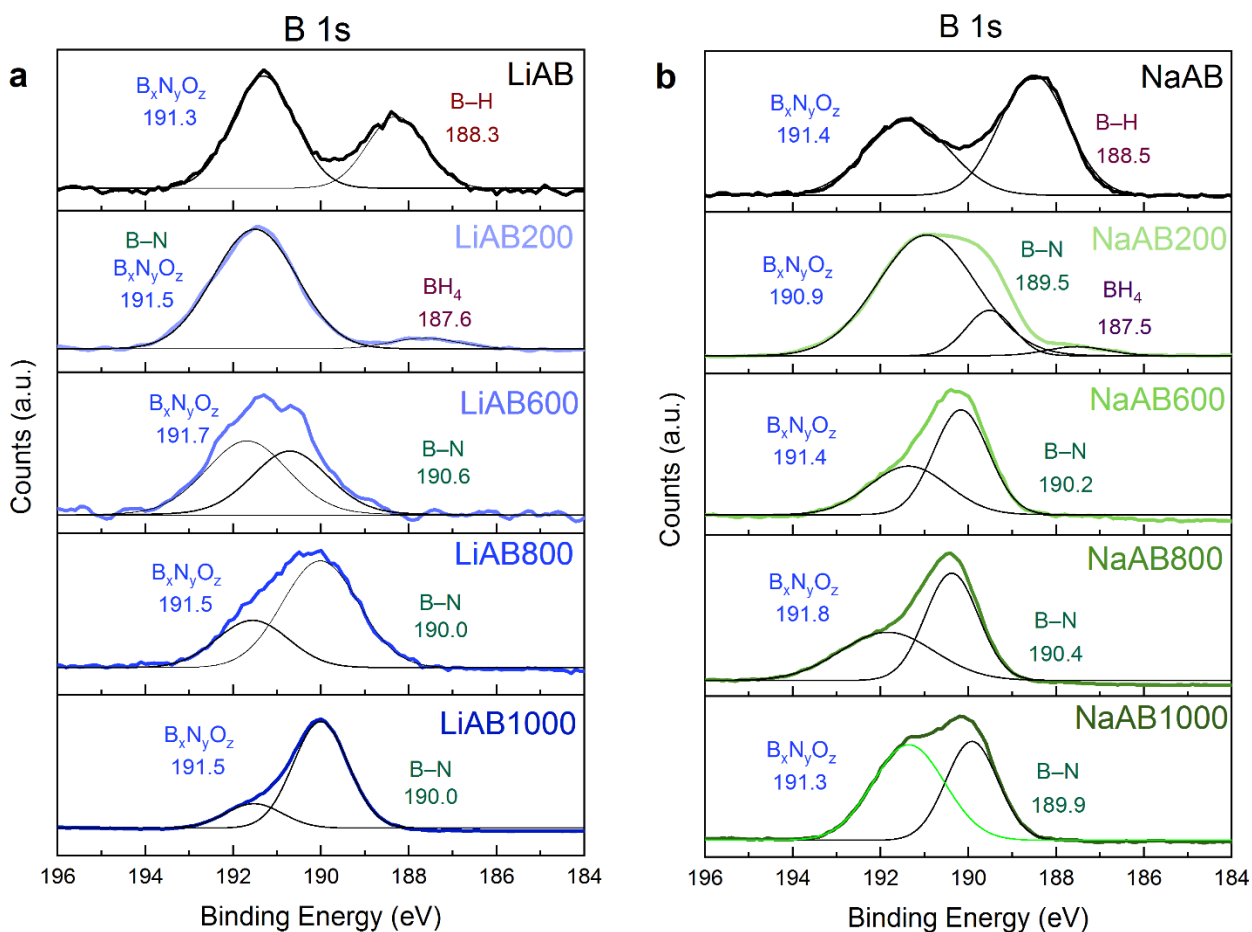


Figure 17. B 1s XPS spectra of the amidoboranes and the solid products after pyrolysis at 200, 600, 800 and 1000°C for a) LiAB and b) NaAB. Component peaks were deconvoluted using a Gaussian fit.

LiAB200 and NaAB200 show a small signal that appeared at ~ 187.5 eV that might indicate the formation of BH_4 -containing species, such as NaBH_4 , LiBH_4 or the DADB-like structures.¹²⁸ This result is in good agreement with the BH_4 environment identified by ^{11}B MAS NMR for the same samples. In the case of LiAB200, a broad band centered at 191.5 eV is observed. It is possible that LiAB200 oxidizes rapidly in contact with air, and this big signal (related to $\text{B}_x\text{N}_y\text{O}_z$ species) overlaps the expected B–N peak at ~ 190 eV. For NaAB200, the two signals are visible: one at 189.5 eV assigned to the B–N species and other at 190.9 eV, which belongs to the $\text{B}_x\text{N}_y\text{O}_z$. Both LiAB and NaAB treated at 600, 800 and 1000°C present two signals. The one at ~ 190 eV is characteristic of the B–N bond in boron nitride-like structures.^{129,130} Also, for all the samples the $\text{B}_x\text{N}_y\text{O}_z$ signal is present at ~ 191.5 eV. However, for NaAB1000, this signal is as intense as the B–N one. This is probably due to O_2 contamination during the pyrolysis process at 1000°C, and the higher sensitivity of NaAB towards water, as observed in the FTIR spectra through the formation of NaOH during the analysis.

Regarding the N 1s, the spectra of the compounds are shown in Figure 18. Both LiAB and NaAB show a peak centered at ~ 399.5 eV, that is assigned to the N–H bond. When the materials are pyrolyzed at 200°C, the spectra was deconvoluted in two signals: one centered at ~ 397.4 eV that is assigned to the N–B bond, and the one at ~ 398.8 eV that is assigned to $\text{B}_x\text{N}_y\text{O}_z$.¹²⁴ However, we do not discard that the bonds N–Li or N–Na can have a contribution to the signal for each one of the amidoboranes.¹²⁹ In the case of LiAB, the sample treated at 600°C starts to show one peak centered at ~ 398 eV, that is assigned to the N–B bond. As the temperature is increased to 1000°C, this signal can be better appreciated. The other signal assigned to the $\text{B}_x\text{N}_y\text{O}_z$ species is still present. The same happens with the NaAB-derived samples. In both cases, it is noticeable that from 200 to 600°C, the binding energy of the N–B bond shifts from ~ 397.3 to ~ 397.8 eV.

The XPS analyses demonstrate that BN is formed through the thermolysis of AB, LiAB and NaAB. However, the identification of $\text{B}_x\text{N}_y\text{O}$ indicates that oxygen is systematically introduced in the BN matrix, either for contamination while the pyrolysis takes place, and/or during the XPS analyses. However, as XPS analyzes only the surface material, it is difficult to determine the exact reason. The doping of BN structures with oxygen has been suggested as a way to improve the sorption capacities of boron nitride.¹³¹ Nevertheless, there is a lack of information in order to do a proper comparison of

free-oxygen BN and O-doped BN. The XPS survey of all the samples can be found in the Annex I, Figures A11 to A13.

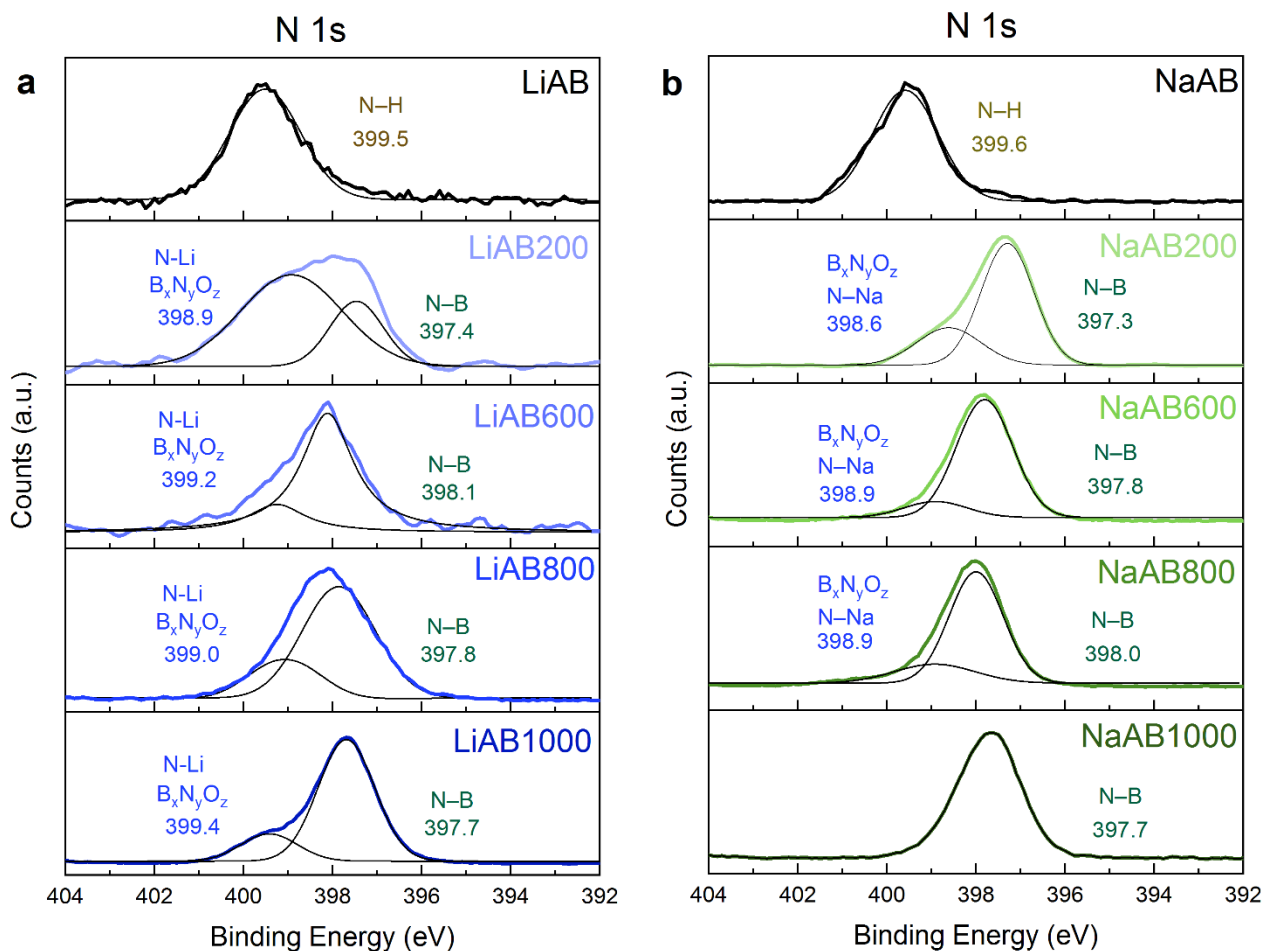


Figure 18. N 1s XPS spectra of the amidoboranes and the solid products after pyrolysis at 200, 600, 800 and 1000°C for a) LiAB and b) NaAB. Component peaks were deconvoluted using a Gaussian fit.

3.3 Information about the Li and Na elements

3.3.1 ^7Li MAS NMR

The pyrolyzed samples derived from LiAB were analyzed by ^7Li MAS NMR, and the spectra is shown in Figure 19. LiAB shows a broad signal centered at 2.36 ppm that can be assigned to the LiNH_2BH_3

environment. LiAB200 shows a peak centered at 0.1 ppm. In another work, a mixture of AB and LiH was analyzed by ^7Li MAS NMR and a single broad peak appeared at 1.5 ppm.¹¹⁴ After dehydrogenation at 95°C of the AB/LiH mixture, this peak shifted to 1 ppm. The shift was related to the removal of hydrogen from LiNH_2BH_3 , due to the reduction of the electronegativity of the N atom and the increase of the electron density on the Li atom. In agreement, in our case the original peak at 2.4 ppm of LiAB shifted to 0.1 ppm. In the case of LiAB600, LiAB800 and LiAB1000, a broad signal appears centered at 2.2 ppm. This might indicate a compound with a tentative formula $(\text{LiNBH}_x)_n$ ($x \leq 2$). For comparison, LiNH_2 presents a signal at ~ 2.4 ppm in ^7Li MAS NMR.^{132–134} LiAB800 presents also two other peaks in the spectrum: one at -0.3 ppm and another at -5.5 ppm. LiH presents a peak at 0.5 ppm,¹³² so the first signal might belong to a dehydrogenated species of LiH. The peak at -5.5 ppm could not being assigned. Due to the lack of a database for these compounds, especially for ^7Li MAS NMR, no conclusive identification of these bands can be done at this point.

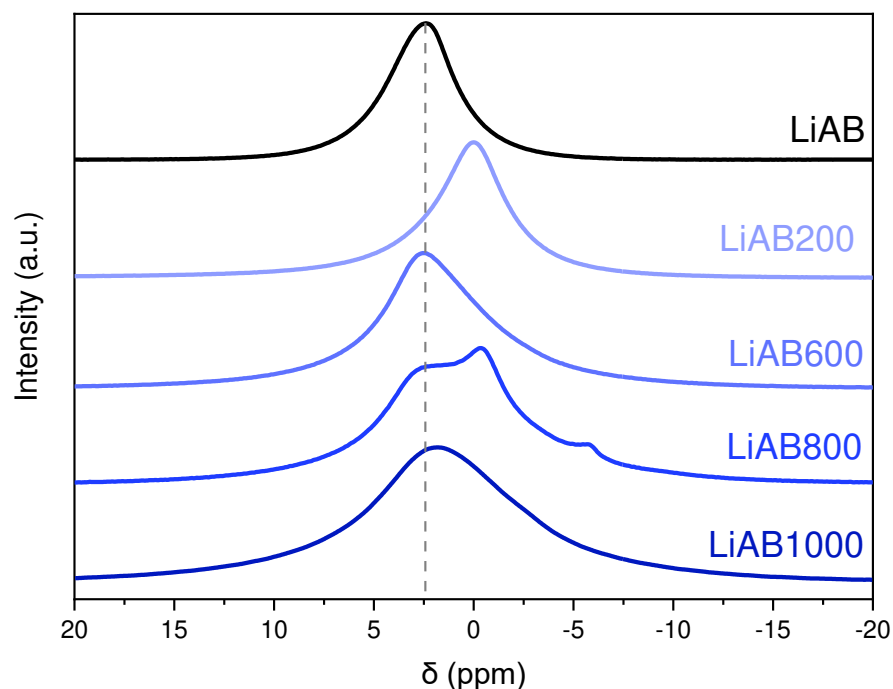


Figure 19. ^7Li MAS NMR spectra for LiAB and the solid products recovered after pyrolysis at 200, 600, 800 and 1000°C.

3.3.2 ^{23}Na MAS NMR

NaAB and the pyrolyzed products were investigated by ^{23}Na MAS NMR (Figure 20). For all samples there is one sharp signal at ~ 18 ppm, corresponding to NaH.^{111,134,135} The broad signal seen at negative chemical shifts belongs to the Na site in NaNH_2BH_3 ; broadened because of the amorphization of NaAB due to the effect of the temperature. In the case of NaAB800 a new peak was observed at ~ 1130 ppm (insert on Figure 20) that is attributed to the formation of metallic Na due to the decomposition of NaH,¹¹¹ or by the reaction proposed in Equation 7 in section 3.2.3. In the case of NaAB1000, a new signal appeared at -1.5 ppm and it might indicate a Na site in a boron nitride-like structure. The formation of NaH during the decomposition of NaAB is explained by the formation of an unstable intermediate following the next mechanism:¹¹⁷

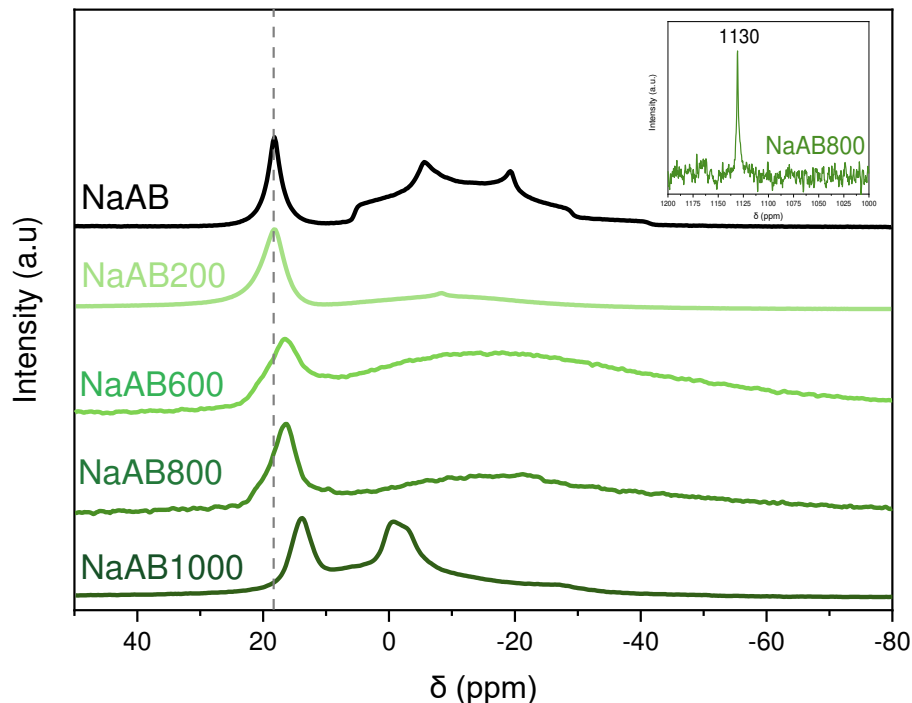
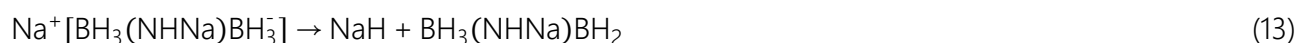
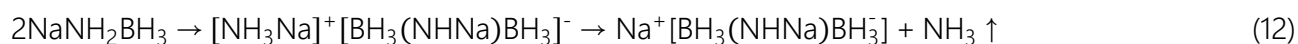


Figure 20. ^{23}Na MAS NMR spectra for NaAB and the solid products recovered after pyrolysis at 200, 600, 800 and 1000°C.

3.3.3 XPS

LiAB, NaAB and the pyrolyzed samples were analyzed by XPS for the Li 1s and Na 1s atoms. The spectra are presented in **Figure 21**.

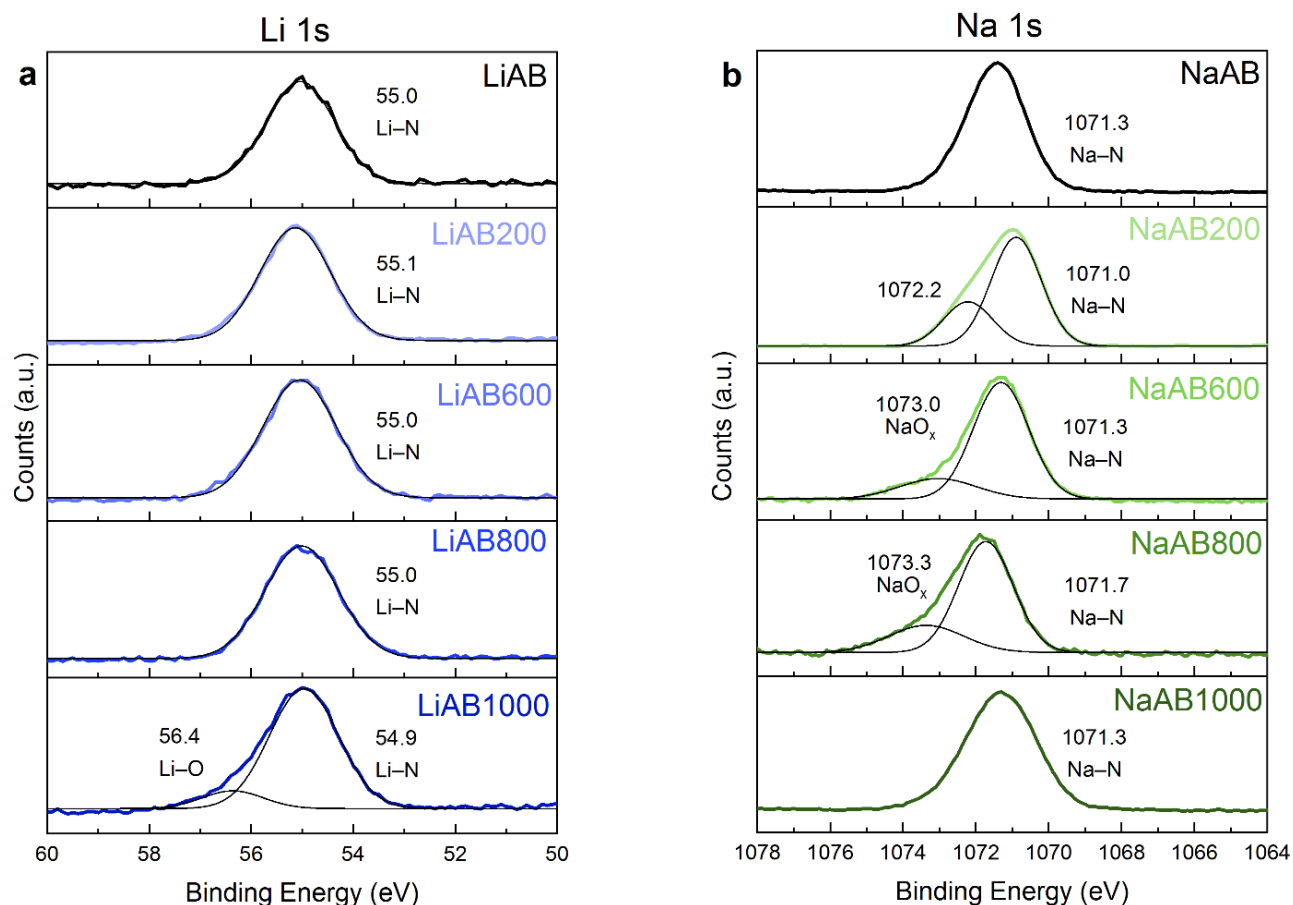


Figure 21. XPS spectra of the amidoboranes and the solid products after pyrolysis at 200, 600, 800 and 1000°C of a) Li 1s for LiAB and b) Na 1s for NaAB.

The spectrum of LiAB shows a broad symmetric signal at 55.0 eV that is assigned to the Li-N bond. As the temperature increases, this peak does not change. LiAB1000 shows a small shoulder at 56.4 eV that is assigned to a Li-O bond,¹²⁹ which can be present due to a partial oxidation of metallic Li.

The spectrum of NaAB presents a broad symmetric signal centered at 1071.3 eV that is assigned to the Na–N bond. As LiAB, this peak lasts for all samples up to the heat treatment of 1000°C. NaAB200 present an unidentified peak at 1072.2 eV. NaAB600 and NaAB800 present another signal at 1073.0 eV (± 0.3 eV) that might indicate the oxidation of some metallic sodium formed during the heat treatment (as evidenced by the MAS NMR analysis). We do not discard the presence of some metallic sodium in NaAB800 (detected by ^{23}Na MAS NMR), but this signal (expected at ~ 1071.8 eV)⁶⁸ can be overlapping with the **Na–N** broad peak.

In any case, the MAS NMR and XPS analyses confirm the previous results about the formation of different species during the thermolysis of the alkali amidoboranes, like oxides due to the presence of air, or even the formation of pure elements, like Na.

3.4 Carbon dioxide sorption properties

The CO₂ sorption capacity of the samples was investigated for all the pyrolyzed samples. All of them were exposed for 3 h to CO₂ at 1.5 bar. As reference, we measured the CO₂ capture capacity of commercial silica (Silica SBA-15, mesostructured, 99 % trace metal basis, Sigma-Aldrich) in our system. A value of 5.7 cm³ g⁻¹ was obtained. We found a reported value of 6.1 cm³ g⁻¹ at 30°C and ambient pressure in the literature.¹³⁶ The results of the pyrolyzed samples of AB, LiAB and NaAB are presented in Table 6 and Figure 22. As reference, the sorption properties of different materials are presented in Table 7. The CO₂ sorption capacities are also presented in different units in the Annex I, Table A 1.

Table 6. Estimated CO₂ sorption capacity (cm³ g⁻¹) by the materials studied in this work at 1.5 bar and 30°C.

	AB	LiAB	NaAB
200°C	8.0	4.4	3.8
600°C	23.6	3.1	16.7
800°C	15.2	4.5	8.0
1000°C	18.9	3.8	7.6

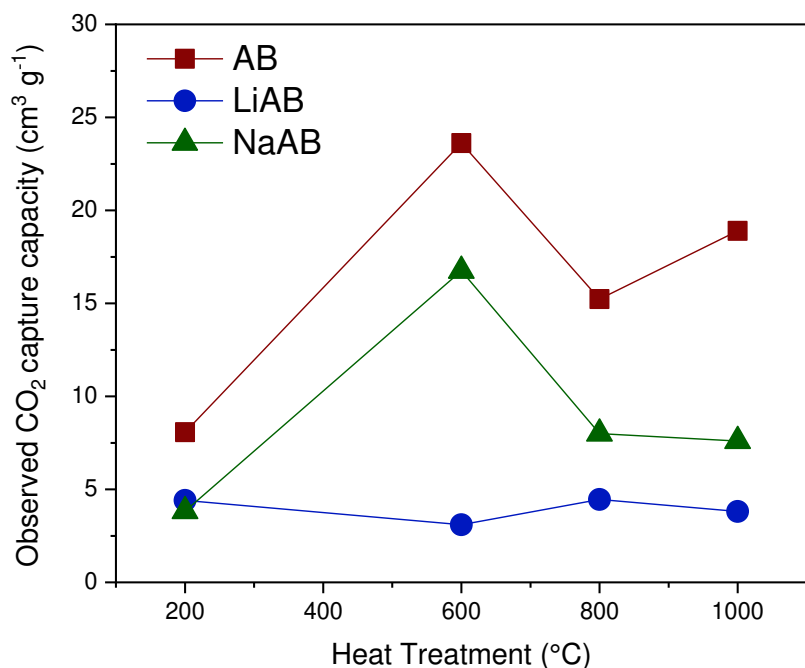


Figure 22. Estimated CO₂ sorption capacity (cm³ g⁻¹) of the pyrolyzed samples of AB, LiAB and NaAB, at 1.5 bar and 30°C.

As it can be observed, the samples treated at 200°C do not present a high uptake of CO₂. As evidenced by the ¹¹B MAS NMR analysis, all samples present the **BN**₃ and **BN**₂H environments. However, AB₂₀₀ presents **BH**₂ and **BH**₄ environments, meanwhile LiAB₂₀₀ and NaAB₂₀₀ present **BH**₄, **BH**₃, **BH**₂ and **BH** environments. The presence of all the different intermediates that provoke these signals (i.e. DADB, PAB) might have an impact in the global uptake of CO₂, inhibiting the sorption capacity of the materials at 200°C. It is likely that having a mixture of different boron- and nitrogen-based polymers does not favor the sorption of CO₂ by the samples. At this temperature, LiAB₂₀₀ and NaAB₂₀₀ present similar uptake values; however, AB₂₀₀ presents the highest value.

With the heat treatment at 600°C, AB and NaAB present an increase on the capacity of CO₂ uptake. The increment of the uptake capacity of AB₆₀₀ is almost 3 times the one of AB₂₀₀. NaAB also increases the value in 4.4 times, passing from 3.8 to 16.7 cm³ g⁻¹. This could be related to the low degree of crystallinity showed by both samples in the PXRD analysis. On the other hand, LiAB₆₀₀

shows poor results increasing the uptake in only 1.2 times in comparison with LiAB200. In fact, the CO₂ uptake capacity shown by the LiAB-derived samples is in general poor. In fact, the values found in this work for the LiAB-derived samples are close to the ones reported for h-BN.²⁴ The results of PXRD for the LiAB samples showed crystallinity from 600°C and this might be related with the sorption capacity of these samples. In any case, the values found in here are higher than the one of h-BN (1 bar, 25°C), suggesting that the Li atom might be enhancing the CO₂ capture properties of the material.

Table 7. CO₂ uptake by different materials. Adapted and completed from reference ¹⁹.

Material	Temperature (°C)	Pressure (bar)	CO ₂ uptake (cm ³ g ⁻¹)	Ref.
Sphere functionalized BN nanosheets/ZnO	0	1	63.4	19
Sphere functionalized BN nanosheets/ZnO	25	1	40	19
Cubic functionalized BN nanosheets/ZnO	0	1	27.8	19
Cubic functionalized BN nanosheets/ZnO	25	1	16.6	19
3D flower-like BN nanosheets	0	1	37.9	24
3D flower-like BN nanosheets	25	1	19.2	24
h-BN	0	1	3.3	24
h-BN	25	1	1.7	24
BN nanosheets	0	1	~16	25
BN nanosheets	25	1	~10	25
Cu-loaded BN nanofibers	0	1	62	22
Polyethyleneimine functionalized BN nanosheets	120	1	69.9	21
P123 ^a modified porous BN	25	1	60.2	20
Pristine porous BN	25	1	44.8	20
SBA-15 mesostructured silica	45	1	10	26
SBA-15 mesostructured silica (commercial)	30	1	5.7	136
SBA-15 functionalized with polyethyleneimine	40	1	31.3	137
Metal Organic Framework NJU-Bai20	25	1	68.0	138
Covalent Organic Framework FCTF-1	25	1	71.9	139

^a Pluronic triblock copolymer surfactant

At 800°C the CO₂ capture capacity of the AB and NaAB pyrolyzed samples decreases. At 1000°C the uptake increases for AB and decreases for NaAB. It is clear that AB presented the highest CO₂ uptake values: AB600 presented the maximum uptake, and this might be related to its amorphous structure (Figure 9). The same is observed for NaAB600; however, the sorption capacity of NaAB800 and NaAB1000 decreased, which coincides with the apparition of the diffraction peaks of h-BN in the PXRD analysis, as observed on Figure 10b. In the case of the LiAB-derived samples, the diffraction peaks were observed from 600°C (Figure 10a), which might be related with the lower values of CO₂ uptake. Nevertheless, all the pyrolyzed samples of LiAB and NaAB show a higher CO₂ uptake than the one reported for bulk h-BN (1.7 cm³ g⁻¹), indicating that the incorporation of an alkali element in the material enhance the CO₂ uptake.

At this point, the results suggest a relation between the crystallinity and the CO₂ sorption capacity of the samples. This could be related to the crystalline conformation of the BN structures. For example, if the AB-derived samples pyrolyzed between 600 and 1000°C mainly have a turbostratic structure, the impurities, incomplete bonds and large surface area characteristics of t-BN might explain the high CO₂ uptake values.⁸⁸ The random orientation of the layers, the defects and the vacancies in t-BN may favor the sorption of CO₂. In comparison, the pyrolysis of both amidoboranes led to a higher degree of crystallinity, and this is reflected in their lower CO₂ uptake. It is likely that a material with random layers conformation would present better sorption properties.

4. Conclusions

Two alkali derivatives of ammonia borane, lithium amidoborane LiNH₂BH₃ (LiAB) and sodium amidoborane NaNH₂BH₃ were studied as precursors of boron nitride for the first time. The synthesis, pyrolysis and characterization of these compounds were performed and compared with the former ammonia borane. All the characterization techniques used in this study confirmed the successful formation of crystalline hexagonal boron nitride from both amidoboranes. At low temperatures, AB, LiAB nor NaAB show any crystallinity, and their composition is mostly amorphous boron- and nitrogen-based polymers. However, at 600°C LiAB started to show the formation of crystalline BN evidenced by PXRD and Raman spectroscopy. The formation of crystalline BN was also detected in

the case of NaAB from 800°C. When the amidoboranes were treated at 1000°C, the presence of hexagonal boron nitride is more evident. In comparison, AB did not show any crystallinity up to 1000°C. This leads us to conclude that the amidoboranes can be used as precursors of crystalline BN. Also, that the alkali cation has an impact in the crystallization of BN. In our study, the LiAB-derived samples presented crystallinity at lower temperatures in comparison with NaAB. However, it is likely that the presence of the Li and Na atoms lead to side reactions and the consequent formation of other compounds during the pyrolysis, such as Li_2NH and metal oxides (if some oxygen is present during the heat treatment). However, the treatment at higher temperatures (1200-1400°C) might lead to a purer BN. In any case, alkali amidoboranes might be considered as viable sources to obtain crystalline BN at lower temperatures than the traditional synthesis.

In addition, the materials presented in this chapter were investigated as potential CO_2 sorbents at nearly room conditions (1.5 bar and 30°C). The results of the sorption experiments showed that the materials were able to uptake CO_2 at these conditions. The AB-derived samples had a better performance than the amidoborane-derived ones: the highest CO_2 uptake was presented by AB pyrolyzed at 600°C. The lowest uptake was exhibited by the LiAB-derived samples. It is likely that the CO_2 uptake capacity of the samples decreases as the crystallinity of the material increases. The AB-derived samples might present a turbostratic structure, so the random disposition of the BN layers and the presence of a higher number of defects may favor the uptake of CO_2 . On the contrary, the Li and Na cations promoted the crystallinity of h-BN at lower temperatures so, in comparison, the uptake values are low. In any case, the LiAB- and NaAB-derived BN structures showed a higher CO_2 uptake capacity in comparison with bulk h-BN,²⁴ possibly due to the incorporation of the Li and Na elements in the material. Besides, we highlight that the materials synthesized in this work are not porous. In this way, the synthesis of a porous structure based on these materials may enhance the CO_2 sorption properties of the compounds.

5. References

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Chapter 6

GENERAL CONCLUSION & PERSPECTIVES

6 General conclusion & perspectives

1. General conclusion

In this thesis, the last alkali members of the derivatives of hydrazine borane (HB, $\text{N}_2\text{H}_4\text{BH}_3$), rubidium (RbHB, $\text{RbN}_2\text{H}_3\text{BH}_3$) and cesium hydrazinidoborane (CsHB, $\text{CsN}_2\text{H}_3\text{BH}_3$), were synthesized for the first time. Through the characterization of both materials, we showed the successful introduction of the alkali metal cation into the hydrazine borane molecule. RbHB is a crystalline solid (monoclinic, s.g. $P2_1$) that carries 4.5 wt. % H; CsHB carries 3.4 wt. % H and is also crystalline (monoclinic, s.g. $P2_1$). The destabilization effect of the metal cation was observed in both cases: the two compounds start to dehydrogenate at lower temperature in comparison to HB. Besides RbHB and CsHB release more equivalents of H_2 at 120°C (1.1 and 2.5 equiv. H_2 respectively) than HB at 140°C (1.1 equiv. H_2) under isothermal conditions. Comparing the dehydrogenation of all the alkali hydrazinidoboranes, the rubidium and lithium ones have a similar behavior: LiHB and RbHB release 2 equiv. H_2 after one hour of isothermal treatment at 140°C . The kinetics presented by CsHB are faster, as it releases nearly 2 equiv. H_2 at only 110°C . However, none of the alkali hydrazinidoboranes overcome the performance of NaHB. In addition, the production of byproducts during the thermolysis was not avoided by RbHB and CsHB. While only ammonia was detected for RbHB, ammonia, hydrazine, and diborane were found in the decomposition of CsHB.

At this point, to have a realistic evaluation of the rubidium and cesium hydrazinidoboranes as hydrogen storage materials, different factors must be taken into account. First, the hydrogen storage capacity: RbHB (4.5 wt. % H) and CsHB (3.4 wt. % H) fall short in comparison with LiHB (11.6 wt. % H) or NaHB (8.8 wt. % H). The weight of the heavy elements like Rb and Cs outshine the gravimetric content of hydrogen the hydrazinidoboranes. Even in the case where the compounds were completely dehydrogenated, this would lead to another problem: the formation of boron

nitride complicates the regeneration of the materials because the hydrogenation of BN is thermodynamically unfavorable. Second, the management of alkali elements such as Rb and Cs is challenging due to their high reactivity, as well as the solid residues after dehydrogenation. Third, Rb and Cs are not abundant. Finally, the synthesis of these compounds did not lead to obtain a pure compound. Taking into account all of these factors, perhaps the Rb and Cs hydrazinidoboranes are not the best candidates for the chemical storage of hydrogen. Rather than hydrogen storage materials, RbHB and CsHB might be envisaged as energetic materials or as boron nitride precursors. However, the findings provided by the synthesis and characterization of RbHB and CsHB contribute to have a better knowledge of the chemistry of boron- and nitrogen-based materials. Some research still lies ahead for these compounds, especially regarding the complicated dehydrogenation mechanisms and the composition of the solid products after thermolysis.

The last part of this work studied the potential use of the alkali derivatives of ammonia borane as boron nitride precursors and their capacity to capture CO₂. The starting point was lithium (LiAB, LiNH₂BH₃) and sodium (NaAB, NaNH₂BH₃) amidoboranes. It is clear that the alkali cation has an impact in the formation of crystalline hexagonal boron nitride (h-BN) when these compounds are pyrolyzed. Diffraction peaks belonging to h-BN appeared in the PXRD patterns of LiAB from 600°C and from 800°C for NaAB. At 1000°C, LiAB presented the highest degree of crystallization among the analyzed compounds, according to the Raman spectroscopy and PXRD analyses. In comparison, pure ammonia borane presented an amorphous structure even when it was pyrolyzed at 1000°C. The composition of the pyrolyzed amidoboranes contained impurities such as Li₂O or Na₂O, as shown by PXRD analysis. At 1000°C, the intensity of these impurities decreased. Further thermal treatment at higher temperatures might lead to obtain a purer h-BN phase.

The pyrolyzed materials from AB, LiAB and NaAB showed interesting results when they were exposed to CO₂. The materials were able to uptake CO₂ at nearly ambient conditions (1.5 bar and 30°C). It is likely that there is a relation between the crystallinity and the sorption capacity of the BN structures. In the one hand, AB pyrolyzed at 600°C (23.6 cm³ g⁻¹) showed the highest CO₂ uptake, likely due to the poor crystallized BN structures and the higher number of defects and vacancies. On the other hand, the LiAB-derived samples presented the lowest CO₂ uptake values, likely due

to the higher degree of crystallization presented by these compounds. The amidoborane-derived materials with the highest degree of crystallization (pyrolyzed at 1000°C) exhibited a higher uptake capacity than bulk h-BN ($3.8 \text{ cm}^3 \text{ g}^{-1}$ for LiAB and $7.6 \text{ cm}^3 \text{ g}^{-1}$ for NaAB vs. $1.7 \text{ cm}^3 \text{ g}^{-1}$ of h-BN). This might confirm the positive effect of the incorporation of alkali elements in the BN structure for enhancing the CO_2 sorption properties. These results are promising, especially because the materials developed in this work are not porous. Thus, new perspectives have been opened.

2. Future perspectives

All of the alkali derivatives of HB have been synthesized and now we have a better overview of these materials. However, it would be interesting to explore new derivatives such as the alkaline-earth ones. Recently, the calcium derivative $\text{Ca}(\text{N}_2\text{H}_3\text{BH}_3)_2$ was reported. In this sense, the magnesium derivative, namely magnesium hydrazinidoborane ($\text{Mg}(\text{HB})_2$, $\text{Mg}(\text{N}_2\text{H}_3\text{BH}_3)_2$), is attractive because it carries more hydrogen (10.5 wt. % H) than almost all of the alkali hydrazinidoboranes (with the exception of LiHB), and due to the earth abundance of magnesium. In the past, some unfruitful efforts have been done in order to obtain this compound. Recently, through a wet method and a different Mg precursor (di-n-butylmagnesium), magnesium hydrazinidoborane was successfully synthesized and identified by FTIR and ^{11}B MAS NMR (Figure 1). The fully characterization of this compound now should be carried out.

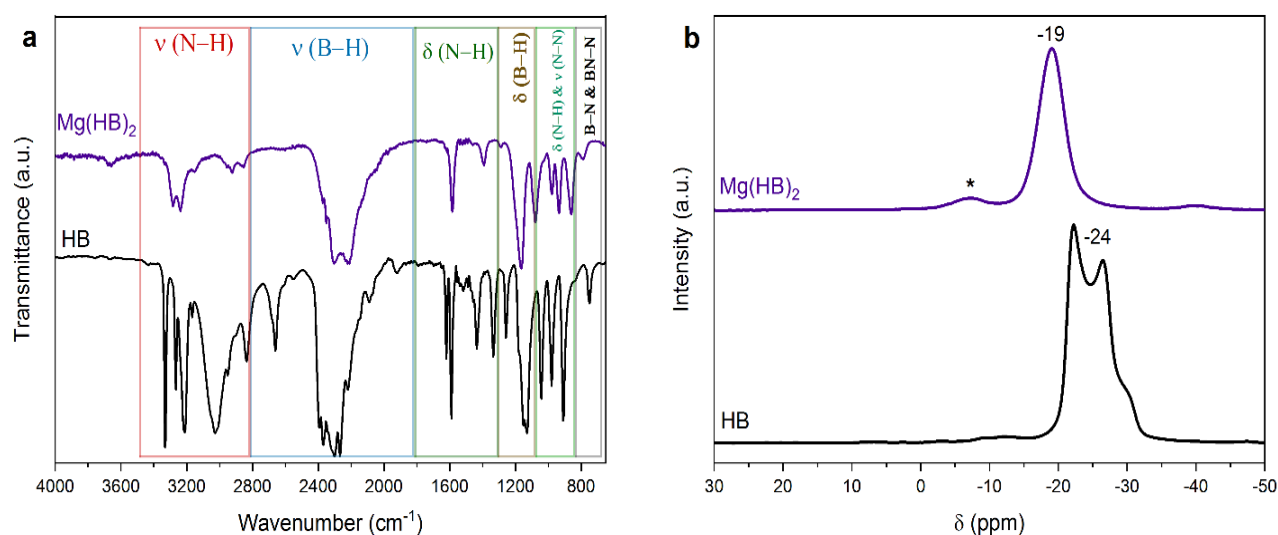


Figure 1. a) FTIR and b) ^{11}B MAS NMR spectra comparison of pristine HB and $\text{Mg}(\text{HB})_2$

Regarding the amidoboranes, the pyrolysis of LiAB and NaAB at higher temperatures ($>1000^{\circ}\text{C}$) might lead to a higher degree of crystallization of boron nitride and this might help to reduce the compounds formed by side reactions detected in this work. The impact of other alkali elements (K, Rb, Cs) in the crystallization of amidoboranes to BN is worth to be analyzed too. The capture of CO_2 by these materials should be evaluated at different conditions of temperature and pressure (for example, the temperature of outlet gas streams of combustion processes in thermal power station is 45°C). Besides, as the materials obtained in this work are bulky, the development of nanostructures or porous structures based on these compounds might lead to improve their CO_2 sorption properties. Finally, the investigation of amidoborane-derived compounds pyrolyzed at lower temperatures (i.e. $300\text{--}500^{\circ}\text{C}$) might confirm the relation established between the crystallinity and the sorption capacity of the materials.

The capture of CO_2 is not the only approach that can be considered for B- and N-based compounds related to CO_2 . They might be also considered as reducing agents for the conversion of CO_2 . For example, PdCl_2 can dehydrogenate AB in a highly exothermic reaction. The energy and the H_2 released by this reaction might help to reduce CO_2 . Some experiments have been performed and evidence of the formation of B–O bonds and some COO^- has been found by ^{11}B and ^{13}C MAS NMR (Figure 2). The simultaneous capture of CO_2 by the sample in these experiments was also observed.

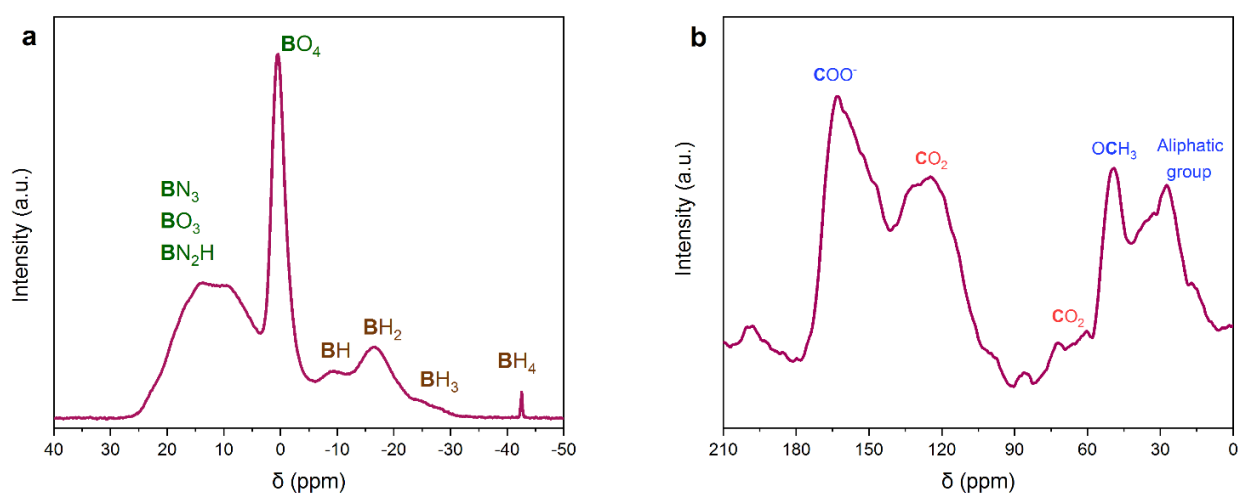


Figure 2. MAS NMR spectra of the solid product after the dehydrogenation of AB catalyzed by PdCl_2 in the presence of CO_2 for a) ^{11}B and b) ^{13}C . The chemical environments are assigned.

Moreover, LiAB has been considered as a reductive agent for aldehydes and ketones. Accordingly, LiAB might be also considered for the reduction of CO_2 . Preliminary experiments have shown that an exothermic reaction occurs during the thermolytic decomposition of LiAB under a CO_2 atmosphere at ca. 110°C . The solid product obtained after the reaction shows different environments assigned to BO_x , BN_3 and BN_2H (Figure 3). These results allowed us to establish an international collaboration with the Yildiz Technical University in Istanbul, Turkey, in order to deepen in the research of these materials.

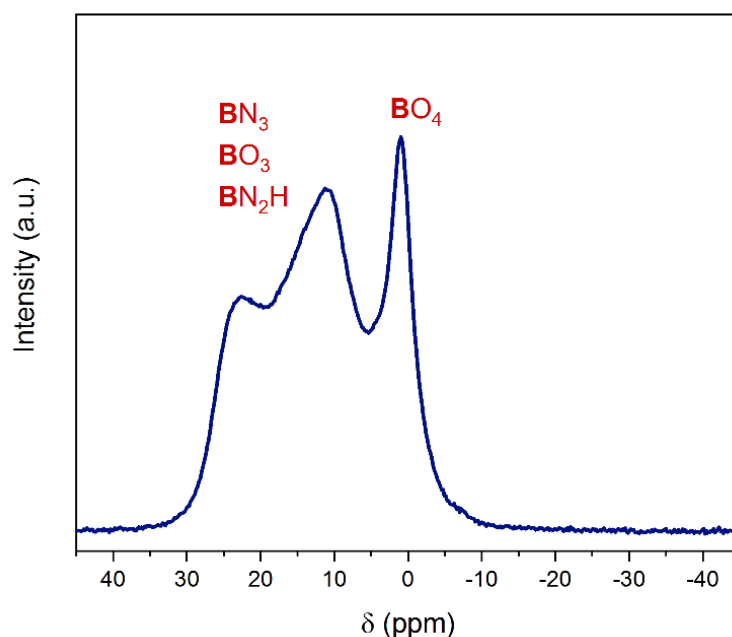


Figure 3. ^{11}B MAS NMR spectrum of the solid product after the thermolysis of LiAB under a CO_2 atmosphere.

In the two mentioned cases, the incorporation of oxygen into the compound evidences the reaction between CO_2 and the borane. Further experiments might be performed to determine the reaction mechanisms and the products formed. A liquid-gas reaction approach between LiAB and CO_2 can also be envisaged. We believe that the conversion/storage of CO_2 by these compounds might open new research lines of the boron- and nitrogen-based compounds and might have an impact in the future. Further research in this field is now expected.

Scientific contributions

Publications

- Castilla-Martinez, C.A., Granier, D., Charmette, C., Maurin, G., Yot, P.G., Demirci, U.B. Rubidium hydrazinidoborane: Synthesis, characterization and hydrogen release properties. *Int. J. Hydrogen Energy* 44, 28252–28261 (2019).
- Castilla-Martinez, C.A., Granier, D., Charmette, C., Cartier, J., Yot, P.G., Demirci, U.B. Cesium hydrazinidoborane, the last of the alkali hydrazinidoboranes, studied as potential hydrogen storage material. *Int. J. Hydrogen Energy*. 45, 16634-16643 (2020).
- Castilla-Martinez, C.A., Moury, R. and Demirci, U.B. Amidoboranes and hydrazinidoboranes: state of the art, potential for hydrogen storage, and other prospects. *Int. J. Hydrogen Energy*. 45, 30731-30755 (2020).
- Turani-I-Belloto, K., Castilla-Martinez, C.A., Cot, D., Petit, E., Benarib, S., Demirci, U.B. Nanosized ammonia borane for solid-state hydrogen storage – Outcomes, limitations, challenges and opportunities. *Int. J. Hydrogen Energy*. 46, 7351-7370 (2021).

Presentations

- New alkaline hydrazinidoborane compounds based on rubidium and cesium. EuroBoron8. June 24-27, 2019, Montpellier, France. Oral presentation.
- Rubidium and cesium hydrazinidoboranes: New derivatives of hydrazine borane as potential hydrogen storage materials. European Material Research Society, Symposium L. September 16-19, 2019, Warsaw, Poland. Oral presentation.

Annex I

SUPPLEMENTARY INFORMATION

AI Supplementary information

Description of Kissinger's method

The change of the heat content in a sample is observed as peaks in the DSC analysis. If all the conditions are constant, except the heating rate φ , the position of the peaks will vary. Using the temperature at which the peaks appear, the apparent activation energy of the process can be calculated. Many reactions of the type solid \rightarrow solid + gas are described by the equation:

$$\frac{dx}{dt} = A(1-x)^n e^{-\frac{E_a}{RT}} \quad (1)$$

where A is the pre-exponential term, x the fraction reacted, n the order of the reaction, E_a the activation energy, R the universal gas constant and T the temperature in Kelvin. If the temperature rises due to the reaction, the rate $\frac{dx}{dt}$ reaches a maximum, and when the reactant is consumed, it goes back to zero. The maximum temperature T_m occurs when $\frac{d}{dt}\left(\frac{dx}{dt}\right)$ is zero:

$$\frac{dx}{dt} \left[-\frac{E_a}{R T_m^2} \frac{dT}{dt} + A e^{-\frac{E_a}{RT_m}} n(1-x)^{n-1} \right] = 0 \quad (2)$$

Kissinger did some assumptions for the method: the heating rate ($\varphi = \frac{dT}{dt}$) is constant and the product $n(1-x)^{n-1}$ is approximately 1. Substituting this in Equation 2, Kissinger equation is obtained:

$$\ln\left(\frac{\phi}{T_m^2}\right) = \alpha - \frac{E_a}{RT_m} \quad (3)$$

where $\alpha = \ln\left(\frac{AR}{E_a}\right)$. With this equation, the apparent activation energy is obtained from plotting $\ln\left(\frac{\phi}{T_m^2}\right)$ against $\frac{1}{T_m}$.

Energy Dispersive X-ray Analysis from pyrolyzed samples (LiAB, NaAB)

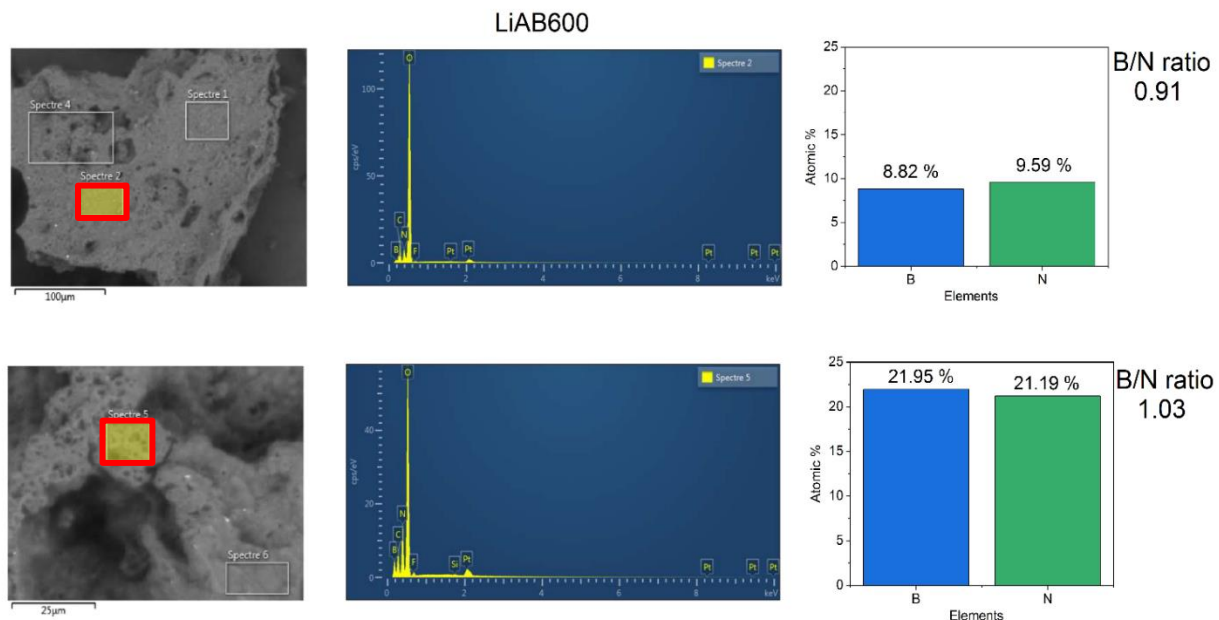


Figure A 1. SEM–EDX analysis of LiAB600 in different zones of the compound.

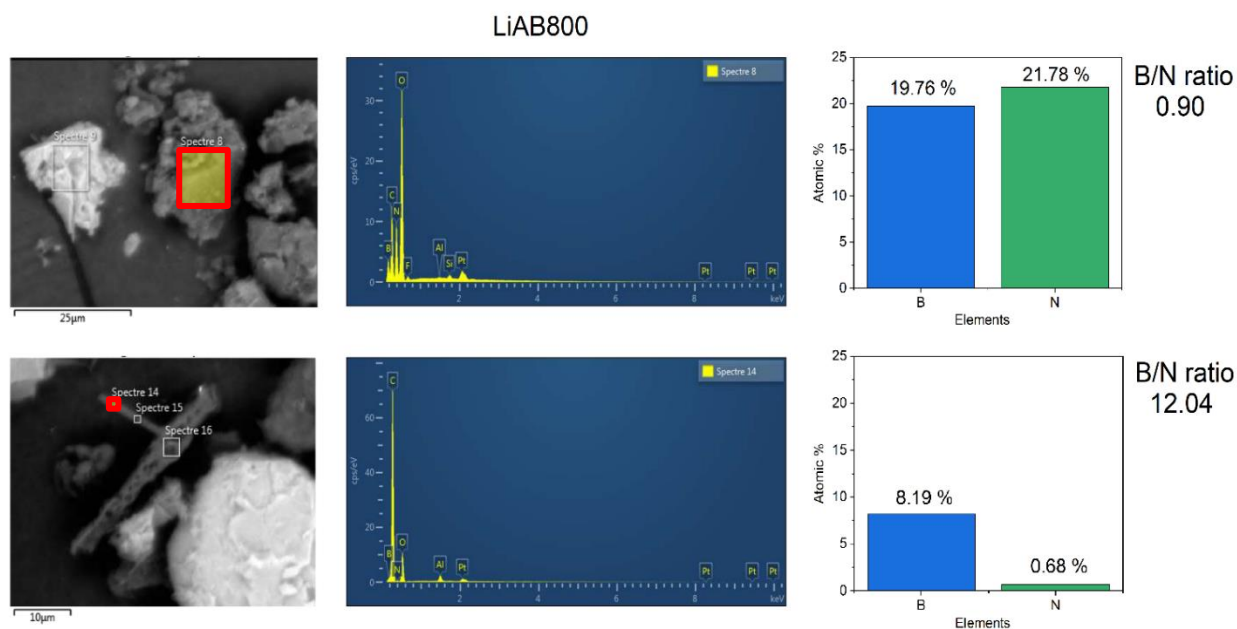


Figure A 2. SEM–EDX analysis of LiAB800 in different zones of the compound. The ratio of 12.04 might be due to some particles that are richer in B rather than N, as observed for BN obtained from polyborazylene.¹

¹ Kho, J., Moon, K., Nouet, G., Ruterana, P., Kim, D. Boron-rich boron nitride (BN) films prepared by a single spin-coating process of a polymeric precursor. *Thin Solid Films*. **389**, 78-83 (2001).

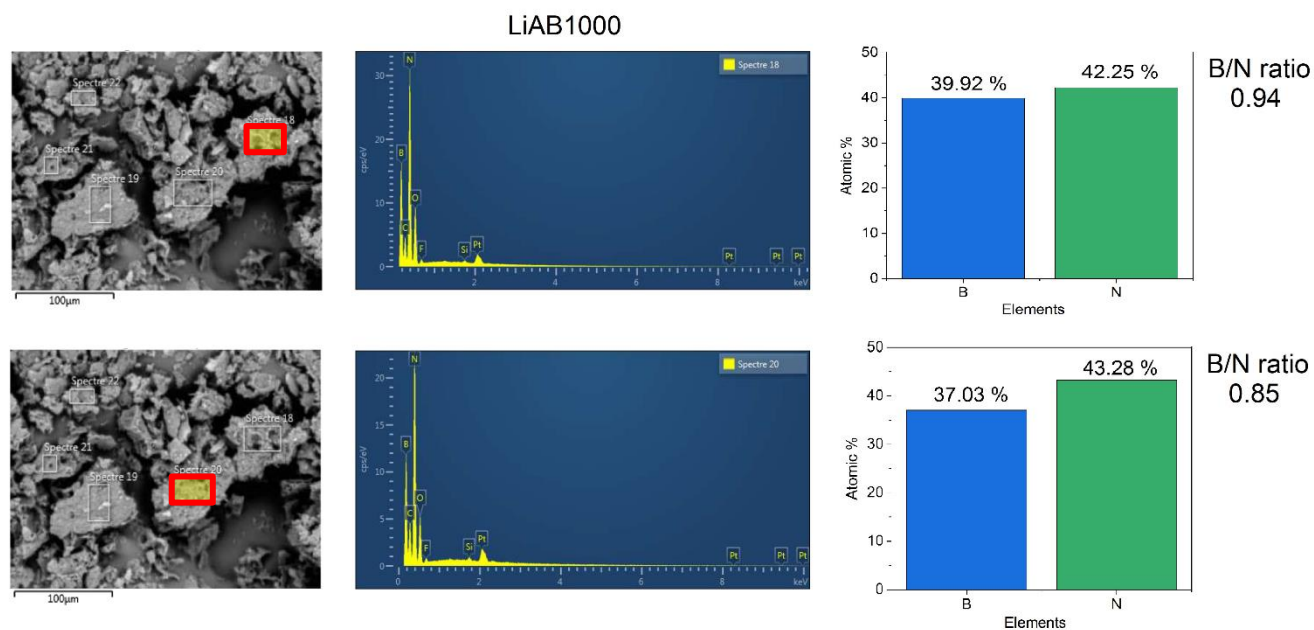


Figure A 3. SEM–EDX analysis of LiAB1000 in different zones of the compound.

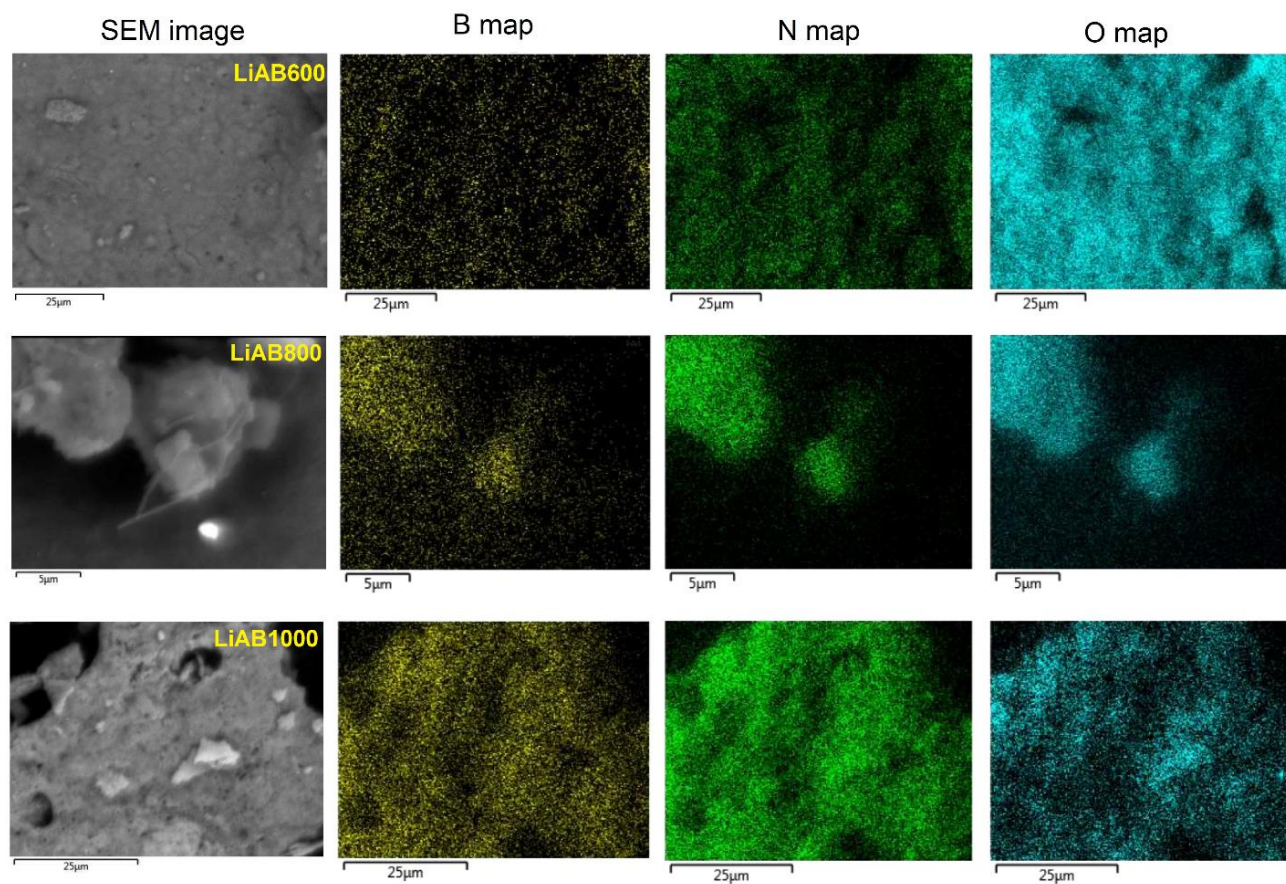


Figure A 4. SEM images and EDX elemental maps of LiAB600, LiAB800 and LiAB1000.

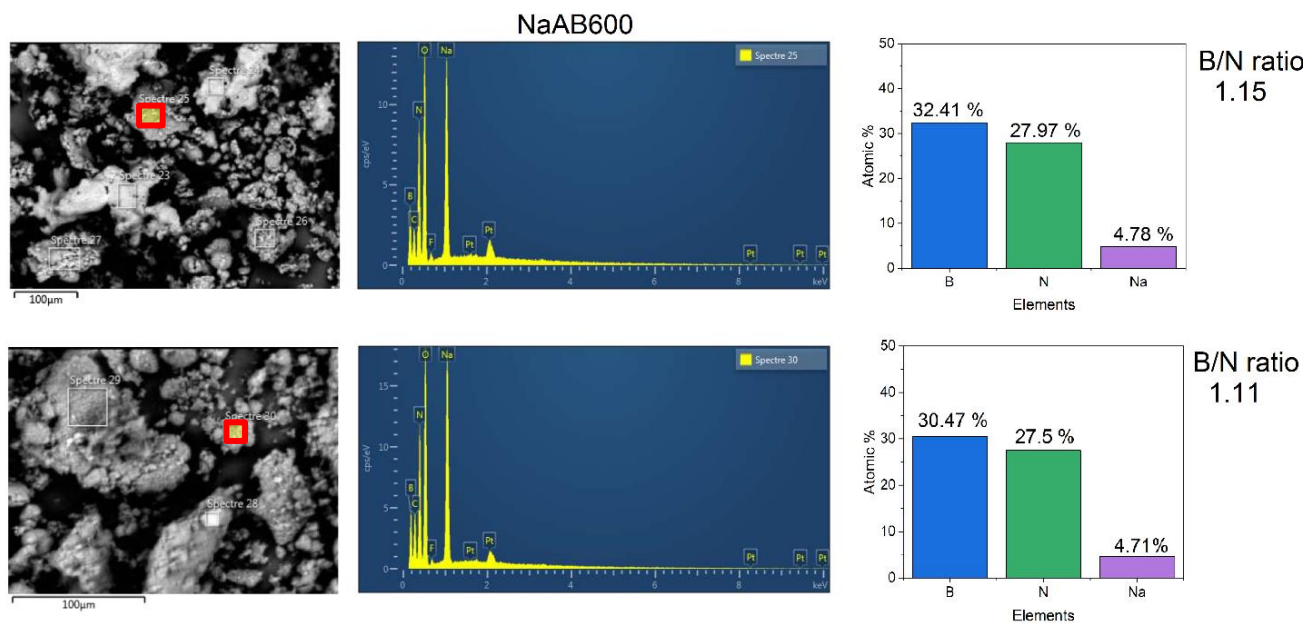


Figure A 5. SEM–EDX analysis of NaAB600 in different zones of the compound.

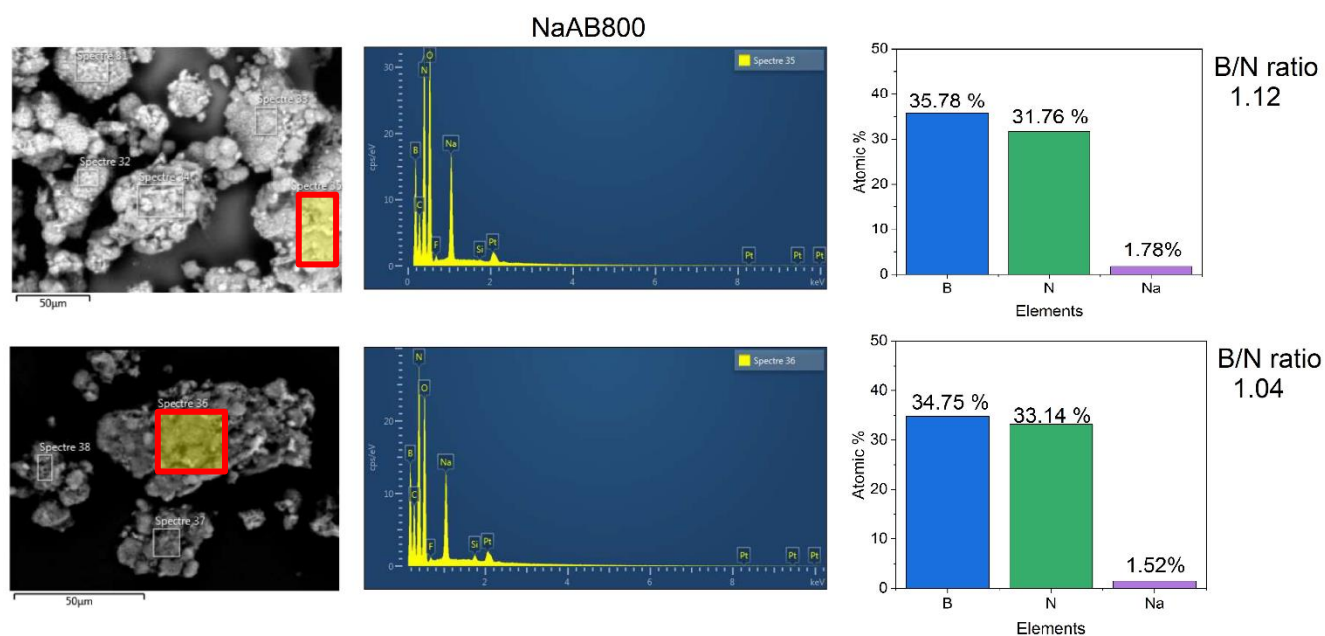


Figure A 6. SEM–EDX analysis of NaAB800 in different zones of the compound.

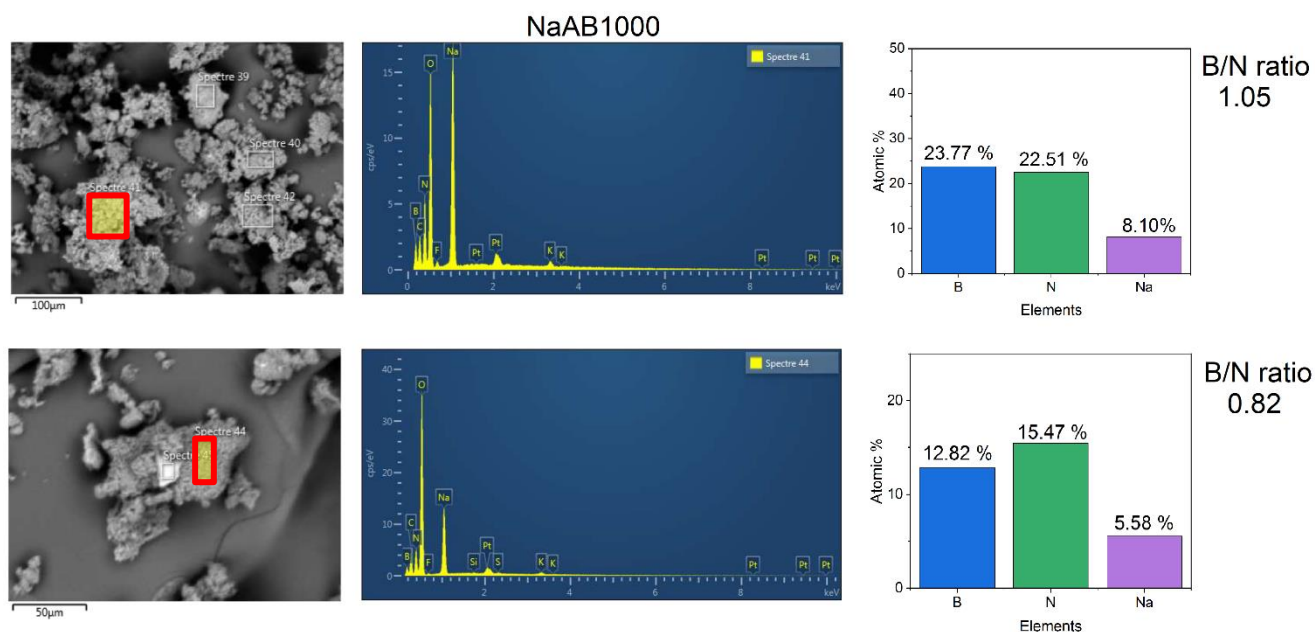


Figure A 7. SEM-EDX analysis of NaAB1000 in different zones of the compound.

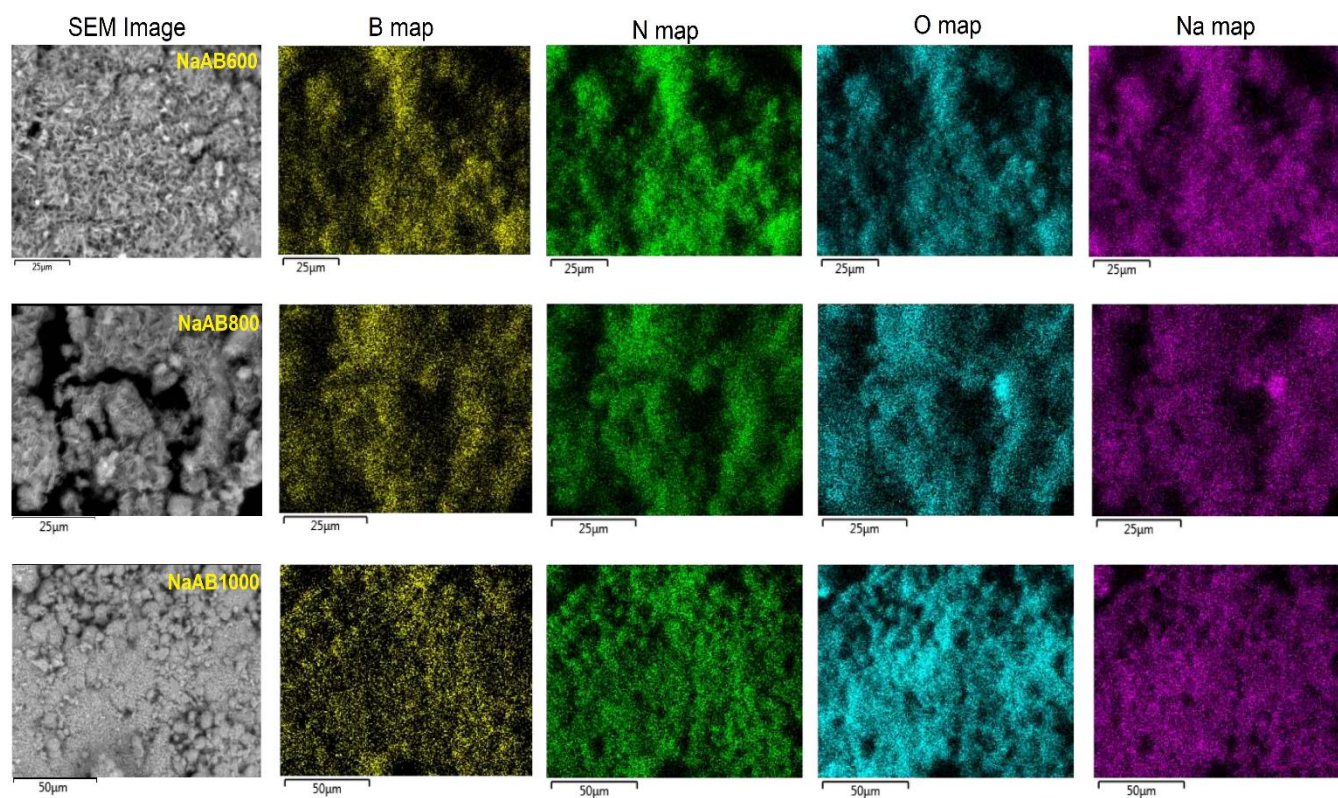


Figure A 8. SEM images and EDX elemental maps of NaAB600, NaAB800 and NaAB1000.

Powder X-Ray Diffraction comparison from samples (AB, LiAB, NaAB) pyrolyzed at 1000°C

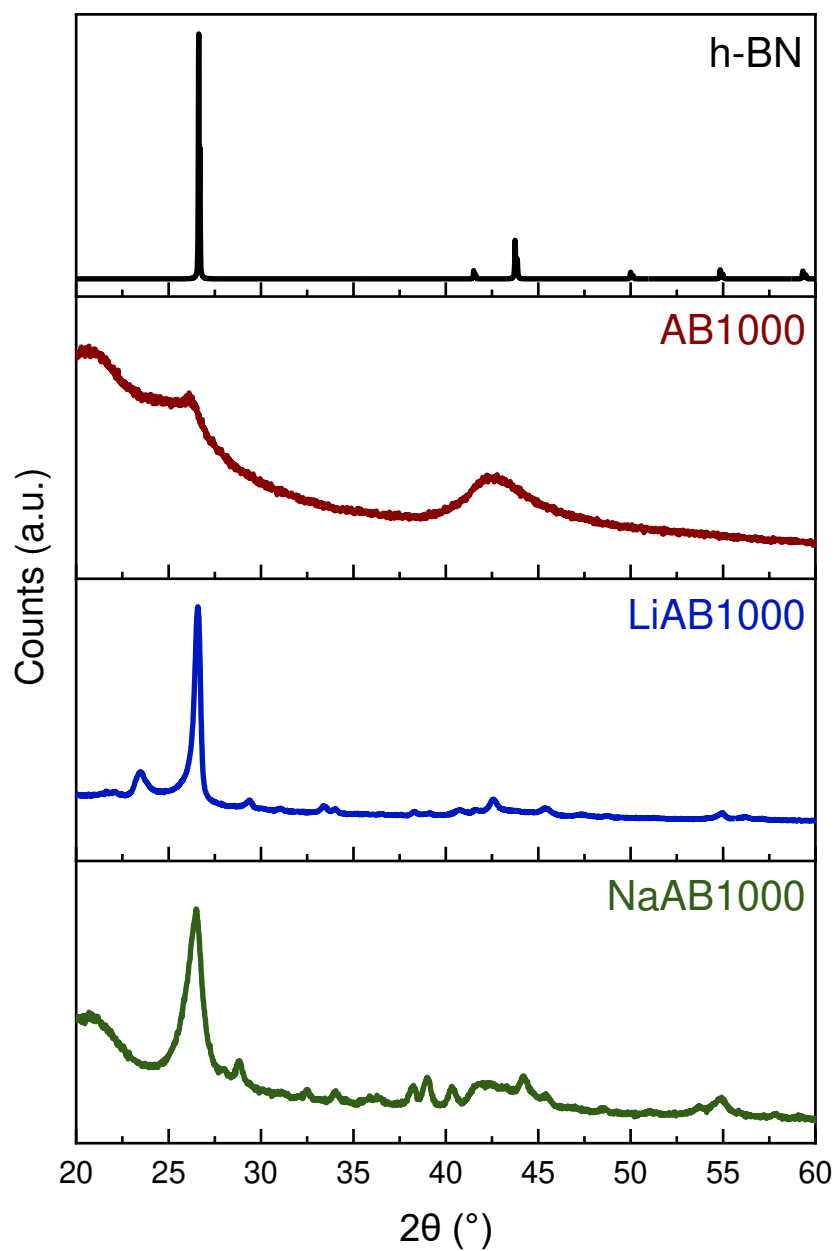


Figure A 9. Comparison between the PXRD patterns of the samples treated at 1000°C and h-BN.

Evolution of boron species determined by ^{11}B MAS NMR from the pyrolyzed samples (AB, LiAB, NaAB)

The peak areas of the BH_4 , NBH_3 , $\text{N}_2\text{BH}_2/\text{N}_3\text{BH}$ and the sp^2 -hybridized boron environments were integrated in the 100 to -100 ppm range and plotted in function of the temperature.

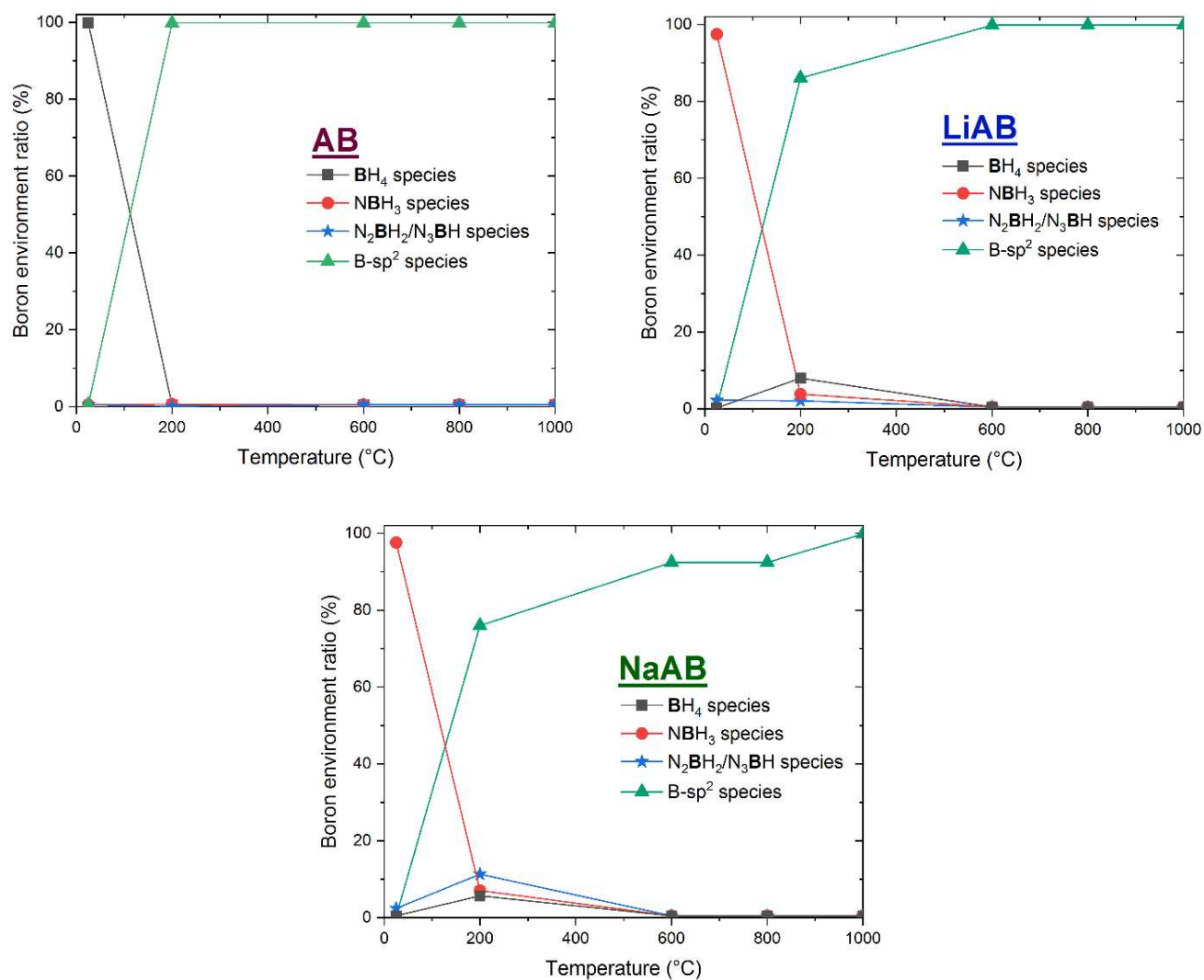


Figure A 10. Peaks area ratios of boron species (BH_4 , NBH_3 , $\text{N}_2\text{BH}_2/\text{N}_3\text{BH}$ and the sp^2 -hybridized B) as a function of the temperature up to 1000 °C. The N_2BH_2 and N_3BH signals were summed up.

XPS survey spectra of the samples derived from AB, LiAB and NaAB

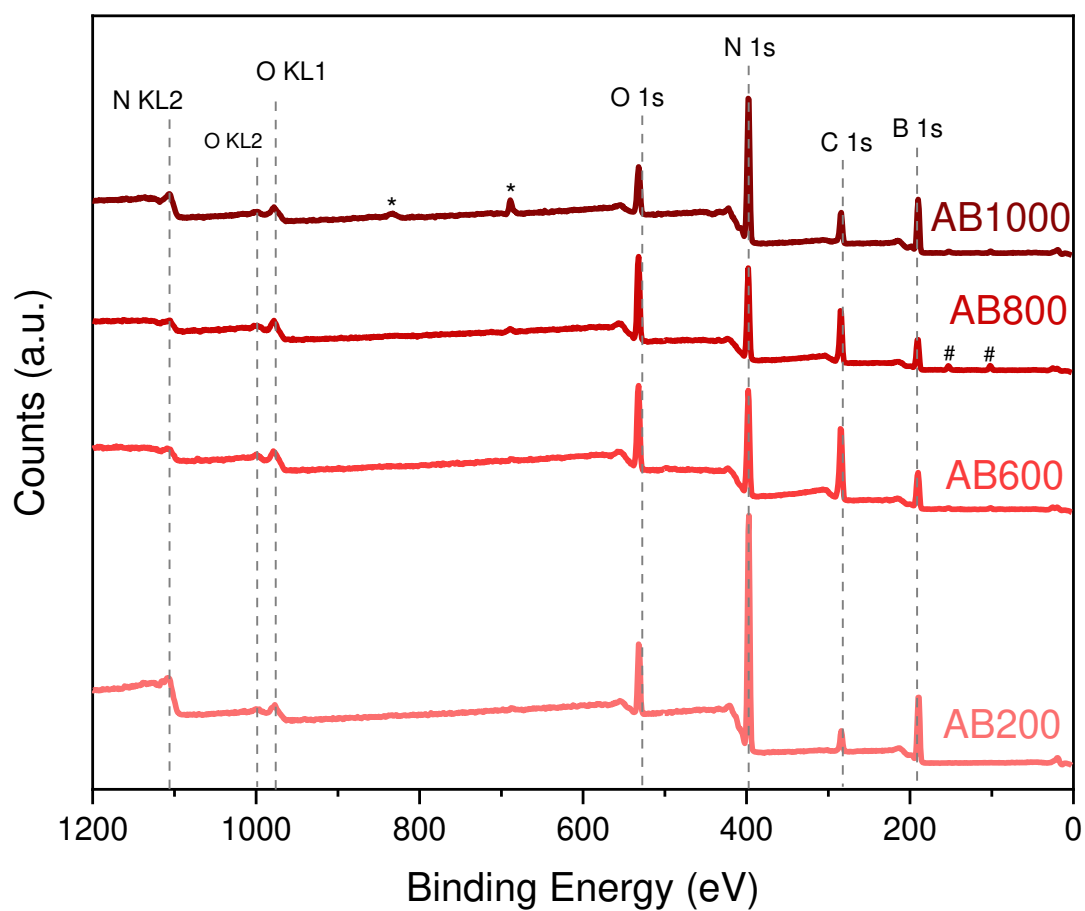


Figure A 11. XPS survey spectra of the AB-derived materials pyrolyzed at 200, 600, 800 and 1000°C. Some impurities peaks were detected and are indicated by a * for F and by # for Si.

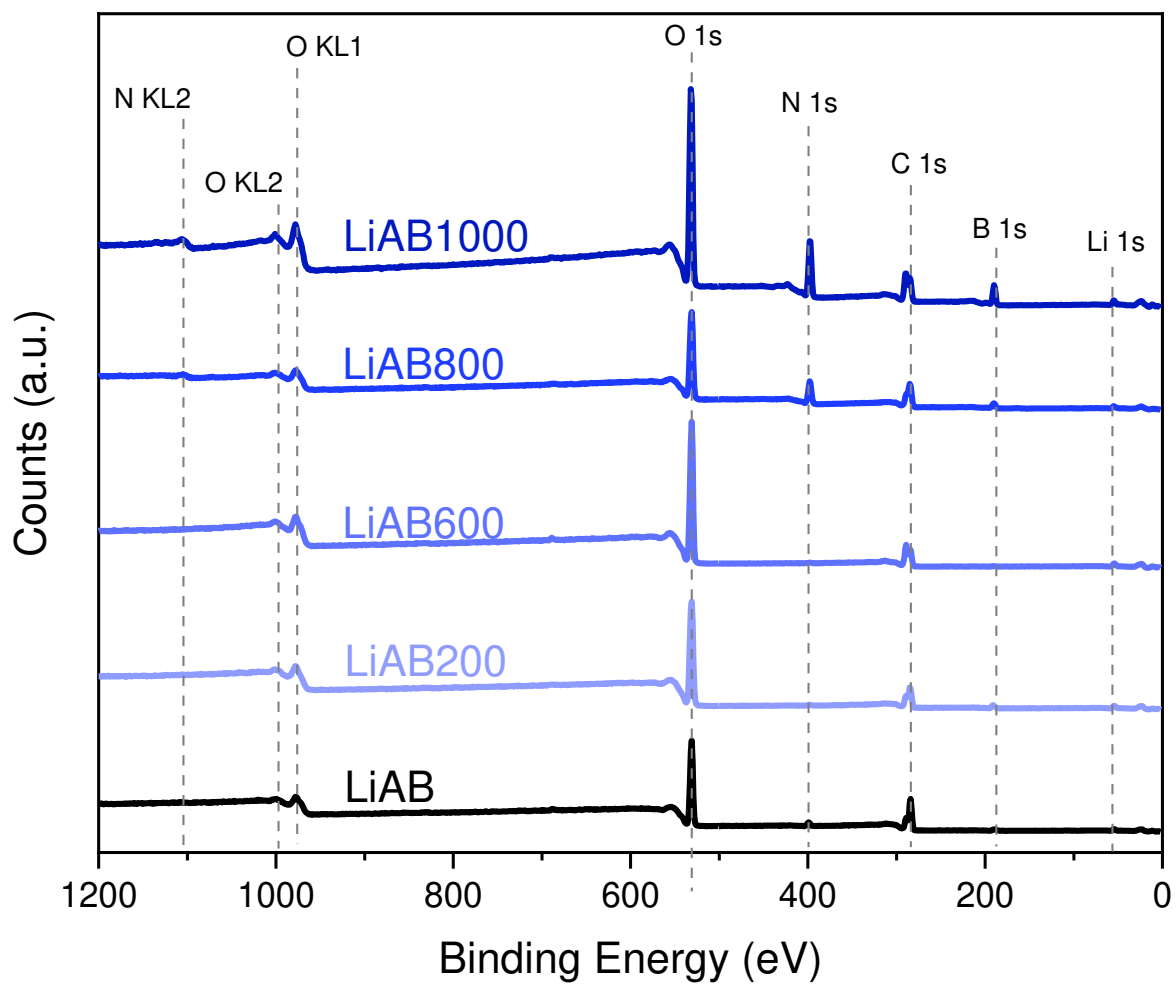


Figure A 12. XPS survey spectra of LiAB and the LiAB-derived materials pyrolyzed at 200, 600, 800 and 1000°C.

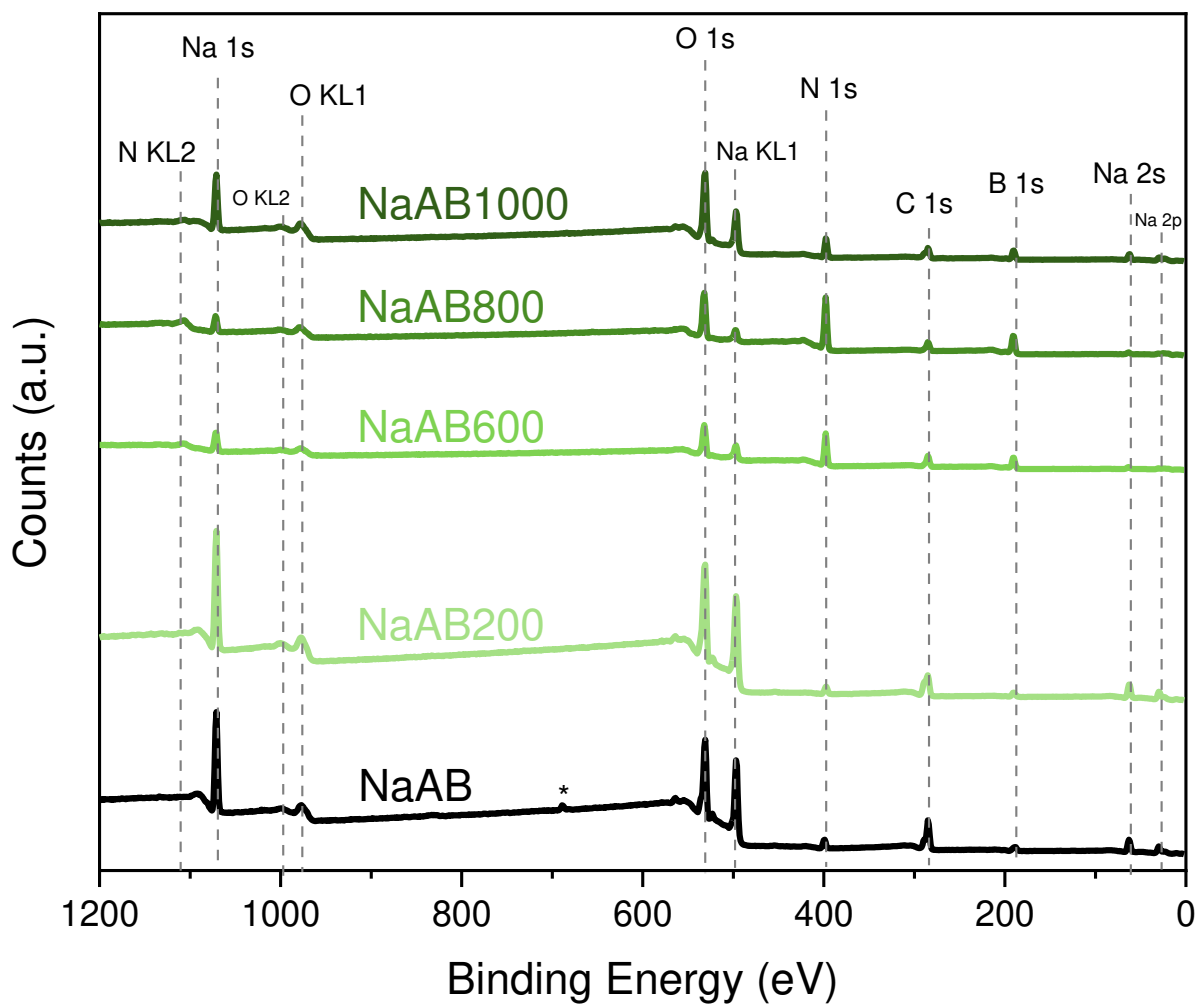


Figure A 13. XPS survey spectra of NaAB and the NaAB-derived materials pyrolyzed at 200, 600, 800 and 1000°C. Some impurities peaks were detected and are indicated by a * for F.

CO₂ uptake by the pyrolyzed samples of AB, LiAB and NaAB

Table A 1. CO₂ sorption capacity by the pyrolyzed samples of AB, LiAB and NaAB at 1.5 bar and 30°C.

Sample	mg g ⁻¹	mmol g ⁻¹	cm ³ g ⁻¹
AB200	15.9	0.4	8.0
LiAB200	8.7	0.2	4.4
NaAB200	7.5	0.2	3.8
AB600	46.4	1.0	23.6
LiAB600	6.1	0.1	3.1
NaAB600	32.9	0.7	16.7
AB800	30.1	0.7	15.2
LiAB800	8.8	0.2	4.5
NaAB800	15.7	0.3	8.0
AB1000	37.1	0.8	18.9
LiAB1000	7.3	0.2	3.8
NaAB1000	14.9	0.4	7.6