Tetrahydroborates: Development and Potential as Hydrogen Storage Medium

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Abstract: The use of fossil fuels as an energy supply becomes increasingly problematic from the point of view of both environmental emissions and energy sustainability. As an alternative, hydrogen is widely regarded as a key element for a potential energy solution. However, different from fossil fuels such as oil, gas, and coal, the production of hydrogen requires energy. Alternative and intermittent renewable sources such as solar power, wind power, etc., present multiple advantages for the production of hydrogen. On one hand, the renewable sources contribute to a remarkable reduction of pollutants released to the air. On the other hand, they significantly enhance the sustainability of energy supply. In addition, the storage of energy in form of hydrogen has a huge potential to balance an effective and synergetic utilization of the renewable energy sources. In this regard, hydrogen storage technology presents a key roadblock towards the practical application of hydrogen as "energy carrier". Among the methods available to store hydrogen, solid-state storage is the most attractive alternative both from the safety and the volumetric energy density points of view. Because of their appealing hydrogen content, complex hydrides and complex hydride-based systems have attracted considerable attention as potential energy vectors for mobile and stationary applications. In this review, the progresses made over the last century on the development in the synthesis and research on the decomposition reactions of homoleptic tetrahydroborates is summarized. Furthermore, theoretical and experimental investigations on the thermodynamic and kinetic tuning of tetrahydroborates for hydrogen storage purposes are herein reviewed.

Keywords: tetrahydroborates; synthesis; decomposition pathways; tailoring; solid state hydrogen storage

1. Introduction

Since the second industrial revolution, in the late 19th century, humankind has experienced an uninterrupted period of industrial and economic growth. The possibility to produce energy using the so far cheap and abundant fossil fuels has represented, beyond doubt, the driving force of this growth period. All of the current energy systems are based on coal, oil, natural gas, as well as nuclear fission, depending on the conditions in a given country and its access to the cheapest primary energy

source. The total final consumption of energy worldwide grew more than twice from the 1970s to the 2000s. Unless an alternative to the use of fossil fuels is found, this trend is going to come soon to an end [1]. Moreover, the massive use of fossil fuels has disturbed the equilibrium of the global climate. The transition from a carbon-based economy to a carbon-free economy is perhaps the greatest challenge of the 21st century. Possible candidates to replace the fossil fuels as energy sources are the so called renewable energy sources (e.g., solar-, wind-, geothermal-, wave-, hydroelectric-energy, etc.). However, the main obstacle to the use of these energy sources is the fact that they are intermittent and un-evenly distributed. To fully exploit these energy sources an efficient energy storage system is required. In this regard, hydrogen is widely considered as an energy vector capable of solving both the increasing CO_2 environmental emissions and future energy sustainability. Hydrogen has a gravimetric energy density of 120 MJ/kg, which is more than twice the energy content of most of the common fossil fuels (e.g., methane 50 MJ/kg, propane 46 MJ/kg and gasoline 45 MJ/kg). That means that only one-third as much hydrogen has to be carried out to cover a similar driving range for vehicles. Unfortunately, when compared to the fossil fuels, being hydrogen the lightest element of the periodic table, it has an extremely low volumetric energy density.

Hydrogen is usually stored in three main forms: as highly pressurized gas under 350 bar and 700 bar, in liquefied form at $-253\ °C$, and in metal hydrides chemically bonded hydrogen. Although, the volumetric energy density improves when hydrogen is compressed and/or liquefied, it still remains low as compared to that of fossil fuels. A significant improvement of the volumetric energy density is achieved when hydrogen is bonded to another element in solid state form [2–5]. It is well known that several metals, and in particular transitions metals, have a high affinity for hydrogen. This high affinity leads to the reaction between hydrogen (H_2) and the metal (M) to form metal hydrides (MH_x). This process can be described as follows:

$$M + (x/2)H_2 \leftrightarrows MH_x \tag{1}$$

Metal hydrides such as those of Mg [6–13] and Pd [14–18] have exhaustively been studied for decades owing to their interesting properties when they interact with hydrogen. On the one hand, Mg has a relative high gravimetric hydrogen density of 7.6 wt %, it is abundant, and it is cheap [12,13]. On the other hand, the Mg/MgH_2 hydride system presents a high thermodynamic stability ($\Delta H_{dehydrogenation} = -74\ kJ/mol\ H_2$) [6], leading to operative temperatures over 300 °C. Thus, the thermal management for large scale use of MgH_2 becomes an important issue, constraining the practical applications of MgH_2 to the stationary ones. In the case of Pd, the absorption of hydrogen already occurs at room temperature and presents excellent catalytic properties for the dissociation of the hydrogen molecule. However, its gravimetric hydrogen density is extremely low (~0.6 wt %) and it is quite expensive. Therefore, Pd is not suitable for any large scale hydrogen storage application.

Other examples of hydrides with high gravimetric hydrogen capacity but improper enthalpy of formation are aluminum hydride (AlH_3, gravimetric hydrogen capacity of ~10.0 wt %), and lithium hydride (LiH, gravimetric hydrogen capacity of ~12.6 wt %). The low formation enthalpy of AlH_3 (5–8 kJ/mol H_2) requires extreme pressure conditions for the hydrogenation of Al [19]. On the contrary, the high formation enthalpy of LiH (140 kJ/mol H_2) leads to a harsh dehydrogenation temperature above 700 °C at 1 bar [4]. Therefore, tailoring the metal hydrides reaction enthalpies and/or developing hydrogen containing materials that are different from the conventional metal hydrides are key issues for the design of vessels based on solid-state hydrogen storage materials towards practical applications. Recently, because of their high hydrogen storage capacity, "complex hydrides" attracted considerable attention as potential hydrogen storage materials [20–23]. The name "complex hydrides" derives from the presence of an anionic non metal–hydrogen complex ($[BH_4]^-$, $[NH_2]^-$, $[AlH_4]^-$) or metal–hydrogen complex ($[NiH_4]^{4-}$, $[CoH_5]^{4-}$, $[FeH_6]^{4-}$, $[MnH_6]^{5-}$, and $[ZnH_4]^{2-}$) bonded to a cationic alkali, alkali-earth, or transition metal. Taking into account this formulation, the complex metal hydrides are classified as non-transition metal complex hydrides (such as $LiBH_4$, $LiNH_2$, $LiAlH_4$) and transition metal complex hydrides (such as Mg_2NiH_4, Mg_2CoH_5, Mg_2FeH_6, Mg_3MnH_7, K_2ZnH_4).

Although this class of hydrides has been known for a long time since the first report on pure metal amides was published in the 1809 [24,25], they had initially not been considered as potential hydrogen storage materials. In the case of the non-transition metal complex hydrides, this lack of initial interest can be traced to their apparent irreversibility and more in general to the difficulty to produce them in a large scale. The interest on hydrogen as an energy carrier began around the 1960s, and it has grown significantly since the 1990s. In 1997, Bogdanovič and Schwickardi were the first to demonstrate the concrete possibility of reversibly store hydrogen in titanium-based doped $NaAlH_4$ at moderate temperature and pressure conditions [26]. Since then, many efforts have been done to investigate and optimize the hydrogen storage properties of complex hydrides.

There are several review works about light complex hydrides in which different aspects of tetrahydroborates are described [20–37]. In some works the synthesis, structure, stability, kinetics, thermodynamics, as well as tailoring of the tetrahydroborates and its hydride mixtures are covered [20–31]. Others are specifically about the synthesis of tetrahydroborates, high metal boranes and rare-earth borohydrides [28,32–34]. There is one review just focused on the hydrogen storage properties of $NaBH_4$ [35]. In addition, some review works are mainly devoted to the crystal structures of tetrahydroborate [28,36,37].

This review comprises the synthesis, decomposition mechanisms and tailoring approaches of the tetrahydroborates. It is the aim of this work to highlight selected aspects of the tetrahydroborates, such as (1) a historical overview about the synthesis of tetrahydroborates, regardless their crystallographic characterization; (2) the different decompositions mechanisms of the homoleptic tetrahydroborates; and, (3) the conceptual background of alternative approaches to tailor their hydrogen storage properties, mainly the concept of the reactive hydride composites (RHC), along with the relevant results and future prospects. Therefore, a novel overview of the progresses made over the last century toward the potential implementation of tetrahydroborates as hydrogen storage media is herein reviewed.

2. From Boron to Tetrahydroborates

In the last two centuries, boron has gained a significant importance in our daily life. This low-abundance element and its compounds are used in a variety of branches, including agriculture, medicine, electronics, chemical synthesis, catalysis, and energy. Highly impure boron was isolated for the first time in 1808 by H. Davy [38] J. L. Gay Lussac and L. J. Thénard [39]. In 1892 H. Moissan obtained boron with a purity of roughly 95% by the reduction of borax with magnesium, as shown in reaction (2) [40]:

$$B_2O_3 + 3Mg \rightarrow 2B + 3MgO \tag{2}$$

However, high-purity boron (>99.9%) was isolated only in 1922 when a new synthetic pathway that was capable to ensure a kilograms scale production was introduced. In that process volatile boron compounds (i.e., BBr_3 and BCl_3) were reduced by H_2 at temperatures between 800 °C and 1200 °C (reaction (3)). The temperature of the process was selective for the final boron allotrope [41].

$$BX_3 + 3/2H_2 \rightarrow B + 3HX \quad (X = Br, Cl) \tag{3}$$
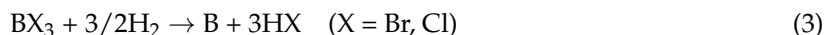
Together with the availability of good purity boron, the preparation and characterization of boron hydrides started in 1912. Thanks to the work of A. Stock and co-workers in the period between the 1912 and 1936, six boron hydrides, i.e., B_2H_6, B_4H_{10}, B_5H_9, B_5H_{11}, B_6H_{10}, and $B_{10}H_{14}$, were isolated and their chemical features investigated [42–44]. The early syntheses of boron hydrides were based upon the reaction between magnesium boride and hydrochloric acid. This preparation pathway was largely inefficient often giving mixtures of products (B_yH_x, y = 4, 5, 6, 10, x = 9, 10, 14), with yields of only 4–5% [44]. A first improvement in the reaction yield (11%) was achieved, replacing the hydrochloric acid with 8N-phosphoric acid.

At this time, diborane was obtained in millimolar quantities by the thermal decomposition of B_4H_{10}, and later in the 1931 H. Schlesinger and A. B. Burg reported the synthesis of B_2H_6 from BCl_3

and H_2, using a high voltage discharge [45]. Despite the fact that the amount of B_2H_6 produced by this method was still small, the reaction provided a considerable yield of 75%. It was necessary to wait until 1947 to find an effective and practical method to synthesize B_2H_6 with a purity of 99% [46]. This method was based on a halide-hydride exchange reaction performed in ethyl ether according to reaction (4):

$$3LiAlH_4 + 4BCl_3 \rightarrow 2B_2H_6 + 3LiCl + 3AlCl_3 \tag{4}$$
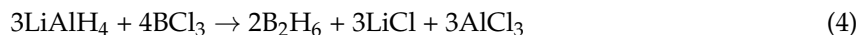
In the following years, several useful routes to synthesize B_2H_6 via halide-hydride exchange reaction were found as for example the reactions between NaH with $B(OCH_3)_3$, BH_4^- with I_2 and BH_4^- with H_2PO_4 [47–51].

Along with the increasing availability of B_2H_6 the synthesis of new compounds was enabled. The first tetrahydroborate, i.e., $Al(BH_4)_3$, was produced in 1940 starting from trimethylaluminium and diborane, reaction (5) [52]:

$$Al_2(CH_3)_6 + 4B_2H_6 \rightarrow 2B(CH_3)_3 + 2Al(BH_4)_3 \tag{5}$$

To synthesize significant quantities of tetrahydroborates and to limit the formation of complex mixtures as side-products, the reaction had to be performed in an excess of diborane. The formula of the aluminum tetrahydroborate was obtained by the characterization of the vapor density and the evaluation of the reaction between the newly synthesized compound with water and hydrogen chloride. The isolated material was a colorless solid below $-64.5\,^{\circ}C$, its vapor pressure measured at $0\,^{\circ}C$ was 119.5 mm Hg, and its extrapolated boiling point was $44.5\,^{\circ}C$.

Encouraged by the close chemical similarities between aluminum and beryllium, A. B. Burg and H. I. Schlesinger [53] successfully synthesized beryllium tetrahydroborate, following the same approach as used for the synthesis of aluminum tetrahydroborate. The reaction of dimethylberyllium with diborane proceeds in several steps towards the formation of beryllium tetrahydroborate, i.e., $Be(BH_4)_2$. In the first step, a solid methyl reach compound with unknown composition is formed. Then, this solid methyl rich compound turns into a non-volatile liquid. Upon further reaction with B_2H_6, an easily sublimable solid is produced. This solid has an approximate composition formula CH_3BeBH_4. The addition of further B_2H_6 leads to the formation of beryllium tetrahydroborate coexisting with a mixture of other derivates of diborane compounds in gas form, such as boron trimethyl and methyl plus a non-volatile beryllium hydroborate species. Due to its complexity, the synthesis of $Be(BH_4)_2$ through this route cannot be summarized in a simple chemical equation.

In the same year, H. I. Schlesinger and H. C. Brown [54] investigated the possibility of forming tetrahydroborates of alkali metals. Because of its simple preparation and purification routes, ethyllithium (LiC_2H_5) was chosen as starting material. Once ethyllithium and B_2H_6 were put into contact, they reacted to form several ethyl derivates of diborane plus the solid tetrahydroborates of lithium $(LiBH_4)$. This compound is characterized by a rather high stability. In fact, differently from the aluminum and beryllium tetrahydroborate that ignite spontaneously when exposed to air at room temperature, $LiBH_4$ is quite stable in dry air.

In 1941, H. I. Schlesinger and co-workers [55] were asked to undertake the synthesis of new volatile compounds of uranium. As a consequence of the fact that the tetrahydroborates of aluminum and beryllium are the most volatile compounds of these elements, the synthesis of uranium tetrahydroborate was attempted [53,56]. Although, the tetrahydroborates of aluminum, beryllium, and lithium were prepared by the reaction of diborane with metal alkyls, no alkyl of uranium was known at that time. Therefore, a new synthetic procedure was developed. Uranium tetrahydroborate was obtained by the interaction of uranium (IV) fluoride with aluminum tetrahydroborate, as shown in reaction (6):

$$UF_4 + 2Al(BH_4)_3 \rightarrow U(BH_4)_4 + 2Al(BH_4)F_2 \tag{6}$$
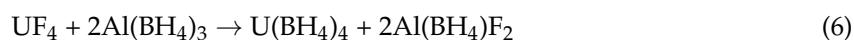
At the time of its first synthesis, uranium tetrahydroborate was the most volatile compound of the known uranium (IV) derivates.

In 1950, E. Wiberg and R. Bauer were the first to synthesize $Mg(BH_4)_2$ by the production of fine magnesium hydride powder, reaction (7), and then its subsequent reaction with diborane, reaction (8) [57]:

$$3Mg(C_2H_5)_2 + B_2H_6 \rightarrow 3MgH_2 + 2B(C_2H_5)_3 \tag{7}$$

$$3MgH_2 + 3B_2H_6 \rightarrow 3Mg(BH_4)_2 \tag{8}$$
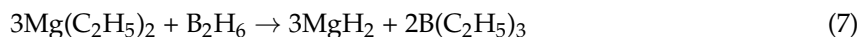
Up to that year the following tetrahydroborates were prepared by the interaction of diborane with metal derivates: $HZn(BH_4)$, $Ga(BH_4)$, $Ti(BH_4)_3$, $Pu(BH_4)_3$, $Zr(BH_4)_4$, $Hf(BH_4)_4$, $Th(BH_4)_4$, $Np(BH_4)_4$ [57].

In 1952–1953, there was a need to synthesized larger amount of borohydride by a more efficient method. The complexity of the process utilized for their synthesis involved slow reaction and repeated treatment with large excess of diborane. Thus, a more satisfactory synthetic method was developed for preparing lithium borohydride, and at that time, unknown sodium and potassium tetrahydroborate was developed.

In solvent environment (ethyl ether) lithium hydride absorbs large quantities of diborane. After the filtration of the insoluble LiH impurities, the evaporation of the solvent from the filtrate leads to the precipitation of $LiBH_4 \cdot (C_2H_5)_2O$ first, and then to high purity $LiBH_4$. It was reported that in the absence of solvents, lithium hydride does not react with diborane even at an elevated temperature because the formation of B–H bonds is not sufficient for $LiBH_4$ formation [55]. However, Friedrichs et al. [58] showed that the solvent-free synthesis of $LiBH_4$ from LiH in a borane atmosphere at room temperature and 120 °C is possible.

Differently from lithium hydride, sodium hydride does not react with diborane even in the presence of solvents. In order to circumvent this inconvenience the use of trimethoxyborohydride as hydride ions was proposed [55,59]. The reaction between trimethoxyborohydride and diborane proceeds rapidly and quantitatively forming sodium tetrahydroborate and trimethylborate, according to reaction (9):
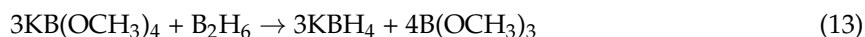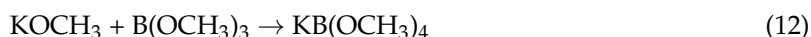
$$B_2H_6 + 2NaBH(OCH_3)_3 \rightarrow 2NaBH_4 + 2B(OCH_3)_3 \tag{9}$$
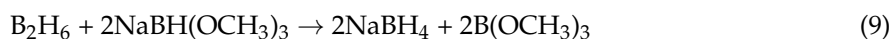
It was also reported that dimethoxiborine reacts with sodium trimethoxyborohydride to form sodium tetrahydroborate and trimethylborate as shown in reaction (10):

$$3(CH_3O)_2BH + NaBH(OCH_3)_3 \rightarrow NaBH_4 + 3B(OCH_3)_3 \tag{10}$$

Similarly, diborane reacts with sodium tetramethoxyborohydride to form sodium tetrahydroborate plus trimethylborate, reaction (11):

$$2B_2H_6 + 3NaB(OCH_3)_4 \rightarrow 3NaBH_4 + 4B(OCH_3)_3 \tag{11}$$
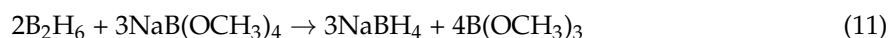
Following the same approach applied for the previously discussed tetrahydroborates, potassium tetrahydroborate was also synthesized for the first time by the reaction of diborane with potassium tetramethoxyborohydride, reaction (13) [59]. The latter was synthesized from potassium methoxyde and methyl borate as shown in reaction (12):

$$KOCH_3 + B(OCH_3)_3 \rightarrow KB(OCH_3)_4 \tag{12}$$

$$3KB(OCH_3)_4 + B_2H_6 \rightarrow 3KBH_4 + 4B(OCH_3)_3 \tag{13}$$

Although, these methods allowed Schlesinger and co-workers to synthesize sodium tetrahydroborates in laboratory scale, they were not appropriate for an industrial scale production. In particular, the risks connected to the use of diborane represented a serious limitation to the scaling up of the above mentioned processes. The first attempt to synthesize sodium tetrahydroborate without the use of diborane was carried out heating sodium trimethoxyborohydride to about 230 °C [59].

At this temperature, the disproportion of the starting material to $NaBH_4$ and $NaB(OCH_3)_4$ takes place via reaction (14):

$$4NaBH(OCH_3)_3 \rightarrow NaBH_4 + 3NaB(OCH_3)_4 \tag{14}$$
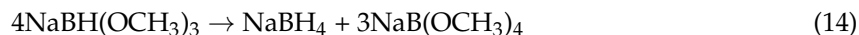
However, the reaction (14) does not proceed to completeness at about 230 °C. Then, the attempts to improve the yield of this reaction were stopped when in the same laboratory it was observed that sodium hydride and methyl borate quickly reacted at high temperature, i.e., 225–275 °C, to form $NaBH_4$ and $NaOCH_3$, reaction (15):

$$4NaH + B(OCH_3)_3 \rightarrow NaBH_4 + 3NaOCH_3 \tag{15}$$

As a consequence of the extremely good yield of this reaction, i.e., 94%, and the high purity of the obtained $NaBH_4$ up to 96%, this method is still the most used synthesis process to obtain sodium tetrahydroborate. Similarly, high purity $LiBH_4$, i.e., 95%, was synthesized by the reaction between lithium hydride and methyl borate with an overall reaction yield of 70%, reaction (16):

$$4LiH + B(OCH_3)_3 \rightarrow LiBH_4 + 3LiOCH_3 \tag{16}$$

The possibility to produce $NaBH_4$ and $LiBH_4$ in large quantities led to the development of a new method to successfully synthesize metal tetrahydroborates. The method consists in the metathesis between metal halides and alkali tetrahydroborates in solvents, reaction (17) [60–62]:

$$yMX_n + yM_a(BH_4)_n \rightarrow yM(BH_4)_n + yM_aX_n \qquad (M, M_a = \text{metals}, X = \text{halide}) \tag{17}$$
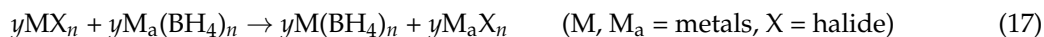
The first example of this reaction reported in literature was the metathesis between lithium tetrahydroborate and aluminum chloride as shown in reaction (18):

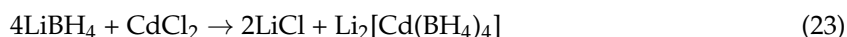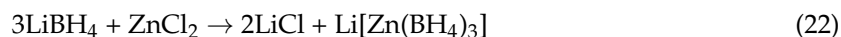$$AlCl_3 + 3LiBH_4 \rightarrow Al(BH_4)_3 + 3LiCl \tag{18}$$

The interaction between tetrahydroborates and metal halides leads also to the formation of multi-cation tetrahydroborates. E. Wiber and W. Henle [61,62] reported on the synthesis of $Li[ZnCl(BH_4)_2]$ and $Li[CdCl(BH_4)_2]$ as intermediates of the syntheses of $Zn(BH_4)_2$ and $Cd(BH_4)_2$ via metathesis between lithium tetrahydroborate and $ZnCl_2$ and $CdCl_2$, respectively, as seen in reactions (19) and (20):

$$ZnCl_2 + 2LiBH_4 \rightarrow Li[ZnCl(BH_4)_2] + LiCl \rightarrow Zn(BH_4)_2 + 2LiCl \tag{19}$$

$$CdCl_2 + 2LiBH_4 \rightarrow Li[CdCl(BH_4)_2] + LiCl \rightarrow Cd(BH_4)_2 + 2LiCl \tag{20}$$
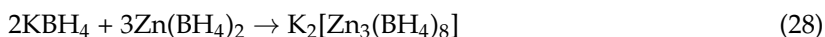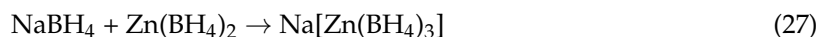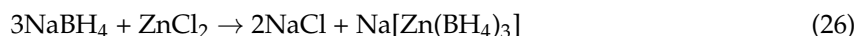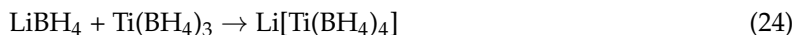
In 1955, E. Wiberg and R. Hartwimmer [63] reported for the first time on the synthesis of calcium, strontium and barium tetrahydroborates, i.e., $Ca(BH_4)_2$, $Sr(BH_4)_2$, $Ba(BH_4)_2$, respectively. The synthesis was performed by the reaction between the hydrides of the mentioned elements and diborane, reaction (21).

$$MH_2 + 2B_2H_6 \rightarrow M(BH_4)_2 \ (M = \text{metal}) \tag{21}$$

In 1961, H. Nöth [64] synthesized several new multi-cation tetrahydroborates via metathesis between lithium, sodium and potassium tetrahydroborates and metal halides or by direct reaction between tetrahydroborates, i.e., $Li[Zn(BH_4)_3]$, $Li_2[Cd(BH_4)_4]$, $Li[Ti(BH_4)_4]$, $Li[Fe(BH_4)_3]$, $Na[Zn(BH_4)_3]$, $K_2[Zn_3(BH_4)_8]$, plus a long series of halogen derivates as for example $Li_2[ZnI_2(BH_4)_2]$, $Li_3[Mn(BH_4)_3I_2]$, etc. The syntheses of some of these multi-cation tetrahydroborates are described in reactions (22)–(28):

$$3LiBH_4 + ZnCl_2 \rightarrow 2LiCl + Li[Zn(BH_4)_3] \tag{22}$$

$$4LiBH_4 + CdCl_2 \rightarrow 2LiCl + Li_2[Cd(BH_4)_4] \tag{23}$$

$$LiBH_4 + Ti(BH_4)_3 \rightarrow Li[Ti(BH_4)_4] \tag{24}$$

$$3LiBH_4 + FeCl_2 \rightarrow 2LiCl + Li[Fe(BH_4)_3] \tag{25}$$

$$3NaBH_4 + ZnCl_2 \rightarrow 2NaCl + Na[Zn(BH_4)_3] \tag{26}$$

$$NaBH_4 + Zn(BH_4)_2 \rightarrow Na[Zn(BH_4)_3] \tag{27}$$

$$2KBH_4 + 3Zn(BH_4)_2 \rightarrow K_2[Zn_3(BH_4)_8] \tag{28}$$

In the following years, it was possible to observe an increasing attention towards this class of material both as laboratory reagents and as energy storage materials. As a consequence, several new tetrahydroborates were synthesized. Nowadays the mono-cation tetrahydroborates of 32 chemical elements, plus an undefined number of multi-cation tetrahydroborates are known [23,38,42–45,52–57,59–78].

The development of the borane chemistry in general, and of the tetrahydroborates in particular, was from the early beginning connected with the research in the field of energy storage. In fact, the research in this field was stirred by the need of finding new propellants for military applications by the U.S. and Soviet Union [79]. Although these war research plans were dismissed around the 1950s, new pacific applications for this class of materials came to light in the field of energy storage.

3. Decomposition Reactions of Li, Na, K, Mg, Ca and U Tetrahydroborates

Homoleptic tetrahydroborates have a high gravimetric hydrogen capacity. However, those compounds stable at room temperature release hydrogen under thermal input. Predictions by first principles calculations suggested that the charge transfer from M^+ to $[BH_4]_n^-$ is a crucial factor for the stability of $M(BH_4)_n$ (M = metal). Moreover, a linear relationship between the enthalpy of $M(BH_4)_n$ and the Pauling electronegativity (X_p) of M was underlined [80–82]. Experimental results also demonstrated that the desorption temperatures (T_d) of the tetrahydroborates are generally correlated with the X_p value of the metal. Gas chromatography experiments showed a decrease of the desorption temperature with the increase of X_p value of the metal, e.g., T_d: (NaBH$_4$) $\approx$ 550 °C > (LiBH$_4$) $\approx$ 470 °C > (Sc(BH$_4$)$_3$) $\approx$ 280 °C > (Zr(BH$_4$)$_4$) $\approx$ 170 °C > (Zn(BH$_4$)$_2$) $\approx$ 125 °C with X_p: Na = 0.9 < Li = 1.0 < Sc = 1.3 < Zr = 1.4 < Zn = 1.6 [82,83]. The Pauling electronegativity of the metal is also correlated with the decomposition products of the tetrahydroborates. Nakamori et al. [84] reported that stable-covalent metal tetrahydroborates (X_p < 1.5) during decomposition release hydrogen, whereas less stable-covalent tetrahydroborates (X_p > 1.5) release a mixture of diborane and hydrogen. An important general feature of the dehydrogenation reaction of $M(BH_4)_n$ (M: K, Na, Li, Mg, Ca, etc.) is the thermodynamically favorable formation of the $M(B_{12}H_{12})_n$ compounds, reaction (29). On one hand, they are reported as an intermediate compounds [85–103]. However, on the other hand, its high stability and highly negative enthalpy of formation suggest that they are a final product of the decomposition of $M(BH_4)_n$ [92,102–106].

$$M(BH_4)_n \rightarrow 1/6M(B_{12}H_{12})_n + 5/6MH_n + 13n/12H_2 \tag{29}$$
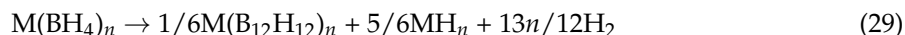
Here, below the decomposition behaviors of KBH$_4$, NaBH$_4$, LiBH$_4$, Mg(BH$_4$)$_2$, Ca(BH$_4$)$_2$, and U(BH$_4$)$_4$ are summarized. It is worth mentioning that the decomposition behavior of U(BH$_4$)$_4$ is here shown because of the scarce information available about this particular borohydride, but it is not regarded as a potential material for hydrogen storage applications.
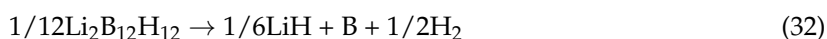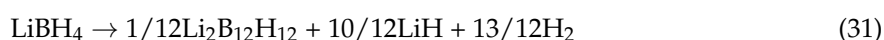
3.1. LiBH$_4$

When LiBH$_4$ is heated, a phase transition from the ordered low-temperature orthorhombic phase to the disordered high-temperature hexagonal polymorph takes place at about 115 °C. Increasing the temperature, LiBH$_4$ releases a small amount of hydrogen of about 0.3 wt % between 100 °C and 200 °C, and melts at around 270 °C [91,107,108]. The two main hydrogen releases occur at 320 °C and

400 °C. When heating up to 600 °C, the final reaction products are solid lithium hydride, solid boron, and gaseous hydrogen, as seen in reaction (30).
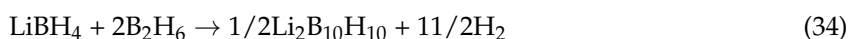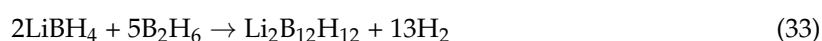
$$LiBH_4 \rightarrow LiH + B + 3/2H_2 \qquad (30)$$

The total weight loss associated with the hydrogen release of reaction (30) is 13.8 wt % and its experimental reaction enthalpy is 75 kJ/mol H_2 [109]. However, reaction (30) proceeds through several different intermediate steps, as predicted via theoretical calculations and verified via experimental evidences [85,86,89,91–93]. Computational and experimental works have reported that the decomposition reaction of $LiBH_4$ undergoes through the formation of the intermediate $Li_2B_{12}H_{12}$ as indicated in reaction (31), and finally, $Li_2B_{12}H_{12}$ decomposes to solid lithium hydride, solid boron and gaseous hydrogen according to reaction (32). This happens because the enthalpy value for reaction the (31) is lower than that for reaction (30), namely 56 kJ/mol H_2 and 75 kJ/mol H_2 [85,86].

$$LiBH_4 \rightarrow 1/12Li_2B_{12}H_{12} + 10/12LiH + 13/12H_2 \qquad (31)$$

$$1/12Li_2B_{12}H_{12} \rightarrow 1/6LiH + B + 1/2H_2 \qquad (32)$$

Caputo et al. [92] studied the decomposition reactions of $LiBH_4$ from a first-principle approach. They argued that the calculated enthalpy of formation of $Li_2B_{12}H_{12}$ is highly negative. Hence, it would be a product and not an intermediate preventing the reversible de-hydrogenation of $LiBH_4$.

Friedrichs et al. [93] reported that together with hydrogen, small quantities of B_2H_6 are released. Once formed, B_2H_6 decomposes to elemental B and hydrogen or it might react with the still present $LiBH_4$ to form $Li_2B_{12}H_{12}$ and possibly $Li_2B_{10}H_{10}$ as in reactions (33) and (34), respectively.

$$2LiBH_4 + 5B_2H_6 \rightarrow Li_2B_{12}H_{12} + 13H_2 \qquad (33)$$

$$LiBH_4 + 2B_2H_6 \rightarrow 1/2Li_2B_{10}H_{10} + 11/2H_2 \qquad (34)$$

The decomposition pathway either via the direct formation of $Li_2B_{12}H_{12}$ (reactions (31) and (32)), or the interaction of $LiBH_4$ and B_2H_6 depends mainly on the applied gas overpressure. Under vacuum conditions the decomposition reaction can go through the formation of B_2H_6, as shown in reactions (33) and (34) [93]. However, under hydrogen or even argon overpressure the decomposition of $LiBH_4$ may not proceed via the intermediate formation of gaseous diborane (B_2H_6) since the gas overpressure kinetically suppresses its release [110,111]. Thus, $LiBH_4$ decomposes through the intermediate formation of $Li_2B_{12}H_{12}$, as indicated in reactions (31) and (32).

3.2. NaBH₄

Upon heating, $NaBH_4$ starts to release hydrogen at 470 °C when it is still in solid form, and continues the dehydrogenation after melting at about 515 °C through a multistep process. From dehydrogenation pressure-composition isotherms (PCI) of $NaBH_4$ measured at 600 °C, 650 °C, and 700 °C under dynamic hydrogen flow, just one plateau was observed. Thus, the decomposition of $NaBH_4$ over 600 °C proceeds in one step and the final products are liquid sodium, solid boron, and gaseous hydrogen, with a total gravimetric H_2 capacity of 10.6 wt % according to reaction (35). The experimental estimated decomposition enthalpy of reaction (35) amounts to 108 ± 3 kJ·mol^{-1} H_2, which is in agreement with the high stability of $NaBH_4$ [112].

$$NaBH_4 \rightarrow Na + B + 2H_2 \qquad (35)$$

Alternatively, $Na_2B_{12}H_{12}$ phase has been reported experimentally as an intermediate of the decomposition of $NaBH_4$ [94–96]. However, the high thermodynamic stability of $Na_2B_{12}H_{12}$ calculated by first-principles approach suggests that it would rather be considered as a product that prevents the

subsequent re-hydrogenation because of its poor reactivity with hydrogen [105]. The mechanism of formation of $Na_2B_{12}H_{12}$ has not been totally understood yet, but theoretical approaches suggest that $Na_2B_{12}H_{12}$ is a product of the reaction between boranes and unreacted $NaBH_4$ as well as in the case of $LiBH_4$ [92,106].
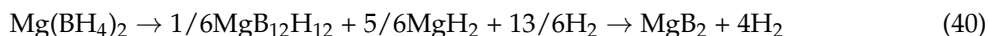
3.3. KBH₄

KBH_4 decomposes after melting at about 585 °C by forming potassium in liquid form, solid boron, and gaseous hydrogen, according to reaction (36). The gravimetric H_2 capacity is 7.48 wt % [21,92]. The intermediate formation of $K_2B_{12}H_{12}$ has been also predicted via first-principles calculations [97].

$$KBH_4 \rightarrow K + B + 2H_2 \tag{36}$$

3.4. Mg(BH₄)₂
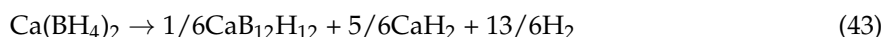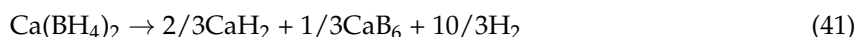
Magnesium tetrahydroborate, i.e., $Mg(BH_4)_2$, has a gravimetric hydrogen storage capacity of 14.9 wt % and an enthalpy of decomposition of about 40 kJ/mol H_2 [76,113–115]. Upon heating $Mg(BH_4)_2$, a phase transition from the hexagonal to the orthorhombic polymorph takes place at 185 °C. However, at room temperature, different polymorphs of $Mg(BH_4)_2$ can be found, depending on the synthesis method. Experimental evidences suggest that the decomposition takes place in several steps between 250 °C and 500 °C, finally forming MgB_2 and hydrogen [29,113,115–118]. The mechanism of decomposition is strongly debated and several different reaction paths can be found in the literature, as described in reactions (37)–(40) [72,98–101]. In this case, as for the $LiBH_4$, the final decomposition products and the presence of reaction intermediate/side product depend strongly on the applied experimental conditions.

$$Mg(BH_4)_2 \rightarrow Mg + 2B + 4H_2 \tag{37}$$

$$Mg(BH_4)_2 \rightarrow MgH_2 + 2B + 3H_2 \tag{38}$$

$$Mg(BH_4)_2 \rightarrow MgB_2 + 4H_2 \tag{39}$$

$$Mg(BH_4)_2 \rightarrow 1/6MgB_{12}H_{12} + 5/6MgH_2 + 13/6H_2 \rightarrow MgB_2 + 4H_2 \tag{40}$$

Experimentally, it was observed that when the decomposition of $Mg(BH_4)_2$ is carried out at temperatures above 450 °C and a hydrogen pressure below the equilibrium pressure of MgH_2, the final products are MgB_2 and H_2 [98,101,108,113]. The formation of MgB_2 upon decomposition is the key for the reversibility of $Mg(BH_4)_2$.

3.5. Ca(BH₄)₂

Calcium tetrahydroborate, i.e., $Ca(BH_4)_2$, has a gravimetric hydrogen storage capacity of 11.6 wt %. Upon heating, it undergoes a polymorphic transition from the orthorhombic α-phase to the tetragonal β-phase at around 170 °C. However, the polymorphs present in the samples, as well as the structural phase transitions between them, depend on the sample synthesis: for instance ball milling leads to the formation of the metastable orthorhombic γ-phase at room temperature [99,119–123]. Like $Mg(BH_4)_2$, the decomposition path of $Ca(BH_4)_2$ is debated and several different reaction mechanisms are reported in the literature as shown in reactions (41)–(45) [102–104]:

$$Ca(BH_4)_2 \rightarrow 2/3CaH_2 + 1/3CaB_6 + 10/3H_2 \tag{41}$$

$$Ca(BH_4)_2 \rightarrow CaH_2 + 2B + 3H_2 \tag{42}$$

$$Ca(BH_4)_2 \rightarrow 1/6CaB_{12}H_{12} + 5/6CaH_2 + 13/6H_2 \tag{43}$$

$$Ca(BH_4)_2 \rightarrow CaB_2H_6 + H_2 \tag{44}$$

$$Ca(BH_4)_2 \rightarrow CaB_2H_2 + 3H_2 \tag{45}$$

Due to extremely similar reaction enthalpies of some of the reported paths, i.e., reaction (41) = 37.04 kJ/mol H_2, reaction (43) = 31.34 − 39.2 kJ/mol H_2 and reaction (44) = 31.09 kJ/mol H_2, the possibility that the decomposition of the $Ca(BH_4)_2$ takes place following more than a single reaction path cannot be excluded [102–104].

3.6. $U(BH_4)_4$

At temperatures below 70 °C, $U(BH_4)_4$ is stable for long periods. However, at about 100 °C it decomposes to form uranium (III) tetrahydroborate, diborane and hydrogen as shown in reaction (46) [124]:
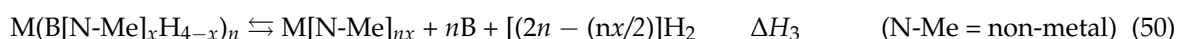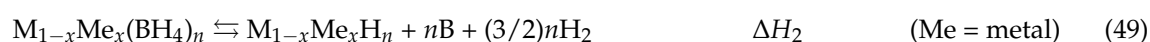
$$2U(BH_4)_4 \rightarrow 2U(BH_4)_3 + B_2H_6 + H_2 \tag{46}$$
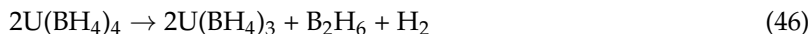
At temperatures above 150 °C, uranium (IV) tetrahydroborate rapidly decomposes to form the uranium boride, i.e., UB_4, or elemental boron and uranium plus hydrogen, as described in reaction (47) [124]:

$$U(BH_4)_4 \rightarrow UB_4 \text{ (or } U + 4B) + 8H_2 \tag{47}$$
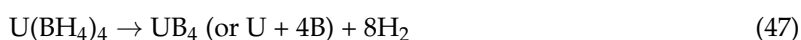
## 4. Tailoring the Hydrogen Storage Properties of Tetrahydroborates

Homoleptic tetrahydroborates are characterized by high decomposition temperature and extremely harsh re-hydrogenation conditions, i.e., temperatures above 400 °C and hydrogen pressures over 100 bar. Until the end of the 1990s, tetrahydroborates have been mostly used as laboratory reagents and have been investigated just sporadically as possible energy storage materials. However, these compounds have caught special attention owing to their promising hydrogen storage properties (light weight and high hydrogen content). Therefore, intensive research has been carried out to improve the hydrogen storage properties of tetrahydroborates, mainly $LiBH_4$, $NaBH_4$, $Mg(BH_4)_2$, and $Ca(BH_4)_2$. Several strategies have been applied to tailor the thermodynamic and kinetic behavior of the above mentioned borohydrides aiming to reach the set US Department of Energy DoE targets [125]. The most relevant strategies are: (1) catalytic additives and reactive additives [126–130]; (2) thermodynamic tuning via hydrides mixtures [131–135]; and, (3) nanoconfinement of tetrahydroborates and their hydride mixtures [95,132–138].

The first strategy refers to the addition of metals or metal compounds, in general transition metals, which leads to an improvement of the hydrogenation and dehydrogenation kinetic behavior because the activation energy barriers are reduced and the intrinsic rate limiting steps are accelerated. In general, the addition of some metals and compounds also promotes a thermodynamic destabilization by changing the reaction pathway. This concept lays on the reduction of the thermodynamic stability and the enhancement of the kinetic behavior of tetrahydroborates (MBH_4) by the partial substitution of M (cation substitution) [126,130], or the partial substitution of hydrogen atoms inside the $[BH_4]^-$ anion (in general by a non-metal such as fluorine; anion substitution) [127–129]. During these processes, it is also possible to attain the formation of a new compound as a product of a favorable thermodynamic interaction between the additive and the tetrahydroborate that provides new catalytic phases. As depicted in the general reactions (48)–(50), the right selection of metal or non-metal can reduced the stability of the tetrahydroborate ($\Delta H_2 < \Delta H_1$ and $\Delta H_3 < \Delta H_1$). On the one hand, the partial cation substitution can reduce the thermodynamic stability and consequently the dehydrogenation temperature by increasing the Pauling electronegative (X_p) (see Section 3) [130]. On the other hand, the partial anion substitution lowers the thermodynamic stability because the B–H bonds are weakened. The following general reactions depict these concepts:

$$M(BH_4)_n \leftrightarrows MH_n + nB + (3/2)nH_2 \qquad \Delta H_1 \tag{48}$$

$$M_{1-x}Me_x(BH_4)_n \leftrightarrows M_{1-x}Me_xH_n + nB + (3/2)nH_2 \qquad \Delta H_2 \qquad \text{(Me = metal)} \tag{49}$$

$$M(B[N\text{-}Me]_xH_{4-x})_n \leftrightarrows M[N\text{-}Me]_{nx} + nB + [(2n - (nx/2)]H_2 \qquad \Delta H_3 \qquad \text{(N-Me = non-metal)} \tag{50}$$

This strategy usually presents limited reversibility since quite stable compounds are formed or an appreciable reduction in the hydrogen capacity owing to formed stable species.

The second strategy is the thermodynamic tuning via hydrides mixtures. This concept was first explored via de-formation of alloys in 1958. That year, Libowitz et al. observed that a given temperature $ZrNiH_3$ has a desorption pressure much higher than the one measured for ZrH_2. Thus, $ZrNiH_3$ has an enthalpy of decomposition lower than that of ZrH_2 [131]. Similarly, in 1967, Reilly et al. [132] reported on the possibility to change the reaction enthalpy of a hydride by mixing it with compounds with a proper stoichiometric ratio, which reversibly react with the hydride during desorption to form a stable compound. In particular, he showed that the reaction enthalpy of $3MgH_2$ + $MgCu_2$ is lower than the one of pure MgH_2. Unfortunately, the gained reduction of the reaction enthalpy is at the expense of the system's hydrogen capacity. In the last 15 years, the approach of Libowitz et al. [131] and Reilly et al. [132] has been improved by P. Chen et al. [133], J. J. Vajo et al. [134] and G. Barkhordarian et al. [135]. These researchers destabilized light-weight hydrides using an appropriate molar ratio of a second hydride. Such hydride mixtures are the so-called Reactive Hydride Composites (RHC). This strategy allows for the reduction of the thermodynamic stability ($\Delta H_4 < \Delta H_1$) upon dehydrogenation because of the exothermic formation of a new and reversible phase, as shown in reaction (51). It offers the advantage of improved reversibility and high gravimetric storage capacity.

$$yM(BH4)n + MeHx \leftrightarrows yMH_n + MeB_{yn} + [(2ny - (x/2)]H_2 \qquad \Delta H_4 \qquad (MeH_x = \text{hydride}) \qquad (51)$$
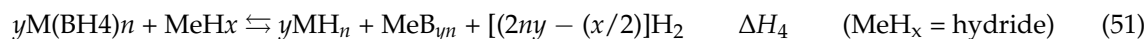
Despite the fact that the RHC strategy has shown good results as for example with the mixture $2LiBH_4$ + MgH_2 [134,135], experimental results have proved that the predicted thermodynamic destabilization is not reached owing to kinetic constraints that lead to multi-step reactions [95,136,137].

Nanoconfinement is the third presented strategy that has been recently applied to the pure tetrahydroborates, doped tetrahydroborates and the undoped and doped RHC [138–141]. It is well known that the physical and chemical properties of the materials can change markedly when entering the nanosize, usually below 100 nm. Under this scale, the materials can be thermodynamically destabilized and their kinetic behavior can also be enhanced. On one hand, concerning thermodynamic destabilization, the enthalpy of reaction can be minimized due to the surface effects [138]. On the other hand, the notable reduction of the diffusion distances and the larger specific area for the hydrogen interaction account for the kinetic enhancement [139,142].

In the following subsections some relevant results regarding the three above described strategies applied to the $LiBH_4$, $NaBH_4$, $Mg(BH_4)_2$, and $Ca(BH_4)_2$ tetrahydroborates are summarized.

4.1. LiBH₄

The first attempts to influence the dehydrogenation and reversibility properties of $LiBH_4$ were made by A. Züttel et al. [142] by mixing the tetrahydroborate with SiO_2. They lowered the hydrogen desorption temperature more than 70 °C. However, the formation of stable silicates upon decomposition prevented the material from being re-hydrogenated [143,144]. This effort was followed by several other researchers, who attempted to improve the hydrogen sorption properties and reversibility of $LiBH_4$ by mixing it with metal halides [126,145–150], pure metals [151–154], and carbon based additives [155,156]. Undoubtedly, the addition of these materials led to a general decrease of the $LiBH_4$ desorption temperature, but the reversibility achieved under elevated temperature and hydrogen pressure conditions (e.g., 600 °C and 100 bar H_2 pressure for $LiBH_4$ doped with Ni) was just partial.

The most prominent RHC system based on tetrahydroborates is $2LiBH_4$ + MgH_2 [134,135,157] According to the reaction (52), it has the reversible hydrogen storage capacity of 11.5 wt % and the theoretical reaction enthalpy of 46 kJ/mol H_2, which implies a hydrogen equilibrium pressure of 1 bar at 170 °C [158].

$$2LiBH_4 + MgH_2 \leftrightarrows 2LiH + MgB_2 + 4H_2 \qquad (52)$$
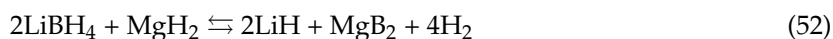
In the last decade this system has been thoroughly investigated with respect to reaction pathway, temperature, hydrogen pressure boundaries, microstructure, effect of additives on the reaction kinetics, and nanoconfinement [159–173].

For the $2LiBH_4 + MgH_2$ system, the value of hydrogen pressure applied during the desorption process is fundamental to ensure the reversibility. In fact, when $2LiBH_4 + MgH_2$ is heated under a hydrogen pressure lower than 1 bar, $LiBH_4$, and MgH_2 decompose individually, forming a series of compounds, which under moderate temperature and hydrogen pressures hardly react together to form again $LiBH_4$ (i.e., $Li_2B_{12}H_{12}$, $Li_2B_2H_6$, LiH, elemental B, and Mg). However, the application of a hydrogen back pressure higher than 1 bar but lower than 5 bar, ensures the possibility to reversibly release under moderate temperature the hydrogen contained in the system. Under dynamic temperature conditions, the decomposition reaction takes place in two distinguished steps. At first, the decomposition of MgH_2 into Mg and H_2 occurs, and then, after a long incubation period, Mg reacts together with $LiBH_4$ to form MgB_2, LiH and H_2 as shown in the reaction (53). Differently from the desorption reaction the hydrogenation process takes place in a single step [136].

$$2LiBH_4 + Mg \leftrightarrows 2LiH + MgB_2 + 3H_2 \tag{53}$$
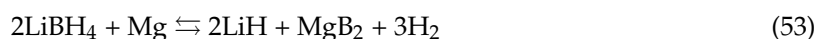
Despite the favorable calculated enthalpy of reaction and the high gravimetric hydrogen capacity, the sluggish kinetics is the primary issue of this system. In the last decade, several studies on the effect of transition metal based additives were carried out. The nucleation of MgB_2 is the key issue for a fast dehydrogenation kinetic behavior and it is enhanced by the presence of transition metal borides that act as nucleation center for the MgB_2 nuclei [159]. Although the reaction times are much different with and without additives, analyses of the reaction kinetics indicate that similar processes limit the sorption reactions for all the composites, independently of the additive and the initial preparation state. The absorption and desorption reactions in the RHC are characterized by significant mass transport through the composite, transport processes, and therefore, the length scales of the phase separation play a significant role in the reaction kinetics.

Another RHC system that presents interesting hydrogen storage properties is the combination of $LiBH_4$ and Mg_2NiH_4, according to the reaction (54). This hydride system exhibits a low reaction enthalpy of 15.4 kJ/mol H_2 and an entropy value of 62.2 J/K mol H_2. Moreover, it starts to release hydrogen at 250 °C [174].

$$4LiBH_4 + 5Mg_2NiH_4 \leftrightarrows 2MgNi_{2.5}B_2 + 4LiH + 8MgH_2 + 8H_2 \tag{54}$$
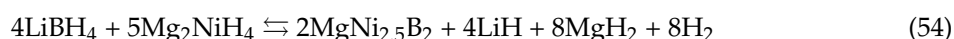
Despite the fact that this system does not display a high hydrogen capacity, i.e., 2.5 wt %, it represents other option of destabilized system since there are few ternary boride phases that reversibly hydrogenate under mild conditions, such as $MgNi_{2.5}B_2$.

4.2. NaBH₄

The effect of the doping on the reversibility of $NaBH_4$ was studied mostly by Mao et al. [175] and Humphries et al. [176]. They observed a sensible enhancement of the hydrogen desorption properties of $NaBH_4$ when Ti-based (i.e., Ti, TiH_2, and TiF_3) and Ni-based additives (i.e., nano-Ni, Ni_3B, $NiCl_2$, and NiF_2) were used. However, partial reversibility was achieved only in case of Ti-based additives. In fact, when using TiF_3, a hydrogen content of 4.0 wt % was stored back in the decomposed $NaBH_4$ after hydrogenation at 55 bar and 500 °C.

In order to improve the hydrogen storage properties of $NaBH_4$, nanocomposites of $NaBH_4$-C with a matrix of 2 to 3 nm pore size diameter were synthesized. It allowed the lowering of the dehydrogenation temperature of $NaBH_4$ down to 250 °C. However, the re-hydrogenation under 60 bar and 325 °C was not completed due to the loss of Na upon dehydrogenation [96].

As in the case of the mixture $2LiBH_4 + MgH_2$, the RHC based on $2NaBH_4 + MgH_2$ presents reversibility because of the formation of MgB_2 upon desorption. The dehydrogenation reactions of the

$2NaBH_4 + MgH_2$ can undergo either as reaction (55) with 7.8 wt % H_2 or reaction (56) with 9.8 wt % H_2, depending on the conditions [177–179].

$$2NaBH_4 + MgH_2 \leftrightarrows 2NaH + MgB_2 + 4H_2 \tag{55}$$

$$2NaBH_4 + MgH_2 \leftrightarrows 2Na + MgB_2 + 5H_2 \tag{56}$$
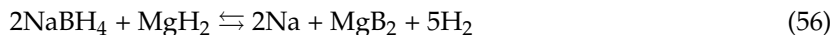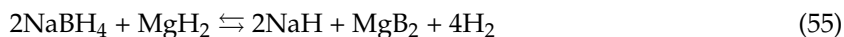
However, the dehydrogenation of this system also goes on in two steps under 1 bar of inert gas, i.e., first the dehydrogenation of MgH_2 and then the subsequent formation of MgB_2 [178,180]. Furthermore, the formation of intermediates such as $Na_2B_{12}H_{12}$ has been also suggested [180]. Under vacuum, the pathway is different and it involves the formation of free Mg and finally free B [181].

As well as the $LiBH_4/Mg_2NiH_4$ mixture, the stoichiometric ration $4NaBH_4 + 5Mg_2NiH_4$ also undergoes to the formation of $MgNi_{2.5}B_2$ lowering the enthalpy of the hydride system to 76 kJ/mol H_2 in respect to the one of pure $NaBH_4$ (108 kJ·mol^{-1} H_2), as shown in the reaction (57) [112,182]. Consequently, the dehydrogenation temperature is reduced up to 360 C. However, the hydrogen capacity of the system is still low, i.e., 4.5 wt %.

$$4NaBH_4 + 5Mg_2NiH_4 \leftrightarrows 2MgNi_{2.5}B_2 + 4NaH + 8Mg + 16H_2 \tag{57}$$
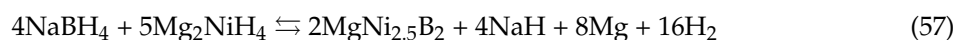
4.3. Mg(BH₄)₂

The effect of additives on the reversibility of $Mg(BH_4)_2$ has been an object of intensive investigation [101,183–188]. The result of the doping seems to be a sensible acceleration of hydrogenation and dehydrogenation processes. However, in the literature, just a few hydrogenation-dehydrogenation cycles are reported and the observed enhancement of the reaction kinetics, in particular for the desorption process, is usually connected with the chemical reaction between the hydride and the additive. Recently, Zavarotynska et al. reported on the partial reversibility of γ-$Mg(BH_4)_2$ in presence of Co-based additives (Co$_{add}$) [187,188]. They investigated the first three absorption-desorption cycles of γ-$Mg(BH_4)_2$ + Co$_{add}$ at 285 °C and 3 bar H_2 pressure. The first desorption yielded 4 wt % of H_2, and the re-absorption at the same temperature but at the pressure of 120 bar H_2 resulted in the uptake of about 2 wt % H_2. Upon re-absorption, γ-$Mg(BH_4)_2$ was not formed back, but instead crystalline β-$Mg(BH_4)_2$ was synthesized. With further cycling, the reversible hydrogen capacity of the samples decreased with an increase in the amount of nano-crystalline MgO and unidentified boron–hydrogen compounds.

Although the addition of selected additives to the tetrahydroborates partially helps to improve the hydrogen absorption and desorption properties, the use of this class of materials as hydrogen storage media is hampered by unfavorable thermal stability.

4.4. Ca(BH₄)₂

As previously mentioned, for $Ca(BH_4)_2$ several decomposition paths (often overlapping) might be observed (Section 3.5), depending on temperature and hydrogen pressure at which the process is carried out [100–102,189]. The reversibility is linked to the final decomposition products. The formation of $Ca(BH_4)_2$ was shown to be partially reversible when the pristine material was doped with Ti and Nb-based additives. Kim et al. [190,191] observed that after desorption at 420 °C in static vacuum, $Ca(BH_4)_2$ can be formed back with a yield of roughly 50% (at 350 °C and 90 bar H_2), if the starting material is milled together with $TiCl_3$ and NbF_5. From these works, it is possible to conclude that the key to the reversibility of $Ca(BH_4)_2$ is the formation of CaB_6. It is known that when using selected additives, $Ca(BH_4)_2$ can be synthesized starting from CaH_2 and CaB_6 [190,192–194]. In fact, Rönnebro et al. successfully synthesized $Ca(BH_4)_2$ with the yield of roughly 60% heating a mixture of CaH_2 and CaB_6 doped with $TiCl_3$ up to 440 °C at a hydrogen pressure of 700 bar [194]. A similar yield of formed $Ca(BH_4)_2$ was obtained by Rongeat et al. [193] via reactive ball milling and following heat

treatment at 350 °C under 90 bar of hydrogen pressure of a mixture of CaH_2 and CaB_6 with the addition of $TiCl_3$ or TiF_3.

Recently, Bonatto Minella et al. [195] based on the work of Bösenberg et al. [159] proposed an interesting approach to explain the effect of the TM-fluorides on the reversibility of the CaB_6/CaH_2–$Ca(BH_4)_2$ system. The formation of transition-metal boride nanoparticles during milling, and hydrogen desorption of the TM-fluorides doped $Ca(BH_4)_2$ is proposed to support the heterogeneous nucleation of CaB_6, maximizing its formation over the one involving irreversible elemental boron and $CaB_{12}H_{12}$. In the case of material doped with NbF_5 and TiF_4, the {111}CaB_6/{1011}NbB_2, {111}CaB_6/{1010}NbB_2, as well as {111}CaB_6/{1011}TiB_2 plane pairs have the potential to be the matching planes because the *d*-value mismatch is well below the *d*-critical mismatch value (6%) [196,197]. This mechanism is similar to that observed for $2LiBH_4 + MgH_2$. Transition-metal borides formed by the reaction of the transition metal based additives with the tetrahydroborates act as heterogeneous nucleation sites for MgB_2, thus improving desorption and absorption reaction kinetics [159].

Despite the fact that the TM-boride species assist the formation of CaB_6, the reversibility of the Ca-RHC system, i.e., $Ca(BH_4)_2 + MgH_2$ as shown in reaction (58), does not happen [137,198–200].

$$Ca(BH_4)_2 + MgH_2 \leftrightarrows Mg + (2/3)CaH_2 + (1/3)CaB_6 + (13/3)H_2 \tag{58}$$
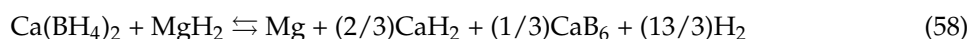
Instead, every time that the material is cycled the stable phase $CaB_{12}H_{12}$ is formed as in reaction (59), thus losing hydrogen capacity and slowing down the kinetic behavior.

$$Ca(BH_4)_2 + MgH_2 \leftrightarrows Mg + (5/6)CaH_2 + CaB_6 + (1/6)CaB_{12}H_{12} + (19/6)H_2 \tag{59}$$
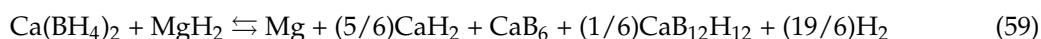
Recently, Bergemann et al. [201] proposed an alternative the combination of $Ca(BH_4)_2$ with Mg_2NiH_4 based on the previous works about $4LiBH_4 + 5Mg_2NiH_4$ [174] and $4NaBH_4 + 5Mg_2NiH_4$ [184]. The reversible ternary boride phase was confirmed $MgNi_{2.5}B_2$ upon dehydrogenation according to reaction (60). There was no evidence of the presence of the irreversible $CaB_{12}H_{12}$. However, $Ca(BH_4)_2$ was partially re-hydrogenated and this is attributed to thermodynamic and kinetic constraints when starting from $MgNi_{2.5}B_2$.

$$Ca(BH_4)_2 + 2.5Mg_2NiH_4 \rightarrow CaH_2 + MgNi_{2.5}B_2 + 4Mg + 8H_2 \tag{60}$$

5. Summary and Future Research Directions

In this review, the most relevant investigated materials in the last decades concerning solid state hydrogen storage in homoleptic tetrahydroborates have been highlighted. As a matter of fact, these materials used alone or as a part of RHC systems have some restrictions, which make their use for practical applications challenging. Owing to their high gravimetric hydrogen capacity (about 8–10 wt %), tetrahydroborates are extremely appealing hydrogen storage materials. However, the contained hydrogen is not easily accessible. Under thermal input, the most investigated tetrahydroborates ($LiBH_4$, $NaBH_4$, $K(BH_4)$, $Mg(BH_4)_2$, and $Ca(BH_4)_2$) decompose at temperatures above 300 °C, and their decomposition products are partially reversible only under extreme temperature and hydrogen pressure conditions (over 100 bar and 350 °C). Additives such as transition metal, transition metal halides, or oxides, sensibly influence the decomposition reaction of these materials, often lowering the starting decomposition temperature by several tenths of degrees. However, the reversibility of the material still remains an issue since stable phases appear. In the case of nanoconfinement, due to the matrix confining the materials, the capacity of the borohydrides or hydride mixtures is still low and sometimes the stability upon absorption-desorption cycling is poor. For these reasons, the hitherto most promising approach to effectively store hydrogen in tetrahydroborates is through the use of RHC strategy. When compared to the pristine materials, this method enables the achievement of full reversibility under milder temperatures and hydrogen pressure

conditions, e.g., 350–400 °C and 3 bar-50 bar for $2LiBH_4 + MgH_2$. Despite the fact that these conditions, mainly temperature, are not even near the ones required for on board practical application (desired temperature $\approx$ 90 °C), there has been just one development of a demonstration hydrogen storage tank based on $2LiBH_4 + MgH_2$ plus $TiCl_3$ as an additive [202]. The pilot tank has been developed for 250 g of RHC + $TiCl_3$. It has been found that during operation, the thermal management becomes an important issue, and moreover, the material undergoes a kind of phase separation, having a negative effect on the kinetic behavior and losing capacity. To the best of our knowledge, this is the first tank design based on borohydrides and it is a starting point to further optimize the scaled-up conditions of tetrahydroborates as hydrogen storage materials. Nowadays, the research is directed to find better destabilized systems that are able to work near the targeted temperature condition of about 90 °C and are capable to reach over 10 wt % of capacity. Besides, the cost of the material is not a minor question at the time to employ it in a large hydrogen storage tank.

In spite of several efforts to find the proper destabilized hydride system, the correct additive and suitable material preparation procedure, it has not yet been possible to achieve complete hydrogen desorption/absorption at the theoretically expected temperature and hydrogen pressure conditions. Moreover, the hydrogenation-dehydrogenation cycling stability is still a roadblock. Although tetrahydroborates are known for more than a century, the major advances towards the utilization of tetrahydroborates have been done in the last 20 years. Based on this perspective, the hydrogen storage properties of tetrahydroborates can be further improved by different strategies that are broadly used nowadays, such as destabilization approaches, addition of catalyst, and/or reactive compounds, or even nanoengineering. Thus, in the near future tetrahydroborates will hopefully fulfill the conditions for a practical application.

Author Contributions: Dr. Claudio Pistidda and Dr. Julián Puszkiel conceieved the design of the structure of the work together with Dr. Sebastiano Garroni, Dr. Chiara Milanese. Dr. Fabiana Gennari contributed also with the writing and correction of the paper. Prof. Thomas Klassen and Dr. Martin Dorhnheim contributed with the correction of the paper.

Conflicts of Interest: The authors declare no conflict of interest.

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