Review

Calcium Borohydride Ca(BH$_4$)$_2$: Fundamentals, Prediction and Probing for High-Capacity Energy Storage Applications, Organic Synthesis and Catalysis

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Abstract: Calcium borohydride (Ca(BH$_4$)$_2$) is a complex hydride that has been less investigated compared to its lighter counterpart, magnesium borohydride. While offering slightly lower hydrogen storage capacity (11.5 wt% theoretical maximum, 9.6 wt% under actual dehydrogenation conditions), there are many improvement avenues for maximizing the reversible hydrogen storage that have been explored recently, from DFT calculations and polymorph investigations to reactive hydride composites (RHCs) and catalytic and nanosizing effects. The stability of Ca(BH$_4$)$_2$, the possibility of regeneration from spent products, and the relatively mild dehydrogenation conditions make calcium borohydride an attractive compound for hydrogen storage purposes. The ionic conductivity enhancements brought about by the rich speciation of borohydride anions can extend the use of Ca(BH$_4$)$_2$ to battery applications, considering the abundance of Ca relative to alkali metal borohydrides typically used for this purpose. The current work aims to review the synthetic strategies, structural considerations of various polymorphs and adducts, and hydrogen storage capacity of composites based on calcium borohydrides and related complex hydrides (mixed anions, mixed cations, additives, catalysts, etc.). Additional applications related to batteries, organic and organometallic chemistry, and catalysis have been briefly described.

Keywords: calcium borohydride; hydrogen storage; thermodynamics; kinetic improvement; batteries; RHC reactive hydride composites

1. Introduction

The road to sustainable energy has an ultimate endpoint: the hydrogen economy. Hydrogen remains the only energy source producing a high amount of clean energy with no carbon-containing by-products [1–12]. However, vehicular and stationary applications relying on hydrogen technology still face major drawbacks and important technological challenges, along with safety risks associated with H$_2$ storage tanks where pressure spikes to 700 bar H$_2$ [1].

In this context, solid-state hydrogen storage represents a safer alternative to classical high pressure H$_2$ tanks, although the strict requirements of the US DOE have yet to be met [2]. The current target for 2025 is a material capable of storing 5.5 wt% hydrogen (1.8 kWh/kg, 1.3 kWh/L, with an estimated cost of $9/kWh). Perhaps the most important aspect of solid-state hydrogen storage is the material’s capability to reversibly store H$_2$ without continual loss of this storage capacity. To this end, most experimental tanks have been fueled by various intermetallics (AB$_2$-type or AB$_5$-type, such as LaNi$_5$H$_6$ with 1.38 wt%), which offer a storage capacity not exceeding, at best, 2 wt% hydrogen. With a storage capacity of up to 20 wt% (Be(BH$_4$)$_2$) and high gravimetric densities (110–150 g H$_2$/L), complex hydrides are the most promising solid-state hydrogen storage materials, and the amount of research in this area has been staggering. Still, the kinetic and thermodynamic factors of absorption/desorption processes hinder their wider use, while the
potentially toxic boron-containing gases (diborane or higher homologues) are of concern for the environment.

Light metal borohydrides $\text{M(BH}_4\text{)}_n$ (M = Li, Na, Mg, Ca) and alanates have received the most attention not only for their increased theoretical hydrogen storage capacity, but also due to promising results pointing to the possibility of reversibility during successive a/d cycles. With a high storage capacity of about 10 wt% (actually attainable under experimental conditions) and a relatively low dehydrogenation temperature, Ca($\text{BH}_4\text{)}_2$ holds promise for a viable and reversible hydrogen storage material under suitable conditions. While dehydrogenation of Ca($\text{BH}_4\text{)}_2$ has been reported in the range 350–500 $^\circ$C, this is still lower than other light metal borohydrides. Driven by the high hydrogen storage capacity of calcium borohydride needed for energy storage applications, particularly in the field of hydrogen storage and fuel cells, researchers have investigated various methods to enhance the hydrogen release kinetics and lower the dehydrogenation temperature. Ca($\text{BH}_4\text{)}_2$ has the potential to offer high energy density, enabling the development of compact and efficient energy storage systems. Calcium borohydride can serve as both a source of energy and a hydrogen reservoir within energy storage devices, such as lithium-ion batteries and sodium-ion batteries.

However, despite its potential, there are several challenges that need to be addressed before the wide acceptance of Ca($\text{BH}_4\text{)}_2$ as an energy storage material. The kinetics of hydrogen release from calcium borohydride are relatively slow, limiting its practical application. Enhancing hydrogen release kinetics is a key research focus. The dehydrogenation reaction mechanisms of calcium borohydride are not yet fully understood, and further investigation is required to gain detailed insights into the underlying processes. Another obstacle comes from an economic point of view. The cost of Ca($\text{BH}_4\text{)}_2$ is high; therefore, the development of cost-effective and scalable synthesis routes for calcium borohydride is another area that requires more research results.

The current review aims to describe the most significant aspects concerning Ca($\text{BH}_4\text{)}_2$, from the synthesis routes, crystal structure and polymorphs, structural variability and modifications (DFT computations, nanoconfinement, destabilization, RHCs, solvates/adducts), characterization methods, hydrogen storage properties, and further applications in battery technology, organic synthesis, and organometallic chemistry. Optimizing the overall performance, stability, and efficiency of energy storage devices utilizing calcium borohydride is a critical research challenge.

### 2. Synthesis Routes

There are various methods reported for the synthesis of borohydrides [5,13] and, in particular, of Ca($\text{BH}_4\text{)}_2$. For instance, Barkhordarian et al. reported the hydrogenation of the RHC: CaH$_2$ + MgB$_2$ at 350 $^\circ$C and 140 bar H$_2$ to produce Ca($\text{BH}_4\text{)}_2$ + MgH$_2$ (Equation (1)) [13].

$$\text{CaH}_2 + \text{MgB}_2 + 4 \text{H}_2 \xrightarrow{250 \, ^\circ\text{C}, 140 \, \text{bar H}_2} \text{Ca(BH}_4\text{)}_2 + \text{MgH}_2 \quad \Delta \text{H} = -27.5 \, \text{kg/mol (1)}$$

However, the layered structure of B in MgB$_2$ was essential for Equation (1) to occur, as no reactivity was observed when substituting MgB$_2$ for B. The reasoning seemed to lie in the structural features of MgB$_2$, where layers of B are located between layers of Mg, a structure bearing similarities to graphite. The authors also reported enhanced kinetics of de-/rehydrogenation when using Ti(O$^{\text{i}}$Pr)$_4$ as an additive [13].

Dodecahydroborates have been obtained by desolvation at ~120 $^\circ$C of the MB$_{12}$H$_{12}$ solvates, or in their pure form, by the following Equation (2) [14]. The mixture of M($\text{BH}_4\text{)}_2$ and B$_{10}$H$_{14}$ is typically milled in a planetary ball mill (10 steel balls, 7 mm diameter, 0.1 MPa Ar, 5 h milling), followed by sintering in stainless steel crucibles at 380 $^\circ$C for 2 h in the case of CaB$_{12}$H$_{12}$ [14].

$$\text{M(BH}_4\text{)}_2 + \text{B}_{10}\text{H}_{14} \rightarrow \text{MB}_{12}\text{H}_{12} + 5 \text{H}_2 \quad (M = \text{Mg, Ca}) \quad (2)$$
Nanostructuring has long been utilized to achieve significantly better yields for reactions where classical synthetic routes have failed [6], while stabilization of reactive species has often been attained via complex formation, i.e., through ligand coordination, as is the case for ammine solvates of M(BH₄)₂ (M = Ca, Sr) [15]. Jepsen et al. reported the synthesis of four such solvates in the case of calcium-based borohydrides: Ca(H₃)₆(BH₄)₂ (n = 1, 2, 4, and 6) (Equation (3)) [15]. The pure Ca(BH₄)₂ absorbs gaseous ammonia, forming the unstable hexa-ammine calcium borohydride Ca(H₃)₆(BH₄)₂, which undergoes a rapid decomposition equilibrium to form the tetra-ammine calcium borohydride Ca(H₃)₄(BH₄)₂.

\[
\text{Ca}(\text{BH}_4)_2 + 6 \text{NH}_3(g) \rightarrow \text{Ca}(\text{NH}_3)_6(\text{BH}_4)_2 \leftrightarrow \text{Ca}(\text{NH}_3)_4(\text{BH}_4)_2 + 2 \text{NH}_3(g) \quad (3)
\]

Karabulut et al. synthesized Ca(BH₄)₂ in a solid-state reaction starting from anhydrous, synthetic colemanite, a calcium borate mineral of formula Ca₅B₆O₁₁·5H₂O [16]. By milling Ca₂B₆O₁₁ and CaH₂ in a 1:12 molar ratio in a spex-mill, calcium borohydride was obtained with a sole by-product in the form of CaO (Equation (4)). Using colemanite as the raw material has a clear economic advantage, as the cost of 1 g Ca(BH₄)₂ would be ~$4, compared to the commercial version’s (~$200).

\[
\text{Ca}_2\text{B}_6\text{O}_{11} + 12 \text{CaH}_2 \rightarrow \text{Ca}(\text{BH}_4)_2 + 11 \text{CaO} \quad (4)
\]

It is also interesting to note that the hydrogen content of Ca(BH₄)₂ could effectively double when subjected to hydrolysis, as Ca(BO₂)₂ is the main product along with H₂ (Equation (5)).

\[
\text{Ca}(\text{BH}_4)_2 + 4 \text{H}_2\text{O} \rightarrow \text{Ca}(\text{BO}_2)_2 + 8 \text{H}_2 \quad (5)
\]

Given the reactivity of metal borohydrides towards water, it follows that the formation of a bimetallic borohydride in the form of LiCa₃(BH₄)₂(BO₃)₃, as isolated and characterized by Lee et al., is not that surprising after all [17]. The mixed borohydride was isolated from hydrogenation studies carried out on RHC based on 0.75 LiBH₄·0.25 Ca(BH₄)₂ embedded in a mesoporous carbon matrix (Vₚ = 1.15 cm³/g), and most likely originates from oxygen-containing impurities (oxygen or water) [17]. The formation of LiCa₃(BH₄)(BO₃)₂ was tracked by XRD and was found to proceed through the intermediacy of mixed anion calcium borohydride, Ca₃(BH₄)₁₁(BO₃)₂ (Equation (6)).

\[
\text{LiBH}_4 + 2 \text{Ca}_3(\text{BH}_4)_3(\text{BO}_3) \rightarrow \text{LiCa}_3(\text{BH}_4)(\text{BO}_3)_2 + 3 \text{Ca}(\text{BH}_4)_2 \quad (6)
\]

The general route to prepare Ca(BH₄)₂ starts from CaH₂ or alkoxide Ca(OR)₂ and B₂H₆, or more conveniently by wet chemistry in a metathesis reaction, where CaCl₂ and NaBH₄ are ball milled in THF (tetrahydrofuran), producing the commercially available THF adduct of calcium borohydride, namely, Ca(BH₄)₂·2THF [18,19] (Equation (7)).

\[
2 \text{NaBH}_4 + \text{CaCl}_2 \xrightarrow{\text{THF}} \text{Ca}(\text{BH}_4)_2 \cdot 2\text{THF} + 2 \text{NaCl} \quad (7)
\]

Other adducts of Ca(BH₄)₂ are also reported; for instance, desolvation of Ca(BH₄)₂·2THF at 80 °C led to the formation of Ca(BH₄)₂·THF, as reported by Richter et al. [20]. Möller et al. reported the synthesis of M(BH₄)ₙ from the systems AlB₂→MHₓ (M = Li, Na, Ca, but not Mg), where AlB₂ served as a boron source, and H₂ was introduced at a pressure in the range of 100–600 bar [21] (Equation (8)).

\[
\text{AlB}_2 + \frac{2}{x}\text{MH}_x + 3 \text{H}_2 \rightarrow \frac{2}{x} \text{M}(\text{BH}_4)_x + \text{Al} \quad (8)
\]

The inclusion of Al in the case of Ca(BH₄)₂ can produce 6.3 wt% with a reaction enthalpy of 64.9 kJ/mol H₂ and an entropy of 156.5 J/k mol H₂, requiring a temperature
of 140 °C at an equilibrium H\textsubscript{2} pressure of 1 bar (Equation (9)). This alone is a marked improvement compared to neat Ca(BH\textsubscript{4})\textsubscript{2} (87.2 kJ/mol H\textsubscript{2}, 158.3 J/K mol H\textsubscript{2}, 280 °C) [21].

\[
Ca(BH_4)_2 + Al \leftrightarrow AlB_2 + CaH_2 + 3 H_2 \tag{9}
\]

Nakagawa et al. used ball milling of CaH\textsubscript{2}–CaB\textsubscript{6} mixtures to obtain Ca(BH\textsubscript{4})\textsubscript{2} near room temperature, noting the important role of crystalline CaB\textsubscript{6} in order to achieve reasonably high rates for hydrogenation [22].

Several experimental aspects have to be considered when synthesizing Ca(BH\textsubscript{4})\textsubscript{2}, along with strong safety protocols. For instance, the influence of chlorides was illustrated in the mixture CaCl\textsubscript{2}:LiBH\textsubscript{4}, when the reactant ratio needs to be carefully optimized, otherwise solid solutions Li(BH\textsubscript{4})\textsubscript{x}Cl\textsubscript{1-x}/Ca(BH\textsubscript{4})\textsubscript{2-x}Cl\textsubscript{x} (milling performed under an Ar atmosphere) are obtained, and CaHCl forms instead of Ca(BH\textsubscript{4})\textsubscript{2} [23]. Ca(BH\textsubscript{4})\textsubscript{2} was also produced by milling CaB\textsubscript{6} with CaH\textsubscript{2} in a 1:2 molar ratio under 700 bar H\textsubscript{2} at 400–440 °C, as evidenced by Ronnebro and Majzoub [11].

Ca(BH\textsubscript{4})\textsubscript{2} can serve as a borohydride source for other metathesis reactions, for instance with M\textsubscript{2}(SO\textsubscript{4})\textsubscript{x} metal sulfates, with the driving force for obtaining M(BH\textsubscript{4})\textsubscript{x} being the formation of the precipitate of CaSO\textsubscript{4} [18]. Other authors have reported a mixed adduct Ca(BH\textsubscript{4})\textsubscript{2}:Al(BH\textsubscript{4})\textsubscript{3} resulted by mixing the unsolvated starting borohydrides, decomposing into starting borohydrides upon heating, and having a postulated structure [Ca(BH\textsubscript{4})]\textsuperscript{+}[Al(BH\textsubscript{4})\textsubscript{4}]\textsuperscript{-} supported by IR spectrum analysis [24].

3. Structural Variability, Polymorphs, Crystal Structure, DFT Predictions, and Phase Transitions

The structural stability aspects of many representative simple and complex hydrides (alanates, borohydrides) have been reviewed in the recent past [25], along with Ca-based RHCs ([Ca(BH\textsubscript{4})\textsubscript{2} + MgH\textsubscript{2} and Ca(BH\textsubscript{4})\textsubscript{2} + MgH\textsubscript{2} + 0.1NbF\textsubscript{3}] [26]). Karimi et al. have highlighted the catalytic role of NbF\textsubscript{5} on the hydrogen sorption kinetics of Ca(BH\textsubscript{4})\textsubscript{2} + MgH\textsubscript{2} (10.5 wt% H\textsubscript{2}), when ~10 nm diameter NbB\textsubscript{2} was evidenced to form and to remain stable during a/d cycles, while also being responsible for producing ~50% finer Ca-RHC + 0.1NbF\textsubscript{5} nanocomposites and preventing agglomeration of calcium-RHCs [26].

The structural features of Ca(BH\textsubscript{4})\textsubscript{2} have been described by Llamas-Jansa et al., who reported the different behavior between α, β, and γ polymorphs of Ca(BH\textsubscript{4})\textsubscript{2} during hydrogenation studies [27]. Vibrational spectroscopy data was employed to correlate the increase in wavenumber to the increased decomposition temperature (15 °C between the α and γ polymorphs). The most effective H\textsubscript{2} release was observed when ramping at 10 °C/min a sample of pure α-Ca(BH\textsubscript{4})\textsubscript{2} [27]. Moreover, Sharma et al. shed light on the B-H bond breaking/formation, using isotope exchange reactions with a D\textsubscript{2} pressure of 20 bar, concluding an activation energy E\textsubscript{a} = 82.1 ± 2.7 kJ mol\textsuperscript{-1} for the transformation of Ca(BH\textsubscript{4})\textsubscript{2} into Ca(BD\textsubscript{4})\textsubscript{2} and proposing a mechanistic scheme involving the formation of an activated complex: Ca((BH\textsubscript{4})\textsubscript{2} + D\textsubscript{2} ↔ Activated complex → Ca(BD\textsubscript{4}H\textsubscript{4}→x)\textsubscript{2} [28].

Considering all the literature data, it seems that the dehydrogenation behavior of Ca(BH\textsubscript{4})\textsubscript{2} depends greatly on the polymorph composition and their respective ratio in the starting sample material, especially considering the typical co-existence of α and β phases during hydrogenation experiments [29]. Soloninin et al. studied the reorientation motion of BH\textsubscript{4} tetrahedra in M(BH\textsubscript{4})\textsubscript{2} (M = Mg, Ca) by proton and \textsuperscript{11}B spin-lattice relaxation rates and found that at low temperatures, the reorientation in the β phase is faster (E\textsubscript{a} = 100–116(5) meV for β-, E\textsubscript{a} = 286(7) meV for α-Ca(BH\textsubscript{4})\textsubscript{2}), and depends on the changes in the local environment of BH\textsubscript{4} groups [29].

3.1. Crystal Structure, Polymorphs, and Phase Transitions

The two most common phases of calcium borohydride are α-Ca(BH\textsubscript{4})\textsubscript{2} (lattice parameters: a = 8.7782(2) Å, b = 13.129(1) Å, c = 7.4887(9) Å; 300 K) and β-Ca(BH\textsubscript{4})\textsubscript{2} (a = 6.9509(5) Å, c = 4.3688(3) Å; 433 K). The alpha phase is stable from 0 K to 440 K, while from 440 K, the high temperature phase, β-Ca(BH\textsubscript{4})\textsubscript{2} becomes dominant. The metastable
\(\gamma\)-Ca(\(\text{BD}_4\)\(\text{H}_2\))\(_2\) crystal structure was reported by combined X-ray and neutron measurements, and was refined in the orthorhombic space group \(Pbca\) (\(a = 7.525(1)\) Å, \(b = 13.109(2)\) Å, \(c = 8.403(1)\) Å) [30,31]. The \(\gamma\) phase is less stable than the \(\alpha\) phase, and its stability decreases with temperature; the expected phase transitions are expected to follow the trend \(\alpha\)-Ca(\(\text{BH}_4\)\(\text{H}_2\)) \(\rightarrow\) \(\gamma\)-Ca(\(\text{BH}_4\)\(\text{H}_2\)) \(\rightarrow\) \(\beta\)-Ca(\(\text{BH}_4\)\(\text{H}_2\)) [30]. There have been some debates regarding the space group of both \(\alpha\) and \(\beta\) phases; for instance, DFT computations conducted by Le et al. [32] over the hydrostatic pressure range 0–40 GPa showed that the \(F2dd\) space group seems to be the preferred structure of \(\alpha\)-Ca(\(\text{BH}_4\)\(\text{H}_2\)) at low temperatures [32]. Crystal structures and total energy have been calculated based on the general gradient approximation (GGA) method for density functional theory (DFT), implemented by the ABINIT simulation package, while Hartwigsen–Goedecker–Hutter pseudopotentials have been used for calculations, and the exchange–correlation interactions were described by the Perdew–Burke–Ernzerhof (PBE) GGA functional [32]. The transition to the beta phase at higher temperatures was supported by calculations performed by Lee et al. [33], who pointed out a vibrational entropy excess of \(\beta\)-Ca(\(\text{BH}_4\)\(\text{H}_2\)) over \(\alpha\)-Ca(\(\text{BH}_4\)\(\text{H}_2\)) of \(16\) J/(mol K). A total of nine possible crystal structures have been proposed in the literature for calcium borohydride: three \(\alpha\) phases, one \(\alpha'\) phase, four \(\beta\) phases, and one \(\gamma\) phase [34]. The most agreed-upon structures are, however, the \(\alpha\) and \(\beta\) phases [35] (Table 1).

<table>
<thead>
<tr>
<th>Metal Borohydride</th>
<th>Decomposition Temperature (°C)</th>
<th>Rehydrogenation Temperature (°C)</th>
<th>Space Group</th>
<th>Crystal System</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\alpha)-Ca((\text{BH}_4)(\text{H}_2))</td>
<td>347–387 °C, 397–497 °C (2-step)</td>
<td>RT stable</td>
<td>(Fddd) or (F2dd)</td>
<td>Orthorhombic</td>
<td>[32,35,36]</td>
</tr>
<tr>
<td>(\beta)-Ca((\text{BH}_4)(\text{H}_2))</td>
<td>(\beta)-Ca((\text{BH}_4)(\text{H}_2)) (\rightarrow) (\beta)-Ca((\text{BH}_4)(\text{H}_2)) (\rightarrow) (\alpha)-Ca((\text{BH}_4)(\text{H}_2)) (\rightarrow) (\gamma)-Ca((\text{BH}_4)(\text{H}_2)) (I-42d), occurring at (\sim)495 K</td>
<td>RT, metastable, HT polymorph</td>
<td>(P4_2/m) or (P4)</td>
<td>Tetragonal</td>
<td>[33,36]</td>
</tr>
<tr>
<td>(\alpha')-Ca((\text{BH}_4)(\text{H}_2))</td>
<td>-</td>
<td>-</td>
<td>(I\bar{4}2d)</td>
<td>Tetragonal</td>
<td>[35]</td>
</tr>
<tr>
<td>(\gamma)-Ca((\text{BD}_4)(\text{H}_2))</td>
<td>-</td>
<td>-</td>
<td>(Pbca)</td>
<td>Orthorhombic</td>
<td>[30,31]</td>
</tr>
<tr>
<td>(\text{CaB}_2\text{H}_12)</td>
<td>-</td>
<td>-</td>
<td>(C2/c)</td>
<td>Monoclinic</td>
<td>[37]</td>
</tr>
</tbody>
</table>

Other reports have dealt with phase variation occurring via desolvation from the adduct Ca(\(\text{BH}_4\)\(\text{H}_2\))\(\text{2THF}\) when a mixture of \(\alpha\)-Ca(\(\text{BH}_4\)\(\text{H}_2\)) and \(\gamma\)-Ca(\(\text{BH}_4\)\(\text{H}_2\)) polymorphs was observed experimentally [35]. Filinchuk et al. have also reported a second-order transition, \(\alpha\)-Ca(\(\text{BH}_4\)\(\text{H}_2\)) \(\rightarrow\) \(\alpha'\)-Ca(\(\text{BH}_4\)\(\text{H}_2\)) (I-42d), occurring at \(\sim\)495 K [35]. The various polymorphs of \(\alpha\)-Ca(\(\text{BH}_4\)\(\text{H}_2\)) (prepared by desolvation of commercially available Ca(\(\text{BH}_4\)\(\text{H}_2\))\(\text{2THF}\) at 433 K for 1 h) have also been investigated under high pressure (10.4 GPa, room temperature) by Liu et al. [38] by combined Raman and IR spectroscopies, and it was found that the transformations are reversible throughout the pressure region investigated [38]. The authors also pointed out the need to start the compression from phase-pure Ca(\(\text{BH}_4\)\(\text{H}_2\)), otherwise \(\text{H}_2\) release and interaction in mixtures \(\alpha\)-Ca(\(\text{BH}_4\)\(\text{H}_2\))\(\rightarrow\) \(\beta\)-Ca(\(\text{BH}_4\)\(\text{H}_2\)) (which are the typical starting point) would further complicate the analysis of lattice, bending, and stretching modes [38]. In order to avoid the \(\alpha\)-Ca(\(\text{BH}_4\)\(\text{H}_2\)) \(\rightarrow\) \(\beta\)-Ca(\(\text{BH}_4\)\(\text{H}_2\)) transition, a more conservative approach was proposed by Paolone et al., who heated Ca(\(\text{BH}_4\)\(\text{H}_2\))\(\text{2THF}\) at 125 °C for 20 h (incomplete conversion of \(\text{THF}\) adduct to \(\alpha\)-Ca(\(\text{BH}_4\)\(\text{H}_2\))) by following the \(\alpha\) \(\rightarrow\) \(\alpha'\) structural phase transition at 180–220 °C, and finally the \(\alpha'\) \(\rightarrow\) \(\beta\) transformation at 320–330 °C [39]. Monitoring the vibration frequency of Ca(\(\text{BH}_4\)\(\text{H}_2\)) via anelastic spectroscopy measurements, the authors also noted that upon further cooling the sample from 320 °C to room temperature, the borohydride did not undergo any phase transitions, consistent with irreversible transformations occurring during heating (\(\alpha\) \(\rightarrow\) \(\alpha'\) \(\rightarrow\) \(\beta\)). Although not detected by DSC, evaluation of the relative variation/decrease of Young’s modulus upon heating can indirectly point out these transitions [39]. Some debate still exists in the literature, as
some authors claim another phase in the C2/c space group for Ca(BH₄)₂ near ambient conditions [40].

Stoichiometric Equations (1)–(7) can describe several possible decomposition pathways for Ca(BH₄)₂ (Figure 1).

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Figure 1. Decomposition pathways possible for calcium borohydride (Equations (1)–(7)).

Judging by how widespread dodecahydro-closo-dodecaborates (B₁₂H₁₂²⁻) are during the dehydrogenation of metal borohydrides M(BH₄)ₙ, it seemed reasonable to further study the implications of these intermediate species on hydrogen storage properties as well as on the unexpected increase in ionic conductivity of related alkali and alkali-metal compounds [41]. Some representative examples of polymorphs of Ca(BH₄)₂, mixed anion borohydrides, and dodecaborate anion are depicted in Figure 2.

Figure 2. (a) Representation of the dodecahedral [B₁₂H₁₂]²⁻ ion of the icosahedral frame. Boron atoms (green), hydrogen atoms (white). (b) Crystal structure of Ca(NH₃)₄(BH₄)₂. Ca, B, N, and H are represented by yellow, red, blue, and gray spheres, respectively; the molecular [Ca(NH₃)₄(BH₄)₂]
octahedra form hexagonal patterns in the bc plane. (c) The layers are stacked in the order AAA along the a direction (reproduced with permission from Ref. [15]). (d) Crystal structures of α-Ca(BH$_4$)$_2$ in space group $Fdar{d}$ and (e) β-Ca(BH$_4$)$_2$ in space group $P4$. The color codes for atoms are green (calcium), pink (boron), and white (hydrogen). Each BH$_4^-$ unit is shown by a tetrahedron. Reprinted with permission from Ref. [38].

The thermal stability of MB$_{12}$H$_{12}$ is rather high, but a tendency towards amorphization (perhaps of the tentative formula B$_{12}$H$_{12-\alpha}^2$-) has been recorded upon heating to 400–450 °C and further, when anion polymerization may occur (CaB$_y$H$_z$)$_n$, but elemental B was not observed even at 750 °C [41].

Jepsen et al. have recently described the DFT-optimized and experimental crystal structures (synchrotron radiation powder XRD data) of Ca(NH$_3$)$_n$(BH$_4$)$_2$ ($n$ = 1, 2, 4, and 6) (Figure 3) [15]. DFT calculations were performed to optimize the structures from the SR-PXD data by using the Vienna Ab-initio Simulation Package (VASP) in the Perdew–Burke–Ernzerhof generalized-gradient approximation [15]. Ca(NH$_3$)$_4$(BH$_4$)$_2$ ($P21/c$) has a molecular structure connected by dihydrogen bonds, and all ammine complexes release ammonia upon gentle heating (at a low partial pressure of NH$_3$), or H$_2$-NH$_3$ (high partial pressure of NH$_3$). These findings suggest metal ammine borohydrides can be used to store ammonia, or to release H$_2$ by catalytic ammonia splitting [15].

Figure 3. (a) In situ SR-PXD pattern of Ca(NH$_3$)$_h$(BH$_4$)$_2$ heated from RT to 350 °C (5 °C min$^{-1}$, p(Ar) = 1 bar, $\lambda$ = 0.9941 Å). (b) Normalized integrated diffraction intensities plotted as a function of temperature. Reprinted with permission from Ref. [15]. (c) Decomposition temperatures for selected ammine metal borohydrides and the respective metal borohydrides under an Ar atmosphere, as a function of the metal M electronegativity. Zn(BH$_4$)$_2$ is not observed experimentally and is considered unstable. Reprinted with permission from Ref. [15].
Ca$^{2+}$ is octahedrally coordinated to six equivalent [BH$_4$] tetrahedra, featuring Ca-B bond distances of 2.82–2.97 Å. The divalent cations in α-Ca(BH$_4$)$_2$ form a close-packed, diamond-type structure where the tetrahydroborate groups exhibit T-shape coordination.

Another interesting intermediate that can be observed during thermal decomposition of Ca([11]BD$_3$)$_2$; after initially being described as belonging to “δ-Ca(BH$_4$)$_2$”, it has been properly assigned to Ca$_3$([11]BD$_4$)$_3$([11]BO$_4$) and its structure was deduced by Riktor et al. based on synchrotron radiation powder XRD and supported by IR measurements [42].

With a decomposition enthalpy in the range 40.6–87 kJ/(mol H$_2$) and an onset decomposition temperature of 278 °C under 1 bar equilibrium pressure, bulk Ca(BH$_4$)$_2$ requires considerable modifications in order to conform to DOE’s restrictions. Overcoming sluggish kinetics, problematic mass transfer, and high reaction enthalpies remain key steps needing further improvement.

### 3.2. Cation Substitution

Cation substitution has been pursued in dual-cation borohydrides in order to decrease the energy barriers in hydrogenation studies of calcium borohydride [43–47]. For instance, Fang et al. studied the dual-cation (Li, Ca) borohydride LiCa(BH$_4$)$_3$ [43]. The mixed borohydride was synthesized by ball milling a 1:1 mixture of LiBH$_4$:Ca(BH$_4$)$_2$, when an intermediate phase Li$_{0.9}$Ca(BH$_4$)$_{2.9}$ was observed to transform into the final stoichiometric mixed-cation borohydride LiCa(BH$_4$)$_3$ upon heating. The dual cation Li$_{0.9}$Ca(BH$_4$)$_{2.9}$ was produced most likely by incorporation of dissolved LiBH$_4$ into β-Ca(BH$_4$)$_2$ (Equation (10)).

$$\text{LiBH}_4 + \text{Ca(BH}_4)_2 \xrightarrow{\text{ball milling}} \text{Li}_{0.9}\text{Ca(BH}_4)_2 + 0.1 \text{LiBH}_4 \xrightarrow{\Delta} \text{LiCa(BH}_4)_3 \quad (10)$$

Contrary to the desorption of individual borohydrides, the mixed-phase LiCa(BH$_4$)$_3$ started to desorb H$_2$ at 200 °C, considerably lower than the onset of LiBH$_4$ (400 °C) or Ca(BH$_4$)$_2$ (300 °C), and lost ~9.6 wt% after heating to 500 °C [43]. The Li-Ca-B-H system also bypassed the formation of the $\text{[B}_2\text{H}_2\text{]F}^-$ anion, following a two-step reaction that yielded 1.2 wt% and 8.1 wt% H$_2$, respectively (Equation (11)). The reversibility of the second dehydrogenation step was, however, only moderate, affording 5.3 wt% H$_2$ recharging [43].

$$\text{LiCa(BH}_4)_3 \xrightarrow{\Delta} \text{LiCaB}_3\text{H}_{11} + \frac{1}{2} \text{H}_2 \xrightarrow{\Delta} \text{LiCa(BH}_4)_3 + \frac{9}{2} \text{H}_2 \quad (11)$$

Jiang et al. observed a new mixed-borohydride adduct when mixing 3 LiBH$_4$:1 CaCl$_2$ in THF, namely, LiBH$_4$:Ca(BH$_4$)$_2$:2THF, which released a mixture of H$_2$:B$_2$H$_6$ upon heating in a complex, 4-step process involving the detection of yet-unknown Li-Ca-B-H phases [44]. Although typically mixing metal halides such as MCl$_n$ with LiBH$_4$ can yield mixed alkali metal-transition metal borohydrides (Equation (12)), a different reaction pathway was revealed when tuning the CaCl$_2$:LiBH$_4$ molar ration, while also using THF as reaction media.

$$\text{MCl}_n + m \text{LiBH}_4 \rightarrow \text{MLi}_{m-n}\text{(BH}_4)_n + n \text{LiCl} \quad (12)$$

Additionally, LiBH$_4$:Ca(BH$_4$)$_2$:2THF was shown to store reversibly up to 5.63 wt.% H$_2$ in the second a/d cycle [44]. Switching LiBH$_4$ with NaBH$_4$, Mattox et al. have reported the influence of the borohydride starting material on the additive used (40% CaCl$_2$), concluding that NaBH$_4$ might interpenetrate the CaCl$_2$ lattice, expanding it [46]. The hypothesized product was marked as CaNa(BH$_4$)$_{1-x}$Cl$_x$, akin to the expected product based on Equation (12).

Lang et al. reported the decomposition of another substituted borohydride, the perovskite-type NH$_4$Ca(BH$_4$)$_3$ (15.7 wt.% hydrogen capacity, Equation (13)) [45]. The origin of the low desorption temperature (65 °C) was found to reside in the destabilization of H$^+$ in NH$_4^+$ and H$^-$ in BH$_4^−$ [45].

$$\text{LiBH}_4 + \text{Ca(BH}_4)_2 + \text{NH}_4\text{Cl} \rightarrow \text{NH}_4\text{Ca(BH}_4)_3 + \text{LiCl} \quad (13)$$
The low onset correlates well with the reaction between NH$_4^+$ and BH$_4^-$, which takes place at 85 °C according to Equation (14).

$$\text{NH}_4^+ + \text{BH}_4^- \rightarrow \text{NH}_3\text{BH}_3 + \text{H}_2 \quad (14)$$

Upon heating, NH$_4$Ca(BH$_4$)$_3$ releases H$_2$ with the formation of Ca(BH$_4$)$_2$NH$_3$BH$_3$, an adduct that further desorbs ammonia borane AB: NH$_3$BH$_3$ (which undergoes a complex decomposition process also releasing H$_2$), and Ca(BH$_4$)$_2$ that can further react with LiCl to form anion-substituted borohydrides (Equation (15)) [45].

$$\text{NH}_4\text{Ca}(\text{BH}_4)_3 \rightarrow \text{Ca}(\text{BH}_4)_3 \cdot \text{NH}_3\text{BH}_3 + \text{LiCl}$$

$$\text{Ca}(\text{BH}_4)_3 \cdot \text{NH}_3\text{BH}_3 + \text{LiCl} \rightarrow \text{Ca}(\text{BH}_4)_y\text{Cl}_{1-x} + \text{Li}(\text{BH}_4)_x\text{Cl}_{1-y} \quad (15)$$

It appears that ~3.8 wt% H$_2$ can be released upon heating to 140 °C for 25 min, with very little other impurity gases such as NH$_3$ or B$_2$H$_6$ (Figure 4).

![Figure 4](image-url)  

Figure 4. (a) XRD patterns of starting materials and as-milled samples; (b) MS profiles of NH$_4$Ca(BH$_4$)$_3$; (c) isothermal hydrogen desorption curves of NH$_4$Ca(BH$_4$)$_3$ at varied temperatures. Reprinted with permission from Ref. [45].

The previous study on NH$_4$Ca(BH$_4$)$_3$ in relation to the proposed destabilization borohydride-ammonium system, was reported by Schouwink et al. [47]. In addition to Equation (13), Schouwink used a novel approach: soft milling Ca(BH$_4$)$_2$ (30 min, 500 rpm) with temperature-stabilized NH$_4$BH$_4$ (cooling at 243 K) (Equation (16)).

$$\text{NH}_4\text{BH}_4 + \text{Ca}(\text{BH}_4)_2 \rightarrow \text{NH}_4\text{Ca}(\text{BH}_4)_3 \quad (16)$$

The crystal structure of NH$_4$Ca(BH$_4$)$_3$ was also reported with a structural model in space group P-43m [47] (Figure 5).

![Figure 5](image-url)  

Figure 5. Structural models for (a) NH$_4$Ca(BH$_4$)$_3$ in space group P-43m; NH$_4^+$ (green), BH$_4^-$ (red), Ca (blue); and (b) Ca(BH$_4$)$_2$-AB; N (green), B (red), H (grey), Ca (blue). Reprinted with permission from reference [47].
3.3. Anion Substitution

Grove et al. have studied halide substitution in Ca(BH$_4$)$_2$ by ball milling the mixtures Ca(BH$_4$)$_{2-x}$CaX$_x$ (X = F, Cl, Br) with various molar ratios (x = 0.5, 1, 2) [48]. The compositions from x = 0–0.6 yield solid solutions of composition β-Ca((BH$_4$)$_{1-x}$Cl$_x$)$_2$ as revealed by Rietveld analysis of diffraction data, but there was no substitution of X$^-$ occurring for X = F or Br, possibly due to the positive enthalpy of mixing (X = F) or the lack of orthorhombic-to-tetragonal phase transition (X = Br) (Equation (17)) [48].

$$x\text{CaCl}_2 + \beta\text{Ca(BH}_4\text{)}_2 \rightarrow (1 + x)\beta\text{Ca((BH}_4\text{)}_{1-x}\text{Cl}_x\text{)}_2$$  \hspace{1cm} (17)

Even though DFT calculations predicted Br$^-$ substitution to be possible, this possibility was experimentally discarded. Additionally, DSC of β-Ca((BH$_4$)$_{0.5}$Cl$_{0.5}$)$_2$ showed a higher decomposition temperature compared to pure Ca(BH$_4$)$_2$. Interestingly, no substitution was observed at temperatures below 250 °C or in the case of α-Ca(BH$_4$)$_2$, the only polymorph undergoing this substitution being β-Ca(BH$_4$)$_2$ (Figure 6) [48]. The calculations were performed applying the periodic quantum-mechanical software CRYSTAL09 within the density functional theory, PBE functional [48].

![Figure 6](image-url)  
**Figure 6.** (a) In situ SR-PXD measured for Ca(BH$_4$)$_2$+Cl$_2$ in molar ratio 1:1, heating rate 3 K min$^{-1}$. The temperature increases from 40 to 360 °C. (a) 3D plot of the selected 2θ area. \(\Lambda = 0.703511\) Å; (b) DSC data for Ca(BH$_4$)$_2$ (dashed) and Ca(BH$_4$)$_2$–CaCl$_2$ (1:1) (solid) with a heating rate of 10 K min$^{-1}$. Reproduced with permission from Ref. [48].

Extending the range of calcium halides used for anion substitution in calcium borohydride, Rude et al. have employed CaI$_2$ in the system Ca(BH$_4$)$_2$–CaI$_2$ and found three new components formed by halide substitution: a solid solution Ca((BH$_4$)$_{1-x}$I$_x$)$_2$ with x = 0.3, the trigonal trt-Ca((BH$_4$)$_{0.70}$I$_{0.30}$)$_2$, and the orthorhombic ort-Ca((BH$_4$)$_{0.64}$I$_{0.36}$)$_2$ [49]. The hydrogen release occurs from tetragonal Ca((BH$_4$)$_{1-x}$I$_x$)$_2$ via CaHI; however, the anion substitution strategy affords borohydrides with a decomposition temperature similar to that of Ca(BH$_4$)$_2$ [49].

3.4. DFT Computation and Predictions

Several DFT computation studies have surfaced related to calcium borohydride, from crystal structure under high pressure [50], predictive evaluation of mixed-anion Ca(BH$_4$)$_2$(NH$_2$)$_2$ [51], simulation of the nanosizing effect of Ca(BH$_4$)$_2$ [52], to the inclusion of metal borohydrides in a combined multidisciplinary approach aimed to further adjust hydride materials for vehicular applications [1]. Aidhy et al. have used a combination of density functional theory (DFT) calculations and a Monte Carlo (MC)-based crystal structure prediction tool, the Prototype Electrostatic Ground State (PEGS) method [51]. Albanese et al. have utilized for the theoretical investigation of Ca(BH$_4$)$_2$ the periodic density functional theory (DFT) calculations employing the PBE functionals as implemented in the CRYSTAL program, with the following all-electron basis set used for all the atoms, namely, 865-1G (2d) for Ca, 6-21G (d) for B, and 31G (p) for H [52]. Other studies have...
investigated the metal electronegativity role in the M(BH$_4$)$_x$–LiNH$_2$ system as a means to enhance dehydrogenation thermodynamics and kinetics in the RHC [53]. Blanchard et al. have combined quasielastic neutron scattering (QENS) and DFT calculations to elucidate the role of hydrogen rotational and translational diffusion in calcium borohydride as an important factor of hydrogen dynamics in crystalline Ca(BH$_4$)$_2$ [54]. The calculations were performed by using the atomic simulation environment (ASE) package, and the DACAPO plane-wave basis-set implementation was used to solve the electronic structure problem within the DFT formalism; the ion cores were described by ultrasoft pseudopotentials, and the exchange and correlation effects were described by the PW91 functional [54].

Alkali-earth metal borohydride stability M(BH$_4$)$_2$ (M=Be, Mg, Ca) has been studied since the 1990s by Bonaccorsi et al. by systematic nonempirical calculations performed on M(BH$_4$)$_2$, HMBH$_4$, and MBH$_4^+$, resulting in optimized geometries [3]. Interestingly, the authors employed the effect of electron correlation in the study of the multi-step decomposition leading to borane elimination, an experimental detail observed in the case of many TM-based borohydrides (Equation (18)).

$$M(BH_4)_2 \rightarrow HMBH_4 + BH_3 \rightarrow MH_2 + 2 BH_3 \rightarrow M + H_2 + 2 BH_3 \ (18)$$

However, a critical point regarding DFT computations is that the agreement with experimental data must be reasonably good; with this goal in mind, Franco et al. used Quantum ESPRESSO to perform DFT computations on seven simple and complex hydrides (including Ca(BH$_4$)$_2$), and found that coupling the GIPAW (gauge-including projected augmented-wave) ab initio method with solid-state NMR experiments led to a good agreement among all investigated samples [55]. For example, $^{11}$B MAS (Hahn echo) spectra of Ca(BH$_4$)$_2$ as a mixture of $\alpha$ and $\beta$ phases showed corresponding signals at $-32.5$ ppm ($\beta$ phase) and $-29.9$ ppm ($\alpha$ phase), and $^1$H SSNMR data also showed good correlation with prediction shifts (PAW: 0.48 ppm error, QE: 0.35 ppm error) (Figure 7) [55].

![Figure 7](image-url)

**Figure 7.** (a) Experimental vs. calculated $^1$H chemical shifts (TMS as reference). (b) Experimental (black) and simulated (red) $^{11}$B MAS (Hahn echo) spectra of $\alpha$-Ca(BH$_4$)$_2$, and Ca(BH$_4$)$_2$ Aldrich ($\alpha$ + $\beta$ form) recorded with a spinning speed of 14 kHz. Reproduced with permission from Ref. [55].

There is, however, an important need to develop new systems for energy storage, and Wolverton et al. employed an atomic scale computational approach using Perdew–Wang GGA (generalized gradient approximation) in this regard, with three-fold advances being recorded: the prediction of hydriding enthalpies and free energies, the prediction of favorable decomposition pathways, and the prediction of low-energy crystal structures of complex hydrides [12]. The results suggest that the DFT approach is useful in evaluating potential decomposition pathways, as was exemplified for Li$_4$BN$_3$H$_{10}$, a metastable phase with three potential decomposition pathways for T < 300 K and thermodynamically possible with $\Delta G < 0$ [12].
4. Characterization and Stability

As previously mentioned, there are several early reports related to the structure and stability of calcium borohydrides [3,35,56]. For instance, Filinchuk et al. [35] and Bosenberg et al. [57] reported the characterization of metal hydride using in situ synchrotron radiation powder X-ray diffraction (SR-PXD). SR-PXD is a powerful tool to track solid-gas reactions, and hydrogenation studies made use of a cell that allows control over wide pressure and temperature ranges (up to 200 bar, 550 °C) [57–59]. The authors reported that β-Ca(BH₄)₂ and MgH₂ were observed when a mixture of CaH₂·MgB₂ was heated, as well as the β → α phase transition of calcium borohydride upon cooling [57]. Dematteis et al. deduced the heat capacities and thermodynamic properties of complex hydrides, which will further ease the thermodynamic data computations (ΔS, ΔH and ΔG) [60].

Other physical characterization methods include inelastic neutron scattering [61], high-resolution laser excitation spectroscopy (albeit for hypothetical, gas phase CaBH₄ molecule) [62], vibrational spectra (IR and Raman, for α-, β-, and mixed (β,γ)-Ca(BH₄)₂ [38,63,64], solid-state NMR (¹H, ¹¹B MAS for α-, β-Ca(BH₄)₂ [29,55,65], confirmation of [B₁₂H₁₂]²⁻ species during borohydride dehydrogenation [66], ¹¹B spin-lattice relaxation [67], analysis of RHCs based on calcium borohydride like LiBH₄–Ca(BH₄)₂ [68]), and various DFT computations (excluding CaB₂H₅ as dehydrogenation intermediate, while favoring CaB₁₂H₁₂ as an intermediate, as argued by Frankcombe, Equation (19) [69], or evaluating [Ca(BH₄)₂]₀n=1–4 clusters for hydrogen storage by Han et al. [70]).

\[
\text{Ca(BH}_4\text{)}_2 \rightarrow \frac{1}{6}\text{CaB}_2\text{H}_{12} + \frac{5}{6}\text{CaH}_2 + \frac{13}{6}\text{H}_2 \rightarrow \frac{1}{3}\text{CaB}_6 + \frac{2}{3}\text{CaH}_2 + \frac{10}{3}\text{H}_2 \quad (19)
\]

Hattrick-Simpers et al. described the use of high-throughput backscattering Raman spectroscopic measurements for combinatorial in situ Raman spectroscopy of Ca(BH₄)₂ and other RHCs (up to 10 Mpa and 823 K) [71].

The stability of Ca(BH₄)₂ has been investigated in many reports, including Miwa et al. [72], Nakamori et al. [73], Riktor et al. [58], and others. Since the decomposition of complex hydrides is related to their hydrogen storage capacity, these results will be discussed in Section 5.

4.1. Neat vs. Nanoconfined

Several aspects of nanosizing are regarded as beneficial for enhancing de-/rehydrogenation of complex hydrides and related RHCs. For instance, when impregnating LiBH₄ into ferrite-catalyzed-graphene, a synergistic effect was observed and an important reduction in activation energy was recorded [74].

4.2. DFT Simulation of the Nanosizing Effect

Albanese et al. have studied the nanostructuring of β-Ca(BH₄)₂ by atomistic thin film models to mimic nanosizing effects (DFT, using CRYSTAL software) in order to evaluate the reduction of dehydrogenation enthalpy of calcium borohydride, showing that for thickness in the range 5–20 Å, the reduction on enthalpy reaches 30–35 kJ/mol H₂, making calcium borohydride an appealing candidate for hydrogen storage under nanosizing conditions [52]. The decomposition pathways for Ca(BH₄)₂ have been investigated by Zhang et al. by means of DFT calculations of free energy, predicting a new CaB₂H₆ compound as a decomposition intermediate [75]. Other groups have evaluated the effectiveness of DFT computations in establishing metastable reaction pathways [76].

Dual-cation borohydrides of form M₁M₂(BH₄)₃(NH₃)₂–₄ have been investigated by Emdadi et al., finding several potentially promising new solvates and stable alloys, including M₂=Ca [77]. Nanosizing was invoked in the case of LiBH₄–Ca(BH₄)₂ RHC when catalyzed by LaMg₃, with an improvement registered in hydrogenation behavior due to nanoparticulate alloy addition affording a dehydrogenation onset at ~200 °C, 100° lower than pristine LiBH₄–Ca(BH₄)₂ and rehydrogenation proceeding at 150 °C [78].
Guo et al. performed first-principles calculations on the system KBH$_4$/Ca(BH$_4$)$_2$ and proposed three new reactions in the mentioned RHC (20), (21) and (22), two of them involving the formation of the [B$_{12}$H$_{12}$]$^{3-}$ anion [79,80].

$$\text{KBH}_4 + \frac{5}{2} \text{Ca(BH}_4)_2 \rightarrow \frac{1}{2} \text{K}_2\text{B}_2\text{H}_{12} + 5 \text{NaH} + \frac{13}{2} \text{H}_2; \text{ 6.0 wt}\% \text{ t}_c = 64 \text{°C} \tag{20}$$

$$\text{KBH}_4 + \frac{1}{10} \text{Ca(BH}_4)_2 \rightarrow \frac{1}{10} \text{CaB}_2\text{H}_{12} + \text{KH} + \frac{13}{10} \text{H}_2; \text{ 4.3 wt}\% \text{ t}_c = 58 \text{°C} \tag{21}$$

$$\text{KBH}_4 + \frac{1}{4} \text{Ca(BH}_4)_2 \rightarrow \frac{1}{4} \text{CaB}_6 + \text{KH} + \frac{5}{2} \text{H}_2; \text{ 7.0 wt}\% \text{ t}_c = 105 \text{°C} \tag{22}$$

Moreover, Kulkarni et al. described by first principles the dodecaborane, amorphous phase CaB$_{12}$H$_{12}$ as a result of an overlap of structurally distinct crystallites [81].

Huang et al. performed first-principles calculations involving Cr-doping of α-Ca(BH$_4$)$_2$ and found half-metallic behavior (0.98 eV for Ca doped sites, 0.63 eV for B) useful for further use in spintronics devices [82]. Computational thermodynamics coupled with CALPHAD (CALculation of PHAse Diagram) modeling revealed the formation of Ca(BH$_4$)$_2$ as a result of Ca addition on LiBH$_4$ along with CaB$_6$, which significantly reduces the H$_2$ releasing temperature of the system [83].

The utilization of Ca(BH$_4$)$_2$ in electrolyte solution for Ca-ion batteries has been shown feasible by a computational approach called AIMD (ab initio molecular dynamics) performed on ether- and ester-based electrolytes on a calcium anode, revealing an aspect that was confirmed experimentally, namely, that the best combination for an electrolyte solution is that of Ca(BH$_4$)$_2$ and the polar, aprotic THF solvent [84]. Calcium borohydride (Ca(BH$_4$)$_2$) has shown potential for use in both lithium-ion batteries (LIBs) and sodium-ion batteries (SIBs) due to its high hydrogen storage capacity and favorable electrochemical properties. Regarding LIBs, it must be noted that Ca(BH$_4$)$_2$ can release H$_2$ through a reversible electrochemical process, enabling its use as an energy and H$_2$ reservoir within the battery. The high capacity of Ca(BH$_4$)$_2$ for Li storage (by theoretical calculations, one mole of Ca(BH$_4$)$_2$ can potentially store four moles of lithium, leading to a high energy density) makes it an attractive solution for LIB applications. However, compared to Mg(BH$_4$)$_2$, which afforded 540 mAh/g (first discharge)/250 mAh/g (recharge), the reported values for Ca(BH$_4$)$_2$ were lower. With good chemical stability, calcium borohydride showed good stability during lithium insertion/extraction, therefore showing good potential for long term cycling stability. Several downsides should be addressed, such as developing the proper electrolyte system that would afford better overall battery performance and stability. As with LIBs, SIBs show similar advantages and downsides for Ca(BH$_4$)$_2$ use in battery applications.

Mikhailin et al. employed potential energy surfaces along minimal energy pathways to study the decomposition of M(BH$_4$)$_2$(NH$_3$)$_{1-2}$ and the [M(BH$_4$)$_2$(NH$_3$)$_2$]$_2$ dimers (M=Be, Mg, Ca, and Zn) using the B3LYP method (DFT). The dimeric structures have almost no effect on the energy barriers, while coordination of the ammonia molecule to the metal center reduced these barriers considerably, affording dehydrogenation at temperatures much lower than those of their corresponding pristine counterparts [85]. The potential decomposition pathways of calcium ammine borohydride complexes would lead to Ca(BH$_2$NH)(BHN), Ca(BH$_4$)(BHN) or Ca$_2$(BH$_4$)$_2$(NH$_3$)$_2$(BH$_3$NH$_2$)$_2$ in the case of the dimer [85]. The case of decomposition of Ca(BH$_4$)$_2$: NH$_3$ was further investigated by Zhang et al. by means of DFT and showed a reasonable agreement with decomposition in the range 190–250 °C, releasing 11.3 wt% hydrogen [86]. Notably, the interaction N-H…H-B was found to play an essential role in favoring H$_2$ release, recognizing the unique role of dihydrogen bonding in H$_2$ release from solid compounds such as complex hydrides and their adducts [86]. Various complementary predictions have been made on the basis of thermodynamic computations by Siegel et al. [87], and Vajeeston et al. [88,89].
4.3. Destabilization Strategies

Destabilization of boron-based materials can be achieved by using additives (various compounds based on Mg, B, Al, C, S, Ti, intermetallics, etc.), chemical modifications, and nanosizing effects [90–98]. Various RHCs have been employed, and most showed improved desorption temperatures compared to pristine components; for instance, Mg(BH₄)₂/Ca(BH₄)₂, Mg(BH₄)₂/CaH₂, or Mg(BH₄)₂/CaH₂/3NaH (Equations (23)–(25)) (Figure 8) [92,94].

\[
5 \text{Mg(BH}_{4}\text{)}_{2} + \text{Ca(BH}_{4}\text{)}_{2} \rightarrow \text{CaB}_{12}\text{H}_{12} + 5 \text{MgH}_{2} + 13 \text{H}_{2} \quad (23)
\]

\[
3 \text{Mg(BH}_{4}\text{)}_{2} + \text{CaH}_{2} \rightarrow 3 \text{MgH}_{2} + \text{CaB}_{5} + 10 \text{H}_{2} \quad (24)
\]

\[
3 \text{Mg(BH}_{4}\text{)}_{2} + \text{CaH}_{2} + 3 \text{NaH} \rightarrow 3 \text{NaMgH}_{3} + \text{CaB}_{5} + 10 \text{H}_{2} \quad (25)
\]

Figure 8. (a) TPD profiles comparing the desorption temperatures of several solid-state hydrogen storage materials. (b) Activation energy plots using the Kissinger equation for several mixtures. Reprinted with permission from Ref. [92].

Ibikunle et al. also studied the RHC Mg(BH₄)₂/Ca(BH₄)₂ and found the H₂ release to be diffusion- and phase boundary-controlled (Figure 9) [94,95].

Figure 9. (a) Plots of reacted fraction versus time for Mg(BH₄)₂, Ca(BH₄)₂, and the Mg(BH₄)₂/Ca(BH₄)₂ mixture at 450 °C. (b) Modeling curves for Mg(BH₄)₂/Ca(BH₄)₂. Reprinted with permission from reference [94].

An extension of the destabilization strategy proposed by Durojaiye in 2010 [92] was employed by Huang et al. in 2016, who used Mg(AlH₄)₂ in order to destabilize Ca(BH₄)₂ instead of magnesium borohydride [93]. The destabilization effect of magnesium alanate Mg(AlH₄)₂ in the 1 Mg(AlH₄)₂:1 Ca(BH₄)₂ RHC was quantified and shown to exhibit a 10-fold faster desorption at 300 °C (0.337 wt.% H₂/min) compared to pristine Ca(BH₄)₂ (2.6 wt% H₂ at the same temperature), releasing 8.4 wt% H₂ at 330 °C in a three-step reaction (with release peaks at 130, 280, and 310 °C) [93]. A key step in the enhancement observed
was attributed to the formation of the Al (Mg) solid solution, effectively destabilizing Ca(BH$_4$)$_2$ [93].

Destabilization in the system NaBH$_4$/Ca(BH$_4$)$_2$ has also been reported (Equation (26)), and the TPD release curves were altered by a decomposition product of Ca(BH$_4$)$_2$; the system behaved reversibly under ~5.5 Mpa H$_2$ at 400 °C when recharged for 10 h [97].

$$4 \text{NaBH}_4 + \text{Ca(BH}_4)_2 \rightarrow 4 \text{Na} + \text{CaB}_6 + 12 \text{H}_2; \text{10.9 wt\% } \text{H}_2$$  (26)

An important aspect of the reversibility reaction of many metal borohydrides is the regeneration of B–H bonds present in the [BH$_4$]$^-$ anion [90]. This issue was tackled by Cai et al., who proposed a general route potentially applicable to M(BH$_4$)$_2$ (M=Mg, Ca), based on the reaction of SiB$_4$ with MH$_{n=1-2}$ to form M(BH$_4$)$_{n=1-2}$ under mild conditions in the case of LiBH$_4$ (10 Mpa, 250 °C) (Equation (27)). The chemical bonding of boron in the reagent (SiB$_4$) was found essential for the best hydrogenation performance; for comparison, the synthesis of LiBH$_4$ from the elements requires 700 °C, while the mildest conditions are required by the solid-gas reaction between LiH and B$_2$H$_6$, yielding LiBH$_4$ at 120 °C.

$$\text{SiB}_4 + 4 \text{LiH} + 6\text{H}_2 \rightarrow 4 \text{LiBH}_4 + \text{Si} ; \Delta \text{H} = -65 \text{ kJ} / \text{molH}_2$$  (27)

5. Hydrogen Storage Properties

Various aspects related to hydrogen desorption behavior have been investigated in recent years, from the detailed decomposition of pristine calcium borohydride by Kim et al. [99,100], to the kinetic and thermodynamic investigation of Ca(BH$_4$)$_2$ decomposition [101], to the further decomposition behavior of the CaB$_{12}$H$_{12}$ intermediate reported by Riktor et al. [102]. Other reports shed light on the H$_2$ backpressure effect [100] or the dehydrogenation temperature used (350 °C vs. 400 °C), which can allow different pathways for the decomposition reaction (via CaB$_6$H$_6$ at 350 °C, or via B and CaH$_2$, leading to CaB$_6$ when heated at 400 °C) [103,104]. Further experimental details related to the H$_2$ desorption potential of Ca(BH$_4$)$_2$ will be discussed in the following sections (Sections 5.1−5.6), as well as the applicability of calcium borohydride to ion conductivity studies and applications (Section 5.7).

5.1. Bulk Ca(BH$_4$)$_2$

As early as 2008, Aoki et al. investigated the hydrogen release properties of Ca(BH$_4$)$_2$ and reported the phase transition (LT, low temperature, to HT, high temperature), while also identifying an unassigned intermediate compound and CaH$_2$ as the final phase identified by XRD data analysis [105]. Decomposition of pristine calcium borohydride has been thought and further demonstrated to proceed through the formation of CaB$_{12}$H$_{12}$ [14,66] or another intermediate type of the general formula CaB$_2$H$_{n}$ (DFT computations) [34]. A pressure investigation performed on a mixture α- and β-Ca(BH$_4$)$_2$ led George et al. to identify a novel phase in which the β– phase transforms when reaching 10.2 Gpa, but no α-to-β transition was observed around 5.3 Gpa, as theoretically predicted [106]. Other DFT computations were run on [Ca(BH$_4$)$_2$]$_{n=1-4}$ clusters and found the smallest dissociation energy to belong to the tetramer [Ca(BH$_4$)$_2$]$_4$, indicative of it being the better hydrogen storage candidate among the investigated clusters [70].

The dehydrogenation of Ca(BH$_4$)$_2$ and that of the destabilized system Ca(BH$_4$)$_2$–MgH$_2$ were investigated by Kim et al., highlighting the essential role of the CaB$_6$ product in achieving system reversibility [107], as corroborated by the findings of Sahle et al. a few years later [108]. It was also suggested that CaB$_6$ forms as the final product of the reaction from intermediate phases likely containing B and CaH$_2$ [108].
As for the decomposition of CaB$_{12}$H$_{12}$, the decomposition pathway differs from that of Ca(BH$_4$)$_2$, producing no CaB$_6$, and can be described by Equation (28) [14]:

$$\text{CaB}_{12}\text{H}_{12} \xrightarrow{2\text{H}_2} \text{CaB}_{12}\text{H}_{12-x} \xrightarrow{\text{H}_2} \frac{1}{n} (\text{CaB}_2\text{H}_4)_n$$  

(28)

Moreover, although there are conflicting reports regarding the role of CaB$_{12}$H$_{12}$ in the dehydrogenation of Ca(BH$_4$)$_2$, it seems unlikely that the dodecaborate is a stable dehydrogenation intermediate [14,37].

5.2. Nanoconfined

Nanoconfinement remains a viable route for tuning the thermodynamic parameters of hydrogen storage materials and of Ca(BH$_4$)$_2$ in particular, with several reports describing marked improvements over the pristine compounds’ thermal behavior [68,74,96,109–118]. Some of the most important characteristics of these systems are summarized in Table 2. A porous borohydride, CaB$_2$H$_7$, was obtained by heating Ca(BH$_4$)$_2$ with Ti(OEt)$_4$ at 160 °C for 1 h and showed improved release and uptake of hydrogen (Equation (29)) [112].

$$\text{Ca(BH}_4)_2 + 0.1\text{Ti(OEt)}_4 \xrightarrow{160^\circ \text{C}, 1 \text{h}} \text{CaB}_2\text{H}_7 + 0.1\text{TiO}_2 + 0.2\text{C}_2\text{H}_6 + 0.2\text{C}_2\text{H}_6\text{O} + 0.2\text{H}_2$$  

(29)

The desorption of the porous borohydride occurred in the 300–420 °C interval, following a two-step dehydrogenation pathway (Equation (30)) [112].

$$\text{CaB}_2\text{H}_7 \xrightarrow{300^\circ \text{C}, 1 \text{h}} 0.6\text{CaB}_2\text{H}_4 + \frac{2}{15}\text{CaB}_6 + \frac{4}{15}\text{CaH}_2 + 3.8\text{H} \xrightarrow{420^\circ \text{C}, 1 \text{h}} \frac{1}{3}\text{CaB}_6 + \frac{2}{3}\text{CaH}_2 + 5.7\text{H}$$  

(30)

When LiBH$_4$ is used in the eutectic mixture 0.7 Li(BH$_4$)$_2$-0.3 Ca(BH$_4$)$_2$ displaying eutectic melting, the reversible coupled RHC system obeys the reversible pathway described by Equation (31).

$$4\text{LiBH}_4 + \text{Ca(BH}_4)_2 \rightarrow \text{CaB}_6 + 4\text{LiH} + 10\text{H}_2$$  

(31)

Other studies have focused on the infiltration and interaction between the eutectic LiBH$_4$-Ca(BH$_4$)$_2$ and mesoporous scaffolds (CMK–3, MCM–41) by means of NMR investigation, including the lack of surface modification of the inert carbon scaffold CMK-3, as revealed by $^{13}$C MAS and $^1$H-$^{13}$C CPMAS (cross-polarization MAS) spectra [68]. Other studies have used mesoporous silica as the host (MCM–41 and SBA–15) for LiBH$_4$-Ca(BH$_4$)$_2$ infiltration and found that the mesoporous structure of the scaffold was altered even with low-energy ball milling [115] or reported on the infiltration of the same RHC into mesoporous carbon [116]. One should also note the affinity of the borohydride for the SiO$_2$ and surface silanol groups, which may lead to another side reaction [115].

Table 2. Hydrogen storage characteristics of nanoconfined Ca(BH$_4$)$_2$ and its RHCs.

<table>
<thead>
<tr>
<th>Ca-Based Storage Material</th>
<th>Nanoscaffold Used</th>
<th>wt% H$_2$ Storage Performance</th>
<th>Obs. (Reversibility, Catalyst)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca(BH$_4$)$_2$ in CMK-3/Ca(BH$_4$)$_2$/TiCl$_3$</td>
<td>CMK-3 with $S_{BET} = 1320$ m$^2$/g, $V_p = 1.48$ cm$^3$/g (wet impregnation from NH$_3$ liq. solution to 70% pore filling)</td>
<td>H$_2$ release onset at 150 °C</td>
<td>TiCl$_3$ as catalyst (1:0.05 molar)</td>
<td>[110]</td>
</tr>
<tr>
<td>Ca(BH$_4$)$_2$ in Ca.(BH$_4$)$_2$=MC-a</td>
<td>MC-a (activated mesoporous carbon 1780 m$^2$/g, 1.01 cm$^3$/g; incipient wetness method)</td>
<td>2.4 (reversible after 18 cycles)</td>
<td>Desorption onset at ~100 °C</td>
<td>[111]</td>
</tr>
<tr>
<td>Ca(BH$_4$)$_2$ in Ca.(BH$_4$)$_2$=MCM-41</td>
<td>MCM–41 (2.4 nm) and fumed silica (7 nm); wet infiltration</td>
<td>–</td>
<td>$^1$H and $^{11}$B VT MAS NMR technique</td>
<td>[113]</td>
</tr>
</tbody>
</table>
Table 2. Cont.

<table>
<thead>
<tr>
<th>Ca-Based Storage Material</th>
<th>Nanoscaffold Used</th>
<th>wt% H₂ Storage Performance</th>
<th>Obs. (Reversibility, Catalyst)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca(BH₄)₂ in Ca.(BH₄)₂=rGO</td>
<td>Graphite and rGO (reduced graphene oxide); ball milling</td>
<td>6.5%</td>
<td>a 50 °C reduction in decomposition onset (220°, graphite; 170 °C, rGO)</td>
<td>[117]</td>
</tr>
<tr>
<td>0.7 Li(BH₄)₂-0.3 Ca(BH₄)₂ (eutectic mixture); ball milling (120 min, BPR 1:18)</td>
<td>CMK–3 mesoporous carbon (5 nm), ASM carbon (20–30 nm), and CD (non-porous carbon disks 20–50 nm thick, 0.8–3 μm diameter)</td>
<td>3.96 (CMK–3), 4.88 (ASM), 6.07 (CD)</td>
<td>Kinetic improvements when pore size ~5 nm, synergically coupled with a catalytic effect</td>
<td>[109]</td>
</tr>
<tr>
<td>0.7 Li(BH₄)₂-0.3 Ca(BH₄)₂ (eutectic mixture)</td>
<td>Two resorcinol-formaldehyde carbon aerogel scaffolds (pristine CA 689 m²/g, CO₂-activated CA–6, 2660 m²/g); 60 vol.% pore filling; melt infiltration method</td>
<td>Up to 12.08% pristine (7.71% CA–6, 3.36% CA)</td>
<td>Reduced Eₐ from 204 bulk to 156€ₐ and 130€ₐ kJ/mol</td>
<td>[114]</td>
</tr>
<tr>
<td>CaB₂H₇/0.1TiO₂₂nano via Ca(BH₄)₂ + Ti(Oet)₄</td>
<td>Porous Ca-based hydride with in situ TiO₂ catalyst</td>
<td>6.2% (300–420 °C, 1 h)</td>
<td>Recharge at 350 °C, 90 bar H₂, 1 h</td>
<td>[112]</td>
</tr>
<tr>
<td>0.68LiBH₄–0.32Ca(BH₄)₂ in LiBH₄–Ca(BH₄)₂–NbF₅@CMK-3 composite</td>
<td>Catalyzed mesoporous carbon host, NbF₅@CMK-3</td>
<td>13.3% (250 min) vs. 10.4% (pristine RHC)</td>
<td>Desorption onset reduced by 120 °C compared to pristine</td>
<td>[37]</td>
</tr>
</tbody>
</table>

5.3. Additives Used to Improve H₂ Storage Features of Calcium Borohydride

While still holding the highest theoretical hydrogen storage capacity of all known materials, complex hydrides still face many shortcomings related to sluggish kinetic and/or thermodynamic barriers that are hard to bypass. To tackle this issue, several additives have been used, with important improvements recorded: MgB₂ yielded Ca(BH₄)₂ + MgB₂ composite with 8.3 wt% gravimetric hydrogen capacity [119]; Co ion-loaded poly(acrylamide-co-acrylic acid) (p(Aam-co-Aac)-Co) hydrogel when a decrease in conversion rate from 98.5 to 83.5% was reported over ten a/d cycles [120,121]; urea yielded a new complex Ca(BH₄)₂·4CO(NH₂)₂, releasing 5.2 wt% hydrogen below 250 °C [122]; 5 wt% CoCl₂ doping in Ca(BH₄)₂-4LiH₂ afforded catalyzed RHC (Co NPs formed during ball milling as active catalytic species), releasing 7 wt% hydrogen at 178 °C [123]; CoCl₂-doped Ca(BH₄)₂·2NH₃ desorbed at 200 °C, releasing 7.6 wt% H₂ with high purity [124]; Mg(BH₄)₂ yielded corresponding RHCs Mg(BH₄)₂/Ca(BH₄)₂ [92], MgF₂ in Ca(BH₄)₂-MgF₂ reversible system [125]; in situ generated TiO₂ to afford novel CaB₂H₇/0.1TiO₂ catalyzed hydride system [112]; particulate LaMg₃ additive in the RHC Ca(BH₄)₂ + LiBH₄ [78]; DFT investigation on Cr-doped α-Ca(BH₄)₂ [82]; TiF₃ introduced via ball milling in Ca(BH₄)₂ [126]; NbF₅ doping in Ca(BH₄)₂ + MgH₂ [127]; Nb and Ti doping on Ca(BH₄)₂ investigated by DFT [128]; Co-Ni-Fe-P alloy as hydrolysis catalyst [129]; TiCl₃ doping of Ca(BH₄)₂ yielded 2 wt% H₂ reversible at 300 °C and 9 Mpa, while also suppressing borohydride melting [103]; 10 mol% addition of CaX₂ (X=F, Cl) produced Ca(BH₄)₂–CaX₂ mixtures, where CaX₂ changed the dehydrogenation pathway [130].

Other reports deal with the additive role of calcium borohydride in the Mg(NH₂)₂–2LiH–0.1Ca(BH₄)₂ system, yielding CaH₂ and LiBH₄ during ball milling to account for 4.5 wt% storage capacity [131]; TiF₃ and NbF₅ doped in Ca(BH₄)₂–MgH₂ RHC, where a slight improvement was seen in the case of NbF₅ doping, and there was evidence of CaB₁₂H₁₆ formation along with the formation of active metal boride nanoparticulate species TiB₂ and NbB₂ (XANES data) with partial reversibility reported [132–134]; Ti(OPr)₄ and CaF₂ [134]; TiF₃ additive in the 2NaAlH₄ + Ca(BH₄)₂ system generating Al₃Ti and CaF₂ with a synergistic catalytic role and affording improved a/d kinetics [135]; investigation of the boron effect in the Ca(BH₄)₂ + B system, showing only minor differences in the
maximum rate of H₂ evolution [136]; CaF₂ replacement of CaH₂ in CaH₂ + MgB₂ yielding the nonstoichiometric CaF₂·xH₂ solid solution with a direct influence over a/d behavior of the system [137]; TiX₃ (X=F, Cl) showing a superior effect of TiF₃ on reversibility (57% yield) but not of TiCl₃, despite their electronic similarities [138].

The catalytic role of additives in the synthesis of calcium borohydride from CaB₆ and CaH₂ was confirmed by Ronnenbro et al. utilizing RuCl₃ or, even better, mixtures of TiCl₃ + Pd [11]. Another synthesis route of calcium borohydride starts from the CaH₂ + MgB₂ system, where the beneficial role of the boride additive AlB₁₃ was reported by Schiavo et al. [119], or the role of fluoride-based additives in the same CaH₂ + MgB₂ system, as shown by Suarez-Alcantara et al., who investigated the systems 9CaH₂ + CaF₂ + 10MgB₂, 10Ca(BH₄)₂ + 9MgH₂ + MgF₂, and 9Ca(BH₄)₂ + Ca(BF₄)₂ + 10MgH₂ [59].

5.4. RHCs—Reactive Hydride Composites Containing Ca(BH₄)₂ or Its Precursors

There have been many attempts to catalyze Ca(BH₄)₂ and its RHCs; however, not all of them showed palpable results. For instance, while MgH₂ was considerably improved using Ni (5 wt%) and Ni₅Zr₂ (5 wt%) catalysts, these catalysts showed very little influence over Ca(BH₄)₂ [140]. On the other hand, the system Ca(BH₄)₂–MgH₂ was shown to produce the species Ca[B₁₂H₁₂] [141]. The same Ca(BH₄)₂–MgH₂ RHC (10.5 wt% H₂ theoretical, 6.4 wt% H₂ desorbed within 3 h) has been characterized when catalyzed by 0.05 mol TiF₃ and NbF₅, yet the catalyst employed did not suppress dodecaborane anion formation, and only some minor improvements were recorded in the case of the NbF₅ anion’s usage of TM fluorides, as shown by XANES data to form TM boride nanoparticles acting as active catalysts [132]. Minella et al. have also extended the study of Ca(BH₄)₂–MgH₂ RHC by using Mg, which behaves as an adjuvant for heterogeneous nucleation of CaB₆ formed during desorption [142]. CaB₆ formation was also reported in the RHC 6LiBH₄ + CaH₂ (11.7 wt% theoretical), which afforded 9.1 wt% reversible storage capacity when catalyzed by 0.25 mol TiF₃ [143,144]. Other authors have investigated the role of the boron source (SiB₄, FeB, and TiB₂) on the production of Ca(BH₄)₂ from the hydrogenation of SiB₄ and CaH₂ [90].

The hydridic–protic interaction has been exploited in a series of RHCs containing borohydride–amide mixtures [145,146]. When the 1:4 molar ratio mixture Ca(BH₄)₂–4LiNH₂ was ball milled, Equation (32) occurred, leading to the formation of Ca(NH₂)₂, LiBH₄, and Li₃(NH₂)₂BH₄, affording a 26.2% reduction in Eₐ compared to LiBH₄–2LiNH₂ chosen as reference [53].

\[
\text{Ca(BH}_4\text{)}_2 + 4 \text{LiNH}_2 \rightarrow \text{Li}_3(\text{NH}_2)_2\text{BH}_4 + \text{LiBH}_4 + \text{Ca(NH}_2\text{)}_2
\]  

Other reports describe a slightly different reaction pathway for the system Ca(BH₄)₂–4LiNH₂, corresponding to Equation (33) [147]. The formation of mixed anion Ca(BH₄)(NH₄)₂–x was also found by Morelle et al. in the RHC system Ca(BH₄)₂–xNaNH₂ (x = 1, 2, and 3), showing release of NH₃ (300 °C) and H₂ (above 350 °C), and a decreasing decomposition temperature as the amide fraction of the composite increased, which advocates for the destabilization of starting Ca(BH₄)₂ by the amide compound (NaNH₂) [148].

\[
\text{Ca(BH}_4\text{)}_2 + 4\text{LiNH}_2 \rightarrow \text{Li}_4\text{B}_4\text{N}_5\text{H}_{10} + [\text{Ca(BH}_4\text{)}(\text{NH}_2)] \rightarrow \frac{1}{4}\text{LiCa}_4(\text{BN}_2)_3 + \frac{5}{4}\text{Li}_3\text{BN}_2 + 8\text{H}_2
\]  

Other molar ratios of Ca(BH₄)₂–xLiNH₂ have also been investigated, for instance, when x = 3 [149]. The intramolecular destabilization in the systems Ca(BH₄)₂–MNH₂ (M=Li, Na) has also been evidenced by Poonyayant et al., when a metathetical reaction led to the formation of cation-mixed, anion-mixed complex hydrides of type mCa(BH₄)₂(NH₂) with a release profile starting at ca. 150 °C through hydridic-protic interactions in a two-step release accounting for 9.3 wt% [98]. The Mn(BH₄)₂–CaH₂ mixture system (1:1 molar, manual grinding) led to the more stable Ca(BH₄)₂ through a double exchange reaction, which effectively suppressed the formation of diborane in the utilized system [150].
Investigation of the Ca(BH$_4$)$_2$-2.5 Mg$_2$NiH$_4$ RHC was shown to proceed through three different pathways, depending on the hydrogen backpressure, which again highlights the aspects of chemical equilibrium (Equations (34) - 2.3 wt%, (35) - 4.2 wt%, (36) - 4.6 wt%) [151]. At 1 bar, the reaction proceeds via Equation (36), whereas at 20 or 50 bar, all three reactions occur simultaneously.

\[
\text{Ca}(\text{BH}_4)_2 + 2.5 \text{Mg}_2\text{NiH}_4 \rightarrow 0.25 \text{Ca}_4\text{Mg}_3\text{H}_{14} + \text{MgNi}_{2.3}\text{B}_2 + 3.25 \text{MgH}_2 + 4\text{H}_2 \quad (34)
\]

\[
\text{Ca}(\text{BH}_4)_2 + 2.5 \text{Mg}_2\text{NiH}_4 \rightarrow 0.25 \text{Ca}_4\text{Mg}_3\text{H}_{14} + \text{MgNi}_{2.3}\text{B}_2 + 3.25 \text{Mg} + 7.25 \text{H}_2 \quad (35)
\]

\[
\text{Ca}(\text{BH}_4)_2 + 2.5 \text{Mg}_2\text{NiH}_4 \rightarrow \text{CaH}_2 + \text{MgNi}_{2.3}\text{B}_2 + 4 \text{Mg} + 8 \text{H}_2 \quad (36)
\]

The influence of alkali metal amides on the desorption properties of calcium borohydride was studied by Chu et al. [152], concluding that the driving force of reactions (37) and (38) must lie in the interaction B–H and N–H present in the milled RHC M(NH$_2$)$_2$-Ca(BH$_4$)$_2$ (M=Mg, Ca).

\[
\text{Ca}(\text{BH}_4)_2 + 2 \text{Mg}(\text{NH}_2)_2 \rightarrow \frac{1}{3} \left[\text{Ca}_3\text{Mg}_6(\text{BN}_2)_6\right] + 8 \text{H}_2 \quad (37)
\]

\[
\text{Ca}(\text{BH}_4)_2 + 2 \text{Ca}(\text{NH}_2)_2 \rightarrow \frac{1}{3} \text{Ca}_9(\text{BN}_2)_6 + 8 \text{H}_2 \quad (38)
\]

Binary, ternary and quaternary mixtures in the LiBH$_4$-NaBH$_4$-KBH$_4$-Mg(BH$_4$)$_2$-Ca(BH$_4$)$_2$ system have been investigated by Dematteis et al. showing that new phases occurring might originate from the interaction Mg(BH$_4$)$_2$-Ca(BH$_4$)$_2$ [153–155]. This interaction in the Mg(BH$_4$)$_2$-Ca(BH$_4$)$_2$ was studied in the 5:1 molar ratio showing a destabilization effect of Ca(BH$_4$)$_2$ over Mg(BH$_4$)$_2$ [34,95].

Another improvement strategy regarding H$_2$ storage performance is utilization of eutectic mixture, and 0.68 LiBH$_4$-0.32 Ca(BH$_4$)$_2$ is a known and tested model system [156,157]. Interestingly, the eutectic mixture of borohydrides can release H$_2$ below each individual components, and even a release onset below the melting of pristine complex hydride [157]. When used as an additive, Ca(BH$_4$)$_2$ can produce very notable improvements; Mg(NH$_2$)$_2$-2LiH-0.1Ca(BH$_4$)$_2$ for instance can release 4.5 wt% H$_2$ with onset at 90 °C, and a rehydrogenation temperature of 60 °C [131]. The synergistic effect of the formed CaH$_2$ and LiBH$_4$ probably played a role in the improvement recorded [131]. Li et al. have studied the system 2LiNH$_2$-MgH$_2$-$x$Ca(BH$_4$)$_2$ with a very low desorption onset of 80 °C and a 8.2 wt% hydrogen storage content ($x = 0.3$); the system 2LiNH$_2$-MgH$_2$-0.1Ca(BH$_4$)$_2$ was also studied. [158]. It’s worth noting that a tentative metathesis reaction of NaBH$_4$ and CaCl$_3$ did not yield the expected Ca(BH$_4$)$_2$ product, and led to CaNa(BH$_4$)$_2$Cl$_x$ instead, which forms as a result of a diffusional process of one reagent into the other [46].

Other additives potentially leading to calcium borohydride have also been employed: 2LiBH$_4$-CaH$_3$ (featuring a lower 1.1 wt% storage capacity at a lower temperature of 270 °C) [159]. A combination of different complex hydrides (alanate–borohydride) was proposed by Moller et al., namely, NaAlH$_4$ + Ca(BH$_4$)$_2$ [160]. This approach led to NaBH$_4$ and Ca(AlH$_4$)$_2$ through a metathesis reaction, releasing ca. 6 wt% H$_2$ below 400 °C [160].

The system NaAlH$_4$ + Ca(BH$_4$)$_2$ has been investigated mechanistically by Mustafa et al., who identified various decomposition intermediates in the multi-step desorption of the RHC, like CaAlH$_5$, Al, CaH$_2$, Al$_2$Ca, and Al$_2$Ca (Figure 10) [135,161].
The ternary system Ca(BH$_4$)$_2$–LiBH$_4$–MgH$_2$ was reported to exhibit long-term cycling stability [162], the precursors CaH$_2$–MgB$_2$ thin films allowed identification of individual steps leading to the formation of Ca(BH$_4$)$_2$ [163], the effect of MgF$_2$ additive was studied in the system Ca(BH$_4$)$_2$–MgF$_2$ with up to 5.8 wt% H$_2$ uptake at 330 °C after 2.5 h during the first three a/d cycles [125], the formation of β-Ca(BH$_4$)$_2$ in the γ-Mg(BH$_4$)$_2$–CaH$_2$ RHC system [164], LaMg$_3$-catalyzed Ca(BH$_4$)$_2$–LiBH$_4$ with H$_2$ release onset at 150 °C and good capacity retention of 70% after five a/d cycles [78], or DFT investigations in the KBH$_4$–Ca(BH$_4$)$_2$ system [79].

When MgH$_2$ is used, destabilization occurs, and a system with a total H$_2$ capacity of 9.1 wt% is generated (Equation (39)) [165]. This type of reactivity was also proven by Kim et al., who demonstrated the reversibility of the Ca(BH$_4$)$_2$+MgH$_2$ RHC, where the formation of CaB$_2$ boride seems to be essential while the formation of a-B is a major downside [107].

$$\text{Ca(BH}_4)_2 + \text{MgH}_2 \rightarrow \frac{2}{3} \text{CaH}_2 + \frac{1}{3} \text{CaB}_6 + \text{Mg} + \frac{13}{3} \text{H}_2; \; 9.1 \text{ wt}\% \text{H}_2 \quad (39)$$

Other RHCs like LiBH$_4$–Ca(BH$_4$)$_2$ were investigated over a wide compositional domain by Lee et al. in xLiBH$_4$+(1-x)Ca(BH$_4$)$_2$ (0 < x < 1) [166], by Yan et al. in the eutectic composite LiBH$_4$+Ca(BH$_4$)$_2$ [167], or when nanoconfined in mesoporous scaffolds of type CMK-3 [68,116,118] or SBA-15 as support, with enhanced interface interaction [115]. In fact, combining nanocatalysts (NbF$_5$) and nanoconfinement (CMK-3 ordered mesoporous carbon) afforded a total capacity of 13.3 wt% for the system LiBH$_4$–Ca(BH$_4$)$_2$ in the resulting nanocomposite 0.68LiBH$_4$–0.32Ca(BH$_4$)$_2$–0.05NbF$_5$@CMK-3 [118].

xNaBH$_4$-(1-x)Ca(BH$_4$)$_2$ composite, however, unlike the Mg(BH$_4$)$_2$ counterpart, yielded no eutectic melting, hence there was no improvement over H$_2$ release temperature [168]. Employing organic borohydrides, such as guanidinium borohydride (GBH), led to a marked improvement in the Ca(BH$_4$)$_2$/Ca(NH$_2$)$_3$ + [BH$_4$]$^-$ coupled system, which suppressed ammonia release and afforded ca. 10 wt% H$_2$ evolution between 60 and 300 °C [169].

There have been attempts to increase the stability of Al(BH$_4$)$_3$ (volatile), and compounding it with Ca(BH$_4$)$_2$ by Titov et al. was one of them, leading to the formation of the complex Ca(BH$_4$)$_2$·Al(BH$_4$)$_3$ (slow reaction: 3–4 days) with a postulated structure [Ca(BH$_4$)$_4$][Al(BH$_4$)$_4$]$^-$, in line with experimental IR data [24]. Some representative RHCs and their hydrogen storage performance are summarized in Table 3.
Table 3. Hydrogen storage characteristics of RHCs based on Ca(BH₄)₂ and its precursors.

<table>
<thead>
<tr>
<th>Ca-Based Storage Material</th>
<th>Synthesis Method</th>
<th>wt% H₂ Storage Performance</th>
<th>Obs. (Reversibility, Catalyst)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>3CaH₂ + 4MgB₂ + CaF₂</td>
<td>Ball milling in a Spex mill (87 h in total)</td>
<td>7.0%</td>
<td>Ca(BH₄)₂ and MgH₂ formed after hydrogenation; Ea = 116.75 kJ mol⁻¹ H₂ after cycling</td>
<td>[170, 171]</td>
</tr>
<tr>
<td>Ca(BH₄)₂ + MgH₂</td>
<td>Ball milling; TiF₅/NbF₅ catalysts</td>
<td>10.5%</td>
<td>60% reversibility (350 °C, 90 bar H₂)</td>
<td>[165]</td>
</tr>
<tr>
<td>Ca(BH₄)₂-3LiNH₂</td>
<td>Ball milling</td>
<td>7.2%</td>
<td>300 °C, 3 h; desorption onset at 220 °C</td>
<td>[146, 149]</td>
</tr>
<tr>
<td>Ca(BH₄)₂-4LiNH₂</td>
<td>Liquid ball milling</td>
<td>8.86%</td>
<td>NH₃ evolution is restrained</td>
<td>[53]</td>
</tr>
<tr>
<td>Ca(BH₄)₂-4LiNH₂ (x = 1, 2, 3)</td>
<td>Hand grinding</td>
<td>7.5-9% (NH₃ + H₂)</td>
<td>Metallization at 100–150 °C to Ca(BH₄)(NH₃)₂; NH₃ release (t &lt; 300 °C) and H₂ (t &gt; 350 °C)</td>
<td>[148, 161]</td>
</tr>
<tr>
<td>Ca(BH₄)₂–Mg₂NiH₄</td>
<td>Fritsch Planetary P6 milling</td>
<td>4.6%</td>
<td>Mutual destabilization; formation of MgNi₂·B₂</td>
<td>[151]</td>
</tr>
<tr>
<td>Ca(BH₄)₂–6Mg₂FeH₆</td>
<td>Ball milling</td>
<td>-</td>
<td>Desorption onset at 310 °C (vs. 350 °C for pristine Ca(BH₄)₂)</td>
<td>[172]</td>
</tr>
<tr>
<td>Mg₂NiH₄·LiBH₄·Ca(BH₄)₂</td>
<td>Ball milling</td>
<td>-</td>
<td>MgNi₂·B₂, Mg, and Mg₂NiH₆·3 as intermediates</td>
<td>[175]</td>
</tr>
<tr>
<td>Ca(BH₄)₂–2Mg(NH₄)₂ and Ca(BH₄)₂–2Ca(NH₂)₂</td>
<td>Ball milling (Retsch PM400 planetary ball mill, 200 rpm, 5 h, Ar)</td>
<td>8.3%, resp. 6.8%</td>
<td>Desorption onset at 220 °C</td>
<td>[152]</td>
</tr>
<tr>
<td>Mg(BH₄)₂–Ca(BH₄)₂ (1/2, 1, 1, 2:1)</td>
<td>Fritsch Pulverisette 6 planetary milling</td>
<td>-</td>
<td>Partial reversibility reported only for 2Mg(BH₄)₂–Ca(BH₄)₂</td>
<td>[94, 153]</td>
</tr>
<tr>
<td>NaAlH₄–Ca(BH₄)₂</td>
<td>Fritsch Pulverisette 6, WC vials and balls, BPR 40</td>
<td>6%</td>
<td>Ca(AlH₄)₂ was partially stable (10 months), yielding Al and CaH₂</td>
<td>[160]</td>
</tr>
<tr>
<td>2NaAlH₄ + Ca(BH₄)₂ (+5 wt% TiF₅ catalyst)</td>
<td>Ball milling (6 h)</td>
<td>4.1 wt% (at 420 °C)</td>
<td>TiF₅ doping reduced release onset from 125 °C (pristine) to 60 °C; Al₄Ti, CaF₂ intermediates (also catalysts)</td>
<td>[135, 161]</td>
</tr>
<tr>
<td>Ca(BH₄)₂–[C(NH₂)₃]⁺[BH₄]⁻ (GBH)</td>
<td>Ball milling</td>
<td>10%</td>
<td>Onset at 60 °C, full release below 300 °C (GBH = guanidinium borohydride)</td>
<td>[169]</td>
</tr>
</tbody>
</table>

5.5. Adduct Formation and Dihydrogen Bonding in Solvates

From molecular insights into the dihydrogen bonding in borohydride ammoniates [174] to DFT modeling of chemical bonding [175, 176] or the dehydrogenation mechanism in Ca(BH₄)₂·2NH₃ [177, 178], as well as experimental confirmation of the theoretical aspects [179], various adducts of Ca(BH₄)₂ have been described and investigated [39, 179, 180], including calcium tetradecahydroundecaborate Ca(B₁₄H₁₄)₂·4Dg (Dg = diglyme) [181]. The first ammoniate of calcium borohydride was synthesized and characterized by Chu et al., who isolated it by direct synthesis from components Ca(BH₄)₂·2NH₃ (space group Pnma) featuring longer B–H and N–H bond lengths due to dihydrogen bonding, which facilitates the release of 11.3 wt% H₂ at 250 °C [182]. DFT studies performed on Ca(BH₄)₂·2NH₃ reveal that the Ea of 1.41 eV for thermal decomposition can be tuned by using metal dopants (Fe, Co, and Ni) that can modify the Fermi level [183]. While the adduct Ca(BH₄)₂·2NH₃ typically releases NH₃ upon heating at 162–250 °C, when a multi-cation strategy was employed by Tang et al., the RHC Ca(BH₄)₂·2NH₃/LiBH₄ released 12 wt% H₂ of high purity (>99%) at 250 °C [184]. The reaction leading to such a behavior was a two-step process described by Equation (40) [184].

\[
\text{Ca(BH}_4\text{)}_2\cdot\text{NH}_3 + \text{LiBH}_4 \rightarrow \text{LiCaNB}_3\text{H}_4 - \frac{3}{2}\text{H}_2 \rightarrow \frac{1}{2}\text{[Li}_4\text{B}_{10}\text{H}_6] + \frac{1}{4}\text{Ca}_3\text{B}_2\text{N}_4 + \frac{1}{4}\text{CaH}_2 \tag{40}
\]

Furthermore, the addition of Mg(BH₄)₂ over Ca(BH₄)₂·nNH₃ (n = 1, 2, 4) revealed an increase in H₂ purity and storage capacity in the system Ca(BH₄)₂·4NH₃–Mg(BH₄)₂, a
synergy that inhibited ammonia release to yield >99% pure H₂ upon thermal treatment at 500 °C [179].

Extending the scope of borohydride adducts of calcium borohydride, Li et al. studied the hydrogen release properties of calcium borohydride hydrazinates Ca(BH₄)₂·nN₂H₄ (n = 1, 4/3, 2, 3). Among these compounds, the monohydradzininate Ca(BH₄)₂·4/3 N₂H₄ showed 10.8 wt% H₂ release with a dehydrogenation temperature of 140 °C when utilizing an Fe-based catalyst (2 wt% FeCl₃) [185].

Other complexes have also been reported, such as the AB (ammonia borane) adducts of complex hydrides, mainly Ca(BH₄)₂(NH₃BH₃)₂ and its lithium counterpart [186]. The AB adduct of calcium borohydride showed partially reversible behavior (2.4 wt%) under moderate conditions (82 bar H₂, 400 °C), with a release of 11 wt% H₂. Guadinate adducts of metal borohydrides have been reported by Wu et al. in the case of Li, Mg, and Ca complex hydrides MBH₄·nCN₃H₅ [187]. The low contamination of gaseous decomposition products with ammonia and diborane was based on the C–N bonds of guanidine and H⁻ anion of borohydrides. Ca(BH₄)₂·2CN₃H₅ released about 10 wt% H₂ under modest conditions [187].

5.6. Reversibility Assessment

As a key element in advancing hydrogen storage materials, reversibility remains one of the toughest problems in solid-state energy storage [11,104,188–190]. The influence that metal fluorides exert on Ca(BH₄)₂ dehydrogenation/rehydrogenation was studied in the case of V₃F₄, TiF₄, and NbF₅ [133]. Several systems were investigated and showed various degrees of reversibility, such as pristine [191] and TiF₄- and NbF₅-catalyzed Ca(BH₄)₂–MgH₂ [132], Ca(BH₄)₂–Mg₂NiH₄ [151,192], LiBH₄–Ca(BH₄)₂ [166], ternary RHCs with higher reversibility Ca(BH₄)₂–LiBH₄–MgH₂ [162], Ca(BH₄)₂–MgF₂ [125], the implications of CaB₁₂H₁₂ on cycling capacity of calcium-based RHCs [41,193–195], eutectic mixture LiBH₄–Ca(BH₄)₂ [156], the use of catalyst (TiCl₃ [196]; TiF₃, NbF₅, NbCl₅ [197]) on the reversibility of Ca(BH₄)₂ (rehydrogenation under 90 bar H₂, 623 K, 3.8 wt% H₂) [196].

The catalytic effect of Ca(BH₄)₂ was explored in a RHC Mg(NH₂)₂–2LiH–0.1Ca(BH₄)₂ composite (4.5 wt% H₂ reversible, onset at 90 °C and release at 140 °C, and rehydrogenation with onset at 60 °C) [131]. Other RHCs serve as precursors for calcium borohydride, and these systems already showed promising results regarding cycling behavior, like LiBH₄–Ca(AlH₄)₂ (4.5 wt% reversible, 450 °C) [198]. TiX₃ (X=F, Cl) has been successfully used to lower the thermodynamic barriers of Ca(BH₄)₂ [138] or in RHCs 6LiBH₄–CaH₂ systems [143]. A critical step for the reversibility of Ca(BH₄)₂ is the formation of CaB₆, presumably from a CaB₁₂H₁₂ precursor that can only be produced between 320 and 350 °C; otherwise, amorphous B would result, which is a clear bottleneck in the cycling pathway of calcium borohydride [104,199].

5.7. Ionic Conductivity

Ionic conductivity [173,200–207] and superconductivity [208,209] have also been investigated recently, with some surprising results and direct implications in the applicability of Ca(BH₄)₂ in electrolytes for batteries or even as high-temperature superconductors when properly doped, as DFT computations have revealed.

It has been hypothesized that Ca²⁺ might be too big for migration in Ca-based electrolytes, preferring an octahedral coordination by binding six ligands, but recent reports imply that using weaker coordinating ligands, such as B₁₂H₁₂⁻ might increase Ca²⁺ mobility.

6. Ca(BH₄)₂ in Organic Synthesis and Organometallic Chemistry

6.1. Catalyst/Initiator

Calcium borohydride extends its utility in organic synthesis as well. For instance, the THF adduct [Ca(BH₄)₂(THF)₂] was prepared from Ca(OMe)₂ and BH₃·THF reacting in THF solvent and used for the polymerization ε-caprolactone and L-lactide in a combined DFT and experimental investigation [210]. The active catalysts employed
were produced by the treatment of \([\text{Ca(BH}_4\text{)}_2(\text{THF})_2]\) with \(\text{KCP}^*\) \((\text{CP}^* = (\eta^5\text{C}_5\text{Me}_5))\) and \(\text{K}((\text{Me}_3\text{SiNPPH}_2)_2\text{CH})\), namely producing dimeric heteroleptic mono-borohydride derivatives \([\text{CP}^*\text{Ca(BH}_4\text{)}(\text{THF})_2]^\text{−}\) and \([((\text{Me}_3\text{SiNPPH}_2)_2\text{CH})\text{Ca(BH}_4\text{)}(\text{THF})_2]^\text{−}\) (Figure 11). These heteroleptic borohydrides were used as initiators for the ring-opening polymerization (ROP) of \(\varepsilon\)-caprolactone and L-lactide in good yields [210].

\[ \begin{align*}
\text{Ca(BH}_4\text{)}_2 + \text{KCP}^* & \rightarrow \text{Ca(BH}_2\text{S}_3\text{)(THF)}_2 \text{Ca(BH}_4\text{)(THF)}_2 + \text{NaBH}_4 \text{NaCl} \\
\text{NaBH}_4 + 3\text{S} & \rightarrow \text{NaBH}_2\text{S}_3 \\
\frac{1}{2}\text{CaCl}_2 & \rightarrow \frac{1}{2}\text{Ca(BH}_2\text{S}_3\text{)}_2 + \text{NaCl}
\end{align*} \]

\(\text{NaBH}_4 + 3\text{S} \rightarrow \text{NaBH}_2\text{S}_3 \rightarrow \frac{1}{2}\text{CaCl}_2 + \frac{1}{2}\text{Ca(BH}_2\text{S}_3\text{)}_2 + \text{NaCl} \)

With a lower reactivity towards esters compared to lithium borohydride, \(\text{Ca(BH}_4\text{)}_2\) was used together with Grignard reagents in a molar ratio of 0.25 \(\text{Ca(BH}_4\text{)}_2:4 \text{EtMgBr}\) to produce the reduction of methyl esters \(\text{RCOOCH}_3\) in \(\text{THF}\) at room temperature to \(\text{RCH}_2\text{OH}\).
alcohol (6%), RCH(OH)Et (83%), and RC(OH)Et$_2$ (11%) [218]. Both Ca(BH$_4$)$_2$ and Zn(BH$_4$)$_2$ were investigated in this reduction and showed similar results.

Another modified borohydride complex, calcium amidoborane Ca(NH$_2$BH$_3$)$_2$ was used successfully to reduce $\alpha$, $\beta$-unsaturated aldehydes and ketones (carbonyl compounds) to allylic alcohols [219]. Its synthesis involves the reaction of CaH$_2$ and AB (ammonia borane) in THF (Equation (42)) [219].

$$\text{CaH}_2 + 2 \text{NH}_3\text{BH}_3 \text{THF} \rightarrow \text{Ca}(\text{NH}_2\text{BH}_3)_2 + 2\text{H}_2$$ (42)

6.3. Promoter of Cyclization in Various Reactions

Calcium borohydride was also involved as an active catalyst in $\sigma$-bond metathesis, a fundamental reaction in organic chemistry [220]. Notably, Bellham et al. reacted amineborane t-BuNH$_2$·BH$_3$ with a $\beta$-diketiminate-supported silylamido calcium complex with elimination of HN(SiMe$_3$)$_2$ while also isolating the active catalyst, characterized by XRD and shown to belong to a polymeric infinite chain of calcium borohydride, in soluble in organic media, namely, [Ca(BH$_4$)$_2$·THF]$_\infty$ [221]. Access to polylactide macrocycles by cyclo-polymerization of L-lactide was reported to proceed in good yield (up to 77%, 20 min) when catalyzed by Ca(BH$_4$)$_2$ by intramolecular transesterification occurring during ROP [222–224].

6.4. Reaction Inhibitor and Miscellaneous Reactivity

There are reports of other derivatives of calcium borohydride, like the cyclopentadienyl complex Cp$_2$Ca(THF)$_2$ (obtained by mixing Ca(BH$_4$)$_2$ and CpNa in THF) and the methyl-substituted analog, (MeCp)$_2$Ca(THF)$_2$ (MeCp = $\eta^5$-CH$_3$C$_5$H$_4$) [225]. Similarly, [Bm$_2$MeBenz]$_2$Ca(THF)$_2$ was also obtained and characterized by the reaction of Ca(BH$_4$)$_2$·2THF with 1-methyl-1,3-dihydro-2H-benzimidazole-2-thione, where Ca is eight-coordinate and features two Ca···H-B interactions [226].

Ca(BH$_4$)$_2$ has served as the starting point for the synthesis of thorium and uranium metallocene borohydride complexes, allowing the isolation and structure determination of (C$_5$Me$_5$)$_2$Th($\eta^3$-H$_3$BH)$_2$ [227].

Alternatively, calcium borohydride found its use as an inhibitor for the synthesis of fluorine-modified polysilazanes, leading to a solid, soluble fluorinated polysilazane suitable for metal substrates coating [228], or as a catalyst for regioselective hydroboration of terminal alkenes [214].

7. Remaining Challenges and Future Prospects

While bearing some similarities to its lighter counterpart Mg(BH$_4$)$_2$, calcium borohydride features some unique features like the relative ease of desolvation from synthesis adducts, different de-/rehydrogenation enthalpies, a lower and thus more feasible activation energy $E_a$, and different decomposition pathways. This decomposition could be further tuned, allowing the generation of high-purity hydrogen with small amounts of boranes.

The use of calcium borohydride as an energy storage material has the potential to impact the environment in several ways. It is essential to consider both the potential benefits and the hazards associated with the production, handling, and disposal of this complex hydride and its related composites. Regarding the production route, hazardous chemicals are involved in the synthesis of calcium borohydride as well as energy-intensive processes such as ball milling. These processes may involve the use of solvents, reagents, and catalysts that could have adverse effects on human health and the environment if not properly handled and managed. The production of calcium borohydride requires significant energy inputs, which, depending on the energy source, could contribute to greenhouse gas emissions. Handling complex hydrides involves some strict safety precautions needed to prevent accidental exposure and ensure safety. It is important to follow established safety protocols to minimize risks during transportation, storage, and usage of Ca(BH$_4$)$_2$. Being reactive towards moisture with the subsequent release of hydrogen gas, calcium
borohydride can be flammable and potentially lead to fire or explosion hazards; therefore, adequate measures must be taken to prevent accidental ignition and control the release of hydrogen gas.

An important aspect linked to the circular economy and a sustainable hydrogen economy is the disposal of end-of-life hydrogen storage materials based on Ca(BH$_4$)$_2$. Since a reaction with water would lead to the release of hydrogen, proper disposal methods should be followed to ensure the safe handling of any H$_2$ generated during disposal processes. The impact associated with the disposal of calcium borohydride waste, if not properly managed, could be linked to adverse environmental effects. It is important to adhere to local regulations and guidelines for the disposal of hazardous waste to prevent contamination of soil, water, or air. Furthermore, the overall environmental impact of calcium borohydride as an energy storage material can be evaluated by life cycle assessment studies that consider the potential environmental impact throughout the entire life cycle of the compound, including production, usage, and disposal, and could guide the development of more sustainable processes.

Reversibility perhaps remains the highest barrier to adopting Ca(BH$_4$)$_2$ as a mainstream hydrogen storage fuel, along with the currently rather cumbersome synthesis procedure. The formation of various rock-stable boron by-products (CaB$_6$, for instance) or other very stable compounds still represents important research avenues to explore. The multistep decomposition can be altered by using catalysts/additives or by conducting the reaction in a suitable solvent capable of decreasing reaction enthalpies by forming borohydride adducts. Among TM-based catalysts, Nb and Ti showed the best results, lowering rehydrogenation conditions (350 °C, 24 h, 90 bar H$_2$). These results add to other reports where nanoconfined Ca(BH$_4$)$_2$ in various nanosized supports, such as carbonaceous hosts [229], achieved a reliable H$_2$ storage capacity, although much lower than the theoretical one.

Additionally, research efforts should focus on developing environmentally friendly synthesis routes, optimizing energy consumption during production, and exploring recycling methods for calcium borohydride waste. Adherence to regulations, responsible waste management, and continuous improvement in production and disposal practices are essential to minimizing the environmental footprint of calcium borohydride and ensuring its safe and sustainable use.

8. Conclusions

With a high production cost, calcium borohydride sits in an awkward place among solid-state hydrogen storage materials; it offers nearly 10 wt% H$_2$ storage but with restricted reversibility and sluggish kinetics, which require the use of catalysts and potentially novel additives. Nanostructuring may be another avenue for researchers to follow in order to achieve improved behavior of Ca(BH$_4$)$_2$ during hydrogenation studies. Calcium borohydride Ca(BH$_4$)$_2$ remains one of the most promising tetrahydridoborates due to its high hydrogen storage capacity, the relative abundance of starting raw materials, and its pivotal role in catalysis for many decades.

The current study has highlighted the synthesis routes for Ca(BH$_4$)$_2$, the identified polymorphs, and various adducts that could potentially yield high-capacity hydrogen storage systems while also significantly reducing production costs. Catalyst/additive compounding is another route to improving a/d kinetics, together with nanosizing and/or nanoconfinement. The wide range of applications of Ca(BH$_4$)$_2$, from energy storage systems to batteries, organic synthesis, organometallic chemistry, and catalysis, have been reviewed.

Understanding the key steps and intermediates of the decomposition pathways of Ca(BH$_4$)$_2$ under different experimental conditions could allow further advances by tuning the thermodynamics and kinetics of hydrogen release/uptake. Other strategies focused on using RHCs containing Ca(BH$_4$)$_2$, while species containing B$_2$H$_4^{2-}$ anion might be suitable in ion conductivity studies. Addressing the challenges related to synthesis methods, reaction mechanisms, hydrogen release kinetics, and overall device performance...
is essential for realizing its full potential. Further research is needed to bridge the existing knowledge gaps and unlock the practical applications of calcium borohydride in energy storage systems. Additionally, several reports of using Ca(BH₄)₂ in catalysis and organic synthesis as a reductant reaffirm the advantages of the plurivalent calcium borohydride.

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