Hydrogenation properties of lithium and sodium hydride – closo-borate, $[B_{10}H_{10}]^{2-}$ and $[B_{12}H_{12}]^{2-}$, composites


The hydrogenation properties of metal closo-borate/metal hydride composites, $M_2B_{10}H_{10}$–8MH and $M_2B_{12}H_{12}$–10MH, $M = \text{Li or Na}$, are studied under high hydrogen pressures to understand the formation mechanism of metal borohydrides. The hydrogen storage properties of the composites have been investigated by in situ synchrotron radiation powder X-ray diffraction at $p(H_2) = 400$ bar and by ex situ hydrogen absorption measurements at $p(H_2) = 526$ to 998 bar. The in situ experiments reveal the formation of crystalline intermediates before metal borohydrides ($M$BH$_4$) are formed. On the contrary, the $M_2B_{12}H_{12}$–10MH ($M = \text{Li and Na}$) systems show no formation of the metal borohydride at $T = 400$ °C and $p(H_2) = 537$ to 970 bar. $^{11}$B MAS NMR of the $M_2B_{10}H_{10}$–8MH composites reveal that the molar ratio of LiBH$_4$ or NaBH$_4$ and the remaining B species is 1:0.63 and 1:0.21, respectively. Solution and solid-state $^{11}$B NMR spectra reveal new intermediates with a B: H ratio close to 1:1. Our results indicate that the $M_2B_{10}H_{10}$ ($M = \text{Li, Na}$) salts display a higher reactivity towards hydrogen in the presence of metal hydrides compared to the corresponding $[B_{10}H_{10}]^{2-}$ composites, which represents an important step towards understanding the factors that determine the stability and reversibility of high hydrogen capacity metal borohydrides for hydrogen storage.

Introduction

The human consumption of energy has increased over the past decades, and has mainly been covered by burning fossil fuels at an increasing rate, which has led to an increase in CO$_2$ levels in the atmosphere.$^{1,2}$ Despite an abundance of available renewable energy from sun and wind, these energy sources are intermittent and fluctuate over time and geography. Thus, energy storage is required to compensate for the variability in renewable energy fluxes, and hydrogen is a promising energy carrier with the highest gravimetric energy density among all known compounds ($\mu_m = 120$ MJ kg$^{-1}$).$^1$ However, compressed hydrogen gas has a low volumetric energy density ($\mu_V = 8.5$ MJ L$^{-1}$).

The volumetric density can be improved by storing hydrogen in a solid, for example in reversible metal hydrides.$^{3-5}$ Metal borohydrides have been proposed as solid-state hydrogen storage media due to their high hydrogen content and potential reversibility.$^6$ The challenge of using metal borohydrides as hydrogen carriers is that they often possess high hydrogen release temperatures, coupled with harsh conditions needed for hydrogenation.$^{10-14}$ These issues have generated interest in the synthesis and investigation of hydrogen storage properties of bi- and tri-metallic main group/transition metal borohydrides with tunable hydrogen desorption temperatures.$^{15-21}$ Another approach has been to stabilize unstable borohydrides $e.g.$ Fe(BH$_4$)$_2$ and Co(BH$_4$)$_2$, using ammonia.$^{22}$ Reactive hydride composites have also been used to thermodynamically destabilize metal borohydrides by altering the decomposition mechanism, $e.g.$ LiBH$_4$–MgH$_2$, or by changing the morphology of the sample, $e.g.$ NaBH$_4$–KBH$_4$, where the solid is transformed into a liquid.$^{23,24}$ Finally, several materials have been studied as catalysts for hydrogen uptake and release, $e.g.$, transition metals and their halides and oxides.$^{25-27}$ However, to the best of our knowledge, an efficient catalyst for breaking and forming B–H bonds has not yet been discovered.
Polyhydro-closo-polyborates (also known as closo-borates), BH₄⁻⁻⁻⁻(n = 6–12), are anions comprised of boron atoms with solely terminal hydrogen in closed polyhedral clusters. These compounds can be prepared through a variety of solid-state and solution synthetic approaches. Higher closo-borates, such as dodecahydro-closo-dodecaborates ([B₁₂H₁₂]⁻ salts) and decahydro-closo-decarboxeborates ([B₁₀H₁₀]⁻ salts) are often assumed to be intermediates in the mechanism for hydrogen release and uptake in metal borohydrides, MBHₓₐᵣ, and their relatively high stability may retard the reversibility of these reactions. The formation of higher closo-borates during decomposition of metal borohydrides may occur in a reaction between the metal borohydride and transient diborane (B₂H₆). The formation of either Li₂B₁₀H₁₀ or Li₂B₁₂H₁₂, depending on temperature, has clearly been observed by mechano-chemical treatment of LiBH₄ in a diborane atmosphere. The formation of Li₂B₁₂H₁₂ is also observed for the reactive hydride composite, LiBH₄-MgH₂-Al, which shows decreasing reversible hydrogen content commensurate with increasing amounts of Li₂B₁₂H₁₂ during cycling of hydrogen release and uptake. In a similar manner, magnesium borohydride, Mg(BH₄)ₓ, decomposes under vacuum at T ≈ 200 °C and forms arachno-Mg(BH₄)ₓ, which is reported to absorb hydrogen at moderate conditions, e.g., p(H₂) = 120 bar and T = 250 °C, in contrast to the closo-borates. Hydrogen release and absorption reactions in boron-based hydrides remain not fully understood. Density functional theory (DFT) calculations have been used to predict reaction enthalpies for multiple chemical reactions that reversibly store hydrogen and to identify promising reactions with large storage capacities and relevant thermodynamic properties. Experiments have revealed that LiBH₄ decomposes into LiH and B, with Li₂B₁₂H₁₂ as an intermediate phase. Theoretical work has suggested formation of LiBH₄ₓ, n ≤ 12, nanoclusters, which decompose into mixed LiₙBaₙ clusters via a series of intermediate clusters of LiₓBaₙH₂ₓ (m ≤ 4n). A variety of other intermediates have also been suggested, with the [B₁₂H₁₂]⁻ as the most stable, which is considered to hamper hydrogen uptake reactions. Experimental determination of structure and composition of intermediates is often hampered by poor crystallinity and difficulties in preparation of phase-pure samples. The closo-borate-hydride composites (Li₂B₁₀A, Li₂B₁₂A, Na₂B₁₀A, and Na₂B₁₂A) were characterized by FT-IR using a NICOLET 360 FT-IR from 500 to 4000 cm⁻¹ and 32 scans, with a spectral resolution of 1 cm⁻¹. Data were collected in the 20 range 5° to 50° at 3' min⁻¹ using a Rigaku D/θex detector. Samples were placed in 0.5 mm boron silicate capillaries and sealed with grease under argon in a glovebox. An overview of the hydrogen-treated samples is given in Table 1. In situ powder X-ray diffraction (PXDI. In situ powder X-ray diffraction patterns were measured on a Rigaku Smart Lab diffractometer using a Cu source and conversion beam mirror (Cu Kα₁ radiation, λ = 1.540593 Å). Data were collected in the 2θ range 5° to 50° at 3° min⁻¹ using a Rigaku D/θex detector. Samples were placed in 0.5 mm boron silicate capillaries and sealed with grease under argon in a glovebox. In-house powder X-ray diffraction (PXDI). In-house powder X-ray diffraction powder X-ray diffraction (PXDI), ex situ powder X-ray diffraction (PXDI), Fourier transform infrared spectroscopy (FT-IR), as well as solution and solid-state ¹¹B NMR and ²³Na magic-angle spinning (MAS) NMR.
Table 1 Overview of the hydrogenated samples. The total pressure allows calculation of hydrogen H2 uptake (Δm/m). Unidentified compounds are denoted, 1, 2, 3, or 4

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*Vessel had a ~4 bar h⁻¹ leak, leading to a large decrease in pressure over the course of the experiment.

Results and discussion

Hydrogenation of metal decahydro-closo-decaborate M2B10H10-8MH compositions

Sample Li2B12H10-8LiH. The Li2B10-A sample was heated to 307 °C (ΔT/Δt = 5 °C min⁻¹) and kept isothermal for 24 hours at p(H2)start = 526 bar, Fig. S1 (ESI†). The hydrogen pressure decreased slowly, 0.054 wt% per h, for the first 6 hours, then ~5× faster (0.262 wt% per h) for 8 hours, and again slower for the remaining 8 hours, suggesting that there was an incubation period before hydrogen absorption could proceed rapidly or that several reactions take place. The pressure decrease corresponds to a total uptake of 2.9 wt% H2, which is about 4× less than the theoretical hydrogen uptake, *i.e.* 11.3 wt%, which would correspond to full conversion of the sample to LiBH4. PXD of the post-hydrogenation sample, Li2B10-B (Fig. 1), reveals that the reactants, Li2B10H10 and LiH, are almost completely consumed during the formation of LiBH4 and 1. PXD of Li2B10-A treated at 400 °C, p(H2) = 998 bar H2 for 48 h (Li2B10-C) (Fig. S2, ESI†) also reveals the formation of LiBH4 and intermediate 1. However, additional Bragg reflections appear at low Bragg angles (2θ), which are assigned to impurities from the reaction vessel. Compound 1 has not previously been reported and may be an intermediate in the formation of LiBH4 with a lithium/boron ratio in between Li2B10H10 and LiBH4, *i.e.*, 0.2 < Li/B < 1. Observed Bragg diffraction data,

![Fig. 1 Normalized powder X-ray diffraction patterns of Li2B10H10-8LiH after manually grinding (Li2B10-A) and after hydrogenation (Li2B10-B) at T = 307 °C and p(H2) = 526 bar for 24 hours (λ = 1.540593 Å). Symbols: ■ o-LiBH4, ● Li2B10H10, ▲ LiH, and compound 1. The dotted pattern is that of pure LiBH4, overlaid for comparison.](image-url)
$d$-spacings and relative intensities, from 1 are listed in Table S1 (ESI†), which can be indexed with an orthorhombic unit cell, $a = 6.0754(2)$, $b = 6.2494(2)$, $c = 21.019(5)$ Å, $V = 778.0(3) \text{ Å}^3$.

The hydrogenation of Li$_2$B$_{10}$H$_{10}$–8LiH was further studied by in situ SR-PXD at high hydrogen pressure, $p(\text{H}_2) = 407$ bar, and isothermal conditions, $T = 300$ °C (Fig. 2). The PXD signatures of the reactants, Li$_2$B$_{10}$H$_{10}$ and LiH, were observed at RT, after ~6 hours the unidentified compound 1 emerged in accordance with ex situ PXD (Fig. 1 and Table S1, ESI†), and reflections from Li$_2$B$_{10}$H$_{10}$ completely disappeared after ~9 hours. This agrees with the induction period observed in Fig. S1 (ESI†). As Bragg reflections from Li$_2$B$_{10}$H$_{10}$ disappear, the reflections from 1 become more pronounced. After ~11 hours the sample is cooled and crystallization of h-LiBH$_4$ (h-hexagonal) is observed ($T_{\text{melt}} = 280$ °C), which transforms into the ambient o-LiBH$_4$ polymorph (o-orthorhombic). This indicates that 1 may be an intermediate in the formation of LiBH$_4$.

The $^{11}$B MAS NMR spectrum of Li$_2$B$_{10}$-B is dominated by the narrow centerband resonance at ~41.1 ppm from LiBH$_4$ (Fig. 3a). In addition, a somewhat broader centerband is observed at ~23 ppm, which is ascribed to boron in compound 1, since the resonance does not match with the chemical shift reported for Li$_2$B$_{10}$H$_{10}$ at ~28.8 ppm. All spinning sidebands for the central and satellite transitions are observed for LiBH$_4$ whereas only a part of the spinning sideband manifold from the satellite transitions is observed for compound 1. Thus, the total intensity for the $^{11}$B central and satellite transitions for LiBH$_4$ is obtained as the sum of intensities of the centerband and all spinning sidebands, whereas the central-transition intensity for compound 1 is obtained from the intensities for the centerband and first-order spinning sidebands after an intensity correction to these peaks from the contribution from the satellite transitions. The central-transition intensity for LiBH$_4$ is obtained as 4/10 of the total intensity, which holds for a spin 3/2 nucleus, and comparison of this value with the central transition intensity for 1 reveals that the molar ratio for boron in LiBH$_4$ and 1 is 1:0.63, which corresponds to an uptake of 2.8 wt% H$_2$, matching well with the observed hydrogenation, 2.9 wt% H$_2$. This indicates that the absorbed hydrogen only goes toward producing LiBH$_4$ as the B: H ratio in the unknown compound 1 is 1:1, consistent with a higher borate, which is also reflected in its characteristic IR mode and $^{11}$B chemical shift. Thus, $^{11}$B MAS NMR reveals that all Li$_2$B$_{10}$H$_{10}$ (~0.9 ppm and ~28.8 ppm) is consumed during hydrogenation and that LiBH$_4$ and 1 are the only reaction products, besides a minor amount of a BO$_3$ species (~20 ppm), corresponding to 3.5% of the boron in the sample. Solution-state $^{11}$B NMR spectra of Li$_2$B$_{10}$-B dissolved in THF obtained without and with $^1$H decoupling (Fig. S4, ESI†) allow identification of resonances at ~14.0 ppm ($^{11}$J$_{\text{BH}} = 142$ Hz), ~15.6 ppm ($^{11}$J$_{\text{BH}} = 120$ Hz), ~16.0 ppm ($^{11}$J$_{\text{BH}} = 120$ Hz), ~16.7 ppm ($^{11}$J$_{\text{BH}} = 120$ Hz), ~18.0 ppm ($^{11}$J$_{\text{BH}} = 150$ Hz) and ~20.7 ppm ($^{11}$J$_{\text{BH}} = 142$ Hz) in addition to the main peak at ~41.8 ppm from the [BH$_4$]$^-$/ units.
All resonances in the $-14.0$ to $-20.7$ ppm region show doublets in the $^1$H-coupled spectra, demonstrating that they originate from boron sites which are directly bonded to one H atom. The resonance and $J_{\text{BH}}$ coupling at $-15.6$ ppm is in agreement with the $^{11}$B NMR data reported for $[\text{B}_{12}\text{H}_{12}]^{2-}$, matching the impurity of Li$\text{B}_{12}\text{H}_{12}$ in the solid-state $^{11}$B NMR spectrum (Fig. 3a). The remaining resonances, and, in particular, the peak at $-20.7$ ppm, may originate from the unknown compound 1 and thereby suggest that this phase contains boron sites directly bonded to a single H atom. Moreover, comparison of the $^{11}$B chemical shifts with those reported for relevant borate species (Table S4, ESI†) strongly suggests that compound 1 contains closo-borate units.

The formation of LiBH$_4$ is also confirmed by FT-IR (Fig. S3, ESI†). The IR spectrum of Li$\text{B}_{10}$A has a single large B–H stretching mode at $2500$ cm$^{-1}$ with minor modes at lower wavenumbers consistent with metal closo-borates.$^{46,47}$ For Li$\text{B}_{10}$B, the B–H stretching mode at $2500$ cm$^{-1}$ has almost disappeared while B–H stretching modes appear around $2300$ cm$^{-1}$, which correspond to those of LiBH$_4$.\footnote{48,49} This work suggests that 1 has a lithium–boron ratio in between Li$\text{B}_{10}$H$_{10}$ and LiBH$_4$, i.e., $0.2 < \text{Li/B} < 1$, and a hydrogen–boron ratio close to 1:1. A hydrogen uptake of $2.9$ wt% H$_2$ was measured, which corresponds to a sample composition 10Li–108–23.6H. After hydrogenation, the sample contains LiBH$_4$ and LiH and, therefore, also some metal borates richer in boron than hydrogen and lithium. However, the spectroscopy and diffraction data do not unambiguously identify any such compounds.

Sample Na$_2$$\text{B}_{10}$H$_{10}$–8NaH. Hydrogenation of Na$_2$$\text{B}_{10}$A was conducted at $T = 289$ °C and $p(H_2) = 534$ bar and kept isothermal for 24 hours, Fig. S5 (ESI†). The hydrogen pressure was steady for the first 3 hours at $p(H_2) = 534$ bar, then decreased, at 0.248 wt% per h, over the next 12 h, and then more slowly at 0.091 wt% per h during the remaining 8 hours (Fig. S5, ESI†). This reveals an induction period of 3 h prior to absorption of 3.2 wt% H$_2$, which is approximately half of the theoretical maximum, i.e., $6.23$ wt%, which would correspond to full conversion to NaBH$_4$.\footnote{44}

PXD of Na$_2$$\text{B}_{10}$B reveals Bragg reflections from NaBH$_4$ along with an unidentified compound, denoted 2, and some unreacted NaH (Fig. 4). PXD of the high-pressure sample, Na$_2$$\text{B}_{10}$C, reveals that NaBH$_4$ is the major crystalline product, along with 2 (Fig. S6, ESI†). The new compound 2 has reflections at low Bragg angles $2\theta < 7^\circ$ ($d > 13$ Å) (Table S2, ESI†), which can be indexed with a relatively large monoclinic unit cell, $a = 12.7068(5)$, $b = 23.3384(7)$, $c = 16.8802(8)$ Å, $\beta = 105.456(4)^\circ$, $V = 4824.95(8)$ Å$^3$. The formation of NaBH$_4$ is further confirmed by IR spectroscopy (Fig. S7, ESI†). The two B–H stretching bands at $\sim 2500$ cm$^{-1}$ from Na$_2$$\text{B}_{10}$H$_{10}$ in Na$_2$$\text{B}_{10}$A are replaced by a single broad band at $\sim 2400$ cm$^{-1}$ in Na$_2$$\text{B}_{10}$B, indicating that a different B–H containing cluster is formed, possibly a closo-, arachno-, or nido-borate, which could potentially be ascribed to the unidentified compound 2. Finally, the two stretching modes between 2350–2250 cm$^{-1}$ are assigned to NaBH$_4$.

The formation of NaBH$_4$ is also confirmed by FT-IR (Fig. S3, ESI†). The IR spectrum of Li$\text{B}_{10}$A has a single large B–H stretching mode at $2500$ cm$^{-1}$ with minor modes at lower wavenumbers consistent with metal closo-borates.$^{46,47}$ For Li$\text{B}_{10}$B, the B–H stretching mode at $2500$ cm$^{-1}$ has almost disappeared while B–H stretching modes appear around $2300$ cm$^{-1}$, which correspond to those of LiBH$_4$.\footnote{48,49} This work suggests that compound 1 contains closo-borate units.

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The hydrogenation of the composite Na$_2$$\text{B}_{10}$H$_{10}$–8NaH was investigated by HP $in$ $situ$ SR-PXD and the diffraction data is presented in Fig. 5. Initially, Bragg reflections from the reactants, Na$_2$$\text{B}_{10}$H$_{10}$ and NaH, are observed followed by the well-known $\alpha$- to $\beta$-Na$_2$$\text{B}_{10}$H$_{10}$ polymorphic transition at $T \sim 130$ °C.\footnote{50} After 20 min at $T = 302$ °C and $p(H_2) \sim 440$ bar ($t = 60$ min), Bragg reflections from 2 are observed, whereas NaBH$_4$ is observed after approximately 220 minutes at $T = 250$ °C during cooling. This reaction time agrees well with the $\sim 4$ hours induction time observed in $ex$ $situ$ hydrogen absorption in Fig. S5 (ESI†). Thus, 2 may represent an intermediate in the formation of NaBH$_4$ from the Na$_2$$\text{B}_{10}$H$_{10}$–8NaH composite.

The $^{11}$B MAS NMR spectrum of Na$_2$$\text{B}_{10}$B (Fig. 3b) reveals at least two different boron environments, with the dominating resonance at $-41.9$ ppm originating from NaBH$_4$.\footnote{51} The second broad resonance is centered at $-28$ ppm and includes a sharp low-intensity component at $-30$ ppm. The main component of the resonance at $-28$ ppm is ascribed to 2 while the sharp resonance at $-30$ ppm is ascribed to a small amount of the Na$_2$$\text{B}_{10}$H$_{10}$ starting material.\footnote{44} The molar ratio for boron in NaBH$_4$ and 2 of 1:0.21 and is derived from the intensities of the central and satellite transitions for NaBH$_4$ and the central transition for the $-28$ ppm resonance.

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Solution $^{11}$B NMR spectra of Na$_2$B$_{10}$-B dissolved in THF and obtained with and without $^1$H decoupling (Fig. 7) show resonances at $-1.7$ ppm ($J_{BH} = 134$ Hz), $-17.5$ ppm ($J_{BH} = 125$ Hz), $-20.7$ ppm ($J_{BH} = 125$ Hz), $-21.3$ ppm ($J_{BH} = 125$ Hz) and $-29.9$ ppm ($J_{BH} = 119$ Hz), all corresponding to boron bonded to one H atom, and a main peak at $-41.8$ ppm from the [BH$_4$]$^-$ units. The peaks at $-1.7$ ppm and $-29.9$ ppm exhibit a 1:4 intensity ratio and are ascribed to the two distinct B sites in [B$_{10}$H$_{10}$]$^2^-$, in accordance with $^{11}$B NMR data from literature.

Thus, the resonances at $-17.5$ ppm, $-20.7$ ppm, and $-21.3$ ppm are assigned to 2 and is in accord with data reported for [B$_{11}$H$_{11}$]$^2^-$ (Table S4, ESI†), which is a closo-borate with terminal hydronens only, i.e., B–H units producing doublets in liquid state NMR spectra.

Thus, the measured hydrogen uptake of 3.2 wt% H$_2$ corresponds to a sample composition of 10Na–10B–29.3H, and Na NMR reveals a sample composition of NaBH$_4$–NaH 1:0.16 and that Na$_2$B$_{11}$H$_{11}$ (denoted 2) accounts for <8.3% of the sodium in the sample. Boron NMR reveals a ratio between NaBH$_4$–Na$_2$B$_{11}$H$_{11}$ of 1:0.21. The products besides NaBH$_4$ and Na$_2$B$_{11}$H$_{11}$ are difficult to determine and may be a mixture of different borates.

Hydrogenation of metal dodec hydro-closo-dodecarbocate
M$_2$B$_{12}$H$_{12}$–10MH compositions

Sample Li$_2$B$_{12}$H$_{12}$–10LiH. PXD of the physical mixture Li$_2$B$_{12}$A is shown in Fig. 8. Li$_2$B$_{12}$A was heated to $T = 402$ °C and kept isothermal for 24 hours at $p(H_2) = 546$ bar. The total pressure decrease corresponds to a H$_2$ uptake of 2.19 wt% H$_2$. However, PXD of Li$_2$B$_{12}$-B reveals no changes in the composite except for weak reflections from Li$_2$O. Experiments conducted on Li$_2$B$_{12}$H$_{12}$–10LiH samples at high pressure, $p(H_2) = 970$ bar and $T = 400$ °C for 48 h (Li$_2$B$_{12}$-C and Li$_2$B$_{12}$-D), confirmed that no LiBH$_4$ or other compounds were produced under the conditions used in this study (Fig. S9, ESI†). Hence, the pressure decrease observed in Fig. S8 (ESI†) is possibly due to a slight hydrogen gas leak.

This finding is further supported by the $^{11}$B MAS NMR spectrum of Li$_2$B$_{12}$-B (Fig. S10a, ESI†) that almost exclusively shows a single resonance peak at $-15.2$ ppm, in agreement with the reported chemical shift for Li$_2$B$_{12}$H$_{12}$.

Sample Na$_2$B$_{12}$H$_{12}$–10NaH. The physical mixture of Na$_2$B$_{12}$H$_{12}$–10NaH (Na$_2$B$_{12}$-A) was heated to $T = 401$ °C and kept isothermal for 24 hours at $p(H_2) = 537$ bar (Fig. S11, ESI†). PXD of Na$_2$B$_{12}$-B (Fig. 9) reveals no formation of NaBH$_4$; however, another unidentified compound is observed, denoted 3. The total pressure decrease corresponds to a H$_2$ uptake of 1.5 wt% H$_2$ (Fig. S11, ESI†). Experiments conducted on Na$_2$B$_{12}$H$_{12}$–10NaH samples at higher pressure, $p(H_2) = 970$ bar and $T = 400$ °C for 48 h (Na$_2$B$_{12}$-C and Na$_2$B$_{12}$-D), confirmed that no NaBH$_4$ was produced (Fig. S12, ESI†); however, both samples show formation of 3. The ball-milled sample, Na$_2$B$_{12}$-C, shows less remaining Na$_2$B$_{12}$H$_{12}$.
compared to the hand-ground sample, Na$_2$B$_{12}$-D, probably due to a smaller particle size and hence a higher reactivity.

The change in structures is investigated by IR spectroscopy (Fig. S13, ESI†). The B–H stretching bands at $2478$ cm$^{-1}$ from Na$_2$B$_{12}$H$_{12}$ in Na$_2$B$_{12}$-A are shifted slightly to a lower value of $2462$ cm$^{-1}$ in Na$_2$B$_{12}$-B, which may be ascribed to $3$ along with a new bending mode at $1650$ cm$^{-1}$.

The formation of $3$ is studied by HP $\textit{in situ}$ SR-PXD (Fig. 10). Initially, Bragg reflections from Na$_2$B$_{12}$H$_{12}$ and NaH are present, and, during heating, the polymorphic transition of $\alpha$ to $\beta$-Na$_2$B$_{12}$H$_{12}$ is observed at $\sim 275$ °C. In addition, an unidentified compound denoted $4$ is observed. No changes in the diffraction pattern are observed at the isothermal temperature, but Bragg reflections from compound $4$ disappear at $T \sim 210$ °C during cooling. At the same time, Bragg reflections from compound $3$ appear, which indicates a phase transition of $4$ into $3$. Reflections from compounds $3$ and $4$ are listed in Table S3 (ESI†) with the $d$-spacing and relative intensities. Indexing suggests an orthorhombic unit cell for $3$: $a = 6.9114(6)\ \text{Å},$ $b = 12.877(2)\ \text{Å},$ $c = 14.296(1)\ \text{Å},$ $V = 1272.2(5)\ \text{Å}^3$, and an orthorhombic unit cell for $4$: $a = 6.3383(2),$ $b = 10.5223(8), c = 14.8283(7)\ \text{Å} \text{ and } V = 987.4(2)\ \text{Å}^3$. 

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Fig. 7 Solution $^{11}$B NMR spectra (14.1 T) of Na$_2$B$_{10}$-B dissolved in THF obtained (a) without and (b) with $^1$H decoupling.

Fig. 8 Normalized powder X-ray diffraction patterns of Li$_2$B$_{12}$H$_{12}$–10LiH after manually grinding (Li$_2$B$_{12}$-A) and after hydrogenation (Li$_2$B$_{12}$-B) at $T = 402$ °C and $p$(H$_2$) = 546 bar for 24 hours ($\lambda = 1.54056$ Å). Symbols: $\bullet$ LT-Li$_2$B$_{12}$H$_{12}$, $\triangle$ LiH, and $\bigstar$ Li$_2$O.

Fig. 9 Normalized powder X-ray diffraction patterns of Na$_2$B$_{12}$H$_{12}$–10NaH after manually grinding (Na$_2$B$_{12}$-A) and after hydrogenation (Na$_2$B$_{12}$-B) at $T = 401$ °C and $p$(H$_2$) = 537 bar for 24 hours ($\lambda = 1.54056$ Å). Symbols: $\bullet$ LT-Na$_2$B$_{12}$H$_{12}$, $\bigcirc$ NaH, and compound $3$.

Fig. 10 $\textit{In situ}$ high pressure synchrotron powder X-ray diffraction pattern of the hydrogenation of Na$_2$B$_{12}$H$_{12}$–10NaH heated from RT to $407$ °C, at $p$(H$_2$) = 417 bar ($\Delta T/\Delta t = 10$ °C min$^{-1}, \lambda = 0.20720$ Å). The sample was kept isothermal at $T = 407$ °C for $\sim 3$ hours. The dashed line indicates the temperature profile. Symbols: $\bullet$ LT-Na$_2$B$_{12}$H$_{12}$, $\bigcirc$ HT-Na$_2$B$_{12}$H$_{12}$, $\bigcirc$ NaH, compound $3$, and compound $4$. 

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The $^{11}$B MAS NMR spectrum of Na$_2$B$_{12}$-B (Fig. S10b, ESI†), exhibits a narrow resonance (full width at half maximum (FWHM) = 0.7 ppm) at −15.7 ppm, in accordance with the $^{11}$B chemical shift reported for Na$_2$B$_{10}$H$_{12}$, which may suggest that 3 has boron coordination similar to that of Na$_2$B$_{10}$H$_{12}$. PXD clearly shows the formation of a new crystalline product after hydrogenation at high temperature, whereas NMR results only indicate the presence of [B$_{12}H_{12}^-$/C$_0$]-containing compounds. A previous study has shown that annealing Li$_2$B$_{10}$H$_{12}$ under hydrogen pressure can result in the formation of additional Bragg diffraction peaks, indicating that other compounds may form at high temperature.$^{25}$ Compound 3 appears to consist of [B$_{12}H_{12}^-$/C$_0$]- anions as suggested by NMR.

The $^{23}$Na MAS NMR spectrum of Na$_2$B$_{12}$-B (Fig. 6b) is dominated by a resonance at 18.2 ppm from NaH. In addition, minor peaks are observed at 32.1 ppm, 11.9 ppm, 2.3 ppm, −11.4 ppm, −28.8 ppm and −38 ppm. A $^{23}$Na MAS NMR spectrum of Na$_2$B$_{12}$H$_{12}$ reveals that the resonance at −11.4 ppm originates from this compound. Moreover, the peaks at −28.8 ppm and −38 ppm are most likely the low-frequency part (singularity and edge) of a second-order quadrupolar lineshape. However, the resonances at 32.1 ppm, 11.9 ppm, 2.3 ppm, −28.8 ppm, and −38 ppm are not assigned and thus they may include contributions from the unidentified compound 3. Spectral integration shows that the four resonances correspond to 10.7% of the total $^{23}$Na centerband intensity.

The Na$_2$B$_{12}$-B sample absorbed 1.5 wt% H$_2$, which corresponds to a sample composition of 12Na$_{12}$-12B-28.4H. Solid state $^{11}$B MAS NMR show that 3 has similar chemical environment as [B$_{12}H_{12}^-$/C$_0$] and diffraction reveal that 4 transforms to 3 upon cooling.

Comparison of the investigated closo-borate composites

Comparison of the reactivity of the Li and Na closo-borate composites, Li$_2$B$_{10}$H$_{10}$–8LiH and Na$_2$B$_{10}$H$_{10}$–8NaH, reveals several important differences. For instance, the Na composites have faster kinetics for hydrogenation than the corresponding Li samples, e.g., Li$_2$B$_{10}$-A absorbs hydrogen slowly for the first 6 hours, then ∼5 fast for 8 hours and then again slower whereas Na$_2$B$_{10}$-A does not absorb hydrogen for the first 3 hours then absorbs quickly for 12 h, and then more slowly. From a kinetic point of view, the shorter induction period for the sodium system may be associated with faster nucleation and growth of intermediate compounds prior to formation of NaBH$_4$, as compared to similar reactions for the analogous lithium composites. This is well documented by solid-state $^{11}$B NMR, which reveals sample compositions of LiBH$_4$–1 (1:0.63) for Li$_2$B$_{10}$H$_{10}$–8LiH and NaBH$_4$–2 (1:0.21) for Na$_2$B$_{10}$H$_{10}$–8NaH after 24 h. In situ HP SR-PXD experiments reveal the formation of NaBH$_4$ after 4 hours of Na$_2$B$_{10}$H$_{10}$–8NaH, whereas LiBH$_4$ forms after 10 hours. A major difference between composites based on M$_2$B$_{10}$H$_{10}$ and M$_2$B$_{12}$H$_{12}$ is their reactivity; those based on M$_2$B$_{10}$H$_{10}$ more readily form the corresponding metal borohydride, MBH$_4$, and intermediate compounds. In contrast, only unidentified compounds are observed in the Na$_2$B$_{12}$H$_{12}$–10NaH composite, whereas no reaction is observed for Li$_2$B$_{12}$H$_{12}$–10LiH under the conditions used in this study.

In a previous study, Li$_2$B$_{12}$H$_{12}$–10LiH and Na$_2$B$_{12}$H$_{12}$–10NaH were fully converted to the respective metal borohydrides, LiBH$_4$ and NaBH$_4$, under harsher conditions, i.e. T = 500 °C, p(H$_2$) = 1.0 bar for 72 h.$^{39}$ Milder conditions are used in this study, i.e. T = 400 °C, p(H$_2$) = 998 bar for 24 h for hydrogenation of M$_2$B$_{12}$H$_{10}$–8MH and T = 400 °C, p(H$_2$) = 970 bar for 48 h for M$_2$B$_{12}$H$_{12}$–10MH, which proves insufficient to form the respective metal borohydride. The M$_2$B$_{10}$H$_{10}$ composites are clearly more reactive and take up hydrogen at milder conditions compared to the M$_2$B$_{12}$H$_{12}$ composites, possibly due to the lower thermodynamic stability of the [B$_{10}H_{10}^-$/C$_0$] anion, which allows B–B bond breaking to occur under milder reaction conditions.

Conclusions

The composites M$_2$B$_{12}$H$_{12}$–10MH and M$_2$B$_{10}$H$_{10}$–8MH (M = Li and Na) have been reacted with hydrogen at elevated pressures and temperatures and studied by X-ray diffraction both PXD and in situ SR-PXD and FT-IR, $^{23}$Na and $^{11}$B NMR spectroscopy. Both the in situ and ex situ characterization results show that the M$_2$B$_{10}$H$_{10}$–8MH composites react with hydrogen gas to form the respective metal borohydride, MBH$_4$, at T = 300 °C and p(H$_2$) > 500 bar. These conditions were deliberately selected to obtain partial hydrogenation of the samples in order to focus on the mechanism of hydrogen uptake. The relatively mild conditions used in this investigation did not allow formation of MBH$_4$ by hydrogenation of the M$_2$B$_{12}$H$_{12}$–10MH composites: no hydrogen absorption was detected for Li$_2$B$_{12}$H$_{12}$–10LiH, but new intermediates were observed for Na$_2$B$_{12}$H$_{12}$–10NaH. Generally, the sodium-containing composites are observed to be more reactive towards hydrogen compared to the lithium analogues under similar conditions of temperature and H$_2$ pressure, and M$_2$B$_{10}$H$_{10}$–8MH are more reactive than M$_2$B$_{12}$H$_{12}$–10MH. The high stability of the [B$_{10}H_{10}^-$/C$_0$]–anions is associated with the pseudoaromatic bonding in dodecaboro-closo-dodecaborate cages and lack of chemically distinct and more reactive apical boron atoms within the closo-borate polyhedra that the decahydro-closo-decaborate cages contain.

The conditions for hydrogenation used in this study are clearly above the thermodynamic limit needed to form the corresponding metal borohydrides, LiBH$_4$ or NaBH$_4$, for the composites containing [B$_{10}H_{10}^-$/C$_0$]. Therefore, the observed differences in the length of the induction periods prior to hydrogen absorption, which occur at different rates, are assigned to kinetic constraints. Remarkably, four different intermediate compounds have been observed in this study for the hydrogenation of the composites. The formation of intermediate compounds appears to be the rate-limiting step of the
reaction, with the slowest kinetics observed for the $\text{M}_2\text{B}_{12}\text{H}_{12}$ compounds. This suggests that the molecular mechanism for hydrogen absorption is different for the two closo-borate cages, $[\text{B}_{10}\text{H}_{10}]^{2-}$ and $[\text{B}_{12}\text{H}_{12}]^{2-}$.

This study not only demonstrates that lithium and sodium $\text{M}_2\text{B}_{10}\text{H}_{10}$ salts can be hydrogenated into the corresponding metal borohydrides, but it also reveals the presence of, at least, four B–H intermediates, which are different to those previously observed experimentally or suggested based on theoretical calculations. Additional investigations are needed to clarify composition, structure, and properties of these intermediate compounds. The analysis of the available solid-state and solution $^{11}\text{B}$ NMR data indicates that these intermediates are not salts of $[\text{B}_3\text{H}_8]^{-}$, $[\text{B}_9\text{H}_{10}]^{2-}$ or $[\text{B}_{11}\text{H}_{12}]^{2-}$ anions. We hypothesize that these could be other closo-polyporoborates, e.g., $[\text{B}_9\text{H}_{9}]^{2-}$ or $[\text{B}_{11}\text{H}_{11}]^{2-}$ salts, or oligomers resulting from $[\text{B}_{10}\text{H}_{10}]^{3-}$ polymerization. For example, closo-decarborate salts are known to form dimeric anions, such as various isomers of $[\text{B}_{10}\text{H}_{18}]^{4-}$ and $[\text{B}_{12}\text{H}_{18}]^{2-}$ anions.\textsuperscript{57}

A detailed understanding of the reactivity of these important compounds may allow further tailoring of the reaction mechanisms of hydrogen storage reactions. Further investigations should focus on identifying reaction pathways in the dehydrogenation of metal borohydrides that avoid the formation of stable $[\text{B}_{12}\text{H}_{12}]^{2-}$ anions, and favoring formation of intermediate B–H species that can be cycled under more reasonable conditions of hydrogen pressure and temperature.

Conflicts of interest

There are no conflicts to declare.

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