THE JOURNAL OF CHEMISTRY C

Understanding and Mitigating the Effects of Stable Dodecahydrocloso-dodecaborate Intermediates on Hydrogen-Storage Reactions

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Supporting Information

ABSTRACT: Alkali metal borohydrides can reversibly store hydrogen; however, the materials display poor cyclability, oftentimes linked to the occurrence of stable *closo*-polyborate intermediate species. In an effort to understand the role of such intermediates on the hydrogen storage properties of metal borohydrides, several alkali metal dodecahydro-*closo*-dodecaborate salts were isolated in anhydrous form and characterized by diffraction and spectroscopic techniques. Mixtures of Li₂B₁₂H₁₂, Na₂B₁₂H₁₂, and K₂B₁₂H₁₂ with the corresponding alkali metal hydrides were subjected to hydrogenation conditions known to favor partial or full reversibility in metal borohydrides. The stoichiometric mixtures of MH and M₂B₁₂H₁₂ salts form the corresponding metal borohydrides



 MBH_4 (M = Li, Na, K) in almost quantitative yield at 100 MPa H₂ and 500 °C. In addition, stoichiometric mixtures of Li₂B₁₂H₁₂ and MgH₂ were found to form MgB₂ at 500 °C and above upon desorption in vacuum. The two destabilization strategies outlined above suggest that metal polyhydro-*closo*-polyborate species can be converted into the corresponding metal borohydrides or borides, albeit under rather harsh conditions of hydrogen pressure and temperature.

1. INTRODUCTION

Light-metal borohydrides are attractive candidates for solidstate hydrogen storage due to their high weight percentages of hydrogen, up to 18.4% for LiBH₄.^{1,2} Unfortunately, the total release of hydrogen as well as the complete reversal of the process have proven difficult, leading to high reaction temperatures and slow rates. One of the major obstacles to reversibility is the formation of pseudoaromatic *closo*-borate intermediates, including $M_nB_{10}H_{10}$ and $M_nB_{12}H_{12}$ (n = 1 for alkaline-earth metals, n = 2 for alkali metals), which act as thermodynamic and kinetic sinks.³⁻¹⁷ Destabilizing these polyboron hydride species can alter the reaction pathways and allow for greater hydrogenation reversibility.

Dodecahydro-*closo*-dodecaborate compounds were first theoretically predicted in 1955 by Longuet-Higgins and Roberts on the basis of MO-LCAO calculations, suggesting that a borane with an icosahedral I_h symmetry would only be stable as a dianion.¹⁸ This stimulated a flurry of experimental research, and, in 1960, Pitochelli and Hawthorne reported the synthesis of the first $[B_{12}H_{12}]^{2-}$ compound, $[Et_3NH]_2[B_{12}H_{12}]$, obtained in small yield as a byproduct of the reaction of 2-iododecaborane and triethylamine in benzene.¹⁹ The existence of such compounds and their chemical properties are determined by the presence of delocalized electrons and the aromatic character of the chemical bonding. The pseudoaromatic nature of the *closo*-borates of general formula $[B_nH_n]^{2-}$

is responsible for their unique properties compared with *nido-*, *hypho-*, *arachno-*, or *klado-*boranes: high thermal and kinetic stability, salt-like behavior, and tendency to undergo B–H substitution rather than B–B bond-breaking reactions.

The occurrence of $[B_{12}H_{12}]^{2-}$ species among the decomposition products of metal borohydrides is not surprising, as multiple preparative synthetic approaches toward $[B_{12}H_{12}]^{2-}$ and $[B_{10}H_{10}]^{2-}$ species involve borohydride compounds as starting materials.² A number of efforts to enhance the dehydrogenation of metal borohydrides have been undertaken, beginning with Vajo et al., who employed MgH₂ to destabilize LiBH₄.²⁰ A variety of additives, particularly alkaline earth and transition metals and metal hydrides, have been found to be effective in partially or fully dehydriding borohydride materials.^{10,11,13,16,21-26} Less work has been done on destabilizing the *closo*-borate intermediates themselves. Ozolins et al. employed first-principles DFT calculations to predict several decomposition reactions involving Li, Mg, and Ca borohydrides and $[B_{12}H_{12}]^{2-}$ salts, the latter of which are formed in the first part of a two-step decomposition pathway.²⁷ However, only one of the predicted *closo*-borate reactions, the dehydrogenation of CaB12H12 with CaH2, has been investigated

Received:September 27, 2016Revised:October 21, 2016Published:October 25, 2016

experimentally thus far.^{14,28} The rehydrogenation of *closo*borates, although occasionally attempted, has not met with success at all,²⁸ even though complete reversibility frequently requires the accessibility of both processes. While *closo*-borates are often, but not always, detected in borohydride decomposition reactions, a variety of other B_xH_y intermediates have also been shown to form.^{16,17,29–32} However, of these compounds, the $[B_{12}H_{12}]^{2-}$ dianion represents the most extreme case of thermal and kinetic stability due to its pseudoaromatic nature compared with the more open and reactive *nido-, hypho-, arachno-,* and *klado*-boranes.³³

In this work, reactions I–IV, which involve either hydrogenation (I–III) or dehydrogenation (IV) of $[B_{12}H_{12}]^{2-}$ salts, were conducted. The alkali *closo*-borates were fully hydrogenated to the borohydrides, unlike the CaB₁₂H₁₂ previously studied. In addition, Li₂B₁₂H₁₂ was destabilized by MgH₂, forming MgB₂. These studies reveal that the stability of the *closo*-borate salts can, in principle, be overcome and lead to greater effective hydrogen capacities for metal borohydrides.

Hydrogenation:

$$Li_2B_{12}H_{12} + 10LiH + 13H_2 \rightarrow 12LiBH_4$$
 (I)

 $Na_2B_{12}H_{12} + 10NaH + 13H_2 \rightarrow 12NaBH_4$ (II)

$$K_2B_{12}H_{12} + 10KH + 13H_2 \rightarrow 12KBH_4$$
 (III)

Dehydrogenation:

$$Li_2B_{12}H_{12} + 6MgH_2 \rightarrow 6MgB_2 + 2LiH + 11H_2$$
 (IV)

2. EXPERIMENTAL METHODS

2.1. Synthesis of M₂B₁₂H₁₂ Compounds (M = Li, Na, K). The preparation of the dodecahydro-closo-dodecaborate compounds was performed as had been previously reported.²⁸ Initially, 4.5 g Cs₂B₁₂H₁₂ (Sigma-Aldrich³⁴) was added to 75 mL of Milli-Q water (18 M Ω), and the mixture was heated almost to boiling to dissolve the salt. The hot solution was eluted with warm Milli-Q water through an Amberlite IR-120 cation-exchange column in H^+ form to yield $[H_3O]_2[B_{12}H_{12}]$, which was detected by measuring the pH of the eluent. The acidic fractions were concentrated with a rotary evaporator to \sim 20 mL and then passed through another protonated Amberlite IR-120 column to ensure complete conversion from the Cs⁺ to the H⁺ form. After concentrating this second eluent, the acid was titrated to a pH of 7 with the hydroxide or carbonate of each of the desired metal cations to generate the dodecahydro-closo-dodecaborate salt. The solution was dried by rotary evaporation, and any remaining water of hydration was removed by heating the residue to 300 °C under vacuum. The $M_2B_{12}H_{12}$ salts, including the lithium salt, prepared by cation exchange have been shown to be stable up to this temperature. However, their synthesis using B₁₀H₁₄ produces a mixture of B_xH_v compounds, including less-stable $M_2B_{10}H_{10}$, some of which do decompose and are likely responsible for the release small quantities of hydrogen below 300 °C.^{31,35}

2.2. Hydrogenation Experiments. The dry $M_2B_{12}H_{12}$ salts (M = Li, Na, K) were ground in a mortar and pestle with their respective metal hydrides (Sigma-Aldrich) in a 1:10 molar ratio in an argon-filled glovebox to prevent rehydration of the $M_2B_{12}H_{12}$ compounds and reaction of the hydrides. The mixed powders were loaded into a 25 mL tungsten carbide milling pod with two tungsten carbide balls and milled in a SPEX 8000 high-energy mill for 15 min. The milled powders

were then pressed into thin pellets and loaded into the reaction vessels. The pellets were heated to 500 $^\circ$ C and exposed to 100 MPa H₂ for 72 h, then cooled to room temperature and depressurized.

2.3. Dehydrogenation Experiments. $Li_2B_{12}H_{12}$ and MgH₂ (molar ratio of 1:6) were ground together with a mortar and pestle, then the mixture was ball-milled for 1 h with a SPEX 8000 high-energy mill. The milled powders were pressed into pellets and heated under vacuum at 500, 600, or 700 °C. Sieverts measurements were performed using a custom-made stainless-steel sample holder, which was equipped with a thermocouple for accurate temperature measurements during the experiments. Pressure changes during the temperature-programmed desorption were quantified with calibrated pressure transducers and recorded using a LabVIEW-based software program. During the dehydrogenation step, the temperature was ramped from ambient to either 600 or 700 °C. Hydrogen capacity data are presented as weight % with respect to the total weight of the solid sample, assuming that H_2 is the only gaseous product of the desorption reaction. Safety note. Metal hydrides react violently with water, acids, protic solvents, and strong oxidizers and must be handled under an inert environment.

2.4. Materials Characterization. X-ray diffraction (XRD) patterns were obtained with either a Rigaku RU-300 rotating anode diffractometer at 40 kV and 60 mA or a Panalytical Empyrean diffractometer at 44 kV and 40 mA. The air-sensitive samples were loaded into 0.7 mm diameter glass capillaries and sealed with vacuum grease inside an argon-filled glovebox. Following collection of the patterns, the background was subtracted to remove the signal from the amorphous glass.

Raman spectra were collected using a 532 nm laser with a power of 0.5 mW directed through an Acton Spectropro-275 monochromator/spectrograph with a 600 grooves/mm grating to a liquid-nitrogen-cooled Spec-10 CCD detector. Fourier transform infrared (FTIR) spectra were obtained using either a Varian 800 or an Agilent Cary 630 FTIR spectrometer. Both were used in the attenuated total reflectance (ATR) mode. Neutron vibrational spectroscopy (NVS) measurements were made at temperatures of 4 K at the NIST Center for Neutron Research using the BT-4 Filter-Analyzer Neutron Spectrometer (FANS) with a Cu(220) monochromator and 20 min of arc for the pre- and post-comonochromator collimations. Solid-state nuclear magnetic resonance spectra of the ¹H and ¹¹B nuclides were gathered by Spectral Data Services on a 360 MHz spectrometer with rotation rates of 10.0 kHz. For all figures, standard uncertainties are commensurate with the observed scatter in the data if not explicitly designated by vertical error bars.

3. RESULTS AND DISCUSSION

3.1. Hydrogenation of M_2B_{12}H_{12} Compounds. The powder XRD patterns of the synthesized and dried $L_{12}B_{12}H_{12}$, $Na_2B_{12}H_{12}$, and $K_2B_{12}H_{12}$ (Figure 1) match well with those previously reported, indicating that these compounds are in the cubic *Pa3*, monoclinic *P2*₁/*n*, and cubic *Fm3* space groups, respectively.^{36–38} In addition, the FTIR spectra of each (Figure S1) and the absence of the O–H stretching band from water indicate that the samples were dried and possessed no water of hydration. The presence of water is detrimental, as alkaline and alkaline-earth metal hydrides irreversibly react with H₂O to form hydroxides and other oxidized species. For all three $M_2B_{12}H_{12}$ salts, the strong B–H stretching mode between 2500



Figure 1. X-ray diffraction patterns of $Li_2B_{12}H_{12}$, $Na_2B_{12}H_{12}$, and $K_2B_{12}H_{12}$, with their corresponding database patterns shown for comparison.

and 2470 cm⁻¹ and the B–H bending mode near 1080 cm⁻¹ confirm the presence of the B₁₂H₁₂^{2–} anion.¹⁵

A pellet of milled $Li_2B_{12}H_{12}$ + 10LiH, before and after exposure to 100 MPa H₂ at 500 °C, is shown in Figure 2. After heating under high hydrogen pressure, the pellet was observed to spread out and fill the bottom of the vessel, indicating the liquefaction of the material during the course of the reaction, followed by resolidification upon cooling back to room temperature. Similar behavior was found for the sodium mixture, while the potassium pellet merely deformed slightly. While the M₂B₁₂H₁₂ compounds persist as solids above 500 °C,¹⁵ the borohydrides have melting points of 268, 400, and 585 °C for Li, Na, and K, respectively.³⁹

The nearly complete conversion of ball-milled $M_2B_{12}H_{12}$ and MH to MBH_4 under high-pressure hydrogen (100 MPa) was confirmed with various characterization techniques. The powder XRD patterns (Figure 3) of each of the reaction product mixtures showed primarily crystalline MBH_4 in each, with small but detectable quantities of $M_2B_{12}H_{12}$ and MH. These are likely simply unreacted species because the equilibrium pressure for the $12LiBH_4 \Leftrightarrow Li_2B_{12}H_{12} + 10LiH + 13H_2$ reaction based on calculations from Ozolins et al. is much lower than the experimental conditions, at only ~120

bar.²⁷ Kinetic barriers, including slow diffusion of solid-state reactants, likely hindered the completion of the reaction. Rietveld refinement was employed to characterize the relative amounts of each crystalline phase. In all three cases, the amount of borohydride was >80% (Table S1). The lattice parameter of the KBH₄ phase, 6.7249(2) Å, did not exactly match that of the database pattern plotted but was within the range of the several refinements catalogued (Table S2). Ball-milling the starting $M_2B_{12}H_{12}/MH$ mixtures increases the borohydride yield, likely due to an improved contact between the hydride and *closo*-borate crystallites, as found for other hydride systems.⁴⁰

XRD, of course, does not take into account amorphous phases, including some intermediate boron-hydride species reported in the dehydrogenation of borohydrides.^{4,9,15} For the detection of such possible products, NVS (Figure 4) and Raman (Figure 5) of the final reacted materials were compared with the pure individual starting materials and expected borohydride products. NVS is a summation of all hydrogen scattering, regardless of the species' crystallinity. The NVS comparison spectra also clearly indicate the conversion to borohydride. The borohydride libration peaks (52 meV for $LiBH_{4}^{41}$ 44 meV for NaBH₄, and 42 meV for KBH₄⁴²) are readily apparent in the spectra of the corresponding resulting materials. Although the lower intensity combination bands at intermediate energies are less visible, the higher energy bending modes (134 and 158 meV for LiBH₄, 140 and 159 meV for NaBH₄, and 140 and 156 meV for KBH₄⁴³) are evident in the product spectra. The peaks for the MH⁴⁴ and $M_2B_{12}H_{12}^{45}$ species are not discernible above the borohydride combination bands, indicating the presence of, at most, only low levels of those compounds, and no peaks corresponding to other intermediate phases such as $\tilde{Li_2}B_{10}H_{10}$ or $\tilde{Na}_2B_{10}\tilde{H_{10}}^{46,47}$ were present above the detection limit either.

Raman spectroscopy is also sensitive to B–H vibrations and would detect partially hydrogenated species. However, only $[BH_4]^-$ and $[B_{12}H_{12}]^{2-}$ peaks are detected, with no other signals corresponding to $[B_{10}H_{10}]^{2-}$ compounds or other boron hydrides.⁴⁸ In the Na Raman spectra, for example, peaks at 589 and 756 cm⁻¹ corresponding to B–H bending modes are seen in both the Na₂B₁₂H₁₂ starting material as well as the sample after the high-pressure experiment. NaH does not scatter strongly and therefore does not show any distinguishable features that can be recognized in the spectrum of the reacted sample. However, accounting for differences in scattering intensity and the possibility of heterogeneity in the sample, the



Figure 2. Photograph of $Li_2B_{12}H_{12}$ + 10LiH in the reaction vessel (a) prior to and (b) after subjection to 100 MPa H_2 at 500 °C.



Figure 3. Posthydrogenation powder diffraction patterns of (a) $Li_2B_{12}H_{12} + 10LiH$, (b) $Na_2B_{12}H_{12} + 10NaH$, and (c) $K_2B_{12}H_{12} + 10KH$. Peaks corresponding to component phases are shown in green (MBH₄), blue ($M_2B_{12}H_{12}$), and red (MH).

borohydride species is the majority phase in each of the product mixtures. The presence of highly hydrogenated B–H species in the hydrogenated $Li_2B_{12}H_{12}$ +10LiH sample was further confirmed using temperature-programmed desorption. The dehydrating behavior upon heating the regenerated $Li_2B_{12}H_{12}$ +10LiH material upon heating from room temperature to 700 °C resembles that of an authentic sample of lithium borohydride (Figure S2), although the amount of hydrogen released is only 12.5 wt % compared with 14.1 wt % for pure LiBH₄.

Magic-angle spinning solid-state nuclear magnetic resonance spectroscopy (Figure S3) was also performed on the three posthydrogenated samples. Each of the ¹¹B spectra, referenced to $BF_3 \cdot OEt_2$, had a large peak corresponding to borohydride: -41.5 ppm for LiBH₄, -42.2 ppm for NaBH₄, and -38.3 ppm for KBH₄, matching the values reported in the literature.^{4,9,10,49} The slight differences in peak position result from minor variations in the chemical environment of the $[BH_4]^-$ anion. Of the three reaction products, only the potassium mixture had a well-defined peak at -15.4 ppm, which corresponds to the $[B_{12}H_{12}]^{2-}$ anion, although the XRD pattern of the lithium mixture also showed detectable amounts of the Li₂B₁₂H₁₂ phase. The ¹H MAS spectra reveal (Figure S3) broad peaks centered at 0.2 ppm for the $[BH_4]^-$ ion. The Li and Na ¹H spectra also possess smaller, sharper peaks that may correspond to the metal hydrides, $[B_{12}H_{12}]^{2-}$ species, or other phases that are amorphous and not detected by XRD.

3.2. Dehydrogenation of *closo*-Borates. In previous studies, the alkali dodecahydro-*closo*-dodecaborates have been found to be too stable for complete dehydrogenation, both on their own and with their corresponding metal hydrides.^{2,31} However, it has been theorized that $B_{12}H_{12}^{2-}$ compounds, with both alkali and alkaline earth counterions, can be destabilized using alkaline earth metals or metal hydrides, from which strongly bound borides are produced.²⁷ Previous work has already shown success with $CaB_{12}H_{12}$ mixed with CaH_2 , yielding crystalline CaB_6 and hydrogen upon heating.²⁸ In this study, $Li_2B_{12}H_{12}$ was dehydrogenated using MgH_2 as a destabilizing agent to form MgB_2 .

The Li₂B₁₂H₁₂ described above for the hydrogenation experiments was also employed for dehydrogenation in the presence of 6 equiv of MgH₂. Reaction IV, in which MgH₂ is employed to destabilize Li₂B₁₂H₁₂, has a theoretical reaction temperature of 215 $^\circ\text{C},^{27}$ whereas $\text{Li}_2\text{B}_{12}\text{H}_{12}$ alone begins to decompose above 250 °C while retaining the B_{12} icosahedral cores.^{15,31} The Li₂B₁₂H₁₂ and MgH₂ powders were ground and then ballmilled together for 1 h, followed by pressing into pellets. The dehydrogenation reaction was performed at several temperatures under vacuum for 18 h. Metallic Mg was formed from the desorption of the MgH₂, as previously observed in the $LiBH_4$ -2MgH₂ system.⁵⁰ However, no MgB₂ was observed below 500 °C. By 700 °C, almost all of the in-situ-generated Mg had been consumed, yielding primarily crystalline MgB₂, indicating the dissociation rather than polymerization of the B_{12} icosahedra but also some MgO (Figure 6). The source of oxygen is unclear, but it might originate from reaction with small amounts of adsorbed water or oxygen on the walls of the reaction vessel. No Li-containing species were observed by XRD after the thermal treatment, possibly due to the high volatility of Li and the decomposition of Li₂B₁₂H₁₂ to amorphous species at 500 °C and above, as previously observed.^{15,31} Experiments with metallic magnesium instead of MgH₂ as the starting material were also attempted to confirm the reaction of Mg⁰ rather than the hydride; however, the soft metal did not mix with the $Li_2B_{12}H_{12}$ salt during milling and thus would not react comparably.

Hydrogen desorption from ball-milled $Li_2B_{12}H_{12} + 6MgH_2$ was measured in a Sieverts apparatus up to a final temperature



Figure 4. Neutron vibrational spectra of the MH (red), $M_2B_{12}H_{12}$ (blue), MBH_4 (green), and the hydrogenated reaction mixtures (black) of (a) Li, (b) Na, and (c) K. Error bars represent one standard deviation. Spectra are vertically offset for clarity.



Figure 5. Raman spectra of the (a) Li, (b) Na, and (c) K systems. Spectra in black are from the reaction mixtures, whereas those in green, blue, and red correspond to the pure MBH_4 , $M_2B_{12}H_{12}$, and MH materials, respectively. Spectra are vertically offset for clarity.



Figure 6. XRD patterns of the $Li_2B_{12}H_{12} + 6MgH_2$ ball-milled mixtures heated to 500, 600, and 700 °C with standard patterns for Mg (orange), MgO (magenta), and MgB₂ (cyan).

of 600 $^{\circ}$ C (Figure 7). The initial stage of desorption did not occur until the measured temperature was above 380 $^{\circ}$ C. The



Figure 7. Temperature-programmed desorption of ball-milled $Li_2B_{12}H_{12} + 6MgH_2$ during heating to 600 °C. The blue curve with markers indicates the wt % H released, while the dotted red curve shows the temperature profile.

desorption achieved its maximum rate after reaching 600 °C and tapered off after about 1 h at that temperature until finally plateauing at 5.9 wt % H, 76.5% of the 7.7 wt % theoretical capacity of the $\text{Li}_2\text{B}_{12}\text{H}_{12}$ + 6MgH₂ mixture. This amount of released hydrogen is slightly above the 5.1 wt % (66% of theoretical) at 700 °C reported by He et al. for pure $\text{Li}_2\text{B}_{12}\text{H}_{12}$, although the latter occurs through the irreversible formation of B_{12}H_z polymers.³¹ The fully hydrogenated mixture, 2LiBH₄ + MgH₂, had an observed hydrogen capacity of 8 to 9 wt % (55–60% of the theoretical hydrogen content) at 425–450 °C and

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only in the presence of catalytic additives such as ${\rm TiCl}_3$ or Ni. $^{\rm 20,50}$

The formation of MgB₂ and the desorption of significant amounts of hydrogen at >250 °C higher than the thermodynamically predicted temperature indicates that significant kinetic barriers exist that inhibit hydrogen release. Ozolins et al. hypothesized that MgH₂ disrupts the pseudoaromatic $B_{12}H_{12}^{2-}$ ion and enables the removal of hydrogen from that species, even when $Li_2B_{12}H_{12}$ is formed in situ from the dehydrogenation of $LiBH_4$.²⁷ However, experimental work by Vajo et al. demonstrated the conversion of $LiBH_4$ and MgH₂ to LiH and MgB₂ at only 450 °C,²⁰ suggesting that the $Li_2B_{12}H_{12}$ intermediate is circumvented, rather than merely destabilized, by the presence of MgH₂ during LiBH₄ decomposition.

4. CONCLUSIONS

The alkali and alkaline earth dodecahydro-closo-dodecaborates have been implicated as highly stable intermediates that prevent the reversible dehydriding of borohydrides, which are otherwise quite promising hydrogen storage materials. Herein we show that metal hydrides can have a destabilizing effect on $[B_{12}H_{12}]^{2-}$ compounds. At 100 MPa H₂ and 500 °C, $Li_2B_{12}H_{12}$, $Na_2B_{12}H_{12}$, and $K_2B_{12}H_{12}$ can be hydrogenated almost quantitatively into the respective alkali borohydrides in the presence of metal hydrides. The high hydrogen pressure hydrogenation could be a promising route to mitigate the occurrence of intermediate boron hydrides in metal borohydrides, especially in the context of the 35 and 70 MPa hydrogen refueling infrastructure currently being deployed. In addition, this route represents an interesting synthetic approach to metal borohydrides. The transformations of $[B_{12}H_{12}]^{2-}$ compounds into the corresponding borohydrides were confirmed with a wide variety of analytical and spectroscopic techniques. In addition, dehydrogenation of Li₂B₁₂H₁₂ was examined utilizing MgH₂ as a destabilizing agent to form MgB₂ at 500 °C and above. The unwillingness of $[B_{12}H_{12}]^{2-}$ to undergo hydrogen release or absorption reactions under milder conditions is clearly associated with the high stability of the B-B bonds in pseudoaromatic dodecahydro-closo-dodecaborate anionic cages. Although further investigations are needed to determine the routes and mechanisms by which $B_{12}H_{12}^{2-}$ and other intermediate boron hydride species are broken down, this study clearly highlights a possible mitigation of this problem by using destabilization approaches, which modify the reaction pathways and favor the hydrogen cycling reactions.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.6b09789.

Infrared spectra of dried $M_2B_{12}H_{12}$ salts, calculated mass fractions postreaction, KBH₄ lattice parameters, and solid-state NMR spectra. (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank Ken Stewart and Jeff Campbell for their skillful technical assistance. J.Z.Z. is grateful to the BES Division of the U.S. DOE for financial support. Sandia National Laboratories is a multiprogram laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000).

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Understanding and Mitigating the Effects of Stable Dodecahydro*closo*-Dodecaborate Intermediates on Hydrogen Storage Reactions

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Figure S1. Infrared spectra of dried $Li_2B_{12}H_{12}$, $Na_2B_{12}H_{12}$, and $K_2B_{12}H_{12}$.

Table S1. Mass percentages of *closo*-borate, metal hydride, and metal borohydride in each of the alkali metal systems after hydrogenation, as determined by Rietveld refinement of the XRD patterns shown in Figure 3.

	Weight Fraction		
Alkali Metal	$M_2B_{12}H_{12}$	MH	MBH ₄
Li	4.1%	0.0%	95.9%
Na	10.2%	8.9%	80.9%
К	13.5%	0.4%	86.1%

Table S2. Lattice parameters of database $Fm\overline{3}m$ KBH₄ patterns and refined parameter of KBH₄ in the reaction mixture.

Lattice Parameter (Å)	Reference
6.6897	1
6.7249	This work
6.72556	2
6.7280	3
6.749	4

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Figure S2. Temperature programmed desorption of hydrogenated $Li_2B_{12}H_{12}+10LiH$ (blue curve) and commercial LiBH₄ (green curve) heating up from room temperature to about 700 °C. The red curve indicates the temperature profile.



Figure S3. MAS solid-state (a) ¹¹B and (b) ¹H NMR spectra of the post-reaction mixtures, performed at spin rates of 10 kHz. In the ¹¹B spectrum, a green circle denotes the BH₄⁻ peak (around -38 to -42 ppm) and a blue triangle indicates the $B_{12}H_{12}^{2-}$ peak in the K spectrum at -16 ppm. Asterisks denote the spinning sidebands. The inset shows a more detailed view near the $B_{12}H_{12}^{2-}$ peak.