Mechanochemical Synthesis and Thermal Dehydrogenation of Novel Calcium-Containing Bimetallic Amidoboranes

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Abstract

Metallic amidoboranes are widely investigated candidates for solid-state hydrogen storage, and much focus shifted recently towards bimetallic amidoboranes. Bimetallic amidoboranes are expected to introduce novel and enhanced physicochemical properties regarding storage and stability. However, these materials are still scarce and mostly grouped around magnesium- or aluminum-containing compounds. We present here a rapid and green mechanochemical solvent-free synthesis of two novel calcium-containing bimetallic amidoboranes, $\text{Li}_2\text{Ca}(\text{NH}_2\text{BH}_3)_4$ and $\text{Na}_2\text{Ca}(\text{NH}_2\text{BH}_3)_4$, from metal hydrides and ammonia borane. The insight into mechanochemical syntheses

is provided by the in situ tandem synchrotron X-ray diffraction and thermal monitoring. The in situ data reveals how the choice of alkali metal hydride governs the course of reactions and their thermal profiles. In situ monitoring of thermal dehydrogenation of these materials is conducted by mass spectrometry and infrared spectroscopy, showing how the course of thermal decomposition varies depending on the structure of the amidoborane, resulting however in the same final products. These new hydrogen-rich bimetallic amidoboranes are structurally characterized by high-resolution powder X-ray diffraction, and they both show potential for hydrogen storage applications: high theoretical gravimetric capacities and low desorption temperatures of hydrogen without the significant presence of harmful gases. We also show how the choice of the milling reactor material can be decisive for the efficiency and overall success of mechanochemical synthetic procedure, which may impact the design of milling syntheses for other thermally labile chemical systems.

Introduction

Indispensable chemical prerequisites of compounds that are candidates for materials for real-world hydrogen storage are: high hydrogen storage capacity, low-temperature hydrogen desorption, purity of the released H_2 , reversibility and fast absorption-desorption kinetics. However, besides these application-level needs, design of materials for hydrogen storage, as well as any other ecologically friendly, sustainable technology, requires a thorough consideration of its whole life cycle, including origin of raw materials and production process.

Although ammonia borane (NH_3BH_3 , further in the text ABH)^{1,2} fulfills most of the mentioned demands, it critically suffers from irreversibility.³ Its derivatives metal amidoboranes (MAB), obtained from metal hydride (MH) and ABH, consist of one or more metal atoms bound to NH_2BH_3 moiety, which is further abbreviated as AB. MABs show major advantages for hydrogen-storage applications with respect to ABH: (i) lower desorption temperatures and; (ii) desorption of hydrogen without or with only a trace amount of unwanted

impurities (borazine and ammonia).^{4,5} Thus, MABs attracted a lot of attention and are very thoroughly investigated during the last decade, being recognised as highly promising candidates for solid-state hydrogen storage.⁴⁻⁸ Derivatives of ammonia borane are generally characterized by lower dehydrogenation temperature, as well as high purity of released H₂ in many cases. However, for the fundamental thermodynamic reasons, irreversibility of their decomposition products remains unsolved, maybe even unsolvable problem.

In comparison with conventional wet synthesis of MABs in dry tetrahydrofuran (THF),⁵ mechanochemical procedures are generally completely solventless, thus providing a very attractive means of preparation from these sensitive reactants.^{9,10} Even more important, they result exclusively in targeted amidoborane and hydrogen as by-product. This was applied to prepare the entire diversity of MABs as they are known today. Beyond mono-metallic amidoboranes with alkali metals (LiAB,⁴ NaAB,^{4,5,7} and KAB¹¹), alkaline earth metals (Ca(AB)₂,¹² Sr(AB)₂¹³) and transition metals (Y(AB)₃,¹⁴ Eu(AB)₂,¹⁵ Yb(AB)₂¹⁵), more recently a series of bimetallic amidoboranes arose as an even more promising class of compounds. Here, a combination of two metals M and N, where differences in their atomic radii, charges, electronegativities, and coordination numbers directly affect bonding interactions with the AB moiety. This combination introduces a rich diversity, thus allowing tailoring of attractive properties. The examples comprise: (i) MN(AB)₂-type bimetallic amidoboranes where both M and N are 1st group metals, such as LiNa(AB)₂;¹⁶⁻¹⁸ (ii) MN(AB)₃-type, where M is a 1st, and N a 2nd group metal, such as NaMg(AB)₃;¹⁹ (iii) M₂N(AB)₄-type, where M is a 1st, and N a 2nd group metal, such as Li₂Mg(AB)₄, Na₂Mg(AB)₄ and K₂Mg(AB)₄;²⁰⁻²² (iv) MN(AB)₄-type, where M is a 1st, and N a 13th group metal, such as LiAl(AB)₄ and NaAl(AB)₄, KAl(AB)₄.²³⁻²⁶ Recently, our group published mechanistic study of mechanochemical preparation of M₂N(AB)₄-type Mg-containing bimetallic amidoboranes (M = Li, Na),²⁰ accomplished by in situ Raman spectroscopic monitoring. The in situ monitoring showed significant differences in the mechanisms of these reactions that depended mostly on alkali metal hydrides.

Although the mechanistic details of synthesis of MABs are important for optimization of preparational process, their dehydrogenation is of central technological importance from the applicative point of view. Thus, it is of the highest interest to thoroughly investigate the details of their thermally-induced desorption.^{4,7,8} Since the MABs consist of NH_2BH_3 groups bound to two metallic cations (alkaline and alkaline earth metal ions), they regularly release unwanted ammonia concurrently with hydrogen, a process that takes place in two steps. Only a few MABs desorb pure hydrogen without impurities: KAB ,¹¹ $\text{Mg}(\text{AB})_2$ ²⁷ and $\text{LiAl}(\text{AB})_4$.²³

Herein, we have developed a green, rapid, and solvent-less mechanochemical procedure for preparation of new $\text{M}_2\text{N}(\text{AB})_4$ -type bimetallic MABs with large divalent cations as calcium, from solid metal hydrides and ABH . The new compounds, $\text{Li}_2\text{Ca}(\text{AB})_4$ and $\text{Na}_2\text{Ca}(\text{AB})_4$, were structurally characterized and their thermal dehydrogenation profiles were monitored by in situ mass spectrometry and IR spectroscopy. The mechanochemical syntheses, conducted by dry ball-milling, were monitored in real-time by tandem synchrotron powder X-ray diffraction (PXRD) and thermal monitoring, revealing how the introduction of different alkali hydrides induces different reaction courses, each having a unique thermal profile. Depending on the alkali cation, these materials follow different decomposition pathways under elevated temperatures, but they end in the same products. After establishing that the large thermal fluctuations in mechanochemical reaction interfere the synthesis of target bimetallic MABs, we also explored the effect of milling reactor material on the reaction.

Results

Synthesis and characterization

Preparations of Ca-containing bimetallic amidoboranes are typically conducted by solvent-free ball milling reaction in argon over 2 h. Stainless steel jars are used for in-house preparations, while PMMA jars are employed to enable in situ monitoring of uninterrupted reactions

Figure 1: IR spectrum (compared with ABH and corresponding Mg-containing amidoboranes²⁰) and PXRD pattern (positions of the lines due to reactants) of (a) $\text{Li}_2\text{Ca}(\text{AB})_4$ and (b) $\text{Na}_2\text{Ca}(\text{AB})_4$. IR spectra are obtained by ATR technique, while PXRD patterns were acquired from 0.3 mm capillary.

by synchrotron X-ray diffraction in real time. More detailed description of synthetic procedures is given in ESI.

Milling of the $2\text{LiH} + \text{CaH}_2 + 4\text{ABH}$ mixture (further in the text LCA) results in white powdered product. The difference of its IR spectrum and PXRD with respect of those for reactants, as well as similarity of IR spectrum to the one for $\text{Li}_2\text{Mg}(\text{AB})_4$ ²⁰ (Fig. 1) indicates a successful production of $\text{Li}_2\text{Ca}(\text{AB})_4$. In situ PXRD monitoring reveals appearance of a series of new lines, attributed mainly to $\text{Li}_2\text{Ca}(\text{AB})_4$, after first 10 min of milling of LCA mixture (Fig. 2 (a)). As evident, these new lines are intensified by further milling with simultaneous decrease of the intensities of original lines due to the depletion of reactants. PXRD patterns of the products obtained in stainless steel and PMMA jars, respectively, evidently show that LCA mixture (Fig. 3 (a) and (b)) results in the same $\text{Li}_2\text{Ca}(\text{AB})_4$ phase, regardless to reaction conditions. After 1.5 h of milling, PXRD pattern consists of $\text{Li}_2\text{Ca}(\text{AB})_4$ and LBN lines, with a small amount of unreacted reactants. Evidently, milling

of ABH powder with LiH is not so prone to temperature change (comparison of temperature profiles between NaH-AB and LiH-AB milling mixtures are shown in ESI file). As a result new $\text{Li}_2\text{Ca}(\text{AB})_4$ phase was synthesized irrespective to milling conditions.

Figure 2: In situ PXRD monitoring of (a) LCA and (b) NCA mixture. Intensities of PXRD lines are represented as defined by scale shown on the left side. Temperature profile of the first 3 min of NCA reaction is shown below the PXRD contour plot. It is evident that the observed significant and instant temperature increase at the very beginning of the reaction, when NaH comes in contact with ABH causes a quick and efficient decomposition of ABH to stable polymeric species, with release of gaseous products such as BH_3 , which, in contact with NaH, gives rise to NaBH_4 . ESR of the amorphous violet product (photo), shown on the right side, undoubtedly shows the presence of radical species in NCA system, which come from NaH. On the other hand, LCA proceeds without such an abrupt temperature rise, thus enabling production of $\text{Li}_2\text{Ca}(\text{AB})_4$, and a small amount of long-tailed $\text{Li}(\text{BH}_2\text{NH}_2\text{BH}_2\text{NH}_2\text{BH}_3)$ (denoted as LBN) as a side-product.

Milling of the $2\text{NaH} + \text{CaH}_2 + 4\text{ABH}$ mixture (further denoted as NCA) in stainless steel jars also resulted in white-powdered product, identified as $\text{Na}_2\text{Ca}(\text{AB})_4$ (Fig. 1 (b)).

Figure 3: Comparison of PXRD patterns at the end of milling. Synchrotron in situ PXRD patterns are shown under a) and c). Ex situ PXRD patterns are shown under b) and d). All patterns are baseline corrected for easier comparison.

However, when carried out in PMMA jars and subjected to in situ PXRD monitoring, the evolution of PXRD patterns indicate a significantly different reaction with respect of the Li-containing system. PXRD patterns clearly show instant disappearance of lines originating from AB, together with a moderate drop of intensity of NaH lines. Simultaneously a series of relatively weak lines appear, which are undoubtedly attributed to NaBH_4 . On the other hand, the CaH_2 lines remain mainly intact. The resulting product is deeply violet coloured. The dominant species is amorphous and its IR spectrum shows that both almost disappeared, indicating a highly decomposed product. Instant change of the composition of NCA system is accompanied by a vigorous release of thermal energy in the first few seconds of the reaction (Fig. 2 (b) - see ESI for detailed comment of temperature profile). Thus, the same experiment was repeated in ex situ conditions with two changes: i) stainless steel milling jars are used instead of PMMA jars; ii) degassing of the jar after 2h of milling and additional milling for 45 min. Milling produces 5 mol of products: 1 mol of bimetallic amidoborane and 4 mol of H_2 . In both cases a white product, identified as $\text{Na}_2\text{Ca}(\text{AB})_4$, was obtained. PXRD patterns of the products of milling of the NCA mixture in stainless steel and PMMA jars, respectively, evidently indicates the above described sensitivity of this reaction in this respect (Fig. 3 (c) and (d)).

PXRD data collected after mechanical milling of LCA and NCA systems in stainless steel jars are used for determination of crystal structure by Rietveld method (ESI, Figs. S5 and S6). The diffraction patterns of synthesized $\text{Li}_2\text{Ca}(\text{AB})_4$ and $\text{Na}_2\text{Ca}(\text{AB})_4$ phase were indexed by assuming orthorhombic and monoclinic unit cell, respectively. The quality of the Pawley fit suggested that the unindexed peaks indicate the presence of impurities. Parts of the pattern with major impurity peaks were at first excluded.

The crystal structure of $\text{Li}_2\text{Ca}(\text{AB})_4$ was solved in direct space by simulated annealing, taking the amidoborane AB moiety as a rigid body. The Li and Ca atoms were treated as independent atoms. Rietveld fitting of the PXRD for $\text{Li}_2\text{Ca}(\text{AB})_4$ (Fig. 4 (a)) shows that it crystallises in the orthorhombic $Fdd2$ space group (No. 43). One Li atom, two AB

moieties and 1/2 of Ca atom comprising the asymmetric unit satisfies the overall charge neutrality. The Ca atom lies on the second order axis. The Ca^{2+} ion is coordinated by 2N atoms of two BH_3NH_2^- groups, and 4B atoms from BH_3 moiety through hydrogen atoms ($\text{Ca}-\text{H}-\text{B}$). Namely, Ca is coordinated with 2 nearly colinear $\text{Ca}-\text{H}$ bonds with amido groups ($\angle(\text{H}_\text{B}-\text{Ca}-\text{H}_\text{B}) = 165^\circ$, $d(\text{Ca}-\text{H}_\text{B}) = 2.374 \text{ \AA}$), two $\text{Ca}-\text{H}$ bonds perpendicular to colinear ones with amido groups ($\angle(\text{H}_\text{B}-\text{Ca}-\text{H}_\text{B}) = 116.5^\circ$, $d(\text{Ca}-\text{H}_\text{B}) = 2.372 \text{ \AA}$) and 2N atoms ($\angle(\text{N}-\text{Ca}-\text{N}) = 96^\circ$, $d(\text{Ca}-\text{N}) = 2.44 \text{ \AA}$). Li is coordinated by 4 hydrogen atoms of 2 BH_3 moieties and 1N atom, in a distorted coordination environment (Fig. 4). Refined PXRD data are also used for assessment of $\text{NH}\cdots\text{HB}$ dihydrogen bonding, although for this purpose more accurate neutron measurements would be needed. In $\text{Li}_2\text{Ca}(\text{AB})_4$ intermolecular $\text{H}_\text{N}-\text{H}_\text{B}$ distances between the neighboring NH_2BH_3^- groups range from (2.103–2.423 $\text{\AA}$), similar to LiAB (2.249 $\text{\AA}$) and $\text{Ca}(\text{AB})_2$ (2.328 $\text{\AA}$).²⁸

Figure 4: Structural details of (a) orthorhombic $\text{Li}_2\text{Ca}(\text{NH}_2\text{BH}_3)_4$ cell where Ca^{2+} ion (green) is coordinated to four nitrogen atoms (blue) from NH_2BH_3^- groups; (b) monoclinic $\text{Na}_2\text{Ca}(\text{NH}_2\text{BH}_3)_4$ cell where one Ca^{2+} ion (green) is coordinated to four NH_2BH_3^- groups, two over hydrogen atoms (gray) from BH_3 moieties and two over nitrogen atoms (blue) from NH_2BH_3^- groups.

Predominant lines of the PXRD pattern obtained by milling NCA mixture are attributed to $\text{Na}_2\text{Ca}(\text{AB})_4$, which contributed with 94.4 %, while the rest of the mixture consists of mi-

Table 1: Geometric parameters of bonding in $M_2Ca(AB)_4$ systems.

	$Li_2Ca(AB)_4$ orthorhombic, $Fdd2$	$Na_2Ca(AB)_4$ monoclinic, $C2$
$d(Ca - H_B)$	2.336 Å	—
$d(Ca - N)$	2.442 Å	(I) 2.292 Å (II) 2.496 Å
$d(M - H)$	1.863 – 2.069 Å	1.415 – 2.189 Å
$d(M - N)$	1.982 Å	—
$\angle(H_B - Ca - H_B)$	166°	—
$\angle(N - Ca - N)$	96°	(I) 129° (II) 171°
$d(NH \cdots HB)$	3.595 Å	3.688 Å

nor amounts of unreacted CaH_2 and AB (Fig. 1 (b)). $Na_2Ca(AB)_4$ crystallises in monoclinic $C2$ space group (No. 5). One Na atom, two AB moieties and 1/2 of Ca atom comprising the asymmetric unit satisfies the overall charge neutrality. The Ca atom lies on the second order axis. The Ca^{2+} ion is coordinated by 4N atoms of four $BH_3NH_2^-$ groups, forming distorted $Ca(AB)_4$ tetrahedron, where the angle between 2N and Ca atoms is 171° ($d(Ca-N) = 2.5$ Å), and between the other 2N and Ca atoms 129° ($d(Ca-N) = 2.3$ Å, which is similar to Ca – N distance in $Ca(AB)_2$ (2.069 – 2.362 Å).¹² Na^+ ion is coordinated by 4 hydrogen atoms of the BH_3 moiety in a distorted coordination environment (Fig. 4 up) with $d(Na - B)$ ranging from 2.634 – 3.059 Å, which is close to Na-B distances in $NaBH_4$ (3.065 Å).²⁹ Thus, the same coordination pattern is evident in both $Li_2Ca(AB)_4$ and $Na_2Ca(AB)_4$, which is analogous to their Mg-containing analogues.²⁰

Thermal decomposition

DSC shows that thermal decomposition of both $Li_2Ca(AB)_4$ and $Na_2Ca(AB)_4$ consists exclusively of exothermal events (Fig. 5).

$Li_2Ca(AB)_4$ shows three intense maxima between 83 and 91 °C (Fig. 5), while a less intense event takes place at 112 °C. After these thermal events, further heating of sample does not induce any change of heat flow. Temperature programmed desorption with mass

spectroscopy (TPD-MS) shows that $\text{Li}_2\text{Ca}(\text{AB})_4$ desorbs all H_2 between 85 and 95 °C (Fig. 6). This is accompanied by a release of NH_3 , but in trace amount, few orders of magnitude lower amount with respect of H_2 , as well as ammonia from $\text{Na}_2\text{Ca}(\text{AB})_4$.

$\text{Na}_2\text{Ca}(\text{AB})_4$ starts to decompose very fast at 66 °C. Until 100 °C, four thermal events are observed, with the most intensive one at 89 °C. The other two very broad exothermal maxima are positioned between 150 and 240 °C. TPD-MS shows that these transitions are mainly associated with chemical transformations resulting in NH_3 , followed by intense H_2 release (Fig. 6). Release of significant amounts of ammonia occurs above 80 °C and remains more or less constant by further heating (up to 300 °C). H_2 is released over a broad 80–120 °C temperature range, peaking at 98 °C.

Figure 5: Heat flow signal of $\text{Li}_2\text{Ca}(\text{AB})_4$ and $\text{Na}_2\text{Ca}(\text{AB})_4$ during thermal heating from room temperature to 250 °C

Figure 6: RGA signals of $\text{Li}_2\text{Ca}(\text{AB})_4$ and $\text{Na}_2\text{Ca}(\text{AB})_4$ samples for $m/z = 2$ and 17 during thermal heating from room temperature to 300°C . Heating rate was set to $10^\circ\text{C min}^{-1}$. Embedded graph represents zoomed NH_3 signal for $\text{Li}_2\text{Ca}(\text{AB})_4$ in the $60 - 120^\circ\text{C}$ region.

Generally, characteristic bands of both compounds are positioned in two regions: $\nu(\text{NH})$ region between $3400 - 3100 \text{ cm}^{-1}$ in and $\nu(\text{BH})$ region between $2400 - 2000 \text{ cm}^{-1}$ (Fig. 1). In line with the previously discussed DSC and TPD-MS measurements, a significant difference in thermal decomposition of $\text{Li}_2\text{Ca}(\text{AB})_4$ with respect to $\text{Na}_2\text{Ca}(\text{AB})_4$ is clearly reflected in thermal evolution of their IR spectra (Fig. 7). Temperature dependant IR spectroscopy shows significant changes in both characteristic regions. In order to extract a detailed information on the thermally induced changes at molecular level, spectral parameters for individual $\nu(\text{NH})$ and $\nu(\text{BH})$ contributions are extracted from Lorentzian profile functions fitted to these envelopes. Thus obtained maximal absorbances $A(\tilde{\nu})$ of individual contributions with respect of temperature are then shown as reaction profiles. For the sake of clarity, maximal $A(t)$ are set to 1, thus giving clear qualitative profiles (Fig. 7).

Both $\nu(\text{NH})$ and $\nu(\text{BH})$ envelopes of $\text{Li}_2\text{Ca}(\text{AB})_4$ show a steep and qualitatively equal decrease above 85°C (Fig. 7). These bands are not present above 120°C . This is accompanied by appearance and increase of 3400 cm^{-1} band. This behaviour is well correlated with most prominent DSC feature (Fig. 5) and TPD/MS evidence of H_2 release (Fig. 6). Additionally, $\nu(\text{BN})$ band disappears over the same temperature range, with appearance of a broad band peaking at 740 cm^{-1} (ESI, Fig. S2). This behaviour clearly indicate a one-step

thermal decomposition of $\text{Li}_2\text{Ca}(\text{AB})_4$ to final decomposition product. Both 3400 cm^{-1} and 740 cm^{-1} bands are attributed to a complex mixture of polymeric species as a decomposition product.

$\text{Na}_2\text{Ca}(\text{AB})_4$ shows a more complicated thermal decomposition. Qualitatively, from the original 3310 and 3250 cm^{-1} contributions of $\nu(\text{NH})$ envelope, significantly narrowed new bands start to grow above 60°C (Fig. 7 (b)). These new bands increase up to 100°C with simultaneous disappearance of original bands. Above 110°C new band at 3400 cm^{-1} appears and starts to increase at the expense of intermediate narrow contributions. Similar behaviour is observed in the $\nu(\text{BH})$ region. Here, the original 2322 cm^{-1} contribution is replaced by the intermediate one at 2275 cm^{-1} , which finally gives rise to 2145 cm^{-1} band. On the other hand, the original bands due to $\nu(\text{BN})$ disappear above 60°C , while the broad envelope at 740 cm^{-1} appear in the last step, together with 3400 cm^{-1} polymeric feature.

After thermal treatment, both $\text{Li}_2\text{Ca}(\text{AB})_4$ and $\text{Na}_2\text{Ca}(\text{AB})_4$ decomposition products show similar spectra, with very intensive $\nu(\text{BH})$ modes around 2300 cm^{-1} and characteristic 3400 cm^{-1} feature. Changes in $\nu(\text{NH})$ modes from starting two strong sharp peaks at 3300 cm^{-1} to final weak and broad maxima at 3400 cm^{-1} is typical for thermally decomposed MAB phases.⁷ Together with this complex amorphous mixture, formation of LiBH_4 , NaBH_4 and $\text{Ca}(\text{BH}_4)_2$ is also expected in these conditions.

Discussion

Mechanochemical synthesis

Generally, synthesis of the Ca-containing amidoboranes is described by the following equation:

Figure 7: Temperature-dependant infrared spectra of (a) $\text{Li}_2\text{Ca}(\text{AB})_4$ and (b) $\text{Na}_2\text{Ca}(\text{AB})_4$ in the 3500 – 2000 cm^{-1} spectral and RT – 200 $^\circ\text{C}$ temperature range. Heating rate was set to 2 $^\circ\text{C min}^{-1}$. Reaction profiles for different $\nu(\text{NH})$ and $\nu(\text{BH})$ bands are shown on the bottom. The profiles show absorbances normalized with respect of their maximal values, and are obtained by fitting the envelopes to Lorentzian profile functions.

where M represents Li or Na. Indeed, reactions involving both LiH and NaH are successfully implemented in stainless steel jars. However, although $\text{Li}_2\text{Ca}(\text{AB})_4$ is obtained in all other here cases, reaction involving NaH shows a high sensitivity to reaction conditions.

In situ monitoring of mechanochemical reaction of LCA mixture shows that production of $\text{Li}_2\text{Ca}(\text{AB})_4$ starts after an initial period of physical shredding and mixing of crystalline reactants. After this initial preparation, the reaction starts, which is evident from simultaneous decrease of PXRD lines due to the reactants and increase of the lines attributed to $\text{Li}_2\text{Ca}(\text{AB})_4$ (Fig. 2 (a)). However, a series of weak lines indicates a side reaction, which results in long-chained amidoborane $\text{Li}(\text{BH}_2\text{NH}_2\text{BH}_2\text{NH}_2\text{BH}_3)$ (further denoted as LBN), a general side product of solid-state reactions of alkaline metal hydrides with ABH.²⁰ The appearance of this phase indicates that the overall reaction undergoes mechanistic pathway which, as a crucial step, involves production of $\text{Li}(\text{AB}) \cdot \text{ABH}$ adduct³⁰ as intermediate phase:

This reaction consumes the entire quantity of LiH. Once produced, intermediate adduct phase can undergo two different pathways: (a) the reaction with CaH_2 , which predominates:

and (b) reaction with remaining ABH:

By analogy with behaviour is observed in the case of Mg-containing bimetallic amidoboranes,²⁰ it is expected that the reaction involving NaH undergoes the same mechanism.

When carried out in PMMA jars, milling of the NCA mixture results in a deep-violet coloured, amorphous product with a minor amount of NaBH_4 (Fig. 2 (b)). PXRD patterns

clearly show instant disappearance of lines originating from ABH, together with a moderate drop of intensity of NaH lines. Simultaneously a series of relatively weak lines appear, which are undoubtedly attributed to NaBH₄. One of the most interesting features of this reaction is a significant and very rapid temperature rise in a first few seconds of the reaction. Such an intense thermal shock causes an irreversible decomposition of ABH to an amorphous polymeric solid, with accompanied with a release of significant amount of NH₃ and BH₃. The later gaseous product partly reacts with NaH giving NaBH₄:

Disappearance of ABH effectively terminates further reaction at its very beginning, in line with our previous observations of the behaviour of the systems consisting of NaH and AB.³¹ It is interesting to note the deeply violet colored product (photograph in Fig. 2 (b)), which is frequently formed in milling reactions of the systems consisting of NaH and AB.^{20,31} The product is amorphous, and its IR spectrum indicates decomposed ABH, with almost invisible $\nu(\text{NH})$ and $\nu(\text{BH})$ regions, and a few extremely broad bands in the region below 1700 cm⁻¹. Violet color indicates the presence of radical species in the system, as confirmed by ESR spectroscopy, which shows a strong and sharp signal with $g = 3.431$ (Fig. 2 (b)). The main component of signal evidently results from off-the-shelf NaH, for which the presence of unpaired electrons is confirmed by comparative ESR measurement. Together with intense color, it indicates a "wandering" electron in the structure.

Na₂Ca(AB)₄ was successfully obtained in stainless steels milling jars, especially when the evolved gas was removed from the system. This is explained by taking into account two orders of magnitude higher thermal conductivity of the stainless steel (14.4 W m⁻¹ K⁻¹) with respect of 0.17 W m⁻¹ K⁻¹ for PMMA. Such a high thermal conduction enables an efficient removal of excess heat released at the start of the reaction and thus temperature regulation of the system during milling. Although we were unable to monitor the temperature in stainless steel

milling jars, composition of the resulting mixture (especially the presence of unreacted ABH) indicate that the reactants inside of these thermally-conductive jars were milled at moderate temperatures (below 50 °C). Under these conditions no irreversible transformation of ABH to violet coloured polymeric product takes place, thus enabling the production of $\text{Na}_2\text{Ca}(\text{AB})_4$, similar to previously discussed systems consisting of NaH and AB.³¹ Milling in stainless steel jars directly mitigate temperature shock in first few second of milling. After "surviving" these opening seconds, NCA mixture starts to react giving 1 mol of product and 4 mol of H_2 . The increased H_2 pressure in closed jar pushes the reaction backward to the reactants side. Thus, in accordance with Le Chatelier's principle, removal of the evolved gaseous H_2 shifts the reaction equilibrium toward the products.³² From the technological point of view, this could be beneficiary in real-world systems, where H_2 produced by dehydrogenation can be constantly released to drive external systems for energy conversion to a useful work, with simultaneous promotion of the reaction.

Structural analysis reveals a coordination of the Ca^{2+} ion with four AB groups, while intermolecular $\text{NH}\cdots\text{HB}$ distance lies in the range 2.352 – 2.688 Å. The range of the values corresponds to $\text{NH}\cdots\text{HB}$ distance in NaAB (2.717 Å).¹¹ Values of intermolecular $\text{NH}\cdots\text{HB}$ bonds are directly responsible for the stabilization of both $\text{Li}_2\text{Ca}(\text{AB})_4$ and $\text{Na}_2\text{Ca}(\text{AB})_4$ structures by forming strong intermolecular dihydrogen bond network between AB groups. At room temperatures, these two phases are stable over weeks.

Thermal decomposition

All here employed techniques undoubtedly show that technologically crucial process of thermal decomposition of $\text{Li}_2\text{Ca}(\text{AB})_4$ and $\text{Na}_2\text{Ca}(\text{AB})_4$ proceeds through two significantly different mechanisms.

A combination of TPD/MS and DSC measurements indicate some generality in ammonia and hydrogen release: i) NH_3 release starts before dehydrogenation; ii) dehydrogenation starts with an event characterized by lower enthalpy (Fig. 5) and lower amount of released

H₂ (Fig. 6), which is succeeded with thermally more prominent event, when majority of H₂ is released; iii) first (less prominent) dehydrogenation event occurs at the equal temperature for both Li₂Ca(AB)₄ and Na₂Ca(AB)₄; iv) exclusively NH₃ impurity was detected in both cases.

Temperature dependant IR spectra reveal molecular background of the processes resulting in release of hydrogen and ammonia. Since in the case of Li₂Ca(AB)₄, ammonia is released only in trace amounts over two events peaking at 86 and 91 °C (Fig. 6), this is not visible in IR spectra. At the same temperatures, a significantly higher amount of ammonia is released from Na₂Ca(AB)₄. The first ammonia emitting event is reflected in IR spectra by simultaneous decrease of 3310 and 2322 cm⁻¹ bands, indicating some rearrangement that includes both -NH₃ and -BH₃ moieties of the AB group. The second amount of NH₃ is not evident by any particular resolved change in IR spectra. The evident thermally induced release of NH₃ from Na-containing amidoboranes^{20,31} can be attributed to the presence of two parallel mechanistic pathways of dehydrogenation. Namely, hydrogen desorption from NaAB⁸ follows two parallel simultaneous desorption mechanisms: (i) the dominant one, through which 90 % of starting amidoborane is decomposed. By this mechanism, exclusively pure H₂ is released. (ii) The less important alternate pathway through which the remaining 10 % of NaAB is decomposed gives rise to emission of NH₃ as a by-product together with H₂. NH₃ evolution is ascribed to formation of "ionic phase" [Na(NH₃)]⁺[H₃B(NHNa)BH₃]⁻ through head-to-tail dimerization.⁸ Decomposition of [Na(NH₃)]⁺ cation causes NH₃ emission. This step leads to Na⁺[H₃B(NHNa)BH₃]⁻ ionic pair, which decomposes finally giving rise to H₂.

TPD measurements (Fig. 6) directly proves that decomposition mechanism as proposed by Fijalkowski is generally applicable to Na-containing amidoboranes. Accordingly, the thermal decomposition of Na₂Ca(AB)₄ is described by (i) the dominant process:

and the simultaneous pathway which results in ammonia as by-product:

$\text{Na}_2\text{Ca}(\text{AB})_4$ releases the first amount of ammonia at 80 °C. Above 85 °C, H_2 evolution becomes a predominant process. Also, we noticed the same mechanism of thermal decomposition of $\text{Na}_2\text{Mg}(\text{AB})_4$, with NH_3 evolution at 75 °C.²⁰ The evidence of NaBH_4 in solid product of decomposition and steady NH_3 release (by equation 7, first step) above 120 °C suggests the following side reaction of thermal decomposition:

For thorough analysis of decomposition products i.e. the exact chemical composition of the formed borohydrides and their environment, ^1H and ^{11}B solid state NMR needs to be employed.

Table 2: Thermal processes resulting in dehydrogenation of $\text{M}_2\text{Ca}(\text{AB})_4$ systems.

$\text{Li}_2\text{Ca}(\text{AB})_4$		
$t/^\circ\text{C}$	% of total H_2	IR processes
88	32.3 %	75 – 110 °C decrease of 3310 and 2321 cm^{-1}
92	67.6 %	90 – 115 °C increase of 3400 cm^{-1}
152	0.1 %	—
$\text{Na}_2\text{Ca}(\text{AB})_4$		
$t/^\circ\text{C}$	% of total H_2	IR processes
—	—	60 – 85 °C decrease of 2322 and 3310 cm^{-1}
89	7.4 %	60 – 95 °C increase of 2275 and 3302 cm^{-1}
97	26.3 %	95 – 115 °C decrease of 2275 and 3302 cm^{-1}
103	52.5 %	95 – 115 °C decrease of 2275 and 3302 cm^{-1} and increase of 2171 and 3400 cm^{-1}
112	13.6 %	95 – 115 °C decrease of 2275 and 3302 cm^{-1} and increase of 2171 and 3400 cm^{-1}
182	0.2 %	—

Although the thermal dehydrogenation of $\text{Na}_2\text{Ca}(\text{AB})_4$ is evidently more complex with respect of $\text{LiCa}(\text{AB})_4$, the processes are conceptually similar (Table 2). 1/3 of total H_2 is released from $\text{Li}_2\text{Ca}(\text{AB})_4$ through a process characterized by a simultaneous decrease of bands due to both $\nu(\text{NH})$ and $\nu(\text{BH})$ bands. This indicates an interaction of $-\text{NH}_3$ with $-\text{BH}_3$ moieties, most probably dimerization of starting amidoborane molecules. The analogous process occurs over two well resolved sub-processes for $\text{Na}_2\text{Ca}(\text{AB})_4$. The remaining 2/3 of H_2 is released by the process in which increase of 3400 cm^{-1} band, characteristic for polymeric $(\text{NH}_2=\text{BH}_2)_n$ species. Only a very small amount of H_2 is released at higher temperatures. The appearance of narrow $\nu(\text{NH})$ intermediate bands for $\text{Na}_2\text{Ca}(\text{AB})_4$ in the $80 - 160^\circ\text{C}$ region is attributed to coordination of ammonia to Lewis acid, i.e. with Na^+ ion. Thus, the new band at 3300 cm^{-1} can be assigned to the $[\text{Na}(\text{NH}_3)]^+$ cation of the ionic salt.⁸ With further heating, at 110°C both $\nu(\text{BH})$ and $\nu(\text{BH})$ modes have reached the highest intensities. By comparing the IR with TPD-MS results we see that this intermediate phase is probably a consequence of head-to-tail dimerization of two amidoborane molecules, as observed for dimerization of NaAB .⁷ Above this temperature, intermediate phase starts to decompose with significant evolution of NH_3 , evolved by decomposition of $[\text{Na}(\text{NH}_3)]^+$ ion.⁸ This is followed by decrease of both characteristic modes. The appearance of 3400 cm^{-1} and 740 cm^{-1} modes characteristic for the final polymeric product shows that, although undergoing a significantly different pathway, $\text{Na}_2\text{Ca}(\text{AB})_4$ decomposition results in practically the same product as $\text{Li}_2\text{Ca}(\text{AB})_4$.

The similarity of IR spectra of the products of thermal decomposition of $\text{Li}_2\text{Ca}(\text{AB})_4$ and $\text{Na}_2\text{Ca}(\text{AB})_4$ indicates the same complex mixture of polymeric species, irrespective of the starting amidoborane. The 740 and 3400 cm^{-1} modes evidently originate from highly complex polymeric decomposition products, together with NaBH_4 (from $\text{Na}_2\text{Ca}(\text{AB})_4$) and LiBH_4 (from $\text{Li}_2\text{Ca}(\text{AB})_4$).^{7,8} These borohydrides are characterised with two bands between $2350 - 2250\text{ cm}^{-1}$.³³ They are kinetically stable at investigated temperatures³⁴ and decompose at 400°C ³⁵ and 505°C ,³⁶ respectively. In principle, formation of $\text{Ca}(\text{BH}_4)_2$ could be also

taken into account. However, although it decomposes at with decomposition temperature of 300 °C,³⁷ its formation is unlikely due to the relative stability of CaH_2 . The formation of these borohydrides is accompanied by a slow, but steady release of NH_3 above 120 °C, as evident in the case of $\text{Na}_2\text{Ca}(\text{AB})_4$ (Fig. 6). In this temperature region, no intermediate phases are detected anymore.

A significantly simpler thermal decomposition of $\text{Li}_2\text{Ca}(\text{AB})_4$ with respect of $\text{Na}_2\text{Ca}(\text{AB})_4$ is additionally explained by taking into account their structures. Namely, from bond length values between alkaline metal and hydrogen (shown in Table S1, ESI) it is clear that both bimetallic amidoboranes posses different span of M-H bond energies (M= Na, Li). Change of Na-H and Li-H bond lengths are 0.765 Å and 0.205 Å, respectively. Due to broader dispersion of bond lengths for around 0.5 Å, $(\text{Na}_2\text{Ca}(\text{AB})_4$ shows broader hydrogen desorption RGA-MS signal (Fig. 6) in comparison to $\text{Li}_2\text{Ca}(\text{AB})_4$). As a consequence of that property, $\text{Na}_2\text{Ca}(\text{AB})_4$ have affinity for transformation through several local energy minima, i.e. to form intermediate metastable phases. Very characteristic for Na-containing amidoboranes is desorption through substantial emission of ammonia.^{7,8} Although we do not know full mechanism, during decomposition of NaAB, the ammonia emission involves head-to-tail dimerization and formation of $\text{Na}^+[\text{BH}_3\text{NH}_2\text{BH}_3]^-$ intermediate phase.⁷ Also, so-called O-step is present during dehydrogenation of Na-containing amidoboranes. The N-B chains of intermolecular oligomerisation are formed between $\text{N}^{\delta-}$ in one moiety and $\text{B}^{\delta+}$ in the other moiety during desorption.³⁸ Behaviour of $\text{Li}_2\text{Ca}(\text{AB})_4$ is in good correspondence with our earlier published results for bimetallic amidoboranes with magnesium²⁰ and other published results from Wu and co-workers²¹ where the whole desorption process was stacked in two events between 100 and 140 °C.

Conclusions

To summarise, we have developed a green and rapid solventless mechanochemical procedure for the synthesis of two bimetallic Ca- and alkaline metal-containing amidoboranes, $\text{Li}_2\text{Ca}(\text{AB})_4$ and $\text{Na}_2\text{Ca}(\text{AB})_4$, using solely metal hydrides and ammonia borane.

The in situ monitoring of mechanochemical syntheses revealed how the course of the reactions, and their thermal profiles strongly depend on the starting alkali metal hydride. For instance, NaH induced sudden and dramatic increase in temperature of reaction mixture, which induced a partial decomposition of thermally labile ABH and influenced the yield and composition of reaction products. Changing of milling reactor material from insulating plastics to thermally-conductive stainless steel readily amended this issue, most likely through more effective heat dissipation.

The crystal structures of $\text{Li}_2\text{Ca}(\text{AB})_4$ and $\text{Na}_2\text{Ca}(\text{AB})_4$ were determined from PXRD, and show that Ca^{2+} central ion is coordinated with four ligands in tetrahedral formation. In $\text{Na}_2\text{Ca}(\text{AB})_4$, the Ca^{2+} ion is coordinated with four amido groups, while in $\text{Li}_2\text{Ca}(\text{AB})_4$, it is surrounded with two amido groups and two BH_3 moieties through their hydride $\text{H}^{\delta-}$ atoms. Their difference in structure, especially in lengths of M-H, Ca-H, and intermolecular $\text{H}_\text{N}\text{-H}_\text{B}$ bonds, affect the dehydrogenation properties.

Both phases show high theoretical gravimetric hydrogen capacities and low H_2 desorption temperatures (11.53 wt % and 91 °C for $\text{Li}_2\text{Ca}(\text{AB})_4$; 9.73 wt % and 98 °C for $\text{Na}_2\text{Ca}(\text{AB})_4$, respectively). The decomposition of $\text{Li}_2\text{Ca}(\text{AB})_4$ is characterized by two hydrogen desorption maxima with minimal ammonia contamination. On the other hand, thermal decomposition of $\text{Na}_2\text{Ca}(\text{AB})_4$ proceeds through four hydrogen release maxima, which is accompanied by a significant quantity of released ammonia. Although both $\text{Li}_2\text{Ca}(\text{AB})_4$ and $\text{Na}_2\text{Ca}(\text{AB})_4$ represent chemically similar members of the wider family of bimetallic amidoboranes, their crystal structures are significantly different. Consequently, they significantly differ in thermal desorption. The presence of NH_3 as a product of thermal decomposition shows that the mechanism of thermal decomposition of Na-containing amidoboranes is more complicated

with respect of Li-containing analogues. Temperature dependent IR measurements indicate the presence of intermediates of thermal decomposition of $\text{Na}_2\text{Ca}(\text{AB})_4$. This means that generally all Na-containing amidoboranes follow two thermal decomposition pathways: (i) the dominant one results in hydrogen evolution without ammonia, and (ii) a side-process leads to release of hydrogen with ammonia as an impurity.

These results strongly indicate that the desorption behaviour of amidoboranes can be tuned by tailoring of ionic interactions in crystal structure, and our future studies will be focused on the development of new stable multimetallic MABs with clean hydrogen desorption.

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Supporting information

Detailed description of all experimental procedures employed in this study; details on synchrotron in-situ PXRD measurements; a comment on the differences between TPD/MS and DSC measurements; IR spectra of starting materials and products; additional temperature dependant IR spectra; details on crystal structure determination from PXRD; bond lengths; temperature profiles of mechanochemical preparations; authors' contributions.

References

- (1) Shore, S. G.; Parry, R. W. Chemical Evidence for the Structure of the Diammoniate of Diborane. II. The Preparation of Ammonia-Borane. *J. Am. Chem. Soc.* **1958**, *80*, 8–12.
- (2) Staubitz, A.; Robertson, A. P. M.; Manners, I. Ammonia-Borane and Related Compounds as Dihydrogen Sources. *Chem. Rev.* **2010**, *110*, 4079–4124.
- (3) Sutton, A. D.; Burrell, A. K.; Dixon, D. A.; Garner, E. B.; Gordon, J. C.; Nakagawa, T.; Ott, K. C.; Robinson, J. P.; Vasiliu, M. Regeneration of Ammonia Borane Spent Fuel by Direct Reaction with Hydrazine and Liquid Ammonia. *Science* **2011**, *331*, 1426–1429.
- (4) Xiong, Z.; Yong, C. K.; Wu, G.; Chen, P.; Shaw, W.; Karkamkar, A.; Autrey, T.; Jones, M. O.; Johnson, S. R.; Edwards, P. P.; David, W. I. F. High-capacity hydrogen storage in lithium and sodium amidoboranes. *Nature Mater.* **2008**, *7*, 138–141.
- (5) Xiong, Z.; Wu, G.; Chua, Y. S.; Hu, J.; He, T.; Xu, W.; Chen, P. Synthesis of sodium amidoborane (NaNH_2BH_3) for hydrogen production. *Energy Environ. Sci.* **2008**, *1*, 360–363.
- (6) Chua, Y. S.; Chen, P.; Wu, G.; Xiong, Z. Development of ammidoboranes for hydrogen storage. *Chem. Commun.* **2011**, *47*, 5116–5129.

- (7) Fijalkowski, K. J.; Grochala, W. Substantial emission of NH₃ during thermal decomposition of sodium amidoborane, NaNH₂BH₃. *J. Mater. Chem.* **2009**, *19*, 2043–2050.
- (8) Fijalkowski, K. J.; Jurczakowski, R.; Kozminski, W.; Grochala, W. Insights from impedance spectroscopy into the mechanism of thermal decomposition of M(NH₂BH₃), M = H, Li, Na, Li_{0.5}Na_{0.5}, hydrogen stores. *Phys. Chem. Chem. Phys.* **2012**, *14*, 5778–5784.
- (9) Yashwantrao, G.; Jejurkar, V. P.; Kshatriya, R.; Saha, S. Solvent-Free, Mechanochemically Scalable Synthesis of 2,3-Dihydroquinazolin-4(1H)-one Using Brønsted Acid Catalyst. *ACS Sust. Chem. Eng.* **2019**, *7*, 13551–13558.
- (10) Jodlowski, A. D.; Yépez, A.; Luque, R.; Camacho, L.; de Miguel, G. Benign-by-Design Solventless Mechanochemical Synthesis of Three-, Two-, and One-Dimensional Hybrid Perovskites. *Angew. Chem. Int. Ed.* **2016**, *55*, 14972–14977.
- (11) Diyabalanage, H. V. K.; Nakagawa, T.; Shrestha, R. P.; Semelsberger, T. A.; Davis, B. L.; Scott, B. L.; Burrell, A. K.; David, W. I. F.; Ryan, K. R.; Jones, M. O.; Edwards, P. P. Potassium(I) Amidotrihydroborate: Structure and Hydrogen Release. *J. Am. Chem. Soc.* **2010**, *132*, 11836–11837.
- (12) Diyabalanage, H. V. K.; Shrestha, R. P.; Semelsberger, T. A.; Scott, B. L.; Bowden, M. E.; Davis, B. L.; Burrell, A. K. Calcium Amidotrihydroborate: A Hydrogen Storage Material. *Angew. Chem. Int. Ed.* **2007**, *46*, 8995–8997.
- (13) Zhang, Q.; Tang, C.; Fang, C.; Fang, F.; Sun, D.; Ouyang, L.; Zhu, M. Synthesis, crystal structure, and thermal decomposition of strontium amidoborane. *Journal of Physical Chemistry C* **2010**, *114*, 1709–1714.
- (14) Genova, R. V.; Fijalkowski, K. J.; Budzianowski, A.; Grochala, W. Towards Y(NH₂BH₃)₃: Probing hydrogen storage properties of YX₃/MNH₂BH₃ (X = F, Cl; M = Li, Na) and YH_{x-3}/NH₃BH₃ composites. *J. Alloys Compds.* **2010**, *499*, 144–148.

- (15) Salupo, T. A. Preparation of Ytterbium and Europium Borides from Yb(II) and Eu(II) Boron Hydride Precursors. Ph.D. thesis, The Ohio State University, 1993.
- (16) Fijalkowski, K. J.; Genova, R. V.; Filinchuk, Y.; Budzianowski, A.; Derzsi, M.; Jaron, T.; Leszczynski, P. J.; Grochala, W. $\text{Na}[\text{Li}(\text{NH}_2\text{BH}_3)_2]$ – the first mixed-cation amidoborane with unusual crystal structure. *Dalton Trans.* **2011**, *40*, 4407–4413.
- (17) Zhang, Y.; Shimoda, K.; Ichikawa, T.; Kojima, Y. Activation of ammonia borane hybridized with alkaline-metal hydrides: A low-temperature and high-purity hydrogen generation material. *J. Phys. Chem. C* **2010**, *114*, 14662–14664.
- (18) Li, W.; Miao, L.; Scheicher, R. H.; Xiong, Z.; Wu, G.; Araújo, C. M.; Blomqvist, A.; Ahuja, R.; Feng, Y.; Chen, P. Li-Na ternary amidoborane for hydrogen storage: Experimental and first-principles study. *Dalton Trans.* **2012**, *41*, 4754–4764.
- (19) Kang, X.; Luo, J.; Zhang, Q.; Wang, P. Combined formation and decomposition of dual-metal amidoborane $\text{NaMg}(\text{NH}_2\text{BH}_3)_3$ for high-performance hydrogen storage. *Dalton Trans.* **2011**, *40*, 3799–3801.
- (20) Biliškov, N.; Borgschulte, A.; Užarević, K.; Halasz, I.; Lukin, S.; Milošević, S.; Milanović, I.; Grbović Novaković, J. In-Situ and Real-time Monitoring of Mechanochemical Preparation of $\text{Li}_2\text{Mg}(\text{NH}_2\text{BH}_3)_4$ and $\text{Na}_2\text{Mg}(\text{NH}_2\text{BH}_3)_4$ and Their Thermal Dehydrogenation. *Chem. Eur. J.* **2017**, *23*, 16274–16282.
- (21) Wu, H.; Zhou, W.; Pinkerton, F. E.; Meyer, M. S.; Yao, Q.; Gadipelli, S.; Udovic, T. J.; Yildirim, T.; Rush, J. J. Sodium magnesium amidoborane: the first mixed-metal amidoborane. *Chem. Commun.* **2011**, *47*, 4102–4104.
- (22) Chua, Y. S.; Li, W.; Wu, G.; Xiong, Z.; Chen, P. From Exothermic to Endothermic Dehydrogenation – Interaction of Monoammoniate of Magnesium Amidoborane and Metal Hydrides. *Chem. Mater.* **2012**, *24*, 3574–3581.

- (23) Xia, G.; Tan, Y.; Chen, X.; Guo, Z.; Liu, H.; Yu, X. Mixed-metal (Li, Al) amidoborane: synthesis and enhanced hydrogen storage properties. *J. Mater. Chem. A* **2013**, *1*, 1810–1820.
- (24) Dovgaliuk, I.; Jepsen, L. H.; Safin, D. A.; Łodziana, Z.; Dyadkin, V.; Jensen, T. R.; Devillers, M.; Filinchuk, Y. A Composite of Complex and Chemical Hydrides Yields the First Al-Based Amidoborane with Improved Hydrogen Storage Properties. *Chem. Eur. J.* **2015**, *21*, 14562–14570.
- (25) Nakagawa, Y.; Shinzato, K.; Nakagawa, T.; Nakajima, K.; Isobe, S.; Goshome, K.; Miyaoka, H.; Ichikawa, T. Synthesis, structural characterization, and hydrogen desorption properties of Na[Al(NH₂BH₃)₄]. *Int. J. Hydrogen En.* **2017**, *42*, 6173–6180.
- (26) Møller, K. T.; Jørgensen, M.; Andreasen, J. G.; Skibsted, J.; Łodziana, Z.; Filinchuk, Y.; Jensen, T. R. Synthesis and thermal decomposition of potassium tetraamidoboranealuminate, K[Al(NH₂BH₃)₄]. *Int. J. Hydrogen En.* **2018**, *43*, 311–321.
- (27) Luo, J.; Kang, X.; Wang, P. Synthesis, formation mechanism, and dehydrogenation properties of the long-sought Mg(NH₂BH₃)₂ compound. *Energy Environ. Sci.* **2013**, *6*, 1018–1025.
- (28) Wu, H.; Zhou, W.; Yildirim, T. Alkali and Alkaline-Earth Metal Amidoboranes: Structure, Crystal Chemistry, and Hydrogen Storage Properties. *J. Am. Chem. Soc.* **2008**, *130*, 14834–14839.
- (29) Filinchuk, Y.; Chernyshov, D.; Dmitriev, V. Light metal borohydrides: crystal structures and beyond. *Z. Kristallogr.* **2008**, *223*, 649–659.
- (30) Wu, C.; Wu, G.; Xiong, Z.; Han, X.; Chu, H.; He, T.; Chen, P. LiNH₂BH₃·NH₃BH₃: Structure and Hydrogen Storage Properties. *Chemistry of Materials* **2010**, *22*, 3–5.

- (31) Milanović, I.; Biliškov, N. Mechanochemical pretreatment of ammonia borane: A new procedure for sodium amidoborane synthesis. *Int. J. Hydrogen En.* **2020**, *45*, 7938–7946.
- (32) Liu, Z. K.; Ågren, J.; Hillert, M. Application of the Le Chatelier principle on gas reactions. *Fluid Phase Equilib.* **1996**, *121*, 167–177.
- (33) Dematteis, E. M.; Baricco, M. Hydrogen Desorption in $\text{Mg}(\text{BH}_4)_2 - \text{Ca}(\text{BH}_4)_2$ System. *Energies* **2019**, *12*, 3230–43.
- (34) Dematteis, E. M.; Santoru, A.; Poletti, M. G.; Pistidda, C.; Klassen, T.; Dornheim, M.; Baricco, M. Phase stability and hydrogen desorption in a quinary equimolar mixture of light-metals borohydrides. *Int. J. Hydrogen En.* **2018**, *43*, 16793–16803.
- (35) Orimo, S.; Nakamori, Y.; Kitahara, G.; Miwa, K.; Ohba, N.; Towata, S.; Züttel, A. Dehydriding and rehydriding reactions of LiBH_4 . *J. Alloys Compds.* **2005**, *404-406*, 427–430.
- (36) Milanese, C.; Garroni, S.; Girella, A.; Mulas, G.; Berbenni, V.; Bruni, G.; Suriñach, S.; Baró, M. D.; Marini, A. Thermodynamic and kinetic investigations on pure and doped $\text{NaBH}_4 - \text{MgH}_2$ system. *J. Phys. Chem. C* **2011**, *115*, 3151–3162.
- (37) Mao, J.; Guo, Z.; Poh, C. K.; Ranjbar, A.; Guo, Y.; Yu, X.; Liu, H. Study on the dehydrogenation kinetics and thermodynamics of $\text{Ca}(\text{BH}_4)_2$. *J. Alloys Compds.* **2010**, *500*, 200–205.
- (38) Kim, D. Y.; Lee, H. M.; Seo, J.; Shin, S. K.; Kim, K. S. Rules and trends of metal cation driven hydride-transfer mechanisms in metal amidoboranes. *Phys. Chem. Chem. Phys.* **2010**, *12*, 5446–5453.
- (39) COST Action CA18112: Mechanochemistry for Sustainable Industry; <http://www.mechsustind.eu/>.

- (40) Baláž, M.; Vella-Zarb, L.; Hernández, J. G.; Halasz, I.; Crawford, D. E.; Krupička, M.; André, V.; Niidu, A.; García, F.; Maini, L.; Colacino, E. Mechanochemistry: a disruptive innovation for the industry of the future. *Chim. Oggi* **2019**, *37*, 32–34.
- (41) Hernández, J. G.; Halasz, I.; Crawford, D. E.; Krupička, M.; Baláž, M.; André, V.; Vella-Zarb, L.; Niidu, A.; García, F.; Maini, L.; Colacino, E. European Research in Focus: Mechanochemistry for Sustainable Industry (COST Action MechSustInd). *Eur. J. Org. Chem.* **2020**, 8–9.

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