

Prediction of thermodynamically reversible hydrogen storage reactions utilizing Ca–M(M = Li, Na, K)–B–H systems: a first-principles study

Yajuan Guo · Ying Ren · Haishun Wu · Jianfeng Jia

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Abstract Calcium borohydride is a potential candidate for onboard hydrogen storage because it has a high gravimetric capacity (11.5 wt.%) and a high volumetric hydrogen content ($\sim 130 \text{ kg m}^{-3}$). Unfortunately, calcium borohydride suffers from the drawback of having very strongly bound hydrogen. In this study, $\text{Ca}(\text{BH}_4)_2$ was predicted to form a destabilized system when it was mixed with LiBH_4 , NaBH_4 , or KBH_4 . The release of hydrogen from $\text{Ca}(\text{BH}_4)_2$ was predicted to proceed via two competing reaction pathways (leading to CaB_6 and CaH_2 or $\text{CaB}_{12}\text{H}_{12}$ and CaH_2) that were found to have almost equal free energies. Using a set of recently developed theoretical methods derived from first principles, we predicted five new hydrogen storage reactions that are among the most attractive of those presently known. These combine high gravimetric densities ($>6.0 \text{ wt.}\% \text{ H}_2$) with low enthalpies [approximately $35 \text{ kJ}/(\text{mol}^{-1} \text{ H}_2)$] and are thermodynamically reversible at low pressure within the target window for onboard storage that is actively being considered for hydrogen storage applications. Thus, the first-principles theoretical design of new materials for energy storage in future research appears to be possible.

Keywords First-principles · $\text{Ca}(\text{BH}_4)_2$ · Thermodynamic · Reversible hydrogen storage reaction

Introduction

Complex borohydrides containing alkali or alkaline earth metal atoms offer high gravimetric and volumetric hydrogen

densities, which are among the key requirements set by the DOE (the US Department of Energy) for onboard vehicular applications [1]. Therefore, alkali and alkaline earth metal tetrahydroborate materials are an important focus of current research into hydrogen storage [2, 3]. Unfortunately, there is no known material that satisfies all of the criteria that define an excellent hydrogen storage material, such as an acceptable H_2 release temperature, fast release of H_2 from the storage material, reversibility, cyclability, and low cost. Among all of the conditions that a candidate hydrogen storage material should satisfy, one of the most difficult to achieve is reversible hydrogen storage at an appropriate temperature [4]. A hydrogen storage candidate should be able to reversibly store and release H_2 at 323–423 K at a pressure of 1–100 bars [5–9].

Recently, Wang and coworkers [10] characterized hydrogen storage reactions of $\text{Ca}(\text{BH}_4)_2$ using experimental and theoretical methods. Their experimental study showed that Ca dehydrogenation produces amorphous $\text{CaB}_{12}\text{H}_{12}$ as an intermediate. Later, Johnson et al. [11] performed first-principles molecular dynamics calculations which indicated that the cations of $\text{CaB}_{12}\text{H}_{12}$ are highly mobile near room temperature, and they experimentally observed an amorphous XRD pattern near room temperature. More recently, Ozolins et al. [12] predicted the crystal structure of $\text{CaB}_{12}\text{H}_{12}$ using first-principles density functional theory (DFT)-based methods, and combined the predicted thermodynamics of $\text{CaB}_{12}\text{H}_{12}$ with a linear programming approach to determine thermodynamically favored reaction pathways and predict H_2 storage reactions. In particular, Minella et al. [13] provided clear experimental evidence that $\text{CaB}_{12}\text{H}_{12}$ is among the decomposition products of a $\text{Ca}(\text{BH}_4)_2 + \text{MgH}_2$ composite.

It is commonly assumed that the decomposition products of the reactions of destabilized borohydrides are binary metal borides and/or hydrides [14]. Based on these assumptions, several of the newly predicted reactions are calculated to have thermodynamic properties that approach the desired window

Y. Guo · Y. Ren · H. Wu (✉) · J. Jia
School of Chemistry and Materials Science,
Shanxi Normal University, Linfen 041004, China
e-mail: gjcom5555@163.com

H. Wu
e-mail: jjf_sxnu@163.com

for reversible onboard storage. In the work reported in the present paper, we utilized DFT to determine thermodynamically favored reaction pathways and predict new H₂ storage reactions. Five previously unsuspected reactions that include the predicted phases X_nB₁₂H₁₂ and CaB₆ as reaction products were predicted in our work. These reactions were found to have some of the most attractive thermodynamic properties and storage densities of all currently known solid-state hydrogen storage systems.

Computation methods

All structural calculations were carried out using DFT as implemented in the CASTEP [15] simulation package. The Kohn–Sham orbitals of the valence electrons were expressed in a plane-wave basis set, and atomic pseudopotentials were used to represent the core electrons of each atom. The PBE functional for exchange and correlation [16] was employed in all calculations. Structural optimizations were performed by minimizing the forces on and displacement of each atom until they were all lower than 0.03 eV/Å and 0.001 Å, respectively. The cell stress was simultaneously optimized until it differed from the target cell stress by less than 0.05 GPa. These structural calculations used norm-conserving pseudopotentials [17]. All of the calculations employed a Fourier grid with a plane-wave kinetic energy cutoff of 500 eV for all atoms, together with a fine mesh of K points and an energy convergence of better than 0.01 meV per atom. Geometry optimizations were carried out using the BFGS routine. Full geometry optimization was performed for all of the investigated structures, and both the internal atomic coordinates and lattice parameters were relaxed [18]. In addition, phonon calculations were performed using CASTEP, which is a computer code for performing electronic structure calculations utilizing DFT theory [19].

The vibration energy of each compound involved in the reaction at zero temperature is not negligible. The enthalpy (H) at $T=0$ K was calculated from the following equations:

$$H = E_{\text{ele}} + E_{\text{zpe}} \quad (1)$$

$$E_{\text{zpe}} = \frac{1}{2} \int h\omega g(\omega) d\omega, \quad (2)$$

where E_{ele} denotes the total energy of all electrons; $g(\omega)$ is the phonon density of states, and E_{zpe} denotes the zero-point energy. The enthalpy (H_{vib}) and entropy (S_{vib}) were obtained from the following equations:

$$H_{\text{vib}}(T) = \int_0^\infty d\omega g(\omega) \left\{ \frac{1}{2} h\omega + h\omega \left[\exp\left(\frac{h\omega}{k_{\text{B}}T}\right) - 1 \right]^{-1} \right\} \quad (3)$$

$$S_{\text{vib}}(T) = k_{\text{B}} \int_0^\infty d\omega g(\omega) \left\{ \frac{1}{k_{\text{B}}T} h\omega \left[\exp\left(\frac{h\omega}{k_{\text{B}}T}\right) - 1 \right]^{-1} - \ln \left[1 - e^{-\frac{h\omega}{k_{\text{B}}T}} \right] \right\}, \quad (4)$$

where k_{B} is the Boltzmann factor, $g(\omega)$ is the phonon density of states, and T is the absolute temperature. For solids, within the harmonic approximation, the reaction enthalpy $H(T)$ and the free energy $G(T)$ of a phase can be obtained using Eqs. 5 and 6 below. For linear (nonlinear) gas molecules, an additional term of $7k_{\text{B}}T/2$ ($4k_{\text{B}}T$) is added to Eq. 5 to account for translational, rotational, and PV degrees of freedom [18].

$$H(T) = E_{\text{ele}}(T) + H_{\text{vib}}[T] \quad (5)$$

$$G(T) = H(T) - TS(T). \quad (6)$$

Temperature barely influences E_{ele} , so we can use $E_{\text{ele}}(T) = E_{\text{ele}}(0 \text{ K})$. S represents either the standard tabulated entropy of a given molecular species in the gas phase at $P=1$ bar [$S_0^{T=300\text{K}} = 130.858(\text{H}_2)$] or the vibrational entropy S_{vib} of a solid-state phase [18]. The reaction enthalpy $\Delta_{\text{R}}H$ at T K can therefore be calculated as follows:

$$\Delta H_{\text{R}}(T) = \sum_p H_p(T) - \sum_r H_r(T), \quad (7)$$

where p denotes a reaction product and r a reactant.

Results and discussion

Structural optimization

Each crystalline structure of a Ca–M (M = Li, Na, K)–B–H system was fully optimized starting from the corresponding experimental structure [3, 4, 19], theoretical computational data [12], and data from the Inorganic Crystal Structure Database (ICSD). All crystal structures were relaxed in the space group, and atomic positions, while the experimental space group and Wyckoff positions were retained.

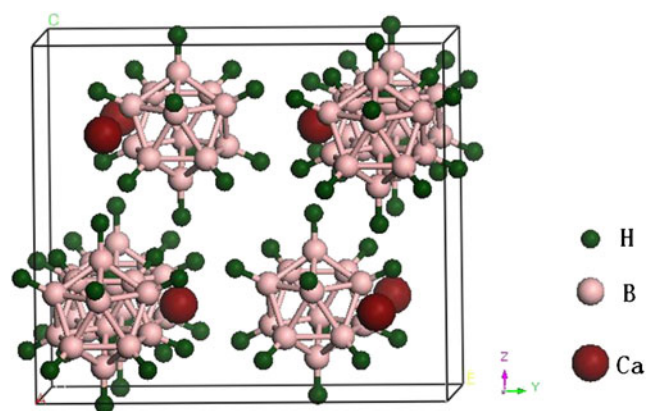
The volume variation due to the optimization process of sodium borohydride (cubic, experimental space group Fm $\bar{3}$ m, computed F43m, Table 1) was small (0.24 %). The optimized unit cell volume of potassium borohydride (same symmetry as sodium, Table 1) was almost the same as the experimental one (it was overestimated by 0.05 %) [20]. Figure 1 shows the optimized crystal structure of CaB₁₂H₁₂, which has monoclinic symmetry and the space group C2/c (no. 15). The optimized structure was found to be in excellent agreement with other calculated data [12]. The cell parameters $a = 7.04 \text{ \AA}$, $b = 12.64 \text{ \AA}$, $c = 11.03 \text{ \AA}$, and $\beta = 90.35$ were only slightly underestimated (errors of ≈ 1 %). CaB₁₂H₁₂ formed a near-trigonal-planar site involving three [B₁₂H₁₂]²⁻ anions, with the six nearest-neighbor H ions at distances ranging from

Table 1 All of the compounds in the Ca–M(M = Li, Na, K)–B–H systems considered in this work

Compound	Space group	ZPE	$E^{T=0K}$	$H_{\text{vib}}^{T=300K}$	$S_{\text{vib}}^{T=300K}$
H ₂		18.1	−31.6	19.6	0
Mg	P63/mmc (194)	16.1	−24.7	29.9	63.7
B	$R\bar{3}m$ (166)	18.9	−77.6	20.4	2.7
LiH	$Fm\bar{3}m$ (225)	17.3	−23.8	20.3	15.7
NaH	$Fm\bar{3}m$ (225)	28.4	−1171.6	35.2	51.8
KH	$Fm\bar{3}m$ (225)	26.6	−799.4	43.7	78.1
CaH ₂	Pnma (62)	32.8	−1036.5	6.2	8.23
MgH ₂	P4 ₂ /mmn (136)	48.8	−56.6	53.5	33.8
CaB ₆	$Pm\bar{3}m$ (221)	115.9	−1471.2	130.7	57.9
LiBH ₄	Pnma (62)	83.4	−150.2	92.6	61
NaBH ₄	$Fm\bar{3}m$ (225)	83.8	−1297.7	89.3	49.8
KBH ₄	$Fm\bar{3}m$ (225)	80.5	−925.4	86.7	57.0
Ca(BH ₄) ₂	F2dd (43)	159.9	−1288.5	169.2	77.6
Li ₂ B ₁₂ H ₁₂	C2/m (12)	162.4	−1141.1	80.5	72.6
K ₂ B ₁₂ H ₁₂	$Fm\bar{3}$ (202)	326.1	−2693.5	340.4	175.2
CaB ₁₂ H ₁₂	C2/c (15)	340.1	−2131.0	353.9	85.1

ZPE refers to the zero-point energy, given by $H_{\text{vib}}(T=0\text{ K})$ (Eq. 3); S_{vib} is the vibrational entropy (Eq. 4). Units are kJ mol^{−1} for ZPE and $H_{\text{vib}}^{T=300K}$, and J mol^{−1} K^{−1} for $S_{\text{vib}}^{T=300K}$.

2.38 to 2.46 Å. This arrangement seemed to optimally satisfy the need for a small ionic radius of Ca²⁺ and short bond lengths to the H atoms of [B₁₂H₁₂]^{2−}. The calculated B–H distances were 1.19–1.21 Å. This means that the experimentally observed bond lengths (1.10–1.20 Å) [21] are considerably shorter than the calculated values. This discrepancy may be due to difficulty in experimentally identifying the positions of the hydrogen atoms. The calculated values for the intricosahedron B–B bond lengths were 1.74–1.77 Å for CaB₁₂H₁₂, which are comparable to the experimentally observed lengths for α -rhombohedral boron (α -B), 1.751–1.806 Å [22]. Since boron crystals have the icosahedral B₁₂ cluster as a common structural component, the decomposition

**Fig. 1** Crystal structure of CaB₁₂H₁₂ (shown in color online)

of a [B₁₂H₁₂]^{2−} anion into a B₁₂ cluster and hydrogen molecule is easy to understand [23].

Reaction thermodynamics: enthalpies and entropies

Table 1 lists thermodynamic data for various reactions of the Ca–B–H system, including energies calculated for $T=0\text{ K}$, vibrational zero-point energies (ZPEs), and vibrational energies and entropies calculated for $T=300\text{ K}$. Utilizing first-principles thermodynamics of the phases of the crystal CaB₁₂H₁₂ and the other known boron hydrides, borides, hydrides, and metals, the DFT linear programming approach [24] was employed to identify all of the thermodynamically favored reactions in Tables 2, 3, and 4.

It should be noted that several of the reactions in Tables 2, 3, and 4 have enthalpies within the window of 20–45 kJ/(mol^{−1} H₂), which is the usual target for reversible onboard storage [12]. Surprisingly, reactions (2), (3), (10)–(16), (18*)–(21*), (23), and (24) seem to show “good” enthalpies for hydrogen release. When a complex hydride is being heated, the entropy plays an important role and should therefore be taken into account too [18]. Indeed, the target enthalpy range 20–45 kJ/(mol^{−1} H₂) was derived from the famous van’t Hoff equation, which relates the pressure to the temperature of hydrogen release via $\ln(p) = (-\Delta H/(RT)) + (\Delta S/R)$, where ΔH and ΔS are the enthalpy and entropy of the dehydrogenation reaction, respectively [11, 16]. It can be seen that there is a linear relationship between $\ln(p)$ and $1/T$, meaning that plotting these quantities against each other would allow the reaction enthalpy to be obtained from the slope and the reaction entropy from the intercept. At the decomposition temperature and at constant pressure, the Gibbs reaction energy is zero, so the temperature of dehydrogenation can be estimated using $T_{\text{dec}} = \Delta H/\Delta S$ [18]. Figure 2 shows these relations (so-called van’t Hoff diagrams) for reactions (10)–(24) from Tables 2, 3, and 4.

Table 2 shows that decomposition paths (1)–(3) are possible for Ca(BH₄)₂, as reported in earlier papers [19, 25, 26]. Similar to Minella et al. [12], we found that not only CaH₂ and H₂ but also B, CaB₆, and CaB₁₂H₁₂ are the products of reactions (1)–(3). At 300 K and an H₂ pressure of 1 bar, the enthalpies of reactions (1)–(3) are 58.7, 41.9, and 38.4 kJ/mol^{−1} H₂, which are in agreement with the previously reported values of 57.3, 37.0, and 39.2 kJ/mol^{−1} H₂ for these enthalpies [19, 25, 26]. It can be seen that reactions (2) and (3) in Table 2 have similar thermodynamics, in that they are two competing decomposition pathways involving Ca(BH₄)₂. The calculated hydrogen-release temperature for the one-step process of reaction (2) is 364 K, whereas the reaction temperatures for two-step processes involving an intermediate CaB₁₂H₁₂ phase via reactions (3) and (4) are 367 and 579 K, respectively. Moreover, the enthalpies of the two reactions (3) and (4)—i.e., Ca(BH₄)₂ → (5/6) CaH₂ + (1/6) CaB₁₂H₁₂ + (13/6) H₂ and

Table 2 Predicted sequence of thermodynamically favored decomposition reactions for the Ca–B–H system

Reaction	wt. % H ₂	$\Delta H^{T=300K}$	$\Delta S^{T=300K}$	T_c (K)
Known decomposition of Ca(BH ₄) ₂				
(1) Ca(BH ₄) ₂ → CaH ₂ + 2B + 3H ₂	8.6	58.7	109.5	536
(2) Ca(BH ₄) ₂ → (2/3)CaH ₂ + (1/3)CaB ₆ + (10/3)H ₂	9.6	41.9	115.0	364
(3) Ca(BH ₄) ₂ → (5/6)CaH ₂ + (1/6)CaB ₁₂ H ₁₂ + (13/6)H ₂	6.3	38.4	104.8	367
Known destabilization of CaB ₁₂ H ₁₂				
(4) CaB ₁₂ H ₁₂ → CaB ₆ + 6B + 6H ₂	6.7	74.6	129.0	579
(5) CaB ₁₂ H ₁₂ + CaH ₂ → 2CaB ₆ + 7H ₂	6.3	48.3	134.1	360
(6) CaB ₁₂ H ₁₂ + 3MgH ₂ → CaB ₆ + 3MgB ₂ + 9H ₂	7.0	55.0	129.7	424
Known destabilization of Ca(BH ₄) ₂ in the presence of MgH ₂				
(7) Ca(BH ₄) ₂ + MgH ₂ → CaH ₂ + MgB ₂ + 4H ₂	8.4	48.0	114.9	417
(8) Ca(BH ₄) ₂ + MgH ₂ → (2/3)CaH ₂ + (1/3)CaB ₆ + Mg + (13/3)H ₂	9.1	45.9	133.1	345
(9) Ca(BH ₄) ₂ + MgH ₂ → CaH ₂ + 2B + Mg + 4H ₂	8.3	58.9	130.4	452

Enthalpies and entropies are given in kJ/(mol⁻¹ H₂) and J/(K mol⁻¹ H₂). ΔH is the calculated enthalpy at $T=300$ K, including vibration energy. T_c is the calculated temperature for hydrogen release at a hydrogen pressure $p=1$ bar

CaB₁₂H₁₂ → CaB₆ + 6B + 6H₂, respectively—are 38.4 and 74.6 kJ/mol⁻¹ H₂ at 300 K. This suggests that all of the hydrogen may be extracted in one step, or at least in two steps with very similar thermodynamics. Calcium borohydride is predicted to have a very promising thermodynamic temperature of H₂ release that is just below 373 K, though further destabilization of this compound would be beneficial [12, 27].

According to the destabilization ideas of Reilly and Wiswall [28], the hydrogen release temperatures of X_nB₁₂H₁₂ systems can be lowered significantly by forming a strongly bound boride product phase; see reactions (5) and (6) in Table 2. In particular, CaB₁₂H₁₂ can be efficiently destabilized by adding CaH₂ in a molar ratio of 1:1, and the resulting decomposition reaction (5) releases hydrogen at 360 K, which is a dramatic decrease from almost 573 K [12], the decomposition temperature of pure CaB₁₂H₁₂. Likewise, another destabilization pathway for CaB₁₂H₁₂ involves the formation of the compound MgB₂ according to reaction (6). Reaction (6) is

predicted to occur at 424 K, which is again a dramatic decrease from almost 573 K, the decomposition temperature of pure CaB₁₂H₁₂. These results are in agreement with those reported by Ozolins et al. [12].

Barkhordarian et al. [29] and Vajo et al. [30] reported that a metal hydride (metal = Li, Na, Ca) reacts with MgB₂ instead of boron during the synthesis of tetrahydroborates [e.g., Ca(BH₄)₂, NaBH₄, and LiBH₄]. The kinetic barrier is drastically reduced and full transformation can be achieved during the abovementioned process. The enhanced kinetics are linked to the peculiar layered structure of MgB₂ [31, 32]. However, upon desorbing Ca(BH₄)₂ + MgH₂, MgB₂ is not necessarily formed [32, 33]. Moreover, CaH₂, Mg, and CaB₆ were reported to be the decomposition products in [32, 34], where a (re)absorption reaction performed at 90 bar H₂ and 623 K for 24 h led to the formation of Ca(BH₄)₂ + MgH₂ (yield of 60 %), thus demonstrating the important role of CaB₆ in reversibility. A standard enthalpy value of 27.5 kJ/mol H₂

Table 3 Predicted new destabilization reactions involving Ca(BH₄)₂/X(BH₄)_n ($n=1, 2$; X = Li, Na, K)

Reaction	wt. % H ₂	$\Delta H^{T=300K}$	$\Delta S^{T=300K}$	T_c (K)
New destabilized reactions involving Ca(BH ₄) ₂ /X(BH ₄) _n ($n=1, 2$; X = Li, Na, K)				
(10) Ca(BH ₄) ₂ + (2/5)LiBH ₄ → (1/5)Li ₂ B ₁₂ H ₁₂ + CaH ₂ + (13/5)H ₂	6.7	35.3	100.2	351
(11*) Ca(BH ₄) ₂ + 10LiBH ₄ → CaB ₁₂ H ₁₂ + 10LiH + 13H ₂	9.0	43.9	96.4	455
(12*) Ca(BH ₄) ₂ + 4LiBH ₄ → 4LiH + CaB ₆ + 10H ₂	12.8	44.7	110.7	404
(13) Ca(BH ₄) ₂ + 10NaBH ₄ → CaB ₁₂ H ₁₂ + 10NaH + 13H ₂	6.0	32.6	97.1	332
(14) Ca(BH ₄) ₂ + 4NaBH ₄ → 4NaH + CaB ₆ + 10H ₂	9.0	38.7	110.9	349
(15) Ca(BH ₄) ₂ + (2/5)KBH ₄ → (1/5)K ₂ B ₁₂ H ₁₂ + CaH ₂ + (13/5)H ₂	5.8	36.2	107.3	337
(16) Ca(BH ₄) ₂ + 10KBH ₄ → CaB ₁₂ H ₁₂ + 10KH + 13H ₂	4.3	42.3	127.3	331
(17*) Ca(BH ₄) ₂ + 4KBH ₄ → 4KH + CaB ₆ + 10H ₂	7.0	47.9	126.8	378

For each reaction, we list the amount of H₂ released (wt.% H₂), the calculated reaction enthalpy ΔH (kJ/mol⁻¹ H₂), and the calculated reaction entropy ΔS (J/mol⁻¹ K) at 300 K. T_c is the calculated temperature for hydrogen release at a hydrogen pressure of $p=1$ bar

Table 4 Predicted thermodynamically reversible hydrogen-release reactions for Ca–(Li, Na)–B–H systems

Reaction	wt % H ₂	$\Delta H^{T=300\text{K}}$	$\Delta S^{T=300\text{K}}$	T_c (K)
New destabilized reactions involving Ca(BH ₄) ₂ and LiBH ₄ , NaBH ₄				
(18*) Ca(BH ₄) ₂ + 2LiBH ₄ + 2NaBH ₄ → 2LiH + 2NaH + CaB ₆ + 10H ₂	10.5	46.5	120.0	387
(19) Ca(BH ₄) ₂ + (2/5)LiBH ₄ + (2/5)NaBH ₄ → (1/5)Li ₂ B ₁₂ H ₁₂ + CaH ₂ + (2/5)NaH + (2/5)B + (16/5)H ₂	6.8	37.8	105.2	359
(20) Ca(BH ₄) ₂ + 4LiBH ₄ + 4NaBH ₄ → (1/3)Li ₂ B ₁₂ H ₁₂ + CaB ₆ + 4NaH + (10/3)LiH + (43/3)H ₂	10.3	38.5	114.6	336
(21*) Ca(BH ₄) ₂ + 10LiBH ₄ + 10NaBH ₄ → 10LiH + 10NaH + CaB ₁₂ H ₁₂ + 10B + 28H ₂	8.4	45.7	116.4	392
(22*) Ca(BH ₄) ₂ + 4LiBH ₄ + 4NaBH ₄ → 4NaH + CaB ₆ + 4LiH + 4B + 16H ₂	10.3	48.5	119.3	407
(23) Ca(BH ₄) ₂ + 10LiBH ₄ + 10NaBH ₄ → (5/6)Li ₂ B ₁₂ H ₁₂ + (25/3)LiH + 10NaH + CaB ₁₂ H ₁₂ + (143/6)H ₂	7.2	36.3	114.2	318
(24) Ca(BH ₄) ₂ + 5LiBH ₄ + 5NaBH ₄ → 5LiH + 5NaH + CaB ₁₂ H ₁₂ + 13H ₂	7.1	42.6	118.1	361

For each reaction, we give the wt.% H₂ released, ΔH at $T=300$ K in kJ/(mol⁻¹ H₂), ΔS at $T=300$ K in J/(K mol⁻¹ H₂), while T_c gives the calculated temperature for hydrogen release at a hydrogen pressure $p=1$ bar

for the reaction involving MgB₂ and CaH₂ as decomposition products [reaction (7)] was estimated by Barkhordarian et al. [32], although temperature and pressure values were not reported. Applying DFT [33], the enthalpy of reaction (7) was found to be 46.9 kJ/mol⁻¹ H₂. In our calculations, reaction (7) has an enthalpy at $T=300$ K of 48.0 kJ/mol⁻¹ H₂, corresponding to a temperature of 422 K at 1 bar H₂. The decomposition reaction leading to CaH₂, CaB₆, and Mg, i.e., reaction (8), has a reaction enthalpy of 45.9 kJ/mol⁻¹ H₂ at 300 K and 1 bar of H₂. This result is in agreement with recent results from Kim et al. [34], who calculated it to be 45 kJ/mol⁻¹ H₂. If B is formed instead of CaB₆ (reaction 9), then the calculated reaction enthalpy is 58.9 kJ/mol⁻¹ H₂, which is in good agreement with another calculated value, 57.9 kJ/mol⁻¹ H₂ [32]. Enthalpy values of 48, 45.9, and 58.9 kJ/mol⁻¹ H₂ were calculated for 300 K and an H₂ pressure of 1 bar. But why do the thermodynamically most favorable decomposition paths involve hydrogen desorption with the formation of MgB₂ and CaB₆? The reason is that these borides form exothermically. More recently, Miella et al. [13] provided, for the first time, clear experimental evidence that CaB₁₂H₁₂ is a product of the decomposition of a Ca(BH₄)₂ + MgH₂ composite. These results imply that, under these experimental conditions, Ca(BH₄)₂ always follows the same two decomposition paths [reactions (2) and (3)] leading to the formation of CaB₆ and CaB₁₂H₁₂.

New reversible hydrogen storage reactions for the Ca–M (M = Li, Na, K)–B–H system

Two classes of reversible hydrogen storage reactions for the Ca–M (M = Li, Na, K)–B–H system are predicted in the present work. First, we predict eight hydrogen storage reactions, (10)–(17*), with X_nB₁₂H₁₂ (X = Li, K, Ca; $n=1, 2$) and CaB₆ phases as products. The reactions (10), (11*), (13), (15), and (16) represent a qualitatively new class of entropically

optimized reactions that use fully hydrogenated high-entropy borohydrides as reactants and result in the formation of low-entropy X_nB₁₂H₁₂ ($n=1, 2$; X = Li, K, Ca) phases as products [12]. However, (12*), (14), and (16) form a CaB₆ phase as a product. It should be noted that reactions (11*), (12*), and (17*) are thermodynamically unreasonable, since the Ca(BH₄)₂ on the left side of each reaction (11*), (12*), and (17*) should decompose first, at ~373 K; see reactions (2) and (3) in Table 3. Reactions (10) and (13)–(16) possess near-ideal thermodynamics, since they pass through the target window for onboard storage in Fig. 2. The first of these, reaction (10), uses a 5:2 molar mixture of Ca and Li borohydrides, leading to the formation of Li₂B₁₂H₁₂ and CaH₂ along with 6.7 wt.% H₂ at 351 K and 1 bar. Reaction (10) was also reported by Ozolins et al. [12], who calculated that the H₂ release temperature of reaction (10) is 356 K. The second reaction, (13), involves a 1:10 molar mixture of Ca and Na borohydrides, leading to the

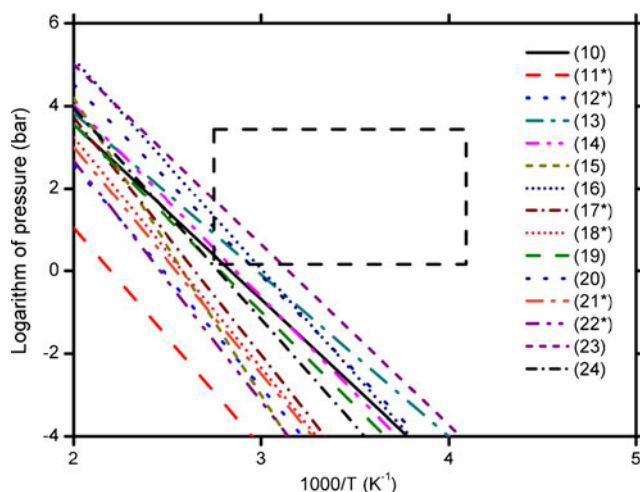


Fig. 2 Calculated van't Hoff plots for reactions (10)–(24) listed in Tables 2, 3, and 4. The region within the rectangular box corresponds to desirable temperatures and pressures for onboard hydrogen storage, $p(\text{H}_2)=1\text{--}700$ bar and $T=233\text{--}355$ K. (Figure shown in color online)

formation of $\text{CaB}_{12}\text{H}_{12}$ and NaH and releasing 6.1 wt.% H_2 at 332 K and 1 bar. The predicted hydrogen storage reaction is in agreement with recent work reported by Caputo et al. [35], who carried out an experiment in which NaBH_4 was heated in vacuo at 443 K for 16 h. They did not witness the formation of $\text{Na}_2\text{B}_{12}\text{H}_{12}$, so they proposed that it is highly improbable that NaBH_4 can form $\text{Na}_2\text{B}_{12}\text{H}_{12}$ via thermal decomposition. In contrast to the above two reactions, reaction (14) uses a ratio of Ca borohydride to Na borohydride of 1:4, and leads to the formation of CaB_6 and NaH and the release of 9.0 wt.% H_2 at 309 K and 1 bar. Recently, reaction (13) was reported by Mao et al. [36], who discussed the use of the additive $\text{Ca}(\text{BH}_4)_2$ to moderate the conditions for dehydrogenation and rehydrogenation of NaBH_4 . In other words, NaBH_4 and $\text{Ca}(\text{BH}_4)_2$ react directly, and the composite system is less stable than the pure NaBH_4 or $\text{Ca}(\text{BH}_4)_2$. However, reactions (15) and (16) have hydrogen storage densities of only 5.8 and 4.3 wt.%, which do not satisfy the guidelines of the US Department of Energy (DOE). Reactions (10), (13), and (14) have low enthalpies [$\sim 35 \text{ kJ}/(\text{mol}^{-1} \text{H}_2)$], which are at the lower limit of the commonly accepted target range 20–45 $\text{kJ}/(\text{mol}^{-1} \text{H}_2)$. They do, however, present excellent thermodynamics due to the low vibrational entropies of the $\text{Li}_2\text{B}_{12}\text{H}_{12}$ and $\text{CaB}_{12}\text{H}_{12}$ product phases. Through the utilization of closely integrated anions, the above demonstrate the previous guideline, to map low-entropy reactions to large product phases. Analysis indicates that linear programming-based reaction prediction based on a theoretical framework is feasible, and that, even in widely researched materials systems, formerly unsuspected reactions occur.

Our work then considered reactant mixtures that are mixtures of $\text{Ca}(\text{BH}_4)_2$, LiBH_4 , and NaBH_4 in different molar ratios, which give slightly different results from those obtained in the previous case. To explore this possibility for achieving a destabilized path to reversible hydrogen storage in the Li–Na–Ca–B–H system, mixtures with equimolar LiBH_4 and NaBH_4 were used to test the thermodynamic approach described above (see Table 4). Similar to the previous case, the results indicated that the reactions (18*), (21*), and (22*) are thermodynamically unreasonable, since the $\text{Ca}(\text{BH}_4)_2$ on the left side of each reaction (18*), (21*), and (22*) should decompose first, at $\sim 373 \text{ K}$. Reactions (19) and (24) do not possess near-ideal thermodynamics, since they do not pass through the target window for onboard storage (see Fig. 2). However, reactions (20) and (23) are candidate reactions for vehicular hydrogen storage. They combine high gravimetric densities (10.3 and 7.2 wt.% H_2) with low enthalpies [approximately 35 $\text{kJ}/(\text{mol}^{-1} \text{H}_2)$], and are thermodynamically reversible at low pressures. Taking reaction (20) as an example, the initial mixture contains LiBH_4 , KBH_4 , and $\text{Ca}(\text{BH}_4)_2$ in the ratio 4:4:1, and this has a total H_2 capacity of 7.1 wt.%. This mixture can undergo two different reactions: a destabilized reaction involving LiBH_4 , i.e., $4\text{LiBH}_4 \rightarrow (1/3)\text{Li}_2\text{B}_{12}\text{H}_{12} +$

$(10/3)\text{LiH} + (13/3)\text{H}_2$; and a similar reaction that involves NaBH_4 and $\text{Ca}(\text{BH}_4)_2$, i.e., $4\text{NaBH}_4 + \text{Ca}(\text{BH}_4)_2 \rightarrow \text{CaB}_6 + 4\text{NaH} + 10\text{H}_2$. Fortunately, reaction (14) involving NaBH_4 and $\text{Ca}(\text{BH}_4)_2$ yields CaB_6 , and this could be a thermodynamically reversible reaction. Another reaction, (23), involves a reactant mixture of LiBH_4 , NaBH_4 , and $\text{Ca}(\text{BH}_4)_2$ at a molar ratio of 10:10:1 and with a total H_2 capacity of 7.2 wt.%. Two separate reactions are considered in the associated reaction scheme of LiBH_4 , NaBH_4 , and $\text{Ca}(\text{BH}_4)_2$. One is a destabilized reaction involving LiBH_4 , i.e., $10\text{LiBH}_4 \rightarrow (5/6)\text{Li}_2\text{B}_{12}\text{H}_{12} + (25/3)\text{LiH} + (65/6)\text{H}_2$, which has already been reported in [12]. The other reaction involves a mixture of NaBH_4 and $\text{Ca}(\text{BH}_4)_2$ [37], i.e., $10\text{NaBH}_4 + \text{Ca}(\text{BH}_4)_2 \rightarrow \text{CaB}_{12}\text{H}_{12} + 10\text{NaH} + 13\text{H}_2$. We assumed that these two separate reactions may occur at the same time, so they were considered to be single-step reactions. A more detailed scheme should be elucidated in future experiments.

The practical usefulness of the new reactions will be dictated not only by their thermodynamics but also their rates of hydrogen release (i.e., by their kinetics) [12, 18]. Indeed, the dehydrogenation kinetics of $\text{Ca}(\text{BH}_4)_2$ have already been studied: hydrogen desorption does not occur until very high temperatures, and the material has not been successfully rehydrided [12, 38, 39]. The evaluation performed in this study leads us to conclude that our new theoretical tool for predicting thermodynamic reversibility is useful and valid. However, kinetically limited reactions are rather different from thermodynamically limited ones. The former have been shown to be more comprehensive and advanced for enhanced reactivity via catalysis, while the latter are no longer considered to be promising candidates for use in future solid storage systems [16]. Our thermodynamic calculations identified five reactions—(10), (13), (14), (20), and (23)—with reaction enthalpies that are potentially of interest for practical applications.

Conclusions

We used DFT at the GGA level to predict thermodynamically reversible hydrogen storage reactions for Ca–M (M = Li, Na, K)–B–H systems. We optimized the atomic positions and lattice parameters of all compounds involved in possible dehydrogenation reactions. Our method was able to predict all thermodynamically favorable hydrogen storage reactions for Ca–M (M = Li, Na, K)–B–H systems with having to explicitly enumerate possible reaction pathways, and can be used to optimize storage capacity within a given window of temperatures and pressures. Our analysis indicated that calcium borohydride undergoes two competing decomposition pathways with very similar thermodynamics. Our thermodynamic calculations predicted that 15 reactions involving $\text{Ca}(\text{BH}_4)_2$ combined with LiBH_4 , NaBH_4 , or KBH_4 release

appreciable amounts of H₂ with reaction enthalpies that are potentially of interest for practical applications. An interesting feature of these calculations is that they showed that a very large number of other possible reactant mixtures involving these borohydrides cannot achieve this important goal. Most importantly, we predicted five new and previously unsuspected reactions in which the predicted phases [B₁₂H₁₂]²⁻ and CaB₆ occur as reaction products, and which possess near-ideal thermodynamics, since they pass through the target window for onboard storage (as shown in Fig. 2). The five reactant mixtures involving Ca(BH₄)₂ and other alkali metal borohydrides would be worth examining experimentally.

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