First-principles study of decomposition mechanisms of Mg(BH4)2$2$NH3 and LiMg(BH4)3$2$NH3

Xiaowei Chen
Fudan University, Jimei University

Renquan Li
Jimei University

Guanglin Xia
University of Wollongong, guanglin@uow.edu.au

Hongsheng He
Jimei University

Xiuqing Zhang
Jimei University

See next page for additional authors

Publication Details
Chen, X., Li, R., Xia, G., He, H., Zhang, X., Zou, W. & Yu, X. (2017). First-principles study of decomposition mechanisms of Mg(BH4)2$2$NH3 and LiMg(BH4)3$2$NH3. RSC Advances: an international journal to further the chemical sciences, 7 (49), 31027-31032.
First-principles study of decomposition mechanisms of Mg(BH4)2$2NH3 and LiMg(BH4)3$2NH3

Abstract
The decomposition mechanisms of Mg(BH4)2$2NH3 and LiMg(BH4)3$2NH3 were studied by using density functional theory calculations. Compared to that of Mg(BH4)2$2NH3, the incorporation of LiBH4 with the formation of LiMg(BH4)3$2NH3 slightly increased Bader charges of B atoms, meanwhile it decreased Bader charges of N atoms. Mg(BH4)2$2NH3 shows a low ammonia vacancy diffusion barrier, but relatively high ammonia vacancy formation energy, which lead to a low concentration of NH3 vacancies and limit NH3 transportation. In contrast to that of Mg(BH4)2$2NH3, LiMg(BH4)3$2NH3 has a relatively high ammonia vacancy formation energy and diffusion barrier, which suppresses ammonia release. The incorporation of LiBH4 and Mg(BH4)2$2NH3 does not decrease but increases the hydrogen formation barrier of LiMg(BH4)3$2NH3, resulting in a slight increase in the dehydrogenation peak temperature, consistent with experimental results.

Keywords
mg(bh4)2$2nh3, limg(bh4)3$2nh3, first-principles, study, decomposition, mechanisms

Disciplines
Engineering | Physical Sciences and Mathematics

Publication Details
Chen, X., Li, R., Xia, G., He, H., Zhang, X., Zou, W. & Yu, X. (2017). First-principles study of decomposition mechanisms of Mg(BH4)2$2NH3 and LiMg(BH4)3$2NH3. RSC Advances: an international journal to further the chemical sciences, 7 (49), 31027-31032.

Authors
Xiaowei Chen, Renquan Li, Guanglin Xia, Hongsheng He, Xiuqing Zhang, Weidong Zou, and Xubin Yu

This journal article is available at Research Online: http://ro.uow.edu.au/aiimpapers/2633
First-principles study of decomposition mechanisms of Mg(BH$_4$)$_2$·2NH$_3$ and LiMg(BH$_4$)$_3$·2NH$_3$

Xiaowei Chen,$^{a,b}$ Renquan Li,$^a$ Guanglin Xia,$^c$ Hongsheng He,$^a$ Xiuqing Zhang,$^a$ Weidong Zou$^a$* and Xubin Yu$^b$

The decomposition mechanisms of Mg(BH$_4$)$_2$·2NH$_3$ and LiMg(BH$_4$)$_3$·2NH$_3$ were studied by using density functional theory calculations. Compared to that of Mg(BH$_4$)$_2$·2NH$_3$, the incorporation of LiBH$_4$ with the formation of LiMg(BH$_4$)$_3$·2NH$_3$ slightly increased Bader charges of B atoms, meanwhile it decreased Bader charges of N atoms. Mg(BH$_4$)$_2$·2NH$_3$ shows a low ammonia vacancy diffusion barrier, but relatively high ammonia vacancy formation energy, which lead to a low concentration of NH$_3$ vacancies and limit NH$_3$ transportation. In contrast to that of Mg(BH$_4$)$_2$·2NH$_3$, LiMg(BH$_4$)$_3$·2NH$_3$ has a relatively high ammonia vacancy formation energy and diffusion barrier, which suppresses ammonia release. The incorporation of LiBH$_4$ and Mg(BH$_4$)$_2$·2NH$_3$ does not decrease but increases the hydrogen formation barrier of LiMg(BH$_4$)$_3$·2NH$_3$ resulting in a slight increase in the dehydrogenation peak temperature, consistent with experimental results.

Introduction

Recently, many efforts have been devoted to B–N based chemical hydrides as potential hydrogen storage materials because of their high theoretical hydrogen capacity. For instance, ammonia borane (AB), with a high H-capacity of 19.6 wt%, is a typical B–N based hydride for chemical hydrogen storage. However, upon decomposition of AB, accompanied volatile compounds of ammonia, diborane, and borazine are evolved, which lead to a reduction of dehydrogenation capacity and are fatal for fuel cell applications. Many different approaches have been adopted to facilitate hydrogen release from AB during the last decade. Recent studies show that the substitution of H atoms in the NH$_3$ unit of AB by alkali metals with the formation of single or double metal amidoborane (MAB) is an effective way to improve the dehydrogenation properties of AB in terms of the reduced H$_2$ release temperatures, accelerated H$_2$ release kinetics, and minimized borazine evolved. Ammine metal borohydrides (AMBs), which show favourable hydrogen storage properties competitive with ammonia borane, have been developed recently as promising materials for hydrogen storage. However, many of these composites suffer from the release of undesirable gas of ammonia during dehydrogenation. Further experimental results show that the purity of gas released and dehydrogenation temperature of AMBs can be improved by using double-cation substitutions approach and tuning BH$_4$/NH$_3$ ration. The experimental and theoretic studies indicate that ammonia is weakly bound to the metal cations with low electronegativity (<1.2) in AMBs, therefore tend to release ammonia at low temperature. Although these studies have provided valuable insight for understanding the decomposition processes of single metal cation AMBs, the results may not be applicable to double cations AMBs. For instance, Mg(BH$_4$)$_2$·2NH$_3$ (with electronegativity of 1.31 for Mg cation) mainly release hydrogen along with a small amount of ammonia. The incorporation of LiBH$_4$ (with low electronegativity of 0.98 for Li cation) and Mg(BH$_4$)$_2$·2NH$_3$ with the formation of double cations ammine borohydride, LiMg(BH$_4$)$_3$·2NH$_3$ results in improving the purity of gas released compared to Mg(BH$_4$)$_2$·2NH$_3$. Further improved dehydrogenation of ammine magnesium borohydride by tuning the NH$_3$/BH$_4$ ratios and combining Mg(BH$_4$)$_2$·2NH$_3$ with MgH$_2$ and NaAlH$_4$ were reported.

The mixed-cation strategy offers a promising route toward tuneable dehydrogenation of ammine metal borohydrides, however, a detail study of the dehydrogenation mechanism is still needed for further improving their dehydrogenation performance. Herein, we presented a comparison study of the electronic structure and dehydrogenation mechanisms of Mg(BH$_4$)$_2$·2NH$_3$ and LiMg(BH$_4$)$_3$·2NH$_3$ by density functional theory (DFT) calculation.
Computational method

Mg(BH₄)₂·2NH₃ crystallizes in the orthorhombic structure with space group of Pcab and lattice parameters of a = 17.4872(4) Å, b = 9.4132(2) Å, c = 8.7304(2) Å.²³ LiMg(BH₄)₂·2NH₃ has a hexagonal structure with space group P6₃ and lattice constants of a = b = 8.0002(1) Å and c = 8.3944 Å.²⁵ The geometric structures were optimized by DFT calculation as implemented in MedeA@VASP code.⁴⁴ To describe the weak van der Waals H···H dihydrogen bonds, the optB86b-vdW functional⁴⁴⁻⁴⁵ was adopted for geometric optimization. Plane waves with kinetic energy cutoff of 500 eV were used. The generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof (PBE) was adapted to treat the exchange and correlation of electrons.⁴⁶ The projector-augmented wave (PAW) approach was used to describe the electron-ion interactions⁴⁶ with 1s2s2p of Li, s2p1 of B, s2p3 of N, s2p⁰ of Mg as the explicit valence electrons. The Brillouin zones were sampled by Monkhorst–Pack k-point meshes⁴⁷ with meshes points spacing less than 0.05 Å for both Mg(BH₄)₂·2NH₃ and LiMg(BH₄)₂·2NH₃. Structural relaxations of atomic positions were carried out until the total energies and residual forces were less than 1.0 × 10⁻⁵ eV and 0.02 eV Å⁻¹, respectively. For the calculation of NH₃ vacancy formation energies and H₂ formation energies, 1 × 2 × 2 supercells of Mg(BH₄)₂·2NH₃ and 2 × 2 × 2 supercells of LiMg(BH₄)₂·2NH₃ were used. Our tests showed that the used of 1 × 2 × 2 supercells of Mg(BH₄)₂·2NH₃ and 2 × 2 × 2 supercells of LiMg(BH₄)₂·2NH₃ with k-point mesh spacing less than 0.05 Å yield energies that converged within 0.01 eV (f.u.)⁻¹. The NH₃ diffusion barriers and H₂ formation barriers were estimated by using climbing image nudged elastic band (CI-NEB) method.⁴⁶⁻⁴⁹

The NH₃ vacancy formation energy was estimated using the following equation:

\[
E_c = E_{\text{total}} - E(\text{AMBs-NH}_3) - E(\text{NH}_3)
\]

where \(E_{\text{total}}\) is the total energy of the AMBs supercells; \(E(\text{NH}_3)\) represents the energy of isolate NH₃ molecule; \(E(\text{AMBs-NH}_3)\) is the total energy of the AMBs supercells after NH₃ molecules are removed. The positive energy of \(E_c\) indicates that the creation of NH₃ vacancy is an endothermic process; while the negative energy of \(E_c\) indicates that the creation of NH₃ vacancy is an exothermic process.

The concentration of ammonia vacancy in Mg(BH₄)₂·2NH₃ and LiMg(BH₄)₂·2NH₃ could be estimated by the following equation⁴⁶

\[
c = N_{\text{sites}}N_{\text{config}} \exp(E_c/kT)
\]

where \(E_c\) is the formation energy of NH₃ vacancy; \(N_{\text{sites}}\) represents the number of sites that the defect can be incorporated; \(N_{\text{config}}\) is the number of configurations per site in which the vacancy can be formed; \(k\) and \(T\) represent Boltzmann constant and temperature, respectively.

Results and discussion

Electronic structure

The electron localization function (ELF) and charge transfer between the H, N, B atoms and metal cations (Li and Mg) were analysed to understand the bonding characters of Mg(BH₄)₂·2NH₃ and LiMg(BH₄)₂·2NH₃. The H atoms bond to N atom and B atom are represent as (NH) and (B)H, respectively. As shown in Fig. 1, the calculated ELF shows the covalent bonding of N–H and B–H. Although the Mg–H bonds are mainly ionic, the distorted ELF isosurfaces around (B)H, (N)H and Mg indicate partial covalent bond feature of Mg–H. The low ELF value around Li indicates the essentially ionic bonding character of Li–H. Table 1 shows the Bader charges of (B)H, (N)H, N, B and Mg for Mg(BH₄)₂·2NH₃ are −0.58/−0.64, 0.44, −1.30, 1.59 and 1.65, respectively. The Bader charge of Li is 0.90 for LiMg(BH₄)₂·2NH₃, indicating a strong ionization of the Li cation. Hence, Li cation transfers most of its 2s electron to neighbouring BH₄ unit, similar to that of LiBH₄. Compared to Mg(BH₄)₂·2NH₃, the incorporation of LiBH₄ with the formation of LiMg(BH₄)₂·2NH₃ barely affects the charge distribution of H
As demonstrated by previous report, Mg(BH₄)₂ dehydrogenation peak located at 221 °C behind the release of ammonia, the formation and dihydrogen network is crucial to the thermodynamics and kinetics of ammonia release.

LiMg(BH₄)₃/C₁₄ release hydrogen at temperature around 120 °C, estimated the hydrogen formation energies. In addition, both Mg(BH₄)₂/2NH₃ and LiMg(BH₄)₃/2NH₃ showed dehydrogenation performance comparable to that of Mg(BH₄)₂/2NH₃, with dehydrogenation peak located at 221 °C. In addition, incorporation of LiBH₄ with Mg(BH₄)₂/2NH₃ suppresses ammonia release.

The calculated ammonia vacancy formation energies and diffusion barriers of NH₃ are crucial to the thermodynamics and kinetics of ammonia release from AMBs. To understand the microscopic mechanisms behind the release of ammonia, the formation and diffusivity of NH₃ were studied. The NH₃ vacancy was created by directly removed a NH₃ unit from Mg(BH₄)₂/2NH₃ and LiMg(BH₄)₃/2NH₃.

As shown in Table 2, the calculated NH₃ removal energies are 1.81 and 1.97 eV for Mg(BH₄)₂/2NH₃ and LiMg(BH₄)₃/2NH₃, respectively. The relatively high NH₃ removal energies indicates that the formation of NH₃ vacancies are thermodynamically unfavourable at low temperature, resulting in low concentration of ammonia vacancy for those two composites. The high formation energy of NH₃ vacancies can attribute to the coordination bond of Mg–N and H⁺...H dihydrogen network.

In addition to the formation energies of NH₃ vacancies, the diffusive of NH₃ vacancies is also importance for ammonia release. The diffusion paths were calculated by moving a NH₃ unit from a nearby lattice site into the vacancy. The diffusion barrier is defined as the energy difference between the saddle point and the ground state. The activation energy (Q) for self-diffusion of ammonia can be obtained by combining the calculated vacancy formation energy with the diffusion barrier.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Mg(BH₄)₂/2NH₃</th>
<th>LiMg(BH₄)₃/2NH₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>1.65</td>
<td>1.64</td>
</tr>
<tr>
<td>Mg</td>
<td>1.59</td>
<td>1.67</td>
</tr>
<tr>
<td>B</td>
<td>−1.30</td>
<td>−1.32/~1.34</td>
</tr>
<tr>
<td>N(H)</td>
<td>−0.58/~0.64</td>
<td>−0.63</td>
</tr>
<tr>
<td>(B)H</td>
<td>0.44</td>
<td>0.45</td>
</tr>
</tbody>
</table>

Ammonia vacancy formation energies and diffusion barriers

As shown in Table 2, the calculated NH₃ removal energies are 1.81 and 1.97 eV for Mg(BH₄)₂/2NH₃ and LiMg(BH₄)₃/2NH₃, respectively. The relatively high NH₃ removal energies indicates that the formation of NH₃ vacancies are thermodynamically unfavourable at low temperature, resulting in low concentration of ammonia vacancy for those two composites. The high formation energy of NH₃ vacancies can attribute to the coordination bond of Mg–N and H⁺...H dihydrogen network.

In addition to the formation energies of NH₃ vacancies, the diffusive of NH₃ vacancies is also importance for ammonia release. The diffusion paths were calculated by moving a NH₃ unit from a nearby lattice site into the vacancy. The diffusion barrier is defined as the energy difference between the saddle point and the ground state. The activation energy (Q) for self-diffusion of ammonia can be obtained by combining the calculated vacancy formation energy with the diffusion barrier.

As summarized in Fig. 2 and Table 2, for Mg(BH₄)₂/2NH₃, the calculated energy barrier and activation energy of ammonia diffusion are 0.26 and 2.07 eV, respectively. It should be noted that the NH₃ diffusion barrier is relatively low, the formation energy of NH₃ vacancy is the dominate term in the activation energy for ammonia diffusion. The relatively high formation energy would result in low concentration of NH₃ vacancy, which limit its transport in Mg(BH₄)₂/2NH₃. This is in agreement with previous report that only a small amount of NH₃ was released during decomposition of Mg(BH₄)₂/2NH₃.

The calculated ammonia vacancy diffusion barrier and activation energy of LiMg(BH₄)₃/2NH₃ are 1.31 and 3.28 eV, respectively. Compared to that of Mg(BH₄)₂/2NH₃, the relatively high ammonia diffusion barrier and activation energy indicate that low concentration and mobility of ammonia vacancy in LiMg(BH₄)₃/2NH₃, in inconsistent with experimental results that the dehydrogenation purity of Mg(BH₄)₂/2NH₃ can be improved by introducing LiBH₄ with the formation of LiMg(BH₄)₃/2NH₃.

Hydrogen formation energies and barriers

Our previous studies suggest that the initial dehydrogenation of AMBs is achieved by combination of H atoms from NH₃ and H atoms from BH₄ groups. Therefore, H₂ formation energies were calculated by moving one (N)H and one (B)H atom away from host N or B atom to form a hydrogen molecule with H–H distance of 0.74 Å in the supercell of AMBs. The geometry optimization was first performed by fixed the H₂ positions and relaxed the rest of the atoms, following by full relaxed all of the atoms in the supercell. In agreement with our previous studies, the formation of H₂ molecules lead to significant rearrangement of the surrounding lattice, which may result in overestimated the hydrogen formation energies. In addition, both Mg(BH₄)₂/2NH₃ and LiMg(BH₄)₃/2NH₃ started to release hydrogen at temperature higher than their melting point. In other word, the crystal structure of Mg(BH₄)₂/2NH₃ and LiMg(BH₄)₃/2NH₃ disappared before hydrogen evolved. Therefore, we further calculated the hydrogen formation energies by using the molecule model in which two formula units of Mg(BH₄)₂/2NH₃ and LiMg(BH₄)₃/2NH₃ were placed in a cubic cell with lattice parameter of 20 Å.

As shown in Table 3, the calculated hydrogen formation energies by using supercell of AMBs are 0.84 and 1.22 eV for Mg(BH₄)₂/2NH₃ and LiMg(BH₄)₃/2NH₃, respectively. In consistent with our previous theoretical study, the dissociation of H₂ results in dramatic movement of around atoms. The hydrogen formation energies calculated by molecule model are −0.11 and 0.08 eV for Mg(BH₄)₂/2NH₃ and LiMg(BH₄)₃/2NH₃, respectively. The combination of the (N)H and (B)H results in rearrangement of the surrounding atoms, similar with our previous report. The NH₂ and BH₃ units reoriented and BH₃ units moved toward NH₂ to form NH₂–BH₃ complexes. The N–B distances reduce to 1.58 Å, indicating the formation of N–B bond during dehydrogenation, in agreement with experimental observation. However, the lengths of Li–...
N, Mg–N, B–H and N–H bonds keep almost the same after structural rearrangements.

The low H₂ formation energies of Mg(BH₄)₂·2NH₃ and LiMg(BH₄)₃·2NH₃ suggest that the formation of hydrogen is thermodynamically favourable at low temperature. Therefore, the energy barrier of H₂ formation is the key of those two composites release hydrogen at temperature above 100 °C.

We further calculated the energy barriers of H₂ formation and the results were summarized in Fig. 3. The calculated energy barrier of H₂ formation from Mg(BH₄)₂·2NH₃ is 2.20 eV. The transition geometric structure of hydrogen release from Mg(BH₄)₂·2NH₃ shows the broken of B–H and N–H bonds with the formation of H₂ molecule. The H₂ molecule is located between NH₂ and BH₃ units with H₂–NH₂ and H₂–BH₃ distances of 2.47 and 2.31 Å, respectively. Meanwhile, the NH₂ unit move toward Mg cation and lead to slightly reduce the Mg–N distance from 2.16 to 1.95 Å. The calculated hydrogen formation energy barrier of LiMg(BH₄)₃·2NH₃ is 2.55 eV, which is 0.35 eV higher than that of Mg(BH₄)₂·2NH₃. Previous experimental results show dehydrogenation peak of 205 °C and 221 °C for Mg(BH₄)₂·2NH₃ and LiMg(BH₄)₃·2NH₃, respectively. The relatively high dehydrogenation peak of LiMg(BH₄)₃·2NH₃ can be attributed to the high hydrogen formation barrier. The transition geometric structure of hydrogen release from LiMg(BH₄)₃·2NH₃ is similar to that of Mg(BH₄)₂·2NH₃. The H₂ molecule is located between NH₂ and BH₃ unit. The H₂–NH₂ distance in transition structure of LiMg(BH₄)₃·2NH₃ is 2.24 Å, which is 0.23 Å shorter than that in Mg(BH₄)₂·2NH₃. And the H₂–BH₃ distance in transition structure of LiMg(BH₄)₃·2NH₃ is 2.11 Å, which is 0.20 Å shorter than that in Mg(BH₄)₂·2NH₃. In addition, the NH₂ unit shortening its distance to the Mg cation from 2.19 to 1.95 Å, similar to that of Mg(BH₄)₂·2NH₃.

Although the above calculations show a low NH₃ diffusion barrier for Mg(BH₄)₂·2NH₃, the formation energy of NH₃ vacancy is relatively high, which results in low concentration of NH₃ vacancy in Mg(BH₄)₂·2NH₃. Therefore, the Mg(BH₄)₂·2NH₃ mainly releases hydrogen accompany with a small amount of ammonia during decomposition. In contrast to that of Mg(BH₄)₂·2NH₃, LiMg(BH₄)₃·2NH₃ shows relatively high formation energy and diffusion barrier of NH₃ vacancy, which limit both the concentration and transport of ammonia, therefore improve the dehydrogenation purity. The calculated hydrogen formation barrier of LiMg(BH₄)₃·2NH₃ is slightly higher than that of Mg(BH₄)₂·2NH₃, therefore incorporation of LiBH₄ with Mg(BH₄)₂·2NH₃ may not decrease the dehydrogenation temperature.

Table 3 Formation energies of H₂ release via (N)H and (B)H combination by using crystal model (Eₜₐₚ-C) and molecule model (Eₜₐₚ-M)

<table>
<thead>
<tr>
<th></th>
<th>Eₜₐₚ-C (eV)</th>
<th>Eₜₐₚ-M (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg(BH₄)₂·2NH₃</td>
<td>0.84</td>
<td>−0.11</td>
</tr>
<tr>
<td>LiMg(BH₄)₃·2NH₃</td>
<td>1.22</td>
<td>0.08</td>
</tr>
</tbody>
</table>

23,35
Conclusions

First-principles calculations based on density functional theory were carried out to investigate the decomposition mechanisms of Mg(BH$_4$)$_2$·2NH$_3$ and LiMg(BH$_4$)$_3$·2NH$_3$. The electronic structure analysis indicates that Mg–H interaction in those two composites are mainly ionic with partial covalent bond feature. The incorporation of LiBH$_4$ and Mg(BH$_4$)$_2$·2NH$_3$ with the formation of LiMg(BH$_4$)$_3$·2NH$_3$ barely affects the charge distribution of H and Mg. The Bader charge of B is slightly increased and Bader charge of N decreased due to the incorporation of LiBH$_4$. Although the NH$_3$ diffusion barrier for Mg(BH$_4$)$_2$·2NH$_3$ is low, the relatively high formation energy of NH$_3$ vacancy lead to low concentration of NH$_3$ vacancy and limit its transportation, in agreement with experimental results that Mg(BH$_4$)$_2$·2NH$_3$ mainly releases hydrogen along with a small amount of ammonia. The LiMg(BH$_4$)$_3$·2NH$_3$ shows relatively high ammonia vacancy formation energy and diffusion barrier, which suppress ammonia release compared to Mg(BH$_4$)$_2$·2NH$_3$. The incorporation of LiBH$_4$ and Mg(BH$_4$)$_2$·2NH$_3$ does not decrease the hydrogen formation barriers, instead slightly increase the hydrogen formation barriers of LiMg(BH$_4$)$_3$·2NH$_3$, in agreement with experimental results that LiMg(BH$_4$)$_3$·2NH$_3$ shows a dehydrogenation peak slightly higher than that of Mg(BH$_4$)$_2$·2NH$_3$.

Acknowledgements

This work is supported by the National Science Fund for Distinguished Young Scholars (51625102), National Natural Science Foundation of China (51601068, 11605073) and Natural Science Foundation of Fujian Province (2016J05129, 2017J05009).

Notes and references

1 A. Staubitz, A. P. M. Robertson and I. Manners, Chem. Rev., 2010, 110, 4079–4124.