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ARTICLE

Theoretical Studies on Dehydrogenation Reactions in $\text{Mg}_2(\text{BH}_4)_2(\text{NH}_2)_2$ Compounds

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Borohydrides have been recently highlighted as prospective new materials due to their high gravimetric capacities for hydrogen storage. It is, therefore, important to understand the underlying dehydrogenation mechanisms for further development of these materials. We present a systematic theoretical investigation on the dehydrogenation mechanisms of the $\text{Mg}_2(\text{BH}_4)_2(\text{NH}_2)_2$ compounds. We found that dehydrogenation takes place most likely via the intermolecular process, which is favorable both kinetically and thermodynamically in comparison with that of the intramolecular process. The dehydrogenation of $\text{Mg}_2(\text{BH}_4)_2(\text{NH}_2)_2$ initially takes place via the direct combination of the hydridic H in BH_4^- and the protic H in NH_2^- , followed by the formation of Mg-H and subsequent ionic recombination of $\text{Mg-H}^{\delta-} \cdots \text{H}^{\delta+}-\text{N}$.

Key words: Hydrogen storage, Density functional theory, Metal borohydride

I. INTRODUCTION

Light metal borohydrides $\text{M}(\text{BH}_4)_n$, where M refers to alkali or alkaline earth metals, are receiving intensive attentions as prospective hydrogen storage materials due to their high gravimetric capacities for hydrogen [1–11]. The theoretical hydrogen contents of these materials, *e.g.*, 18.3% for LiBH_4 [3–6], 14.9% for $\text{Mg}(\text{BH}_4)_2$ [7–9], and 11.6% for $\text{Ca}(\text{BH}_4)_2$ [10, 11], all satisfy the target criteria set by the U.S. Department of Energy. Among all these known light metal borohydrides, $\text{Mg}(\text{BH}_4)_2$ has the greatest potential for being a reversible hydrogen storage material because of its desirable thermodynamic properties ($\Delta H=39$ kJ/mol) [12]. Nonetheless, the dehydrogenation temperature of $\text{Mg}(\text{BH}_4)_2$ is too high to be applied as an efficient hydrogen storage material [9].

The introduction of amides is an effective way to lower the dehydrogenation temperatures of metal borohydrides [13–18]. $\text{LiBH}_4\text{-LiNH}_2$ is the first metal amidoborane sample, which exhibits significantly improved dehydrogenation properties as compared to that of LiBH_4 [15, 16]. Since then, a lot of works have been conducted on other light metal borohydrides to improve

the dehydrogenation kinetics [17–19]. However, the dehydrogenation mechanisms of these systems are rarely investigated due to the lack of detailed structural information. Very recently, Xiong *et al.* investigated the $\text{Mg}(\text{BH}_4)_2\text{-Mg}(\text{NH}_2)_2$ mixture and found that a novel complex hydride, $\text{Mg}_2(\text{BH}_4)_2(\text{NH}_2)_2$, could be formed and crystallized in a tetragonal structure through heating the post-milled $\text{Mg}(\text{BH}_4)_2$ and $\text{Mg}(\text{NH}_2)_2$ mixtures [20]. This system undergoes dehydrogenation reaction according to the following formula:



The onset temperature of this newly synthesized complex hydride for hydrogen desorption is found to be much lower than that of $\text{Mg}(\text{BH}_4)_2$ [20]. With the structural information in hand, it is now feasible to explore in depth this new material, which shall be useful in tuning the reactions to improve the properties for future applications in hydrogen storage.

In this work, we present the first mechanistic research on the dehydrogenation processes of $\text{Mg}_2(\text{BH}_4)_2(\text{NH}_2)_2$. Our calculations demonstrate that it is the intermolecular, instead of the intramolecular process, that plays a predominant role in H_2 release. The intermolecular process consists of two competing pathways, a direct (denoted as D-) pathway via the combination of $\text{B-H}^{\delta-} \cdots \text{H}^{\delta+}-\text{N}$ and a metal-mediated (denoted as M-) pathway involving the com-

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combination of $\text{Mg}-\text{H}^{\delta-} \cdots \text{H}^{\delta+}-\text{N}$. Our calculations suggest that the D-pathway is more favorable than the M-pathway during the initial dehydrogenation process, while the M-pathway becomes predominant in the subsequent steps of the second H_2 release.

II. MODEL CHOICE AND COMPUTATIONAL DETAILS

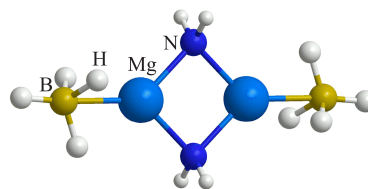
Since the dehydrogenations of B, N based hydrogen storage materials often occur after the melting point [20–22], a cluster model is relevant and adopted here to investigate the dehydrogenation mechanisms of $\text{Mg}_2(\text{BH}_4)_2(\text{NH}_2)_2$. During the phase transformation from $\text{Mg}_2(\text{BH}_4)_2(\text{NH}_2)_2$ crystal to liquid, many small clusters are formed, in which $\text{Mg}_2(\text{BH}_4)_2(\text{NH}_2)_2$ with a planar four-membered ring, as shown in Scheme 1, is the most stable conformation according to our theoretical calculations. Therefore, this cluster was chosen as the model compound for our dehydrogenation mechanism study.

For the geometry optimization, 6-31G(d) [23] basis set was used in conjunction with the B3LYP functional [24, 25]. All stationary and saddle points were characterized by subsequent frequency calculations at the same level of theory, which were then used to determine the corresponding thermodynamic properties. Intrinsic reaction coordinate (IRC) [26] calculations were employed to confirm the connections between a transition state and the corresponding reactants as well as the products. The electronic energies were corrected with single point calculations at the level of XYGJ-OS [27]/6-311+G(2d,2p) [28]. Energies reported here are free energies at 453.15 K and 101 kPa, which generally correspond to the experimental conditions.

In this work, all other calculations were performed with the Gaussian 09 package [29], while the XYGJ-OS calculations were performed with the Q-Chem package [30].

III. RESULTS AND DISCUSSION

Originally, it is proposed that the driving force leads to the dehydrogenation process when LiNH_2 reacts with LiH , due to the redox reaction between $\text{H}^{\delta+}$ in LiNH_2 and $\text{H}^{\delta-}$ in LiH . Similar mechanism was proposed in the $\text{Li}-\text{Mg}-\text{N}-\text{H}$ and $\text{Li}-\text{Ca}-\text{N}-\text{H}$ systems [13, 14]. Recently, Kim and coworkers have performed a thorough theoretical study of the $\text{H}^{\delta-} \cdots \text{H}^{\delta+}$ combination on various alkali/alkaline-earth metal amidoboranes, $\text{M}(\text{NH}_2\text{BH}_3)$, exploiting several reaction pathways [31, 32]. Our new system $\text{Mg}_2(\text{BH}_4)_2(\text{NH}_2)_2$ shall bear some mechanistic similarities with Kim's. In particular, we have studied the D-pathway, in which H_2 is released through a direct $\text{B}-\text{H}^{\delta-} \cdots \text{H}^{\delta+}-\text{N}$ dihydrogen bond formation, as well as the M-pathway, where the hydride is first transferred from boron to Mg^{2+} to form $\text{Mg}-\text{H}$,



Scheme 1 The $\text{Mg}_2(\text{BH}_4)_2(\text{NH}_2)_2$ monomer.

and then the redox reaction of the $\text{Mg}-\text{H}^{\delta-} \cdots \text{H}^{\delta+}-\text{N}$ dihydrogen bond formation takes place. In this work, we have considered both pathways through intramolecular and intermolecular processes.

The monomeric $\text{Mg}_2(\text{BH}_4)_2(\text{NH}_2)_2$ is shown in Scheme 1, where $\text{Mg}^{\delta+}-\text{N}^{\delta-}-\text{Mg}^{\delta+}-\text{N}^{\delta-}$ forms a planar four-membered ring. The BH_4^- group and the NH_2^- group are spatially apart and the distance between the hydridic H in BH_4^- and the protic H in NH_2^- is more than 3.4 Å, which is far beyond the range of dihydrogen bond. Hence, the reorganization energy is too high to release one H_2 through the direct combination of $\text{B}-\text{H}^{\delta-} \cdots \text{H}^{\delta+}-\text{N}$. As a result, we could not locate a transition state for the D-pathway from a monomeric $\text{Mg}_2(\text{BH}_4)_2(\text{NH}_2)_2$.

Two steps are involved in the M-pathway as shown in Fig.1 for the desorption of H_2 from a monomeric $\text{Mg}_2(\text{BH}_4)_2(\text{NH}_2)_2$. The magnesium hydride ($\text{Mg}-\text{H}$) is initially formed as an intermediate (LM1M) by transferring a hydride from $\text{H}^{\delta-}-\text{BH}_3$ to Mg (via TS1M). Then, dehydrogenation takes place to release the first H_2 via the combination of $\text{Mg}-\text{H}^{\delta-} \cdots \text{H}^{\delta+}-\text{N}$. It is noteworthy that the barrier height of TS1M for the formation magnesium hydride is quite high (284.9 kJ/mol), which is probably due to the breakage of the more stable $\text{Mg}-\text{N}$ bond. On the other hand, TS2M is considerably stabilized (200.8 kJ/mol), as the $\text{Mg}^{\delta+}-\text{N}^{\delta-}-\text{Mg}^{\delta+}-\text{N}^{\delta-}$ ring structure is reformed.

For the release of the second H_2 , both the D-pathway and the M-pathway were located. Our calculations showed that the stepwised M-pathway (TS3M/TS4M) is more favorable than the D-pathway (TS2D) (129.3/262.8 *vs.* 401.2 kJ/mol). This implies that $\text{Mg}-\text{H}^{\delta-}$ is a stronger Lewis base as compared with $\text{H}_2\text{B}-\text{H}^{\delta-}$. This is in line with the previous finding by Kim *et al.* on their $\text{M}(\text{NH}_2\text{BH}_3)$ systems [31, 32]. However, TS1M (284.9 kJ/mol) has created a kinetic bottleneck, while LM3 (179.1 kJ/mol) has put a thermodynamic constraint, showing that the overall intramolecular dehydrogenation process from a monomeric $\text{Mg}_2(\text{BH}_4)_2(\text{NH}_2)_2$ is unfavorable from both kinetic and thermodynamic points of view. This is most likely due to the relative high reorganization energies during the dehydrogenation processes.

Figure 2 illustrates the dehydrogenation mechanism through the intermolecular processes in the dimeric system. According to our calculations, a $(\text{Mg}_2(\text{BH}_4)_2(\text{NH}_2)_2)_2$ dimer can be formed from two

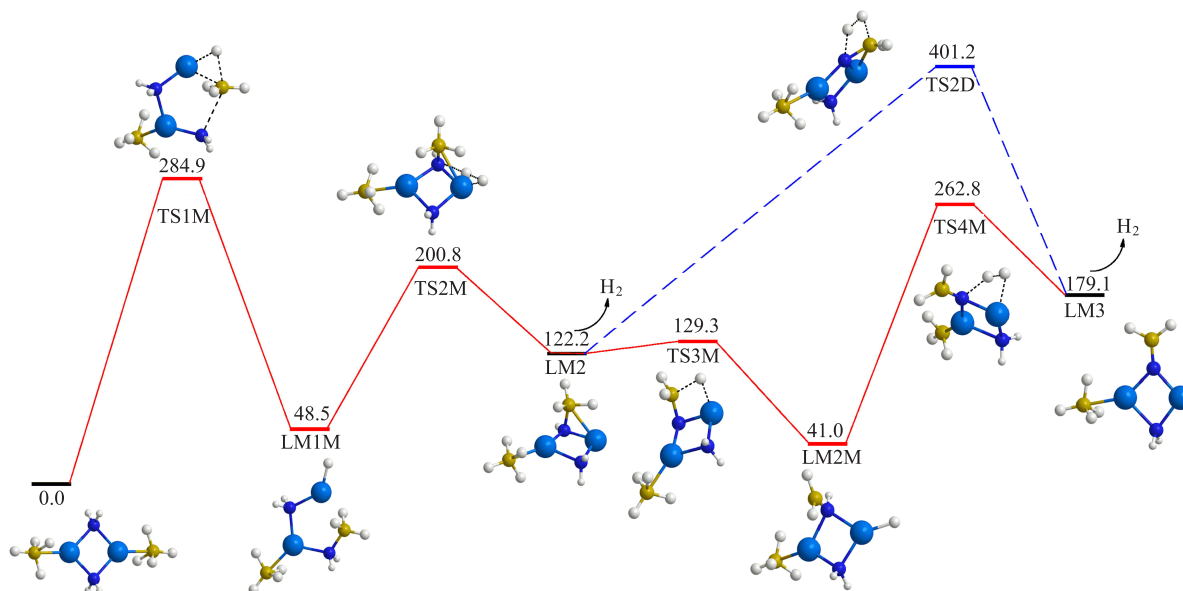


FIG. 1 Relative free energy profiles for the dehydrogenation reaction in $\text{Mg}_2(\text{BH}_4)_2(\text{NH}_2)_2$ monomer (unit in kJ/mol). D or M is used as suffix to specify the D- (broken line) or M-pathway (solid line), respectively.

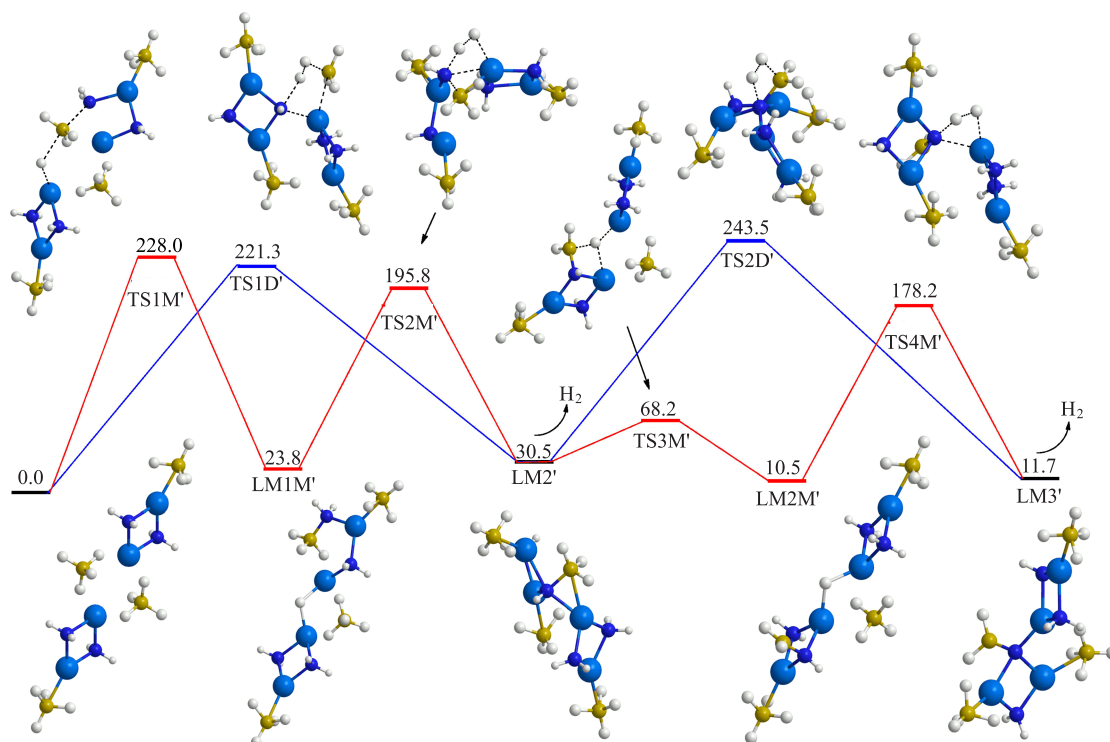


FIG. 2 Relative free energy profiles for the dehydrogenation reaction in $(\text{Mg}_2(\text{BH}_4)_2(\text{NH}_2)_2)_2$ dimer (unit in kJ/mol). D or M is used as suffix to specify the D- (broken line) or M-pathway (solid line), respectively.

monomeric $\text{Mg}_2(\text{BH}_4)_2(\text{NH}_2)_2$ with a stabilization energy of 32.6 kJ/mol. It should be noted that this dimer has a similar structure as crystal $\text{Mg}_2(\text{BH}_4)_2(\text{NH}_2)_2$, in which Mg^{2+} is tetrahedrally coordinated with two BH_4^- and two NH_2^- groups. On the contrary to the

intramolecular processes, both mechanistic pathways, the D-pathway and the M-pathway, could be located for the release of two H_2 . While Kim *et al.* suggested that the M-pathway is the dominant way for dehydrogenation of all metal amidoboranes $\text{M}(\text{NH}_2\text{BH}_3)$ [32], our

calculations suggest that, on $\text{Mg}_2(\text{BH}_4)_2(\text{NH}_2)_2$, two pathways compete with each other for the initial H_2 desorption. Thus, different systems may favor different mechanisms. Indeed the D-pathway is found here to be kinetically more favorable in comparison with the M-pathway with a single barrier height of 221.3 kJ/mol, whereas the M-pathway has to overcome two barriers (228.0 and 195.8 kJ/mol) successively to release the first H_2 . Certainly, the lower barrier of the M-pathway in the case of dimeric system suggests that the intermolecular process could efficiently reduce the reorganization energy as compared to that in the monomeric system (228.0 *vs.* 262.8 kJ/mol). The dimeric system may release the second H_2 via both pathways. The M-pathway is more favorable than the D-pathway as shown in Fig.2 (178.2 *vs.* 243.5 kJ/mol). This is probably due to the relative low basicity of $\text{H}_2\text{B}-\text{H}^{\delta-}$, and this finding is consistent with the results of intramolecular dehydrogenation in monomeric $\text{Mg}_2(\text{BH}_4)_2(\text{NH}_2)_2$. In view of the overall kinetic and thermodynamic data for dehydrogenation of dimeric $\text{Mg}_2(\text{BH}_4)_2(\text{NH}_2)_2$, the first H_2 release is supposed to go along the D-pathway, and the second H_2 release occurs by the formation of $\text{Mg}-\text{H}$ at the first place, followed by the ionic recombination of the $\text{Mg}-\text{H}^{\delta-} \cdots \text{H}^{\delta+}-\text{N}$ dihydrogen bond. As shown in Fig.2, the activation of B-H bond in either D-pathway or M-pathway is the rate-limiting step (221.3/228.0 *vs.* 178.2 kJ/mol). Any possibility that can reduce the barrier for B-H activation shall catalyze the whole reaction. We note that previous investigations on $\text{Li}_3(\text{BH}_4)(\text{NH}_2)_2$ and $\text{Li}_4(\text{BH}_4)(\text{NH}_2)_3$ have shown that the CoB alloy is particularly effective in activating the B-H bond in BH_4^- [33–36]. Hence we predict that the CoB alloy can also catalyze the dehydrogenation of the present $\text{Mg}_2(\text{BH}_4)_2(\text{NH}_2)_2$ system according to our mechanisms. Indeed, a recent experiment has verified the catalytic improvement of the dehydrogenation kinetics of $\text{Mg}_2(\text{BH}_4)_2(\text{NH}_2)_2$ by mixing 5%CoB catalyst [20], lending strong support to the present mechanisms.

IV. CONCLUSION

By investigating the molecular model of the dehydrogenation mechanism of $\text{Mg}_2(\text{BH}_4)_2(\text{NH}_2)_2$ compounds, we find that dehydrogenation takes place most likely via the intermolecular process, which is favorable both kinetically and thermodynamically. The dehydrogenation mechanism of $\text{Mg}_2(\text{BH}_4)_2(\text{NH}_2)_2$ is quite different from that of metal amidoboranes, for which the dehydrogenations all follow the metal-mediated pathway. Our calculations demonstrated that dehydrogenation of $\text{Mg}_2(\text{BH}_4)_2(\text{NH}_2)_2$ initially takes place via the direct combination of the hydridic H in BH_4^- and the protic H in NH_2^- , followed by the formation of $\text{Mg}-\text{H}$ and subsequent ionic recombination of $\text{Mg}-\text{H}^{\delta-} \cdots \text{H}^{\delta+}-\text{N}$. The activation of the H-B bond in BH_4^- is the rate-

limiting step for the release of H_2 and this finding fits well with the catalytic improvement by Co-B alloy reported in the recent experiments. Our present work constructed a detailed mechanistic picture for the dehydrogenation in $\text{Mg}_2(\text{BH}_4)_2(\text{NH}_2)_2$, which provides better understanding of this new material and is of help in tuning the reactions to improve its properties for future applications in hydrogen storage.

V. ACKNOWLEDGEMENT

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