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Decomposition Mechanism of Zinc Ammine Borohydride: A First-Principles Calculation

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Abstract

The decomposition mechanism of zinc ammine borohydride ($[\text{Zn}(\text{NH}_3)_2][\text{BH}_4]_2$) has been studied by density functional theory calculation. The release of B_2H_6 and BH_3 is predicted to be kinetically and/or thermodynamically unfavorable for $[\text{Zn}(\text{NH}_3)_2][\text{BH}_4]_2$, in agreement with experimental results that no boranes were detected during decomposition. The climbing image nudged elastic band calculation and ab initio molecular dynamics simulations indicate the formation of NH_3BH_3 and B_2H_7^- intermediates during decomposition of $[\text{Zn}(\text{NH}_3)_2][\text{BH}_4]_2$, which is different from that observed for other reported ammine metal borohydrides. The dehydrogenation occurs through reaction pathways involving transfers of hydrides from the Zn cation to BH_4^- or transfers of protons from NH_3BH_3 to NH_3 .

1. Introduction

Hydrogen is an ideal clean energy carrier because of its abundance, high heating value per mass and environmentally friendly product of water.¹⁻³ Developing hydrogen storage materials with high gravimetric hydrogen densities and favorable de-hydrogenation/re-hydrogenation properties is one of the key challenges in using hydrogen as an alternative energy source for mobile or stationary applications.² Metal borohydrides ($M(BH_4)_x$) with high gravimetric and volumetric densities of hydrogen have received great attention in the past few decades.⁴⁻⁸ The experimental and theoretical studies suggest a correlation between the hydrogen desorption temperature and the Pauling electronegativity of the cation (χ_p) of metal borohydrides.^{9, 10} The metal borohydrides with low χ_p tend to release hydrogen at high temperature. For instance, $NaBH_4$, $LiBH_4$ and $Mg(BH_4)_2$ with χ_p lower than 1.3 start to release H_2 at temperature above 300 °C.¹¹⁻¹⁴ On the other hand, metal borohydrides with high χ_p tend to release an undesired byproduct of diborane (B_2H_6) at low temperatures. For example, $Al(BH_4)_3$ and $Zn(BH_4)_2$ with χ_p of 1.6 and 1.65, respectively, are volatile at room temperature and release a significant volume of B_2H_6 byproduct upon heating.^{8, 15, 16}

The use of NH_3 ligands to saturate and immobilize the metal cation with formation of ammine metal borohydrides (AMBs, $[M(NH_3)_x][BH_4]_y$) is an effective strategy to improve thermo-dynamic stability of metal borohydrides.¹⁷⁻³² Although AMBs show improvement of dehydrogenation properties and prevention of B_2H_6 release compared to metal borohydrides, many of these AMBs tend to release ammonia during thermal decomposition. It has been reported that $[Li(NH_3)_x][BH_4]$ and $[Ca(NH_3)_x][BH_4]_2$ ($x=1, 2$ and 4) release a significant amount of ammonia below 300 °C under dynamic situation.^{17, 19, 21} The $[Mg(NH_3)_2][BH_4]_2$ and $[Al(NH_3)_6][BH_4]_3$ mainly release hydrogen with a certain amount of ammonia detected during decomposition.^{23, 33} Among these AMBs, zinc ammine borohydride, $[Zn(NH_3)_2][BH_4]_2$, shows favorable dehydrogenation properties in terms of hydrogen desorption temperature and purity of gas release. As

reported in a previous literature study, $[\text{Zn}(\text{NH}_3)_2][\text{BH}_4]_2$ is able to release 8.9 wt% hydrogen below 115 °C within 15 min without concomitant release of undesirable gases such as ammonia and boranes.²²

The dehydrogenation of some of the AMBs may be achieved through combining hydrides from $[\text{BH}_4]^-$ and protons from NH_3 , ultimately yielding amorphous metal boronitrides.^{19, 23-26, 34-36} The experimental observation of the formation of well-crystallized Zn during dehydrogenation indicates that the decomposition pathway of $[\text{Zn}(\text{NH}_3)_2][\text{BH}_4]_2$ is slightly different from those of the other reported AMBs, in which the metal cations in the dehydrogenated products are always bonded to the BN species.²² Although a previous report suggested the formation of the NH_3BH_3 intermediate,³⁷ the dehydrogenation mechanism of $[\text{Zn}(\text{NH}_3)_2][\text{BH}_4]_2$ is still unclear. Therefore, a detailed study of the decomposition mechanism of $[\text{Zn}(\text{NH}_3)_2][\text{BH}_4]_2$ will provide useful insights for improving its dehydrogenation performance and offer guidelines for designing novel Zn-based ammine borohydrides for hydrogen storage.

Herein, the decomposition mechanism of $[\text{Zn}(\text{NH}_3)_2][\text{BH}_4]_2$ was studied by density functional theory (DFT) calculation. We performed climbing image nudged elastic band (CI-NEB) calculation and ab initio molecular dynamics (AIMD) simulations to illustrate that the dehydrogenation mechanism of $[\text{Zn}(\text{NH}_3)_2][\text{BH}_4]_2$ is different from those of other reported AMBs which release hydrogen via combining hydrides from $[\text{BH}_4]^-$ and protons from NH_3 . Our calculation indicates the formation of NH_3BH_3 and B_2H_7^- intermediates during decomposition of $[\text{Zn}(\text{NH}_3)_2][\text{BH}_4]_2$.

2. Computational Method

As reported in a previous literature study, the $[\text{Zn}(\text{NH}_3)_2][\text{BH}_4]_2$ crystallize in the orthorhombic structure with a space group of $P2_1$ and cell parameters of $a = 6.392(4)$ Å, $b = 8.417(6)$ Å, $c = 6.388(4)$ Å, $\alpha = \gamma = 90^\circ$ and $\beta = 92.407(4)^\circ$.²² The geometric structure was optimized by DFT calculation as implemented in MedeA@VASP code³⁸. To describe the weak van der Waals $\text{H}^+ \cdots \cdots \text{H}$ dihydrogen bonds, the optB86b-vdW functional³⁹⁻⁴¹ was

adopted for geometric optimization. The projector-augmented wave (PAW) approach was used to describe the electron-ion interactions⁴². Plane wave with kinetic energy cutoff of 400 eV was used. The generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) was adopted to describe the exchange and correlation of electronics^{43, 44}. The Brillouin zone was sampled by Monkhorst-Pack k -point meshes⁴⁵ with mesh point spacing less than $0.05 \text{ \AA}^{-1}$. Structural relaxations of atomic positions were carried out until the residual forces on each atoms were less than $0.02 \text{ eV} \cdot \text{\AA}^{-1}$. The NH_3 diffusion barriers and H_2 formation barriers were estimated by using the climbing image nudged elastic band (CI-NEB) method^{46, 47} until the forces on each atoms were less than $0.02 \text{ eV} \cdot \text{\AA}^{-1}$.

The NH_3 vacancy was created by removing one NH_3 molecule from $2 \times 1 \times 2$ supercell of $[\text{Zn}(\text{NH}_3)_2][\text{BH}_4]_2$. The NH_3 vacancy formation energy was estimated using the following equation:

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

where E_{total} is the total energy of $[\text{Zn}(\text{NH}_3)_2][\text{BH}_4]_2$; $E(\text{NH}_3)$ represents the energy of isolated NH_3 molecule; and $E(\text{Zn-NH}_3)$ is the total energy of $[\text{Zn}(\text{NH}_3)_2][\text{BH}_4]_2$ after a NH_3 molecule is removed. The positive energy of E_c indicates that the creation of NH_3 vacancy is an endothermic process, and the negative energy of E_c indicates that the creation of NH_3 vacancy is an exothermic process.

Previous differential scanning calorimetry and in-situ X-ray diffraction data suggested that $[\text{Zn}(\text{NH}_3)_2][\text{BH}_4]_2$ started to release hydrogen at temperature higher than its melting point.²² In other word, $[\text{Zn}(\text{NH}_3)_2][\text{BH}_4]_2$ undergoes a phase change from the solid state to viscous liquid before hydrogen released. Hence, the CI-NEB calculation of hydrogen formation energy and barrier were calculated by using a molecular model in which one formula unit of $[\text{Zn}(\text{NH}_3)_2][\text{BH}_4]_2$ was placed in a cubic cell with a lattice parameter of $20 \text{ \AA}$. The formation of a H_2 molecule was achieved by moving a proton and a hydride away from host N and B atoms to form a hydrogen molecule with the H-H distance of

0.74 Å. All of the atoms in the cell were relaxed during geometry optimization.

The vibrational enthalpies are important to estimate the reaction barrier and enthalpies. Therefore, we further investigate the reaction barrier and enthalpies of these reactions by including the zero-point energy (ZPE) and vibrational enthalpy contributions. Phonons are calculated using the supercell force-constant method and the vibrational enthalpies are obtained by directly summing the calculated phonon frequencies.

Ab initio molecular dynamics simulations (AIMD) were performed to further examine the decomposition mechanism. We used a $2 \times 1 \times 2$ supercell of $[\text{Zn}(\text{NH}_3)_2][\text{BH}_4]_2$ which contains 152 atoms to prevent the spurious interactions between neighboring supercells. The canonical ensemble (NVT) following the Born-Oppenheimer (BO) implementation was adopted. The ionic equations of motion were integrated using the Nose-Hoover algorithm with a time step of 1.0 fs; deuterium mass was used for the hydrogen atom in order to enable a larger time step. The simulated system was initially equilibrated at a temperature of 300 K for 2 ps (2 000 steps). Then, the simulation temperature increased from 300 K to 3000 K uniformly over 40 ps (40 000 steps). The high temperatures used in simulation allowed reactions to be observed within 40 ps. To analyze the fragments during the simulation, we used a bond length cut-off of ~ 1.3 times of the normal bond length.

3. Results and Discussion

3.1 Formation and Diffusion of NH_3 Vacancy

The transport property of NH_3 vacancy is crucial to the thermodynamics and kinetics of ammonia release or intermediate formation. To understand the microscopic dehydrogenation mechanism of $[\text{Zn}(\text{NH}_3)_2][\text{BH}_4]_2$, the formation and diffusion of NH_3 were studied.

Our calculated formation energy of NH_3 vacancy is 1.13 eV for $[\text{Zn}(\text{NH}_3)_2][\text{BH}_4]_2$, which is 0.68 eV lower than that of $[\text{Mg}(\text{NH}_3)_2][\text{BH}_4]_2$. In addition, as shown in Figure 1, the energy barrier of ammonia diffusion is calculated to be 0.96 eV for $[\text{Zn}(\text{NH}_3)_2][\text{BH}_4]_2$.

The activation energy (E_a) for self-diffusion of ammonia (combining the vacancy formation energy with the diffusion energy barrier) is calculated to be 2.09 eV, comparable to that of $[\text{Mg}(\text{NH}_3)_2][\text{BH}_4]_2$. Our previous reports suggest that AMBs with low E_a tend to release ammonia during decomposition.^{34, 35} Ammonia was not detected during thermal decomposition of $[\text{Zn}(\text{NH}_3)_2][\text{BH}_4]_2$, unlike that of $[\text{Mg}(\text{NH}_3)_2][\text{BH}_4]_2$ which released a small amount of NH_3 during decomposition.^{22, 23} With a relatively low ammonia diffusion energy barrier of 0.96 eV, NH_3 may be able to diffuse and involve in the formation of amorphous intermediate(s) before the dehydrogenation of $[\text{Zn}(\text{NH}_3)_2][\text{BH}_4]_2$, which prevents its release upon heating.

Figure 1. Calculated energy barrier, and initial (IS), transition (TS) and final (FS) geometric structures of NH_3 diffusion in $[\text{Zn}(\text{NH}_3)_2][\text{BH}_4]_2$. E_b represents the calculated energy barrier.

3.2 Direct Release of Hydrogen

Figure 2. Calculated hydrogen release energy barriers for AMBs (via directly combining a hydride from BH_4^- and a proton from NH_3) plotted as a function of experimental peak temperature of dehydrogenation. The experimental peak temperature of dehydrogenation is adapted from refs 22, 23, 26, 33 and 36. The H_2 releases energy barrier is adapted from refs 33 and 34.

Figure 3. Calculated energy barrier, and initial (IS), transition (TS) and final (FS) geometric structures of H_2 release from $[\text{Zn}(\text{NH}_3)_2][\text{BH}_4]_2$ via directly combine hydride from $[\text{BH}_4]^-$ and proton from NH_3 . E_b represents the calculated energy barrier.

Our previous studies about AMBs (seeing Figure 2) show a correlation between the peak dehydrogenation temperature and the calculated H₂ release energy barrier (H₂ released via combining a hydride from BH₄⁻ and a proton from NH₃).^{34, 35} The AMBs with higher energy barriers tend to release hydrogen at higher temperatures. Therefore, we calculated a similar reaction pathway in which H₂ is form via combining a hydride from BH₄⁻ and a proton from NH₃. For making the discussion easier to understand, the reaction pathway was simplified as the following equation:

As shown in Figure 3, the energy barrier of this process is 2.02 eV, which is 0.66 eV higher than that of [Al(NH₃)₆][Li₂(BH₄)₅].³⁵ The experimental results, however, show peak dehydrogenation temperature of 127 and 138 °C for [Zn(NH₃)₂][BH₄]₂ and [Al(NH₃)₆][Li₂(BH₄)₅], respectively.^{22, 33} Thus, different from that of [Al(NH₃)₆][Li₂(BH₄)₅], the dehydrogenation of [Zn(NH₃)₂][BH₄]₂ may not through the direct combination of a proton from NH₃ and a hydride from [BH₄]⁻. [Zn(NH₃)₂][BH₄]₂ presents an amorphous phase at 69 °C,²² and with the temperature increase, some amorphous intermediate(s) may be formed.

3.3 Formation of B₂H₆ or BH₃

The above discussion indicates that the formation of intermediate(s) may be a key aspect to uncover the dehydrogenation mechanism of [Zn(NH₃)₂][BH₄]₂. Previous experimental results show the release of B₂H₆ during decomposition of Zn(BH₄)₂.¹⁶ Although no borane byproducts were detected during the dehydrogenation of [Zn(NH₃)₂][BH₄]₂, the B₂H₆ or BH₃ intermediate(s) may be formed before dehydrogenation, which may further react with NH₃ to release hydrogen.

Figure 4. Calculated energy barrier, and initial (IS), transition (TS) and final (FS) geometric structures of (a) B₂H₆ formation and (b) BH₃ formation. E_b represents the calculated energy barrier.

We first calculated the formation of B₂H₆ via combination of two BH₃ from [BH₄]⁻ with two remaining hydrides bonding to the Zn cation. This reaction pathway was simplified as the following equation:

As shown in Figure 4a, the CI-NEB energy profile indicates that [Zn(NH₃)₂][BH₄]₂ first overcomes an energy barrier of 1.62 eV to form a local minimize configuration with B₂H₇⁻-like anion fragment (LM as shown in Figure 4a). The B₂H₇⁻-like anion fragment subsequently transforms to B₂H₆ through an endothermal process with a reaction enthalpy of 0.68 eV. This indicates that B₂H₆ formation via LM→FS2 is kinetically and thermodynamically unfavorable because the reverse reaction to form B₂H₇⁻-like anion fragment (FS2→LM) is a barrierless exothermal process.

We also examined the pathway in which two hydrides from BH₄⁻ directly combine with

each other to form H₂, and the two remaining BH₃ fragments bond to the Zn cation. This reaction pathway was simplified as the following equation:

As shown in Figure 4b, the final configuration (FS3) shows that two BH₃ bond to the Zn cation with Zn-B and B-B distances of 2.072 and 1.932 Å, respectively. This process is also an endothermal process with the reaction enthalpy and barrier of 1.23 and 2.58 eV, respectively. The high reaction barrier indicates that this process is kinetically unfavorable.

The above discussion indicates that the formation of B₂H₆ and BH₃ is kinetically and/or thermodynamically unfavorable, in consistent with experimental results that not boranes were detected during decomposition of [Zn(NH₃)₂][BH₄]₂.²²

3.4 Formation of the B₂H₇⁻ Intermediate

Figure 5. Calculated energy barrier, and initial (IS), transition (TS) and final (FS) geometric structures of B₂H₇⁻ formation. E_b represents the calculated energy barrier.

We further calculated the formation of B₂H₇⁻ intermediate via the combination of two BH₄⁻ with a remaining hydride bonding to the Zn cation. This reaction pathway was simplified as the following equation:

As shown in Figure 5, the formation of the B₂H₇⁻ intermediate through IS1→TS4→FS4

is an endothermal process with reaction enthalpy and barrier of 0.56 eV (0.62 eV at 300 K) and 1.58 eV (1.52 eV including zero-point energy correction), respectively. The geometry of TS4 shows that a hydride from BH_4^- migrates and ultimately bonds to Zn cation with a Zn-H distance of $\sim 1.56 \text{ \AA}$, which is $0.33 \text{ \AA}$ shorter than Zn-H distances in crystalline phase of $[\text{Zn}(\text{NH}_3)_2][\text{BH}_4]_2$.²² Thus, the Zn cation assists the formation of B_2H_7^- intermediate by extracting a hydride from BH_4^- to form Zn-H ionic bond. Compared to that of H_2 release via combining a hydride from BH_4^- and a proton from NH_3 ($\text{BH}_4^- + \text{NH}_3 \rightarrow \text{BH}_3\text{NH}_2^- + \text{H}_2$, $\text{IS} \rightarrow \text{TS} \rightarrow \text{FS}$ as shown in Figure 2), the formation of B_2H_7^- intermediate is 0.44 eV lower in energy barrier. This indicates that $[\text{Zn}(\text{NH}_3)_2][\text{BH}_4]_2$ may first undergo a phase transformation to form B_2H_7^- rather than directly release H_2 upon heating.

3.5 Formation of NH_3BH_3 Intermediate

Figure 6. Calculated energy barrier, and initial (IS), transition (TS) and final (FS) geometric structure of NH_3BH_3 formation via (a) combining BH_3 from B_2H_7^- with NH_3 (b)

combining BH_3 from BH_4^- with NH_3 . E_b represents the calculated energy barrier.

A previous study suggests that B_2H_7^- would combine with NH_3 to form NH_3BH_3 and BH_4^- in gas phase.³⁷ It would be interesting to examine whether or not this process can occur in $[\text{Zn}(\text{NH}_3)_2][\text{BH}_4]_2$. As shown in Figure 6a, we calculated the rearrangement pathway in which a BH_3 from B_2H_7^- combines with a NH_3 to form NH_3BH_3 and BH_4^- fragments through $\text{FS4} \rightarrow \text{TS5} \rightarrow \text{FS5}$. The reaction pathway was simplified as the following equation:

This rearrangement is an exothermal process with a reaction barrier of 1.15 eV (1.30 eV including zero-point energy correction). To take the rearrangement enthalpy from BH_4^- to B_2H_7^- into account, the effective barrier for NH_3BH_3 formation via $\text{IS1} \rightarrow \text{TS4} \rightarrow \text{FS4} \rightarrow \text{TS5} \rightarrow \text{FS5}$ is 1.71 eV (1.93 eV including zero-point energy correction).

An alternative pathway to form the NH_3BH_3 intermediate can be achieved through combination of a BH_3 from BH_4^- and a NH_3 in $[\text{Zn}(\text{NH}_3)_2][\text{BH}_4]_2$, with a remaining hydride bonding to the Zn cation (Figure 6b). This reaction pathway was simplified as the following equation:

As shown in Figure 6b, the geometry of TS6 shows that the Zn cation assists the formation of the NH_3BH_3 intermediate by extracting a hydride from BH_4^- to form the Zn-H ionic bond. The Zn-H distance in TS6 is $\sim 1.55 \text{ \AA}$, similar to that in TS4. As shown in Figure 6b, the calculated energy barrier of direct formation of NH_3BH_3 intermediate via $\text{IS1} \rightarrow \text{TS6} \rightarrow \text{FS6}$ is 1.59 eV (1.54 eV including zero-point energy correction), which is comparable to the formation of B_2H_7^- ($2\text{BH}_4^- \rightarrow \text{B}_2\text{H}_7^- + \text{H}^-$, $\text{IS1} \rightarrow \text{TS4} \rightarrow \text{FS4}$ as shown in Figure 5). Therefore, the NH_3BH_3 and B_2H_7^- intermediates may co-exist during the decomposition of $[\text{Zn}(\text{NH}_3)_2][\text{BH}_4]_2$.

3.6 Discussion

Our above calculation compared the numbers of possible reaction pathways and indicated that the release of B_2H_6 and BH_3 is kinetically and/or thermodynamically unfavorable for $[Zn(NH_3)_2][BH_4]_2$, in agreement with experimental results that no borane byproducts were detected during decomposition.

To better illustrate the decomposition mechanism of $[Zn(NH_3)_2][BH_4]_2$, the calculated reaction pathways with relatively low energy barriers including zero-point energy correction were summarized in Figure 7 and Table S1. As shown in Figure 7, our calculation results indicate the formation of NH_3BH_3 (via $IS1 \rightarrow TS6 \rightarrow FS6$) and $B_2H_7^-$ intermediates (via $IS1 \rightarrow TS4 \rightarrow FS4$) with comparable reaction barrier.

Figure 7 Energy profile of the formation of NH_3BH_3 and $B_2H_7^-$ intermediates (including the zero-point energy correction).

Figure 8. Bond number analysis for decomposition of $[\text{Zn}(\text{NH}_3)_2][\text{BH}_4]_2$.

To further examine the decomposition mechanism discussed above, AIMD simulation was performed using a $2 \times 1 \times 2$ supercell of $[\text{Zn}(\text{NH}_3)_2][\text{BH}_4]_2$ which contains 152 atoms. As shown in Figure 8a, from 0 to 10 ps (10 000 fs), the number of Zn-N bonds remains unchanged, indicating that the NH_3 molecules still coordinates with Zn cations. The number of Zn-B bonds fluctuates from 16 to 10 because of the rotation of BH_4^- around Zn cations. With the simulation time increasing from 10 to 20 ps (20 000 fs), the number of Zn-N bonds starts to decrease, indicating that some of NH_3 molecules detach from Zn cations. Figure 8b shows that the number of N-B and H-H bonds remains zero before 20 ps (20 000 fs), suggesting that no N-B relative intermediates or H_2 were formed. With the simulation time increasing from 20 to 40 ps (40 000 fs), the formation of N-B (started at ~ 21 000 fs) and H-H bonds (started at ~ 24 000fs) were observed.

Figure 9. Schematics of the formation of NH_3BH_3 (a-c) and B_2H_7^- (d-e) observed in our AIMD simulations. The intermediates are highlighted as ball and stick, other atoms are represent as line.

The MD trajectories in Figure 9a-9c show the formation of the NH_3BH_3 intermediate via combination of NH_3 and BH_4^- with a remainder H^- bonding to the Zn cation from simulation time of 20 869 fs to 21 025 fs. As shown in Figure 9d and 9e, two BH_4^- combine to form B_2H_7^- from the simulation time of 24 166 fs to 24 173 fs. The above MD calculation results indicate that the Zn cation assists the formation of NH_3BH_3 and B_2H_7^- intermediates by extracting a hydride from BH_4^- to form the Zn-H ionic bond, in consistent with our above CI-NEB calculation results.

Figure 10. Schematics of the release of H_2 observed in our AIMD simulations. The intermediates are highlighted as ball-and-stick models, and the other atoms are represent as line.

The MD trajectories show two initial dehydrogenation pathways as presented in Figure 10 and 11. As discussed above, the Zn cation extracts a hydride from BH_4^- to facilitate the formation of NH_3BH_3 and B_2H_7^- intermediates. Figure 10a-10c shows that the extra hydride on Zn cation transfers to the neighboring BH_4^- with the formation of $\text{BH}_3\text{-H}_2$ intermediate. $\text{BH}_3\text{-H}_2$ intermediate further combines with NH_3 to form H_2 and NH_3BH_3 (Figure 10d). The simplified reaction pathways were summarized as following:

Figure 11. Schematics of the formation of NH_4^+ (a-b) and release of H_2 (c-e) observed in our AIMD simulations. The intermediates are highlighted as ball and stick, other atoms are represent as line.

As shown in Figure 11a and 11b, the formation of NH_3BH_3 facilitates the H_2 release by transferring a proton from NH_3BH_3 intermediate to NH_3 , with the formation of NH_4^+ and NH_2BH_3^- . The NH_2BH_3^- fragment further rotates and bonds to the vicinal Zn cation. The NH_4^+ fragment migrates and combines with a BH_4^- to form H_2 , NH_3 and BH_3 as shown in Figure 11c-11e.

The simplified reaction pathways were summarized as following:

The remaining BH_3 fragment could combines with NH_3 to form NH_3BH_3 or combine with BH_4^- to form B_2H_7^- as discussed above.

4. Conclusions

DFT calculation has been employed to investigate the decomposition mechanism of $[\text{Zn}(\text{NH}_3)_2][\text{BH}_4]_2$. Our calculation indicates that the formation of B_2H_6 and BH_3 is kinetically and/or thermodynamically unfavorable for $[\text{Zn}(\text{NH}_3)_2][\text{BH}_4]_2$, which explains the experimental observation that no B_2H_6 or BH_3 byproducts were detected during thermal decomposition. On the other hand, our calculation indicates that the decomposition mechanism of $[\text{Zn}(\text{NH}_3)_2][\text{BH}_4]_2$ is different from those of other reported AMBs, which releases H_2 via directly combining hydrides from BH_4^- and protons from NH_3 . The $[\text{Zn}(\text{NH}_3)_2][\text{BH}_4]_2$ is able to form NH_3BH_3 and B_2H_7^- intermediates during decomposition. The Zn cation assists the formation of NH_3BH_3 and B_2H_7^- intermediates by extracting a hydride from BH_4^- to form the Zn-H ionic bond. Our calculation also indicates that the dehydrogenation occurs through the following two reaction pathways: transfer of a hydride from the Zn cation to BH_4^- with the formation of $\text{BH}_3\text{-H}_2$, which further combines with NH_3 to form H_2 and NH_3BH_3 and transfer of a proton from NH_3BH_3 to NH_3 with the formation of NH_4^+ , which combines with BH_4^- to release hydrogen. We hope that our findings may provide useful insights for improving the dehydrogenation properties of $[\text{Zn}(\text{NH}_3)_2][\text{BH}_4]_2$ as well as offer guidelines for designing novel Zn-based ammine borohydrides for hydrogen storage.

Conflicts of interest

There are no conflicts to declare

Supporting Information

Calculated reaction pathways of $[\text{Zn}(\text{NH}_3)_2][\text{BH}_4]_2$ with relatively low energy barriers including zero-point energy correction.

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