

PAPER



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Promotion mechanisms of LiBH_4 dehydrogenation dominated by charge redistribution†

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LiBH_4 is a promising solid-state hydrogen storage material, but its complex dehydrogenation reaction mechanism severely hinders the regulation of dehydrogenation barriers and reversibility. To elucidate the micro-mechanism of its dehydrogenation reaction, the potential of mean force method, *ab initio* molecular dynamics simulations, and the electronic structure through density functional theory with Grimme D3 dispersion corrections have been conducted for different surfaces of LiBH_4 . The dehydrogenation barriers of various surfaces typically fall within the range of 110.84–122.96 kJ mol^{-1} . The dehydrogenation barrier can be remarkably reduced from 110.84 to 70.6 kJ mol^{-1} , as the concentration of Li vacancies varies from 0 to 12.5%. Besides, doping transition metals (TMs) can effectively reduce the dehydrogenation barrier of LiBH_4 (74.28–104.06 kJ mol^{-1}). The existence of Li vacancies results in the loss of electrons in the shared electron pairs of B–H bonds and weakens the strength between B–H covalent bonds. The TMs doping makes the B–H bonds gain electrons, which occupy the antibonding orbitals and result in weakening the B–H bond strength. Consequently, the dehydrogenation barriers of LiBH_4 are significantly reduced. This work reveals two different promotion mechanisms for Li vacancies and TMs doping, and provides a new perspective for lowering its dehydrogenation temperature in future experiments.

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1 Introduction

In the current common hydrogen storage measures, solid-state hydrogen storage is recognized as a promising technology owing to its high density and good safety.^{1,2} Therefore, various hydrogen storage materials have been studied, such as metal hydrides,^{3–6} nano-carbon materials,⁷ and metal–organic frameworks.⁸ Amongst these, lithium borohydride (LiBH_4) has garnered considerable attention as a light metal hydride due to its high hydrogen storage capacity up to 18.4 wt%.^{9,10} However, the dehydrogenation temperature of LiBH_4 is relatively high, which severely hinders its engineering application. In experiments, the dehydrogenation temperature of LiBH_4 has been found to range between 400 and 500 °C,^{10,11} and the corresponding theoretical calculation dehydrogenation barrier range is from 101 to 156 kJ mol^{-1} .^{12–14}

To promote further development and utilization of LiBH_4 , various experimental approaches have been employed to lower the dehydrogenation temperature, such as nano-engineering,^{15,16} catalyst doping,^{17,18} substitution,^{19,20} and

component mixing.²¹ For example, the dehydrogenation temperature of LiBH_4 can be reduced from 347 °C to 217 °C by doping SrH_2 into LiBH_4 .¹⁸ The $\text{LiBH}_4/\text{SrH}_2$ system can reduce the dehydrogenation enthalpy from 67 to 48 $\text{kJ mol}^{-1} \text{H}_2$,²² and activation energy from 156 to 64 kJ mol^{-1} .²³ Other similar results can be observed in LiBH_4 -nanoporous carbon scaffolds,¹⁶ LiBH_4 -Ca instead of Li,¹⁹ LiBH_4 -chromocene and nickelocene,¹⁷ and LiBH_4 - $\text{Mg}(\text{BH}_4)_2$.²¹ Nevertheless, there is still a certain gap between the current experimental results and the target of dehydrogenation temperature proposed by U.S. DOE (60 °C). Therefore, reducing the dehydrogenation temperature of LiBH_4 to achieve the application target remains a challenge. The dehydrogenation mechanism of LiBH_4 remains unclear due to the complex dehydrogenation pathways, the presence of multiple intermediates, and the occurrence of phase transitions. This has resulted in the absence of a key factor that affects the dehydrogenation barriers being identified. Therefore, unraveling the micro-mechanism of dehydrogenation is the key to breaking through the current dilemma of LiBH_4 application.

Recently, density functional theory (DFT) calculations have been successfully applied to reveal the micro-mechanism of dehydrogenation processes, such as the “burst effect” of MgH_2 dehydrogenation²⁴ and the kinetic model of metal hydrides.²⁵ Therefore, applying DFT calculations to the micro-mechanism of dehydrogenation of LiBH_4 should be significant and effective. To improve the dehydrogenation performance of LiBH_4 , Liu *et al.*²⁶ doped Ti on different surfaces of LiBH_4 . This results

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in weakening the strength of B–H bonds and reducing the dehydrogenation barriers. Du *et al.*^{12,27} applied the DFT method to calculate the dehydrogenation barrier of LiBH_4 . By using the (010) surface model and the climbing-image nudged elastic band (CI-NEB) method, the calculated value ($349.44 \text{ kJ mol}^{-1}$) is approximately 194 kJ mol^{-1} higher than the experimental result.¹⁰ Although many DFT calculations have been carried out to reveal the micro-mechanism, the difference between DFT calculations and experimental results is still obvious. This is because of the difference between the melting disordered structure in experiments²⁸ and the ordered crystal structure in DFT calculations.^{12,29} In addition, the dehydrogenation paths obtained by transition state theory (TST) are random and insufficient, compared to complex dehydrogenation paths and various intermediates in experiments. Therefore, selecting a better method, which can calculate the disordered structure based on the molten state and has statistical characteristics, can describe the dehydrogenation barrier of LiBH_4 more accurately.

In this work, the dehydrogenation mechanism of LiBH_4 on different surfaces was comprehensively explored through DFT calculations. The melted disordered structure of LiBH_4 has been successfully observed through *ab initio* molecular dynamics (AIMD) simulation. The dehydrogenation barrier of LiBH_4 was calculated through the potential of mean force (PMF) method based on the statistical average characteristics in the dynamic simulation process. The promoting effect of Li migration on the dehydrogenation of LiBH_4 was revealed. Importantly, constructing Li vacancies (V_{Li}) and doping transition metals (TMs) can remarkably reduce the dehydrogenation barrier, providing an efficient avenue for tuning the dehydrogenation temperature of LiBH_4 .

2 Computational method

In this study, the bulk LiBH_4 structure is shown in Fig. 1a. It has lattice parameters of $a = 7.14 \text{ \AA}$, $b = 4.29 \text{ \AA}$, and $c = 6.748 \text{ \AA}$,

which is consistent with experimental reports^{10,14,28} (with errors less than 5%, as shown in Table S1†). Besides, the X-ray diffraction (XRD) pattern of the LiBH_4 primitive cell is consistent with that reported in previous experiments (as shown in Fig. 1a).^{10,14} DFT implementation in CP2K/Quickstep³⁰ was based on a hybrid Gaussian plane wave (GPW) scheme, the orbitals were described by an atom centered Gaussian-type basis set, and an auxiliary plane wave basis set was used to re-expand the electron density in the reciprocal space. The Perdew–Burke–Ernzerhof (PBE) functional was employed to describe the exchange–correlation functional, with all calculations incorporating Grimme D3 (DFT-D3)^{31,32} dispersion correction. The calculations used Goedecker–Teter–Hutter (GTH) pseudopotentials^{33,34} and the Gaussian basis set was double-zeta with one set of polarization functions (DZVP).³⁵ Initially, the structure of LiBH_4 was optimized. In the structural optimization, a matrix diagonalization procedure was used to optimize the wave function. In addition, geometrical configurations were optimized using the Broyden–Fletcher–Goldfarb–Shanno (BFGS) minimizer in calculations with the plane wave cutoff energy set to 400 Ry and a $(5 \times 5 \times 5)$ Monkhorst–Pack k -point grid was employed. The k -point and cutoff parameter test results are shown in Tables S2 and S3.† The convergence of the self-consistent field was set at 10^{-6} a.u. The convergence of maximum displacement and force of each atom were set at 0.003 bohr and $0.00045 \text{ hartree bohr}^{-1}$, respectively; the convergence of root-mean-square displacement and force of each atom were set at 0.0015 bohr and $0.0003 \text{ hartree bohr}^{-1}$, respectively. The geometries were deemed to be relaxed when all four criteria were met. Then, the optimized structure was sliced into different facets, each with a 15 Å vacuum layer in the Z -direction to avoid periodic effects.

For sampling the melted structure of the LiBH_4 , AIMD simulations were employed and canonical ensemble conditions were imposed by canonical sampling through a velocity rescaling thermostat. The MD time step was set to 1 fs. For all the MD trajectories, the initial simulation results of 2 ps (2000

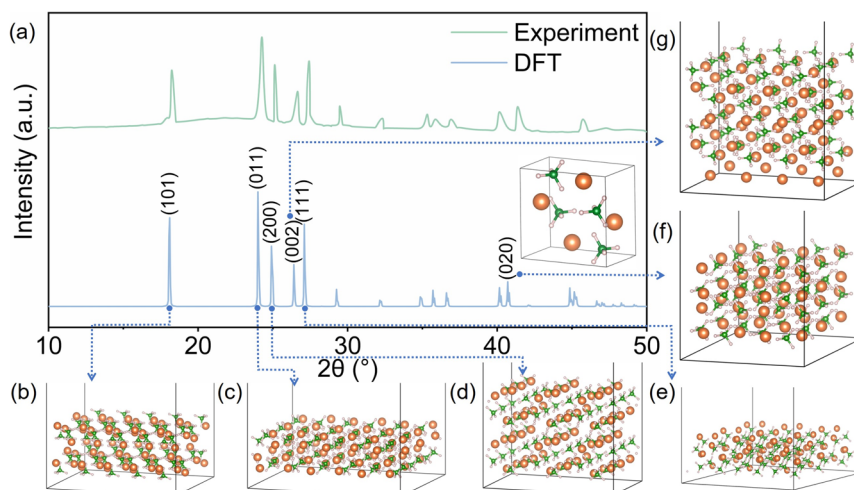


Fig. 1 (a) The XRD of the calculated structure is compared with experiments, and the primitive cell of LiBH_4 . (b)–(g) Initial structures after cell expansion for the LiBH_4 (101), (011), (200), (111), (020) and (002) surfaces. White, yellow, and green spheres represent H, Li, and B, respectively.

steps) were abandoned to avoid the effect of non-equilibrium, and then subsequent results of 8 ps (8000 steps) were selected for dehydrogenation simulation. To increase the authenticity of the simulation, all surfaces were expanded and the specific expansion multiples and test values of cutoff are shown in Table S4.† Therefore, all MD calculations used the orbital transformation algorithm and the Γ point with cutoff energy was set to 300 Ry to relax the structures after expansion.

The post-processing analysis of AIMD used the visualization program VMD³⁶ to calculate the radial distribution functions (RDFs³⁷) of the B–H bonds. The potential of mean force (PMF^{38,39}) between B–H bonds can be obtained by further processing the RDFs of B–H bonds using eqn (1). The PMF can be calculated as:

$$\Delta G_a(r) = k_B T \ln \frac{g_{\max}(r)}{g_{\min}(r)} \quad (1)$$

where k_B is Boltzmann's constant, T is the environmental temperature, but this is always 1100 K in our calculations, $\Delta G_a(r)$ is the dissociation energy of B–H bonds, and $g_{\max}(r)$ and $g_{\min}(r)$ are, respectively, the maximum and minimum values of RDFs. Besides, to obtain the mean squared displacement (MSD) curves and the fitting slopes for different atoms, GROMACS⁴⁰ was used to further process the MD trajectories. The diffusion coefficient was calculated using the following equation:

$$D = \lim_{t \rightarrow \infty} \left[\frac{1}{2dt} \left\langle [\vec{r}(t)]^2 \right\rangle \right] \quad (2)$$

where d is the dimension ($d = 3$), $[\vec{r}(t)]^2$ is the MSD and t is the simulation time. In this study, Mayer bond order values were obtained using Multiwfn3.8 (dev).⁴¹ The electronic density difference was calculated to analyze the electron transfer upon LiBH₄ with V_{Li} and TMs doping. To analyze the stability of B–H bonds, the Crystal Orbital Hamiltonian Population (COHP) method was employed,^{42,43} and the results were calculated using the LOBSTER package.^{44,45} To quantitatively analyze the strength of B–H bonds, Integrated Crystal Orbital Hamilton Population (ICOHP) was calculated. The opposite of ICOHP (–ICOHP) was selected as the independent variable, which ensured consistency with the normal understanding that small values correspond to weaker strengths.

3 Results and discussion

3.1 Surface structures of LiBH₄ and atomic migration in AIMD simulation

According to the XRD of LiBH₄ bulk in the experiment,¹¹ the dominant surfaces are selected based on its intensity peak of XRD, including (002), (020), (011), (200), (101) and (111) surfaces, as illustrated in Fig. 1b–g. The specific parameters of the six surfaces, including cell parameters and atomic numbers, are provided in Table S5.† Considering the consistency of the six surfaces, the surfaces with orthorhombic crystal structures ((002), (020), (011), (200) and (101)) were chosen for the subsequent investigations.

Numerous experiments^{11,28,46} have demonstrated that the dehydrogenation process of LiBH₄ is accompanied by a phase transition (from solid to molten state). However, the structural evolution and atomic migrations that occur during the melting process remain unrevealed. To observe the dynamic change

process, AIMD simulation with time-evolving properties is employed to observe the dynamics evolution. According to the experimental results,¹⁰ the melting temperature of LiBH₄ is around 280 °C and the dehydrogenation temperature is approximately 460 °C. Therefore, to facilitate the observation of the experimental phenomena, the target temperatures of simulations were selected to be 500 K, 700 K, 900 K and 1100 K. Each MD time step was set to 1 fs and the total period was 10 ps (10 000 steps). Fig. 2a illustrates the MD trajectories on (101) at different temperatures in detail, while Fig. S1–S4† depict the MSD curves of other surfaces. To verify the consistency between our calculations and experimental phenomena, the snapshots corresponding to 0, 3333, 6666, and 10 000 fs at $T = 1100$ K were selected as references. A comparison between the ordered structures at 0 fs and the disordered structures at 3333 fs reveals a notable transformation. The corresponding dynamic graphs are presented in Table S6,† which clearly illustrates the transformation process of different surfaces from an ordered state to a disordered one. The disordered structures cause the diversity and complexity of the intermediate products in the LiBH₄ dehydrogenation process. The process of LiBH₄ transformation from order to disorder has been successfully observed through MD simulations, thereby deepening the understanding of the underlying micro-mechanism. Since the RDFs can be used to investigate the order of a material, the RDFs of the initial (0 fs) and final (10 000 fs) simulation structures of LiBH₄ (101) at different temperatures are calculated (as shown in Fig. 2c and d). In comparison to the final structure, the initial structure has much higher and deeper peaks. The peaks of B–H are higher than those of B–B, but the RDFs curve of B–B displays more obvious peaks, which is due to the characteristics of crystal order in the initial structure. In contrast, when heated to temperatures of 700 K, 900 K and 1100 K, the ordered structure melts into disordered structures, making the RDFs curves continuous and smooth. The RDFs curves of other surfaces are shown in Fig. S5–S12.†

As shown in Table S6,† the internal atoms of LiBH₄ exhibit disorder at high temperatures. However, the underlying mechanism governing the migration of these atoms remains unclear. Therefore, investigating the process of atomics migration is the significant emphasis of the subsequent work. Since the BH₄ group displays collective motion, the H and Li atoms are chosen for calculating the MSD; the corresponding curves are shown in Fig. S13–S17.† As shown in Fig. 2a and S1–S4,† the movement of H atoms at low temperatures ($T = 500$ K, 700 K) is not significant. Consequently, the variation curves of the MSD of H along with the MSD of Li at 900 K for all different surfaces are plotted (as shown in Fig. 2b), demonstrating that the MSD of H increases with the increase of Li. The differences in the synergistic effects of Li and H exist in different surfaces, but they are insignificant. Similarly, the migration of Li has an evident promoting effect on the migration of H. Among them, the surface of LiBH₄ (002) has a slightly significant effect.

3.2 Dehydrogenation barrier of LiBH₄

Due to the complex and various dehydrogenation pathways of LiBH₄, using the traditional TST is difficult to capture

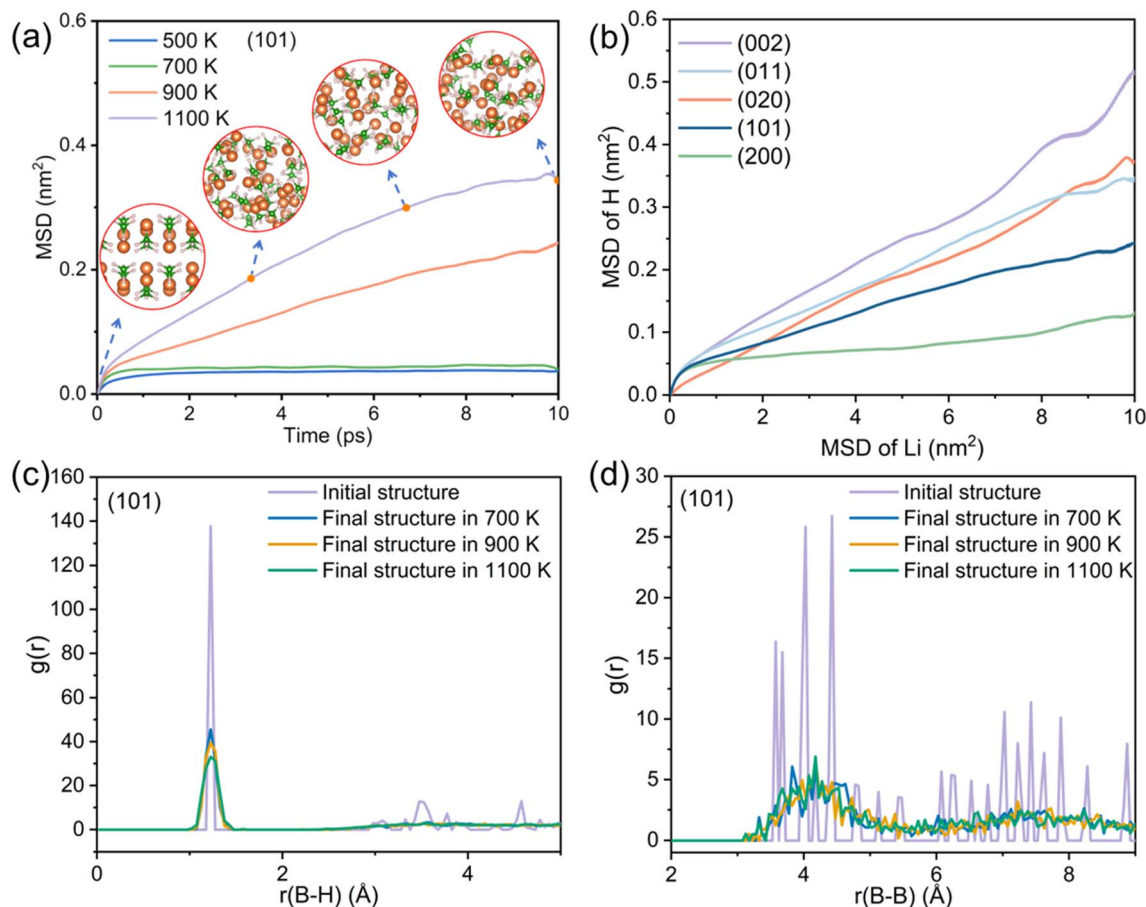


Fig. 2 (a) The MSD curves of hydrogen atoms at different temperatures for the LiBH₄ (101) surface. The red circle shows the atomistic snapshots at the corresponding time. White, yellow, and green spheres represent H, Li, and B, respectively. (b) The change curves of the MSD of H along with the MSD of Li for different surfaces at $T = 900$ K. (c and d) RDFs of B-H and B-B of initial and final structures at different temperatures for the LiBH₄ (101) surface.

a comprehensive reaction pathway. The gap in dehydrogenation barriers between calculated and experimental results is still significant. Therefore, the PMF algorithm is employed to calculate dehydrogenation barriers to avoid the randomness in calculation. In our studies, the PMF is based on the calculations of RDFs between B and H, which are obtained by the statistical average of the entire process of MD. Subsequently, the RDFs obtained at 1100 K is selected and the PMF of different surfaces is calculated using eqn (2). Finally, the dehydrogenation barriers calculated in this work (histogram) and previous studies (green dots) on different surfaces are shown in Fig. 3a. The light grey background represents the range of experimentally measured dehydrogenation barriers for LiBH₄.

As shown in Fig. 3a, the dehydrogenation barriers calculated in this study are distributed within the range of 110.84–122.96 kJ mol⁻¹, which is within the range of the experimental measurements (101–156 kJ mol⁻¹).^{10,13,16} The results indicate that our DFT calculation results are reasonable and reliable. Compared with previous DFT calculation results,^{12,27,29,47} our calculations are closer to experimental results due to consideration of the statistical characteristics. According to the experimental results,¹⁰ the dehydrogenation of LiBH₄ occurs

subsequent to melting; different surfaces need to melt and then dehydrogenate. Therefore, although the different surfaces exhibit certain differences, the dehydrogenation barriers only have some slight differences (the maximum is approximately 12 kJ mol⁻¹). This also indirectly demonstrates the rationality of our calculation results. So far, this work has produced the most closely aligned theoretical calculation results with experimental reports. Subsequently, an investigation is conducted into the relationship between the dehydrogenation barriers and the corresponding diffusion coefficients of Li on different surfaces, as illustrated in Fig. 3b. The results demonstrate a clear linear relationship between the dehydrogenation barriers and the corresponding diffusion coefficients of Li, indicating a reduction in the barriers with an increase in the diffusion coefficients. Our theoretical research indicates that there is a promotion effect of Li migration on the dehydrogenation of LiBH₄, which is consistent with the current experimental results.⁴⁸

3.3 The effect of Li vacancies on dehydrogenation of LiBH₄

Since Li migration can facilitate the reduction of dehydrogenation barriers, a hypothesis is put forward: after the migration

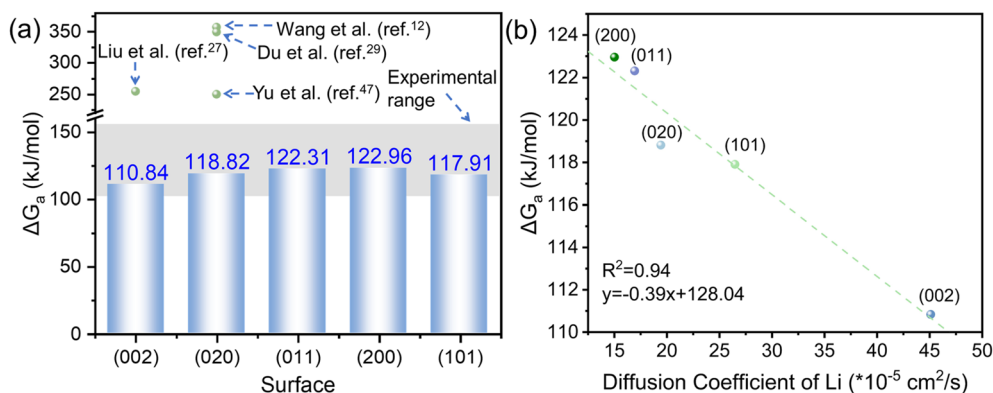


Fig. 3 (a) Histogram of dehydrogenation barriers on different surfaces; the light grey background and green dots represent the dehydrogenation barriers of the experimental range and the previous theoretical calculations, respectively. (b) The relationship between dehydrogenation barriers of different surfaces and the corresponding diffusion coefficients of Li ions.

of Li ions, the corresponding BH_4 group changes the electron distribution, which weakens the strength of B–H bonds and reduces the dehydrogenation barrier. Then, some simulation experiments are performed with V_{Li} on LiBH_4 (002), which has the lowest dehydrogenation barriers. The same method (PMF) is used to calculate the dehydrogenation barriers of the surface with V_{Li} . The structures with V_{Li} are presented in a graph of dehydrogenation barriers *versus* the concentration V_{Li} (as shown in Fig. 4), and the dehydrogenation process at different V_{Li} concentrations can be clearly seen in Table S7.† The dynamic process clearly demonstrates that the existence of V_{Li} contributes to dehydrogenation.

As shown in Fig. 4, the structures with V_{Li} concentrations of 0%, 3.13%, 6.25%, 9.38% and 12.5% are selected for presentation. Besides, the dehydrogenation barrier is only $96.33 \text{ kJ mol}^{-1}$ when the system exists with 1.56% V_{Li} concentration, which is a reduction of $14.51 \text{ kJ mol}^{-1}$ compared to that of the original system. When the V_{Li} concentration is increased to 3.13%, the dehydrogenation barrier decreases to $79.96 \text{ kJ mol}^{-1}$. This is $16.37 \text{ kJ mol}^{-1}$ lower than the barrier when the concentration is 1.56%. As the concentration of V_{Li} increases,

the change of barrier becomes less noticeable. From the fitting curve, the barrier decreases significantly when the concentration of V_{Li} is low. However, when the concentration of V_{Li} exceeds 3.13%, the changes of barrier become smoother. Furthermore, this phenomenon demonstrates our hypothesis that the presence of V_{Li} promotes dehydrogenation. In current theoretical calculations, decreasing the dehydrogenation barriers by increasing the concentrations of V_{Li} is an extremely effective measure,^{12,27} which can reduce the original barrier by 36.3%.

3.4 The effect of transition metals doping on dehydrogenation of LiBH_4

Previous experimental study has indicated that doping TMs can effectively reduce the dehydrogenation temperature.⁴⁹ In detail, LiBH_4 doping with Ti, V and Cr can reduce the dehydrogenation temperature from 450°C to approximately 420°C .⁴⁹ Besides, numerous experiments have used the mixture of LiBH_4 and MCl_2 ($\text{M} = \text{Mn, Fe and Co}$) to form $\text{M}(\text{BH}_4)_2$, thereby reducing the stability and the dehydrogenation temperature of LiBH_4 .^{50,51}

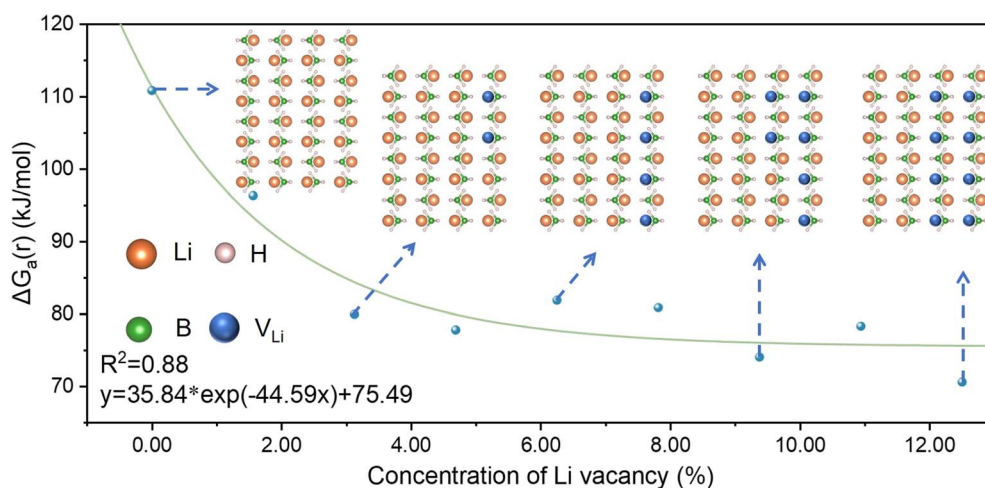


Fig. 4 The relationship of the dehydrogenation barrier of the LiBH_4 (002) surface with the concentrations of V_{Li} .

By doping MCl_2 , the dehydrogenation temperature of LiBH_4 can be effectively reduced to 230–300 °C. TMs play a major role in the process of MCl_2 doping. Therefore, to explore the effect of TMs doping, LiBH_4 with TMs doping (including Ti, V, Cr, Mn, Fe, Co and Cu) is investigated by calculating the dehydrogenation barriers.

The structure of the doping system is illustrated in Fig. 5a and b. To compare the effects of doping and vacancy, the position of TMs doping is maintained in accordance with that of V_{Li} . The dehydrogenation barriers of TMs doping are shown in Fig. 5, with the range of 74.28–104.06 kJ mol^{-1} . In comparison to the original system, TMs doping has also been demonstrated to be an effective method for reducing the dehydrogenation barrier of LiBH_4 . This is consistent with the phenomenon of decreasing the dehydrogenation temperature after TMs doping in the experiment.^{49,50} Compared with other TMs doping systems, the dehydrogenation barrier of Co doping is the lowest. In the experiment, compared with MnCl_2 and FeCl_2 , the doping of CoCl_2 can most effectively reduce the

dehydrogenation temperature of LiBH_4 from 450 °C to 230 °C.^{50,51} This is consistent with our theoretical calculation results.

3.5 Electronic structure analysis

Although there is a promotion effect of V_{Li} and TMs doping on decreasing dehydrogenation barriers, the inherent mechanism remains unclear.

First, to further uncover the internal reason that the surface containing V_{Li} can reduce the barriers, an analysis is conducted on the charge distribution. The charge of BH_4 groups which are arranged in the surface layer is calculated (Fig. 6a). As shown in Fig. 6a, the charge of the original BH_4 groups distributes within the range of -0.5 to $-0.4e$. When considering the effect of V_{Li} , the charge distribution range of the BH_4 groups becomes larger (-0.6 to $0.4e$), and the average charge of BH_4 groups gets closer and closer to zero, indicating that with the increase of V_{Li} , the BH_4 groups lose electrons. Furthermore, to reveal the inherent reasons for the weakening of the B–H bond strength, the structure with V_{Li} concentration of 1.56% is selected to calculate the electronic density difference (Fig. 6b). According to Fig. 6b,

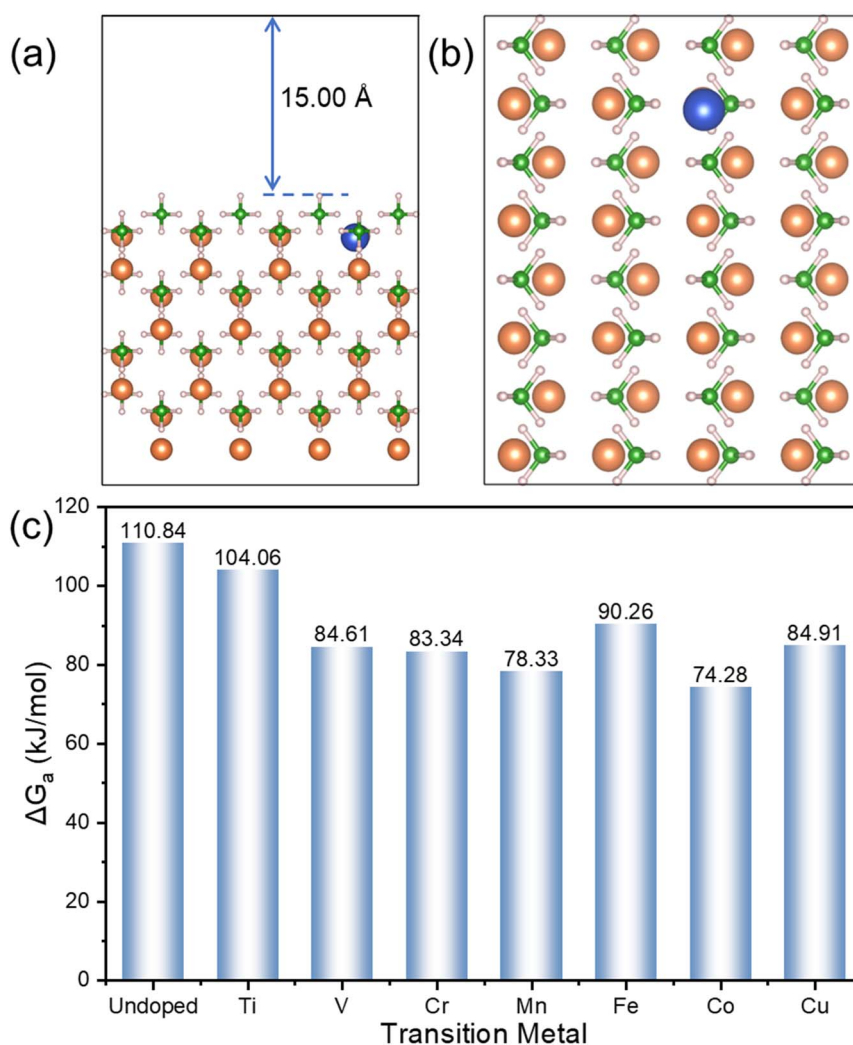


Fig. 5 Structure of LiBH_4 (002) with TMs doping, (a) front view; (b) top view. White, yellow, green, and blue spheres represent H, Li, B, and TMs (including Ti, V, Cr, Mn, Fe, Co and Cu), respectively. (c) Dehydrogenation barriers histogram of LiBH_4 (002) with TMs doping.

these BH_4 groups lose electrons and the gained electrons are mainly concentrated at the V_{Li} sites. As the B–H bonds lose electrons, the number of electrons in the covalent bonds may decrease. To verify this assumption, the Mayer bond order of the B–H bond with different concentrations of V_{Li} was calculated (Fig. 6c). The physical essence of the Mayer bond order reflects the number of electrons shared between atoms. For bonds of the same type, there is a positive correlation between bond order and bond strength. As shown in Fig. 6c, with the

increase of V_{Li} , the bond order of the B–H bond is significantly reduced. This indicates that the V_{Li} can weaken the strength of B–H bonds. Moreover, as shown in Fig. S18,[†] there is a significant linear relationship between the dehydrogenation barrier and the Mayer bond order. Based on the above analysis, the introduction of V_{Li} will cause the BH_4 groups to lose electrons, reducing the number of shared electrons in the B–H bond and thereby weakening the strength of the covalent B–H bond.

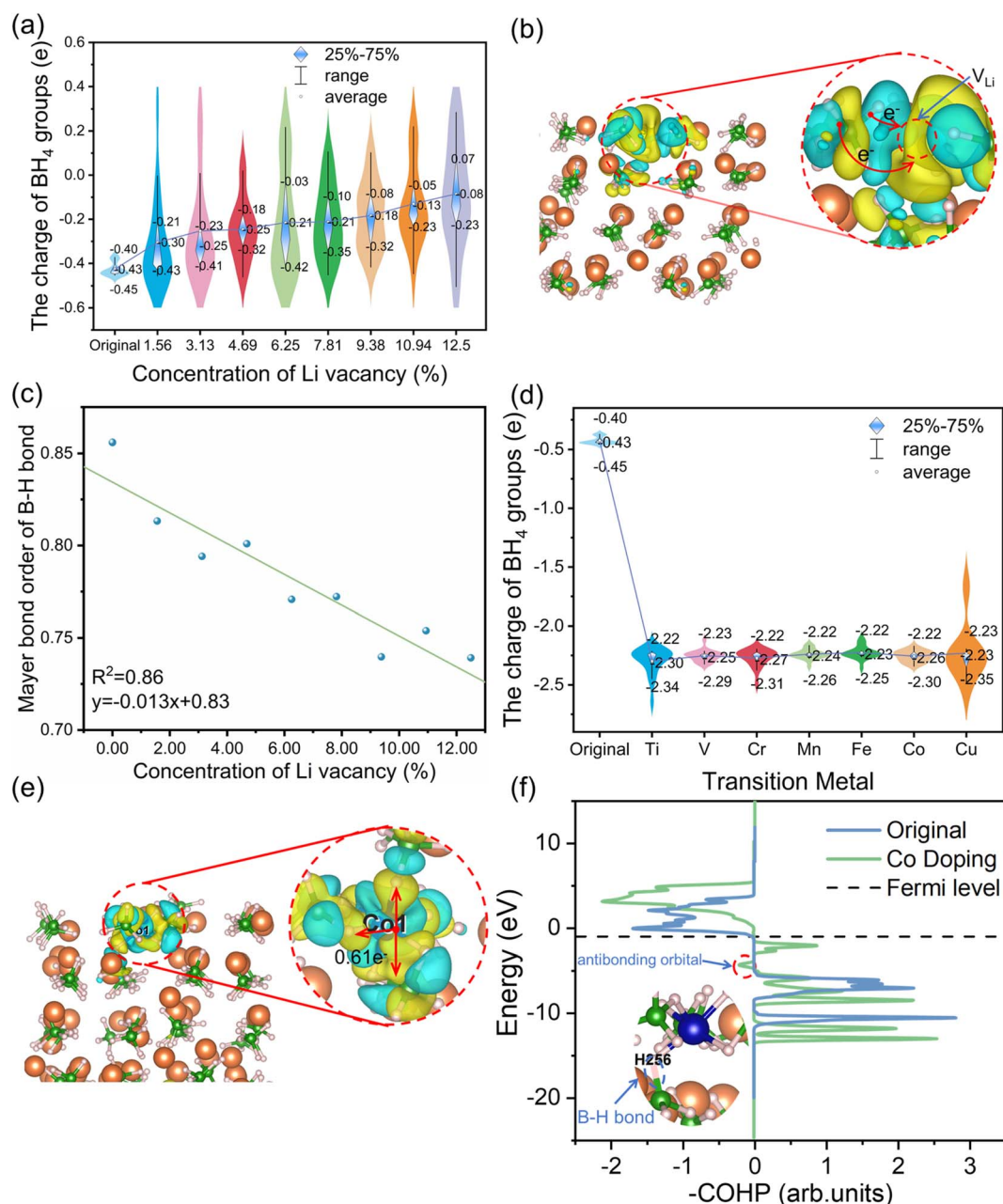


Fig. 6 (a) Charge distribution of the BH_4 group in the surface layer with the concentrations of V_{Li} . (b and e) Electronic density difference of V_{Li} and TM Co doping. The yellow and blue isosurfaces indicate electron accumulation and loss, respectively. The result is plotted with an isovalue of $0.001 \text{ e } \text{\AA}^{-3}$. The red arrows represent the direction of electron transfer. (c) The relationship of the average Mayer bond order of the B–H bonds in the surface layer and concentrations of V_{Li} . (d) Charge distribution of the BH_4 group in the surface layer with the TMs (Ti, V, Cr, Mn, Fe, Co and Cu) doping. (f) COHP analysis of the B–H bond in LiBH_4 (002) and Co doping; the dotted line indicates the Fermi level. White, yellow green, and blue spheres represent H, Li, B, and Co, respectively.

For the TMs doping systems, since the charge number carried by TMs is greater than that carried by Li, TMs tend to lose more electrons and exhibit a higher valence state. Therefore, during the pairing reaction of TMs with the BH_4 group, more electrons on the TMs transfer to the B–H bonds. The charge of the BH_4 group in TMs doping is calculated in Fig. 6d. The average charge of BH_4 groups becomes more negative after TMs doping. By comparing Fig. 6a and d, the charge distribution in TMs doping is more concentrated and the average charge drops from -0.43 to $-2.25e$, indicating that the BH_4 groups gain more electrons. Moreover, according to the electronic density difference, the direction and specific amount of electron transfer are also shown in Fig. 6e and S19.† The electrons of the TMs are transferred to the BH_4 groups. These gained electrons are mainly concentrated at the BH_4 groups (especially in the B–H bond). To further identify the electrons occupation of the B–H bond after gaining electrons, the COHP curves of the B–H bond are plotted in Fig. 6f. Compared with the original system, there is an obvious occupation of the B–H antibonding orbitals, which is marked by a red circle. Based on the above analysis, introduction of TMs doping will cause the BH_4 groups to gain more electrons, making the gained electrons occupy the antibonding orbitals of the B–H bond, thereby weakening the strength of the B–H bond.

To further demonstrate that there are two different promotion mechanisms for V_{Li} and TMs doping, ICOHP of B–H bond was calculated to quantitatively explain the changes in B–H bond strength. The relationship between the dehydrogenation barrier and -ICOHP in V_{Li} and TMs doping is shown in Fig. S20 and S21.† In the systems with V_{Li} , there is no obvious correlation, which indicates that antibonding orbital occupation may not play a dominant role. However, Mayer bond order and the concentration of Li vacancies show an obvious linear relationship, suggesting that the covalent electron number in the B–H bond should play a crucial role. In the TMs doping systems, an obvious correlation exists between the dehydrogenation barrier and the -ICOHP. The dehydrogenation barrier lowers accordingly with the -ICOHP value decreasing, which further confirms the rationality of the promotion mechanism based on antibonding orbital occupation. Therefore, the different relationships between the dehydrogenation barrier and -ICOHP value in the system of V_{Li} and TMs doping can well demonstrate that the promotion mechanisms corresponding to V_{Li} and TMs doping are different.

In general, there are two different promotion mechanisms for V_{Li} and TMs doping. The essence of the two promotion mechanisms is to weaken the strength of the B–H bond and thereby reduces the dehydrogenation barrier. Specifically, for the V_{Li} , the electron flow direction is from the BH_4 groups to the V_{Li} , leading to a reduction in the number of electrons in the shared electron pairs of the B–H bond and weakening the strength of the B–H covalent bond. However, for TMs doping, the electron flow direction is from the doped metal to the BH_4 groups. The gained electrons occupy the antibonding orbitals of the B–H bond, thereby weakening the strength of the B–H bond.

4 Conclusion

Based on *ab initio* molecular dynamic simulations, the structural phase transition from ordered crystal to disordered molten state was well observed during the dehydrogenation process of LiBH_4 . Using the potential of mean force method with radial distribution functions, the dehydrogenation barrier of LiBH_4 was accurately evaluated by considering statistical characteristics. Different surfaces of LiBH_4 had similar dehydrogenation barriers in the range of 110.84 – $122.96 \text{ kJ mol}^{-1}$, which was consistent with the experimental results (101 – 156 kJ mol^{-1}). Interestingly, there is a promotion effect of Li vacancies and TMs doping on the reduction of LiBH_4 dehydrogenation barrier. The dehydrogenation barrier of LiBH_4 can be reduced to 70.6 kJ mol^{-1} when the Li vacancies concentration reaches 12.5% . Besides, TMs doping can also efficiently reduce the dehydrogenation barrier of LiBH_4 from 110.84 to $74.28 \text{ kJ mol}^{-1}$. Most importantly, the micro-mechanism of the promotion effect was successfully revealed by analyzing the charge distribution and electronic transformation. The existence of Li vacancies results in the loss of electrons in B–H bonds, which weakens the strength of B–H covalent bonds. However, TMs doping makes the B–H bonds gain more electrons, causing the gained electrons to occupy the antibonding orbitals, thereby weakening the strength of the B–H bond. The essence of the two promotion mechanisms is to weaken the strength of the B–H bond and thereby reduce the dehydrogenation barrier. This work shows that there are two different promotion mechanisms for Li vacancies and TMs doping, indicating the optimization direction for improving the dehydrogenation kinetics of LiBH_4 .

Data availability

Data are available upon request from the authors.

Author contributions

Weijie Yang: conceptualization, funding acquisition, supervision, resources, writing – original draft, writing – review & editing. Han Ge: data curation, formal analysis, investigation, methodology, software, validation, visualization, writing – original draft, writing – review & editing. Tongao Yao, Qiyong Chen, Feiyang Liu, and Mingye Huang: investigation, formal analysis, software. Junwei Sun: supervision, formal analysis. Shuai Dong: funding acquisition, supervision, resources, writing – review & editing. Yanfeng Liu: supervision, writing – review & editing. Zhengyang Gao: supervision, writing – review & editing. All authors contributed to writing the manuscript and have granted their approval for the final version.

Conflicts of interest

There are no conflicts to declare.

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