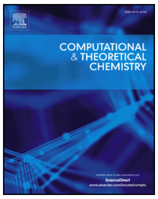
Computational and Theoretical Chemistry 1133 (2018) 33–39

Contents lists available at ScienceDirect

Computational and Theoretical Chemistry

journal homepage: www.elsevier.com/locate/comptc



Influence of transition metals Fe, Co, Ni, Cu and Ti on the dehydrogenation characteristics of $LiBH_4$: A first-principles investigation

Zhuonan Huang[a,b], Yuqi Wang[a,*], Di Wang[a], Fusheng Yang[c], Zhen Wu[c], Zaoxiao Zhang[c]

[a] School of Chemical Engineering, Northwest University, Xi'an 710069, PR China
[b] College of Chemistry and Chemical Engineering, Baoji University of Arts and Sciences, Shaanxi 721013, PR China
[c] School of Chemical Engineering and Technology, Xi'an Jiaotong University, Xi'an 710049, PR China

ARTICLE INFO

Keywords:
Density functional theory
Lithium borohydride
Hydrogen storage
Electronic structure

ABSTRACT

$LiBH_4$ is among a few chemicals with the highest hydrogen storage capacities. In this paper, the crystal structure, electronic structure and dehydrogenation properties of both pure and transition metal (TM = Fe, Co, Ni, Cu and Ti)-modified $LiBH_4$ were investigated by using first-principles calculations based on density functional theory. According to the computing results, the occupation energies of TM-doped $LiBH_4$ suggest that the metal atoms prefer to occupy interstitial sites rather than substitute a Li atom site. Meanwhile, the calculation results show that the TM-modified $LiBH_4$ could have decreased stability and that all the TM substitutions may kinetically favour H-desorption, due to the decrease in hydrogen removal energy during the H atom release process from the bulk. The electronic structure further proves that the TM modification tends to weaken the B—H bonding interaction, and that Ti-doped $LiBH_4$ has a good dehydrogenation performance, which is also confirmed by the reported experimental results.

1. Introduction

Hydrogen has attracted much attention due to its high abundance, light weight and environmental friendliness [1–3]. However, the lack of safe, efficient and economical hydrogen storage technologies hinders its practical application [4,5]. Compared with the traditional hydrogen storage methods such as high-pressure gas and liquid hydrogen, solid storage has the most potential and is the most prospective technology in the near future [6,7]. Among the solid materials developed for hydrogen storage, lithium borohydride ($LiBH_4$) has gained considerable interest due to its outstanding gravimetric and volumetric hydrogen densities of 18.5 wt% and 121 kg H_2/m^3 [8–10], respectively. Nevertheless, $LiBH_4$ desorbs hydrogen gas at a relatively high temperature (> 300 °C) due to the strong ionic bond between Li^+ and $[BH_4^-]$ [11,12]. Many investigations have been undertaken to improve the dynamic and kinetic properties of $LiBH_4$ in the past decades. The most common approach is to produce a complex hydride with $LiBH_4$ through the addition of oxides [13,14], amides [15], metals [16–19], metal halides [20] or metal hydrides [21,22].

Züttel et al. [12] reported that 75% $LiBH_4$ mixed with 25% SiO_2 can reduce the initial hydrogen release temperature to 200 °C. Yu et al. [14] studied the dehydrogenation of $LiBH_4$ destabilized with TiO_2, Nb_2O_5, Fe_2O_3, V_2O_5 and SiO_2, and found that Fe_2O_3 has a better destabilization effect on $LiBH_4$ than that of the others. The effect of divalent metal-dopants, Mg, Ca and Zn, on the stability of $LiBH_4$ was studied by Lee et al. [23], and they observed that the additions of Mg, Ca, and Zn do not significantly reduce the hydrogen storage capacity of $LiBH_4$. Moreover, the addition of Ca significantly reduces the H_2 release temperature due to the formation of highly stable CaB_6. An experimental study by Au et al. [24] discovered that metal additives such as $TiCl_3$, TiF_3 and ZnF_2 could effectively reduce the dehydrogenation temperature of $LiBH_4$. Guo et al. [25] found that $LiBH_4$-TiF_3 (mole ratio: 3:1) samples started to release hydrogen at approximately 100 °C, and that the hydrogen desorption capacity reached 5.0 wt% at 250 °C. Zhang et al. [26] presented the effects of MCl_2 (M = Fe, Co, and Ni) addition in various quantities on the dehydrogenation characteristics of $LiBH_4$, and the results indicated that the doping of small amounts of MCl_2 into $LiBH_4$ can effectively improve dehydrogenation kinetics of $LiBH_4$.

Although a number of effective or ineffective metal additives have been experimentally identified, the catalytic mechanism of transition metals is not fully understood, especially for the $LiBH_4$ system. In this work, we conducted the related calculations of pure and transition metal-doped $LiBH_4$ based on first principles. The geometrical structures, electronic structures, bonding interactions among atoms, and hydrogen removal energies of pure and TM-substituted $LiBH_4$ are discussed in detail. Understanding the effects of these substitutions in the $LiBH_4$

---

[*] Corresponding author.
E-mail address: wangyuqi@nwu.edu.cn (Y. Wang).

https://doi.org/10.1016/j.comptc.2018.04.017
Received 12 March 2018; Received in revised form 25 April 2018; Accepted 25 April 2018

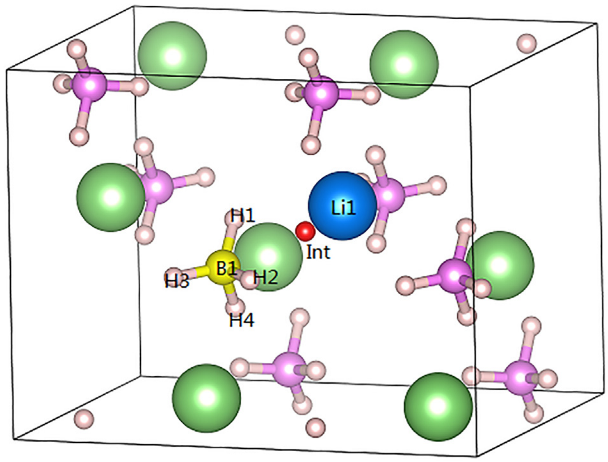


Fig. 1. Model of $LiBH_4$ with 1 × 2 × 1 supercell (Green, purple and pink spheres denote Li, B and H atoms). Blue and red spheres represent the substitution positions of Li1 atom site (0.345, 0.375, 0.611) and interstitial site (0.5, 0.5, 0.5). In $[BH_4]$ group, the four H atoms surrounding B1 atom (yellow sphere) are labeled with H1, H2, H3 and H4. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

systems contributes to the rational design and practical application of modified materials.

2. Models and computational details

Density functional theory (DFT) calculations with spin-polarization were carried out using the VASP code [27]. The electron-ion interactions were described by the projector augmented wave (PAW) [28,29]. The Perdew-Burke-Ernzerhof generalized gradient approximation (GGA-PBE) was used to describe the electronic exchange correlation functionals [30]. The plane-wave cutoff energy of 750 was found to be sufficient for pure $LiBH_4$ and TM-substituted $LiBH_4$. The Brillouin zones were sampled using 4 × 6 × 4 Monkhorst-Pack k-point meshes. A Gaussian smearing of 0.1 eV was employed in structure optimization. The electron self-consistent total energy was performed within 1.0×10^{-6} eV/atom, and the residual force was within 0.02 eV/Å in all cases. Spin polarization was considered for the transition metal-containing systems.

The crystal structure of $LiBH_4$ is an orthorhombic structure with the space group *Pnma* at room temperature and lattice parameters of a = 7.179 Å, b = 4.437 Å, c = 6.803 Å [31]. As is shown in Fig. 1, each $[BH_4]^-$ anion is surrounded by four Li^+ (lithium cations), and each Li^+ cation is surrounded by four $[BH_4]^-$ anions in both tetrahedral configurations. Pure $LiBH_4$ was fully relaxed to obtain the optimized lattice parameters a = 7.264 Å, b = 4.378 Å, c = 6.649 Å in our theoretical calculations. These values are in satisfactory agreement with experimental values [31].

3. Results and discussion

3.1. Structural properties and substituted $LiBH_4$

A TM is designed to add into the 1 × 2 × 1 supercell $Li_8B_8H_{32}$ by substitution for a Li atom and interstitial site, producing TM-Sub and TM-Int, respectively. The structures of TM-Sub and TM-Int were fully relaxed, in which the Li1 atom (0.345, 0.375, 0.611) or interstitial site (0.5, 0.5, 0.5) were substituted with a Fe, Co, Ni, Cu or Ti atom. The calculated lattice parameters (R_{op}), cell volume (V), and occupation energy (E_{occu}) in the pure and doped $LiBH_4$ are listed in Table 1. As illustrated in Table 1, TM doping should break the symmetry of $LiBH_4$ because of the different atomic radii of Li (1.58 Å), Fe (1.26 Å), Co (1.25 Å), Ni (1.25 Å), Cu (1.28 Å) and Ti (1.47 Å), which causes different lattice parameters and cell volumes for pure $LiBH_4$ and TM-doped $LiBH_4$. To investigate the dehydrogenation mechanisms of pure and TM-doped $LiBH_4$, we analysed the average bond lengths (d_{B-H}) and maximum bond lengths (max d_{B-H}) between the B atoms and H atoms near the doping centre, and the bond lengths between transition metal atoms and H atoms ($d_{M\text{-}H}$) are listed in Table 1. After doping, the d_{B-H} and max d_{B-H} increase to different degrees, and these results indicate that substitution weakens some B–H bonds, favouring hydrogen release. Moreover, we calculated the vibrational frequencies of the B–H bonds in $LiBH_4$ and TM-doped $LiBH_4$. The vibrational frequency of the B–H bonds in $LiBH_4$ is approximately 2410 cm^{-1}, and the vibrational frequencies of the B–H bonds adjacent to the TM are reduced to different degrees after doping (2364 cm^{-1} (Fe-doped system), 2375 cm^{-1} (Co-doped system), 2324 cm^{-1} (Ni-doped system), 2380 cm^{-1} (Cu-doped system), and 2063 cm^{-1} (Ti-doped system)), which implies that the substitution of transition metal atoms weakens the B–H bonds.

Table 1
Unit cell parameters (R_{op}) and cell volume (V), selected bond lengths (Distance) and occupation energies (E_{occu}) for pure and TM-doped $LiBH_4$.

System	R_{op} (Å)			V (Å^3)	Distance (Å)			E_{occu} (eV)
	a	b	c		d_{B-H}	max d_{B-H}	d_{M-H}	
Pure	7.264	8.756	6.65	422.9	1.23	1.23	–	–
Fe-Int	8.532	8.594	6.532	475.2	1.27	1.32	1.65	3.87
Fe-Sub	7.338	8.791	6.444	415.7	1.25	1.30	1.64	4.22
Co-Int	8.294	8.681	6.562	470.6	1.26	1.30	1.66	2.99
Co-Sub	7.270	8.806	6.523	417.6	1.24	1.28	1.73	3.50
Ni-Int	7.946	8.751	6.767	468.3	1.26	1.30	1.67	2.095
Ni-Sub	7.213	8.832	6.599	420.4	1.24	1.27	1.77	3.24
Cu-Int	8.204	8.888	6.710	483.66	1.24	1.25	1.84	2.94
Cu-Sub	7.232	8.789	6.654	422.9	1.23	1.25	1.76	2.25
Ti-Int	7.314	9.561	6.832	470.0	1.26	1.30	1.96	3.96
Ti-Sub	7.470	8.670	6.654	430.5	1.24	1.27	2.10	3.85

To illustrate the site preference of the TM dopant in bulk $LiBH_4$, the occupation energy for TM dopant is determined using the following formula:

$$E_{occu} = E_{doped} - E_{pure} - (nE_{TM} - mE_{Li})$$

where (n = 1, m = 1) stands for substitutional sites and (n = 1, m = 0) means the interstitial site; E_{doped} is the total energy of the TM substituted system; E_{pure} is the total energy of pure $LiBH_4$; E_{Li} is the total energy of pure metal Li atom; and E_{TM} (TM = Fe, Co, Ni, Cu and Ti) is the total energy of the pure metal Fe, Co, Ni, Cu and Ti atoms. The energy per atom of the pure metal is calculated from the crystal of the pure metal. As seen in Table 1, the occupation energy of the TM (TM = Fe, Co, Ni, Cu and Ti) substitution for Li is in increasing order as follows: Cu (2.25 eV) < Ni (3.24 eV) < Co (3.5 eV) < Ti (3.85 eV) < Fe (4.22 eV), which indicates that the Cu atom can most easily substitute for the Li1 atom. The occupation energy of the TM (TM = Fe, Co, Ni, Cu and Ti) inserted into the interstitial site is in increasing order as follows: Ni (2.095 eV) < Cu (2.94 eV) < Co (2.99 eV) < Fe (3.87 eV) < Ti (3.96 eV), which denotes that the Ni atom can most easily occupy an interstitial site. In general, a TM atom prefers to occupy an interstitial site relative to the Li atom site. The occupation energy for Cu and Ti doped at the Li site (2.25 eV and 3.85 eV, respectively) is smaller than that of those metals doped at the interstitial site (2.94 eV and 3.96 eV), which may be because Ti atoms and Cu atoms have a relatively large atomic radius (1.47 Å and 1.28 Å) so that Cu and Ti atoms cannot easily insert into the interstitial site. The positive value of occupation energy indicates that the doping process is endothermic. Jiang et al. [32] investigated the substitution of the Li atom with a Ti atom in 1 × 2 × 1 $LiBH_4$ supercell by using the CASTEP package and found the occupation energy was 3.82 eV, which is in agreement with our calculated result.