INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 41 (2016) 1662–1671

Available online at www.sciencedirect.com

ScienceDirect

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

Influence of alloying elements on the stability and dehydrogenation properties on $Y(BH_4)_3$ by first principles calculations

Jianhong Dai, Yuying Chen, Ruiwen Xie, Zhou Hu, Yan Song [*]

School of Materials Science and Engineering, Harbin Institute of Technology at Weihai, 2 West Wenhua Road, Weihai 264209, China

ARTICLE INFO

Article history:
Received 25 August 2015
Received in revised form
6 October 2015
Accepted 1 November 2015
Available online 22 November 2015

Keywords:
First principles calculations
$Y(BH_4)_3$
Alloying elements
Stability
Dehydrogenation

ABSTRACT

First principles calculations are performed to study the influence of alloying elements Li, Na, K, Ti, Mn, and Ni and Y vacancy on the stability and dehydrogenation properties of $Y(BH_4)_3$. The formation energies of low and high temperature (LT and HT) phases of alloyed $Y(BH_4)_3$ are evaluated. Ti, Mn, and Ni elements and the Y vacancy containing $Y(BH_4)_3$ systems are endothermic. The Y vacancy is difficult to be generated due to the high energy demand. The alkali metals of Li, Na, and K prefer to occupy the interstitial sites in both the LT and HT phases of $Y(BH_4)_3$, especially the K element. The K containing systems show negative formation energy, even if eight K atoms are introduced. The K containing systems show similar structure characteristics with the $KY(BH_4)_4$ compound. Therefore, a phase transition from the K alloyed $Y(BH_4)_3$ to $KY(BH_4)_4$ is expectable. However, the transition from Li/Na alloyed $Y(BH_4)_3$ to corresponding Li/Na–$Y(BH_4)_4$ compounds is energetically unfavorable. Electronic structures of alloyed $Y(BH_4)_3$ are investigated to explore the reasons that why only K alloyed $Y(BH_4)_3$ can transform to $KY(BH_4)_4$ compound. In term of dehydrogenation properties, all alloyed systems show smaller dehydrogenation energies than the pure $Y(BH_4)_3$. The concentrations of alloying elements can greatly affect the dehydrogenation properties of alloyed $Y(BH_4)_3$.

Introduction

It is crucial to develop an efficient and safe way to store hydrogen for the application of hydrogen energy. Solid storage approach owns great advantages in cost and safety. Some hydrogen storage media have been extensively studied, such as MgH_2, coordination compounds of $M[BH_4]$ and $M[AlH_4]$ (M = metal element), and so on. Among them, the $M[BH_4]$ compounds are the most promising media due to their high energy density. For example, the hydrogen capacity in $LiBH_4$ is high to 18 wt%, but its dehydrogenation is hindered by the strong bonding interaction between H and B [1].

The catalytic dopant can improve the de/hydrogenation properties of hydrogen storage materials. Ti is one of the widely used catalysts for enhancing hydrogen storage performance of metal hydrides. It was found that the reversible de/hydrogenation of $NaAlH_4$ could be achieved by effect of catalysts, such as Ti and its compounds [2,3]. TiO_2 and $TiCl_3$ can improve the kinetics of the dehydrogenation of borohydrides, but their catalytic effects are poor for those of aluminum hydrides. It is believed that the catalytic effects

---

[*] *Corresponding author.*
E-mail address: sy@hitwh.edu.cn (Y. Song).

http://dx.doi.org/10.1016/j.ijhydene.2015.11.005

connect to the bonding characteristics of catalysts with coordination cluster [4]. Transition metals have great catalytic effects on borohydrides [5–8].

For the B–H coordination, $LiBH_4$ and $NaBH_4$ are too stable for dehydrogenation, while the transition metal borohydrides are unstable under normal conditions. The effects of dopants on the de/hydrogenation of borohydrides have been extensively studied. The alkali oxide additions can greatly affect the formation of BH_4 [9]. Ball-milling $LiBH_4$ with $RECl_3$ (RE = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Er, Yb, and Lu) will form numerous rare-earth metal (RE) borohydrides and LiCl [10]. A mixed-cation borohydride ($K_2Mn(BH_4)_4$) can be synthesized by ball milling of KBH_4 and $MnCl_2$ with 2:1 mole ratio [11], and other complex borohydrides i.e., $KHo(BH_4)_4$ [12], $Mn(BH_4)_2$ [13] by ball milling method. They all show potential application as hydrogen storage material.

The Ni and Ti can improve the dehydrogenation and rehydrogenation properties of $LiBH_4$ and $NaBH_4$ [14,15]. However, the Ti has a limited effect in lowering the decomposition temperature of $LiBH_4$ [16], which may be associated with the oxidation states of Ti cations. Theoretical studies show the Ti ions cannot dope into $LiBH_4$, while high oxidation states of Ti^{n+} ($n > 3$) cations may become thermodynamically stable in $NaAlH_4$ [17].

$Y(BH_4)_3$ is one of candidates for hydrogen storage containing 9.06 wt% of hydrogen. The thermodynamics of $Y(BH_4)_3$ exhibits a lower dissociation temperature than $Mg(BH_4)_2$ under 1 bar of H_2 [18]. The solid–solid metathesis reaction occurs between $LiBH_4$ and YCl_3 [19,20], while the $NaBH_4$ does not react with YF_3 during ball milling [21]. High-energy milling of $Y(BH_4)_3$ with KBH_4 leads to $KY(BH_4)_4$, while no chemical reaction is observed for milling of $LiBH_4$ and $NaBH_4$ with yttrium compounds [22]. The mechanochemical solid–solid reactions ($MBH_4 + 3YX_3^- > Y(BH_4)_3 + 3\,LiCl$, where M = Li and Na; X = F and Cl) have been succeeded only for the $LiBH_4$ and YCl_3 reagents [23]. The $Y(BH_4)_3$ can also be synthesized by reactive ball milling of yttrium hydride in diborane/hydrogen atmosphere [24].

The primitive cubic low-temperature (LT) phase, the α-$Y(BH_4)_3$ phase, transforms to face-centered cubic high-temperature (HT) phase, the β-$Y(BH_4)_3$ phase, under 10 MPa and 475 K [19]. The β-$Y(BH_4)_3$ can be easily formed through phase transition at approximate 180 °C and will be decomposed at 190 °C to YH_3, and further transformed to YH_2 at 543 K [25,26]. In the decomposition process of $Y(BH_4)_3$, yttrium octahydrotriborate, *i.e.*, $Y(B_3H_8)_3$, rather than the stable $Y_2(B_{12}H_{12})_3$, is formed as the main intermediate [27]. The activation energy of HT is nearly three times lower than the LT polymorph for the first step of the thermal decomposition, although the α-$Y(BH_4)_3$ and the β-$Y(BH_4)_3$ show slight differences in the crystal structure [28]. The high energy barrier for the $[BH_4]^-$ reorientation partly accounts for the slow phase transition observed in $Y(BH_4)_3$ [18,29]. The phase transformation of $Y(BH_4)_3$ can be shown through following reaction [18],

$$\alpha\text{-}Y(BH_4)_3 \leftrightarrow \beta\text{-}Y(BH_4)_3,\ -4.2\ \text{kJ/molH}_2 \quad (1)$$

The dehydrogenation energy is 37.4 kJ/molH_2 for β-$Y(BH_4)_3$ with 8.5 wt% hydrogen capacity [18]. The activation energies for the I step decomposition of α-$Y(BH_4)_3$ and β-$Y(BH_4)_3$ are high to 785 and 281 kJ/molY [28]. Therefore, it is crucial to improve the reaction kinetic properties under dehydrogenation of $Y(BH_4)_3$. Furthermore, it is interesting to study why the $KY(BH_4)_4$ can be formed but no Li/Na–$Y(BH_4)_4$ were observed during high-energy milling of $Y(BH_4)_3$ with Li, Na, or K–BH_4. Alloying elements are usually applied to improve the dehydrogenation property of metal hydrides. In the present work, the influence of alloying elements (Li, Na, K, Ti, Mn, and Ni) on the stability and dehydrogenation properties of $Y(BH_4)_3$ are studied via first-principles. The method used in this paper is briefly described in Section 2, and results are presented in Section 3. Electronic structures are analyzed to identify the intrinsic mechanisms of influence of alloying elements. Conclusions are presented in the last part.

Computation methods

Vienna *Ab initio* Simulation Package (VASP) is employed to perform all calculations [30,31] based on generalized gradient approximation (GGA). The Projector Augmented Wave (PAW) potentials were used [32] with a cutoff energy of 350 eV of plane wave basis set. The valence electron configurations used in the present calculations are: H $1s^1$, B $2s^22p^1$, Y $4s^24p^65s^24d^1$, Li $2s^12p^0$, Na $3s^13p^0$, K $3p^64s^1$, Ti $3d^34s^1$, Mn $3d^64s^1$, Ni $3d^94s^1$. The 2 × 2 × 2 Monckhorst-Pack [33] k-point grid is used in all calculations. The convergence criteria of self-consistency calculations are that the differences between two consecutive energies and forces are less than 0.01 meV and 0.01 eV/Å, respectively. The LT phase (α-$Y(BH_4)_3$) and HT phase (β-$Y(BH_4)_3$) both occur in cubic structure as shown in Fig. 1. The β-$Y(BH_4)_3$ can be achieved by quenching, and it is actually metastable at room temperature. The lattice parameters of LT and HT phases are 10.852 Å and 11.008 Å [19], respectively. The number of atoms containing in an unit cell of $Y(BH_4)_3$ is 8 (Y), 24 (B), and 96 (H) for both phases, respectively. The calculated lattice parameters for the LT and HT phases are 10.638 and 10.825 Å, respectively, which are well consistent with experimental values. The molecular dynamics (MD) calculations employed in this work were based on the density functional theory using VASP code. A canonical ensemble (*NVT*) with a Nosé thermostat procedure was used at the temperature of 300 K. The MD simulations were ran for 10,000 steps containing with equilibration and data sampling procedures with a time step of 1 fs.

Results and discussions

Stability and dehydrogenation properties

(a) Single-element alloyed systems

The calculation models of single-element alloyed LT and HT phases are shown in Fig. 1. The interstitial and substitutional sites for alloying element are selected as (0.5, 0.5, 0.5) and (0.2187, 0.2187, 0.2187) for LT phase, and (0.25, 0.25, 0.25) and (0.5, 0.5, 0.5) for HT phase, respectively. Table 1 shows the lattice parameters of LT phase after full relaxations. The α, β, and γ angles are still equivalent and only slightly deviated