Journal of Alloys and Compounds 580 (2013) S292–S295

Contents lists available at SciVerse ScienceDirect

Journal of Alloys and Compounds

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

Comparative study on the reversibility of pure metal borohydrides

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ARTICLE INFO

Article history:
Available online 6 April 2013

Keywords:
Hydrogen storage
Borohydride
Reversibility
Hydrogen
Hydride

ABSTRACT

Improvement of the reversibility of metal borohydrides is a key issue for hydrogen storage applications. In this study, we carefully investigated the first rehydrogenation of pure $Mg(BH_4)_2$ and $Ca(BH_4)_2$ under a hydrogen pressure of 40.0 MPa. $Mg(BH_4)_2$ is produced even at a relatively low temperature of 473 K, and its amount increases with the temperature up to 673 K, leading to the increased rehydrogenation content and a maximum (7.6 mass%, equivalent to 51% of $Mg(BH_4)_2$) at 673 K. Under the same condition, more than 90% of rehydrogenation is confirmed through the formation of α-$Ca(BH_4)_2$ as clearly observed by XRD and NMR measurements. Comparison of the rehydrogenation properties of $Mg(BH_4)_2$ and $Ca(BH_4)_2$ suggests that control of dehydrogenation products would be an important approach to improve the reversibility of metal borohydrides.

1. Introduction

Metal borohydrides $M(BH_4)_n$ have been regarded as potential hydrogen storage materials owing to their high hydrogen densities. Most of $M(BH_4)_n$ suffer from their relatively high thermodynamics and sluggish kinetics. In the last decade, great efforts have been devoted to solve these problems, and lots of progresses have been achieved such as using electronegativity as an indicator for estimating the thermodynamics [1]; making a composite system with other element or their compounds (also called reactive hydride composites) [2,3], and nanoconfinement technology [4], as summarized in recent review papers [5–8].

Reversibility (reversible dehydrogenation/rehydrogenation) of $M(BH_4)_n$ is an important issue for onboard hydrogen storage application. Generally dehydrogenation/rehydrogenation reactions proceed through decomposition and recombination of $M(BH_4)_n$ itself together with the formation of intermediate compounds such as $MB_{12}H_{12}$ regarded as one of the main reasons causing the degradation of reversibility [9–11]. Rehydrogenation of $LiBH_4$ has been reported to proceed at a temperature higher than 873 K under a hydrogen pressure of 15.0 or 35.0 MPa [12,13]. The first rehydrogenation experiment of $Mg(BH_4)_2$ found that $MgB_{12}H_{12}$ was the main rehydrogenated phase at 543 K under a hydrogen pressure of 40.0 MPa [14]. The addition of 5 mol% TiF_3 and $ScCl_3$ was reported to improve the rehydrogenation of $Mg(BH_4)_2$ [15]. Also, $Mg(BH_4)_2$ was produced by hydrogenation of the dehydrogenated product MgB_2 at 673 K under a hydrogen pressure of 95.0 MPa for 108 h [16]. The hydrogenation of MgB_2 can be significantly promoted by introduction of the nanostructures with defects [17,18]. Approximately 60% of $Ca(BH_4)_2$ have been produced by rehydrogenation at 623–713 K under a hydrogenation pressure of 9.0–70.0 MPa with various additions, such as NbF_5 [19], TiF_3 [20] or $TiCl_3$ + Pd [21]. It is noteworthy to mention that most reports focus on the rehydrogenation of doped $Mg(BH_4)_2$ and $Ca(BH_4)_2$ without comparison with those of pure samples. Therefore, it is of great importance to systematically investigate the rehydrogenation of pure $Mg(BH_4)_2$ and $Ca(BH_4)_2$ as a reference point for comparison prior to depict the improvement effect of additives.

In this study, we carefully investigate the rehydrogenation of pure $Mg(BH_4)_2$ and $Ca(BH_4)_2$ under a hydrogen pressure of 40.0 MPa by using thermogravimetric (TG) analysis. Also, the phase changes after dehydrogenation and rehydrogenation are analyzed by X-ray diffraction (XRD) and nuclear magnetic resonance (NMR). Moreover, the rehydrogenation properties are compared in order to provide insightful information for substantial improvement of reversibility of metal borohydrides.

2. Experimental

$Mg(BH_4)_2$ was synthesized by means of the metathesis reaction of $MgCl_2$ (Aldrich; purity, 95%) and Na(BH4) (Aldrich; purity, 99.99%), as described in the previous report [22]. The single high-temperature phase β-$Mg(BH_4)_2$ was used as the starting material. $Ca(BH_4)_2$ was synthesized by heating the commercial reagent

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http://dx.doi.org/10.1016/j.jallcom.2013.03.264

$Ca(BH_4)_2 \cdot 2THF$ (Sigma–Aldrich) under vacuum at 503 K for 16 h. This sample consists of β-$Ca(BH_4)_2$ phase mainly. The dehydrogenation of $Mg(BH_4)_2$ was performed under vacuum at 623 K and kept for 6 h, and the obtained product was used as the starting material of rehydrogenation. The dehydrogenated $Ca(BH_4)_2$ samples were prepared under 1.0 MPa Ar at 643 and 743 K, respectively, and kept for 3 h. The rehydrogenation was carried out under a hydrogen pressure of 40.0 MPa in a specially designed pressure-resistant reaction tube.

The crystal structures were examined via XRD (PANalytical X'PERT with Cu Kα radiation) at room temperature. The hydrogen content was analyzed by using thermogravimetry (TG, Rigaku TG-8210) under a He flow of 150 ml/min at a heating rate of 5 K/min. The chemical bonding states of boron atoms were further investigated via ^{11}B MAS NMR measurement at room temperature (JEOL Ltd., JNM-ECA600 spectrometer operated at a magnetic field of 14.1 T; resonance frequency, 192.57 MHz; spinning rate of 4.0 mm diameter sample rotor, 16 kHz). Spectra were obtained by using a single pulse sequence without a high power 1H decoupling during signal acquisition. The pulse width of 1 μs was used, which was set equivalent to a $\pi/9$ of the solution $\pi/2$ pulse to minimize the nutation effect on the quantitative peak area analysis of the spectrum. For each spectrum, 6000 scans were accumulated with repetition time of 2 s. Chemical shift was referenced to $BF_3 \cdot Et_2O$ in ether solution as 0 ppm. All the samples were always handled in a glove box filled with purified Ar/He gas (water and oxygen concentration, <1 ppm) in order to avoid (hydro-)oxidation.

3. Results and discussion

3.1. Rehydrogenation property of $Mg(BH_4)_2$

The dehydrogenated product of $Mg(BH_4)_2$ are analyzed by XRD (not shown) and ^{11}B MAS NMR (Fig. 1). Only diffraction peaks of Mg are observed in the XRD profile. $MgB_{12}H_{12}$ reported to be amorphous are confirmed in ^{11}B MAS NMR spectra, as evidenced by the peak at approximately −15 ppm. Thus the dehydrogenated product is a mixture consisting of crystalline Mg and amorphous $MgB_{12}H_{12}$, which are used as the starting material for rehydrogenation.

After rehydrogenation at 473–773 K, diffraction peaks of MgH_2 are cleared observed in all the XRD profiles. Also, MgB_2 is confirmed when rehydrogenated at 773 K, suggesting the interaction between Mg and $MgB_{12}H_{12}$. Some selected rehydrogenated samples are examined by ^{11}B MAS NMR and the spectra are shown in the inset of Fig. 1. At 473 K, the formation of small amount $Mg(BH_4)_2$ is evidenced by a very weak peak at −40 ppm. With increasing the rehydrogenation temperature up to 543 K, the intensity ratio of $Mg(BH_4)_2$ to $MgB_{12}H_{12}$ increases largely, suggesting the increment of rehydrogenation content. At 773 K, no evidence of $Mg(BH_4)_2$ can be found and the main phase becomes $MgB_{12}H_{12}$ and MgB_2 as confirmed at −15 and 100 ppm (not shown), respectively [15]. The change in the chemical composition of MgH_2, $MgB_{12}H_{12}$, $Mg(BH_4)_2$ and MgB_2 dominates not only the rehydrogenation content but also the sample colors, as given in Fig. 1.

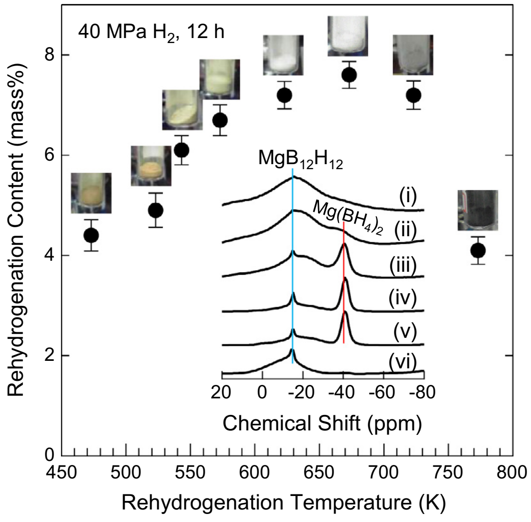

Fig. 1. Rehydrogenation content (black close circle) as a function of rehydrogenation temperature under a hydrogen pressure of 40.0 MPa for 12 h. Photos of rehydrogenated product powders are shown to compare the color changes. Inset presents the ^{11}B MAS NMR spectra of selected samples: (i) dehydrogenated product, rehydrogenated products at (ii) 473 K, (iii) 543 K, (iv) 623 K, (v) 673 K and (vi) 773 K.

The rehydrogenation content examined by TG increases and reaches the maximum (7.6 mass%, equivalent to 51% of the total hydrogen content in $Mg(BH_4)_2$) when increasing the temperature from 473 to 673 K, while reduces when the temperature higher than 673 K. The increased hydrogen content attributes to the improved kinetics because higher temperature would thermally activate the rehydrogenation reaction. On the other hand, if the temperature is higher than the decomposition temperature under a hydrogen pressure of 40.0 MPa, $Mg(BH_4)_2$ becomes thermodynamically unstable and results in the reduced hydrogen content.

3.2. Rehydrogenation property of $Ca(BH_4)_2$

XRD profiles and NMR spectra of $Ca(BH_4)_2$ and its dehydrogenated products at 643 and 743 K are shown in Figs. 2 and 3, respectively. Both the diffraction peaks and the chemical shift at −32 ppm consistently indicate that β-$Ca(BH_4)_2$ is the main phase of $Ca(BH_4)_2 \cdot 2THF$ after desolvation [23]. CaH_2 and CaB_2H_x [24] are identified in the XRD profiles of $Ca(BH_4)_2$ dehydrogenated at 643 K, while only CaH_2 is confirmed as dehydrogenated product at 743 K. The presence of CaO may originate from the impurities in the lines and reaction tube. A series of signals at ∼15, ∼2, ∼−14 and ∼−30 ppm are observed for dehydrogenated samples at both 643 K and 743 K. In reference to the ^{11}B MAS NMR spectrum of pure CaB_6 [25], the broad peak at 15 ppm should belong to CaB_6, which is also clearly detected by Raman analysis (not shown here). The peak at −30 ppm appears in between α- (−29 ppm) and β-$Ca(BH_4)_2$ (−32 ppm), suggesting the quite similar chemical environment with $Ca(BH_4)_2$. Also, the intensity decreases significantly when the dehydrogenation temperature

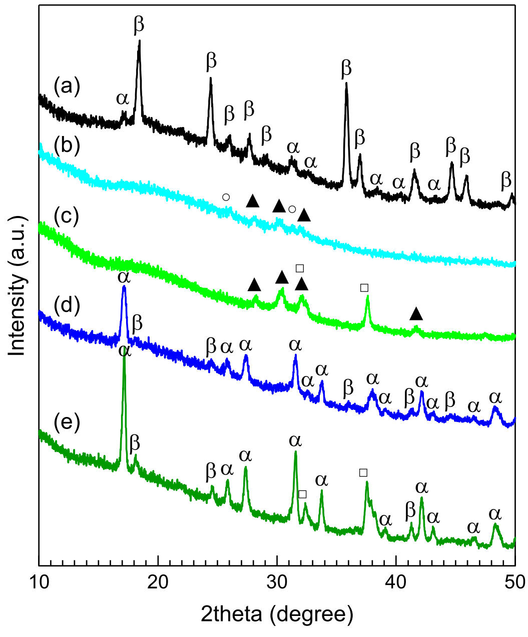

Fig. 2. Powder XRD profiles of (a) $Ca(BH_4)_2$ prepared by desolvation of $Ca(BH_4)_2 \cdot 2THF$, dehydrogenated products at (b) 643 K and (c) 743 K, as well as their rehydrogenation products (d and e), respectively, under a hydrogen pressure of 40.0 MPa at 673 K. α, β, triangle, circle and square symbols indicate α-$Ca(BH_4)_2$, β-$Ca(BH_4)_2$, CaH_2, CaB_2H_x and CaO, respectively.

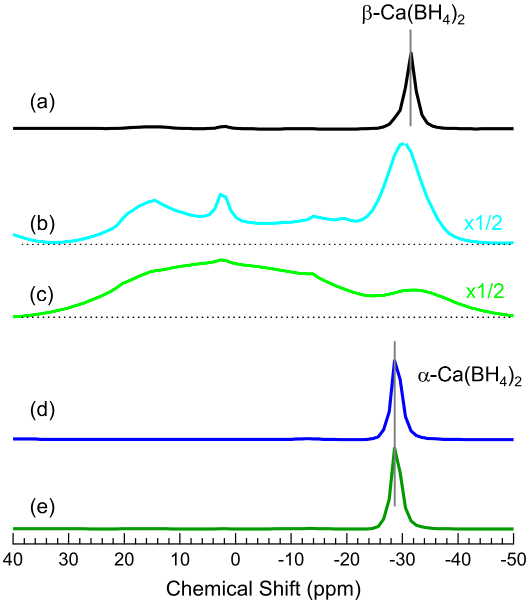

Fig. 3. ^{11}B MAS NMR spectra of (a) $Ca(BH_4)_2$ prepared by desolvation of $Ca(BH_4)_2$·2THF, dehydrogenated products at (b) 643 K and (c) 743 K, scale adjusted by 2 times, as well as their rehydrogenation products (d and e), respectively.

increased from 643 to 743 K. These results suggest that the peak at −30 ppm could be residual $Ca(BH_4)_2$, as observed in the previous reports [23,25]. In addition, the peak at −14 ppm can be assigned to $CaB_{12}H_{12}$ in reference to the ^{11}B MAS NMR spectrum (−15.6 ppm) of pure $CaB_{12}H_{12}$ [25]. A very broad signal centered at around ~0 ppm suggests the presence of element boron for the dehydrogenated at 743 K [25].

The rehydrogenated products are identified mainly as α-$Ca(BH_4)_2$ from both XRD profiles and NMR spectra, regardless of dehydrogenation temperature, as shown in Figs. 2 and 3. Surprisingly, no obvious traces of dehydrogenated products including CaH_2, CaB_6, $CaB_{12}H_{12}$ and CaB_2H_x are observed in the XRD and NMR profiles. This indicates the good rehydrogenation property of $Ca(BH_4)_2$ at present experimental condition, which is well supported by the rehydrogenation content shown in Fig. 4. The rehydrogenation contents are 7.4 and 7.0 mass%, respectively, for samples dehydrogenated at 643 and 743 K. These values are equivalent to 96% and 91% of the dehydrogenation amount (7.7 mass%) of the starting $Ca(BH_4)_2$ prepared in this study, demonstrating the superior rehydrogenation property than the previous reports [11,19–21,23]. The loss of rehydrogenation content may originate from the impurities included in the lines and reaction tube, or from the very small amount formation of stable $CaB_{12}H_{12}$.

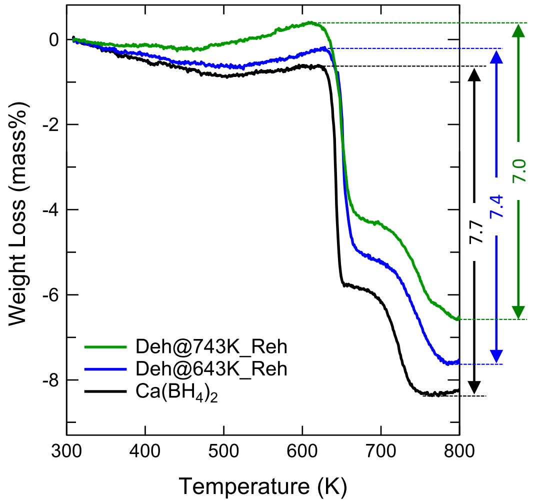

Fig. 4. Hydrogen content examined by TG of $Ca(BH_4)_2$ prepared by desolvation of $Ca(BH_4)_2$·2THF, rehydrogenated products after dehydrogenation at 643 and 743 K.

3.3. Comparison of reversibility of $Mg(BH_4)_2$ and $Ca(BH_4)_2$

Rehydrogenation of both $Mg(BH_4)_2$ and $Ca(BH_4)_2$ are thermodynamically favorable, whereas need to overcome the kinetic obstacle originating from the migration of constituent element and the rearrangement of chemical bonding. Under the same rehydrogenation condition (40 MPa H_2, 673 K), $Ca(BH_4)_2$ shows superior reversibility in the first rehydrogenation than that of $Mg(BH_4)_2$, i.e. more than 90% formation of $Ca(BH_4)_2$ and only 51% formation of $Mg(BH_4)_2$. This may originate from the different dehydrogenation products, especially for the main boron-related species: $MgB_{12}H_{12}$ in the case of $Mg(BH_4)_2$ (Fig. 1i), while CaB_6 and CaB_2H_x in $Ca(BH_4)_2$ (Fig. 3b). This is the case similar to the previous report that MgB_3H_8 and MgB_2 shows better reactivity with hydrogen to produce $Mg(BH_4)_2$ than that of $MgB_{12}H_{12}$ [16,26]. Effective control of dehydrogenation pathway to avoid the formation of too stable intermediate compounds like $MB_{12}H_{12}$, therefore, is an important approach to develop metal borohydrides with good reversibility.

4. Conclusions

The dehydrogenated product consisting of crystalline Mg and amorphous $MgB_{12}H_{12}$ transformed into MgH_2, $MgB_{12}H_{12}$ and $Mg(BH_4)_2$ after hydrogenation under a hydrogen pressure of 40.0 MPa at 473–673 K. With increasing the rehydrogenation temperature, the composition ratio of $Mg(BH_4)_2$ to $MgB_{12}H_{12}$ increased, leading to the increased hydrogen content and its maximum reached 7.6 mass% (equivalent to 51% of $Mg(BH_4)_2$) at 673 K. More than 90% of rehydrogenation were confirmed through the formation of α-$Ca(BH_4)_2$ by hydrogenation of the dehydrogenated products including CaH_2, CaB_6 and/or CaB_2H_x at 673 K. The different boron-related species between the dehydrogenated $Mg(BH_4)_2$ and $Ca(BH_4)_2$ would afford different rehydrogenation performance, suggesting that control of dehydrogenation products is an effective approach to develop metal borohydrides with good reversibility.

Acknowledgements

The authors would like to thank Drs. S. Towata, K. Miwa, M. Aoki, M. Matsumoto, and T. Noritake for their valuable discussions. This study was partially supported by NEDO, 'Development for Hydrogen Production, Transportation and Storage System' Project, JSPS KAKENHI (23760658) and The International Institute for Carbon Neutral Energy Research (WPI-I2CNER), sponsored by the Japanese Ministry of Education, Culture, Sports, Science and Technology.

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