



Dehydrogenation properties and crystal structure analysis of Mg(BH₄)(NH₂)



Tatsuo Noritake^{a,*}, Kazutoshi Miwa^a, Masakazu Aoki^a, Mitsuru Matsumoto^a, Shin-ichi Towata^a, Hai-Wen Li^b, Shin-ichi Orimo^c

^a Toyota Central R&D Labs., Inc., Nagakute, Aichi 480-1192, Japan

^b International Research Center for Hydrogen Energy, Kyushu University, Fukuoka 819-0395, Japan

^c Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

ARTICLE INFO

Article history:

Available online 21 March 2013

Keywords:

Hydrogen absorbing materials
Crystal structure
X-ray diffraction
Synchrotron radiation

ABSTRACT

Dehydrogenation properties and crystal structure of the double anion complex hydride Mg(BH₄)(NH₂) were studied by thermal analyses and synchrotron X-ray diffraction. The stoichiometric mixture of Mg(BH₄)₂ and Mg(NH₂)₂ were ball-milled and then heated to 453 K to form Mg(BH₄)(NH₂) crystal. The dehydrogenation of Mg(BH₄)(NH₂) occurs in two-stage at 513 K and 688 K. The following reaction sequence is suggested by the results of thermal analyses; Mg(BH₄)(NH₂) → MgH₂ + BN + 2H₂ (7.3 mass% weight loss) → Mg + BN + 3H₂ (11.0 mass% weight loss in total). The dehydrogenation temperature of Mg(BH₄)(NH₂) is approximately 50 K lower than that of the other double anion complex Li₂(BH₄)(NH₂). The crystal structure of Mg(BH₄)(NH₂) was determined by the measurement at 300 K (crystal system: tetragonal, space group: I4₁ (No. 80), lattice constants: *a* = 5.792(1), *c* = 20.632(4) Å at 300 K). In the crystal of Mg(BH₄)(NH₂), the cation (Mg²⁺) and the anions (BH₄⁻ and NH₂⁻) are stacked alternately along the *c*-axis direction. The Mg²⁺ cation is tetrahedrally coordinated with two BH₄⁻ anions and two NH₂⁻ anions.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Hydrogen storage is one of the most important technologies towards a future sustainable hydrogen society. Many materials, for example, hydrogen storage alloys, complex hydrides, carbon materials, metal organic frameworks and so on, have been studied as new hydrogen storage systems over the past decade [1]. Particularly, complex hydrides consisting of light elements have received significant attention because of their high gravimetric hydrogen storage capacities [2]. The major issue to be solved is to lower the dehydrogenation temperature of complex hydrides. The novel complex hydrides with lower dehydrogenation temperature should be developed for practical use such as fuel cell vehicles [3]. As the pursuit of novel complex hydrides, the mixture system of LiBH₄ + *n* LiNH₂ (*n* = 1–3) was found. The dehydrogenation temperature of this mixed system is much lower than pristine LiBH₄ [4–8]. Following this finding, many mixture systems of borohydride and amide compounds have been studied; for example, LiBH₄–Mg(NH₂)₂ [9], Mg(BH₄)₂–LiNH₂ [10], NaBH₄–NaNH₂ [11], Ca(BH₄)₂–LiNH₂ [12].

It is already known that the double anion complex hydrides, Li₂(BH₄)(NH₂) and Li₄(BH₄)(NH₂)₃, are crystallized by ball-milling or heat treatment of the mixture LiBH₄ + *n* LiNH₂ (*n* = 1–3) [13–15].

It is suggested that the double anion complex environment, i.e. cation(s) equally surrounded by BH₄⁻ and NH₂⁻, is the one reason to desorb hydrogen at lower temperature. In order to lower in dehydrogenation temperature further, the mixture system of Mg(BH₄)₂ + Mg(NH₂)₂ was studied because Mg(BH₄)₂ is thermodynamically less stable than LiBH₄ [16–18]. In the previous study [19,20], the novel complex hydride Mg(BH₄)(NH₂), which was created from mixture Mg(BH₄)₂ + Mg(NH₂)₂ at temperature 453 K, was investigated by in situ synchrotron X-ray measurement. In this paper, the thermal analysis of Mg(BH₄)₂ + Mg(NH₂)₂ is performed and the crystal structure of Mg(BH₄)(NH₂) at room temperature (300 K) is studied.

2. Materials and methods

2.1. Synthesis

The synthesis method of Mg(BH₄)₂ from magnesium hydride MgH₂ and tri-ethylamine borazane Et₃N–BH₃ is described in Ref. [21]. Mg(NH₂)₂ was prepared by the reaction of MgH₂ powder and ammonia gas as described in Ref. [22]. The powder of Mg(BH₄)₂ and Mg(NH₂)₂ were mixed (1:1 M ratio) using agate mortar, then the mixture was mechanically milled for 2 h under Ar atmosphere using the planetary ball mill (Fritsch P-5).

2.2. Thermal analysis

For the obtained mixture sample of Mg(BH₄)₂ + Mg(NH₂)₂, thermogravimetry (TG) and differential thermal analysis (DTA) were carried out under He gas flow at heating rate of 5 K/min (Rigaku TG-8120). In addition, mass spectrometry was

* Corresponding author. Tel.: +81 561 71 7804; fax: +81 561 63 6136.

E-mail address: e0553@mosk.tytlabs.co.jp (T. Noritake).

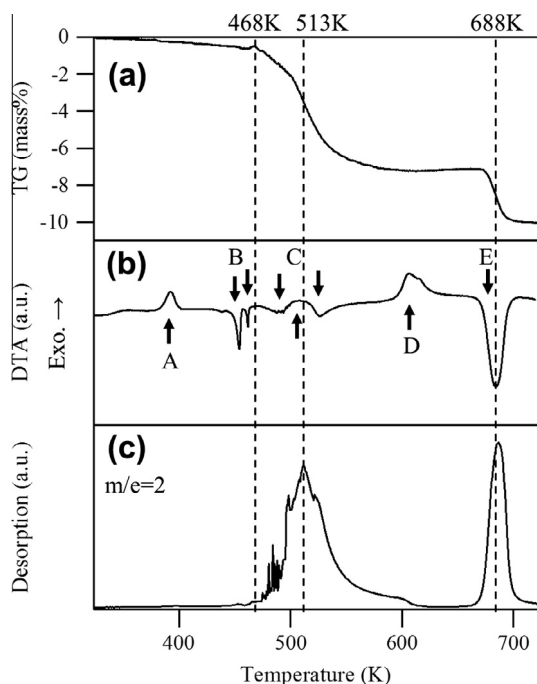


Fig. 1. (a) Thermogravimetry analysis curve, (b) differential thermal analysis curve and (c) TPD-MS spectrum for the mixture sample of $\text{Mg}(\text{BH}_4)_2 + \text{Mg}(\text{NH}_2)_2$ in the dehydrogenation process (heating rate: 5 K/min). The dehydrogenation begins at about 468 K and actively reacts in two-stage at 513 K and 688 K.

measured using the equipment (Anelva M-QA200TS) directly connected with the TG/DTA apparatus. The handling of the samples was always performed in a glove box filled with purified Ar gas (dew point below 180 K, oxygen concentration lower than 1 ppm) to avoid oxidation or hydroxylation of samples.

2.3. X-ray diffraction

The mixture sample of $\text{Mg}(\text{BH}_4)_2 + \text{Mg}(\text{NH}_2)_2$ was inserted into a glass capillary (diameter: 0.3 mm) and then the capillary edge was sealed by an epoxy adhesive. The synchrotron X-ray diffraction experiment was carried out by use of a large Debye-Scherrer camera with an imaging plate as detectors at the beam-line BL19B2 in SPring-8 [23]. The powder X-ray diffraction data were measured with incident X-ray of wavelength 0.80 Å and collected with a 0.01° step from 4.0° to 74.0° in 2θ . The temperature was controlled by blowing heated nitrogen gas to the glass capillary. The temperature was brought from room temperature (300 K) to 453 K and then cooled down to 300 K. The X-ray diffraction intensity was measured for 15 min after waiting for 5 min at each temperature. The obtained data were analyzed by Rietveld method using computer program RIETAN [24].

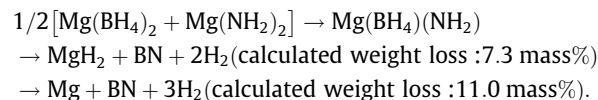
3. Results and discussion

3.1. Dehydrogenation properties

The thermal analysis results of the mixture sample of $\text{Mg}(\text{BH}_4)_2 + \text{Mg}(\text{NH}_2)_2$ during heating process are shown in Fig. 1. By the X-ray diffraction measurements (Section 3.2), it is confirmed that this sample has been changed to single phase $\text{Mg}(\text{BH}_4)(\text{NH}_2)$ at 453 K. Consequently, in the present thermal analysis, the dehydrogenation properties of $\text{Mg}(\text{BH}_4)(\text{NH}_2)$ are indicated at higher temperature than 453 K.

Many fine peaks that appear in the range from 480 K to 490 K in the TPD-MS (Temperature Programmed Desorption-Mass Spectrometry) curve (Fig. 1c) are noises in the measurement. The cause of noises is unexplained but these noises often appear in the early dehydrogenation stage of some complex hydrides. The dehydrogenation begins at about 468 K and actively reacts in two-stage at 513 K and 688 K. The measurement value of weight loss by the dehydrogenation is 7.2 mass% at 600 K and 10.0 mass% at 723 K (Fig. 1a). It is confirmed that ammonia is not released with this

dehydrogenation reaction by the TPD-MS measurement. These results indicate that the dehydrogenation of this sample is expressed in the following reaction formula;



From the X-ray diffraction measurements, it was confirmed that MgH_2 and Mg are crystalline phase and BN is amorphous phase. The second reaction temperature 688 K is higher than the dehydrogenation of mechanically milled MgH_2 and is about the same as that of no milled MgH_2 reagent [25]. Therefore, in the present measurement, it is estimated that the generated MgH_2 crystalline phase is in a grain growth state.

Several peaks, which are indicated by the labels (A–E) in Fig. 1b, appear in the DTA curve. It is estimated that these peaks are corresponding to the following structural changes; mixture of $\text{Mg}(\text{BH}_4)_2 + \text{Mg}(\text{NH}_2)_2$.

- A: crystallization to $\text{Mg}(\text{BH}_4)(\text{NH}_2)$ (exothermic peak at 392 K).
- B: structural change to intermediate or amorphous phase (endothermic peaks at 454 K and 462 K).
- C: dehydrogenation (exothermic peak at 508 K or endothermic peaks at 490 K and 526 K).
- D: crystallization to MgH_2 (exothermic peak at 607 K).
- E: dehydrogenation from MgH_2 to Mg (endothermic peak at 688 K).

It is reported that the initiation temperature of dehydrogenation in $\text{LiBH}_4 + n\text{LiNH}_2$ ($n = 1-3$) is about 523 K [5,6]. Therefore, the dehydrogenation temperature of $\text{Mg}(\text{BH}_4)(\text{NH}_2)$ is about 50 K lower than that of $\text{Li}_2(\text{BH}_4)(\text{NH}_2)$.

The mixture of $\text{Mg}(\text{BH}_4)_2 + 2\text{Mg}(\text{NH}_2)_2$ was studied in the same way as $\text{Mg}(\text{BH}_4)_2 + \text{Mg}(\text{NH}_2)_2$. As a result, it was found that the

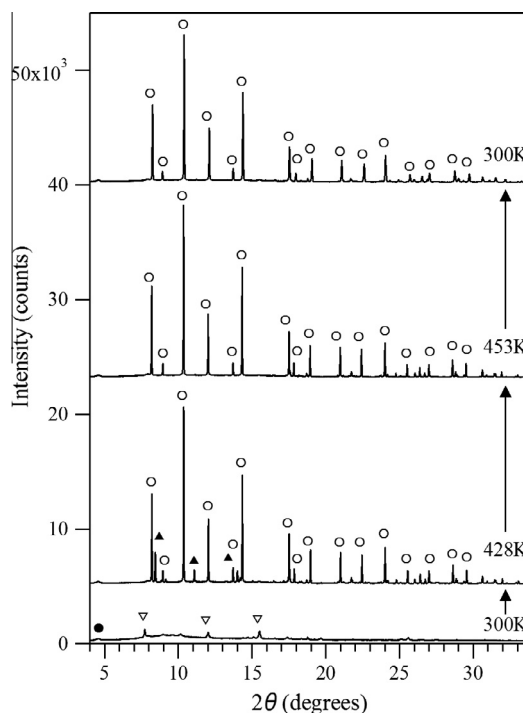


Fig. 2. X-ray diffraction patterns for the mixture sample of $\text{Mg}(\text{BH}_4)_2 + \text{Mg}(\text{NH}_2)_2$ at each temperature in the heating and cooling process. Each marks represent peaks of the following compounds; ○: $\text{Mg}(\text{BH}_4)(\text{NH}_2)$, ▲: unknown, ▽: $\text{Mg}(\text{NH}_2)_2$, ●: MgNH .

Download English Version:

<https://daneshyari.com/en/article/1613371>

Download Persian Version:

<https://daneshyari.com/article/1613371>

[Daneshyari.com](https://daneshyari.com)