

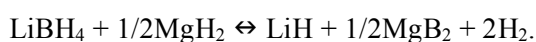
HYDROGEN DESORPTION PROPERTIES AND NMR CHARACTERIZATION OF $\text{ScH}_2 + \text{MB}_n$ ($M = \text{Mg}, \text{Ca}$) COMPOSITES

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Introduction

Hydrogen energy is a potential resource that enables to replace the fossil fuel. Therefore, hydrogen storage materials such as hydride and metal alloys have been extensively studied recent years. Among them, light metal borohydride $M(\text{BH}_4)_n$ is one of attractive candidates because of their high hydrogen capacity. However, almost all $M(\text{BH}_4)_n$ have poor reversibility because of quite slow kinetics. Vajo et al. reported reversible reaction of hydrogen storage composite [1];



According to the reverse reaction, the hydride and boride mixture gives a borohydride at 300 – 350°C under 10 MPa H_2 pressure. By analogy, we here show the hydrogenation of mixtures of scandium hydride and borides under H_2 pressure. To accelerate the hydrogenation reaction, we applied the ball-milling technique. The products were investigated on their gas desorption properties by using thermogravimetry (TG) and thermal desorption mass spectroscopy (MS), and characterized by using high-energy synchrotron X-ray diffraction (SR-XRD) and solid-state nuclear magnetic resonance (NMR) spectroscopy.

Experimental

Materials

A starting material ScH_2 was prepared by the hydrogenation of metal scandium (99.9%, Sigma-Aldrich) at 250°C under 9.0 MPa H_2 pressure for < 1 h. Then, ScH_2 and metal boride, which was MgB_2 (99%, Rare Metallic) or CaB_6 (99.5%, Alpha Aesar), were put into Cr-steel vessels with 20 steel balls (7 mm in diameter). The molar ratios of $\text{ScH}_2:\text{MgB}_2$ and $\text{ScH}_2:\text{CaB}_6$ were 2:3 and 2:1, respectively. The samples were finely milled at room temperature under 6.0 MPa H_2 by using rocking-mill apparatus for 80 h. Additionally, scandium diboride (ScB_2), magnesium borohydride ($\text{Mg}(\text{BH}_4)_2$), and calcium borohydride ($\text{Ca}(\text{BH}_4)_2$) were used as references. ScB_2 was synthesized by heating the mixture of scandium oxide and boron under vacuum condition at ~1300 °C for 40 min. $\text{Mg}(\text{BH}_4)_2$ was synthesized by milling and heating of mixture of magnesium chloride and lithium borohydride with 1:2 of molar ratio under hydrogen pressure. $\text{Ca}(\text{BH}_4)_2$ was obtained by heating of $\text{Ca}(\text{BH}_4)_2 \cdot 2\text{THF}$ (98%, Sigma-Aldrich) at 160 °C for 1 h under vacuum condition. All the sample preparations were performed in a purified Ar-filled glove box (Miwa MFG Co., Ltd., MPP60W) to keep a low dew point (< -80 °C) and oxygen concentration (< 1 ppm).

Apparatus and Procedures

The gas desorption properties of the products were investigated by TG (Rigaku TG-8120) equipped with MS (Anelva M-QA200TS) under He gas flow condition. The samples were heated up to 500°C with a heating rate of 5°C/min. SR-XRD measurements were performed for the sample powders before/after dehydrogenation at the beam line BL02B2 in SPring-8 (Figures are not shown). The samples were stuffed into a glass capillary and sealed with epoxy adhesive to avoid exposure to the air. NMR spectra were acquired for ^{11}B nucleus (resonance frequency of 192.5 MHz) at a magnetic field of 14.1 T (JEOL JNM-ECA600). The samples were stuffed in 4-mm rotors with tight-sealing caps and spun at 15 kHz (magic-angle spinning, MAS). H_3BO_3 saturated solution was used as an external reference at 19.49 ppm.

Results and discussion

The gas desorption properties of $2\text{ScH}_2 + 3\text{MgB}_2$ and $2\text{ScH}_2 + \text{CaB}_6$ milling products were shown in Fig. 1. All the products released H_2 and no other components such as toxic B_2H_6 . Because neat ScH_2 , MgB_2 , and CaB_6 do not release hydrogen, these results indicate that hydrogenation of mixtures ScH_2 and metal borides were proceeded by milling. The weight losses of $2\text{ScH}_2 + 3\text{MgB}_2$ and $2\text{ScH}_2 + \text{CaB}_6$ 3.4 mass % and 2.3 mass %.

SR-XRD profiles of $2\text{ScH}_2 + 3\text{MgB}_2$ milling product before/after dehydrogenation showed relatively broad peaks attributable to ScB_2 , and small amounts of Fe peaks coming from ball and vessel. Similarly, the $2\text{ScH}_2 + \text{CaB}_6$ products showed the ScB_2 , Fe and unreacted CaB_6 . There were few differences between the XRD profiles before and after

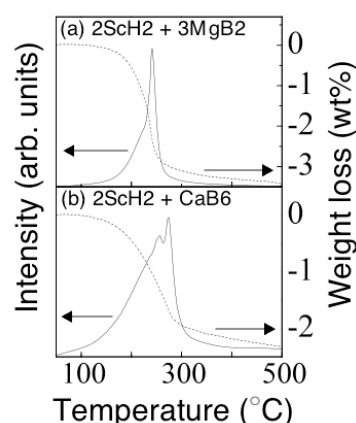


Fig. 1 TG-MS profiles of milled (a) $2\text{ScH}_2 + 3\text{MgB}_2$ and (b) $2\text{ScH}_2 + \text{CaB}_6$. The MS profiles are shown for H_2 .

heating. These results indicate that ScB₂ was produced from ScH₂ and borides. From above results, there are two possibilities of the origin of hydrogen desorption: hydrogen stored in ScB₂ or the other amorphous phases.

To clarify the origin of hydrogen desorption, we performed NMR spectroscopy. NMR spectroscopy is the best tool to investigate the amorphous structures. ¹¹B MAS NMR spectra of 2ScH₂ + 3MgB₂ and 2ScH₂ + CaB₆ milling products before/after dehydrogenation were examined in Figs. 2, along with the other reference materials Mg(BH₄)₂, Ca(BH₄)₂, ScB₂, MgB₂ and CaB₆ (these references are unmilled and crystalline).

The spectrum of 2ScH₂ + 3MgB₂ before dehydrogenation shows a relatively sharp peak at -39 ppm and a broad peak between 50 and 125 ppm (Fig. 2(a)). It is found that the -39 ppm peak strictly coincides with the single peak in the crystalline Mg(BH₄)₂. The broad peak around 50 – 125 ppm will be related to borides, especially ScB₂ according to the SR-XRD result mentioned above, although both the references ScB₂ and MgB₂ have a close chemical shift each other. It should be noted that the milled ScB₂ had a broader peak similar to that in Fig. 2(a). In the spectrum of 2ScH₂ + 3MgB₂ milling product after dehydrogenation (Fig. 2(b)), the -39 ppm peak disappears, strongly suggesting that the hydrogen was desorbed by the thermal decomposition of Mg(BH₄)₂.

The spectrum of 2ScH₂ + CaB₆ milling product before dehydrogenation also shows a relatively sharp peak at -28 ppm and a broad peak between 50 – 125 ppm (Fig. 2(c)). The -28 ppm peak agrees well with the single peak in the crystalline Ca(BH₄)₂. The broad peak around 50 – 125 ppm is again related to ScB₂, and the small peak around 0 ppm is coming from residual CaB₆, being consistent with the SR-XRD result. The spectrum of 2ScH₂ + CaB₆ after dehydrogenation do not have any peak at -28 ppm (Fig. 2(d)), indicating that the dehydrogenation is responsible for the decomposition of Ca(BH₄)₂ into CaB₆, CaH₂, and H₂ [2].

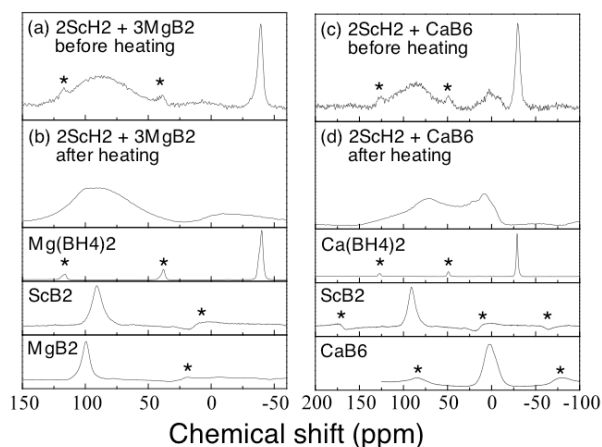
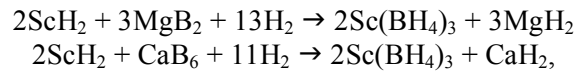
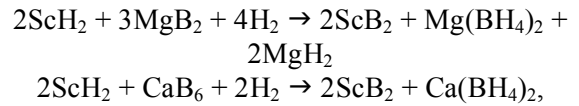


Fig. 2 ¹¹B MAS NMR spectra of the 2ScH₂ + 3MgB₂, 2ScH₂ + CaB₆ milling products before/after heat treatment, and references. Spinning side bands are shown as asterisks.

According to the results of Vajo et al. [1], the following reactions were inferred on the hydrogenation process;



where Sc(BH₄)₃ is expected to have lower H₂ desorption temperature among metal borohydrides [3]. However, this study offers the alternative reactions;



where the presence of amorphous MgH₂ will be confirmed in the future works. We here note that in the proposed reactions by mechanical milling under H₂ pressure, the hydrogen-bearing products Mg(BH₄)₂ and Ca(BH₄)₂ are X-ray amorphous and should be confirmed by NMR. This study indicates that the ScB₂ forms by replacing hydrogen in ScH₂ by boron, and does not act as a hydrogen storage.

Conclusion

We studied the hydrogen storage properties (hydrogenation/dehydrogenation) of ScH₂ + MB_n (M = Mg, Ca) composites mechanically-milled under H₂ pressure by using TG-MS, and characterized the composites by SR-XRD and NMR spectroscopy. The results of dehydrogenation properties suggested that the hydrogenation of ScH₂ + MB_n were proceeded by milling at room temperature. ¹¹B MAS NMR spectra clarified that the composites after milling consisted of low-crystalline ScB₂ and non-crystalline M(BH₄)₂-like materials, and that H₂ desorption was coming from the decomposition of the borohydrides.

Acknowledgements

The authors are grateful to Dr. Shinji Michimura (Hiroshima University) for preparing ScB₂. This work was supported by New Energy and Industrial Technology Development Organization (NEDO) under the project “Advanced Fundamental Research Project on Hydrogen Storage Materials”.

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