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Hydrogen storage properties of $LiBH_4$ destabilized by SrH_2

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ABSTRACT

In this work, we have succeeded in destabilizing $LiBH_4$ by the addition of SrH_2, *via* the reaction $6LiBH_4 + SrH_2 \rightarrow SrB_6 + 6LiH + 10H_2$ with a theoretical hydrogen capacity of 9.1 wt.%. According to the van't Hoff and Arrhenius equations, the dehydrogenation enthalpy change and activation energy for the $LiBH_4/SrH_2$ system were experimentally determined to be 48 kJ/mol H_2 and 64 kJ/mol, respectively. Both are remarkably reduced in comparison with the pristine $LiBH_4$, which is responsible for the improved dehydrogenation property of the $LiBH_4/SrH_2$ system. The dehydrogenated products $SrB_6 + 6LiH$ can be rehydrogenated to form $LiBH_4$ and $LiSrH_3$ at 723 K under an initial hydrogen pressure of 8.0 MPa.

1. Introduction

Hydrogen, as a highly efficient and clean secondary energy carrier, is an ideal substitute for conventional fossil fuels in the future. For large-scale utilization of hydrogen as an energy carrier, hydrogen storage systems with high efficiency and safety should be developed. Various solid-state materials, such as metal hydrides, alanates and borohydrides, have been widely investigated for this purpose. Among them, $LiBH_4$ is one of the most promising candidates for on-board hydrogen storage, due to its high gravimetric (18.4 wt.%) and volumetric (121 kg/m^3) hydrogen density [1–3]. However, $LiBH_4$ alone has a reaction enthalpy change as high as 74 kJ/mol H_2 for its decomposition into LiH and B, and therefore a dehydrogenation temperature above 370 °C is required under 0.1 MPa hydrogen pressure [4]. Furthermore, the dehydrogenation process of $LiBH_4$ is rather sluggish and the rehydrogenation is hardly possible under mild temperature and pressure conditions [4,5].

During the last decade, $LiBH_4$ multicomponent reactive systems have been intensively investigated to destabilize $LiBH_4$ and enhance its dehydrogenation kinetics [6–20]. For example, Vajo et al. [6] reported that $LiBH_4$ could release hydrogen with a reduced reaction enthalpy by the addition of MgH_2, because of the change in reaction pathway as described below:

$$2LiBH_4 + MgH_2 \rightarrow MgB_2 + 2LiH + 4H_2 \quad (1)$$

Moreover, the formation of MgB_2 could overcome the chemical inertness of pure boron, thus greatly improving the rehydrogenation to form $LiBH_4$. Following this strategy, the $LiBH_4/CaH_2$ system with a small amount of catalyst was also investigated [7,21–24]. It was found that a dehydrogenation enthalpy change of 56.5 kJ/mol H_2 could be obtained by incorporating $LiBH_4$ with CaH_2, based on the formation of calcium hexaboride CaB_6 [21].

In view of the previous results mentioned above, a question arises as to whether other binary alkaline-earth metal hydrides than MgH_2 and CaH_2 can be used as the destabilizing additives for $LiBH_4$. Stimulated by this question, the dehydrogenation and rehydrogenation properties, as well as the destabilization mechanism involved for the $LiBH_4/SrH_2$ system have been investigated in this work. No catalysts were doped into the $LiBH_4/SrH_2$ system, which enables the investigation of the pure effect from SrH_2.

2. Experimental details

2.1. Sample preparation

Commercial $LiBH_4$ powder (95%, Alfa Aesar) was used as-received without further purification. SrH_2 powder was synthesized by reacting metallic Sr scraps (99%, Alfa Aesar) with hydrogen (99.999%). The $6LiBH_4 + SrH_2$ mixture was ball-milled under 0.5 MPa hydrogen pressure at a rotation speed of 400 rpm for only 2 h by using a QM-1SP planetary mill. Stainless steel vials (250 mL in volume) and balls (10 mm in diameter) were used. The ball to sample weight ratio was 20:1. To avoid air-exposure, all sample handling was carried out in an Ar-filled glove box equipped with a purification system keeping the typical O_2/H_2O levels below 1 ppm.

2.2. Sample characterization

Dehydrogenation and rehydrogenation properties of the samples were examined based on the volumetric method by using a carefully calibrated Sieverts-type apparatus (Suzuki Shokan Co., Ltd., Japan). The temperature dependence of dehydrogenation was determined by heating the sample from ambient temperature to

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873 K at a heating rate of 2 K/min. Isothermal dehydrogenation was performed by quickly heating and then keeping the sample at a given temperature. The hydrogen back pressure for the above temperature ramp and isothermal dehydrogenation examinations was below 0.1 MPa. Pressure–composition (P–C) isotherms were measured at 693, 723 and 753 K to investigate the thermodynamic property of the $LiBH_4/SrH_2$ system in the dehydrogenation process. The rehydrogenation experiment was carried out at 723 K under an initial hydrogen pressure of 8.0 MPa.

To elucidate the phase components of the ball-milled, dehydrogenated and rehydrogenated $6LiBH_4 + SrH_2$ mixtures, X-ray diffraction (XRD) measurements were performed using a Rigaku D/Max 2500VL/PC diffractometer with Cu Kα radiation at 50 kV and 150 mA. The XRD samples were loaded and sealed in a special holder that can keep the sample under argon atmosphere in the course of measurement.

3. Results and discussion

3.1. Dehydrogenation behavior

3.1.1. Thermal behavior upon dehydrogenation

For understanding the dehydrogenation stage of the $LiBH_4/SrH_2$ system, Fig. 1 gives the amount of hydrogen desorbed as a function of temperature for the as-milled $6LiBH_4 + SrH_2$ mixture at a heating rate of 2 K/min. For comparison, the hydrogen desorption curve of the pristine $LiBH_4$ sample ball-milled for 2 h was also measured. It is observed that dehydrogenation of the $LiBH_4/SrH_2$ system starts around 490 K, and the majority of hydrogen is released in the temperature range of 660–760 K. A dehydrogenation amount of 8.7 wt.% was totally achieved. In contrast, the pristine $LiBH_4$ released hydrogen sluggishly, and the amount of hydrogen desorbed up to 873 K is only 6.8 wt.%. This value is much lower than the theoretical one (13.8 wt.%). Evidently, the thermal stability of $LiBH_4$ can be remarkably reduced by using SrH_2 as a destabilizing additive.

It should be noted from Fig. 1 that dehydrogenation of the $LiBH_4/SrH_2$ system proceeds in a single step, i.e., through a direct reaction between $LiBH_4$ with SrH_2. In comparison with the two-step dehydrogenation in the $LiBH_4/MgH_2$ system [25], such a feature enables the $LiBH_4/SrH_2$ system to release hydrogen prior to the decomposition of SrH_2. That is, $LiBH_4$ is also effective in lowering the stability of SrH_2, which is similar to the results observed in the $LiBH_4/CaH_2$ and $LiBH_4/CaF_2$ systems [7,21,26].

Fig. 2 presents the XRD patterns of the $6LiBH_4 + SrH_2$ samples after ball-milling and dehydrogenation at 723 K. It can be seen that the as-milled sample consists mainly of $LiBH_4$ and SrH_2, indicating that no definite reaction occurred between the starting materials during milling. After dehydrogenation, as indicated in Fig. 2b, SrB_6 and LiH can be formed without the remaining $LiBH_4$ or SrH_2. The XRD results suggest that the $LiBH_4/SrH_2$ system is dehydrogenated according to the following reaction:

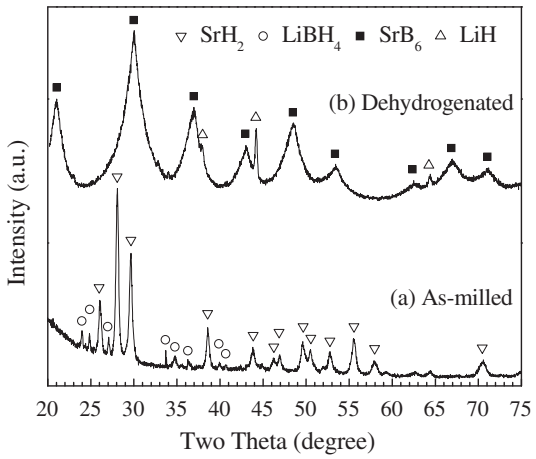

Fig. 2. XRD patterns of the $LiBH_4/SrH_2$ system: (a) as-milled and (b) dehydrogenated at 723 K.

$$6LiBH_4 + SrH_2 \rightarrow SrB_6 + 6LiH + 10H_2 \quad (2)$$

The theoretical hydrogen amount desorbed from this reaction can be calculated to be 9.1 wt.%, which is consistent with the measured value of 8.7 wt.% (see Fig. 1).

3.1.2. Dehydrogenation thermodynamics

In order to evaluate the dehydrogenation thermodynamics of the $LiBH_4/SrH_2$ system, P–C isotherms (see Fig. 3) were measured at 693, 723 and 753 K, respectively. It can be seen that the dehydrogenation isotherms have a well-defined plateau region, and the equilibrium pressures vary from 0.49 MPa at 693 K to 0.94 MPa at 753 K. It is well known that the enthalpy change (ΔH) and entropy change (ΔS) for a dehydrogenation reaction can be calculated from the van't Hoff equation:

$$\ln P = [-\Delta H/(RT)] + \Delta S/R \quad (3)$$

where P is the equilibrium pressure at absolute temperature T, and R is the gas constant. Fig. 4 gives the van't Hoff plot of the $LiBH_4/SrH_2$ system by using the dehydrogenation equilibrium pressures at 4.0 wt.% (see Fig. 3). According to the equation shown in Fig. 4, the enthalpy and entropy changes for the dehydrogenation of the $LiBH_4/SrH_2$ system can be determined to be 48 kJ/mol H_2 and 82 J/(mol K) H_2, respectively. The ΔS value here is rather different from the typical value of ~130 J/(mol K) H_2 for most metal hydrides. This difference can be mainly attributed to the higher entropy of $LiBH_4$

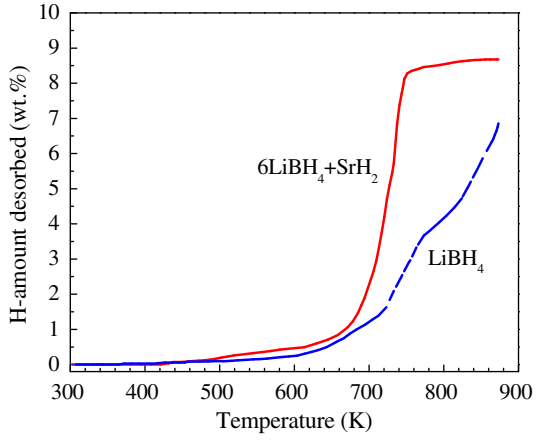

Fig. 1. Temperature dependence of dehydrogenation for the 2 h ball-milled $6LiBH_4 + SrH_2$ mixture and the pristine $LiBH_4$ at a heating rate of 2 K/min.

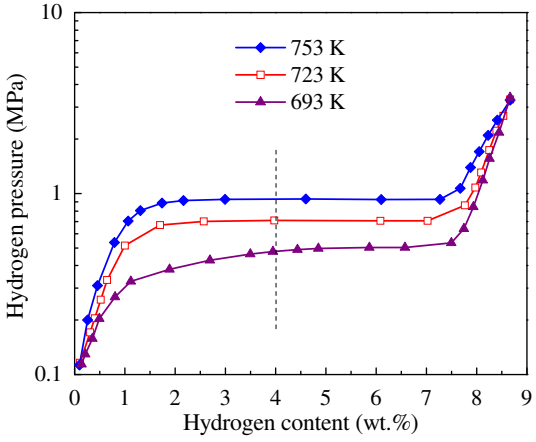

Fig. 3. Dehydrogenation P–C isotherms of the $LiBH_4/SrH_2$ system at different temperatures.