Improved Dehydrogenation and Rehydrogenation Properties of LiBH₄ by Nanosized Ni Addition

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The complex hydride LiBH₄, with a hydrogen density of 18.5 mass%, has been attracting significant interests for hydrogen storage, while suffers from its high dehydrogenation and rehydrogenation temperature. In this work, we systematically investigated the improvement effects of nanosized Ni on the dehydrogenation and rehydrogenation reactions of LiBH₄ using thermogravimetry, quadrupole mass spectrometry and pressure-composition-isotherm analyses. Nanosized Ni was homogeneously dispersed on the surface of LiBH₄ after ball milling. The dehydrogenation peak temperature of LiBH₄ was reduced from 743 to 696 K with addition of 25 mass% Ni. First, LiBH₄ tended to react with Ni to form Ni₄B₃, which suggests the thermodynamic destabilization effect of Ni. Then, the *in-situ* formed Ni₄B₃ was suggested to play a catalytic role on the dehydrogenation of the unreacted LiBH₄. Moreover, the rehydrogenation content of LiBH₄ was improved from 4.3 to 10.8 mass% by addition of 25 mass% Ni, suggesting the significant improvement effect of Ni₄B₃ on the rehydrogenation. [doi:10.2320/matertrans.MG201407]

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1. Introduction

Metal borohydride, generally expressed as $M(\text{BH}_4)_n$ (n denotes the valence of metal M), has been attracting interest for high density hydrogen storage.^{1,2)} LiBH₄, as a typical $M(\text{BH}_4)_n$, possessing the hydrogen density of 18.5 mass%, was firstly reported as a potential hydrogen storage material in 2003.³⁾ Upon heating, LiBH₄ releases approximately 13.8 mass% of hydrogen according to the following reaction.

The dehydrogenation reaction was reported to occur above 600 K (at a heating rate of 5 K/min) and rehydrogenation reaction from LiH and B proceeds at 873 K under 35 MPa of hydrogen.⁴⁾ To reduce the de/rehydrogenation temperatures of LiBH₄ for practical applications, an important approach is to tailor the enthalpy change of dehydrogenation by combination LiBH₄ with metal or metal hydrides.^{5–14)} For example, the addition of MgH₂^{5,8)} to LiBH₄ reduces the enthalpy changes of dehydrogenation reaction by 25 kJ/mol H₂ according to eq. (2).

Moreover, due to the formation of MgB₂ with weaker B–B bonds compared to the amorphous boron, reaction (2) can be fully reversed at 573–623 K.⁵⁾

LiBH₄–Ni system is expected to dehydrogenate at near room temperature, because the dehydrogenation enthalpy to the supposed products of Ni₄B₃, Ni₂B or Ni₃B according to eqs. (3)–(5), can be estimated as 18, 24 or 34 kJ/mol H₂, respectively.

Further, the supposed dehydrogenated product of nickel boride such as Ni₂B has been widely known as a heterogeneous hydrogenation catalyst.¹⁵⁾ LiBH₄–Ni system, therefore, is expected to be a good candidate for hydrogen storage material which may possess better thermodynamic and kinetic properties than those of LiBH₄.

In this study, nanosized Ni was chosen as a starting material for facilitating the reaction with LiBH₄. In order to maintain the hydrogen capacity at approximately 10 mass% in the LiBH₄–Ni system, the weight ratio of nanosized Ni to LiBH₄ was set as 25 mass% (equal to 8.5 mol%). The de/rehydrogenation properties of LiBH₄–Ni system were compared with those of the pristine LiBH₄, in order to reveal the improvement effect of Ni. Moreover, mechanistic discussion based on the phase transformations during de/rehydrogenation will provide insightful information for designing new LiBH₄ related system with improved hydrogen storage properties.

2. Experimental Procedure

Starting materials of LiBH₄ (Aldrich, 95% purity) and Ni powder (Aldrich, 99.5% purity, particle size of 100–500 nm) were used as received. The sample of LiBH₄–Ni was prepared by mechanical milling (Fritsch P-7, 400 rpm, ball to powder ratio of 30 : 1) in a hardened steel vial (30 cm³ in volume) under 0.1 MPa Ar. The milling process was paused for 5 min every 15 min milling, in order to avoid temperature increment in the sample during milling. Nanosized Ni was found to homogeneously disperse on the surface of LiBH₄, as shown in Fig. 1. Dehydrogenation of LiBH₄–Ni was carried out under 1.0 MPa Ar at 773 K and kept for 2 h, thus obtained

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Fig. 1 SEM image of ball milled LiBH₄-Ni. The white particle homogeneously dispersed on the surface was detected as Ni.

product was used as the starting material of rehydrogenation. The rehydrogenation was carried out under a hydrogen pressure of 35.0 MPa at 823 K for 24 h in a specially designed pressure-resistant reaction tube.

The microstructure was observed by scanning electron microscope (SEM, JEOL, SM7000). The crystal structures were examined via XRD (PANalytical X'PERT with Cu K α radiation) at room temperature. The dehydrogenation content and thermal desorption spectra as a function of temperature was examined by thermogravimetry (TG, Rigaku TG-8210) connected directly with quadrupole mass spectroscopy (QMS, Anelva M-QA200TS). The combined TG and QMS apparatuses are installed in a glove box filled with purified He gas. The samples were heated at a rate of 5 K/min under a flow of high-purity He (99.9999%) at 150 mL/min. The isothermal dehydrogenation at 723 K was carried out by pressure-composition-temperature (PCT, Suzuki Shokan, PCT-4SDWIN) measurements with a maximum equilibrium judging time of 2 h. 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 Discussions

3.1 De/rehydrogenation of LiBH₄-Ni system

Dehydrogenation of ball milled LiBH₄ and LiBH₄-Ni as a function of temperature examined by TG and QMS are shown in Figs. 2(a) and 2(b), respectively. No impurity gas except for hydrogen was detected under present measurement condition, which suggests the weight loss means the dehydrogenation content. The dehydrogenation content referring to LiBH₄ reaches to 12.3 mass% when LiBH₄-Ni was heated up to 800 K, which is almost same as that of the pristine LiBH₄. Further, the main dehydrogenation peak temperature is decreased from 743 to 696 K with the addition of nanosized Ni. These results consistently proved the improvement effect of nanosized Ni on the dehydrogenation of LiBH₄.

Apparent activation energy E_A was evaluated by the Kissinger's peak shift method, including the application of the next equation.

Fig. 2 (a) TG and (b) QMS measurement results of ball milled LiBH₄ and LiBH₄-Ni as well as their rehydrogenated samples.

Fig. 3 Kissinger plot for the dehydrogenation of ball milled LiBH₄ and LiBH₄-Ni.

$$\ln(C/T_p^2) = -(E_A/RT_p) + A \quad (6)$$

Here, C is the heating rate, T_p is the peak temperature, E_A is the apparent activation energy, R is the gas constant, and A is a constant. Figure 3 shows a Kissinger plot for the dehydrogenation of ball milled LiBH₄ and LiBH₄-Ni. From the slope of the fitted line, E_A were therefore determined. E_{A1} for the dehydrogenation of pristine LiBH₄ was estimated as 187 ± 24 kJ/mol, which is largely reduced to 100 ± 4 kJ/mol with addition of nanosized Ni. Such significant reduction of E_A suggests that nanosized Ni may play a role in the improvement of kinetics.

Fig. 4 PCT curves at 723 K for dehydrogenation of the ball milled LiBH_4 and $\text{LiBH}_4\text{-Ni}$.

The isothermal dehydrogenation curves at 723 K of as-milled samples are shown in Fig. 4. Taking the sluggish kinetics and the poor reversibility under the present experimental condition into account, it would be reasonable to call the “equivalent pressure” as “apparent plateau”. The apparent plateau of LiBH_4 at 723 K is increased from 0.35 to 1.2 MPa by addition of nanosized Ni. Further, another short apparent plateau is observed at a hydrogen pressure higher than 6.0 MPa. These suggest a possible thermodynamic improvement by Ni, whereas kinetic effect should be also taken into account due to the small amount (only 8.5 mol%) addition. These thermodynamic and/or kinetic improvement effects also increased the dehydrogenation content (from approximately 9.8 to 11.6 mass%) which was referred to the pure LiBH_4 . Detailed improvement effect of nanosized Ni will be discussed later.

The rehydrogenation properties of LiBH_4 are also found to be improved by addition of Ni, as shown in the TG and QMS measurement results in Fig. 2. Here, the weight loss means the rehydrogenation content for the dehydrogenated samples. The rehydrogenation content of LiBH_4 is remarkably increased from 4.3 to 10.5 mass% by addition of nanosized Ni. Further, the dehydrogenation temperature of the rehydrogenated $\text{LiBH}_4\text{-Ni}$ is approximately 40 K lower than that of the rehydrogenated LiBH_4 .

3.2 Phase transformations during de/rehydrogenation

The XRD profiles of the as-milled, dehydrogenated and rehydrogenated products are shown in Fig. 5. Diffraction peaks of low temperature phase LiBH_4 are confirmed in LiBH_4 and $\text{LiBH}_4\text{-Ni}$ after ball milling. Only LiH is identified after dehydrogenation at 773 K, indicating that LiBH_4 decomposes into LiH and amorphous B.³⁾ On the other hand, in addition to LiH, a new compound of Ni_4B_3 is detected in $\text{LiBH}_4\text{-Ni}$ after dehydrogenating at 773 K. Therefore, the reaction between LiBH_4 and nanosized Ni can be expressed as eq. (3).

Fig. 5 XRD profiles of as-milled, dehydrogenated (Dehy) and rehydrogenated (Rehy) samples of (a) pristine LiBH_4 and (b) $\text{LiBH}_4\text{-Ni}$.

The formation of LiBH_4 is confirmed in the XRD profiles (Fig. 5) of both rehydrogenated samples of LiBH_4 and $\text{LiBH}_4\text{-Ni}$. The differences between these two samples are also clearly observed: (a) in the rehydrogenated $\text{LiBH}_4\text{-Ni}$, the peak density of remained LiH is largely reduced, which agrees with its improved rehydrogenation properties; (b) a new compound of Ni_2B is identified in the rehydrogenated $\text{LiBH}_4\text{-Ni}$. Therefore, the improved rehydrogenation properties by Ni addition are considered to mainly result from the following reaction:

3.3 Improvement effect of nanosized Ni on the de/rehydrogenation of LiBH_4

Since the dehydrogenation enthalpy of $\text{LiBH}_4\text{-Ni}$ to form Ni_4B_3 according to eq. (3) is smaller than that of pristine LiBH_4 , higher plateau examined by PCT and lower dehydrogenation temperature examined by TG and QMS were observed in $\text{LiBH}_4\text{-Ni}$. Judging from the dehydrogenation enthalpy assuming the entropy change is 130 J/(mol·K), the short apparent plateau above 6.0 MPa should attribute to the reaction between LiBH_4 and Ni, while the apparent plateau at 1.2 MPa may originate from the dehydrogenation of LiBH_4 which is considered to be kinetically improved by the *in-situ* formed Ni_4B_3 . This explanation is well supported by the phase transformation during the dehydrogenation of $\text{LiBH}_4\text{-Ni}$, i.e., formation of Ni_4B_3 and large amount of undecomposed LiBH_4 are confirmed even at the dehydrogenation peak temperature of 700 K by XRD, suggesting that the reaction between LiBH_4 and Ni proceed prior to the decomposition of LiBH_4 . We believe the reaction between LiBH_4 and Ni should be responsible for dehydrogenation at

the short plateau above 6.0 MPa. The *in-situ* formed Ni₄B₃, therefore, is considered to subsequently facilitates the dehydrogenation of undecomposed LiBH₄, similar to that of TiB₂ formed in LiBH₄-MgH₂ with addition of Ti-isopropoxide¹⁶ or Mg(BH₄)₂ with addition of TiCl₃.^{17,18}

During rehydrogenation, Ni₄B₃ react with LiH to form LiBH₄ and Ni₂B according to eq. (7). Generally, the rehydrogenation from LiH and metal boride will generate LiBH₄ together with metal or metal hydride, like the system of LiH/MgB₂,^{5,8} LiH/AlB₂^{11–13} or LiH/CaB₆.¹⁴ Noticeably, not Ni but Ni₂B is formed in the rehydrogenation reaction of LiH/Ni₄B₃ system. Thus formed Ni₂B also showed comparable kinetic improvement effect to that of Ni₄B₃ on the subsequent dehydrogenation.

Further investigation on the changes in chemical bonding state and microstructures of Ni species during the de/rehydrogenation are ongoing, which is expected to contribute to the clarification of the improvement mechanism of nickel borides on de/rehydrogenation of LiBH₄.

4. Conclusion

In this study, we demonstrated the improvement effects of nanosized Ni on the de/rehydrogenation of LiBH₄. The *in-situ* formed Ni₄B₃ through chemical reaction between LiBH₄ and Ni during dehydrogenation showed significant effects on the reduction of dehydrogenation temperature and the increase of rehydrogenation content of LiBH₄. Ni₄B₃ transformed into Ni₂B after rehydrogenation reaction. Thus formed Ni₂B was found to show similar catalytic effect to Ni₄B₃ on the reduction of dehydrogenation temperature. Clarification of the improvement mechanism of nickel boride on the de/rehydrogenation of LiBH₄ is of great importance for the development of advanced borohydride-based high density hydrogen storage materials.

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