Investigation of the dehydrogenation behavior of the 2LiBH$_4$:CaNi$_5$ multicomponent hydride system

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ABSTRACT

LiBH$_4$ has gained much attention as a potential hydrogen storage material due to its high hydrogen storage capacity of 18.5 wt%. However, LiBH$_4$ only releases its full hydrogen capacity at temperatures greater than 600 °C and requires hydrogen pressures of at least 350 bar to rehydrogenate the end products. The dehydrogenation temperature can be altered by thermodynamic tuning through the addition of a reactive agent resulting in a lower enthalpy of dehydrogenation. Most multicomponent hydride systems display dehydrogenation temperatures above 300 °C, making them less desirable for automotive applications. In this work we report the solid-state decomposition of LiBH$_4$ in the 2LiBH$_4$:CaNi$_5$ system below the LiBH$_4$ melting temperature of 270 °C. In situ neutron diffraction measurements confirmed the decomposition took place in the solid state at 200 °C, forming LiD, CaD$_2$, Ni$_3$B and Ni$_2$B phases as end products. The solid-state decomposition was further supported by SEM and TEM measurements showing the presence of nano-crystalline particles.

Introduction

With increasing levels of atmospheric CO$_2$ due to the consumption of fossil fuels, alternative energy sources have the potential to relieve the strain on fossil fuels as well as to reduce CO$_2$ emissions. However, for alternative energy technologies to succeed, practical and efficient energy storage is required. Hydrogen has become an attractive energy carrier for renewable energy sources due to its high energy density, however a suitable hydrogen storage system remains a significant challenge [1]. Solid state hydrogen storage has the potential to provide higher hydrogen storage capacities than conventional storage methods such as compressed or liquefied hydrogen [2–4]. Complex metal hydrides have recently gained much attention due to their high hydrogen storage capacities, e.g. 18.5 wt% for LiBH$_4$, making them suitable to meet the U.S. Department of Energy gravimetric hydrogen storage target of 5.5 wt% for 2015 [5]. However, many of these materials suffer from poor kinetic and thermodynamic properties. For example, LiBH$_4$ only releases its full hydrogen capacity at temperatures greater than 600 °C [6,7] and hydrogenation does not occur below 600 °C and then only

under a hydrogen pressure of 350 bar [8]. Dehydrogenation of $LiBH_4$, as indicated by Scheme 1, does not release all the hydrogen due to formation of LiH, a more thermodynamically stable metal hydride having a T(1 bar) of 910 °C (the temperature required for a 1 bar equilibrium pressure), lowering the total available hydrogen capacity to 13.4 wt% [9,10].

Scheme 1. Decomposition pathway of $LiBH_4$

$$LiBH_4 \rightarrow LiH + B + 3/2H_2$$
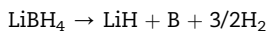
Tuning the thermodynamics for dehydrogenation from $LiBH_4$, in order to reduce the temperature at which hydrogen is evolved has been the focus of much research [6–9,11–18]. This is achieved through the addition of a second phase, a reactive agent, which will lead to the formation of a more thermodynamically stable product upon decomposition and thereby reducing the enthalpy for dehydrogenation [14–16]. This concept has been successfully demonstrated through additions of binary hydrides [7,12,18], complex metal hydrides [11,17], and metal additions [13]. The hydrogen storage properties of the intermetallic $CaNi_5$ have shown to be similar to the intermetallic $LaNi_5$ in terms of fast hydrogen kinetics, but $CaNi_5$ possesses a higher hydrogen capacity (1.8 wt%) than the $LaNi_5$ alloy (1.5 wt%) [19]. $CaNi_5H_6$ is an interesting system showing five reversible single phase regions during hydrogenation, α, β, γ', γ'' and δ with the largest plateau $\beta - \gamma'$ having an enthalpy of hydrogenation of -33.7 kJ mol^{-1} and change in entropy of -105 ± 2 J mol^{-1} K^{-1} [20] resulting in a lower plateau pressure than $LaNi_5H_6$. It has been shown to be stable through cycling at temperatures up to 30 °C [20], however at higher temperatures $CaNi_5H_6$ can suffer from disproportionation to CaH_2 and Ni [21]. It has so far found little attention within the research field of multi-component hydrogen storage systems.

Ibikunle et al. reported the use of $CaNi_5H_4$ with $LiBH_4$ as an alternative calcium source to CaH_2, postulating that the free nickel should serve as a dopant and that the overall reaction pathway would follow Scheme 2 [22–24]. However, they found no enhanced effect from the presence of Ni on the dehydrogenation temperature in comparison to using just CaH_2. Furthermore, the added weight of the nickel reduced the hydrogen capacity of the system [23].

Scheme 2. Reaction pathway with $CaNi_5$ hydride

$$6LiBH_4 + CaNi_5H_4 \rightarrow 6LiH + CaB_6 + 5Ni + 11H_2$$

In the work reported below, $CaNi_5$ alloy was added to $LiBH_4$ in the expectation that the calcium would react with the boron and nickel would act as a catalyst, as nickel is reported to improve the dehydrogenation and rehydrogenation of $LiBH_4$ [25–30]. To our knowledge no other stoichiometric ratios other than 6:1 have been investigated for the $LiBH_4$:Ca-containing systems and in this study we report the results for a 2:1 M ratio $LiBH_4$:$CaNi_5$ system which resulted in the solid-state decomposition of $LiBH_4$ (a first for reversible $LiBH_4$ multicomponent systems). The effect of niobium as a catalyst for the system was also investigated.

Experimental

$LiBH_4$ (95%, Sigma Aldrich), $^7Li^{11}BD_4$ (Katchem, 98%), and $CaNi_5$ (Sigma Aldrich Hy-STOR) were used as received without any further purification. All handling and storage of samples were performed in an inert atmosphere (Ar) glove box with <1 ppm O_2. Ball milling was performed in a Fritsch Rotary P5 ball mill under an Ar atmosphere at 400 rpm. Mixtures of $2LiBH_4$:$CaNi_5$ and $2LiBD_4$:$CaNi_5$ of sample weight 1.0 g were prepared and milled for 3 h with a ball to powder weight ratio of 80:1. The catalyzed samples were prepared by the addition of 2 mol% NbF_5.

Thermal analysis of 1.5–4.0 mg samples was undertaken by thermal gravimetric analysis, TGA (Netzsch 209 F1) and differential scanning calorimeter, DSC (Netzsch 204 HP). Both techniques were run using a heating ramp of 10 °C min^{-1} under 1 bar of argon or hydrogen with a flow rate of 100 ml min^{-1}. The samples were loaded into alumina crucibles and hermitically sealed within an aluminum pan and lid. The sample lid was pierced immediately before loading the sample into the instrument to minimize air contamination of the sample. The reversibility of the 3 h milled decomposed uncatalyzed $2LiBH_4$:$CaNi_5$ sample was conducted on a Sieverts apparatus at 175 °C under pressures ranging from 0.1 bar to 85 bar of H_2.

Powder XRD was recorded on a Bruker D8 Advance, with a 2θ range of 10–80°, a step size of 0.02° and dwell time of 4 s with a CuKα source (λ = 1.5418 Å). Samples were placed on a Si single crystal wafer and covered with an amorphous polymer film to protect against oxidation during analysis of the sample.

In situ powder neutron diffraction, PND, measurements on the $2LiBD_4$:$CaNi_5$ ratio were performed on the neutron diffractometer D20 at the Institute Laue-Langevin (ILL) in Grenoble, France (λ = 2.42 Å) [31]. Data was analyzed using Large Array Manipulation Program (LAMP) version 6. A sample of 2.65 g was loaded inertly into 316 L stainless steel vessel and sealed under argon atmosphere. The vessel was then evacuated in situ using a scroll pump and a static pressure of 1 bar deuterium was applied over the sample. The sample was then heated at a rate of 1 °C min^{-1} to 500 °C. Individual PND scans were accumulated over 5 min.

Results

As-milled samples

XRD data of catalyzed (with NbF_5) and uncatalyzed $2LiBH_4$:$CaNi_5$ samples after 1 h and 3 h of milling are shown in the electronic supplementary information, Fig. S1. The amorphous hump centered at a 2θ of 19°, evident in all the patterns, was due to the amorphous polymer film over the sample. For both catalyzed and uncatalyzed systems the 1 h milled samples show two broad peaks at 2θ values of approximately 40° and 45° together with $CaNi_5$ and $LiBH_4$ diffraction lines. After 3 h of milling no distinct diffraction lines were evident, except for a broad feature between 2θ values of 35°–55°.