Solvent-free synthesis and decomposition of Y(BH₄)₃

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The direct and solvent-free synthesis of yttrium borohydride was achieved by reactive ball milling of yttrium hydride in diborane/hydrogen atmosphere. The product contains only the solid elemental hydride as remaining contaminant. Yields above 75% were obtained. The product crystallizes in the cubic α phase and releases hydrogen above 460 K. The decomposition was measured by in situ X-ray diffraction and the hydrogen release was monitored gravimetrically in conjunction with infrared gas analysis. No diborane was detected during the decomposition.
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The implementation of a future hydrogen society relies on safe and economic ways to produce, store and distribute hydrogen. Among different techniques to store hydrogen [1,2], solid-state hydrogen storage in borohydrides $M(BH_4)_n$ (M = Li, Na, Mg, Ca, Al, etc.; n = 1, 2, 3, 4) is attractive due to the high gravimetric and volumetric hydrogen density in these compounds [2–5]. Some of the most intensively investigated tetrahydroborates (e.g. $LiBH_4$, $Ca(BH_4)_2$ and $Mg(BH_4)_2$) exhibit a rather high hydrogen desorption temperature because of the thermodynamic stability or because of a kinetic barrier [2–5]. The stability of the borohydrides is determined by the charge transfer from the metal cation to the $(BH_4)^-$ anion. Empirically, a relation between the Pauling electronegativity χ of the constituting cations and the decomposition temperature T_{dec} of selected borohydrides has been established [6–8]. Applying this empirical rule to Y ($\chi_Y = 1.2$), a decomposition temperature of 500 K, well below those of $LiBH_4$ and $Ca(BH_4)_2$, is expected [9]. Together with a hydrogen content of 9.1 wt.%, this makes $Y(BH_4)_3$ an attractive candidate for hydrogen storage.

Sato et al. and Frommen et al. [9,10] synthesized $Y(BH_4)_3$ by ball milling anhydrous YCl_3 and $LiBH_4$. The metathesis reaction results in the formation of $Y(BH_4)_3$ and LiCl according to the reaction

$$3LiBH_4 + YCl_3 \rightarrow Y(BH_4)_3 + 3LiCl \tag{1}$$
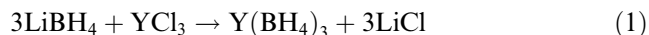
The by-product of the reaction, LiCl, is completely contained in the final product. To increase the purity of $Y(BH_4)_3$, LiCl has to be removed. Due to its low solubility, LiCl can be separated from $Y(BH_4)_3$ by using diethyl ether (Et_2O) [11]. Yan et al. [12] used the solubility of $LiBH_4$ and YCl_3 in Et_2O and performed the metathesis reaction in solution, resulting in $Y(BH_4)_3$ dissolved in Et_2O, while the by-product (LiCl) is readily separated as a precipitation. Jarón and Grochala [13] examined further possible approaches to synthesize $Y(BH_4)_3$, involving other educts (borohydrides other than $LiBH_4$ and/or yttrium halides other than YCl_3) or different solvents, but none of them were successful. Only the metathesis reaction described by Eq. (1) results in the desired product.

The crystal structure of $Y(BH_4)_3$ at room temperature is simple cubic, of space group $Pa\bar{3}$ (No. 205) with a lattice constant of 10.852 Å [9,10]. At 453 K, close to the onset of thermal decomposition, the low-temperature phase (the α-phase) transforms into the β-phase [10,11,13]. The decomposition of $Y(BH_4)_3$ proceeds stepwise, involving several intermediates. The onset of hydrogen evolution is observed between 423 K [13] and 463 K [12,11]. Details of the decomposition path and the role of intermediate phases such as YB_4 are still under discussion. While Jarón and Grochala notice contamination of the evolving hydrogen gas by toxic boron hydrides and products of their pyrolysis, the other groups explicitly rule out the evolution of diborane. The stability of crystalline $Y(BH_4)_3$ was described by

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density functional calculations. Thereby the ionic contribution to the bonding is responsible for the room temperature stability. The calculations predict thermal decomposition into boron, yttrium hydride and hydrogen at elevated temperature. The evolution of diborane is not expected [14].

In the present study we demonstrate the direct, solvent-free synthesis of $Y(BH_4)_3$ at room temperature by a gas–solid reaction of YH_3 with B_2H_6 and H_2. The thermal decomposition is measured gravimetrically and by in situ X-ray diffraction (XRD). The evolved gas is investigated via infrared (IR) spectroscopy.

The synthesis uses elemental Y (powder, 99.9%) and $ZnCl_2$ (anhydrous, beads, 99.99%, purchased from Sigma–Aldrich), $LiBH_4$ (powder, 95%, Katchem) and pressurized H_2 (99.999%, Messer) as starting materials. All solids were exclusively handled in vacuum, in hydrogen or in inert Ar atmosphere.

The synthesis was carried out using a custom made mill connected to a gas/vacuum supply [15]. The gas supply uses $LiZn_2(BH_4)_5$ as a diborane and hydrogen desorbing material [16]. It was prepared according to the protocol of Ravensbæk et al. [17] by milling a mixture of $ZnCl_2$ and $LiBH_4$. The set-up may be evacuated or pressurized with hydrogen ($p_{max} = 200$ bar).

CuK_α radiation with a wavelength of $\lambda_{CuK\alpha} = 1.5418$ Å from a Bruker D8 diffractometer equipped with a Goebel mirror was used to characterize the initial materials, and the products of the synthesis and of the desorption process. The samples were measured in glass capillaries (Hilgenberg, diameter: 0.7 mm, wall thickness: 0.01 mm). The XRD patterns were analyzed by quantitative phase analysis using TOPAS software.

Decomposition was investigated by the weight change using a magnetic suspension balance (Rubotherm, Bochum) in combination with infrared gas analysis (Bruker Alpha spectrometer) equipped with a 8 cm gas cell at a resolution of 0.9 cm^{-1} [18]. To guarantee defined thermodynamic conditions, a dynamic H_2 atmosphere (flow of 250 ml min^{-1}) of 1 bar was applied during the decomposition.

The formation of $Y(BH_4)_3$ from elemental yttrium, diborane and hydrogen is accomplished in two subsequent reactions. First, YH_3 was prepared by heating 1 g of elemental Y in an applied H_2 atmosphere of 60 bar. Above 530 K the pressure drops as the gas is absorbed and the hydride is formed. The hydride formation is verified by XRD. The sample contains 87 wt.% YH_3 and 13 wt.% YH_2. No traces of elemental Y or other impurities could be detected. The preparation of YH_3 is crucial. Attempts to directly synthesize $Y(BH_4)_3$ by reactive ball milling of elemental yttrium in B_2H_6/H_2 failed.

In a second step, $Y(BH_4)_3$ is prepared by reactive ball milling of the YH_3/YH_2 sample in a 1:1 mixture of B_2H_6 and H_2. First, the as-prepared yttrium hydride added to the milling vial and connected to the diborane source, then the whole system is purged with hydrogen and evacuated. Subsequently, the source is heated to 400 K to fill the system with a borane/hydrogen atmosphere. After the complete desorption of the diborane source, the mill containing the yttrium hydride is started. The progress of the subsequent reaction is monitored by

the pressure drop in the milling vial. Within 5 days the pressure drops by 3 bar, from an initial pressure of 24.4 bar down to 21.4 bar. Similar time scales have been observed for the formation of $Ca(BH_4)_2$ and $Mg(BH_4)_2$ using the same set-up [13].

One gram of Y correspond to 11.3 mmol, which convert to 11.3 mmol of YH_3 when fully hydrogenated. Assuming the net reaction

$$YH_3 + 3/2B_2H_6 \rightarrow Y(BH_4)_3 \qquad (2)$$
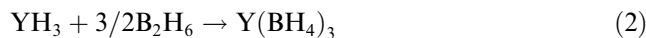
17 mmol or 400 ml diborane is required for the complete conversion to $Y(BH_4)_3$. With a system volume of about 100 ml, we therefore expect a pressure drop of 4 bar. The observed pressure drop indicates an incomplete reaction.

Figure 1 shows the XRD pattern of the product. All Bragg peaks can either be attributed to $Y(BH_4)_3$, YH_3 or YH_2. There are no unidentified reflections. The qualitative phase analysis yields 77 wt.% $Y(BH_4)_3$, 17 wt.% YH_3 and 6 wt.% YH_2. Given the hydrogen contents of 9.1 wt.% for $Y(BH_4)_3$, 3.3 wt.% for YH_3 and 2.2 wt.% for YH_2, respectively, the sample contains 7.7 wt.% hydrogen.

Figure 2 shows the gravimetric data (rate of the mass loss $d/dt(\delta m/m_0)[\% \, min^{-1}]$) at a heating rate of 1 K min^{-1} as a black dotted curve. The red solid curve represents the optical signal diborane, determined by IR spectroscopy.

A small weight loss due to the release of diborane sets in around 370 K, where the signal rises from the background level to about 0.01% min^{-1}. However, weight loss due to diborane is negligible. Diborane desorption reaches its maximum at 390 K. Above 430 K no diborane evolution is detectable any more. Integration of the signal results in a total weight loss due to diborane desorption of 0.058%, which is much lower than the totally observed weight loss of 6.8%. It is probable that the diborane released originates from the sample preparation. It might be unreacted diborane, adsorbed at the surface of the sample.

The onset of the hydrogen desorption lies at about 460 K, in agreement with earlier reports [11,12]. The maximum occurs at 523 K, with a desorption rate of 0.12% min^{-1}. The integrated weight loss is 6.8%, which is well below the theoretical value of 7.7 wt.% contained

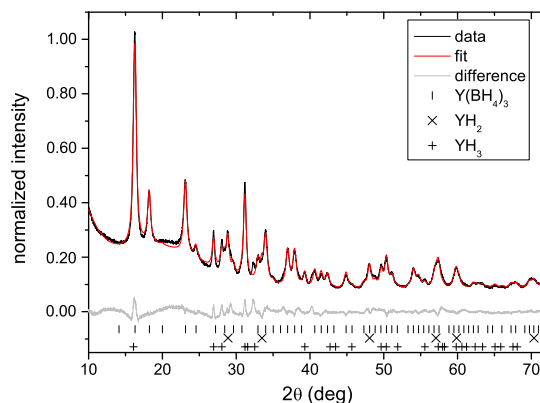Fig. 1. XRD pattern of the as-prepared $Y(BH_4)_3$.