



In situ thermodiffraction to monitor synthesis and thermolysis of hydrazine borane-based materials



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ABSTRACT

Hydrazine borane $N_2H_4BH_3$ (HB) and its alkali metal derivatives, *i.e.* sodium hydrazinidoborane $NaN_2H_3BH_3$ (NaHB) and lithium hydrazinidoborane β - $LiN_2H_3BH_3$ (β -LiHB), are novel materials under investigation for solid-state chemical hydrogen storage. Herein, we report *in situ* thermodiffraction experiments developed to monitor synthesis of NaHB at low temperatures (from -173 °C) and a thermolysis of each of the boranes, manifesting the following main observations. (i) Dehydrogenation of HB starts with the liquid phase and dehydrocoupling involves the formation of a crystalline intermediate (at 90 – 197 °C). (ii) NaHB forms from -38 °C, melts at *ca.* 60 °C, and decomposes upon melting at higher temperatures. (iii) β -LiHB dehydrogenates to a small extent starting from 40 °C, but mostly transforms to the high-temperature phase α -LiHB at 91 °C; up to around 150 °C, the two crystalline phases dehydrogenate according to a complex stepwise mechanism. Our results help in gaining insight in synthesis and thermolysis of the aforementioned novel hydrazine borane-based materials.

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1. Introduction

In the field of solid-state chemical hydrogen storage, boron- and nitrogen-containing materials are attractive hydrogen-dense compounds although the storage is irreversible in practical and acceptable conditions (in terms of temperature and pressure of hydrogen) [1]. The most typical example is ammonia borane NH_3BH_3 , which carries 19.5 wt% of both protic and hydridic hydrogens ($3 H^{\delta+}$ vs. $3 H^{\delta-}$). Under heating, it melts at around 100 °C and then decomposes. The decomposition is stepwise over the range 100 – 200 °C, with liberation of $1 + 1$ equiv. H_2 in two successive steps and of large amounts of undesired gaseous by-products such as ammonia, borazine and diborane especially during the second decomposition step [2]. To improve the dehydrogenation properties of ammonia borane, different destabilization strategies have been investigated so far: *i.e.* solvation in organic solvent/ionic liquid with and without the presence of homogeneous catalyst [3–5]; chemical doping with solid-state oxidant or

hydride [6,7]; confinement into the porosity of host material (scaffold) [8]; and chemical modification with synthesis of amido-borane derivatives [9].

Another example of boron- and nitrogen-containing materials is hydrazine borane $N_2H_4BH_3$ (15.4 wt% H; with $4 H^{\delta+}$ vs. $3 H^{\delta-}$). It can be considered as a derivative of ammonia borane where the NH_3 moiety is substituted by N_2H_4 . Hydrazine borane (denoted HB) was discovered in the 1960s [10] but was thereafter little studied [11]. It gained new interest in the recent years [12]. In 2009, Hügler et al. [13] showed that an equimolar mixture of lithium hydride LiH and HB, with a balanced number of protic and hydridic hydrogen atoms ($4 H^{\delta+}$ vs. $4 H^{\delta-}$), is able to dehydrogenate in suitable conditions. In 2012, Moury et al. [14] confirmed the unsuitability of hydrazine borane in pristine state for solid-state chemical hydrogen storage whereas in 2011 Hannauer et al. [15] showed a real potential for liquid-state chemical hydrogen storage (*i.e.* catalytic dehydrogenation in hydrolysis conditions). However, HB has not been eliminated as a candidate solid-state chemical hydrogen storage material by the fact that like ammonia borane it can be chemically modified towards formation of derivatives [11].

By the reaction with an alkali metal hydride MH (with $M = Li, Na$ and K), HB can be transformed into an alkali metal hydrazinidoborane $MN_2H_3BH_3$. The first derivative, $LiN_2H_3BH_3$ (11.6 wt% H;

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denoted α -LiHB) was reported by Wu et al. [16]. Another polymorph, β -LiHB, was reported by Moury et al. [17]. The former is the high-temperature phase, while the latter is the low-temperature one, the transition taking place at about 90 °C. Both polymorphs can be synthesized by ball-milling but in different conditions [17]. An accurate determination of the phase transition temperature between these two phases is one of the objectives of the present work.

Sodium hydrazinidoborane $\text{NaN}_2\text{H}_3\text{BH}_3$ (8.9 wt% H; denoted NaHB) [18] and potassium hydrazinidoborane $\text{KN}_2\text{H}_3\text{BH}_3$ (7.2 wt% H; denoted KHB) were also reported [19] as derivatives of HB. Nevertheless, the reaction of NaH and KH with HB is exothermic, even highly exothermic with the latter hydride, taking an explosive nature. Synthesis of $\text{KN}_2\text{H}_3\text{BH}_3$ can be conducted in safe conditions in an autoclave [19]. With respect to the synthesis of $\text{NaN}_2\text{H}_3\text{BH}_3$, it can be done in safe conditions by milling both reactants in a jar kept at low temperatures (e.g. by immersing the jar in liquid nitrogen) [18]. Determining a “safe” temperature of the reaction between NaH and HB towards the formation of NaHB and, for that, developing a novel *in situ* method are the objectives of the present work.

The aforementioned hydrazinidoborane derivatives possess an equal number of protic and hydridic hydrogen atoms ($3\text{H}^{\delta+}$ vs. $3\text{H}^{\delta-}$). Thus, the dehydrogenation could theoretically reach high yield, probably quantitative, likely at moderate temperatures. Indeed, the hydrazinidoboranes have shown much better dehydrogenation kinetics than pristine HB [16–19]. For example, LiHB is able to release 9.3 wt% H (out of a maximum of 11.6 wt% H) under heating at 130 °C for 1 h [16] and NaHB liberates 8.8 wt% H (out of a maximum of 8.9 wt%) at 100 °C in less than 10 min [18]. Accordingly, alkali metal hydrazinidoboranes are positioned as potential candidates for solid-state chemical hydrogen storage. Nonetheless, technological application and viability of these compounds is strongly dependent on recyclability of the solid residues to regenerate the starting materials or at least a compound like sodium/lithium borohydride, ammonia borane or HB. A promising way is reduction by using hydrazine in ammonia medium, which has already shown to be efficient for hydrogenating polyborazylene into ammonia borane [20,21]. Recyclability is certainly the most challenging issue in the field.

The present work is dedicated to *in situ* thermodiffraction of HB, β -LiHB and NaHB. Specifically, we aim at gaining more insight, from a crystallographic point of view, into (i) the synthesis of NaHB from -173 °C to ambient conditions followed by a novel *in situ* method, (ii) the thermal decomposition of HB from 20 °C to 220 °C, paying attention to possible formation of an intermediate, (iii) the phase transition β -LiHB \rightarrow α -LiHB over the range 90–155 °C as well as the thermal decomposition of these phases from 20 °C to 200 °C, and (iv) the thermal decomposition of NaHB from 20 °C to 200 °C.

2. Experimental

Sodium borohydride NaBH_4 (Acros, 99%), hydrazine hemisulfate $\text{N}_2\text{H}_4 \cdot 1/2(\text{SO}_4)$ (Sigma–Aldrich, >99%), anhydrous 1,4-dioxane $\text{C}_4\text{H}_8\text{O}_2$ (Sigma–Aldrich, >99%), lithium hydride LiH (Sigma–Aldrich, 95%) and sodium hydride NaH (Sigma–Aldrich, 95%) were used as-received, stored and handled in an argon-filled glove box (MBraun M200B, $\text{H}_2\text{O} \leq 0.1$ ppm, $\text{O}_2 \leq 0.1$ ppm).

Hydrazine borane $\text{N}_2\text{H}_4\text{BH}_3$ (purity $\geq 99\%$) was synthesized from NaBH_4 and $\text{N}_2\text{H}_4 \cdot 1/2(\text{SO}_4)$ in 1,4-dioxane following an optimized procedure described in details elsewhere [14]. The synthesis of sodium hydrazinidoborane ($\text{NaN}_2\text{H}_3\text{BH}_3$) is described in details elsewhere [18]. In the present study, the procedure was adapted to *in situ* XRD. In the argon-filled glove box, equimolar amounts of NaH and $\text{N}_2\text{H}_4\text{BH}_3$ were introduced in a stainless steel milling jar while taking care not to put the reactants into contact; they were

separated by 5 stainless steel balls (\varnothing 70 mm). The jar was carefully taken out the glove box and put in a Dewar container filled with liquid nitrogen (-196 °C) for 1 h. Then, the cold jar was placed in the ball mill (FRITSH Pulverisette 7 Premium Line) and the mixture was milled for 5 min at 250 rpm. The jar was placed in liquid nitrogen once again and then placed in a nitrogen glove box. Several glass capillaries (\varnothing 0.7 mm) were filled with the mixture while keeping the temperature close to -196 °C. The samples in capillaries were finally analyzed by XRD.

Lithium hydrazinidoborane has two known polymorphs: the low-temperature phase β -LiHB [17] and the high-temperature α -LiHB [16]. In the present work, β -LiHB was prepared from equimolar amounts of LiH and $\text{N}_2\text{H}_4\text{BH}_3$ by ball-milling in the following conditions: ambient temperature; PM100 ball mill from RETSCH; balls-to-reactants weight ratio of ~ 100 ; 180 min by alternating 10 min milling at 200 rpm with 20 min break. With respect to α -LiHB, it was prepared with another ball mill (FRITSH Pulverisette 7 Premium Line) and by applying 3 different cycles at ambient temperature: 180 min of milling at 200 rpm for 10 min alternated with 20 min break; 160 min of milling at 250 rpm for 10 min with 10 min break; and, 360 min of milling at 300 rpm for 10 min with 20 min break.

The synthesis of NaHB from NaH and $\text{N}_2\text{H}_4\text{BH}_3$ has to be done at low temperatures [18]. To precisely define the reaction temperature, the pressure in the milling jar was monitored from -100 °C to 20 °C and the gas composition was analyzed at the end of the experiment. Typically, a jar equipped with a quick connect gas outlet was used in milling under the conditions reported above. The variations in pressure and temperature were recorded. The jar was connected to a gas chromatograph (GC; Shimadzu, GC-14B; Column Chromosorb 103; 40 °C; detector TCD; 2250 points recorded every 0.4 s for 15 min) and upon the completion of the reaction, the jar atmosphere was analyzed. The GC results showed the presence of H_2 (retention time of 1.57 min) only. No other by-product was found.

The synthesis of NaHB was also followed by *in situ* XRD. An X-ray diffractometer, with an image plate detector MAR345 positioned at 250 mm, a Rigaku rotated anode generator and a molybdenum radiation ($\lambda_{\text{K}\alpha} = 0.71069$ Å), was used. The detector geometry was calibrated with the LaB_6 standard. The temperature was controlled using a programmable gas blower Oxford Cryostream 700. The temperature was first set at -173 °C and then increased at 0.5 °C min^{-1} . The same diffractometer was used to verify the successful synthesis of α -LiHB.

The thermal behavior of HB, NaHB and β -LiHB was studied using synchrotron radiation at the BM01-A beamline (ESRF). The wavelength was $\lambda = 0.69405$ Å. A 2D Pilatus detector positioned at 411 mm from the sample was used. The detector geometry was calibrated with the LaB_6 standard. The temperature was controlled using a Cyberstar hot blower. The analysis was performed from room temperature to 250 °C with a heating rate of 5 °C min^{-1} . The thermal behavior of HB was also studied by thermogravimetric analysis (TGA) coupled to mass spectrometry (MS). The measurements were performed in an argon-filled glove box using a Rigaku TG8120 TGA (3 mg of product in a platinum crucible; 2 °C min^{-1}) and an M-QA200TS MS under helium flux respectively. The thermal behavior of NaHB and β -LiHB are reported elsewhere [17,18].

3. Results and discussion

3.1. *In situ* monitoring of NaHB synthesis

At ambient temperature and under argon atmosphere, NaH and HB spontaneously react [18]. The reaction can be controlled by gradually increasing the temperature. This interesting feature was used to successfully develop an *in situ* approach to monitor the low-

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