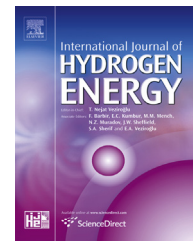




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Borohydride-induced destabilization of hydrazine borane

F. Toche^a, R. Chiriac^a, U.B. Demirci^{b,*}, P. Miele^b

^a Université Lyon 1, CNRS, UMR 5615, Laboratoire des Multimatériaux et Interfaces, 43 boulevard du 11 Novembre 1918, F-69622 Villeurbanne, France

^b IEM (Institut Européen des Membranes), UMR 5635 (CNRS-ENSCM-UM2), Université Montpellier 2, Place E. Bataillon, F-34095 Montpellier, France

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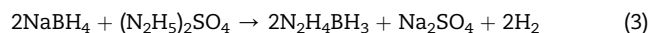
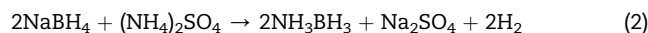
ABSTRACT

We investigated the destabilization of 4 mol of hydrazine borane $N_2H_4BH_3$ in the presence of 1 mol of an alkaline borohydride ($LiBH_4$ or $NaBH_4$) and, in a second step, of 1 mol of NH_3BH_3 in addition. The destabilization was followed by TGA, DSC and μ GC. The solid residues were analyzed by solid-state ^{11}B NMR, IR and XRD. The presence of the borohydride effectively destabilizes $N_2H_4BH_3$ which is thus able to liberate H_2 from 50 °C. Seeing the results from the other side, one could consider that the alkaline borohydrides are destabilized by $N_2H_4BH_3$. Such destabilization approach is attractive as it involves boron-based materials only. The best decomposition results were obtained with the sample containing 4 mol of $N_2H_4BH_3$ and 1 mol of $LiBH_4$ (containing 16 equiv. H_2). Upon heating up to 300 °C at 5 °C min^{-1} , this sample releases 12.1 mol of H_2 (dehydrogenation extent of 76%) and 1.1 mol of N_2H_4 . A solid residue of empirical formulae $LiB_5N_{5,8}H_{3,4}$ is formed. It is composed of polyborazylene- and/or boron nitride-like materials. This is an attractive feature as it implies recyclability of the polymer and elaboration of inorganic ceramics at relatively low temperatures. Our main results are reported herein.

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Introduction

Borohydrides and boranes have been widely investigated as candidates for chemical hydrogen storage. Typical examples are lithium borohydride $LiBH_4$ [1], sodium borohydride $NaBH_4$ [2], ammonia borane NH_3BH_3 [3] and the recent hydrazine borane $N_2H_4BH_3$ [4]. Sodium borohydride is however the most important of them as it is the parent of each [5]:



These materials are constituted of light heteroatoms and, the B and N atoms bond to 2–4 hydrogen elements. Accordingly, the theoretical gravimetric hydrogen storage capacities of

* Corresponding author. Tel.: +33 (0) 4 67 14 91 60; fax: +33 (0) 4 67 14 91 19.

E-mail address: umit.demirci@um2.fr (U.B. Demirci).

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LiBH₄, NaBH₄, NH₃BH₃ and N₂H₄BH₃ are 18.4, 10.8, 19.5 and 15.4 wt% respectively.

Boron ($\chi = 2.04$) is less electronegative than hydrogen ($\chi = 2.2$) and the hydrogen atoms of BH₃ and BH₄⁻ have a hydride character H^{δ-}. Nitrogen ($\chi = 3$) is more electronegative than hydrogen, and the hydrogen atoms of NH₃ and N₂H₄ are protic H^{δ+}. Accordingly, the borohydrides store only H^{δ-} while the boranes carry both H^{δ-} and H^{δ+}, and these features strongly determine the dehydrogenation properties of the respective borohydrides and boranes [6].

In the presence of a protic solvent (e.g. water or methanol) and in ambient conditions, the borohydrides and boranes are subjected to dehydrogenation by catalytic solvolysis. The H^{δ+} of the solvent reacts with the H^{δ-} of BH₄⁻ or BH₃ to give 3–4 moles H₂ per mole of boron hydride. The dehydrogenation of the NH₃ moiety of NH₃BH₃ is thermodynamically impossible [7], whereas that of the N₂H₄ group of N₂H₄BH₃ is possible in the presence of an active and selective nickel-based bimetallic catalyst [8].

The presence of H^{δ-} and H^{δ+} in the aforementioned boranes allows thermolytic dehydrogenation under acceptable conditions. These hydrogens can couple via inter- or intramolecular interactions leading to dehydrocoupling of NH₃BH₃ and N₂H₄BH₃. The former borane, which attractively has 3H^{δ-} and 3H^{δ+}, has been much investigated since the mid-2000s [9]. It decomposes from ca. 100 °C and releases 2 equiv. H₂ and some unwanted borazine B₃N₃H₆ within the range 100–200 °C [10]. With respect to N₂H₄BH₃, the presence of 3H^{δ-} vs. 4H^{δ+} has appeared as being an imbalance in thermolytic dehydrocoupling. Accordingly, Hügle et al. proposed the addition of a source of H^{δ-} (i.e. LiH) and then showed improved dehydrogenation properties [4]. Wu et al. and Moury et al. reported, respectively, the mechano-synthesis of lithium and sodium hydrazinidoboranes (LiN₂H₃BH₃ and NaN₂H₃BH₃) by reaction of LiH and NaH with N₂H₄BH₃ [11,12]. Both derivatives have 3H^{δ-} and 3H^{δ+}. Note that pristine N₂H₄BH₃ is not appropriate for solid-state hydrogen storage because of the generation of significant amounts of hydrazine under heating (over the range 100–200 °C) [13].

In the present work, we considered the destabilization of N₂H₄BH₃ in the presence of LiBH₄ or NaBH₄, and/or of NH₃BH₃. Binary/ternary mixtures were prepared so that they contain as many H^{δ-} as H^{δ+}. The thermolytic dehydrogenation of the binary/ternary mixtures was then studied. Our main results are reported herein.

Experimental

Lithium borohydride LiBH₄, sodium borohydride NaBH₄ and ammonia borane NH₃BH₃ were purchased from Sigma–Aldrich and used as received. Hydrazine borane N₂H₄BH₃ was prepared according to an optimized procedure as described elsewhere [13]. All of these materials were stored in an argon-filled glove box. Four binary/ternary mixtures of boranes and borohydrides, with equal amounts of H^{δ-} and H^{δ+} (Table 1), were prepared in the argon-filled glove box. The binary mixtures were made of N₂H₄BH₃ as main component and one of the borohydrides (samples 1 and 2). The ternary mixtures were made of N₂H₄BH₃ as main component, NH₃BH₃ and

one of the borohydrides (samples 3 and 4). The mixtures were prepared as follows. The materials composing a mixture were weighted, transferred in a mortar, and gently milled in order to homogenize the solids. The samples were analyzed by attenuated total reflectance infrared spectroscopy (IR, SAFAS IR600), X-ray diffraction (XRD, PANalytical X'pert pro MPD powder diffractometer, CuK α radiation, $\lambda = 1.5406$ Å) and solid-state ¹¹B MAS NMR (Varian VNMR400, 128.37 MHz). To prevent the analyzed sample from air during the XRD analysis, the sample was covered with a polyimide film. The data were collected in the range $2\theta = 10$ – 50° with a step of 0.0167° .

Thermogravimetric analyses (TGA) were carried out with a TGA/SDTA 851^e (Mettler Toledo). The calibration was made over the range 25–300 °C at 1 °C min⁻¹. The melting onset temperatures of 3 compounds (phenyl salicylate, indium and tin) obtained from the differential thermal analysis (DTA) signals were used for the sample temperature calibration. Calcium oxalate monohydrate was used to check the sample mass calibration. The TGA analyses were performed in the following experimental conditions. The sample (2–3 mg) was transferred in an aluminum crucible of 100 μ l with a pinhole ($\varnothing = 670$ μ m) in the argon-filled glove box. The TGA experiments were carried out with a heating rate of 1 °C min⁻¹, within the temperature range of 25–300 °C, and under N₂ atmosphere (50 mL min⁻¹). To integrate the different mass loss steps, we used the TGA first derivative curve (the mass loss rate curve).

Differential scanning calorimetry (DSC; DSC1 Mettler Toledo) was also employed to study the decomposition of the binary/ternary mixtures. The DSC device was calibrated within the range 25–300 °C. The melting points and enthalpies of standards were used for the calibration in terms of heat flow (indium and zinc) and temperature (indium and tin). Experimental conditions identical to those in TGA were employed.

The purity of generated H₂ was analyzed with a portable micro-chromatograph, μ GC M200 from Agilent M Series. This apparatus has 2 columns and 1 micro-thermal conductivity detector (μ -TCD). Hydrogen was separated on a molecular sieve column (12 m \times 0.32 mm; diameter mesh of 5 Å; argon as carrier gas; column pressure and temperature fixed at 27.6 psi and 70 °C, respectively) and quantified with the μ -TCD detector. Another OV1 column (10 m \times 0.15 mm i.d.; helium as carrier gas; column pressure and temperature fixed at 30.8 psi and 90 °C, respectively) was used to separate any gaseous by-products (e.g. borazine B₃N₃H₆, ammonia NH₃, and diborane B₂H₆). Their identification was done by coupling the μ GC with a mass selective detector (MSD). The μ GC is commercialized by S.R.A. Instruments. The μ GC runtime was 60 and 120 s for H₂ and the by-products, respectively. The injection time was fixed at 200 ms. In order to quantify the amounts of H₂, the μ GC was calibrated with a gas sample of known concentration, i.e. 2000 ppm of H₂ in a N₂ balance.

Results

The binary/ternary mixtures 1–4 were prepared so that the mole numbers of H^{δ-} and H^{δ+} were equal (Table 1). With the samples 1 and 2, obtained by mixing 4 mol of N₂H₄BH₃ with

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