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Metal hydride–hydrazine borane: Towards hydrazinidoboranes or composites as hydrogen carriers

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ABSTRACT

In the present work, the behavior of hydrazine borane $N_2H_4BH_3$ in the presence of alkali/alkaline-earth hydrides is investigated. (i) Hydrazine borane $N_2H_4BH_3$ is readily destabilized by an alkali hydride MH ($M=Li, Na, K$). The electronic properties of M drive the reactivity of MH_1 towards $N_2H_4BH_3$. KH is the most reactive (at 25 °C, $\Delta_rH = -70.25 \text{ kJ mol}^{-1}$) while K is the least electronegative and the biggest element. Hydrazinidoboranes $MN_2H_3BH_3$ form. (ii) Hydrazine borane $N_2H_4BH_3$ is destabilized by MH_x ($x = 2, 3; M=Mg, Ca, Al$). In comparison to pristine $N_2H_4BH_3$, better dehydrogenation properties are found: MgH_2 has a catalytic effect; CaH_2 strongly destabilizes $N_2H_4BH_3$; and, unstable AlH_3 is able to destabilize $N_2H_4BH_3$ under heating. Though the synthesis of hydrazinidoboranes $M(N_2H_3BH_3)_x$ is difficult, the mixtures $MH_x-N_2H_4BH_3$ leads to composites. The most efficient composite is $CaH_2-N_2H_4BH_3$. The aforementioned hydrazinidoboranes and composites may have potential as solid-state hydrogen storage materials. This is discussed herein.

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Introduction

Boron- and nitrogen-containing materials have shown to be attractive for solid-state chemical hydrogen storage owing to

high gravimetric hydrogen densities and presence of protic $H^{\delta+}$ and hydridic $H^{\delta-}$ hydrogen atoms in the same molecule [1,2]. Ammonia borane NH_3BH_3 is a typical example, with 3 $H^{\delta+}$ carried by the NH_3 moiety, 3 $H^{\delta-}$ for the BH_3 group, and a capacity of 19.6 wt% H. Under heating, these hydrogen atoms

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react, via intra- and/or inter-molecular interactions. The liberation of H_2 proceeds from $\sim 100^\circ C$ [3]. This is much lower than the dehydrogenation temperature of a material containing only protic hydrogen atoms like ammonia NH_3 ($>600^\circ C$) or only hydridic hydrogen atoms like lithium borohydride $LiBH_4$ ($>300^\circ C$) [4,5].

Alternatives to ammonia borane have been explored [1,2,6]. Hydrazine borane $N_2H_4BH_3$, with 4 H^+ and 3 H^- (15.4 wt% H), is one them [7,8]. Pristine, it is not suitable for solid-state chemical hydrogen storage because of safety problems (emission of pure hydrazine N_2H_4 at $>100^\circ C$ and formation of shock-sensitive solid residue at $>300^\circ C$) [9]. However, it is a precursor of derivatives that show better dehydrogenation properties. Alkali hydrazinidoboranes $MN_2H_3BH_3$ with $M=Li, Na, K$ were indeed synthesized by reaction of hydrazine borane with an alkali hydride MH [10–13].

The recent works on hydrazinidoboranes showed that the reactivity of the alkali hydrides MH towards hydrazine borane is different. The short-term stability of the equimolar mixture $LiH-N_2H_4BH_3$ is satisfactorily in ambient conditions and under neutral atmosphere; the destabilization of the borane is achieved under heating [14], or by ball-milling (e.g. argon atmosphere; weight ratio of balls over reactants of 200; 10 min of milling, followed by a 20 min break, 18 times, at 200 rpm, and in ambient conditions) [15]. In other words, the binary mixture $LiH-N_2H_4BH_3$ is a composite that has a potential for solid-state hydrogen storage [14]. With respect to NaH , it is much reactive towards hydrazine borane in ambient conditions and under neutral atmosphere [11]. As reported herein, the reactivity of KH with hydrazine borane is even more important; it can be described as being “explosive”. The synthesis of $KN_2H_3BH_3$ has thus to be done in closed stainless-steel pressure vessel [12].

With the initial objective of exploring the possibility to synthesize novel hydrazinidoboranes, we investigated mixtures of $N_2H_4BH_3$ with MH_x ($M=Li, Na, K, Mg, Ca, Al$ and $x=1, 2, 3$). Interestingly, hydrazine borane showed different behaviors depending on MH_x . We then conducted a systematic work to study the stability of $MH_x-N_2H_4BH_3$ by using characterization techniques such as Calvet calorimetry, thermogravimetric analysis (TGA), differential thermal analysis (DTA), powder X-ray diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopy. Such a work enabled us to state if the mixture $MH_x-N_2H_4BH_3$ leads to the formation of hydrazinidoboranes or composite systems.

Experimental

Hydrazine borane $N_2H_4BH_3$ was prepared according to an optimized procedure reported in details elsewhere [9]. Hydrides of lithium LiH , sodium NaH , potassium KH , magnesium MgH_2 , and calcium CaH_2 were purchased from Sigma-Aldrich and used as received. Aluminum hydride $\alpha-AlH_3$ was prepared according to a procedure reported in details elsewhere [16]. All of these materials were stored and handled in an argon-filled glove box (MBraun M200B, $H_2O < 0.1$ ppm, $O_2 < 0.1$ ppm).

The reactivity of the metal hydrides MH_x ($x=1, 2, 3$) towards $N_2H_4BH_3$ was qualitatively assessed in an agate mortar in the argon-filled glove box. Typically, 10 mg of $N_2H_4BH_3$ were

put in the mortar, and few grains of MH_x were added slowly onto the borane. No reactivity was noticed with LiH, MgH_2, CaH_2 and AlH_3 . Then, equimolar mixtures $MH_x-N_2H_4BH_3$ were prepared and ground; there was no observable reactivity. However, with NaH and KH , the addition of the first grains showed high reactivity, which was characterized by an explosive evolution of gas and the dispersion of the solids around the mortar.

The reactivity of NaH and KH towards $N_2H_4BH_3$ was studied by Calvet Calorimetry. For comparison purpose, LiH was also tested. The calorimetric experiments were done on a C80 Calvet calorimeter [17] from Setaram. Reversal mixing cells (made of stainless steel and hermetic) were used. They can be used for regular pressures, i.e. 5 bar. They are composed of two compartments separated by a lid. In the glove box, the starting materials, MH and $N_2H_4BH_3$, were put in the cell so that one was placed in the lower compartment (1.3 mL) and the other in the upper compartment (4.2 mL). A reference cell, kept empty, was used. Both cells were installed in the C80 calorimeter. The mixing of MH and $N_2H_4BH_3$ was obtained by inverting the calorimeter (using the reversal mechanism). The inversion was stopped when the maximum of the reaction peak was reached. The mixing was done at $25^\circ C$ and the heat flow was monitored against time. The calorimeter gives an enthalpy of reaction in $J g^{-1}$. The enthalpy was then calculated per mole of mixture (e.g. a molecular mass of $53.83 g mol^{-1}$ was taken for $LiH-N_2H_4BH_3$), but also per mole of metal hydride by taking the molecular mass of MH only (the presence of $N_2H_4BH_3$ was neglected in that approach). Both are used hereafter.

For safety reasons, KH was then discarded from the study. It is however very important to stress on the risk and danger of putting NaH and KH into contact with $N_2H_4BH_3$. The reader is invited to refer to the previous sections for more details. Also, the freshly ball-milled mixtures $MH_x-N_2H_4BH_3$ are not stable in the presence of protic solvents. Slow oxidation under air (under a hood) followed by treatment with isopropanol is an efficient way to neutralize them.

The samples 1 to 6 (Table 1) were prepared by ball-milling according to a procedure optimized by varying the milling conditions (1–18 cycles; 10–30 min; 200–450 rpm). The selected procedure was as follows. In the glove box, both MH_x and $N_2H_4BH_3$ (molar ratio 1:1) were transferred in a stainless steel jar (20 mL) while avoiding any contact between both materials. Stainless balls were also added; the weight ratio of balls over reactants was 200:1. The sealed jar was carefully put outside the glove box and immersed in liquid nitrogen for 20 min. The cooled mixture was milled 10 min at 300 rpm. Finally, the sample was recovered in the argon-filled glove

Table 1 – Samples 1 to 6 consisting of equimolar amounts of MH_x and $N_2H_4BH_3$, both in solid states (GHD as gravimetric hydrogen density).

Notation	The borane	MH_x	Mole ratio	GHD (wt%)
1	$N_2H_4BH_3$			15.4
2	$N_2H_4BH_3$	LiH	1:1	14.9
3	$N_2H_4BH_3$	NaH	1:1	11.5
4	$N_2H_4BH_3$	MgH_2	1:1	12.5
5	$N_2H_4BH_3$	CaH_2	1:1	10.2
6	$N_2H_4BH_3$	AlH_3	1:1	13.2

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