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Abstract

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Keywords

behavior, hydrazinates, synthesis, crystal, structures, thermal, sodium, decomposition, borohydride

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Sodium Borohydride Hydrazinates: Synthesis, Crystal Structures, and Thermal Decomposition Behavior

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Abstract

Metallic borohydride hydrazinates are novel boron- and nitrogen-based materials that appear to be promising candidates for chemical hydrogen storage. Herein, sodium borohydride hydrazinates, including $\text{NaBH}_4 \cdot \text{N}_2\text{H}_4$ and $\text{NaBH}_4 \cdot 2\text{N}_2\text{H}_4$, were synthesized via a facile solution synthesis approach based on the solid-liquid reaction between NaBH_4 and hydrazine in tetrahydrofuran (THF) solution. The crystal structure of $\text{NaBH}_4 \cdot 2\text{N}_2\text{H}_4$ was solved to a monoclinic structure with unit cell parameters $a = 8.4592(2) \text{ \AA}$, $b = 11.7131(2) \text{ \AA}$, $c = 6.4584(1) \text{ \AA}$, and $\beta = 100.0777(14)^\circ$, with space group $A1a1$ (9). Each Na^+ ion interacts with four neighboring N_2H_4 molecules, leading to the formation of $\text{Na}_4[\text{N}_2\text{H}_4]_4^{4+}$ cationic chains along the a direction. Such cationic chains are surrounded by BH_4^- anions. The $\text{NaBH}_4 \cdot x\text{N}_2\text{H}_4$ ($x = 1, 2$) was characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC), and mass spectroscopy (MS) to obtain a full picture of the relationship of the structure to the decomposition, which will be useful for future work on borohydride hydrazinates or the study of other B-N materials. Furthermore, magnesium borohydride hydrazinates were synthesized by ball milling the sodium borohydride hydrazinates with magnesium borohydride, and their thermal decomposition was investigated as well.

KEYWORDS: Hydrogen storage; borohydride; B-N compounds

1. Introduction

Hydrogen is regarded as one of the best alternative energy carriers for sustainable energy because of its abundance, high energy density, and environmental friendliness. Nevertheless, an important challenge to realizing the so-called "hydrogen economy" is finding an efficient way to achieve compact, safe, and high density hydrogen storage.¹ Great interest has been ignited in studying the light metal hydrides and complex hydrides such as metal alanates, amides/imides, and borohydrides for hydrogen storage.^{2,3} Among them, metal borohydrides such as NaBH_4 , LiBH_4 , $\text{Mg}(\text{BH}_4)_2$, and $\text{Ca}(\text{BH}_4)_2$, are regarded as promising hydrogen storage materials because they can offer high gravimetric and volumetric hydrogen densities.⁴ For example, NaBH_4 and $\text{Mg}(\text{BH}_4)_2$ possess a gravimetric hydrogen density of 10.6 and 14.9 wt %, respectively, which can meet the system targets of 5.5 wt % set by the US Department of Energy (DOE).⁵⁻¹² The required operating temperature for dehydrogenation occurs at over 300 °C, however, which would considerably exceed the upper limit demanded for practical application in hydrogen fuel cell vehicles.

In order to overcome the thermodynamic and kinetic limitations of the thermal decomposition of borohydrides, several novel strategies, such as catalytic doping,¹³ nano-engineering,¹⁴ additive destabilization,¹⁵ and chemical modification,¹⁶ have been employed in the past decade. One of the most fascinating strategies is to combine the borohydrides with $\text{H}^{\delta+}$ enriched nitrogen-containing compounds such as amide, guanidinium, and NH_3 to form new boron and nitrogen based compounds or

composites.¹⁷⁻²³ The B-N-H materials contain both hydridic and protic hydrogens, and are therefore expected to release hydrogen under more mild conditions, since a local combination of the $\text{N}-\text{H}^{\delta+}\cdots\text{H}^{\delta-}-\text{B}$ dihydrogen bonds will be achieved in these materials upon heating. For example, a series of metal borohydride ammoniates, including $\text{LiBH}_4\cdot\text{NH}_3$,¹⁸ $\text{Mg}(\text{BH}_4)_2\cdot 2\text{NH}_3$,¹⁹ $\text{Ca}(\text{BH}_4)_2\cdot 2\text{NH}_3$,²⁰ $\text{Zn}(\text{BH}_4)_2\cdot 2\text{NH}_3$,²¹ $\text{Al}(\text{BH}_4)_3\cdot 6\text{NH}_3$,²² and $\text{Li}_2\text{Al}(\text{BH}_4)_5\cdot 6\text{NH}_3$ ²³ have been synthesized and investigated as hydrogen storage media. Compared to the high decomposition temperature for the borohydrides, the ammoniate complexes showed much lower decomposition temperature. For example, $\text{Zn}(\text{BH}_4)_2\cdot 2\text{NH}_3$ and its composite are able to release more than 5 wt % hydrogen below 115 °C within 15 min, without concomitant release of undesirable gases such as ammonia and/or boranes, which makes it interesting as a hydrogen storage candidate.²¹

As one of the $\text{H}^{\delta+}$ enriched nitrogen-containing compounds, hydrazine (N_2H_4) is also interesting to coordinate with borane or borohydrides, since it contains 12.5 wt% hydrogen and four $\text{H}^{\delta+}$ hydrogens. Actually, it was already known in the early 1960s that hydrazine can complex with borane to form hydrazine borane ($\text{N}_2\text{H}_4\text{BH}_3$) and hydrazine bisborane ($\text{N}_2\text{H}_4(\text{BH}_3)_2$), but studies on these two materials are rare up to the present day.²⁴⁻²⁶ Recently, the hydrazine (bis)boranes were revisited due to their high hydrogen capacity, and today they can be considered as novel chemical hydrogen storage materials.²⁷⁻³⁰

More recently, it was reported that hydrazine can also complex with borohydrides, and a series of borohydride hydrazinates, including $\text{NaBH}_4 \cdot \text{N}_2\text{H}_4$, $\text{LiBH}_4 \cdot x\text{N}_2\text{H}_4$ ($x = 0.5, 1, 2$), and $\text{Mg}(\text{BH}_4)_2 \cdot 3\text{N}_2\text{H}_4$, were synthesized and investigated as hydrogen storage media.^{31,32} It was demonstrated that the Li and Na borohydride hydrazinates prefer to release part or all of their hydrazine under dynamic conditions, but $\text{Mg}(\text{BH}_4)_2$ hydrazinates can directly generate hydrogen under the same conditions. The different decomposition behaviour may be attributed to the different metal-ligand coordination strength, since the electronegativity, charge, and ionic radii of the cations are different, which affects the bonding properties between BH_4 and N_2H_4 , and thus leads to different dehydrogenation behavior. On the other hand, the development of hydrazinates requires a better understanding of the relationships of the crystal and electronic structures of the materials to the decomposition behavior in order to attempt targeted design and to further improve their dehydrogenation performance.

As for the sodium borohydride hydrazinates, only $\text{NaBH}_4 \cdot \text{N}_2\text{H}_4$ has been reported.³² The structure was found to be crystallized in a monoclinic $P2_1/c$ cell with lattice parameters $a = 7.6307 \text{ \AA}$, $b = 6.6135 \text{ \AA}$, $c = 9.1099 \text{ \AA}$, $\beta = 107.399^\circ$, and $V = 438.70 \text{ \AA}^3$. Each Na^+ ion interacts with two neighboring N_2H_4 molecules, leading to the formation of $\text{Na}_2[\text{N}_2\text{H}_4]_2^{2+}$ cationic chains, which are spread along the c direction. Such cationic chains are then surrounded by BH_4^- anions. The detailed thermal decomposition has not been clearly investigated, however. On the other hand, NaBH_4 can coordinate more than one equivalent of N_2H_4 .

In this paper, $\text{NaBH}_4\cdot\text{N}_2\text{H}_4$ and $\text{NaBH}_4\cdot 2\text{N}_2\text{H}_4$ were synthesized via a facile solution synthesis approach based on a solid-liquid reaction between NaBH_4 and hydrazine in tetrahydrofuran (THF) solution. The thermal decomposition behavior of these two compounds was systematically investigated by a series of structural analyses and property evaluations. The structure of $\text{NaBH}_4\cdot 2\text{N}_2\text{H}_4$ in particular was successfully solved. In addition, magnesium borohydride hydrazinates were synthesized by using sodium borohydride hydrazinates as starting materials.

2. Experimental

NaBH_4 (Sigma-Aldrich, 98.0 %) and hydrazine-THF solution (1.0 M) were purchased from Sigma-Aldrich. The sodium borohydride hydrazinate complexes were synthesized by the reaction of sodium borohydride and hydrazine in a certain ratio (1:1 and 1:2) in THF solution. In a typical synthesis process, the THF solution of hydrazine was dropped slowly into half or one equivalent of sodium borohydride. The reaction flask was stirred for 2 h at room temperature, and then the solvent was removed under vacuum, yielding a white polycrystalline solid. The final products were denoted as $\text{NaBH}_4\cdot\text{N}_2\text{H}_4$ and $\text{NaBH}_4\cdot 2\text{N}_2\text{H}_4$, respectively, according to whether 1 or 2 equivalents of hydrazine-THF solution were added. Note, however, that in this paper single phase NaBH_4 coordinated with one or two equivalents of hydrazine is denoted as $\text{NaBH}_4\cdot\text{N}_2\text{H}_4$ or $\text{NaBH}_4\cdot 2\text{N}_2\text{H}_4$, respectively. Adduct-free $\text{Mg}(\text{BH}_4)_2$ powders were prepared by drying commercial $\text{Mg}(\text{BH}_4)_2\cdot x\text{S}(\text{CH}_3)_2$ powders (Sigma-Aldrich) under vacuum at 473 K for 5 h. The magnesium borohydride

hydrazinate complexes were synthesized by ball milling magnesium borohydride and sodium borohydride hydrazinate complexes in a molar ratio of 1:1 in a Fritsch Pulverisette P7 planetary mill at 200 rpm under an inert atmosphere for 5 h. All syntheses and reactions were performed in a standard high vacuum line or a glove box filled with high purity argon unless otherwise stated.

Powder X-ray diffraction patterns for phase identification were collected on a Stoe STADI P diffractometer (Bragg–Brentano geometry) in reflection geometry (Cu $K\alpha_{1,2}$). Diffraction data for phase identification were typically collected for $5^\circ \leq 2\theta \leq 85^\circ$ with scan times of ~ 1 h. Additional data for the structure refinement of selected samples were collected over longer scan times (12 h; $5^\circ \leq 2\theta \leq 85^\circ$ with a step size of 0.017°) in a Bruker D8 Advance X-ray powder diffractometer, which employs a Ge 111 Vario monochromator at the X-ray tube with Cu $K\alpha_1$ radiation ($\lambda = 1.5406 \text{ \AA}$). Due to their sensitivity to air and moisture, samples were ground and loaded into 0.5 mm glass capillary tubes under argon, and the capillary tubes were sealed to prevent exposure to air before the measurements. Fourier transform infrared (FTIR) measurements were performed on a Varian 3100 unit.

Thermal decomposition behavior was investigated by simultaneous thermogravimetry – differential thermal analysis – mass spectrometry (TG-DTA-MS) measurements, which were conducted under Ar flow from room temperature to 250°C at a heating rate of $10^\circ\text{C}/\text{min}$ using a Netzsch STA 449C thermal analyzer coupled with a quadrupole mass spectrometer for analysis of the evolved gas. The thermogravimetry

– differential scanning calorimetry (TG-DSC) measurements were performed on a TG/DSC1 STAR system (METTLER TOLEDO). The measurements were carried out under argon flow at a rate of 50 ml min⁻¹, using typically 5-6 mg of sample, which was heated in an alumina crucible with a heating rate of 10 °C/min.

3 Results and discussion

3.1 Synthesis of sodium borohydride hydrazinates

The sodium borohydride hydrazinates NaBH₄·*x*N₂H₄ (*x* = 1 and 2) were synthesized by the reaction of NaBH₄ and hydrazine in various molar ratios (1:1, and 1:2) in THF solution. Figure 1 presents the powder X-ray diffraction (PXRD) patterns of the as-prepared NaBH₄·*x*N₂H₄ (*x* = 1 and 2) before and after hydrazination. For the molar ratio of 1:1, in addition to some residual NaBH₄ peaks, a set of new diffraction peaks appeared, which can be assigned to the single phase NaBH₄·N₂H₄, agreeing well with the previous report on NaBH₄·N₂H₄ produced through the ball-milling synthesis method.³² On further increasing the relative amount of hydrazine to the molar ratio of 1:2, the NaBH₄ phase disappeared, and in addition to the NaBH₄·N₂H₄ peaks, a set of new peaks appeared. Combining the PXRD and thermal decomposition analysis, the set of new peaks can be assigned to single phase NaBH₄·2N₂H₄. Further FTIR examination confirmed the formation of the sodium borohydride hydrazinates. Figure 2 presents the infrared transmittance of the NaBH₄ and hydrazinate complexes. Clearly, the typical features of the [BH₄] group can be observed in the spectrum for

the NaBH_4 and its hydrazinate complex samples, where the B–H bending vibration ($\sim 1110\text{ cm}^{-1}$) and the B–H stretching vibrations ($2010\text{--}2516\text{ cm}^{-1}$) were detected. In addition, numerous bands associated with the characteristic N_2H_4 absorption were detected for the hydrazinate complexes, which can be assigned as follows: (i) several bands with different strengths in the N–H stretching region over the range of $3119\text{--}3600\text{ cm}^{-1}$; (ii) two very strong sharp bands in the N–H asymmetric bending region (1595 and 1622 cm^{-1}); (iii) two sharp bands in the N–H symmetric bending region (1321 and 1293 cm^{-1}); (iv) two sharp and strong bands in the N–H rocking region (1022 and 876 cm^{-1}); and (vi) a band in the BN–N asymmetric stretching region and in the N–N symmetric stretching region (571 cm^{-1}). These FTIR spectral data with respect to N_2H_4 match well with the previous report on the molecular structure of hydrazine borane.²⁹

3.2 Thermal decomposition behavior

The thermal decomposition behavior of the sodium borohydride hydrazinates was derived from the simultaneous TGA-DTA-MS measurements. Figure 3 shows the TGA curves of the as-prepared $\text{NaBH}_4\text{-N}_2\text{H}_4$ and $\text{NaBH}_4\text{-2N}_2\text{H}_4$ at the heating rates of $10\text{ }^\circ\text{C/min}$. Thermogravimetric investigation of both the $\text{NaBH}_4\text{-N}_2\text{H}_4$ and the $\text{NaBH}_4\text{-2N}_2\text{H}_4$ showed a similar weight loss beginning at about $50\text{ }^\circ\text{C}$ and finishing at approximately $180\text{ }^\circ\text{C}$. The PXRD results (see inset of Fig. 3) demonstrated the final product for both $\text{NaBH}_4\text{-N}_2\text{H}_4$ and $\text{NaBH}_4\text{-2N}_2\text{H}_4$ at $180\text{ }^\circ\text{C}$ to be NaBH_4 . This fact indicated that the decomposition of $\text{NaBH}_4\text{-N}_2\text{H}_4$ and $\text{NaBH}_4\text{-2N}_2\text{H}_4$ below $200\text{ }^\circ\text{C}$

can be regarded as the desorption of hydrazine due to the weak coordination bonds of N_2H_4 with NaBH_4 . The weight loss for the $\text{NaBH}_4\text{-N}_2\text{H}_4$, approximately 43 wt%, corresponds exclusively to the loss of hydrazine (the theoretical loss for $\text{NaBH}_4\cdot\text{N}_2\text{H}_4$ being ~ 46 wt%), agreeing well with the PXRD results (Fig. 1), since the as-prepared $\text{NaBH}_4\text{-N}_2\text{H}_4$ sample includes much $\text{NaBH}_4\cdot\text{N}_2\text{H}_4$ and some small amount of NaBH_4 residue. In contrast, the weight loss for the $\text{NaBH}_4\text{-2N}_2\text{H}_4$, approximately 56 wt%, is much lower than the theoretical loss of $\text{NaBH}_4\cdot 2\text{N}_2\text{H}_4$ (~ 63 wt%). Nevertheless, the results are reasonable, since the as-prepared $\text{NaBH}_4\text{-2N}_2\text{H}_4$ includes 39 wt% $\text{NaBH}_4\cdot\text{N}_2\text{H}_4$ and 61wt% $\text{NaBH}_4\cdot 2\text{N}_2\text{H}_4$ according to the PXRD refinement (Fig. 7).

The decomposition properties of $\text{NaBH}_4\text{-N}_2\text{H}_4$ and $\text{NaBH}_4\text{-2N}_2\text{H}_4$ were further analyzed by mass spectrometry (MS) measurements (Fig. 4). It is well known that the decomposition of hydrazine follows two competing routes, giving rise to H_2 , N_2 , and NH_3 as follows:^{33,34}

For both the $\text{NaBH}_4\text{-N}_2\text{H}_4$ and the $\text{NaBH}_4\text{-2N}_2\text{H}_4$ samples, N_2H_4 and its decomposed products (i.e., NH_3 , N_2 , and H_2) were detected in the temperature range of 140-200 °C under dynamic Ar flow. The release of H_2 as the major constituent, especially in the $\text{NaBH}_4\text{-2N}_2\text{H}_4$ sample, indicates that Reaction (1) is preferred. It is well known that the hydrazine can only release hydrogen via Reaction (1) in the present of catalysts,

indicating that storing the hydrazine in sodium borohydride produces a good storage medium favoring the release of hydrogen without using catalysts.^{35,36}

Also, the thermal decomposition behavior of $\text{NaBH}_4\text{-N}_2\text{H}_4$ and $\text{NaBH}_4\text{-2N}_2\text{H}_4$ was further investigated by DTA, as presented in Figure 5. Both the $\text{NaBH}_4\text{-N}_2\text{H}_4$ and the $\text{NaBH}_4\text{-2N}_2\text{H}_4$ are white solids (Fig. 6a, c), and melt at around 60 °C (Fig. 6b, d). From the DTA curves, there are two similar endothermic peaks for the $\text{NaBH}_4\text{-N}_2\text{H}_4$ and $\text{NaBH}_4\text{-2N}_2\text{H}_4$, with the peak positions shifting to lower temperature for the $\text{NaBH}_4\text{-2N}_2\text{H}_4$. Based on the TGA curves (Fig. 3) and the photographs (Fig. 6), the first peak can be assigned to the melting point, while the second peak is associated with hydrazine desorption. Both the TGA and the DTA curves indicate that the hydrazine complex decomposes in a single step. The release of H_2 , N_2 , and NH_3 in MS measurements, however, indicates the desorption of hydrazine as well as with its self-decomposition.

Furthermore, the compatible melting characteristic of hydrazinate complexes can be used to fabricate nanoscale NaBH_4 . It has been reported that nanoconfinement of NaBH_4 in nanoporous scaffolds is an effective way to improve the kinetic and/or thermodynamic properties of the NaBH_4 material.^{37,38} The fabrication of NaBH_4 in the host materials is not easy, however, as the melting point of NaBH_4 is quite close to the decomposition temperature, and the solubility of NaBH_4 in organic solvent is poor.³⁹ Because of the low melting temperature and low hydrazine desorption temperature, these sodium borohydride hydrazinate complexes can be easily infiltrated into a

nanoporous scaffold via a simple melt impregnation method. After desorption of the hydrazine, the nanoconfined NaBH₄ would be synthesized.

3.3 Structure identification of NaBH₄·2N₂H₄

NaBH₄·2N₂H₄ was indexed from the PXRD pattern (Fig. 7) as having a monoclinic unit cell and space group *A1a1* (No. 9) with the lattice constants $a = 8.4592(2) \text{ \AA}$, $b = 11.7131(2) \text{ \AA}$, $c = 6.4584(1) \text{ \AA}$, $\beta = 100.0777(14)^\circ$, and $V = 630.05(2) \text{ \AA}^3$. The crystal structure was then solved using the direct space method, in which the BH₄ and N₂H₄ units were input as rigid bodies with common bond lengths and bond angles. Rietveld structural refinement was then conducted for this compound using the structure model shown in Figure 8, where the Rietveld fit is highly consistent with the experimental PXRD profile, yielding the following agreement factors: weighted profile R-factor, $R_{wp} = 5.64\%$, Bragg R-factor, $R_B = 3.65\%$, and goodness of fit, $GoF = 1.412$. The Rietveld refinement gave the relative amounts of NaBH₄·2N₂H₄ and NaBH₄·N₂H₄ in the final product as 61 wt% and 39 wt%, respectively. The detailed experimental and crystallographic data are summarized in Table 1 and Table S1 in the Supporting Information.

The crystal structure of NaBH₄·2N₂H₄ is shown in Figure 8, in which each Na⁺ ion is surrounded by two NH₂NH₂ molecules, with Na⁺ in a distorted tetrahedral coordination with Na-N distances of 2.346-2.762 Å. With lone pairs on N atoms, the NH₂NH₂ molecules act as a connecting bridge to link the Na⁺ tetrahedra through an

edge-sharing chain complex along the a -axis. The free BH_4^- anions fill the space in between these chain complexes, with Na-B distance of 2.978-3.354 Å. The typical interatomic distances of $\text{NaBH}_4 \cdot 2\text{N}_2\text{H}_4$ are summarized in Table S2.

3.4 Synthesis of magnesium borohydride hydrazinates

For metal borohydrides, it has been theoretically and experimentally demonstrated that a clear correlation exists between the thermodynamic stability of metal borohydrides and the Pauling electronegativity of the respective metal cations.^{40,41} Specifically, the dehydrogenation temperature of $\text{M}(\text{BH}_4)_n$, where M is a metal cation of valence n , decreases linearly with the increasing electronegativity of M. For example the dehydrogenation temperature of $\text{Mg}(\text{BH}_4)_2$ is 100 °C lower than that of NaBH_4 .⁵ Regarding the borohydride hydrazinates, it was also shown that cations with high Pauling electronegativity hold hydrazine strongly in the vicinity of the borohydride, resulting in direct dehydrogenation at elevated temperatures.^{31,32} For example, $\text{Mg}(\text{BH}_4)_2$ hydrazinates can directly generate hydrogen when heated under flowing Ar.³² Therefore, it is of particular interest to improve the dehydrogenation of sodium borohydride hydrazinates via the partial replacement of Na^+ cations by other cations with larger electronegativities or by synthesizing dual-cation borohydride hydrazinates.

Ball milling is a good method to synthesize these anticipated materials. XRD patterns were obtained for the ball-milled $\text{NaBH}_4\text{-N}_2\text{H}_4 + \text{Mg}(\text{BH}_4)_2$ and $\text{NaBH}_4\text{-}2\text{N}_2\text{H}_4 +$

Mg(BH₄)₂ composites. For comparison purposes, the starting material, Mg(BH₄)₂, obtained from commercial Mg(BH₄)₂•xS(CH₃)₂ powders, was also included. These data, as shown in Figure 9, revealed similar peak characteristics for these two samples. Interestingly, the peaks assigned to NaBH₄-xN₂H₄ (x = 1, 2) completely disappeared after ball milling for 5 h. Meanwhile, the present peaks can be assigned to residual Mg(BH₄)₂, newly formed NaBH₄, and a set of other new peaks. These new peaks agree well with a previous report on Mg(BH₄)₂-xN₂H₄, indicating the formation of Mg(BH₄)₂-xN₂H₄ (x = 1, 2).³² The results indicated that the following reaction: NaBH₄-xN₂H₄ + Mg(BH₄)₂ → Mg(BH₄)₂-xN₂H₄ + NaBH₄ was likely to have occurred during ball milling.

The thermal decomposition behavior for the milled NaBH₄-N₂H₄ + Mg(BH₄)₂ and NaBH₄-2N₂H₄ + Mg(BH₄)₂ samples is presented in Figure 10. As expected, both samples showed the thermal characteristics of Mg(BH₄)₂-xN₂H₄ (x = 1, 2). The TGA curves for the NaBH₄-N₂H₄ + Mg(BH₄)₂ sample showed two decomposition steps from 130 to 270 °C, agreeing well with the DSC results, where two exothermic peaks were observed at 162 and 221 °C, respectively. The NaBH₄-2N₂H₄ + Mg(BH₄)₂ sample showed similar characteristics, but featured a slightly higher decomposition temperature. Its TGA curves showed two decomposition steps in the temperature range from 147 to 300 °C, and the DSC results featured two peaks, a small exothermic peak at 160 °C and a much larger peak at 260 °C.

Conclusion

In summary, sodium borohydride hydrazinates, including $\text{NaBH}_4 \cdot \text{N}_2\text{H}_4$ and $\text{NaBH}_4 \cdot 2\text{N}_2\text{H}_4$, have been synthesized via a simple solution synthesis method. The crystal structure of $\text{NaBH}_4 \cdot 2\text{N}_2\text{H}_4$ was solved by the powder X-ray diffraction method, which is also supported by evidence from FTIR spectroscopy. Pyrolysis of $\text{NaBH}_4 \cdot x\text{N}_2\text{H}_4$ ($x = 1, 2$) lead to the formation of hydrogen gas together with appreciable amounts of volatile nitrogen and ammonia below 200 °C through desorption of hydrazine. Interestingly, the $\text{NaBH}_4 \cdot x\text{N}_2\text{H}_4$ showed a melting characteristic at around 60 °C before desorption of hydrazine. This melting characteristic at low temperature and low hydrazine desorption temperature can be used to synthesize NaBH_4 nanoparticles through infiltration of $\text{NaBH}_4 \cdot x\text{N}_2\text{H}_4$ into a nanoporous scaffold via a simple melt impregnation method. Furthermore, magnesium borohydride hydrazinates were synthesized by ball milling the sodium borohydride hydrazinates with magnesium borohydride.

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Figure and Table Captions

Table 1. Experimental and crystallographic details for $\text{NaBH}_4 \cdot 2\text{N}_2\text{H}_4$.

Figure 1. PXRD patterns of NaBH_4 (a), $\text{NaBH}_4 \cdot \text{N}_2\text{H}_4$ (b), and $\text{NaBH}_4 \cdot 2\text{N}_2\text{H}_4$ (c).

Figure 2. FTIR spectra of NaBH_4 (a), $\text{NaBH}_4 \cdot \text{N}_2\text{H}_4$ (b), and $\text{NaBH}_4 \cdot 2\text{N}_2\text{H}_4$ (c).

Figure 3. TGA curves of $\text{NaBH}_4 \cdot \text{N}_2\text{H}_4$ (a) and $\text{NaBH}_4 \cdot 2\text{N}_2\text{H}_4$ (b). Inset shows the PXRD patterns of $\text{NaBH}_4 \cdot \text{N}_2\text{H}_4$ and $\text{NaBH}_4 \cdot 2\text{N}_2\text{H}_4$ after heating to 200 °C.

Figure 4. MS spectra of (a) $\text{NaBH}_4 \cdot \text{N}_2\text{H}_4$ and (b) $\text{NaBH}_4 \cdot 2\text{N}_2\text{H}_4$.

Figure 5. DTA curves of $\text{NaBH}_4 \cdot \text{N}_2\text{H}_4$ (a) and $\text{NaBH}_4 \cdot 2\text{N}_2\text{H}_4$ (b).

Figure 6. Photographs of $\text{NaBH}_4 \cdot \text{N}_2\text{H}_4$ (a, b) and $\text{NaBH}_4 \cdot 2\text{N}_2\text{H}_4$ (c, d) before and after heating to their melting temperature.

Figure 7. Rietveld refinement profile for the as-prepared $\text{NaBH}_4 \cdot 2\text{N}_2\text{H}_4$. Experimental (blue), fitted (red), and difference (grey line below observed and calculated patterns) PXRD profiles. Vertical bars indicate the calculated positions of Bragg peaks for $\text{NaBH}_4 \cdot \text{N}_2\text{H}_4$ and $\text{NaBH}_4 \cdot 2\text{N}_2\text{H}_4$.

Figure 8. Three-dimensional crystal structure of $\text{NaBH}_4 \cdot 2\text{N}_2\text{H}_4$ (a) presented in a unit cell, (b) viewed along the *a*-axis, and (c) viewed along the *c*-axis.

Figure 9. PXRD patterns of the milled $\text{NaBH}_4\text{-}2\text{N}_2\text{H}_4 + \text{Mg}(\text{BH}_4)_2$ (a) and $\text{NaBH}_4\text{-N}_2\text{H}_4 + \text{Mg}(\text{BH}_4)_2$ (b). The PXRD pattern of $\text{Mg}(\text{BH}_4)_2$ is also concluded for comparison (c).

Figure 10. TGA-DSC (inset) curves of the milled $\text{NaBH}_4\text{-}2\text{N}_2\text{H}_4 + \text{Mg}(\text{BH}_4)_2$ (a) and $\text{NaBH}_4\text{-N}_2\text{H}_4 + \text{Mg}(\text{BH}_4)_2$ (b).

Table 1

Chemical formula	NaBH ₄ ·2N ₂ H ₄
Formula weight	101.923 g mol ⁻¹
Crystal system	monoclinic
Space group	<i>A</i> 1 <i>a</i> 1 (9)
Unit cell dimensions	$a = 8.4592(2) \text{ \AA}$ $\alpha = 90^\circ$ $b = 11.7131(2) \text{ \AA}$ $\beta = 100.0777(14)^\circ$ $c = 6.4584(1) \text{ \AA}$ $\gamma = 90^\circ$
Z	4
Density (calculated)	1.07443 g/cm ³
Volume	630.05(2) Å ³
2 θ [°]	2 $\theta_{\min} = 10$, 2 $\theta_{\max} = 85$
Diffractometer	Bruker D8
Wavelength	1.5406 Å
Measurement temperature	25 °C
R _B	3.65%
R _{wp}	5.64%
GoF	1.412

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10