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Keywords

high, release, capacity, hydrogen, hydrolysis, nab₃h₈

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High-capacity hydrogen release through hydrolysis of NaB₃H₈

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Abstract

NaB₃H₈ has advantages over NaBH₄ and NH₃BH₃, two most widely studied chemical hydrides for hydrogen storage via hydrolysis. NaB₃H₈ has an extraordinary high solubility in water and thus possesses a high theoretical capacity of 10.5 wt % H via hydrolysis, in contrast to 7.5 wt % for NaBH₄ and 5.1 wt % for NH₃BH₃. NaB₃H₈ is reasonably stable in water which makes it unnecessary to add corrosive NaOH as a stabilizer as the case for NaBH₄. Furthermore, hydrolysis of NaB₃H₈ can be catalyzed by a Co-based catalyst with fast kinetics that is comparable to Ru-based catalysts. Therefore, cost-effective hydrolysis of NaB₃H₈ is possible for practical applications. A high capacity of 7.4 wt % H was achieved when water was included in the materials weight.

Keywords: hydrogen storage, hydrogen generation, NaB₃H₈, hydrolysis

1. Introduction

Safe and efficient on-board hydrogen storage is a major barrier to the use of hydrogen as a transportation fuel. Due to their high hydrogen content, boranes and borohydrides have been considered as potential candidates for chemical hydrogen storage. Among them, NH₃BH₃ [1,2] and NaBH₄ [3,4] have attracted the most attention. Through pyrolysis, NH₃BH₃ gives off 12 wt % hydrogen at 150 °C, but it suffers from low rates of H₂ release and the formation of the volatile impurity—borazine [5,6]. Hydrolytic dehydrogenation (eqn. 1) facilitated by catalysts has demonstrated

improved kinetics and the elimination of borazine formation, but the formation of NH_3 was observed [7,8]. Furthermore, due to the low solubility in water (~26 wt % at 25 °C [9]), extra water (than required for eqn 1) is needed which results in a lower theoretical material weight density [$\text{wt \%} = \text{H}_2 / (\text{NH}_3\text{BH}_3 + \text{H}_2\text{O} + \text{catalyst})$] of less than 5.1 wt % [9]. Dehydrogenation of NH_3BH_3 in solvents led to enhanced kinetics and hydrogen purity, but the hydrogen density decreased significantly due to the presence of auxiliary solvents [10]. As for NaBH_4 , controllable H_2 release was developed through hydrolysis (eqn 2). However, NaBH_4 reacts rapidly with water and as a result a strong basic solution (commonly 3 wt % NaOH) is required to minimize the degradation [3,4]. The addition of NaOH not only forms a corrosive environment but also reduces the solubility of NaBH_4 [11]. Its low solubility in water (~35 wt % at 25 °C [12]) necessitates extra water to be carried on board, which lowers the theoretical hydrogen density [$\text{wt \%} = \text{H}_2 / (\text{NaBH}_4 + \text{H}_2\text{O} + \text{catalyst})$] to ~7.5 wt %. Moreover, the variation in solubility with temperature makes only ~24 wt % solubility practical, which results in a lower hydrogen density of ~5.0 wt % [13].

The enormous variety and very distinct properties of boron compounds prompt us to search for new materials that would satisfy the requirements for hydrogen storage. With the same metal cation, the properties of metal-boron-hydrogen (M-B-H) compounds change dramatically as the number of boron atoms increases from 1 to 12, with NaBH_4 reacting intensively with water and $\text{Na}_2\text{B}_{12}\text{H}_{12}$ staying intact in water [14]. For hydrogen storage, it is crucial to find a suitable combination of light-weight metal cation and H-rich B_mH_n anion. NaB_3H_8 (sodium octahydrotriborate) becomes very attractive considering its 12.6 wt % H capacity. However, for more than seven decades, the reported syntheses of unsolvated NaB_3H_8 used dangerous starting materials such as B_2H_6 or BF_3 that requires extremely careful handling and disposal [15,16]. We have recently developed a simple and efficient route to unsolvated NaB_3H_8 , making it possible to synthesize and study it in an average chemistry lab [17]. Here we report the hydrogen release properties of this

compound through hydrolysis (eqn 3). The interesting results indicate that NaB₃H₈ has advantages over NaBH₄ and NH₃BH₃ and a high capacity hydrogen generation through cost-effective hydrolysis of NaB₃H₈ is possible for practical applications.

2. Materials and methods

Unsolvated NaB₃H₈ was prepared according to the procedure recently developed in our lab [17]. Due to its hygroscopic nature, unsolvated NaB₃H₈ was stored and handled under an inert atmosphere except for the hydrolysis. For the stability study, NaB₃H₈ and NaBH₄ aqueous solutions (2 M, distilled water) were compared at 28 °C. The degradation was monitored using NMR technique. NMR spectra were obtained on a Bruker Avance DPX 250 NMR spectrometer. The ¹¹B NMR spectra were obtained at 80.3 MHz and externally referenced to BF₃·OEt₂ in C₆D₆ at 0.00 ppm. The degree of degradation was calculated based on the integration ratio of ¹¹B NMR peaks.

In a two-neck flask connected to a vacuum line, 1 mmol NaB₃H₈ was mixed with 0.01 mmol Pt (Pt/C, 10 wt % Pt). After evacuating all the gases via dynamic vacuum, the flask was sealed and 14 mmol water was injected. At the reaction conclusion, the flask was opened to a vacuum line, and the evolved gas passed through a liquid nitrogen trap in order to isolate any volatile non-hydrogen products, including water. The hydrogen was then quantitatively measured using a Toepler pump. Mass spectrum of the gas released from hydrolysis was recorded through Balzer's Quadstar 422 Quadropole Mass Spectrometer. The heat of the hydrolysis reaction of NaB₃H₈ was calculated based on the same method used by Sneddon [18] .

For catalysts screening, a gas buret was set up to measure the amount of H₂ gas and to determine the rates of H₂ release [18]. Pt/C (10 wt % Pt), Ru/Al₂O₃ (5 wt % Ru), RuCl₃, CoCl₂, NiCl₂ and FeCl₃ were all tested as received. For the catalyst loading, 1 mol % (with reference to NaB₃H₈) of noble metal (Pt or Ru) was loaded, while 4 mol % of transition metal (Co, Ni, or Fe) was used unless otherwise stated.

3. Results and discussion

In contrast to both NH_3BH_3 and NaBH_4 , NaB_3H_8 has a significantly higher solubility in water. A visual observation reveals a value > 74 wt % at room temperature, and > 60 wt % at 0°C . Therefore, based on eqn 3, the solubility is not a limiting factor for the hydrogen density. The limited solubility of both NH_3BH_3 and NaBH_4 in water, in contrast, significantly lowers the hydrogen density of their respective systems. Quantitative measurements of hydrogen released using a Toepler pump and a gas buret showed that upon adding 14 mmol water to 1 mmol NaB_3H_8 with Pt/C (1 mol % Pt), a near theoretical value of 8.85 mmol hydrogen was released in 20 min. Mass spectrum of the gaseous product from the hydrolysis indicates the existence of hydrogen only. Therefore, this system has a high theoretical hydrogen weight density [$\text{wt \%} = \text{H}_2 / (\text{NaB}_3\text{H}_8 + \text{H}_2\text{O})$] of 10.5 wt %, which will be lowered slightly considering the weight of the catalyst. This number is much higher than those from NH_3BH_3 (5.1 wt %) and NaBH_4 (7.5 wt %).

Unlike NaBH_4 , NaB_3H_8 is significantly more stable in water (distilled water is used through this study). At 28°C , for the same molar concentration (2 M), ^{11}B NMR studies (Fig. 1 a-e) show that more than 50 percent of NaBH_4 hydrolyzed over a day, while less than 10 percent of NaB_3H_8 hydrolyzed over a week. The hydrolysis products of the two compounds were quite different as indicated by the ^{11}B NMR spectra. Boric acid is present in the solution for NaBH_4 (Fig. 1a). For NaB_3H_8 , the ^{11}B NMR spectrum (Fig. 1 inset) exhibits one broad peak centered at 16 ppm which is likely associated with $\text{B}_3\text{O}_3(\text{OH})_4^-$ and $\text{B}_5\text{O}_6(\text{OH})_4^-$, and the other sharp peak situated at around 0 ppm is also due to $\text{B}_5\text{O}_6(\text{OH})_4^-$ [19,20]. The difference in the composition is associated with the concentration of $\text{B}(\text{OH})_3$ in the solution. For the same molar concentration, NaB_3H_8 produces a higher concentration of $\text{B}(\text{OH})_3$ than NaBH_4 , and as a result, $\text{B}_3\text{O}_3(\text{OH})_4^-$ and $\text{B}_5\text{O}_6(\text{OH})_4^-$ become dominant.

Since NaB_3H_8 is fairly stable in water, catalysts have to be used to accelerate the hydrolysis. For an aqueous solution with a 1:14 molar ratio of NaB_3H_8 to H_2O , the commercially available Pt/C catalyst (10 wt % Pt, 1 mol % Pt loading with reference to NaB_3H_8) shows the best catalytic activity, with complete hydrolysis in less than 20 min (Fig. 2). $\text{Ru}/\text{Al}_2\text{O}_3$ (5 wt % Ru, 1 mol % Ru loading with reference to NaB_3H_8) is

also very effective and full hydrolysis was complete in about 30 min. RuCl_3 displayed excellent catalytic activity, and this is likely associated with the formation of Ru (0) as indicated by the formation of a black powder, which was also observed during hydrolysis of both NaBH_4 [3] and NH_3BH_3 [8]. The high cost of these noble metals, however, will likely prevent their wide applications in practical chemical hydrogen storage systems. Cost-effective transition metal based catalysts were explored in our study and fairly good catalytic activity was observed for CoCl_2 . NiCl_2 is less effective and the H_2 evolution rate decreased after 20 min. FeCl_3 displayed negligible catalytic activity.

With 4 mol % loading of CoCl_2 , full hydrolysis was completed in about 30 min and this performance is comparable to that of Ru-based catalysts. A black powder appeared instantly when CoCl_2 was brought in contact with an aqueous NaB_3H_8 solution. The black powder was collected through filtration. It is amorphous as revealed by XRD pattern. Once hydrochloric acid is added to the black powder, a rose red solution was obtained, which is a typical color of a CoCl_2 aqueous solution. The ^{11}B NMR spectrum of the solution reveals the existence of boric acid. It was therefore contemplated that the black powder is a Co-B compound. Similar compounds were reported for the hydrolysis of NaBH_4 catalyzed by Co salts [3].

The H_2 release rates can be tuned by modifying the loadings of the catalyst. As illustrated in Fig. 3, for the 2 mol % CoCl_2 loading, it took about 100 min to give off 6 H_2 equiv., while a 4 mol % loading led to the release of almost 9 H_2 equiv. in only ~30 min.

Eqn (3) indicates that NaB_3H_8 aqueous solution has a high theoretical hydrogen density of 10.5 wt %. For practical applications, however, due to the mass transfer limitations, this value could only be achieved with slow H_2 evolution rates. In order to obtain both high hydrogen density and satisfactory kinetics, a proper NaB_3H_8 to H_2O ratio is necessary. Molar ratios of 1:10, 1:14 and 1:20 have been investigated (Fig. 4). These aqueous solutions have a hydrogen density of 7.4 wt %, 5.7 wt % and 4.2 wt %, respectively, with the addition of CoCl_2 (4 mol %) lowering the density slightly. As expected, both 1:14 and 1:20 solutions yielded about 9 H_2 equiv. in ~30 min, in contrast to ~100 min for the 1:10 solution to complete the hydrolysis.

Calculations of the standard heats of hydrolysis from the standard enthalpies of formation indicate that H_2 release from NaB_3H_8 is slightly less exothermic (60.96 kJ/mol H_2 [21,22]) than from either NaBH_4 (63.6 kJ/mol H_2) or $\text{NH}_3\text{B}_3\text{H}_7$ (79.1 kJ/mol H_2), but higher than NH_3BH_3 (53.16 kJ/mol H_2) [23]. Hydrolysis of NaB_3H_8 is much less exothermic than that of metal hydrides (LiAlH_4 (121.34 kJ/mol H_2), MgH_2 (140.16 kJ/mol H_2), and LiH (132.2 kJ/mol H_2) [24, 25]).

The ^{11}B NMR spectrum of the solution obtained after the catalyzed hydrolysis of a 26 wt % solution (1:10 molar ratio of NaB_3H_8 to H_2O) reveals the co-existence of $\text{B}_3\text{O}_3(\text{OH})_4^-$ and $\text{B}_5\text{O}_6(\text{OH})_4^-$ (Fig. 5). As in the cases of NaBH_4 , NH_3BH_3 , $\text{NH}_3\text{B}_3\text{H}_7$ and $\text{NH}_4\text{B}_3\text{H}_8$ [26], the formation of borates may affect the performance of the catalysts if the borate precipitates cover the active sites. It should be noted that the removal and transportability of the borates depend on the starting materials and reaction conditions, and thus can be improved [27]. The ultimate utility of NaB_3H_8 as a chemical hydrogen storage material for transportation will depend on the development of an efficient “off-board” regeneration of NaB_3H_8 from the borates.

US Department of Energy (DOE) recently modified vehicular hydrogen storage targets to 4.5 wt % by 2010, 5.5 wt % by 2015 and 7.5 wt % for the ultimate [28]. We show that NaB_3H_8 has a high solubility and reasonable stability in water, and a high hydrogen density through hydrolysis using transition metal based catalysts. This represents an opportunity for meeting the hydrogen storage targets. Further investigation on the improvement of the stability is underway. But the fairly stable aqueous NaB_3H_8 solution without additives can be a good candidate for certain applications where hydrogen is consumed continuously.

4. Conclusions

As a chemical hydride for hydrogen storage, unsolvated NaB_3H_8 outperforms NaBH_4 and NH_3BH_3 in several key aspects.

1. NaB_3H_8 has an extraordinary high solubility in water, >74 wt % at room temperature, in contrast to 26 wt % of NH_3BH_3 and 35 wt % of NaBH_4 . Therefore, hydrolysis of NaB_3H_8 renders a high theoretical material capacity of 10.5 wt %, in contrast to 5.1 wt % of NH_3BH_3 and 7.5 wt % of NaBH_4 .

2. NaB_3H_8 is reasonably stable in water which makes it unnecessary to add corrosive NaOH as a stabilizer as the case for NaBH_4 . This renders an easier system assembly than using NaBH_4 .
3. Hydrolysis of NaB_3H_8 produces high quality hydrogen gas. Cost-effective Co-based catalyst displays fast kinetics comparable to Ru-based catalysts. A high capacity of 7.4 wt % H was achieved when water was included in the materials weight.

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References

- [1] Zhang Y, Shimoda K, Miyaoka H, Ichikawa T, Kojima Y. Thermal decomposition of alkaline-earth metal hydride and ammonia borane composites. *Inter J Hydrogen Energy* 2010; 35: 12405-9.
- [2] Diwan M, Hanna D, Varma A. Method to release hydrogen from ammonia borane for portable fuel cell applications *Inter J Hydrogen Energy* 2010; 35: 577-84.
- [3] Liu BH, Li, ZP. A review: Hydrogen generation from borohydride hydrolysis reaction. *J Power Sources* 2009; 187: 527-34.
- [4] Liu BH, Li Q. A highly active Co-B catalyst for hydrogen generation from sodium borohydride hydrolysis. *Inter J Hydrogen Energy* 2008; 33: 7385-91.
- [5] Wolf G, Baumann J, Baitalow F, Hoffmann FP. Calorimetric process monitoring of thermal decomposition of B–N–H compounds. *Thermochim Acta* 2000; 343: 19-25.
- [6] Hu MG, Geanangel RA, Wendlandt WW. The thermal decomposition of ammonia borane. *Thermochim Acta* 1978; 23: 249-55.
- [7] Yan J, Zhang X, Han S, Shioyama H, Xu Q. Iron-nanoparticle-catalyzed hydrolytic dehydrogenation of ammonia borane for chemical hydrogen storage. *Angew Chem Int Ed* 2008; 47: 2287-9.

- [8] Ramachandran PV, Gagare PD. Preparation of ammonia borane in high yield and purity, methanolysis, and regeneration. *Inorg Chem* 2007; 46: 7810-7.
- [9] Brockman A, Zheng Y, Gore J. A study of catalytic hydrolysis of concentrated ammonia borane solutions. *Inter J Hydrogen Energy* 2010; 35: 7350-6.
- [10] Bluhm ME, Bradley MG, Butterick R, Kusari U, Sneddon LG. Amineborane-based chemical hydrogen storage: enhanced ammonia borane dehydrogenation in ionic liquids. *J Am Chem Soc* 2006; 128: 7748-9.
- [11] Shang Y, Chen R. Hydrogen storage via the hydrolysis of NaBH_4 basic solution: optimization of NaBH_4 concentration. *Energy Fuels* 2006; 20: 2142-8.
- [12] Rohm and Haas: the Sodium Borohydride Digest, 2003; 8.
- [13] US Department of Energy Independent Review: Go/no-go recommendation for sodium borohydride for on-board vehicular hydrogen storage, 2007.
- [14] Muetterties EL, Balthis JH, Chia YT, Knoth WH, Miller HC. Chemistry of boranes. VIII.¹ Salts and acids of $\text{B}_{10}\text{H}_{10}^{2-}$ and $\text{B}_{12}\text{H}_{12}^{2-}$. *Inorg Chem* 1964; 3: 444-51.
- [15] Hough WV, Edwards LJ, McElroy AD. The sodium-diborane reaction. *J Am Chem Soc* 1956; 78: 689.
- [16] Goedde DM, Windler GK, Girolami GS. Synthesis and characterization of the homoleptic octahydrotriborate complex $\text{Cr}(\text{B}_3\text{H}_8)_2$ and its lewis base adducts. *Inorg Chem* 2007; 46: 2814-23.
- [17] Huang Z, King G, Chen X, Hoy J, YisgeduT, Lingam HK, Shore SG, Woodward PM, Zhao J-C. A Simple and efficient way to synthesize unsolvated sodium octahydrotriborate. *Inorg Chem* 2010, 49, 8185-7.
- [18] Yoon CW, Sneddon LG. Ammonia Triborane: A promising new candidate for amineborane-based chemical hydrogen storage. *J Am Chem Soc* 2006; 128: 13992-3.
- [19] Momii RK, Nachtrieb NH. Nuclear magnetic resonance study of borate-polyborate equilibria in aqueous solution. *Inorg Chem* 1967; 6: 1189-92.
- [20] Salentine CG. High-field ^{11}B NMR of alkali borates. Aqueous polyborate equilibria. *Inorg Chem* 1983; 22: 3920-4.
- [21] Rozenberg AS, Nechiporenko GN, Titov LV, Levicheva MD. Kinetics of the thermal decomposition of sodium octahydrotriborate. *Russ J Inorg Chem* 1982; 27: 1527-9.

- [22] CRC Handbook of Chemistry and Physics, 90th Edition.
- [23] Yoon, CW, Carroll PJ, Sneddon LG. Ammonia Triborane: A new synthesis, structural determinations, and hydrolytic hydrogen-release properties. *J Am Chem Soc* 2009; 131: 855-64.
- [24] Messer CE, Fasolino LG, Thalmayerm CE. The heats of formation of lithium, sodium and potassium hydrides. *J Am Chem Soc* 1955; 77: 4524-6.
- [25] Davis WD, Mason LS, Stegeman G. The heats of formation of sodium borohydride, lithium borohydride and lithium aluminum hydride. *J Am Chem Soc* 1949; 71: 2775-81.
- [26] Huang Z, Chen X, Yisgedu T, Meyers EA, Shore SG, Zhao J-C. Ammonium Octahydrotriborate ($\text{NH}_4\text{B}_3\text{H}_8$): New Synthesis, Structure and Hydrolytic Hydrogen Release. *Inorg Chem* accepted, 2011.
- [27] Basu S, Diwan M, Abiad MG, Zheng Y, Campanella OH, Varma A. Transport characteristics of dehydrogenated ammonia borane and sodium borohydride spent fuels. *Inter J Hydrogen Energy* 2010; 35: 2063-72.
- [28] U.S. Department of Energy.
https://www1.eere.energy.gov/hydrogenandfuelcells/storage/pdfs/targets_onboard_hydro_storage.pdf US DOE recently modified vehicular hydrogen storage targets. 2009.

Fig. 1 ^{11}B NMR spectra of 2 M aqueous solution taken after a: 24 hrs for NaBH_4 ; b: 12 hrs, c: 24 hrs, d: 7 days and e: 11 days for NaB_3H_8 . Inset is an expanded spectrum of e.

Fig. 2 Hydrogen evolution from aqueous NaB_3H_8 solution (molar ratio of NaB_3H_8 : H_2O being 1:14) containing Pt/C (1 mol % Pt); Ru/ Al_2O_3 (1 mol % Ru), RuCl_3 (1 mol % Ru), CoCl_2 (4 mol % Co), NiCl_2 (4 mol % Ni) and FeCl_3 (4 mol % Fe). Molar ratios are referenced to NaB_3H_8 .

Fig. 3 Hydrogen evolution from aqueous solution (NaB_3H_8 : H_2O being 1: 14) containing 2, 4, and 8 mol % of CoCl_2 (with reference to NaB_3H_8).

Fig. 4 Hydrogen evolution from aqueous solution with molar ratio of NaB_3H_8 : H_2O being 1:10, 1:14 and 1:20. CoCl_2 (4 mol % Co) was used as the catalyst.

Fig. 5 ^{11}B NMR spectrum of the catalyzed hydrolysis solution (NaB_3H_8 to H_2O being 1:10).