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Hydrogen liberation from the hydrolytic dehydrogenation of hydrazine borane in acidic media

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ABSTRACT

Addressed herein, the hydrolytic dehydrogenation of hydrazine borane (NH_4BH_3, HB) was reported in acidic media using nitric acid (HNO_3) as a catalyst at room conditions. The aqueous hydrazine borane was treated with HNO_3 solution in different concentrations to liberate H_2. Besides, kinetic data were collected to idetificate the activation parameters, the effect of temperature, acid and hydrazine borane concentrations on the hydrogen production for the hydrolytic dehydrogenation of hydrazine borane in acidic media. It can be said that the acid catalyzed hydrazine borane system can be regarded as a simple system for hydrogen production.

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Introduction

The storage and liberation of hydrogen at high gravimetric density and volume are known the most important technological challenges of the hydrogen economy [1–20]. For this purpose, various materials have been investigated for the storage of hydrogen. Especially, ammonia triborane [2], ammonia borane [3], amine borane adducts [4,5] and ammonium borates [6] which are B–N compounds show high gravimetric hydrogen storage. Hydrazine borane ($N_2H_4BH_3$, HB) is one of the remarkable hydrogen carrier. Because, while its gravimetric hydrogen storage capacity is high (15.4% by weight), molecular weight is low. This value is higher than 9 wt % hydrogen given for the 2015 target by the US Department of Energy (DOE) for a practical material [7]. It has been shown that the effective hydrogen release at room temperature can be obtained by the hydrolysis of HB as shown in Eq. (1). Hydrogen production from the hydrazine borane by the help of acid catalyzed hydrolysis is an alternative method to metal catalyzed hydrolytic dehydrogenation under the desired conditions (at room temperature) [10–12].

$$N_2H_4BH_3 + 2H_2O \rightarrow N_2H_5^+ + BO_2^- + 3H_2 \quad (1)$$

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Previous studies have shown that hydrogen can be obtained in different ratios from the hydrolytic dehydrogenation of ammonia borane, ammonia triborane and sodium borohydride in acidic media [13–15]. The current study reports that the solution of the hydrazine borane undergoes to hydrolytic dehydrogenation in acidic media (Eq. (2)) to release H_2 at high acid concentrations in the presence of a mineral acid (like nitric acid HNO_3). Nitric acid has certain advantageous as accelerators for single-use applications as follows [16,17]: a) It is possible to prepare and maintain the aqueous solution of the acid in different concentrations. b) Accelerated species (H^+) don't have to be recovered or recycled because of the conversion of the entire hydrogen is provided. c) The volume of hydrogen liberated can be adjusted by changing the amount of acid solution.

$$N_2H_4BH_3 + H^+ + 3H_2O \rightarrow N_2H_5^+ + B(OH)_3 + 3H_2 \quad (2)$$

Experimental

Hydrazine borane was synthesized and characterized by the steps in accordance with literature [8]. HB can be obtained from the reaction between sodium borohydride and dihydrazine sulphate in tetrahydrofuran at room temperature as shown in Eq. (3).

$$2N_2H_4.\frac{1}{2}H_2SO_4 + 2NaBH_4 \xrightarrow[THF,RT]{} 2N_2H_4BH_3 + Na_2SO_4 + 2H_2 \quad (3)$$

Experimental method for the hydrogen liberation, kinetic studies, identification of activation parameters and monitoring of hydrazine borane by ^{11}B NMR spectroscopy for the hydrolytic dehydrogenation of hydrazine borane in acidic media were given in detail in supporting information.

Results and discussion

In literature, effective H_2 release was mostly obtained from aqueous solutions of the hydrazine borane by adding the specified metal catalyst [10–12]. However, previous studies [13–16] have shown that hydrogen can also be obtained from the hydrolysis of ammonia borane, ammonia triborane and sodium borohydride by use of an acid catalayst. For this purpose, nitric acid has been used as catalyst for the hydrolysis of $N_2H_4BH_3$. This strong mineral acid is stable under mild conditions. It can be said that HNO_3 is a preferred acid to catalyze the hydrolysis of $N_2H_4BH_3$ with high hydrogen production rates. NMR spectroscopy was used to observe acid-catalyzed hydrolysis of the hydrazine borane by treatment with HNO_3. Fig. 1 shows the ^{11}B NMR spectra of solutions taken at different times of hydrolysis study. The $N_2H_4BH_3$ solution prepared freshly is colorless and has alkalinity which is pH 8.4. This solution gave a quartet at $\delta = -20.1$ ppm in accordance with the literature [10,12]. The liberation of 3.0 mol H_2 per mol of $N_2H_4BH_3$ was observed after the addition of nitric acid to the hydrolysis media. At the end of the 10 min reaction, the relative intensity of the quartet peak decreases, and a remarkable singlet is obtained at $\delta = 18.5$ ppm in the ^{11}B NMR spectrum as shown in Fig. 1 and as the reaction progresses, the resonance signal at 18.5 ppm for the product increases, while the resonance signal of the hydrazine borane (−20.1 ppm) gradually loses its intensity and eventually disappears within 130 min. The pH of the solution approaches to 0.5 in the reaction time within 130 min. The previous ^{11}B NMR study [19] showed whether the product of the hydrolysis of the ammonia borane is boric acid or metaborate ion, depending on the pH. In acidic solution, the dominant form is H_3BO_3, while in basic solution the hydrolysis product is in the form of BO_2^- ion. As a result, the hydrolytic dehydrogenation of hydrazine borane takes place by the catalytic effect of HNO_3 and the hydrolysis product is boric acid by the use of HNO_3 as catalyst. The ^{11}B NMR spectrum at 18.5 ppm is attributed to the boric acid which is in line with the literature [13]. The proposed mechanism for the hydrolysis of ammonia borane catalyzed by acid has also been adopted for the hydrolysis of hydrazine borane in acidic media [20]. In acidic solutions, H^+ attacks the B–N bond that forms the hydrazinium ion and releases the rapidly hydrolyzed BH_3 molecule after the rate limiting steps. In terms of the reaction mechanism for hydrogen production from the hydrolytic dehydrogenation of $N_2H_4BH_3$ with HNO_3, it is reasonable to assume that the acidic proton of HNO_3 in aqueous media promotes the breaking of the B–N bond whereby the proton attacks the electron rich nitrogen atom, thus forming the $N_2H_5^+$ ion. The fast hydrolysis of BH_3 released produces boric acid and H_2 gas as the solution is still acidic.

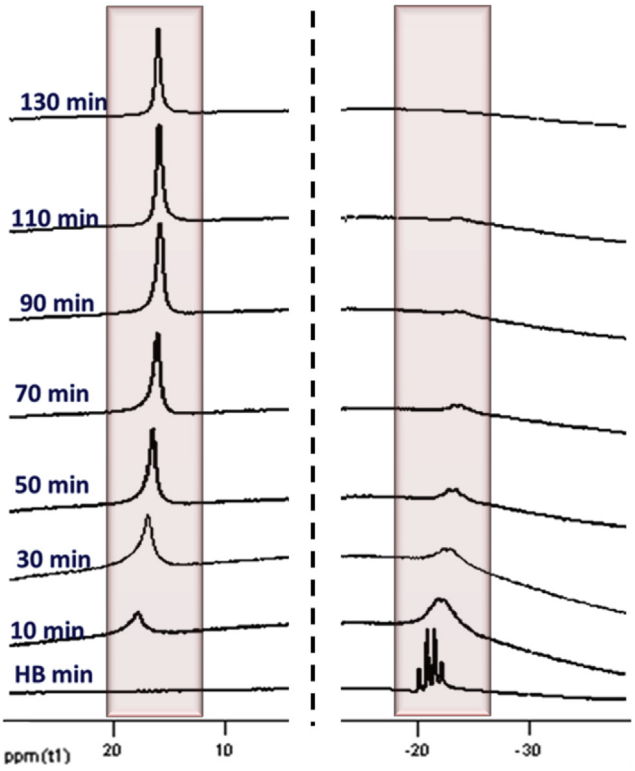

Fig. 1 – ^{11}B NMR spectra of the solutions concerning the hydrolysis of $N_2H_4BH_3$ (100 mM) with HNO_3 measured at different times at 25 ± 0.5 °C.

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