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Low-temperature synthesis of ammonia borane using diborane and ammonia

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ABSTRACT

Ammonia borane (NH_3BH_3), as a source material for energy generation and hydrogen storage, has attracted growing interest due to its high hydrogen content. We have investigated the synthesis of ammonia borane from diborane (B_2H_6) and ammonia (NH_3) utilizing a low-temperature process. From our results, a maximum synthetic yield of 92.2% was obtained, for an ammonia borane complex of 0.35 M. The diammoniate diborane (DADB) was detected in about 5–10 mol% within the solid ammonia borane by solid-state ^{11}B -NMR analysis. The synthesized solid ammonia borane products were studied to characterize hydrogen release upon thermal dehydrogenation.

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Introduction

Ammonia borane (AB), as an energy source material, exists as a white polycrystalline powder in the solid state that is stabilized under ambient conditions because of its strong polarity and intermolecular forces. AB is formed through a dative bond in which the lone pair of the NH_3 interacts with the empty p_z -orbital of boron in BH_3 , and is considered a promising solid state hydrogen storage material due to its high relative hydrogen content of 19.6 wt% [1–7]. Because hydrogen can be released from AB by either hydrolysis or thermolysis, its production from AB does not demand the need for special methods and equipment such as cryogenic processes and high pressure compressive tanks.

AB is a non toxic, environmentally benign, and stable material that can be safely transported without hydrogen loss, which dictates the success of any chemical for hydrogen storage [8]. The development of an efficient, strategy, both in terms of energy and cost, for the recycling of waste products resulting from hydrogen released from AB, conversion of the polymeric aminoborane back to the starting AB is of importance [9]. Recently, research efforts directed at synthetic strategies toward AB have been continually reported. In the commercial process, AB is produced from the reaction of NaBH_4 and NH_4Cl at a low temperature below -78°C [10]. In previous research, Shore and Bøddeker [11] reported the reaction conditions that enabled the preparatory-scale synthesis of diammoniate of diborane (DADB) and mixtures of DADB with AB. They showed that passing diborane gas into liquid

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ammonia afforded the asymmetric cleavage product, DADB, in quantitative yield at temperatures below $-78\text{ }^{\circ}\text{C}$. On the other hand, when they distilled liquid NH_3 into a solution of $\text{BH}_3\text{-THF}$ complex at $-78\text{ }^{\circ}\text{C}$, they observed both DADB and the symmetric cleavage product, AB, in equimolar amounts. Fig. 1 shows the scheme for symmetric (2) and unsymmetric (1) cleavage of diborane by ammonia. Mayer [12,13] reported that AB could be prepared with 68–76% yields in diglyme if gaseous ammonia was added to diborane solutions of ethers.

Research on the dehydrogenation of AB has been performed extensively; one of the methods by which hydrogen can be generated from AB is through thermal decomposition. Autrey et al. [14] described mechanistic details for the thermal dehydrogenation of AB to polyaminoborane, which involved an induction period and nucleation formation. Research toward improving hydrogen release from AB from an engineering point of view has been recently reported [11,15,16]. In addition, metal and organic catalysts have also been reported to promote the dehydrogenation reaction of AB [17].

In this work, we discuss the optimization of the synthetic conditions of AB under various process operating conditions, and the results of the characterization of hydrogen release properties. The synthetic process described in this work offers two safety advantages, namely, i) fast reaction control and liquefaction of NH_3 gas, and ii) fast and quantitative feed into the reactor system of the diborane complex with THF. The transition states of AB samples synthesized by this process were characterized by solid-state ^{11}B NMR. The proposed synthetic process from this study is feasible for the continuous operation need to the commercial plant of large scale.

Experimental and procedures

Experimental materials

Diborane and ammonia were used as the raw materials for AB synthesis. In this work, diborane (15% $\text{B}_2\text{H}_6/\text{N}_2$, purity 99.99%) was obtained from Voltaix Co., Ltd. (USA). Ammonia (purity 99.999%) was provided by Wonik Materials Co., Ltd. (Korea). Anhydrous tetrahydrofuran (THF; purity 99.99%), which is used as a solvent in this process, was purchased from Sigma–Aldrich (USA). Commercial AB was provided by JSC Avabor Chemical Company (purity 98%, Russia) for comparison of hydrogen release and characterization with the synthesized AB in this work.

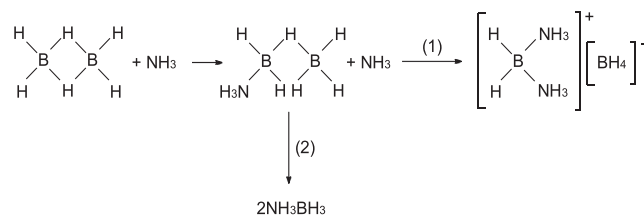


Fig. 1 – Symmetric (2) and unsymmetric (1) cleavage of diborane by ammonia.

Experimental setup

AB synthesis was conducted in two reactors as schematically shown in Fig. 2. We adopted a system of two high-pressure reactors to provide a constant feed of diborane and ammonia. The two reactors had a cryogenic nitrogen chamber in which liquid N_2 was continuously supplied to the system for low-temperature reactions. The temperature of the reactor was constantly maintained at an extremely low temperature using an isothermal controller. The internal volumes of the two reactors were each $2,000\text{ cm}^3$ (Reactor 1) and 3000 cm^3 (Reactor 2); the reactors themselves were fabricated using a stainless steel 316L cylindrical vessel-type autoclave equipped with magnetic drive agitator having variable speed arrangements. The reaction temperature was stable within $\pm 2\text{ }^{\circ}\text{C}$ over the time frame of the experiment. Diborane (0.09 mol) and anhydrous ammonia (0.18 mol) were added to each reactor fitted with a stir bar. The diborane and anhydrous THF mixture in Reactor 1 was cooled to $-78\text{ }^{\circ}\text{C}$ in a chamber closed off to liquid N_2 , and was converted to the diborane complex. The diborane complex was transferred into Reactor 2 and reacted with anhydrous NH_3 . These contents were vigorously stirred at various temperatures and pressures. Upon completion, the reaction mixture was slowly warmed to room temperature and the influence of warming time on AB yield was confirmed, and the product was then collected. After warming the reactor to room temperature, the product was collected as the THF-soluble material formed with the added THF, and the insoluble salts were filtered. After filtration, THF was removed by rotary evaporation. The filtered solid samples were characterized by solid-state ^{11}B magic-angle spinning (MAS)-NMR, using a Varian Inova 300 MHz spectrometer to record the spectra and using NaBH_4 as an external reference for calibration. To perform characterization and to understand the continuous hydrogen release properties from AB, the coarse AB power synthesized in this reaction was initially ground into a fine powder using a commercial grinder under an atmosphere of N_2 . The fine AB powder was then pelletized into spherically shaped beads. Experiments on the thermally induced hydrogen release properties of the synthesized AB were conducted at various temperatures using the dehydrogenation equipment at the Korea Institute of Science and Technology (KIST) [4].

Results and discussion

Synthetic of AB

In this work, material-based diborane yields were calculated using the following Equation (1):

$$\text{AB yield}(\%) = \frac{\text{Weight of AB produced}}{\text{Weight of B}_2\text{H}_6} \times 100 \quad (1)$$

On the basis of the synthetic conditions used, we obtained a maximum AB yield of 92.2% and a minimum of 51.7%. Table 1 presents the synthetic yields of AB according to the materials (B_2H_6 and NH_3), solvent (THF), temperature, and pressure variations. The general procedure for preparing AB has been

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