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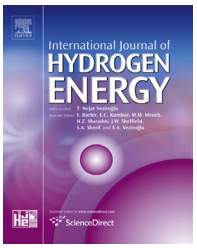

Synthesis, structural characterization, and hydrogen desorption properties of $Na[Al(NH_2BH_3)_4]$

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ABSTRACT

$Na[Al(NH_2BH_3)_4]$, a mixed-metal amidoborane, was synthesized by ball-milling (solid method) and the chemical reaction in THF (solution method). Solid method has a tendency to remain unreacted $NaAlH_4$ and AB. In the solution method, the partial decomposition of $Na[Al(NH_2BH_3)_4]$ would proceed during mixing in THF. The local structural characterization of as-synthesized material was performed by MAS NMR and FT-IR. While $Na[Al(NH_2BH_3)_4]$ desorbed hydrogen in two steps as reported, the results of structural characterization suggested that the hydrogen desorption in the 2nd step would originate from the Al–N–B–H phase. Effect of hydrogen pressure during ball-milling was also investigated for nNH_3BH_3–$NaAlH_4$ ($n = 1, 4$) composites. In the case of $n = 4$, $Na[Al(NH_2BH_3)_4]$ was formed under both Ar and H_2 atmosphere. However, in the case of $n = 1$, $Na[Al(NH_2BH_3)_4]$ was only formed under H_2 atmosphere, whereas most of H_2 was desorbed during ball-milling under Ar atmosphere. Thus, the hydrogen pressure is necessary for the synthesis in the case of $n = 1$. Potential energy diagram of AB-$NaAlH_4$ system was described.

Introduction

Materials based on a boron-nitrogen (B–N) bond (structure) are promising hydrogen storage materials. In particular, ammonia borane (NH_3BH_3, AB) [1,2], metal amidoborane ($M(NH_2BH_3)_n$) [3], hydrazine borane ($N_2H_4BH_3$) [4,5], and metal borohydride ammoniates ($M(BH_4)_n \cdot mNH_3$) [6] are attractive materials because of their high gravimetric hydrogen densities. In general, they desorb hydrogen in exothermic reactions between $H^{\delta+}$ and $H^{\delta-}$, indicating that the hydrogen absorption of the spent material is thermodynamically impossible [7,8]. The slow desorption kinetics and by-product gases emission (e.g., ammonia (NH_3), diborane (B_2H_6), and borazine ($B_3H_6N_3$)) are also drawbacks for applications [7,8].

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Among various kinds of B–N based materials, Al–B–N–H phases have shown excellent hydrogen storage properties [9]. For instance, $Al(BH_4)_3 \cdot 6NH_3$ releases more than 10 mass% of hydrogen below 140 °C with favorable kinetics by a weak exothermic reaction [10]. In another instance, $Al(BH_4)_3 \cdot NH_3BH_3$ can desorb 2 equiv. of hydrogen at 70 °C with an endothermic reaction, suggesting that direct rehydrogenation is possible [11]. AB-$MAlH_4$ (M = Na, Li) system consists of Na(Li), Al, N, B and H, which is similar composition as Al–B–N–H system. By-product gases emitted from AB-$MAlH_4$ (M = Na, Li) composites were effectively suppressed during the hydrogen desorption compared with those from AB [12]. In the case of 4AB-$NaAlH_4$ system, the crystal structure and hydrogen desorption properties of $Na[Al(NH_2BH_3)_4]$ have been reported [13]. This Al-based amidoborane was synthesized by ball-milling with the following reaction:

$$NaAlH_4 + 4\,NH_3BH_3 \rightarrow Na\left[Al(NH_2BH_3)_4\right] + 4\,H_2 \quad (1)$$

$Na[Al(NH_2BH_3)_4]$ showed a large amount of hydrogen desorption (9 mass%) and a partial reversibility by pressurising hydrogen [13]. Therefore, this material has attracted much attention as a promising hydrogen storage material. The formation of the Al-based amidoborane was also suggested in nAB-Li_3AlH_6 (n = 4–6) system, which can desorb around 10 mass% H_2 below 200 °C and can be partially regenerable by chemical treatments [14].

In the present study, the structural characterizations of $Na[Al(NH_2BH_3)_4]$ by using XRD, MAS NMR, and FT-IR were performed to obtain the insights about hydrogen desorption process of $Na[Al(NH_2BH_3)_4]$. NMR is a useful technique to characterize the local structure of metal amidoborane because their dehydrogenated states are amorphous(-like) structure [15–17]. The single-phase synthesis of $Na[Al(NH_2BH_3)_4]$ is also important to characterize the material. Although the synthesis of mixed-metal amidoboranes such as $Na[Al(NH_2BH_3)_4]$ and $Na[Li(NH_2BH_3)_2]$ were performed by ball-milling method [13,14,18,19], the reported $Na[Al(NH_2BH_3)_4]$ was not single-phase. On the other hand, there are some reports which focus on the liquid state synthesis of mixed-metal amidoborane [20] and solution synthesis of mono-metal amidoborane [21,22]. In this study, both the ball-milling (solid method) and the chemical reaction in THF (solution method) were employed as the synthesis methods in order to obtain the single-phase of $Na[Al(NH_2BH_3)_4]$. Since the synthesis of metal amidoborane causes the exothermic dehydrogenation reaction, the solution method would be effective for unstable material to minimize unfavourable decomposition during the synthesis. We also studied the dependency of milling atmosphere (Ar or H_2) for nAB-$NaAlH_4$ (n = 1, 4) composites because hand-mixing of AB and $MAlH_4$ (M = Na, Li) in an agate mortar in an Ar-purified glovebox often causes the gas eruption [12].

Experimental section

Sample synthesis

The starting materials, NH_3BH_3 and $NaAlH_4$ (purity 97% and 90%, respectively), were purchased from Sigma Aldrich Co. Ltd. All samples were handled in a glovebox filled with purified Ar or N_2. $Na[Al(NH_2BH_3)_4]$ was synthesized by ball-milling (solid method) and the chemical reaction in THF (solution method). The solid method was performed by using a planetary ball-milling apparatus (Fritsch Pulverisette 7) with 20 stainless steel balls (7 mm in diameter) and 300 mg samples (NH_3BH_3: $NaAlH_4$ molar ratio = 4: 1, ball: powder weight ratio = 70: 1). The milling was executed under 1.0 MPa H_2 atmosphere with 300 rpm for 3 h with six cycles of 30/30 min operation/interval per each cycle in order to avoid an excess heating of sample. This composite was labelled as BM composite. For the solution synthesis method, $NaAlH_4$ and NH_3BH_3 were mixed by using magnetic stirrer for 3 h in anhydrous THF (Kanto Chemical Co. Inc.) and then solvent was removed by evacuation. Since the product was still sticky paste just after simple evacuation and AB was used more than 4 equivalents of $NaAlH_4$, the sample was flushed and AB was removed with anhydrous diethyl ether for three times by the following procedure: ether was introduced and stirred for 30 min; filtration was operated in order to remove the excess AB from the sample and then; residual substance was evacuated. Finally, we obtained white solvent-free powder. This composite was labelled as SL composite. We also tried solution method using other solvents and finally we optimized that THF is the best solvent for this reaction. In this case, the ratio of $NaAlH_4$/THF was about 17 mmol/L. The ratio of $NaAlH_4$/THF is important for the synthesis of $Na[Al(NH_2BH_3)_4]$ because $Na[Al(NH_2BH_3)_4]$ was not formed when small amount of THF was used.

Characterization

Powder X-ray diffraction (XRD, PANalytical, X'Pert Pro with Cu Kα radiation) measurements were performed to investigate the crystalline phases of mixtures. The samples for XRD were placed on a greased glass plate in a glovebox and then covered with a polyimide sheet (Kapton, The Nilaco Co. Ltd.) and sealed by grease in order to avoid the oxidation during measurement. Hydrogen desorption properties were examined by a thermogravimetry and differential thermal analysis equipment (TG-DTA, Bruker, 2000SA) connected to a mass spectrometer (MS, ULVAC, BGM-102). The desorbed gases were carried from TG-DTA to MS through a capillary by 300 mL min^{-1} stream of high purity He as a carrier gas. The samples were heated from room temperature to 260 °C with a heating rate of 5 °C min^{-1}. Solid-state magic angle spinning - nuclear magnetic resonance (MAS-NMR) spectra were recorded on a JNM-ECA600 spectrometer (JEOL) at a magnetic field of 14.1 T with the ^{11}B, ^{23}Na and ^{27}Al resonant frequency of 192.6, 159.1 and 156.7 MHz, respectively. All the samples were spun at 15 kHz, using 4 mm ZrO_2 rotors filled in argon atmosphere. Chemical shifts were calibrated by saturated aqueous solutions of H_3BO_3 for ^{11}B, NaCl for ^{23}Na, and $AlCl_3$ for ^{27}Al at 19.49, 0.00, and −0.10 ppm, respectively. Fourier transform infrared spectrometer (FT-IR, JASCO Co., FT/IR-6100) was operated in order to observe their vibration modes of the synthesized materials. Each sample was diluted with KBr (mass ratio of sample/KBr = 1:10) and then pelletized for the measurement.

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