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Ammonia borane destabilized by aluminium hydride: A mutual enhancement for hydrogen release

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ABSTRACT

Destabilized by aluminum hydride, the dehydrogenation properties of ammonia borane (AB) can be improved significantly, including enhanced dehydrogenation kinetics, reduced induction period and suppressed formation of volatile byproducts. Furthermore, a lowered dehydrogenation temperature was also achieved for AlH_3 , indicating a mutual dehydrogenation enhancement for both AB and AlH_3 in this mixture. The destabilized sample, 3AB/ AlH_3 , can totally release more than 12 wt% of high-pure hydrogen (>99 wt%) without any detectable by-products below 250 °C. Mechanism investigations indicated that the mutual dehydrogenation enhancement in the mixture is attributed to the Coulombic attraction between the hydridic $\text{H}^{\delta-}$ in AlH_3 and the protonic $\text{H}^{\delta+}$ in the NH_3 group of AB. Copyright © 2014, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

Introduction

Hydrogen is considered as an ideal candidate for solving the energy and environment issues for its abundance, lightness and environmental benignancy [1]. After decades of development, how to achieve safe and high efficient density hydrogen storage is still one of the main obstacles on the application of hydrogen-based energy [2]. Besides two well-established methods of high pressure tanks and hydrogen liquification, solid hydrogen storage materials have been developed continuously over the past few decades [3–6], showing a great advantage with respect to gravimetric hydrogen content. Among the studied solid hydrides, ammonia borane (NH_3BH_3 ,

AB) has drawn the most and ever-increasing attention for its great potential for hydrogen storage [7–12].

AB is a colour-less solid crystal material with stability at room temperature and solubility in relatively polar solvents [13–15]. With a fabulous hydrogen capacity of 19.6 wt%, AB contains both hydridic B–H and protonic N–H bonds and a strong enough B–N bond so that dehydrogenation proceeds prior to dissociation to ammonia and borane. At relatively moderate temperature, AB can release 2 equivalents of hydrogen via a two-step dehydrogenation process [16]. However, the practical application of pristine AB as on-board hydrogen source is greatly restricted by its sluggish dehydrogenation kinetics below 100 °C, severe foaming and volume expansion during thermal decomposition, in addition with large amount of undesirable volatile by-products (such as

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borazine, ammonia, and diborane), which are not only poisonous to the proton membrane fuel cell but also cause the component loss (B, N elements) that will degrade the regeneration efficiency of AB [5]. Recently, several approaches have been adopted to promote hydrogen release from AB, including catalytic dehydrogenation by acids [17], bases [18,19] and transition-metals [20–22], activating by ion liquids [23,24], modifying by nanoscaffolds [25–29] and partial substitution of the protonic $H^{\delta+}$ in AB by metal cations [30–34].

Among the strategies mentioned above, substitution one of the protonic $H^{\delta+}$ attached to N atom of AB with a metal cation to form a series of amidoboranes (such as LiAB, NaAB, KAB and CaAB), makes the kinetics and thermodynamics of hydrogen release be improved significantly, along with effective suppression of volatile by-products. Previous researches have even demonstrated that ball-milled AB with LiH [35], MgH_2 [36] or Mg powder [37] with destabilization of AB can also dramatically improve the dehydrogenation properties.

Herein we report our recent results on the dehydrogenation properties of aluminum hydride (AlH_3) destabilized AB. Aluminum hydride is a covalent binary hydride which is metastable at room temperature. With a 10.1 wt% of hydrogen, it can be decomposed by modest heating, typically in the 60–200 °C range [38], which makes itself a possible hydrogen carrier. Based on the destabilizing strategies applied to the MgH_2 modified AB [36], we found that aluminum hydride is also an effective promoter for AB dehydrogenation. The prepared 3AB/ AlH_3 sample showed 12 wt% hydrogen capacity below 250 °C with no detectable amount of volatile byproducts.

Experimental section

The starting materials, $LiAlH_4$ (97%), $AlCl_3$ (99%), MgH_2 (95%) and BH_3NH_3 (97%), were purchased from Sigma–Aldrich and used in as received form without further purification. Anhydrous diethyl ether (99.9%) was purchased from Sigma–Aldrich and used with further desiccation. All solid samples were handled in a glovebox equipped with a recirculation and regeneration system where oxygen and water concentrations were maintained below 1 ppm.

Samples of AlH_3 were synthesized by mixing stoichiometric ratios (3: 1) of $LiAlH_4$ and $AlCl_3$ in diethyl ether as previously reported method [39]. XRD pattern verified the successful preparation of AlH_3 . The AB/ AlH_3 mixtures in varied molar ratios were prepared by vigorously stirring in an anhydrous diethyl solution for 12 h and evacuate at 60 °C under vacuum for 5 h. The sample of 2AB/ MgH_2 were prepared by ball-milling of AB with stoichiometric MgH_2 at an agitation frequency of 400 rpm for 2 h. The ball-to-powder ratio was 40: 1.

Temperature-programmed-desorption (TPD) measurement was carried out on a semi-automatic Sieverts' apparatus under argon atmosphere (~1 bar) with a heating rate of 5 °C/min. Dehydrogenation properties of the prepared samples were examined by simultaneous thermal gravimetric analysis (TGA) synchronized with a mass spectrometer (MS, QMS 403), in which about 5 mg samples were heated up 5 °C/min ranging from room temperature to 300 °C under argon flow.

The isothermal dehydrogenation performances of the samples (with a typical amount of 100 mg) were examined by using a carefully calibrated semi-automatic Sieverts' apparatus under argon atmosphere (~1 bar). Precise pressure measurement and temperature controlling were accomplished by using a high-precision pressure transducer and silicon oil bath, respectively.

Powder X-ray diffraction data were collected by a Bruke X'PERT diffractometer (Cu K α radiation, 16 Kw). All the samples were mounted in a glovebox. In order to avoid oxidation, an amorphous polymer tape was used to cover the surface of the powder. For phase identification during the dehydrogenation, the sample was loaded into a pre-dried 0.7 mm boron-silica glass capillary whilst inside an argon-filled glovebox. In-situ high-resolution synchrotron powder X-ray diffraction data were collected by a Mythen-II detector with the wavelength 1.0329 Å at the Powder diffraction beamline, Australian Synchrotron. The capillary was sealed with vacuum grease for X-ray diffraction measurements. Time-resolved in-situ measurements were conducted by using a Cyberstar hot-air blower to heat the sample from 40 to 200 °C at a ramping rate of 2 °C/min. Data were collected with an exposure time of 150 s at every 10 °C step.

Fourier transform infrared (FTIR) (Magna-IR 550 II, Nicolet) analyses were used to confirm the chemical bonds in all solid products. Samples (KBr pellets) were loaded into a sealed tube with CaF_2 window for the measurement. Raman spectra of the samples were recorded using a Dilor LABRAM-1B spectrometer excited by a 632.8 nm laser.

Results and discussion

Dehydrogenation properties

The xAB/ AlH_3 mixtures with molar ratio x ranging from 1 to 4 were prepared as mentioned above. A preliminary study (see in Fig. S1) found that the overall dehydrogenation property of the xAB/ AlH_3 (x = 1–3) samples reached its maximum when the molar ratio to be 3:1 (AB: AlH_3). And when x > 3, x = 4 for example, besides higher dehydrogenation temperature, impurity has been proved to be the main drawback compared with the 3AB/ AlH_3 sample (see in Fig. S2). So the 3AB/ AlH_3 sample was selected for further detailed property examinations. Fig. 1 shows the comparison of 3AB/ AlH_3 and neat AB on thermal decomposition behaviours using synchronous TPD/TG/MS. Compared with neat AB, the 3AB/ AlH_3 sample has shown a serial of dehydrogenation advantages. Firstly, the dehydrogenation temperature was significantly lowered with the addition of AlH_3 . For neat AB, as previously reported, two dehydrogenation peaks were observed centred at 124 and 162 °C (Fig. 1b) with the formation of polymeric amidoboranes ($(NH_2BH_2)_n$, PAB) and polymeric imidoboranes ($(NHBH)_n$, PIB) respectively [16,40–44]. Dehydrogenation of the 3AB/ AlH_3 sample was initiated below 100 °C, and the rapid release of the first and the second equivalent of H_2 occurred at around 112 and 154 °C, respectively, which showed great improvement for the decomposition kinetics. Secondly, the evolution of volatile byproducts has been suppressed with the participation of AlH_3 . As shown in the MS spectra (Fig. 1b), companied

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