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Regeneration of alkaline metal amidoboranes with high purity

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ABSTRACT

In this manuscript, we report a facile and safe process for highly efficient regeneration of dehydrogenated alkaline metal amidoboranes (MNH_2BH_3 , MAB, $M = Li, K$), in which CH_3OH is employed as a digestion reagent; then $LiAlH_4$ is used as a reduction reagent in the presence of NH_4Cl giving ammonia borane (NH_3BH_3 , AB) as the intermediate; finally the generated AB reacts with corresponding metal hydride to complete the whole self-contained cycle. Using this chemical process, MABs are reproduced in a high purity of 98%. The byproducts of regeneration procedure can be converted to mass commodity chemicals as recyclable auxiliary reagents utilizing the recycling pathways. More importantly, our finding of successful scission of dehydrogenated polymeric MAB residues into small molecule B species that guarantees to facilitate the following regeneration process, provides a general strategy for the efficient regeneration for other MAB compounds and a potentially viable route for the chemical recycling of metal-B-N containing hydrogen storage materials.

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Introduction

In the endeavor to decrease greenhouse gas emissions and fossil fuel dependence, hydrogen has been considered as one of the best alternative energy carriers because of its abundance, high energy density, and environmental friendliness. Highly efficient and convenient hydrogen storage materials/technology are still the main challenge for today's development of the hydrogen economy [1]. A reliable and economical

hydrogen storage system has to satisfy several criteria, including high storage capacity, safety, low operation temperature, reversibility, and low cost [2,3].

Recently, the ammonia–borane (H_3NBH_3 , AB) complex has been identified as one of the leading candidates as a hydrogen reservoir owing to its high hydrogen content (19.6 wt %, mat.-based), high air-stability, and nontoxicity [4–6]. The practical application of AB and its derivatives, however, is still obstructed by crucial issues, especially, slow kinetics at low temperatures (below 90 °C) and excessive volatile impurities

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(borazine, ammonia, and diborane) during its pyrolysis dehydrogenation [7–14]. To overcome the above drawbacks, significant efforts have been made to investigate improvement of the dehydrogenation of AB [15–22]. As part of this research effort, modifying the structure of AB to enhance the kinetics and dynamics of H₂ release has been extensively studied. For example, replacing one H atom on the N of AB with a metal cation generates a metal amidoborane (MAB), such as LiNH₂BH₃ (LiAB), KNH₂BH₃ (KAB), etc., which not only has fast kinetics and decreased enthalpy for H₂ release but also suppresses the emission of gaseous impurities [23–27].

The viability of any storage system is critically dependent on efficient recyclability. Reports on the regeneration of metal amidoboranes are quite sparse, however. In our previous work, regenerable hydrogen storage of LiAB was first achieved through the route of chemical hydrogenation of its dehydrogenated products by treatment with hydrazine in liquid ammonia [28]. Nevertheless, only ~60% of the LiAB was obtained, because during regeneration, some of LiAB react with liquid ammonia to form aminelithium amidoborane (LiNH₂BH₃NH₃), which decomposes at the regeneration temperature, thus resulting in a severe degradation of regeneration purity. In addition, hydrazine is energetically demanding, dangerously unstable, and toxic, so it is very difficult to handle on an industrial scale [29]. Therefore, it is highly preferable to design new strategies for the regeneration of MAB that feature safety, practicability, and high purity. In this paper, we develop a chemical recycling for MAB (M = Li, K), in which some common reagents are used to accomplish the whole cycle, and high regeneration purity of MAB can be achieved at mild conditions.

Experimental

Materials and preparation

The materials, ammonia borane (NH₃BH₃, AB, 97%), LiH (95%), KH (30 wt% in paraffin), LiAlH₄-tetrahydrofuran (THF) solution (2 M L⁻¹), NH₄Cl (99%), anhydrous CH₃OH (99.9%), B(OCH₃)₃ (99.5%) and anhydrous THF (99.9%), were purchased from Sigma–Aldrich and used in as-received form without further purification. KH was washed to remove the paraffin in THF prior to use. AB (200 mg) was dissolved in THF (20 mL) under magnetic stirring for 3 min. LiH (51.9 mg) and KH (260 mg) was added into AB solution in the glove box, respectively. Then, the mixture was allowed to react for 60 min at 40 °C under N₂ atmosphere. At the end of the reaction, white metal amidoborane (MNH₂BH₃, MAB, M = Li, K) powder was obtained by vacuum drying the solution overnight at room temperature. The dehydrogenated MAB, MNBH (89 mg LiNBH and 94.1 mg KNBH), was obtained by heating 100 mg MAB to 250 °C using a rate of 5 °C min⁻¹. The decomposition process were monitored by a mass spectrometry and a Sieverts' type apparatus, in which about 2 equiv. high pure hydrogen release were observed for MNH₂BH₃ (M = Li, K), indicating the decomposition products have a molecular formula of MNBH. All the sample handling was performed in an N₂-filled glove box equipped with a recirculation system to keep the H₂O and O₂ levels below 1 ppm.

Characterizations

The crystalline structure of the samples was characterized by X-ray diffraction (XRD) conducted on a Rigaku D/max-kA diffractometer with Cu K α radiation. (An amorphous tape was used to prevent the oxidation and moisture contamination of samples during XRD measurements.) The chemical composition was investigated using Fourier transform infrared spectroscopy (FTIR, Nicolet Nexus 470). The ¹¹B nuclear magnetic resonance (NMR) experiments were performed on a Bruker Avance III 500 MHz spectrometer. The ¹¹B shifts were referenced to BF₃·OEt₂ (δ = 0 ppm). For all samples, the spectra were measured with and without decoupling. NMR solvents were used without further purification.

Gas evolution measurements

During the reaction process, gaseous products were analyzed by mass spectrometry (MS). Based on species identified in an initial survey with a Hiden system that sampled all mass channels from 6 to 199 amu, the MS monitored the partial pressures for 2 amu (H₂), 16 amu (NH₃), 18 amu (H₂O), 27 amu (B₂H₆), 32 amu (O₂), and 80 amu (B₃N₃H₆). The molecular weight and cracking pattern of each species was taken into account in extracting semi-quantitative information. Typical sample quantities were 5–10 mg, which are sufficient for obtaining accurate results due to the high sensitivity of the employed equipment. Volumetric release for quantitative measurements of hydrogen desorption from samples was carried out with a homemade Sieverts' type apparatus under Ar (1 atm). All gas evolution measurements were conducted using a heating rate of 5 °C min⁻¹.

Recyclable regeneration procedure for MAB (M = Li, K)

89 mg LiNBH and 94.1 mg KNBH was mixed with 10 mL CH₃OH, respectively. The mixtures were heated for 12 h at 40 °C with stirring. ¹¹B NMR spectroscopy indicated the formation of LiB(OCH₃)₄ and KB(OCH₃)₄, respectively. The solid products (385 mg LiB(OCH₃)₄ and 252 mg KB(OCH₃)₄) were obtained after filtrating and evacuating for 6 h to remove the residual CH₃OH. After heating the LiB(OCH₃)₄ and KB(OCH₃)₄ using a distillation apparatus at 350 °C, B(OCH₃)₃ (267.9 mg for LiB(OCH₃)₄ and 143.1 mg for KB(OCH₃)₄) could be well gathered in the condensation collector, leaving the LiOCH₃ and KOCH₃ powder, respectively. The commercial B(OCH₃)₃ (915 mg) then was added under nitrogen atmosphere to a suspension of NH₄Cl (948 mg) in THF (44 mL) at 0 °C. Under vigorous stirring, LiAlH₄-THF solution (11 mL) was added, dropwise, over a period of 1 h at the same temperature. The reaction mixture was warmed to room temperature and stirred for 2 h. The ¹¹B NMR shows the formation of AB. The solvent was distilled under reduced pressure using cannula distillation at room temperature to obtain a powdery solid residue, which was suspended in cold diethylether at 0 °C and stirred for 30 min. The cold ether layer was filtered, and the solvent was removed in vacuo to obtain AB (234 mg) as a white crystalline solid. Finally, the AB was reacted with the corresponding metal hydride (MH) to reproduce MAB for completing the whole regeneration cycle. XRD tests on the obtained powdery materials confirmed the

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