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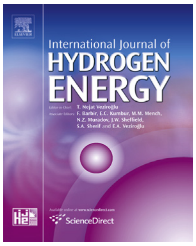

Review Article

Ammonia borane, a material with exceptional properties for chemical hydrogen storage

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ABSTRACT

Ammonia borane $H_3N{-}BH_3$, first reported in 1955, is isoelectronic with ethane $H_3C{-}CH_3$, but it has much different properties owing to (*i*) the nitrogen and boron atoms (leading to a dipole moment), (*ii*) the protic and hydridic hydrogens, and (*iii*) the heteropolar dihydrogen bonding (rationalizing its solid state at ambient conditions). Ammonia borane has exceptional properties for chemical hydrogen storage and the recent years have witnessed many efforts in making it implementable for both thermolytic and hydrolytic dehydrogenations. The present article aims at (1) giving an exhaustive overview of the 1955–2016 literature dedicated to ammonia borane's fundamentals and exceptional properties, and then (2) surveying the main achievements, limitations and challenges for chemical hydrogen storage.

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Introduction

In the recent years ammonia borane $H_3N{-}BH_3$ ($M_w = 30.8$ g mol^{-1}; $\rho = 0.78$ g cm^{-3} at 25 °C) as hydrogen carrier has been the subject of intense research. Research on ammonia borane is a minor part of the huge efforts dedicated to solve the issues hindering the development of a near-future hydrogen economy (including production, storage, distribution and end-use) but this research is a major part of the efforts dedicated to address the specific problems of hydrogen storage [1].

Hydrogen storage has proved to be an overwhelming challenge. Beyond the classical ways of gas storage, *i.e.* high pressure (up to 80 MPa) and liquefaction (at −253 °C) [2], alternative and/or novel approaches have been searched for. A variety of materials emerged, including among others porous structures for H_2 cryo-adsorption, metal hydrides, inorganic carriers such as B–(N–)H and Al–H compounds, organic carriers like the cycloalkane/aromatic couples, and sustainable liquid-state carriers like hydrous hydrazine $N_2H_4{\cdot}H_2O$ and formic acid HCCOH [3,4]. Depending on their intrinsic properties, these materials display specific advantages and particular drawbacks. For example, the porous structures and metal hydrides enable reversible sorption of H_2 but in small amounts, whereas the inorganic/organic carriers are able to release high amounts of H_2 but irreversibly. This is the key difference between physical hydrogen storage and chemical hydrogen storage [5].

Ammonia borane, which is solid at ambient conditions, has high potential for chemical hydrogen storage. It is isoelectronic with gaseous ethane $H_3C{-}CH_3$ ($M_w = 30$ g mol^{-1}; $\rho = 0.001356$ g cm^{-3} at 0 °C) but it has radically different properties, making it attractive for the above-mentioned application [6]. Ammonia borane and ethane have similar gravimetric hydrogen densities (20 *vs.* 19.4 wt%, respectively) but the borane has a considerably higher volumetric density (<0.3 *vs.* 146 g_H L^{-1}). The H_3N and BH_3 fragments carry three protic $H^{\delta+}$ and three hydridic $H^{\delta-}$ hydrogens that polarize the bonds and the molecule. Such polarity facilitates the release of H_2 *via* intra-/inter-molecular $H^{\delta+}\cdots H^{\delta-}$ interactions. Ammonia borane dehydrogenates at much lower temperature because ethane suffers from unfavorable thermodynamics on account of strong C–H bonds. About 13 wt% H_2 can be recovered from ammonia borane below 200 °C; this is an attractive dehydrogenation property [7–11].

Ammonia borane is not a new compound. The first report on its synthesis was published in 1955 by Shore and Parry [12], but the first attempts date from the 1930s. Indeed, Schlesinger and Burg failed in their attempt to obtain the borane by ammoniation of diborane B_2H_6 at −120 °C [13]. Instead they synthesized the dimer called diammoniate of diborane $[H_2B(NH_3)_2^+][BH_4^-]$. As discussed in details in the next section, the conditions were perhaps inadequate (*e.g.* low temperature) and/or the spectral signatures of ammonia borane and diammoniate of diborane were comparable making any distinction even more difficult