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The destabilising effect of alkali metal (Na and K) of hydrazine-borane $N_2H_4BH_3$ for hydrogen storage: *Ab-initio* study

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ABSTRACT

In this research work, we have investigated the crystal structure, thermodynamic and electronic properties to elucidate the chemical bonding features of $N_2H_4BH_3$ and $MN_2H_3BH_3$ ($M = Na$ and K), using both plane waves and pseudopotentials methods applied in density functional theory. The as-optimized crystal structures are found to be in a good agreement with the experimental. The bond lengths of these materials have been compared to show the effect of alkali metal (Na and K) in $N_2H_4BH_3$. The density of states (DOS) indicated that these materials are considered as an insulator with wide band-gap: 5.78, 4.35 and 4.36 eV for $N_2H_4BH_3$, $NaN_2H_3BH_3$ and $KN_2H_3BH_3$, respectively. This indicated that the substitution of one hydrogen atom from $N_2H_4BH_3$ by alkali atom (Na or K) could reduce the band-gap. The partial DOS, Hirshfeld method and charge density distribution have been used to understand the nature of the chemical bond. It is found that the chemical bonding in each group namely $[N_2H_4]$ and $[BH_3]$ for $N_2H_4BH_3$ or $[N_2H_3]$ and $[BH_3]$ for $MN_2H_3BH_3$ ($M = Na$ and K) have mainly a covalent nature. While, an ionic character between M (Na and K) and the rest of $N_2H_3BH_3$ group is suggested for $MN_2H_3BH_3$ ($M = Na$ and K). Interestingly, both N-H and B-H bonds are destabilized in $MN_2H_3BH_3$ ($M = Na$ and K) with a less protic character of $[BH_3]$ than that of $N_2H_4BH_3$. Finally, it is observed that each group $[BH_3]$ is bonded covalently to another $[N_2H_3]$ for $MN_2H_3BH_3$ ($M = Na$ and K) similarly to $N_2H_4BH_3$ (covalent bonding between $[BH_3]$ and $[N_2H_4]$). The standard enthalpies of formation of $KN_2H_3BH_3$ and $NaN_2H_3BH_3$ are calculated for the first time in this research work.

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Introduction

Several studies have shown the existence of a direct relationship between climate change and the emission of carbon

dioxide (CO_2) originating from the massive use of fossil fuels [1,2]. Therefore, reducing CO_2 implies necessarily the use of clean and renewable energies that can substitute efficiently fossil fuels. Among them, hydrogen (H_2) appears to be the

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perfect clean and sustainable energy knowing that its combustion produces energy and water (no CO₂) [1].

Despite the above cited advantages, the wide-use of H₂ in mobile applications is hampered by the on-board storage issues due to the low H₂ storage density. Thus, the development of a viable, low cost and secure method for H₂ storage is mandatory to boost the marketing of vehicles with fuel-cells [3].

Three methods of H₂ storage are known: cryogenic-hydrogen (up to -253 °C), compressed-hydrogen (up to 350 Bar) and solid state-hydrogen. The latest method (also known as hydride) offers important improvements in terms of weight and price in addition to its safety [4]. Thus, the fundamental research and development are devoted on the search of practical solid-state hydrogen tank that exhibit the required criteria at ambient conditions necessary for each particular application [5], including ideal solid H₂ storage medium, excellent H₂ absorption/desorption kinetics at ambient temperature and pressure. In addition, lightweight has always been the most drawback to overcome for practical automotive vehicle applications. Since, they can satisfy most of the above criteria, some boron- and nitrogen-based materials (such ammonia borane) have been identified as attractive and promising H₂-storage compounds [6].

Among B and N based materials, ammonia borane NH₃BH₃ has a very high H₂ capacity of 19.6 wt% (exceeding that of gasoline) and stands as a potential candidate for chemical H₂ storage applications [6]. Nevertheless, the release of H₂ from solid ammonia borane is accompanied with the production of borazine [7] (which represents a danger for the fuel cell by disabling the catalyst) and the reaction kinetics is not faster enough. The same features and issues were observed for the aqueous hydrazine bisborane H₃B-N₂H₄-BH₃ (HBB) (16.8 wt% with instability in water) [7,8].

On the other side, hydrazine borane has been identified as another promising candidate of new B-N-hydride material for H₂ storage. Therefore, many experimental researches [9–15] have been carried out using different methods such as hydrolysis, thermal decomposition, and thermogravimetric analysis in order to evaluate its characteristics for H₂ storage applications.

In fact, with a theoretical H₂ mass capacity of 15.4%, hydrazine borane (N₂H₄BH₃) can produce (in 12 min and at 140 °C) 5.8 wt% H₂ [9]. This amount can reach 11 wt% H₂ at 150 °C in less than an hour [9], if N₂H₄BH₃ is mixed with an equal quantity of LiH. It must be noted that N₂H₄BH₃ can be simply synthesized by the reaction of sodium borohydride (NaBH₄) with dihydrazine sulfate (H₁₀N₄O₄S) [9]. However, the decomposition of N₂H₄BH₃ is an exothermic process, and its dehydrogenation is accompanied by the emission of N₂H₄ and NH₃, which can damage the fuel cell.

It is noteworthy to highlight that few studies in the literature related to hydrazine borane reported some interesting results. Moury et al. [12] concluded that hydrazine borane in pure solid state storage may be unsuitable for H₂ storage applications. Meanwhile, Hannauer et al. [13] indicated that using Ni and Pt nanoparticles as dehydrogenation catalyst, hydrazine borane released up to 9.7 wt% H₂ (in hydrolysis conditions), hence can be used as material for on-board H₂ storage. However, other authors used different catalysts in order to improve the dehydrogenation of hydrazine borane

such as: NiCl₂ [16], Cu@SiO₂ [17] or Rh_{0.8}Ni_{0.2}@CeOx/rGO [18]. Recently, Yao et al. [19] reported, for the first time, that the noble-metal-free catalyst CuNiMo nanocatalyst can release 100% H₂ from N₂H₄BH₃ in alkaline solution. Therefore, N₂H₄BH₃ was reconsidering again as a potential medium in solid-state H₂ storage following several routes such as: catalytic dehydrogenation [13,16–19], chemical modifications towards the formation of derivatives [20,21,23], or using destabilization reactions [22–26].

Indeed, Petit et al. [22] investigated the destabilization of ammonia borane by hydrazine borane and vice versa. According to the authors, the simultaneous presence of the two compounds resulted in destabilising Hδ⁺...Hδ⁻ network in both compounds and making the mixture unstable compared to both compounds taken separately [22]. However, Sen et al. [27] proposed the use of the mineral acid (HNO₃) as a catalyst on hydrolysis of hydrazine borane. Moury et al. [23] reported a thermolysis study of hydrazine borane and its alkali metal derivatives: N₂H₄BH₃, NaN₂H₃BH₃ and LiN₂H₃BH₃. It was observed that at low temperature (-173 °C), the synthesis of sodium hydrazinidoborane NaN₂H₃BH₃ using *in-situ* thermodiffraction experiments [23]. Esrafilii et al. [24] have studied the adsorption and the mechanism of N₂H₄BH₃ decomposition over both boron nitride nanotubes (BNNTs) and Aluminum-doped boron nitride nanotubes (Al-BNNTs), using charge transfer analyses and electron density difference and via density functional theory (DFT) calculations. The obtained results showed that N₂H₄BH₃ is strongly adsorbed in the two cases (BNNTs and Al-doped BNNTs) with a slightly larger activation energy for Al-doped BNNTs than for BNNTs [24]. Pylypko et al. [25] investigated experimentally the destabilization of N₂H₄BH₃ by alkali/alkaline-earth hydrides MH_x (M = Li, Na, K, Mg, Ca, Al and x = 1, 2, 3). Using characterization methods (thermogravimetric analysis, Calvet calorimetry, differential thermal analysis) [25], it was established that alkali hydride MH (M = Li, Na, K) can react and destabilize N₂H₄BH₃. Interestingly, the authors try to explain the behavior of reactivity of different alkali hydride with N₂H₄BH₃, by the Pauling electronegativity: the reactivity is higher when the electronegativity of the alkali hydride is lower [25]. Chua et al. [28] have synthesized and determined the crystal structures of NaN₂H₃BH₃ and KN₂H₃BH₃. A comparative study of the dehydrogenation behavior of the two hydrides with N₂H₄BH₃ indicated a clear dependence between the melting temperature and desorption temperature. It was concluded that the alkali-metal-hydrazinborane showed a suitable dehydrogenation behavior (compared to hydrazine borane) with the elimination of the undesirable emission of N₂H₄ and NH₃.

To the best knowledge of the authors, no experimental or theoretical studies about electronic structure and the nature of chemical bonds of alkali metal derivatives of hydrazine borane have been so far reported in the literature. Indeed, the practical use of such materials in H₂ storage require in-depth understanding of the fundamental chemical interactions (particularly when H₂ atoms are absorbed), which can be described by the electronic structure investigation. In this research work, the crystal structure and electronic structure of hydrazine and alkali metal derivatives of hydrazine borane were investigated, i.e. sodium hydrazinidoborane NaN₂H₃BH₃ and potassium hydrazinidoborane KN₂H₃BH₃, using first-

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