

Recent advances in sodium borohydride for hydrogen storage

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Abstract. Hydrogen energy is an efficient and renewable clean energy source, and the key issue for its application right moment is the development of hydrogen storage technology with high density and safety. Among many available hydrogen storage materials, metal complex hydrides with the advantages of high hydrogen storage capacity and good safety, are promising for future applications. However, high-capacity hydrogen storage composites suffer from disadvantages such as high hydrogen release temperature and poor reversibility, which severely limit their application. This paper provides a detailed summary of existing approaches to improve the kinetic and thermodynamic properties of NaBH₄ for hydrogen storage, including the addition of catalysts, the incorporation of appropriate reactants and the preparation of nanoscale NaBH₄, as well as an outlook on the future direction of pyrolysis.

1. Introduction

Energy shortage will be one of the major problems confronting human society in the 21st century, with the world's energy demand expected to nearly double by 2050. Currently, the structure of energy consumption is shifting from monoculture to diversification. Hydrogen as a fuel energy source has many advantages such as wide source, high combustion value, and minimal harm to the environment [1].

The energy produced by chemical combustion per unit mass of hydrogen (142 MJ/kg) [2] is three times greater than that produced by burning the same mass of gasoline (47 MJ/kg). For borohydrides, hydrogen exists as a covalent bond in [BH₄]⁻, resulting in a high mass hydrogen storage density and volume hydrogen storage density. NaBH₄, with a bulk density of 113 kg/m³ and a weight density of 10.6 wt%, is regarded as a very promising solid hydrogen storage material and has piqued the interest of researchers [3]. The complete decomposition of NaBH₄ and the reaction equation are as in (1),

$$\text{NaBH}_4 \rightarrow \text{Na} + \text{B} + 2\text{H}_2 \quad (1)$$

The operating temperature of NaBH₄ for hydrogen release typically exceeds 500 °C due to its high thermodynamic stability and slow kinetics. More importantly, the hydrogen produced by NaBH₄ is very limited due to phase separation and sodium evaporation during dehydrogenation [4]. In this paper, we take sodium borohydride (NaBH₄) with high hydrogen storage density as the research object and review the catalyzing, compositing [5, 6], and nano-confining [7] approaches to improve the reaction thermodynamic and kinetic properties of NaBH₄, with the primary objective of improving the performance of NaBH₄ to achieve its efficient and reversible hydrogen storage.

2. CATALYSIS

A good catalyst accelerates hydrogen physisorption and chemisorption on the adsorbate's surface and allows hydrogen diffusion within the adsorbate. Thus, the adsorbate's uptake is accelerated. The effect of catalysts such as TiH and TiF on the dehydrogenation of NaBH₄ was investigated by Mao et al [8]. Christian et al. found the hydrogen storage capacity of NaBH₄@Ni composite reached 5% [9]. It was also confirmed that the core-shell NaBH₄@m (m = Co, Cu, Fe, Ni, Sn) can achieve cyclic stability for at least several cycles [10]. Khazaei et al. discovered that pre-hydrogenated graphene substituted with Li atoms has a hydrogen storage capacity of 3.8 wt% [11].

The addition of a new catalyst to the hydride results in a homogeneous dispersion on the surface and interface of the hydride, facilitating hydrogen decomposition and recombination. For example, the addition of NdF₃ reduces the enthalpy of hydrogen release of NaBH₄ from 100 kJ/mol H₂ for pure NaBH₄ to 86.4 kJ/mol H₂ for the NaBH₄-3NdF₃ system [5]. Furthermore, Milanese et al. investigated the effect of MgF₂ on the hydrogen adsorption properties of NaBH₄, focusing on the fact that the decomposition temperature of NaBH₄ was reduced by 30 °C with the addition of MgF₂ [12]. Zhu et al. discovered that ball-milled BN compounds have a hydrogen storage capacity of 3.1 wt% at 175 °C for NaBH₄ [13]. Meanwhile, Ali et al. improved the hydrogenation performance of NaBH₄ by adding 10% wt MgFe₂O₄ as a catalyst, the hydrogen storage capacity was 6.2 weight percent in 60 minutes [14].

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3. COMPOSITING

Despite its good properties, the application of NaBH₄ is limited by its high enthalpy of decomposition (106.8 kJ/mol H₂), excessive thermodynamic stability, and higher dehydrogenation temperature (1 bar > 500 °C) [15]. The addition of one or more complex hydrides to form "active hydride composites" can lower the hydrogen release temperature and improve the hydrogen release kinetics of NaBH₄ [16, 17].

Compared to pure NaBH₄, the hydrogen storage performance of NaBH₄-LiAlH₄, NaBH₄-MgH₂, and NaBH₄-CaH₂ composite hydrogen storage systems,

formed by adding LiAlH₄, MgH₂, or CaH₂, was greatly improved. In this regard, Gorrioni et al demonstrated that when NaBH₄ was composited with MgH₂, the starting desorption temperature was reduced to 330 °C [18]. Also, the NaBH₄/LiAlH₄ system released hydrogen at a lower temperature than pure NaBH₄ [15]. Yahiya et al. discovered that the NaBH₄-Li₃AlH₆ complex could achieve 4.1 wt% capacity in 60 minutes at 420 °C [19]. The absorption kinetic curve is shown in figure 1, the optimum molar ratio for the NaBH₄-Li₃AlH₆ destabilized system was 1:1, and it disintegrated in two levels: Li₃AlH₆ decomposed at 170 °C and NaBH₄ decomposed at 400 °C.

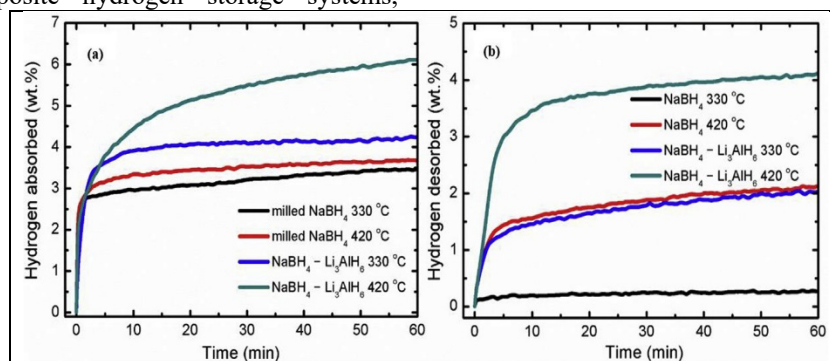


Figure 1 (a) Milled NaBH₄ and NaBH₄-Li₃AlH₆ absorption kinetics profiles at 330 and 430 °C under 30 atm pressure (b) profiles of the milling NaBH₄ and NaBH₄-Li₃AlH₆ desorption kinetics at 330 °C and 430 °C under 1 atm pressure [19]

In another study, Mao et al. demonstrated that the CaB₆ formed by the addition of CaH₂ or Ca(BH₄)₂ during heating destabilized NaBH₄ [15]. On the other hand, the regeneration of metal borides was much easier than monomeric boron because the energy required to open the metal-B bond was lower than that required to open the B-B bond [20]. The generation of metal borides, such as AlB₂, MgB₂ and CaB₆, is crucial for the reversible hydrogen performance in the above-mentioned systems when hydrogen is released. In this case, in addition to AlB₂, MgB₂ and CaB₆, other metal borides such as LaB₆, CeB₆, NdB₆, PrB₆, PrB₄, SmB₄, GdB₄ and YbB₄ may also favor the reversible hydrogen storage of NaBH₄. Meanwhile, Lanthanide hydrides such as YH₂ and CeH₂ [21], LaH₂

[22], and GdH₂ [23] have been shown to improve the reversible hydrogen release properties of NaBH₄.

In addition, Manoharan investigated efficient hydrogen storage on non-carbon (Ah-BN) and storage media containing NaBH₄, where the presence of Ah-BN greatly reduced the decomposition temperature of NaBH₄ with a hydrogen storage capacity of 3.8 wt% (similar to the hydrogenation setup of Sievert). The hydrogen storage schematic of NaBH₄/Ah-BN is shown in figure 2 [24]. Zheng et al. used multi-hydroxyl xylitol to make hydrogen easily available from NaBH₄ below 80 °C effectively, proposing a new strategy to destabilize NaBH₄ by multi-hydroxyl xylitol [25].

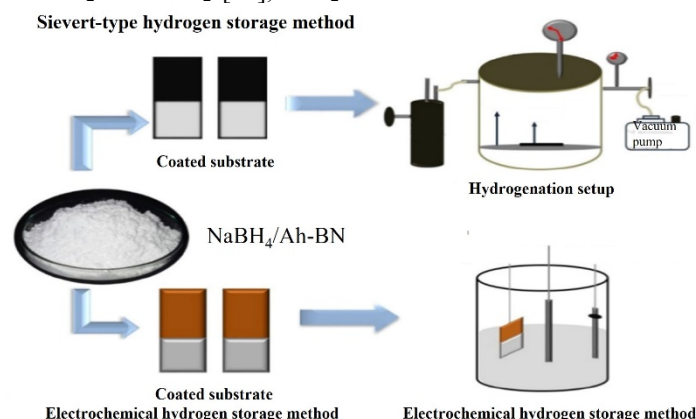


Figure 2 Schematic illustration of hydrogen storage press of NaBH₄/Ah-BN [24].

4. Nano-confinement

NaBH_4 is difficult to use for practical solid hydrogen storage due to its poor adsorption kinetics and thermodynamics [26]. Recent research has discovered that controlling the size of metal hydrides on the nanoscale can significantly improve their ability to store hydrogen. Chen et al. created a nanosheet derived from the carbonization of NiCo-MOF nanosheets. The nanosizing of NaBH_4 in NiCo-NC not only led to the homogeneous formation of NaBH_4 NPs but also made the NPS uniformly distributed inside NiCo-NC, facilitating the thermodynamically unstable reaction between NaBH_4 and NiCo alloy NPs [27].

Dorthe et al. produced $\text{NaZn}_2(\text{BH}_4)_5$ and $\text{NaZn}_3(\text{BH}_4)_3$ bimetallic borohydrides by ball milling of NaBH_4 and ZnCl_2 [28]. Then, the hydrogen release properties of NaBH_4 were improved by loading $\text{NaZn}_3(\text{BH}_4)_3$ into microporous SBA-15 [29]. Jeon et al. successfully encapsulated magnesium nanocrystals in a polymer,

which rapidly absorbed hydrogen and maintained a stable high capacity over three cycles [30], while nanocrystallization experiments were performed by infiltrating NaBH_4 into the microporous pores to obtain NaBH_4 nanoparticles with lower dehydrogenation temperature and better reversibility. However, this approach is still very limited due to its contamination caused by emitted by-products [31].

Chong et al. investigated novel hydrogen storage composites in which the hydride was nanowrapped by graphene, which limits the separation/polymerization of the hydride phase and improves the dehydrogenation/rehydrogenation performance of graphene-catalyzed hydrogenation, while also effectively preventing the leakage of dehydration products. It was found that the pure complex could reach a hydrogen production capacity of 7.0 wt% at 350 °C and 4 MPa with an initial hydrogen release temperature of 40 °C and a significant desorption effect after reaching 200 °C. The hydrogen absorption kinetic curves and cycling performance over six cycles are shown in figure 3, in addition, no by-products were found in the process [32].

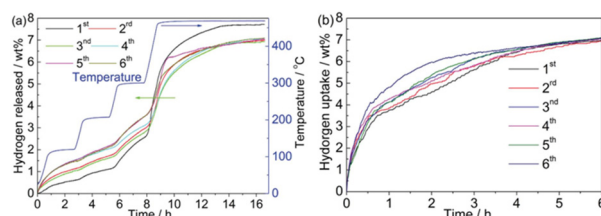


Figure 3 a) H_2 desorption cycling property of NaBH_4 @graphene. b) NaBH_4 @graphene for six cycles of hydrogen uptake kinetics [32].

5. Summary and outlook

This paper investigates the advantages and disadvantages of NaBH_4 for hydrogen storage. On the one hand, it is described in detail that the thermodynamic and kinetic properties of NaBH_4 for dehydrogenation and rehydrogenation are greatly improved using catalysis and compositing. On the other hand, by controlling the size of the metal hydride at the nanoscale, its hydrogen storage capacity can be stellarly improved. This nano-encapsulation prevents the agglomeration, dispersion, and loss of NaBH_4 during dehydrogenation and rehydrogenation, especially the volatilization of Na at higher temperatures, thus improving the reversible storage capacity of NaBH_4 . This paper provides a theoretical basis for the future selection of appropriate additives to optimize the hydrogen storage performance of metal boron hydride. Although some progress has been made in the study of NaBH_4 hydrogen storage, there is still much-uncharted space to be explored. According to the previous discussion, the hydrogen storage performance of this material can be improved or extended in the following ways.

1. Although the addition of catalysts or mixed hydrides to light metal borohydrides can effectively improve their hydrogen storage properties, there is a large gap between the hydrogen storage performance of existing hydrogen storage systems and their actual use, so it would be of great practical importance to conduct extensive research in this area to find the best hydrogen storage material system.

2. The proportion of the second hydride in the composite system should be reduced, and the thermodynamic and kinetic properties of the system should be improved by adding other small amounts of catalysts to increase the hydrogen storage capacity of the system.

3. The preparation and experimenting conditions should be optimized to keep increasing storage capacity, lowering the operating temperature, and improving the kinetics of nanoscale NaBH_4 .

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