



Article Sustainable Additives for the Production of Hydrogen via Sodium Borohydride Hydrolysis

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Abstract: Finding stable solutions for hydrogen storage is one of the main challenges to boosting its deployment as an energy vector and contributing to the decarbonization of the energy sector. In this context, sodium borohydride (NaBH₄) has been largely studied as a hydrogen storage material due to its significant advantages, such as low pressure, stability, and high hydrogen storage density. The development of catalysts and additive materials for the on-demand hydrolysis of NaBH₄ for hydrogen release is a key research area. This work studies the effects of non-toxic and environmentally friendly additives for the hydrolysis process in terms of yield, lag time, hydrogen generation rate, and gravimetric density. Specifically, four additives, including sodium carboxymethylcellulose (CMC), polyacrylamide (PAM), sodium dodecyl sulfate (SDS), and β -cyclodextrin (BCD), were studied for their application in the storage and release of hydrogen. The best results were provided by the use of sodium carboxymethyl cellulose and polyacrylamide. In the first case, a hydrolysis yield of 85%, a lag time of 70 s, a hydrogen production rate of 1374 mL·min⁻¹·gcat⁻¹, and a storage capacity of 1.8 wt% were obtained. Using polyacrylamide as additive, a hydrolysis yield of almost 100% was achieved, although it required a significantly higher time period for complete conversion.

Keywords: hydrogen storage; sodium borohydride; additives; hydrolysis; hydrogen release rate; lag time

1. Introduction

The abusive use of fossil fuels for energy production since the industrial revolution has caused an incessant increase in the concentration of carbon dioxide (CO₂) in the atmosphere. CO₂ is the primary greenhouse gas (GHG) emitted by human activity and it is considered one of the main contributors to climate change [1]. In this sense, urgent measures to avoid the emission of GHG are mandatory. The Intergovernmental Panel on Climate Change (IPCC) claimed the necessity of limiting the increment in the temperature of the Earth to below 2 °C, preferably 1.5 °C, to compared to the pre-industrial era, otherwise, climate change may be irreversible. The United Nations (UN), through 17 sustainable development goals (SGDs), promotes a better and more sustainable future, including two specific objectives associated with energy supply and consumption without compromising the planet. These are SGD number 7, 'affordable and clean energy', and SGD number 13, 'climate action', which set the basis to reduce CO₂ emissions [2].

One of the key aspects that must be addressed to mitigate climate change is the development of new renewable sources of energy which can compete with conventional



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). sources based on fossil fuels. Nevertheless, the most widespread green energies nowadays, solar and wind, have major drawbacks such as low performance and power generation intermittency. In this context, the use of hydrogen as an energy vector presents a promising alternative, although there are still challenges to be overcome, especially in terms of storage for onboard applications [3]. At present, traditional systems for hydrogen storage are based on its use either in (i) gaseous form, which allows working at 273 K but requires the use of high pressures, and (ii) liquid form, which can be operated at ambient conditions of pressure but also demands cryogenic temperatures below 25 K [4].

In line with the necessity for new systems capable of achieving high storage and regeneration capacities and lower costs [5], hydrogen storage in solid materials could constitute a step forward to reach this objective. These materials must offer safe handling while providing high gravimetric and volumetric densities, low temperatures for H₂ release, and the possibility of operating at atmospheric pressure. Nowadays, the materials that are gaining interest for this application are adsorbents (e.g., MOF-5) [6], organic liquids (e.g., BN-methyl cyclopentane) [7], metal hydrides (e.g., MgH₂) [8], ammonia boranes (e.g., NH₃BH₃) [9], and chemical hydrides (e.g., NaBH₄) [10]. In this context, two main approaches have shown significant results for hydrogen generation using ammonia boranes and chemical hydrides: methanolysis [11,12] and hydrolysis [13,14]. While methanolysis offers advantages such as higher hydrogen yields, lower required temperatures, and faster reaction rates, it does have some drawbacks. For example, the production of methanol as a byproduct requires proper handling and disposal due to its flammability and toxicity. Additionally, the need to separate methanol from the hydrogen gas stream adds an extra step and cost to the process. On the other hand, hydrolysis provides simplicity as a straightforward process, requiring only water as a reactant, and also offers lower costs and is considered safe and environmentally friendly.

Specifically, in recent years, increasing attention has been paid to the hydrogen generation of metal hydrides due to their high theoretical hydrogen yield [15]. Specifically, the chemical hydride sodium borohydride (NaBH₄) stands out as a promising hydrogen carrier due to its inherent advantages, (i) stability under a wide range of temperatures, (ii) low working pressures, (iii) high hydrogen purity, (iv) high hydrogen storage capacity (10.8 wt%), (v) exothermic hydrolysis ($\Delta H = -210 \text{ kJ} \cdot \text{mol}^{-1}$), (vi) capacity of simultaneous hydrogen generation and storage, (vii) direct H₂ release to feed electrochemical systems, such as PEM fuel cells, to generate electric energy, and (viii) non-toxic character [16–21].

The low hydrogen generation rate from NaBH₄ at ambient temperature is considered a barrier to its commercialization. However, the employment of catalysts enhances the rate of hydrogen release, whereas the use of additives may help in stabilizing the process kinetics [18,19]. Platinum has shown high catalytic activity for the hydrolysis of NaBH₄, however, its scarcity and high cost hinder its widespread use [22]. Thus, many efforts have been devoted to developing new catalysts to enhance the dehydrogenation process, especially based on non-noble metals due to their low price, abundant reserves, and relatively high activities [20–24]. The most investigated elements are cobalt, ruthenium, and nickel as heterogeneous catalysts [25]. Among them, bimetallic catalysts based on Ni-Ru have been commonly used in the hydrolysis of NaBH₄ because of their large specific surface area [26]. Regarding the structural form of the catalyst, different alternatives have been studied, including powder as the most common type, aerogels, and foam [25,27].

Additionally, additives can be introduced to optimize the hydrolysis of NaBH₄ by increasing the stability and improving hydrogen generation rates, leading to higher yields and better overall process performance. Several works have studied the effect of additives in NaBH₄ hydrolysis, including common chemicals and organic polymers [28,29]. Xu et al. [28] employed ammonia borane NH₃BH₃ to prevent particle agglomeration, improving the dispersibility of NaBH₄ and making the resulting composite more porous. With this additive, 90% of hydrogen could be released at 70 °C after 1 h, with hydrogen yields of 9 wt% (considering reacted water). On the other hand, Ferreira et al. [29] analyzed the effect of the addition of a cellulose derivative, observing a rise in the rate

and yield of hydrogen generation by increasing the non-polar hydrogen–electrolyte interactions and, consequently, improving the affinity for H₂ storage in the liquid phase due to its solubility. Another interesting work highlights the use of metal nanoparticles supported on polyacrylamide (PAM), known for its highly water-absorbent character, in NaBH₄ methanolysis [30]. Furthermore, the use of NaOH-poly(acrylamide) hydrogels for the hydrolysis of NaBH₄ has been explored for H₂ generation [31]. Moreover, Loghmani et al. [32] studied sodium dodecyl sulfate (SDS) as a surfactant and stabilizing agent to investigate its effect on the size, morphology, and catalytic activity for H₂ production using NaBH₄. Other authors, such as Huff et al. [33], utilized β -cyclodextrin (BCD) as a capping agent in the synthesis of nanoparticles. This approach was selected to prevent agglomeration and ensure stability.

Nevertheless, the number of works dealing with additives in the hydrolysis of NaBH₄ remains scarce in the literature and, thus, this work aims to optimize the hydrolysis of sodium borohydride through the employment of four different additives that improve the rate of hydrogen generation. The selected additives were non-toxic, environmentally friendly, and had the ability to enhance the reaction efficiency and stability, including sodium carboxymethyl cellulose (CMC), polyacrylamide (PAM), sodium dodecyl sulfate (SCS), and β -cyclodextrin (BCD). The obtained results provide valuable insights into the storage and production of hydrogen through NaBH₄ hydrolysis in the presence of sustainable additives. The use of these additives improves the reproducibility and stability of the reaction, facilitating its control and scalability for industrial applications.

2. Materials and Methods

2.1. Catalyst

The decomposition of sodium borohydride to produce hydrogen is a relatively slow reaction, and it requires a significant input of energy to overcome the activation barrier. Therefore, a catalyst is typically used to speed up the reaction and increase the yield of hydrogen. In this case, the catalyst employed was composed of Ni-Ru in powder form, nanometric particle size, and was prepared from a mixture of precursors in deionized water by impregnating small amounts of Ru in Ni salts (Riedel-de Haën, Seelze, Germany) via reaction with a 10 wt% stabilized NaBH₄ solution (Rohm and Haas, Philadelphia, PA, USA), which acted as reducing environment. In the second step, when the reduction was completed, the catalyst was appropriately settled, washed, filtered, and dried, and, finally, subjected to thermal treatment at 110 °C and stored in a desiccator until use [34]. Each experiment was performed using 5 mL of the solution and a mass ratio of 0.4 catalysts—NaBH₄ was used after the results obtained in previous works. The catalyst was placed inside the reactor and then the reactant solution was injected, with this moment considered the beginning of the experiment. Further details regarding the experimental setup and procedures can be found in previous works [10,26,29].

2.2. Additives

The influence of four additives on the kinetics and stability of hydrogen release was studied. Sodium carboxymethyl cellulose (CMC, Sigma Aldrich (St. Louis, MO, USA), average Mw \approx 700,000), polyacrylamide (PAM, Polysciences. Inc. (Warrington, PA, USA), Mw = 18,000,000), sodium dodecyl sulfate (SDS, Sigma Aldrich, \geq 98.5%), and β -cyclodextrin (BCD, Sigma Aldrich, \geq 97.0%) were respectively added to the hydrolysis tests at a concentration of 1 wt%.

PAM is often used as a viscosity modifier and friction reducer, and thus it could help to control the rate of hydrogen release [35]. For its part, CMC is a derivative of cellulose, non-toxic and generally non-allergenic, which dissolves rapidly in cold water. Its viscosity drops during heating, which could promote the hydrogen release rate [29]. In the case of SDS, this additive has been widely used to improve the storage capacity and induction time of multiple compounds [36,37]. Finally, BCD is a non-toxic, green, and cyclic oligosaccharide that was selected due to its potential to provide a strong interaction between the metal in the catalyst and the solution, which can be beneficial to improve the reaction performance [38].

Hydrolysis tests in the absence of additives (control test) were also performed for comparison.

2.3. Hydrolysis Test

Hydrogen gas can be generated through the hydrolysis of NaBH₄ in the presence of a catalyst at moderate temperatures, as described by Equation (1). To increase the yield of H₂, an excess of water (denoted as x) is required, which helps to prevent the formation of intermediate boranes that can decrease the yield in hydrogen production. In this study, a value of x = 15 was chosen, as this provides sufficient water excess to achieve the complete hydrolysis of NaBH₄ while avoiding excessive dilution of the reaction mixture. Using lower values of x can result in incomplete hydrolysis of NaBH₄, leading to lower yields of H₂ and the formation of byproducts such as intermediate boranes. Additionally, inadequate alkalinity may reduce the reaction rate, leading to longer reaction times. Conversely, choosing a value of x higher than 15 can lead to excessive dilution of the reaction mixture, reducing the efficiency of the hydrolysis reaction, and resulting in lower H₂ yields and longer reaction times.

$$NaBH_4 + (2+x) H_2O \rightarrow NaBO_2 \cdot xH_2O + 4 H_2 \tag{1}$$

Aqueous solutions of sodium borohydride (Sigma Aldrich, powder \geq 98.0%) at 10 wt% were prepared to perform the experiments. Moreover, sodium hydroxide (NaOH) (PanReac, Barcelona, Spain, pellets, 98.0%) at 7 wt% was added to ensure the reaction stability. The solutions were prepared by first mixing NaBH₄ and NaOH in deionized water and afterward they were fed to the reactor. Once both components were thoroughly mixed, the additives were added. All experiments were conducted at room temperature ($26 \pm 1 \,^{\circ}$ C) in a stainless-steel batch reactor with a free internal volume of 229 cm³. Once in the reactor, the tests were performed without stirring and in duplicate, under the same conditions, to study the reproducibility of the process [26,34].

2.4. Data Collection and Analysis

The reactor used was equipped with a k-thermocouple and a pressure probe connected to the Lab View software to record the data simultaneously every 2 s. The yield of hydrogen production in the reaction was calculated as the ratio between the total pressure in the hydrogen gas and the theoretical pressure considering a complete NaBH₄ conversion (100%). In addition, the lag time was determined as the time required to achieve 0.5 bar overpressure in all hydrolysis tests according to Figure 1.

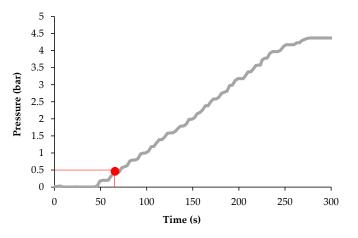


Figure 1. Lag time.

3. Results

3.1. Influence of the Additives on the Yield of Hydrogen

Among the critical process parameters, the hydrogen yield is intimately related to the overall performance efficiency of NaBH₄ hydrolysis. Figure 2 illustrates the mean values of hydrogen yield in the presence of each of the tested additives CMC, PAM, SDS, and BCD. The results are compared with those obtained in the conventional process in the absence of additives. The deviation of the results is also presented for each case. It is important to remark that the yields were calculated considering the real and theoretical pressure of the system. In all the cases, the additives were added to the aqueous solution in a concentration of 1 wt%.

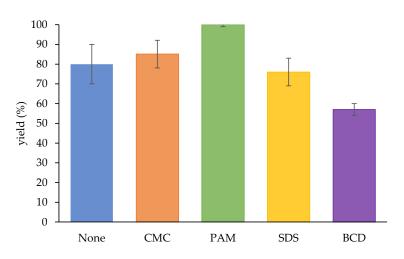


Figure 2. Hydrogen generation yield (%) achieved in a batch reactor using different additives.

Based on the results, PAM can be considered a promising additive for hydrogen production given that it enables hydrogen yields close to 100% with standard deviations below 1.5%. PAM is a water-soluble polymer that functions as a stabilizing agent and rheological modifier. When added to a NaBH₄–water mixture, PAM can reduce the formation of gas bubbles, which can hinder the release of hydrogen gas. Moreover, PAM is relatively inexpensive and easily available, thus facilitating large-scale industrial applications.

In contrast, the additive BCD led to the lowest yield of 57%, which is far from the desirable values for NaBH₄ hydrolysis. Furthermore, hydrolysis tests in the presence of BCD showed lower values compared to those achieved with the conventional process (control). This is because BCD has a lower ability to stabilize the reaction mixture and prevent the formation of gas bubbles as compared to PAM. In addition, BCD can reduce the availability of hydroxide ions (OH⁻) in the solution, which slows down the rate of the hydrolysis reaction. Intermediate values of around 85% and 76% were obtained with the additives CMC and SDS, respectively, with standard deviations in the range of 5–7%. It is worth noting that the traditional method without additives showed a significantly wider variability. In this case, although the average yield was 80%, the standard deviation was about 10%. In the case of CMC, this additive promotes the yield of H₂ by facilitating the reaction between NaBH₄ and water and improves the efficiency of the H₂ production process. Thus, the presence of PAM and CMC is clearly beneficial for NaBH₄ hydrolysis given that their yields outperformed the control test. In addition, the use of all additives showed narrower variability, contributing to the stabilization performance of the process.

3.2. Hydrogen Generation Rates

In order to understand NaBH₄ hydrolysis, it is essential to monitor hydrogen generation over time. In this regard, this section discusses the evolution of hydrogen release in the batch reactor in the presence of the four different additives employed in the previous section and compares the results with values provided in the literature so far. Figure 3 depicts the evolution of hydrogen generation curves for CMC, PAM, SDS, and BCD, including the results of the control test. Figure 3a shows the pressure variation inside the reactor over time until it stabilized. According to Section 3.1, PAM offered the highest hydrogen yield, however, it also required a longer period of time until a plateau was reached. The stabilization of the pressure for PAM was seen after 4000 s, representing up to four times the stabilization time required for the rest of the additives and the control test. This suggests that this admixture could be used when low and controlled quantities of hydrogen are required.

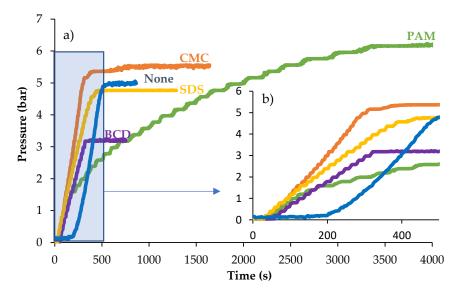


Figure 3. (a) Hydrogen generation plots obtained for the reaction of NaBH₄ hydrolysis at room temperature. • Control, • BCD additive, • SDS additive, • CMC additive, • PAM additive. (b) Zoom of subfigure (a) to show slopes differences.

On the other hand, when CMC was added, the final pressure was obtained in the shortest time. In this case, only 300 s were required to achieve the maximum volume of hydrogen. As seen before, CMC reported a hydrogen yield of 85% (the second-best value). Consequently, considering both the release time and yield, CMC could be among the most prominent options to control NaBH₄ hydrolysis. The tests with SDS and the system without precursor showed similar stabilization times, 450 and 500 s, respectively. Finally, despite the bad performance provided by BCD, Figure 3 demonstrates that this additive offers rapid kinetics before stabilization of the hydrogen release (app. 300 s).

Figure 3b shows the slopes of the curves, which lead to the hydrogen rates. Table 1 includes the calculated release velocities with regard to the mass of the catalyst and the comparison with results previously reported working with 10 wt% of NaBH₄ in the presence of NaOH and operating at room temperature, as in this work.

Additive	H ₂ Rate (mL∙min ⁻¹ ∙gcat ⁻¹)	Conditions	Ref
Control	1000 ± 500	10 wt% NaBH4, 7 wt% NaOH, 1 wt% additive Catalyst: Ni-Ru	This work
СМС	1374 ± 40	10 wt% NaBH ₄ , 7 wt% NaOH, 1 wt% additive Catalyst: Ni-Ru	This work
PAM	721 ± 62	10 wt% NaBH ₄ , 7 wt% NaOH, 1 wt% additive Catalyst: Ni-Ru	This work
SDS	688 ± 66	10 wt% NaBH ₄ , 7 wt% NaOH, 1 wt% additive Catalyst: Ni-Ru	This work

Table 1. Hydrogen generation rates.

Additive	H₂ Rate (mL∙min ⁻¹ ∙gcat ⁻¹)	Conditions	Ref
BCD	788 ± 120	10 wt% NaBH ₄ , 7 wt% NaOH, 1 wt% additive Catalyst: Ni-Ru	This work
None	980	10 wt% NaBH4, 7 wt% NaOH Catalyst: Ni-Ru	[10]
None	220	10 wt% NaBH4, 5 wt% NaOH Catalyst: Co-Al ₂ O ₃	[39]
None	400	10 wt% NaBH4, 5 wt% NaOH Catalyst: Ni-Ru nanocomposite	[40]
None	1466 2446	10 wt% NaBH4, 5 wt% NaOH, Ni- Catalyst: Ni-Co ₃ O ₄ Catalyst: Co-Co ₃ O ₄	[41]

Table 1. Cont.

Among the additives tested, CMC provided promising values in terms of kinetics and stability in hydrogen production, specifically $1374 \pm 40 \text{ mL} \cdot \text{min}^{-1} \cdot \text{gcat}^{-1}$, showing a clear positive effect of its use for NaBH4 hydrolysis. The rest of the additives offered lower generation rates in comparison to the control test. In detail, the velocity of SDS was almost half the value obtained with CMC, achieving rates of $688 \pm 66 \text{ mL} \cdot \text{min}^{-1} \cdot \text{gcat}^{-1}$, but with high reproducibility (error lower than 9%). A similar trend was observed with BDC, which accomplished values of 788 \pm 120 mL·min⁻¹·gcat⁻¹. In contrast, when the control test was studied, the results showed higher values of hydrogen generation rates compared to PAM, SDS, and BCD additives. However, the variability was remarkably high $(1000 \pm 500 \text{ mL} \cdot \text{min}^{-1} \cdot \text{gcat}^{-1})$. This is probably because, in the control group, the reaction mixture had a simpler composition, consisting only of NaBH₄ and water. This point leads to a simpler reaction system, where the reaction kinetics and rate of H_2 generation are less controlled, resulting in higher variability in the H₂ generation rates. On the other hand, additives act as stabilizers, helping to control the reaction kinetics and, therefore, the rate of H₂ generation. This results in a more controlled and reproducible reaction, which can be beneficial for industrial applications where stability and reproducibility are paramount.

In comparison to previous results reported in the literature, the hydrogen rates from the hydrolysis of NaBH₄ using CMC were significantly higher than those obtained with nanocomposites based on Co-Al₂O₃ and Ni-Ru as catalysts in the absence of additives (400 and 220 mL·min⁻¹·gcat⁻¹ respectively) [39,40] and with Ni-Ru as catalyst (980 mL·min⁻¹·gcat⁻¹) [10]. Other works have reported noticeable hydrogen generation rates (2446 mL·min⁻¹·gcat⁻¹) in the absence of additives, but using a different catalyst (Co-Co₃O₄) to the one used in this work, which comparatively was more expensive [41]. This suggests the necessity of future works to simultaneously optimize the presence of additives and catalysts for the hydrolysis of NaBH₄.

3.3. Lag Time

This section discusses the influence of the studied additives on the lag time values. Table 2 shows the lag times obtained in the presence and the absence of the different additives, following an increasing order. SDS reported the lowest value of lag time (50 s), while the test in the absence of additives offered the highest value (211 s). SDS can negatively impact H_2 production by accelerating the decomposition of NaBH₄, causing an uncontrolled release of hydrogen gas, which can lead to safety concerns and reduce the overall yield of H_2 . On the other hand, the precursor CMC, which showed the shortest stabilization release time, offered a threefold decrease in the lag time (70 s) in comparison to the value achieved without additives (115 s) but still half the lag time of the control test. This is because PAM acts as a dispersant, which helps to break up the agglomerates of the catalyst, allowing for better dispersion of the catalyst available for the reaction, resulting

in a shorter lag time and faster onset of hydrogen generation. Moreover, PAM can also enhance the mass transfer in the reaction mixture, which can improve further the efficiency of the hydrogen production process. Finally, BCD achieved a lag time of 80 s, which can be considered acceptable. The values obtained in this section demonstrate that the use of additives can improve the lag time required for H₂ release. Thus, all the additives can be used to accelerate the initial hydrogen release, which is desirable when small but rapid hydrogen production is necessary for process control. Furthermore, for higher demands, the use of CMC, BCD, and PAM additives can facilitate the production of larger quantities of hydrogen safely.

Additive	Lag Time (s)
SDS	50
СМС	70
BCD	80
PAM	115
None	211

Table 2. Lag times for different additives.

3.4. Critical Comparison between the Additives

From the comparison between the gravimetric density and hydrogen generation rates depicted in Figure 4, it is possible to observe the general trends obtained with the four additives used in this study. Gravimetric density refers to the amount of a substance that can be contained per unit mass. Thus, in the context of hydrogen production using NaBH₄, gravimetric density determines how much hydrogen can be produced from a given amount of NaBH₄.

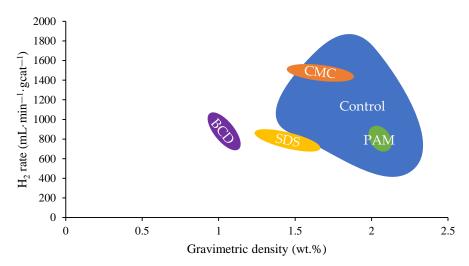


Figure 4. Comparison between gravimetric density and H₂ rate. • Control, • BCD additive, • SDS additive, • CMC additive, • PAM additive.

As seen, the BCD admixture provided a poor performance, with lower values in comparison to the experiment without an additive. To this respect, the control experiment demonstrated that NaBH₄ hydrolysis leads to low reproducible values given that replicate tests reported high variability.

For its part, SDS provided replicable experiments, reaching reasonable values of density, close to 1.5%. Still, the hydrogen rate was low, implying the necessity of either (i) increasing the quantity of this additive or (ii) exploring new routes of catalyst to promote a higher release rate. In the case of PAM, the results demonstrated its high gravimetric density and hydrogen rate. In addition, these experiments exhibited the lowest variations

in terms of reproducibility. However, PAM required the longest time to achieve a high yield, implying that its use could be mainly recommended in processes in which low and controllable hydrogen requirements are needed. Finally, CMC, again, has been presented as the additive with optimal performance among the materials studied given that it allowed the highest values of velocity with acceptable values of gravimetric density.

As a general trend, it is seen that the use of additives helps to achieve higher stability and replicability in the results. Nevertheless, future optimization works are necessary to make progress on the use of additives to promote NaBH₄ as a hydrogen carrier in order to obtain gravimetric densities close to the maximum values expected from sodium borohydrides (10.8 wt%).

4. Conclusions

Sodium borohydrides are currently positioned among the most promising strategies for hydrogen storage in a solid state. However, the maximum hydrogen release and the reaction kinetics are challenges ahead to reach higher TRLs and, therefore, full industrial implementation. In this regard, additives represent an option to overcome some of the most frequently reported performance limitations. The present work contributes to making a step forward in the use of additives in low quantities, specifically at 1 wt%, studying the effects on the hydrolysis of NaBH₄ and describing the most relevant process variables. For this purpose, four additives with different viscosities and natures have been evaluated, analyzing the yields, hydrogen generation rates, lag time, and gravimetric densities.

The results showed that the additive polyacrylamide (PAM) presented the highest yield, close to 100%, and a relatively high H₂ release rate, with a total value of 721 mL·min⁻¹·gcat⁻¹. The time required to obtain the total amount of hydrogen (4000 s) was significantly longer in comparison to the rest of the additives tested. In contrast, sodium carboxymethyl cellulose (CMC) provided reasonable hydrogen yield values (85%), safe values of lag time (70 s), the highest value of hydrogen generation rate at 1374 mL·min⁻¹·gcat⁻¹, and the lowest time for stabilization, only 300 s, positioning it as the most valuable additive under the studied reaction conditions. The other two additives, β -cyclodextrin and sodium dodecyl sulfate, achieved lower values in terms of H₂ release rate and yield but, in both cases, higher replicability and safety were obtained in comparison with the control test.

Further efforts are still required to optimize the effects of additives such as polyacrylamide and sodium carboxymethyl cellulose for the use of sodium borohydrides in hydrogen storage and release. The employment of additives could be of great importance to achieve a safe, stable, and reproducible system for sodium borohydride hydrolysis.

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References

- 1. Climate Change: Atmospheric Carbon Dioxide | NOAA Climate.Gov. Available online: https://www.climate.gov/news-features/understanding-climate/climate-change-atmospheric-carbon-dioxide (accessed on 13 September 2021).
- 2. United Nations THE 17 GOALS | Sustainable Development. Available online: https://sdgs.un.org/goals (accessed on 20 January 2022).
- 3. Hydrogen Storage Challenges | Department of Energy. Available online: https://www.energy.gov/eere/fuelcells/hydrogenstorage-challenges (accessed on 9 September 2021).
- 4. Hassan, I.A.; Ramadan, H.S.; Saleh, M.A.; Hissel, D. Hydrogen Storage Technologies for Stationary and Mobile Applications: Review, Analysis and Perspectives. *Renew. Sustain. Energy Rev.* **2021**, *149*, 111311. [CrossRef]
- Nunes, H.X.; Silva, D.L.; Rangel, C.M.; Pinto, A.M.F.R.; Nunes, H.X.; Silva, D.L.; Rangel, C.M.; Pinto, A.M.F.R. Rehydrogenation of Sodium Borates to Close the NaBH 4-H 2 Cycle: A Review Rehydrogenation of Sodium Borates to Close the NaBH 4-H 2 Cycle: A Review. *Energies* 2021, 14, 3567. [CrossRef]
- Hardy, B.; Tamburello, D.; Corgnale, C. Hydrogen Storage Adsorbent Systems Acceptability Envelope. *Int. J. Hydrogen Energy* 2018, 43, 19528–19539. [CrossRef]
- Verevkin, S.P.; Konnova, M.E.; Zherikova, K.V.; Pimerzin, A.A. Sustainable Hydrogen Storage: Thermochemistry of Amino-Alcohols as Seminal Liquid Organic Hydrogen Carriers. J. Chem. Thermodyn. 2021, 163, 106591. [CrossRef]
- 8. Wu, Z.; Zhu, L.; Yang, F.; Nyamsi, S.N.; Porpatham, E.; Zhang, Z. Toward the Design of Interstitial Nonmetals Co-Doping for Mg-Based Hydrides as Hydrogen Storage Material. *J. Mater. Res.* **2018**, *33*, 4080–4091. [CrossRef]
- 9. Demirci, U.B. Mechanistic Insights into the Thermal Decomposition of Ammonia Borane, a Material Studied for Chemical Hydrogen Storage. *Inorg. Chem. Front.* **2021**, *8*, 1900–1930. [CrossRef]
- 10. Nunes, H.X.; Ferreira, M.J.F.; Rangel, C.M.; Pinto, A.M.F.R. Hydrogen Generation and Storage by Aqueous Sodium Borohydride (NaBH4) Hydrolysis for Small Portable Fuel Cells (H2–PEMFC). *Int. J. Hydrogen Energy* **2016**, *41*, 15426–15432. [CrossRef]
- Liao, J.; Shao, Y.; Feng, Y.; Zhang, J.; Song, C.; Zeng, W.; Tang, J.; Dong, H.; Liu, Q.; Li, H. Interfacial Charge Transfer Induced Dual-Active-Sites of Heterostructured Cu0.8Ni0.2WO4 Nanoparticles in Ammonia Borane Methanolysis for Fast Hydrogen Production. *Appl. Catal. B* 2023, *320*, 121973. [CrossRef]
- Feng, Y.; Li, Y.; Liao, Q.; Zhang, W.; Huang, Z.; Chen, X.; Shao, Y.; Dong, H.; Liu, Q.; Li, H. Modulation the Electronic Structure of Hollow Structured CuO-NiCo2O4 Nanosphere for Enhanced Catalytic Activity towards Methanolysis of Ammonia Borane. *Fuel* 2023, 332, 126045. [CrossRef]
- 13. Kirk, J.; Kim, Y.; Lee, Y.; Kim, M.; Min, D.; Soon, P.; Hui, J.; Kim, Y.; Lee, J.; Woo, J.; et al. Pushing the Limits of Sodium Borohydride Hydrolysis for On-Board Hydrogen Generation Systems. *Chem. Eng. J.* **2023**, *466*, 143233. [CrossRef]
- Avcı Hansu, T. A Novel and Active Ruthenium Based Supported Multiwalled Carbon Nanotube Tungsten Nanoalloy Catalyst for Sodium Borohydride Hydrolysis. Int. J. Hydrogen Energy 2023, 48, 6788–6797. [CrossRef]
- 15. Chen, W.; Ouyang, L.Z.; Liu, J.W.; Yao, X.D.; Wang, H.; Liu, Z.W.; Zhu, M. Hydrolysis and Regeneration of Sodium Borohydride (NaBH4)—A Combination of Hydrogen Production and Storage. J. Power Sources 2017, 359, 400–407. [CrossRef]
- 16. Mao, J.; Gregory, D.H. Recent Advances in the Use of Sodium Borohydride as a Solid State Hydrogen Store. *Energies* **2015**, *8*, 430–453. [CrossRef]
- Yao, Q.; DIng, Y.; Lu, Z.-H. Noble-Metal-Free Nanocatalysts for Hydrogen Generation from Boron- And Nitrogen-Based Hydrides. Inorg. Chem. Front. 2020, 7, 3837–3874. [CrossRef]
- 18. Demirci, U.B. About the Technological Readiness of the H<inf>2</Inf> Generation by Hydrolysis of B(-N)–H Compounds. *Energy Technol.* **2018**, *6*, 470–486. [CrossRef]
- 19. Tan, Y.; Yu, X. Chemical Regeneration of Hydrogen Storage Materials. RSC Adv. 2013, 3, 23879–23894. [CrossRef]
- 20. Muir, S.S.; Yao, X. Progress in Sodium Borohydride as a Hydrogen Storage Material: Development of Hydrolysis Catalysts and Reaction Systems. *Int. J. Hydrogen Energy* **2011**, *36*, 5983–5997. [CrossRef]
- 21. Retnamma, R.; Novais, A.Q.; Rangel, C.M. Kinetics of Hydrolysis of Sodium Borohydride for Hydrogen Production in Fuel Cell Applications: A Review. *Int. J. Hydrogen Energy* **2011**, *36*, 9772–9790. [CrossRef]
- 22. Zhang, H.; Zhang, L.; Rodríguez-Pérez, I.A.; Miao, W.; Chen, K.; Wang, W.; Li, Y.; Han, S. Carbon Nanospheres Supported Bimetallic Pt-Co as an Efficient Catalyst for NaBH4 Hydrolysis. *Appl. Surf. Sci.* **2021**, *540*, 148296. [CrossRef]
- 23. Demirci, U.B.; Miele, P. Cobalt-Based Catalysts for the Hydrolysis of NaBH₄ and NH₃BH₃. *Phys. Chem. Chem. Phys.* **2014**, *16*, 6872–6885. [CrossRef]
- 24. Simagina, V.I.; Ozerova, A.M.; Komova, O.V.; Netskina, O.V. Recent Advances in Applications of Co-B Catalysts in NABH4-based Portable Hydrogen Generators. *Catalysts* **2021**, *11*, 268. [CrossRef]
- 25. Demirci, U.B. The Hydrogen Cycle with the Hydrolysis of Sodium Borohydride: A Statistical Approach for Highlighting the Scientific/Technical Issues to Prioritize in the Field. *Int. J. Hydrogen Energy* **2015**, *40*, 2673–2691. [CrossRef]
- 26. Ferreira, M.J.F.; Gales, L.; Fernandes, V.R.; Rangel, C.M.; Pinto, A.M.F.R. Alkali Free Hydrolysis of Sodium Borohydride for Hydrogen Generation under Pressure. *Int. J. Hydrogen Energy* **2010**, *35*, 9869–9878. [CrossRef]
- 27. Brack, P.; Dann, S.E.; Upul Wijayantha, K.G. Heterogeneous and Homogenous Catalysts for Hydrogen Generation by Hydrolysis of Aqueous Sodium Borohydride (NaBH4) Solutions. *Energy Sci. Eng.* **2015**, *3*, 174–188. [CrossRef]
- Xu, Y.; Wu, C.; Chen, Y.; Huang, Z.; Luo, L.; Wu, H.; Liu, P. Hydrogen Generation Behaviors of NaBH4-NH3BH 3 Composite by Hydrolysis. J. Power Sources 2014, 261, 7–13. [CrossRef]

- 29. Ferreira, M.J.F.; Fernandes, V.R.; Gales, L.; Rangel, C.M.; Pinto, A.M.F.R. Effects of the Addition of an Organic Polymer on the Hydrolysis of Sodium Tetrahydroborate in Batch Reactors. *Int. J. Hydrogen Energy* **2010**, *35*, 11456–11469. [CrossRef]
- Khan, S.B.; Ali, F.; Asiri, A.M. Metal Nanoparticles Supported on Polyacrylamide Water Beads as Catalyst for Efficient Generation of H2 from NaBH4 Methanolysis. *Int. J. Hydrogen Energy* 2020, 45, 1532–1540. [CrossRef]
- Seven, F.; Sahiner, N. NaOH Modified P(Acrylamide) Hydrogel Matrices for in Situ Metal Nanoparticles Preparation and Their Use in H2 Generation from Hydrolysis of NaBH4. J. Appl. Polym. Sci. 2014, 131, 1–9. [CrossRef]
- Loghmani, M.H.; Shojaei, A.F.; Khakzad, M. Hydrogen Generation as a Clean Energy through Hydrolysis of Sodium Borohydride over Cu-Fe-B Nano Powders: Effect of Polymers and Surfactants. *Energy* 2017, 126, 830–840. [CrossRef]
- Huff, C.; Long, J.M.; Heyman, A.; Abdel-Fattah, T.M. Palladium Nanoparticle Multiwalled Carbon Nanotube Composite as Catalyst for Hydrogen Production by the Hydrolysis of Sodium Borohydride. ACS Appl. Energy Mater. 2018, 1, 4635–4640. [CrossRef]
- Pinto, A.M.F.R.; Ferreira, M.J.F.; Fernandes, V.R.; Rangel, C.M. Durability and Reutilization Capabilities of a Ni-Ru Catalyst for the Hydrolysis of Sodium Borohydride in Batch Reactors. *Catal. Today* 2011, 170, 40–49. [CrossRef]
- Xiong, B.; Dettam Loss, R.; Shields, D.; Pawlik, T.; Hochreiter, R.; Zydney, A.L.; Kumar, M. Polyacrylamide Degradation and Its Implications in Environmental Systems. NPJ Clean Water 1982, 1, 17. [CrossRef]
- 36. Da Silva Lirio, C.F.; Pessoa, F.L.P.; Uller, A.M.C. Storage Capacity of Carbon Dioxide Hydrates in the Presence of Sodium Dodecyl Sulfate (SDS) and Tetrahydrofuran (THF). *Chem. Eng. Sci.* **2013**, *96*, 118–123. [CrossRef]
- 37. Zhang, J.S.; Lo, C.; Somasundaran, P.; Lee, J.W. Competitive Adsorption between SDS and Carbonate on Tetrahydrofuran Hydrates. *J. Colloid Interface Sci.* **2010**, *341*, 286–288. [CrossRef]
- Liu, X.; Gao, D.; Chi, Y.; Wang, H.; Wang, Z.; Zhao, Z. Ultrafine AuPd Nanoparticles Supported on Amine Functionalized Monochlorotriazinyl β-Cyclodextrin as Highly Active Catalysts for Hydrogen Evolution from Formic Acid Dehydrogenation. *Catal. Sci. Technol.* 2020, 10, 5281–5287. [CrossRef]
- 39. Ye, W.; Zhang, H.; Xu, D.; Ma, L.; Yi, B. Hydrogen Generation Utilizing Alkaline Sodium Borohydride Solution and Supported Cobalt Catalyst. *J. Power Sources* **2007**, *164*, 544–548. [CrossRef]
- 40. Liu, C.H.; Chen, B.H.; Hsueh, C.L.; Ku, J.R.; Jeng, M.S.; Tsau, F. Hydrogen Generation from Hydrolysis of Sodium Borohydride Using Ni-Ru Nanocomposite as Catalysts. *Int. J. Hydrogen Energy* **2009**, *34*, 2153–2163. [CrossRef]
- 41. Bozkurt, G.; Özer, A.; Yurtcan, A.B. Hydrogen Generation from Sodium Borohydride with Ni and Co Based Catalysts Supported on Co3O4. *Int. J. Hydrogen Energy* **2018**, *43*, 22205–22214. [CrossRef]

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