Review

Rehydrogenation of Sodium Borates to Close the NaBH$_4$-H$_2$ Cycle: A Review

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Abstract: In 2007, the US Department of Energy recommended a no-go on NaBH$_4$ hydrolysis for onboard applications; however, the concept of a NaBH$_4$-H$_2$-PEMFC system has the potential to become a primary source for on-demand power supply. Despite the many efforts to study this technology, most of the published papers focus on catalytic performance. Nevertheless, the development of a practical reaction system to close the NaBH$_4$-H$_2$ cycle remains a critical issue. Therefore, this work provides an overview of the research progress on the solutions for the by-product rehydrogenation leading to the regeneration of NaBH$_4$ with economic potential. It is the first to compare and analyze the main types of processes to regenerate NaBH$_4$: thermo-, mechano-, and electrochemical. Moreover, it considers the report by Demirci et al. on the main by-product of sodium borohydride hydrolysis. The published literature already reported efficient NaBH$_4$ regeneration; however, the processes still need more improvements. Moreover, it is noteworthy that a transition to clean methods, through the years, was observed.

Keywords: hydrogen; sodium borohydride; regeneration of sodium borohydride; thermochemical processes; mechano-chemical processes; electrochemical processes; hydrogen cycle

1. Introduction

The negative impact of the excessive use of fossil fuels has been a major concern since the beginning of the century, mainly in the current decade [1]. Thus, the need to reduce greenhouse gas concentrations to sustainable levels is mandatory to allow the future generations to live on an Earth at least as habitable as today, which has resulted in a demand for clean and abundant energy technologies [2]. In this context, hydrogen (H$_2$) arises as one of the most promising fuels of the future. Hydrogen can be efficiently oxidized in Polymer Electrolyte Membrane Fuel Cells (PEMFC) to provide electricity to a wide range of applications (e.g., portable and maritime applications) [3,4], involving an electrode (anode and cathode)/membrane electrolyte system. The energy stored in the H$_2$ fuel is converted into electricity and heat, producing only water as a by-product [5,6]. Thus, hydrogen is supplied in the anode and splits into electrons and protons, while oxygen is reduced at the cathode. The protons are carried through a polymer electrolyte membrane (PEM) to recombine with oxygen, whereas the electrons proceed to the cathode through an external circuit, providing the electrical output [6].

Hydrogen is an energy vector with a strong potential for energy storage due to its high gravimetric density (142 MJ.kg^{-1}) and lightness. Nevertheless, it is lighter than air, flammable, and is usually combined with other elements [3,7]. Due to its abundance, hydrogen can be produced by several methods using a wide range of sources, through fossil fuels to renewable energy resources. Currently, 96% of worldwide hydrogen is

generated from fossil fuels; nevertheless, to be a low-carbon energy carrier, new generation methods must be developed [2,7–9].

Chemical hydrides, such as metal–boron hydrides and ammonia borane, have received strong attention, since they exhibit an impressive volumetric hydrogen storage density on a material-only basis and simultaneously allow the generation and storage of hydrogen [10,11]. Among chemical hydrides, sodium borohydride ($NaBH_4$) is a promising hydrogen carrier due to its high hydrogen storage capacity (10.8 wt %), safe handling, and fast kinetics of hydrogen release [12–14]. $NaBH_4$ releases molecular hydrogen via hydrolysis, at room pressure and temperature, as described by the chemical reaction presented in Equation (1) [3,15].

$$NaBH_4 + 2\,H_2O \ \rightarrow\ NaBO_2 + 4\,H_2 \tag{1}$$
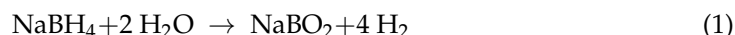
The reaction is spontaneous and exothermic ($\Delta H = -217$ kJ.mol^{-1}), and the release of hydrogen can be accelerated by a catalyst [16,17]. The only by-product that forms upon hydrolysis usually retains two or four molecules of water, which decreases the hydrogen yield and generation rate. Therefore, an excess of water is needed, and the effective hydrolysis reaction of $NaBH_4$ is observed according to Equation (2), where $\times$ represents the hydration factor [18–20].

$$NaBH_4 + (2+x)\,H_2O \ \rightarrow\ NaBO_2 \bullet x\,H_2O + 4\,H_2 \tag{2}$$
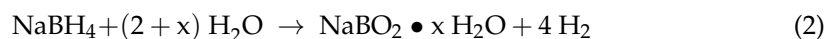
Since the early 2000s, many efforts have been dedicated to the hydrolysis of $NaBH_4$; however, there is no consensus about the chemical structure of the by-product [21,22]. Although the majority of the published studies described sodium metaborate ($NaBO_2$) as the by-product of the reaction, several studies reported that the only by-product that forms is sodium tetrahydroxyborate ($NaB(OH)_4$) [21–33], since the solution is stabilized with pH beyond 11 [3]. Therefore, the appropriate equation would be written as follows:

$$NaBH_4 + (2+x)\,H_2O \ \rightarrow\ NaB(OH)_4 + 4\,H_2. \tag{3}$$

Although the hydrolysis of $NaBH_4$ combines the best properties for hydrogen generation and storage, including solubility in water, rapid controllable hydrolysis, overall stability, and moderate exothermicity, in 2007, the US Department of Energy (DOE) recommended a no-go on $NaBH_4$ hydrolysis for onboard applications [34]. This decision was based on three key issues: storage capacity targets, regeneration of $NaBH_4$, and costs [35]. In order to address these issues, the research dedicated to the synthesis and regeneration of $NaBH_4$ improved [36].

Bearing in mind the research articles concerning the $NaBH_4$ hydrolysis by-product recycling that have been published in peer-reviewed international journals since the early 2000s, only three studies were dedicated to this topic [37–39] prior to the US DOE report in 2007. About 96% of the papers on this topic [20,40–68] were published after the DOE no-go recommendation (Figure 1). Despite the efforts, since 2009, to develop an efficient and reliable method to regenerate $NaBH_4$, the reported research is low when compared with the total number of published studies on $NaBH_4$ hydrolysis.

In the past 20 years, 12 review-type articles were published regarding the hydrogen generation through boron-based hydrides [21,22,35,36,69–76]. Although 10 of these articles focused on $NaBH_4$ hydrolysis, only five overviews highlight the importance to recycling the by-product in order to close the $NaBH_4$-H_2 cycle [21,22,35,36,71].

In 2015, Demirci et al. [21] analyzed 260 research articles published between 2000 and 2013 that were dedicated to "the hydrogen cycle with hydrolysis of sodium borohydride" and reported that only 8.9% of the papers were related with $NaBH_4$ regeneration. According to the authors, more than 60% of the research articles focused on catalysis. There is a noteworthy lack of research in recycling, which is a key issue to close the $NaBH_4$-H_2 cycle. Therefore, 217 research papers [11,17,20,23,24,28–31,50,52–61,77–273], published from 2014 up to the publication of this paper, were selected to understand the evolution of the research on "hydrogen from $NaBH_4$ hydrolysis" after the report by Demirci et al. [21]. The

selected articles were published in peer-reviewed international journals, and all the review-type articles and conference proceedings were discarded. According to their main focus, the research articles were divided in four topics: "catalysis", "fundamentals", "others", and "regeneration" (Figure 2). The "catalysis" topic highlights the performance and characterization of catalysts; "fundamentals" focuses on reaction mechanisms, kinetics, and thermodynamics; the topic "other" emphasizes the experimental and computational study of reactors, prototypes, and developed systems; and the "regeneration" topic is dedicated to the synthesis of $NaBH_4$ from the reaction by-products. It is noteworthy that the high majority of the studies, about 80%, continue to be dedicated to the topic "catalysis". Despite the need to close the hydrogen cycle from $NaBH_4$ hydrolysis, which is strongly dependent on the development and implementation of an efficient, low-cost, and reliable recycling method [21,36,61], only 5.5% of the published articles highlight the topic "regeneration". Although important advances have been made through the years, there is still a low impact of this topic.
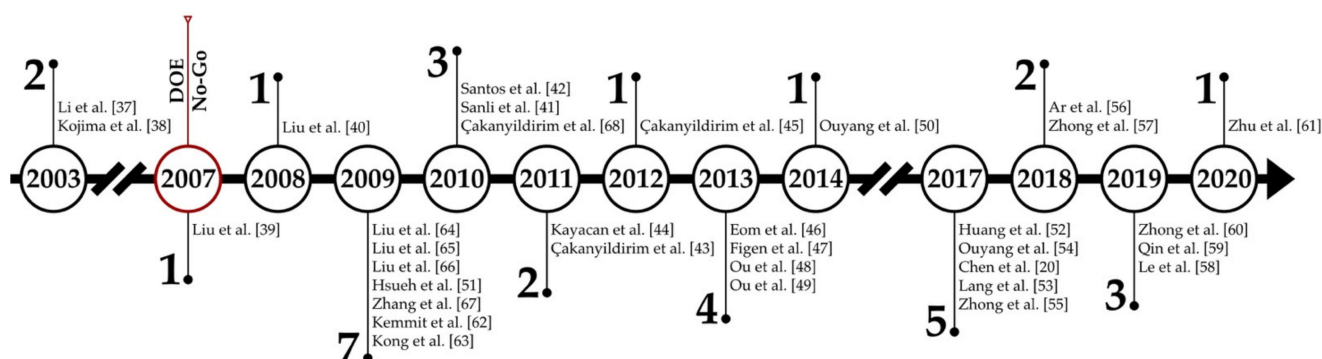
Figure 1. Timeline of published articles dedicated to $NaBH_4$ regeneration.

Figure 2. Infographic view of the main focus of research articles, published between 2014 and 2021, dedicated to the regeneration of $NaBH_4$.

The usual path to synthesize $NaBH_4$ is the Brown–Schlesinger process, which was developed in the early 1950s [15,22]. This process is expensive, not clean, and inefficient. It consists of seven steps, which require high pressures and temperatures and produce

various by-products [36,58]. The main reaction is presented in Equation (4), where sodium hydride (NaH) and trimethylborate (B(OCH$_3$)$_3$) react at 225 to 275 °C [15,42].

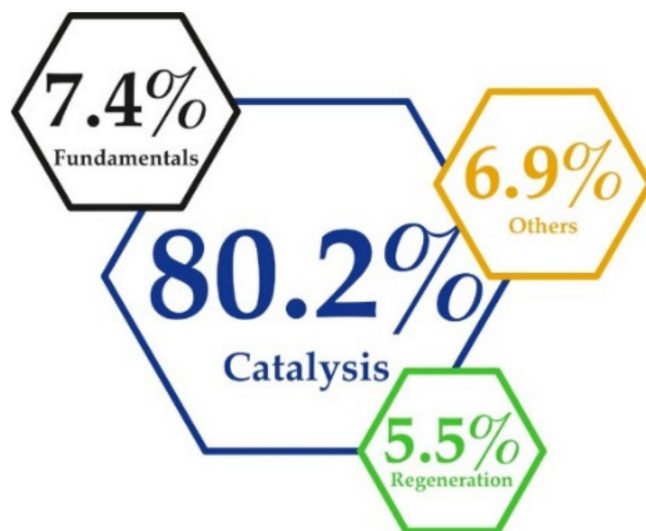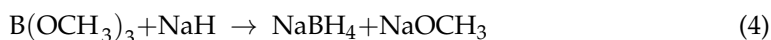$$B(OCH_3)_3 + NaH \; \rightarrow \; NaBH_4 + NaOCH_3 \tag{4}$$

An alternative method to produce NaBH$_4$ at industrial scale is the Bayer process, which is represented in Equation (5) [33,37]. Na$_2$B$_4$O$_7$•7SiO$_2$ reacts with Na at 400–500 °C under a hydrogen atmosphere. It is noteworthy that this process exhibits high potential risks due to the high temperature and hydrogen pressure operations. Moreover, it produces Na$_2$SiO$_3$ as a by-product, which is a residue with low commercial value that is difficult to discard [33,58].

$$Na_2B_4O_7 \bullet \, 7SiO_2 + 16Na + 8H_2 \; \rightarrow \; 4NaBH_4 + 7Na_2SiO_3 \tag{5}$$
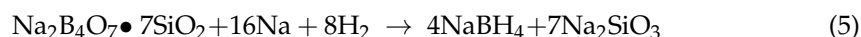
Although the synthesis of NaBH$_4$ from hydrolysis by-products remains a great challenge, the studies published to date present promising advances [25,33]. Nevertheless, a low-cost fully reliable alternative method to synthesize NaBH$_4$ has not yet been developed. Closing the NaBH$_4$-H$_2$ cycle is essential to implement a NaBH$_4$-H$_2$-PEMFC system as a primary energy source to provide on-demand power for portable and maritime applications [4,11]. Moreover, NaBH$_4$-H$_2$-PEMFC systems emerge as a promising off-grid technology capable of providing a fully reliable electricity supply in emerging countries and locations without a reliable grid.

Among the many possible hydrogen carriers, liquid ammonia and LOHC (liquid organic hydrogen carriers) have been gaining increased importance [22,70,274]. Ammonia has a very high hydrogen content (17.8% in weight) and simultaneously an impressive volumetric hydrogen density (108 kg H$_2$/m^3 in liquid ammonia at 20 °C and 8.6 bar). However, ultra-pure hydrogen recovery from the ammonia cracker in the reconversion to hydrogen process is still a great challenge [28,275]. LOHC exhibit moderate H$_2$ content, reversibility, moderate dehydrogenation temperature, commercial availability, and compatibility with the existing gasoline infrastructure, but the reactor systems, process heat integration, and concerns such as catalyst recovery and regeneration, separation, and capture of CO$_2$ from the gaseous products formed need further developments [274]. In comparison, chemical hydrides present, as referred above, a high hydrogen content and low to moderate dehydrogenation temperatures (the hydrolysis reaction is an easy and controllable process and allows simultaneously hydrogen storage), but they suffer from irreversibility and energy-consuming regeneration. Therefore, a major challenge for the effective use of these hydrogen carriers is the development of alternative or improved routes to rehydrogenate the by-products formed. The specific advantages of the sodium borohydride carrier were already enlightened. Thus, this overview focuses on the published alternative methods to rehydrogenating the borates leading to the NaBH$_4$ regeneration, since this is a critical issue that needs to be overcome in order to close the NaBH$_4$-H$_2$ cycle and allow the implementation of this technology [36,59,61].

2. Regeneration of NaBH$_4$

The regeneration of sodium borohydride can be organized into three major groups of processes based on the energy source: thermochemical, mechano-chemical, and electrochemical. Thermochemical processes are based on reactions that involve high pressure and/or temperature, and they comprise most of the reactions to effectively regenerate NaBH$_4$. The mechano-chemical processes are similar to the thermochemical ones, but the source of energy used in this type of process relies on mechanical forces. Lastly, the electrochemical processes use electric energy to produce sodium borohydride by reducing or oxidizing other borates. Until 2015, the regeneration of sodium borohydride was mainly achieved through thermochemical processes [41,42] (Figure 3). However, since 2016, there has been a transition to cleaner processes to regenerate this compound, with mechano-chemical processes being the most used ones [20,43,45,50,52–61,68]. The lack of efficient

$NaBH_4$ electrosynthesis also contributed to this "mechano-chemical processes boom" to regenerate $NaBH_4$.

An overview of the $NaBH_4$ regeneration yields through thermochemical and mechano-chemical processes is presented in Figures 4 and 5, respectively. Regeneration yields based on thermochemical processes are presented according to the temperature (closed circles) and pressure (open circles) of the reaction (Figure 4). Almost all experiments were performed using pressure values between 2 and 4 MPa and temperature values between 800 and 900 K. For mechano-chemical processes, the regeneration yields are presented along with the time of milling (closed circles) and the year of publication of the articles (open circles) (Figure 5). As observed, higher yields are achieved when using higher milling times; nevertheless, regenerating $NaBH_4$ for more than 35 h (2000 min) is a considerable energy-consuming process. These higher yield values have been obtained since 2017, which may reflect a gradual improvement of these processes. It is noteworthy that the same color points in both figures correspond to the same first author, indicating that a wider variety of groups has progressively been focusing on mechano-chemical sodium borohydride regeneration.
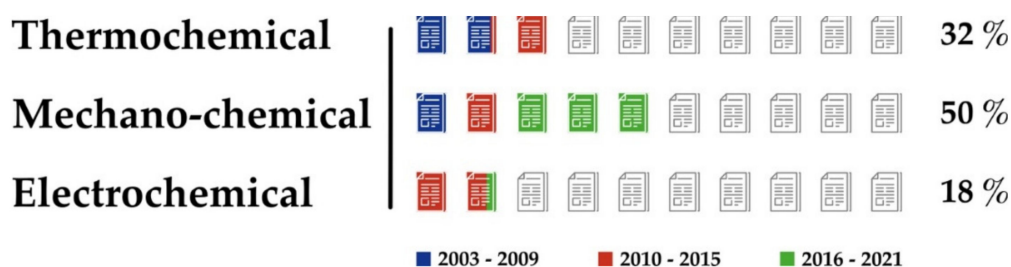

Figure 3. Infographic view of the type of process reported in the research articles, published since 2000, dedicated to $NaBH_4$ regeneration.
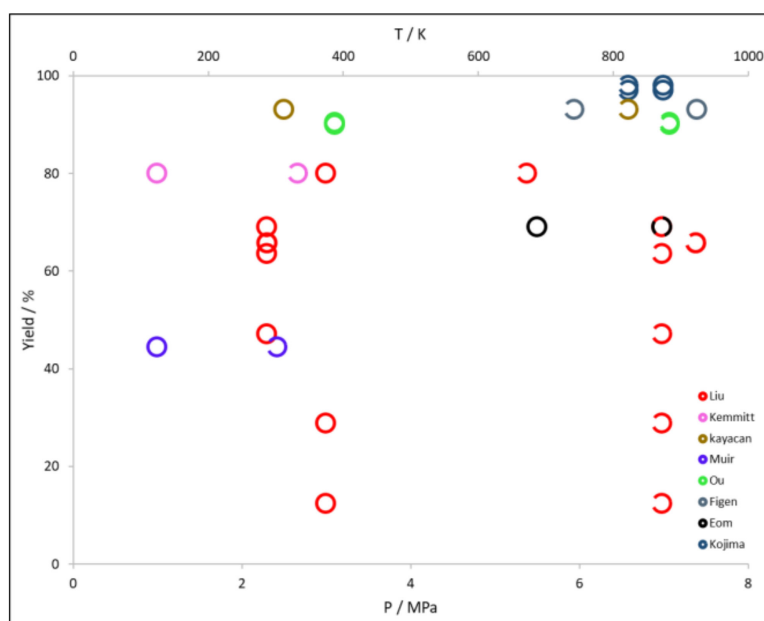

Figure 4. Reported yields for $NaBH_4$ regeneration through thermochemical processes.

Figure 5. Reported yields for NaBH$_4$ regeneration through mechano-chemical processes.

Regarding the electrochemical synthesis of NaBH$_4$, studies conducted at Penn State University (PSU), in combination with DOW Jones Industrial Average and Los Alamos National Lab (LANL), indicated that no NaBH$_4$ was electrochemically obtained, and it would not be possible to effectively regenerate it from NaBO$_2$. This statement contributed to a lack of papers on the subsequent years using electrochemical methods to regenerate NaBH$_4$. Moreover, although several patents have claimed that the electrochemical regeneration was achieved, there are no published studies reproducing the results. It is noteworthy to highlight some papers that synthesize NaBH$_4$ through electrochemical processes as an intermediate step for desulfurization experiments [276–279].

The following sub-sections describe the results reported so far regarding the regeneration of NaBH$_4$. It is noteworthy that most of these results were obtained using commercially available boron compounds. Thus, there is an emergent need for developing synthesized boron compounds to regenerate NaBH$_4$, as the ultimate goal is to use the by-products of its hydrolysis for the regeneration process, which can react differently compared to commercial boron compounds.

2.1. Thermochemical Processes

Thermochemical processes are chemical reactions that occur at high pressure and/or temperature. As previously referred, NaBH$_4$ is usually synthesized through two thermochemical processes: (i) the Brown and Schlesinger process and (ii) the Bayer process.

The main disadvantage of the Brown and Schlesinger process is the formation of several by-products. To overcome this issue, Liu et al. [280] developed a modified closed system where NaBO$_2$ and ammonia borate ((NH$_4$)$_3$(BO$_3$)) are simultaneously produced and recycled from NaBH$_4$. According to the authors, the metallic Na is obtained by the electrolysis of sodium chloride (NaCl) in a seawater treatment. Although this study presents a major improvement to the Brown and Schlesinger process, it continues to be a multi-step process that needs to use metallic Na. In contrast, the Bayer process allows a direct production of NaBH$_4$. Nevertheless, it has some associated issues: (a) the need to use metallic Na, (b) the disposal of the by-product (Na$_2$SiO$_3$), and (c) the risk of explosion due to high temperature (873 K) and hydrogen pressure [33,58].

Therefore, several authors attempted to synthetize NaBH$_4$ through different methods. Since the early 2000s, only 12 papers were published reporting the NaBH$_4$ hydrolysis by-

product recycling through thermochemical processes (Table 1) [38–40,44,46–49,62,64–66]. All reported studies were carried out using either magnesium hydride (MgH_2) or magnesium under a hydrogen atmosphere. The thermochemical studies using MgH_2 reported higher conversion yields; however, this method also presents high costs due to the commercial value of MgH_2 [47]. On the other hand, although the $NaBH_4$ regeneration using Mg under a hydrogen atmosphere presented lower costs, this method is not suitable due to the need to use hydrogen as a reactant. Since the basis of these studies is to generate hydrogen as an energy carrier, this method does not seem to be profitable to close the $NaBH_4$-H_2 cycle.

Table 1. Summary of thermochemical processes for $NaBH_4$ regeneration.

Author	Boron Compound	Other Reactants	Yield/%	Ref.
Kojima	$NaBO_2$	MgH_2	97.0	[38]
		Mg, Si	98.0	
Liu	$Na_4B_2O_5$	Al, H_2, Na_2O	65.8	[39]
	Na_3BO_3	Si	47.0	[40]
	$NaBO_2$	Al	69.0	[64]
		Mg	63.5	
	$NaBO_2 \bullet 0.5\,H_2O$	Mg	28.8	[66]
	$NaBO_2 \bullet H_2O$	Mg	12.3	
	$NaBO_2$	Mg + 23.5% Ni	80.0	[65]
Kemmitt	$NaBO_2$	CH_3OH, $NaAlH_4$	80.0	[62]
Kayacan	$Na_2B_4O_7$	Mg, H_2	93.0	[44]
Ou	$NaBO_2$	MgH_2	90.4	[48]
		MgH_2	90.0	[49]
Figen		MgH_2	93.0	[47]
Eom		Mg	69.0	[46]

2.1.1. Effect of Temperature, Pressure, and Time of Reaction

The thermochemical reactions are highly affected by the parameters considered, as observed in Figure 4. The published articles analyzed in this overview focus on two main parameters: the reaction temperature and pressure. Moreover, some articles also studied the influence of time and the benefit of specific additives.

In 2003, Kojima et al. [38] studied the mixture of $NaBO_2$ with MgH_2 (Equation (6)), at 7 MPa H_2 and 823 K, after 2 h of reaction, and they obtained a conversion yield of 97.0%. This is the higher yield reported for the $NaBH_4$ regeneration using a thermochemical process without additives.

$$NaBO_2 + 2\,MgH_2 \;\rightarrow\; NaBH_4 + MgO \tag{6}$$
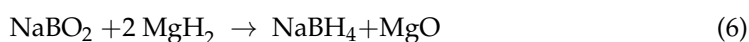
Ten years later, Ou et al. [48] studied the influence of temperature variation in Equation (6) at 3.1 MPa H_2. The authors increased the reaction temperature from 293 to 884 K followed by a consequent decrease to 293 K and reported a $NaBH_4$ regeneration of 90.4% yield. The calculus of the conversion yield was based on H_2 pressure variation, and 85.2% of the obtained value had been associated to the formation of $NaBH_4$ during the isothermal period between T = 873 K and T = 884 K. Therefore, Ou et al. [49] added two more parameters to the study: pressure and time of reaction (tr). In order to promote the hydrogen adsorption for $NaBH_4$ formation, the authors set the H_2 pressure between 2.1 and 3.1 MPa and observed that after 1.5 h, at 907 K, they achieved the maximum borate conversion. Nevertheless, at 857 K, the authors observed that it took 8 h to obtain the same $NaBH_4$ conversion.

Eom et al. [46] also studied Equation (6), in turn, at 6 MPa. After 1 h of reaction, the authors observed that the conversion yield increased with temperature (Figure 6a). The results obtained stand out, since the yield is considerably lower than the ones previously reported [38,48,49]. However, the authors justified the results with the tough in MgH_2 decomposition promoted by the high H_2 pressure.
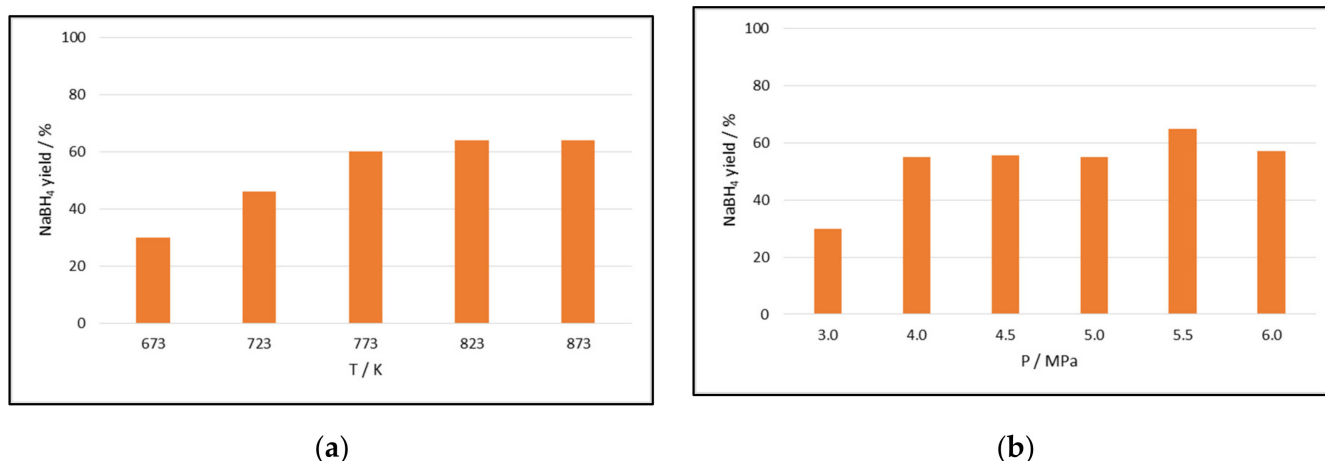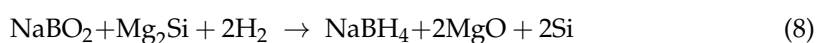

(**a**)

(**b**)

Figure 6. Values of $NaBH_4$ yield vs. (**a**) Temperature *T* and (**b**) Pressure *P* for *t* = 1 h. Adapted from [46].

According to these results, it is possible to conclude that the temperature presents a main role in thermochemical processes.

Eom et al. [46] also studied, at 873 K, the influence of H_2 pressure (Figure 6b) as well as other reducing agents. Thermodynamically, Ca is more suitable than Mg as a reducing agent. Nevertheless, the authors concluded that Ca does not act as an effective catalyst in the H_2-H^- conversion, since only a small amount of $NaBH_4$ was formed.

2.1.2. Effect of Additives and the Hydration of the Boron Compound

In addition to the effect of temperature, Kojima et al. [38] also studied the influence of additives in the reaction. The authors performed experiments with silicon (Equations (7) and (8)) at 7 MPa H_2 and 823 K, and they obtained $NaBH_4$ with a 98% yield after 2 h of reaction.

$$NaBO_2 + 2\,Mg + Si + 2H_2 \; \rightarrow \; NaBO_2 + Mg_2Si + 2H_2 \tag{7}$$

$$NaBO_2 + Mg_2Si + 2H_2 \; \rightarrow \; NaBH_4 + 2MgO + 2Si \tag{8}$$

In 2007, Liu et al. [39] studied the influence of Al as a reducing agent and observed that the formation of $NaBH_4$ did not occur. However, the authors reported a maximum $NaBH_4$ conversion of 65.8% when the compounds tetrasodium diborate ($Na_4B_2O_5$) and sodium oxide (Na_2O) were combined with Al (Equation (9)).

$$4\,Al + 6\,H_2 + Na_4B_2O_5 + NaBO_2 + Na_2O \; \rightarrow \; 3\,NaBH_4 + 4\,NaAlO_2 \tag{9}$$
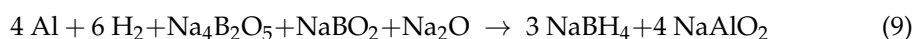
The studies were carried out at 873 K with a $NaBO_2/Na_2O$ molar ratio between 1.5 and 4 (Figure 7). The authors concluded that although the presence of Na_2O has a positive impact on the regeneration of $NaBH_4$, the $NaBO_2/Na_2O$ molar ratio must be optimized [64].

Furthermore, Liu et al. [40] studied the influence of several additives in the reaction of $NaBO_2$ with Mg and H_2, such as Fe, Co, Ni, and Cu. The authors reported that Fe and Ni affect the reaction similarly. The addition of 5 wt % of these metals not only increased the $NaBH_4$ yield (Fe: 88%; Ni: 82%) but also decreased the reaction temperature (Fe: $\approx$283 K; Ni: $\approx$313 K). Moreover, increasing the Fe concentration up to 20 wt % promotes the $NaBH_4$ generation rate with similar conversion yields. The authors also observed that the addition

of 5 wt % of Co converted $NaBH_4$ with 85% yield, and the addition of the same amount of Cu did not show any significant effect in the reaction. Additionally, the authors concluded that none of the additives decreased the activation energy of the reaction (156.3 kJ.mol^{-1})
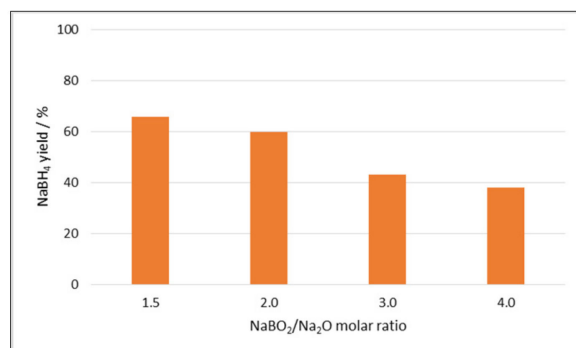

Figure 7. Values of $NaBH_4$ yield vs. $NaBO_2$/Na_2O molar ratio. Adapted from [38].

A year later, Liu et al. [65] reported a eutectic alloy of Mg with 23.5% Ni in the recycling of $NaBO_2$. The studies were performed at 673 K and 3.0 MPa H_2, and a slight increase of 3 wt % H_2 absorbed on the Mg surface was observed, which promoted an increase of 8% in $NaBH_4$ conversion yield. The authors concluded that the Mg alloy induced the hydrogen dissociation and diffusion during the reaction.

Furthermore, Liu et al. [66] also studied the $NaBH_4$ by-product recycling without performing its initial dehydration. Bearing in mind Equation (2), the authors studied the influence of the by-product hydration between x = 0 and x = 2 and observed that while the hydration factor increases, the conversion yield considerably decreases. Moreover, the authors reported that for x = 4, no $NaBH_4$ was formed. Therefore, the authors realized that although it is a high-energy consumption step, the dehydration of the by-product is necessary.

2.2. Mechano-Chemical Processes

The mechano-chemical processes use mechanical movement instead of heat to generate the required energy to form the products of the reaction. These reactions are typically performed in a high-energy ball mill, at room temperature, with the reactants in the solid state (powder). The impact of the milling balls on the reactants reduces the size of the particles, which increases the contact between them and, consequently, promotes the reaction. It is noteworthy that although these reactions occur at room temperature, there is an increase of temperature inside the mill during the reaction that promotes the formation of $NaBH_4$. Similar to thermochemical processes, the mechano-chemical processes are carried out using MgH_2 or Mg under hydrogen atmosphere as reactants. Although mechano-chemical processes are more environmentally friendly, since they are low-energy consumption processes, the high times of milling are a considerable limitation. Moreover, the implementation of the ball milling process to synthesize $NaBH_4$ in a larger scale is not feasible mainly due to cost issues [58].

Since 2003, several authors reported the regeneration of $NaBH_4$ through ball milling (Table 2). In addition to MgH_2, some authors studied the reaction with Si compounds in order to find a low-cost alternative. Moreover, the influence of several additives was studied, such as sodium peroxide (Na_2O_2), sodium hydroxide (NaOH), sodium carbonate (Na_2CO_3), sodium hydride (NaH), and methanol (CH_3OH). The influence of the hydration of sodium borates was also studied, and it is noteworthy that $NaBH_4$ was regenerated with high yield without an initial dehydration step.

**Table 2.** Summary of mechano-chemical processes for $NaBH_4$ regeneration.

Author	Borate	Other Reactants	Excess of Reactant/%	Additive	t/min	Yield/%	Ref.
Li	$Na_2B_4O_7$	MgH_2	100	-	60	43.0	[37]
			2.70	Na_2O_2		67.0	
			-	NaOH		64.0	
			15.50	Na_2CO_3		78.0	
Hsueh	$NaBO_2$	MgH_2	40	-	120	76.0	[51]
Kong	$NaBO_2$	MgH_2	3.50	-	120	71.0	[63]
Zhang	$NaBO_2$	NaH, SiO_2	-	-	360	32.0	[67]
Çakanyldirim	$NaBO_2$	MgH_2	27	-	700	73.9	[68]
	B_2O_3		30	Na	800	25.0	[43]
	$Na_2B_4O_7$		10	-	400	84.0	[45]
Ouyang	$NaBO_2$	Mg	37.50	-	900	67.7	[54]
Lang	$NaBO_2$	MgH_2	35	CH_3OH	480	89.0	[53]
Chen	$NaBO_2 \bullet 2\,H_2O$	MgH_2	25	-	900	89.8	[20]
	$NaBO_2 \bullet 4\,H_2O$		37.50	-	1 200	88.3	
	$NaBO_2 \bullet 2\,H_2O$, $NaBO_2 \bullet 4\,H_2O$		40	-	360	82.0	
Huang	$NaBO_2 \bullet 2\,H_2O$	Mg, Mg_2Si	25	-	1 200	86.0	[52]
Zhong	$NaBO_2 \bullet 2\,H_2O$	Mg_2Si	50	-	1 200	78.0	[55]
	$NaBO_2 \bullet 4\,H_2O$		100	-	1 200	74.0	[57]
Ar	B_2O_3	$NaNH_2$, MgH_2	30	-	500	53.0	[56]
Qin	$NaBO_2 \bullet 2\,H_2O$	$Mg_{17}Al_{12}$	-	NaH	1 200	57.0	[59]
Le	$NaBO_2$	Mg, Al	-	-	2 160	99.7	[58]
	$NaBO_2 \bullet 4\,H_2O$		-	-	2 160	99.5	
Zhu	$Na_2B_4O_7 \bullet 10\,H_2O$	Mg, Na_2CO_3	23.75	-	1 800	78.9	[61]

Nevertheless, the $NaBH_4$ regeneration through ball milling is a multi-step process, since after the ball mill reaction, it is necessary to proceed to $NaBH_4$ extraction. In this additional step, it is necessary to use a solvent (e.g., isopropyl amine) to dissolve $NaBH_4$ from the final reaction mixture and then filter and dry to obtain the final $NaBH_4$.

The information regarding the conditions inside the mill, mainly the inside temperature achieved and the inside pressure atmosphere, are rarely provided. However, it is possible to conclude from the reported articles that the inside temperature is strongly influenced by the time of milling, the speed of milling, and the ball mill material composition. Moreover, despite the poor information, researchers clearly observed a preference for H_2 or Ar atmospheres inside the mill.

2.2.1. Effect of Time, Ball to Powder Ratio, and Excess of Reactant

Kong et al. [63] were one of the first authors to report the ball mill reaction of $NaBO_2$ with MgH_2 (Equation (10)). The influence of the following parameters was studied and optimized: $MgH_2/NaBO_2$ molar ratio, ball to powder ratio (BPR), and time of milling (t).

$$NaBO_2 + 2\,MgH_2 \;\rightarrow\; NaBH_4 + 2\,MgO \tag{10}$$
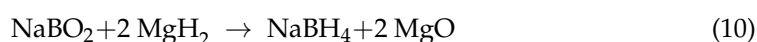
According to the authors, it took 1 h of ball milling to start to synthesize $NaBH_4$ and an extra hour for the conversion to be complete, with a yield of 71%. The authors also

concluded that BPR considerably influences the conversion yield, which is higher with the increase of BPR [63].

In 2010, Varin et al. [281] studied the milling of MgH_2 up to 100 h in H_2 and Ar atmospheres. Although it was concluded that both atmospheres did not influence MgH_2 molecules, the formation of $Mg(OH)_2$ was observed. However, in the H_2 atmosphere studies, the formed $Mg(OH)_2$ was naturally reduced to MgH_2 and water during the reaction, which allowed the authors to conclude that a H_2 atmosphere is more suitable to perform this process.

Çakanyldirim et al. [68] analyzed the effect of the milling time and the excess of MgH_2 in the synthesis of $NaBH_4$ through ball milling (Figure 8). The higher conversion yield reported (73.90%) was achieved after about 12 h of milling, with 27% excess of MgH_2. Lang et al. [53] studied the optimization of the amount of MgH_2 and reported similar results: a 71% yield of $NaBH_4$ after 12 h, with 35% of MgH_2 in excess.
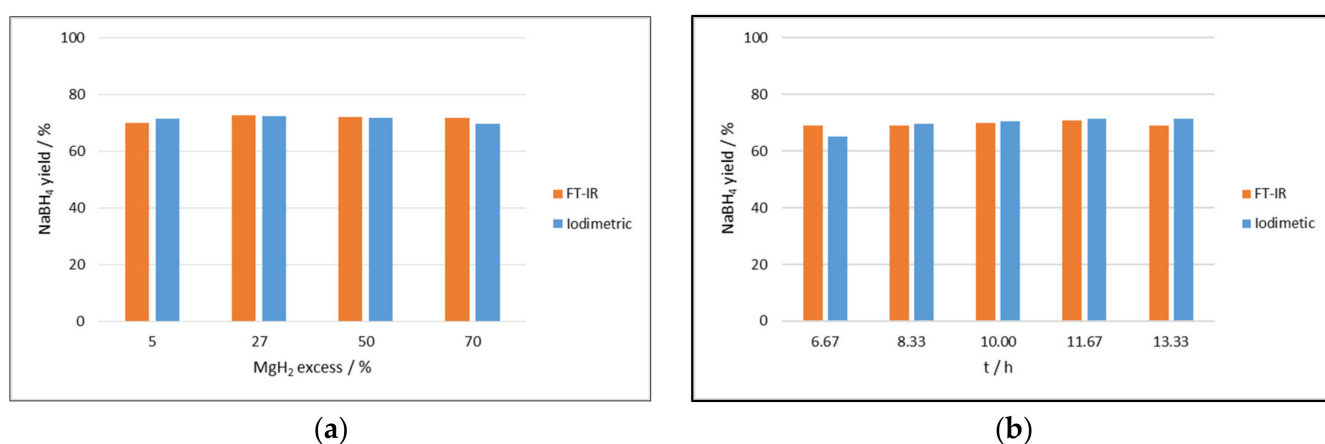
Figure 8. Values of $NaBH_4$ yield vs. (**a**) excess of MgH_2 and (**b**) *t*. Adapted from [68].

In 2017, Ouyang et al. [54] also studied the influence of the same parameters (milling time, excess of Mg and BPR) in the ball milling reaction of $NaBO_2$ with Mg, expecting to achieve higher yields by increasing those parameters. Nevertheless, the obtained conversion was below the expectations, and a maximum yield of 67.7% was reported after 15 h of milling, with 37.5% excess of Mg and a BPR of 30:1.

Furthermore, bearing in mind the borates structure presented in the $NaBH_4$ regeneration process, Ar et al. [56] reported ball mill studies where B_2O_3 reacts with $NaNH_2$ and MgH_2 (Equation (11)).

$$NaNH_2 + 3\,MgH_2 + B_2O_3 \ \rightarrow \ NaBH_4 + 3\,MgO + NH_4BH_4 \tag{11}$$
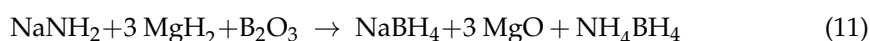
Several experiments were carried out with time of milling between 400 and 800 min. According to the authors, the optimal value for the time parameter is 500 min of milling, since above this value, researchers observed the formation of MgO instead of the desirable $NaBH_4$. Moreover, Ar et al. reported that the excess of MgH_2 is necessary since, at the end of the reaction, it was observed that a portion of this compound was fixed to the reactor walls and did not react. On the other hand, if the amount of MgH_2 is too high, it may decrease the contact between the reactants and, consequently, the $NaBH_4$ yields will be lower. Thus, the authors concluded that the optimal value for the amount of MgH_2 is 35% excess, which is in agreement with the results published by Çakanyldirim et al. [68].

In 2019, Le et al. [58] reacted $NaBO_2$ with a Mg-Al based alloy at 7 MPa H_2 with a BPR of 20:1. The reported results showed a conversion close to 100% after 36 h of milling. Moreover, the authors stated that the milling time could be reduced to 12 h without any considerable loss since, at that point, the $NaBH_4$ conversion was about 97%.

2.2.2. Effect of Additives and the Hydration of the Boron Compound

In addition to the influence of the parameters mentioned before, Çakanyldirim et al. [68] also studied the influence of several additives (Al, Na, and Na_2CO_3) and observed that the all the studied additives promoted a negative effect in the conversion yield (Figure 9).
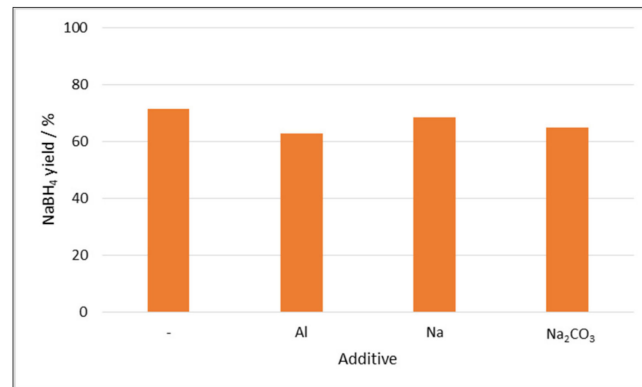

Figure 9. Effect of additive on the $NaBH_4$ yield. Adapted from [68].

Lang et al. [53] studied the influence of methanol (CH_3OH) as an additive to the $NaBO_2$-MgH_2 mixture and reported a slight increase of $NaBH_4$ conversion yield when the time of milling was superior to 10 h (Figure 10).

(**a**)　　　　　　　　　　　　　　　　　　(**b**)
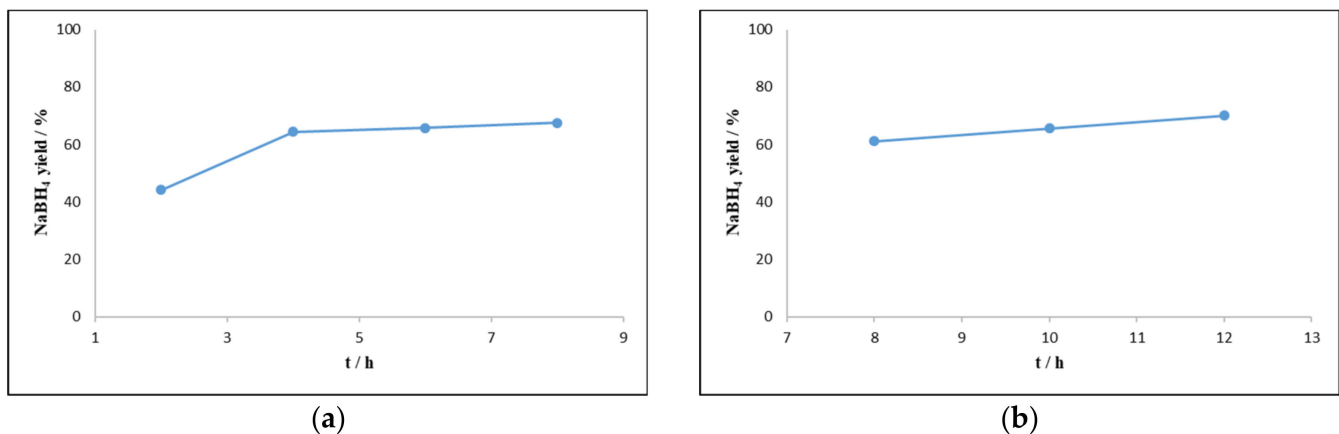
Figure 10. Values of $NaBH_4$ yield vs. t without (**a**) and with (**b**) CH_3OH. Adapted from [53].

Furthermore, several authors researched the possibility to regenerate $NaBH_4$ through ball milling using the borates in its hydrated form. Since the by-product of $NaBH_4$ hydrolysis is usually obtained in its hydrated form, and its dehydration is a high-energy consumption step, the possibility of ball milling the hydrated borates with high conversion yields makes this method more feasible. Thus, Huang et al. [52] studied the ball milling of the hydrated $NaBO_2$ with Mg and Mg_2Si (Equation (12)).

$$NaBO_2 \bullet 2\,H_2O + 2\,Mg + Mg_2Si \;\rightarrow\; NaBH_4 + 4\,MgO + Si \tag{12}$$
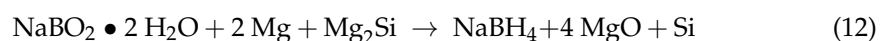
The reaction was performed in a vibrational ball mill under Ar atmosphere, and the time of milling as well as the reactants molar ratio were analyzed. The results presented a conversion yield of 86%, after 20 h, with a Mg:Mg_2Si:$NaBO_2$ molar ratio of 2.5:1:1.

Zhong et al. [57] also studied the recycling of the dehydrated sodium metaborate at room temperature in an Ar atmosphere; however, it was ball milled with Mg_2Si
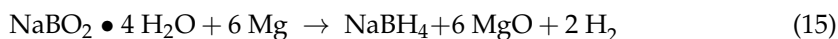
(Equation (13)). The process regenerates $NaBH_4$ with 78% yield, after 20 h of milling, with a $Mg_2Si/NaBO_2 \bullet 2H_2O$ molar ratio of 3:1.

$$NaBO_2 \bullet 2\,H_2O + 2\,Mg_2Si \rightarrow NaBH_4 + 4\,MgO + 2\,Si \tag{13}$$

Therefore, Zhong et al. [55] studied the recycling of tetrahydrated sodium metaborate in the same conditions and tried to optimize the reaction parameters. The results indicated a higher $NaBH_4$ yield of 74%, after 20 h, with a $Mg_2Si/NaBO_2 \bullet 4H_2O$ molar ratio of 4:1 [57].

Chen et al. [20] and Ouyang et al. [54] also studied the regeneration of $NaBH_4$ through the ball milling of $NaBO_2 \bullet 2H_2O$ and $NaBO_2 \bullet 4H_2O$. In the work published by Chen et al. [20], the borates were mixed with MgH_2. The experiments with $NaBO_2 \bullet 2H_2O$ were performed with 25% excess of MgH_2, and after 5 h, 84.5% yield was obtained. This value increased to 90% after 15 h. $NaBO_2 \bullet 4H_2O$ experiments were performed with 37.5% excess of MgH_2, and a maximum yield of 88.3%, achieved after 20 h, was reported.

In the work of Ouyang et al. [54], the experiments were carried out by reacting the borates with Mg (Equations (14) and (15)) in a high-energy ball mill at room temperature and pressure during 15 h. Both borates were mixed in a 1:12.5 molar ratio and 68.6% and 64.1% of $NaBH_4$ were obtained for the $NaBO_2 \bullet 2H_2O$ and $NaBO_2 \bullet 4H_2O$, respectively.

$$NaBO_2 \bullet 2\,H_2O + 4\,Mg \rightarrow NaBH_4 + 4\,MgO \tag{14}$$

$$NaBO_2 \bullet 4\,H_2O + 6\,Mg \rightarrow NaBH_4 + 6\,MgO + 2\,H_2 \tag{15}$$

The reaction of $NaBO_2 \bullet 2H_2O$ with $Mg_{17}Al_{12}$ in the presence of NaH, as additive, was studied by Qin et al. [59]. The authors optimized the parameters to 20 h of milling and 5 wt % of NaH, and the results showed that NaH had a considerable impact, since the reaction yield has doubled. Nevertheless, the obtained yield of 57.0% is considerably lower when compared with other values published in the literature.

The conversion of $NaBO_2 \bullet 4H_2O$ into $NaBH_4$ was also studied by Le et al. [58]. The borate was ball milled with a Mg-Al-based alloy, up to 36 h, at 0.1 MPa in an Ar atmosphere, with a BPR of 20:1, and it resulted in a conversion close to 100%.

Moreover, Zhu et al. [61] developed a low-cost system to close the $NaBH_4$-H_2 cycle based on the recycling of borax ($Na_2B_4O_7 \bullet 10H_2O$) with Na_2CO_3 and Mg (Equation (16)).

$$Na_2B_4O_7 \bullet 10\,H_2O + Na_2CO_3 + 20\,Mg \rightarrow 4\,NaBH_4 + 20\,MgO + CH_4 \tag{16}$$
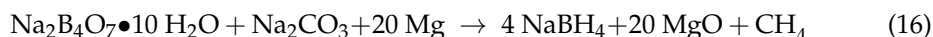
According to the authors, borax presents more similarities with $NaBH_4$ and has a reactivity higher than $NaBO_2$, which makes the regeneration of $NaBH_4$ easier. A maximum yield of 78.9% was obtained after 30 h of milling and 23.75% excess of Mg.

The $NaBH_4$ regeneration from $Na_2B_4O_7$ with MgH_2 was previously studied by Li et al. [37] in 2003. The experiments were carried out during 1 h, and the influence of three additives was studied: Na_2O_2, NaOH, and Na_2CO_3. The higher $NaBH_4$ conversion (78%) was achieved with the use of Na_2CO_3 as an additive.

2.2.3. Effect of the Mill

As referred above, there are different types of ball mills, which can also influence the reaction. The work published by Hsueh et al. [51] compares the results of $NaBH_4$ regeneration, which are presented in Equation (10) and were performed in a planetary ball mill and a shaker mill. Initially, the reactant mixture was ground for 6 h. Then, the experiments were performed by maintaining the amount of borate constant and increasing the excess of MgH_2 in both mills (Figure 11). Hsueh concluded that the shaker mill was more suitable than the planetary mill due to the difficulty of decomposing the reaction and promoting the $NaBH_4$ formation.
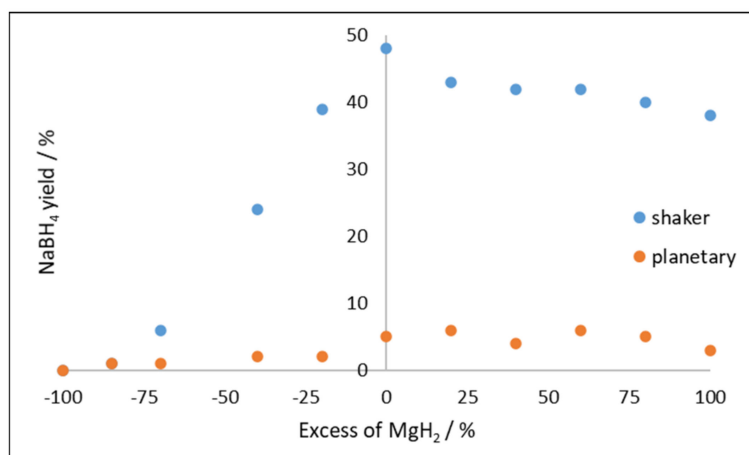
**Figure 11.** $NaBH_4$ dependence on the ball mill. Adapted from [51].

2.2.4. $NaBH_4$ Formation and Energy Efficiency

To better optimize the $NaBH_4$ synthesis, it is essential to understand $NaBH_4$ formation.

Ouyang et al. [54] studied the $NaBO_2 \bullet 2H_2O$ conversion into $NaBH_4$ and reported the structural rearrangement of the borate to $NaB(OH)_4$. The authors analyzed and described the ball mill reaction between $NaBO_2 \bullet 2H_2O$ and Mg and observed the formation of magnesium hydroxide ($Mg(OH)_2$), after 10 min of milling, as an intermediate in the reaction. This compound was also consumed after 1 h, as shown in Equation (17). The formation of $Mg(OH)_2$ plays an important role in this reaction, since its consumption during the process is responsible for its appearance of molecular hydrogen in the reaction medium. Those observations were also reported by Chen et al. [20], Huang et al. [52], and Qin et al. [59].

$$2\,Mg(OH)_2 + 2\,Mg \;\rightarrow\; 4\,MgO + 2\,H_2 \tag{17}$$
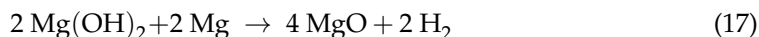
Zhong et al. [55] studied the reaction mechanisms of $NaBO_2 \bullet 4H_2O$ with Mg_2Si_2 and observed that $NaBO_2 \bullet 2H_2O$ and molecular hydrogen are formed in an intermediate step (Equation (18)). The authors reported that this step is important to promote the $NaBH_4$ regeneration yield.

$$NaBO_2 \bullet 4\,H_2O + Mg_2Si \;\rightarrow\; NaBO_2 \bullet 2\,H_2O + 2\,MgO + Si + H_2 \tag{18}$$
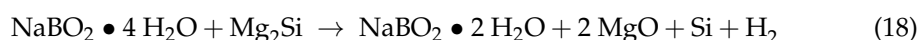
Furthermore, in 2014, Ouyang et al. [50] calculated the energy efficiency of the consumption/regeneration of $NaBH_4$ based on the recycling of $NaBO_2$ with MgH_2 in a high-speed vibrating mill. The results showed an energy efficiency of about 50%, which led to the conclusion that the system is feasible. Nevertheless, it is important to find novel techniques to improve the energy efficiency of this process, for example by reusing the heat released from the reactions.

2.3. Electrochemical Processes

As previously referred, the regeneration of $NaBH_4$ can occur through the input of electric energy. When it is applied in the right conditions, it can reduce or oxidize compounds. This process takes place inside an electrochemical cell, which consists of an anode (where oxidation reaction occurs) and a cathode (where reduction reaction occurs). The electrolyte is essential to warrant the correct means to promote the reduction and/or oxidation of any intended compound. Moreover, the electrochemical cell can also be used to convert the chemical energy of a compound in electric energy. These processes are desired due to its low energy consumption, cleanliness, and reduced cost compared to the thermochemical processes.

The regeneration of sodium borohydride from sodium metaborate can theoretically be obtained mainly through the direct electroreduction, as shown in Equations (19) and (20).
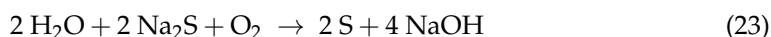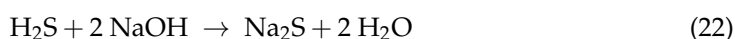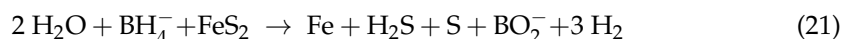
Cathode:

$$BO_2^- + 6H_2O + 8e^- \rightarrow BH_4^- + 8OH^- \tag{19}$$

Anode:

$$8OH^- \rightarrow 4H_2O + 2O_2 + 8e^-. \tag{20}$$
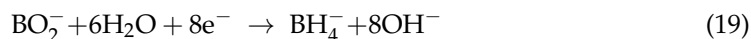
Although there have been claims of sodium borohydride synthesis, those results have not been replicated. This fact is associated with the formation of other compounds at the potentials applied at the cathode: for example, the water decomposition into H_2 and OH^-. Other electrochemical processes have been referred in the literature; however, the results obtained were similar to the direct electroreduction process. From what the authors could find, the first paper reported in the literature that confirms the $NaBH_4$ electrosynthesis was that of Zhu et al. [280,282] The authors reported a 15.1% current efficiency for the $NaBH_4$ electrosynthesis at atmospheric pressure and room temperature. The electrochemical cell was composed of a copper working electrode and a lead counter-electrode. Then, 1 mol/L H_2SO_4 solution was added to the anode and 1 mol/L NaOH and 0.2 mol/L $NaBO_2$ solution was added to the cathode. A cathodic peak was observed at -1.17 V, which is indicative of the BO_2^- reduction. Moreover, the increase of NaOH favors the electrosynthesis; however, excessive NaOH hardens the products' adsorption and conduction. Similar observation was made for the $NaBO_2$ concentration. Nevertheless, the process' efficiency is too low.

Efficient electrosynthesis of $NaBH_4$ was achieved by Shen et al. [276]. Given the use of $NaBH_4$ as an effective reducing agent and its high cost, the authors considered its electrosynthesis as an intermediate step in a desulfurization experiment of a coal water slurry at ambient pressure and room temperature. The electrochemical cell consisted of cathode and anode reservoirs separated by a KCl bridge. On the cathode side, a solution containing 0.1 to 0.45 mol/L $NaBO_2$ and 0.025 mol/L NaOH was initially added. Then, the coal was added, and the mix was maintained under stirring. The anode side was composed of an iron sulfide (FeS_2) and NaOH solution. The cathode was Pb and the anode was graphite (C). After the synthesis of BH_4^- in the cathode, its hydrolysis promoted the formation of hydrogen that reduced the FeS_2 to hydrogen sulfide (H_2S). Then, in the anode, the reaction with NaOH allowed the separation and removal of the sulfur. Equations (19) and (21)–(23) represent the primary reactions of the experiment.

$$2\,H_2O + BH_4^- + FeS_2 \rightarrow Fe + H_2S + S + BO_2^- + 3\,H_2 \tag{21}$$

$$H_2S + 2\,NaOH \rightarrow Na_2S + 2\,H_2O \tag{22}$$

$$2\,H_2O + 2\,Na_2S + O_2 \rightarrow 2\,S + 4\,NaOH \tag{23}$$

The BO_2^- concentration, electrolytic time, and voltage were studied between 6 and 30 g/L, 1 and 5 h, and 2.5 and 3.3 V, respectively. An optimal total sulfur removal (TSR) of 36.6% was achieved with 12 g/L, 4 h, and 3.0 V, respectively. Considering the BO_2^- as an intermediate essential step of the process, these parameters also benefited the BH_4^- formation.

The group continued the experiments in the years forward, and the electrochemical cell for the process was also optimized, promoting the TSR and the BH_4^- formation. Considering similar electrochemical cells—however, with a combined anode and cathode reservoir [277]—the group studied again the BO_2^- concentration, electrolytic time, and voltage. However, the optimal values did not suffer a considerable change (0.2 mol/L, 4 h and 3.5 V). Moreover, the NaOH concentration and electrodes were analyzed. The NaOH concentration was studied up to 0.375 mol/L. It was observed that 0.05 mol/L was the optimal value to promote the TSR, since further increase favored the pH and reduced the hydrogen generation from the BH_4^- hydrolysis. Regarding the electrodes, five anode/cathode combinations were considered: Pb/Pb, C/Pb, Ti/Pb, C/Cu, and C/Zn. The results were in favor of the last. In this way, graphite not only better promotes the TSR but also presents significant advantages to consider, such as easy to process, reduced waste and price, and good thermostability and conductivity.

Following that, the group studied the desulfurization of gasoline [278]. The electrochemical cell was composed of a BDD electrode in the cathode (working electrode) and a C electrode in the anode (counter electrode) and the cathode and anode were separated by a cation exchange membrane. After BH_4^- formation, a gasoline model was added to the cathode, and after the reaction, $NiCl_2 \bullet 6H_2O$ was added to the last. Moreover, pulse voltage was studied during the BH_4^- electrosynthesis, and the researchers observed a considerable increase in the TSR (almost twice higher). Cyclic voltammetry tests were performed using 0.15 mol/L $NaBO_2$, and a reduction peak was observed between -1.2 and -1.8 V, while the hydrogen and oxygen evolution reactions were initiated at voltage below -1.8 V and above 0.6 V, respectively. Forward and reverse pulse voltages were optimized considering these limits. Overall, the best TSR achieved was with a forward and reverse pulse of -1.5 V (applied after 1.5 s) and 0.3 V (applied after 0.5 s), respectively, which were explained considering that it avoided at maximum the hydrogen evolution reaction (happening simultaneously with the BH_4^- electrosynthesis), and the reverse pulse voltage was enough to attract the BO_2^- ions to the BDD electrode while avoiding the oxygen evolution reaction. Regarding the BH_4^- electrosynthesis step, other cell parameters were also studied: $NaBO_2$ and NaOH concentrations, electrolytic time, and stirring rate. First, 0.15 mol/L of $NaBO_2$ was maintained as an optimized value, since higher concentrations did not contribute to further increasing the TSR. The optimal NaOH concentration was 0.1 mol/L, since although it is important to maintain the cell as alkaline to avoid too fast BH_4^- hydrolysis, its excess reduces the oxygen evolution voltage, promoting it and making the BO_2^- transfer to the BDD electrode difficult. Excess stirring rate was also observed to affect the BO_2^- transfer, so 400 rpm was the best value defined. The higher efficiency of the desulfurization process was 97%.

More recently, the group studied the addition of ionic liquids (IL) to the desulfurization process of gasoline. The use of ILs as electrolyte has been increasingly reported in the literature due to their characteristics, which make them more suitable than water and other electrolytes. In the BH_4^- electrosynthesis, they avoid the need to control the hydrogen and oxygen evolution reactions and present a wider electrochemical window. Moreover, they can be recovered at the end of the experiment. Similar electrochemical cells to previous study were considered by the group. In this experiment, the working electrode was a glassy carbon electrode, and the counter-electrode was a Pt wire. The IL was added to both the electrodes reservoirs in the cell, while water was only present due to the $NaBO_2$ solution and the need of hydrogen for the BH_4^- electrosynthesis. Cyclic voltammetry tests were performed, which indicated a reduction peak between -2.2 and -3.0 V, which was associated to the BH_4^-. Moreover, the hydrogen and oxygen evolution reactions were observed at -3.0 and 2.0 V, respectively. As expected, the electrochemical window using IL is wider than that of water. Forward and reverse pulse voltage was equally applied, and their parameters were optimized. The optimal values to promote the BH_4^- electrosynthesis and the TSR (97%) were a forward pulse voltage of -2.6 V (0.6 s forward pulse time), reverse pulse voltage of 0.5 V (0.5 s reverse pulse time), and pull-off time of 0.8 s. The times that were associated to the ones referred and applied were the forward and reverse pulse voltage and turn-off. If they are too long, the reactions do not benefit; if they are too short, the reactions do not occur.

Based on these results of the group and assuming that an efficient electrosynthesis of BH_4^- is essential for the desulfurization of the coal water slurry, it is possible to affirm that $NaBH_4$ can be obtained through an electrochemical process and that it is an alternative to the thermo- and mechano-chemical processes. Nevertheless, it is essential to promote the $NaBH_4$ regeneration as the main aim instead of an intermediate step in another process. In addition, as noted in the thermo and mechano-chemical regeneration processes section, the study of hydrated $NaBO_2$ is crucial, since it is the main by-product of the $NaBH_4$ hydrolysis and it is demonstrated that its recycling is not as easy. Considering the practicability and possibly low cost of these processes, the electrochemical regeneration of $NaBH_4$ must be

considered. In that order, both the use of ILs and the pulse voltage are improvements to the process and must be studied.

3. Conclusions

Sodium borohydride stands as a promising hydrogen carrier for on-demand power supply. Despite the DOE no-go recommendation in 2007 for $NaBH_4$ hydrolysis for onboard applications, over 13 years later, several findings and improvements have been made in this area. Therefore, $NaBH_4$-H_2-PEMFC systems have emerged as a feasible candidate to supply energy for portable applications, maritime applications, as well as an off-grid technology capable of providing an electricity supply in emerging countries and locations without a reliable grid. Nevertheless, closing the $NaBH_4$-H_2 cycle is strongly dependent on the regeneration of $NaBH_4$. In this overview, a survey of alternative methods to recycle $NaBH_4$ hydrolysis by-products was made, and three types of methods stands out: thermo-, mechano-, and electrochemical. Although the first published studies were mostly dedicated to thermochemical processes, since they present high conversion yields, over the years, they have been replaced by mechano-chemical processes. This transition shows a concern for the development of environmentally friendly methods, since mechano-chemical processes use a mechanical source of energy instead of heat and, consequently, do not require high temperatures and pressures. Nevertheless, although it is possible to obtain $NaBH_4$ conversion yields as high as in thermochemical processes, they require high milling times to achieve those same yields. Moreover, both methods typically use expensive hydrides, such as MgH_2, to promote the $NaBH_4$ synthesis. Thus, electrochemical processes arise as a promising low-cost and clean alternative. Although the regeneration of $NaBH_4$ from $NaBO_2$ has been confirmed, as an intermediate step in a desulfurization experiment, the study of this process is very limited, and published articles dedicated to electrochemical methods to regenerate $NaBH_4$ are rare. There are a few issues in this process that need to be overcome: mainly, the water decomposition and the formation of other by-products. Thus, further studies to find alternative electrochemical reactions are needed in order to take advantage of the potential of this process. Therefore, the rehydrogenation of the borates formed in the $NaBH_4$ regeneration is a technology that needs urgent improvement, and it is essential to close the $NaBH_4$-H_2 cycle and, consequently, implement $NaBH_4$-H_2-PEMFC on-demand systems. After all, these systems may be the future off-grid technology that would address the increasing renewable energy supply.

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Conflicts of Interest: The authors declare no conflict of interest.

References

1. Fazelpour, F.; Markarian, E.; Soltani, N. Wind energy potential and economic assessment of four locations in Sistan and Balouchestan province in Iran. *Renew. Energy* **2017**, *109*, 646–667. [CrossRef]
2. Hanley, E.S.; Deane, J.; Gallachóir, B.P.Ó. The role of hydrogen in low carbon energy futures—A review of existing perspectives. *Renew. Sustain. Energy Rev.* **2018**, *82*, 3027–3045. [CrossRef]
3. Amendola, S.C. A safe, portable, hydrogen gas generator using aqueous borohydride solution and Ru catalyst. *Int. J. Hydrog. Energy* **2000**, *25*, 969–975. [CrossRef]
4. Arzac, G.; Fernandez, A.; Justo, A.; Sarmiento, B.; Jimenez, M.M. Optimized hydrogen generation in a semicontinuous sodium borohydride hydrolysis reactor for a 60W-scale fuel cell stack. *J. Power Sources* **2011**, *196*, 4388–4395. [CrossRef]
5. Sopian, K.; Daud, W.R.W. Challenges and future developments in proton exchange membrane fuel cells. *Renew. Energy* **2006**, *31*, 719–727. [CrossRef]

6. Lototskyy, M.V.; Tolj, I.; Pickering, L.; Sita, C.; Barbir, F.; Yartys, V. The use of metal hydrides in fuel cell applications. *Prog. Nat. Sci.* **2017**, *27*, 3–20. [CrossRef]

7. Dawood, F.; Anda, M.; Shafiullah, G. Hydrogen production for energy: An overview. *Int. J. Hydrog. Energy* **2020**, *45*, 3847–3869. [CrossRef]

8. Veras, T.D.S.; Mozer, T.S.; da Costa Rubim Messeder dos Santos, D.; César, A. Hydrogen: Trends, production and characterization of the main process worldwide. *Int. J. Hydrog. Energy* **2017**, *42*, 2018–2033. [CrossRef]

9. Baykara, S.Z. Hydrogen: A brief overview on its sources, production and environmental impact. *Int. J. Hydrog. Energy* **2018**, *43*, 10605–10614. [CrossRef]

10. Demirci, U.B.; Akdim, O.; Hannauer, J.; Chamoun, R.; Miele, P. Cobalt, a reactive metal in releasing hydrogen from sodium borohydride by hydrolysis: A short review and a research perspective. *Sci. China Ser. B Chem.* **2010**, *53*, 1870–1879. [CrossRef]

11. Nunes, H.; Ferreira, M.; Rangel, C.; Pinto, A. Hydrogen generation and storage by aqueous sodium borohydride (NaBH4) hydrolysis for small portable fuel cells (H2–PEMFC). *Int. J. Hydrog. Energy* **2016**, *41*, 15426–15432. [CrossRef]

12. Amendola, S.C.; Sharp-Goldman, S.L.; Janjua, M.; Kelly, M.T.; Petillo, P.J.; Binder, M. An ultrasafe hydrogen generator: Aqueous, alkaline borohydride solutions and Ru catalyst. *ACS Div. Fuel Chem. Prepr.* **1999**, *44*, 864–866. [CrossRef]

13. Demirci, U.B.; Miele, P. Sodium tetrahydroborate as energy/hydrogen carrier, its history. *Comptes Rendus Chim.* **2009**, *12*, 943–950. [CrossRef]

14. Santos, D.; Sequeira, C. Sodium borohydride as a fuel for the future. *Renew. Sustain. Energy Rev.* **2011**, *15*, 3980–4001. [CrossRef]

15. Schlesinger, H.I.; Brown, H.C.; Finholt, A.E. The Preparation of Sodium Borohydride by the High Temperature Reaction of Sodium Hydride with Borate Esters1. *J. Am. Chem. Soc.* **1953**, *75*, 205–209. [CrossRef]

16. Kojima, Y.; Suzuki, K.-I.; Fukumoto, K.; Sasaki, M.; Yamamoto, T.; Kawai, Y.; Hayashi, H. Hydrogen generation using sodium borohydride solution and metal catalyst coated on metal oxide. *Int. J. Hydrog. Energy* **2002**, *27*, 1029–1034. [CrossRef]

17. Brack, P.; Dann, S.E.; Wijayantha, K.G.U. Heterogeneous and homogenous catalysts for hydrogen generation by hydrolysis of aqueous sodium borohydride (NaBH4) solutions. *Energy Sci. Eng.* **2015**, *3*, 174–188. [CrossRef]

18. Marrero-Alfonso, E.Y.; Gray, J.R.; Davis, T.A.; Matthews, M.A. Minimizing water utilization in hydrolysis of sodium borohydride: The role of sodium metaborate hydrates. *Int. J. Hydrog. Energy* **2007**, *32*, 4723–4730. [CrossRef]

19. Stepanov, N.; Uvarov, V.; Popov, I.; Sasson, Y. Study of by-product of NaBH4 hydrolysis and its behavior at a room temperature. *Int. J. Hydrog. Energy* **2008**, *33*, 7378–7384. [CrossRef]

20. Chen, W.; Ouyang, L.; Liu, J.; Yao, X.; Wang, H.; Liu, Z.; Zhu, M. Hydrolysis and regeneration of sodium borohydride (NaBH4)—A combination of hydrogen production and storage. *J. Power Sources* **2017**, *359*, 400–407. [CrossRef]

21. 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. Hydrog. Energy* **2015**, *40*, 2673–2691. [CrossRef]

22. Demirci, U.B. Impact of H.I. Schlesinger's discoveries upon the course of modern chemistry on B-(N-)H hydrogen carriers. *Int. J. Hydrog. Energy* **2017**, *42*, 21048–21062. [CrossRef]

23. Lai, Q.; Alligier, D.; Aguey-Zinsou, K.-F.; Demirci, U.B. Hydrogen generation from a sodium borohydride-nickel core@shell structure under hydrolytic conditions. *Nanoscale Adv.* **2019**, *1*, 2707–2717. [CrossRef]

24. Tignol, P.; Demirci, U.B. Nickel-based catalysts for hydrogen evolution by hydrolysis of sodium borohydride: From structured nickel hydrazine nitrate complexes to reduced counterparts. *Int. J. Hydrog. Energy* **2019**, *44*, 14207–14216. [CrossRef]

25. Aydın, K.; Kulaklı, B.N.; Filiz, B.C.; Alligier, D.; Demirci, U.B.; Figen, A.K. Closing the hydrogen cycle with the couple sodium borohydride-methanol, via the formation of sodium tetramethoxyborate and sodium metaborate. *Int. J. Energy Res.* **2020**, *44*, 11405–11416. [CrossRef]

26. Demirci, U.; Garin, F. Kinetics of Ru-promoted sulphated zirconia catalysed hydrogen generation by hydrolysis of sodium tetrahydroborate. *J. Mol. Catal. A Chem.* **2008**, *279*, 57–62. [CrossRef]

27. Ferreira, M.; Gales, L.; Fernandes, V.; Rangel, C.M.; Pinto, A. Alkali free hydrolysis of sodium borohydride for hydrogen generation under pressure. *Int. J. Hydrog. Energy* **2010**, *35*, 9869–9878. [CrossRef]

28. Demirci, U.B.; Miele, P. Cobalt-based catalysts for the hydrolysis of NaBH4 and NH3BH3. *Phys. Chem. Chem. Phys.* **2014**, *16*, 6872–6885. [CrossRef]

29. Kahri, H.; Flaud, V.; Touati, R.; Miele, P.; Demirci, U.B. Reaction intermediate/product-induced segregation in cobalt–copper as the catalyst for hydrogen generation from the hydrolysis of sodium borohydride. *RSC Adv.* **2016**, *6*, 102498–102503. [CrossRef]

30. Eugénio, S.; Demirci, U.B.; Silva, T.M.; Carmezim, M.J.; Montemor, M.F. Copper-cobalt foams as active and stable catalysts for hydrogen release by hydrolysis of sodium borohydride. *Int. J. Hydrog. Energy* **2016**, *41*, 8438–8448. [CrossRef]

31. Koska, A.; Toshikj, N.; Hoett, S.; Bernaud, L.; Demirci, U.B. Volcano Plot for Bimetallic Catalysts in Hydrogen Generation by Hydrolysis of Sodium Borohydride. *J. Chem. Educ.* **2017**, *94*, 1163–1166. [CrossRef]

32. Demirci, U.B. About the Technological Readiness of the H2 Generation by Hydrolysis of B(-N)-H Compounds. *Energy Technol.* **2018**, *6*, 470–486. [CrossRef]

33. Demirci, Ü.B. Sodium borohydride for the near-future energy: A rough diamond for Turkey. *Turk. J. Chem.* **2018**, *42*, 193–220. [CrossRef]

34. U.S. Department of Energy. *Go/No-Go Recommendation for Sodium Borohydride for On-Board Vehicular Hydrogen Storage*; U.S. Department of Energy: Washington, DC, USA, 2007.

35. Demirci, U.; Akdim, O.; Miele, P. Ten-year efforts and a no-go recommendation for sodium borohydride for on-board automotive hydrogen storage. *Int. J. Hydrog. Energy* **2009**, *34*, 2638–2645. [CrossRef]

36. Ouyang, L.; Zhong, H.; Li, H.-W.; Zhu, M. A Recycling Hydrogen Supply System of NaBH4 Based on a Facile Regeneration Process: A Review. *Inorganics* **2018**, *6*, 10. [CrossRef]

37. Li, Z.P.; Morigazaki, N.; Liu, B.H.; Suda, S. Preparation of sodium borohydride by the reaction of MgH$_2$ with dehydrated borax through ball milling at room temperature. *J. Alloys Compd.* **2003**, *349*, 232–236. [CrossRef]

38. Kojima, Y.; Haga, T. Recycling process of sodium metaborate to sodium borohydride. *Int. J. Hydrog. Energy* **2003**, *28*, 989–993. [CrossRef]

39. Liu, B.H.; Li, Z.P.; Zhu, J.K.; Morigasaki, N.; Suda, S. Sodium Borohydride Synthesis by Reaction of Na$_2$O Contained Sodium Borate with Al and Hydrogen. *Energy Fuels* **2007**, *21*, 1707–1711. [CrossRef]

40. Liu, B.; Li, Z.; Morigasaki, N.; Suda, S. Kinetic characteristics of sodium borohydride formation when sodium meta-borate reacts with magnesium and hydrogen. *Int. J. Hydrog. Energy* **2008**, *33*, 1323–1328. [CrossRef]

41. Sanli, A.E.; Kayacan, I.; Uysal, B.Z.; Aksu, M.L. Recovery of borohydride from metaborate solution using a silver catalyst for application of direct rechargable borohydride/peroxide fuel cells. *J. Power Sources* **2010**, *195*, 2604–2607. [CrossRef]

42. Santos, D.; Sequeira, C. On the electrosynthesis of sodium borohydride. *Int. J. Hydrog. Energy* **2010**, *35*, 9851–9861. [CrossRef]

43. Çakanyildirim, Ç.; Gürü, M. The Production of NaBH4 from Its Elements by Mechano-chemical Reaction and Usage in Hydrogen Recycle. *Energy Sources Part A Recover. Util. Environ. Eff.* **2011**, *33*, 1912–1920. [CrossRef]

44. Kayacan, I.; Dogan, Ö.M.; Uysal, B.Z. Effect of magnesium on sodium borohydride synthesis from anhydrous borax. *Int. J. Hydrog. Energy* **2011**, *36*, 7410–7415. [CrossRef]

45. Çakanyildirim, Ç.; Gürü, M. The Processing of NaBH$_4$ from Na$_2$B$_4$O$_7$ by Mechano-chemical Synthesis and Its Catalytic Dehydrogenation. *Energy Sources Part A Recover. Util. Environ. Eff.* **2012**, *34*, 1104–1113. [CrossRef]

46. Eom, K.; Cho, E.; Kim, M.; Oh, S.; Nam, S.-W.; Kwon, H. Thermochemical production of sodium borohydride from sodium metaborate in a scaled-up reactor. *Int. J. Hydrog. Energy* **2013**, *38*, 2804–2809. [CrossRef]

47. Figen, A.K.; Pişkin, S. Microwave assisted green chemistry approach of sodium metaborate dihydrate (NaBO$_2$·2H$_2$O) synthesis and use as raw material for sodium borohydride (NaBH$_4$) thermochemical production. *Int. J. Hydrog. Energy* **2013**, *38*, 3702–3709. [CrossRef]

48. Ou, T.; Giuliano, A.; Panizza, M.; Barbucci, A.; Cerisola, G. Thermochemical recycling of hydrolyzed NaBH4. Part I: In-Situ and Ex-Situ evaluations. *Int. J. Hydrog. Energy* **2013**, *38*, 15269–15274. [CrossRef]

49. Ou, T.; Panizza, M.; Barbucci, A. Thermochemical recycling of hydrolyzed NaBH4. Part II: Systematical study of parameters dependencies. *Int. J. Hydrog. Energy* **2013**, *38*, 15940–15945. [CrossRef]

50. Ouyang, L.; Zhong, H.; Li, Z.; Cao, Z.; Wang, H.; Liu, J.; Zhu, X.; Zhu, M. Low-cost method for sodium borohydride regeneration and the energy efficiency of its hydrolysis and regeneration process. *J. Power Sources* **2014**, *269*, 768–772. [CrossRef]

51. Hsueh, C.-L.; Liu, C.-H.; Chen, B.-H.; Chen, C.-Y.; Kuo, Y.-C.; Hwang, K.-J.; Ku, J.-R. Regeneration of spent-NaBH4 back to NaBH4 by using high-energy ball milling. *Int. J. Hydrog. Energy* **2009**, *34*, 1717–1725. [CrossRef]

52. Huang, M.; Zhong, H.; Ouyang, L.; Peng, C.; Zhu, X.; Zhu, W.; Fang, F.; Zhu, M. Efficient regeneration of sodium borohydride via ball milling dihydrate sodium metaborate with magnesium and magnesium silicide. *J. Alloys Compd.* **2017**, *729*, 1079–1085. [CrossRef]

53. Lang, C.; Jia, Y.; Liu, J.; Wang, H.; Ouyang, L.; Zhu, M.; Yao, X. NaBH$_4$ regeneration from NaBO$_2$ by high-energy ball milling and its plausible mechanism. *Int. J. Hydrogen Energy* **2017**, *42*, 13127–13135. [CrossRef]

54. Ouyang, L.; Chen, W.; Liu, J.; Felderhoff, M.; Wang, H.; Zhu, M. Enhancing the Regeneration Process of Consumed NaBH4for Hydrogen Storage. *Adv. Energy Mater.* **2017**, *7*, 1–8. [CrossRef]

55. Zhong, H.; Ouyang, L.Z.; Ye, J.S.; Liu, J.W.; Wang, H.; Yao, X.; Zhu, M. An one-step approach towards hydrogen production and storage through regeneration of NaBH$_4$. *Energy Storage Mater.* **2017**, *7*, 222–228. [CrossRef]

56. Ar, I.; Güler, Ö.U.; Gürü, M. Synthesis and characterization of sodium borohydride and a novel catalyst for its dehydrogenation. *Int. J. Hydrog. Energy* **2018**, *43*, 20214–20233. [CrossRef]

57. Zhong, H.; Ouyang, L.; Liu, J.; Peng, C.; Zhu, X.; Zhu, W.; Fang, F.; Zhu, M. Sodium borohydride regeneration via direct hydrogen transformation of sodium metaborate tetrahydrate. *J. Power Sources* **2018**, *390*, 71–77. [CrossRef]

58. Le, T.T.; Pistidda, C.; Puszkiel, J.; Milanese, C.; Garroni, S.; Emmler, T.; Capurso, G.; Gizer, G.; Klassen, T.; Dornheim, M. Efficient Synthesis of Alkali Borohydrides from Mechanochemical Reduction of Borates Using Magnesium-Aluminum-Based Waste. *Metals* **2019**, *9*, 1061. [CrossRef]

59. Qin, C.; Ouyang, L.; Wang, H.; Liu, J.; Shao, H.; Zhu, M. Regulation of high-efficient regeneration of sodium borohydride by magnesium-aluminum alloy. *Int. J. Hydrog. Energy* **2019**, *44*, 29108–29115. [CrossRef]

60. Zhong, H.Z.; Ouyang, L.; Zeng, M.; Liu, J.; Wang, H.; Shao, H.; Felderhoff, M.; Zhu, M. Realizing facile regeneration of spent NaBH4 with Mg–Al alloy. *J. Mater. Chem. A* **2019**, *7*, 10723–10728. [CrossRef]

61. Zhu, Y.; Ouyang, L.; Zhong, H.; Liu, J.; Wang, H.; Shao, H.; Huang, Z.; Zhu, M. Closing the Loop for Hydrogen Storage: Facile Regeneration of NaBH 4 from its Hydrolytic Product. *Angew. Chem. Int. Ed.* **2020**, *59*, 8623–8629. [CrossRef]

62. Kemmitt, T.; Gainsford, G. Regeneration of sodium borohydride from sodium metaborate, and isolation of intermediate compounds. *Int. J. Hydrog. Energy* **2009**, *34*, 5726–5731. [CrossRef]

63. Kong, L.; Cui, X.; Jin, H.; Wu, J.; Du, H.; Xiong, T. Mechanochemical Synthesis of Sodium Borohydride by Recycling Sodium Metaborate. *Energy Fuels* **2009**, *23*, 5049–5054. [CrossRef]

64. Liu, B.H.; Li, Z.P.; Suda, S. Influences of alkali in borates on recovery of sodium borohydride. *J. Alloys Compd.* **2009**, *474*, L6–L9. [CrossRef]

65. Liu, B.H.; Li, Z.P.; Suda, S. Improving MgH2 formation kinetics and its effect on NaBH4 synthesis. *J. Alloys Compd.* **2009**, *474*, 321–325. [CrossRef]

66. Liu, B.H.; Li, Z.P.; Zhu, J.K. Sodium borohydride formation when Mg reacts with hydrous sodium borates under hydrogen. *J. Alloys Compd.* **2009**, *476*, L16–L20. [CrossRef]

67. Zhang, H.; Zheng, S.; Fang, F.; Chen, G.; Sang, G.; Sun, D. Synthesis of NaBH4 based on a solid-state reaction under Ar atmosphere. *J. Alloys Compd.* **2009**, *484*, 352–355. [CrossRef]

68. Çakanyıldırım, Ç.; Gürü, M. Processing of NaBH4 from NaBO2 with MgH2 by ball milling and usage as hydrogen carrier. *Renew. Energy* **2010**, *35*, 1895–1899. [CrossRef]

69. Moussa, G.; Moury, R.; Demirci, U.B.; Şener, T.; Miele, P. Boron-based hydrides for chemical hydrogen storage. *Int. J. Energy Res.* **2013**, *37*, 825–842. [CrossRef]

70. Abdelhamid, H.N. A review on hydrogen generation from the hydrolysis of sodium borohydride. *Int. J. Hydrogen Energy* **2021**, *46*, 726–765. [CrossRef]

71. Wu, Y.; Kelly, M.T.; Ortega, J.V. *Review of Chemical Processes for the Synthesis of Sodium Borohydride*; Under DOE Cooperative Agreement DE-FC36-04GO14008; Millennium Cell Inc.: Eatontown, NJ, USA, 2004.

72. Çakanyıldırım, Ç.; Guru, M. Hydrogen cycle with sodium borohydride. *Int. J. Hydrogen Energy* **2008**, *33*, 4634–4639. [CrossRef]

73. Liu, B.; Li, Z. A review: Hydrogen generation from borohydride hydrolysis reaction. *J. Power Source* **2009**, *187*, 527–534. [CrossRef]

74. 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]

75. 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]

76. Wang, K.; Pan, Z.; Yu, X. Metal B-N-H hydrogen-storage compound: Development and perspectives. *J. Alloys Compd.* **2019**, *794*, 303–324. [CrossRef]

77. Li, S.-C.; Wang, F.-C. The development of a sodium borohydride hydrogen generation system for proton exchange membrane fuel cell. *Int. J. Hydrogen Energy* **2016**, *41*, 3038–3051. [CrossRef]

78. Li, X.; Fan, G.; Zeng, C. Synthesis of ruthenium nanoparticles deposited on graphene-like transition metal carbide as an effective catalyst for the hydrolysis of sodium borohydride. *Int. J. Hydrogen Energy* **2014**, *39*, 14927–14934. [CrossRef]

79. Li, Y.; Hou, X.; Wang, J.; Feng, X.; Cheng, L.; Zhang, H.; Han, S. Co-Mo nanoparticles loaded on three-dimensional graphene oxide as efficient catalysts for hydrogen generation from catalytic hydrolysis of sodium borohydride. *Int. J. Hydrogen Energy* **2019**, *44*, 29075–29082. [CrossRef]

80. Li, Y.; Zhang, X.; Zhang, Q.; Zheng, J.; Zhang, N.; Chen, B.H.; Smith, K.J. Activity and kinetics of ruthenium supported catalysts for sodium borohydride hydrolysis to hydrogen. *RSC Adv.* **2016**, *6*, 29371–29377. [CrossRef]

81. Li, Z.; Li, H.; Wang, L.; Liu, T.; Zhang, T.; Wang, G.; Xie, G. Hydrogen generation from catalytic hydrolysis of sodium borohydride solution using supported amorphous alloy catalysts (Ni-Co-P/γ-Al$_2$O$_3$). *Int. J. Hydrogen Energy* **2014**, *39*, 14935–14941. [CrossRef]

82. Li, Z.; Wang, L.; Zhang, Y.; Xie, G. Properties of Cu Co P/γ-Al$_2$O$_3$ catalysts for efficient hydrogen generation by hydrolysis of alkaline NaBH 4 solution. *Int. J. Hydrogen Energy* **2017**, *42*, 5749–5757. [CrossRef]

83. Liang, Z.; Li, Q.; Li, F.; Zhao, S.; Xia, X. Hydrogen generation from hydrolysis of NaBH4 based on high stable NiB/NiFe$_2$O$_4$ catalyst. *Int. J. Hydrogen Energy* **2017**, *42*, 3971–3980. [CrossRef]

84. Liao, J.; Huang, H. Magnetic sensitive *Hericium erinaceus* residue chitin/Cu hydrogel nanocomposites for H2 generation by catalyzing NaBH4 hydrolysis. *Carbohydr. Polym.* **2020**, *229*, 115426. [CrossRef]

85. Lin, K.-Y.A.; Chang, H.-A. Efficient hydrogen production from NaBH4 hydrolysis catalyzed by a magnetic cobalt/carbon composite derived from a zeolitic imidazolate framework. *Chem. Eng. J.* **2016**, *296*, 243–251. [CrossRef]

86. Liu, Q.; Zhang, J.; Du, X.; Mi, G.; Dong, Y. Immobilization of Amorphous NiB Nanoparticles on Mesoporous Supports: Superior Catalysis for Controllably Hydrolyzing NaBH4 to Release H2. *J. Chem.* **2019**, *2019*, 4372794. [CrossRef]

87. Liu, T.; Wang, K.; Du, G.; Asiri, A.M.; Sun, X. Self-supported CoP nanosheet arrays: A non-precious metal catalyst for efficient hydrogen generation from alkaline NaBH4 solution. *J. Mater. Chem. A* **2016**, *4*, 13053–13057. [CrossRef]

88. Liu, Y.; Guo, H.; Sun, K.; Jiang, J. Magnetic CoOx@C-Reduced graphene oxide composite with catalytic activity towards hydrogen generation. *Int. J. Hydrogen Energy* **2019**, *44*, 28163–28172. [CrossRef]

89. Liu, Y.; Han, G.; Zhang, X.; Xing, C.; Du, C.; Cao, H.; Li, B. Co-Co3O4@carbon core–shells derived from metal−organic framework nanocrystals as efficient hydrogen evolution catalysts. *Nano Res.* **2017**, *10*, 3035–3048. [CrossRef]

90. Loghmani, M.H.; Shojaei, A.F. Hydrogen production through hydrolysis of sodium borohydride: Oleic acid stabilized Co–La–Zr–B nanoparticle as a novel catalyst. *Energy* **2014**, *68*, 152–159. [CrossRef]

91. 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]

92. Luo, C.; Fu, F.; Yang, X.; Wei, J.; Wang, C.; Zhu, J.; Huang, D.; Astruc, D.; Zhao, P. Highly Efficient and Selective Co@ZIF-8 Nanocatalyst for Hydrogen Release from Sodium Borohydride Hydrolysis. *ChemCatChem* **2019**, *11*, 1643–1649. [CrossRef]

93. Ma, T.; Qiu, Y.; Zhang, Y.; Ji, X.; Hu, P.-A. Iron-Doped Ni5P4 Ultrathin Nanoporous Nanosheets for Water Splitting and On-Demand Hydrogen Release via NaBH4 Hydrolysis. *ACS Appl. Nano Mater.* **2019**, *2*, 3091–3099. [CrossRef]

94. Makiabadi, M.; Shamspur, T.; Mostafavi, A. Performance improvement of oxygen on the carbon substrate surface for dispersion of cobalt nanoparticles and its effect on hydrogen generation rate via NaBH4 hydrolysis. *Int. J. Hydrogen Energy* **2020**, *45*, 1706–1718. [CrossRef]

95. Manna, J.; Roy, B.; Pareek, D.; Sharma, P. Hydrogen generation from NaBH4 hydrolysis using Co-B/AlPO4 and Co-B/bentonite catalysts. *Catal. Struct. React.* **2017**, *3*, 157–164. [CrossRef]

96. Manna, J.; Roy, B.; Sharma, P. Efficient hydrogen generation from sodium borohydride hydrolysis using silica sulfuric acid catalyst. *J. Power Source* **2015**, *275*, 727–733. [CrossRef]

97. Manna, J.; Roy, B.; Vashistha, M.; Sharma, P. Effect of Co+2/BH4-ratio in the synthesis of Co-B catalysts on sodium borohydride hydrolysis. *Int. J. Hydrogen Energy* **2014**, *39*, 406–413. [CrossRef]

98. Minkina, V.G.; Shabunya, S.I.; Kalinin, V.I.; Smirnova, A. Hydrogen generation from sodium borohydride solutions for stationary applications. *Int. J. Hydrogen Energy* **2016**, *41*, 9227–9233. [CrossRef]

99. Mostajeran, M.; Prévot, V.; Mal, S.S.; Mattiussi, E.; Davis, B.R.; Baker, R.T. Base-metal catalysts based on porous layered double hydroxides for alkaline-free sodium borohydride hydrolysis. *Int. J. Hydrogen Energy* **2017**, *42*, 20092–20102. [CrossRef]

100. Muir, S.S.; Chen, Z.; Wood, B.J.; Wang, L.; Lu, G.; Yao, X. New electroless plating method for preparation of highly active Co-B catalysts for NaBH4 hydrolysis. *Int. J. Hydrogen Energy* **2014**, *39*, 414–425. [CrossRef]

101. Nabid, M.R.; Bide, Y.; Fereidouni, N. Boron and nitrogen co-doped carbon dots as a metal-free catalyst for hydrogen generation from sodium borohydride. *N. J. Chem.* **2016**, *40*, 8823–8828. [CrossRef]

102. Narasimharao, K.; Abu-Zied, B.M.; Alfaifi, S.Y. Cobalt oxide supported multi wall carbon nanotube catalysts for hydrogen production via sodium borohydride hydrolysis. *Int. J. Hydrogen Energy* **2021**, *46*, 6404–6418. [CrossRef]

103. Netskina, O.; Kochubey, D.I.; Prosvirin, I.P.; Kellerman, D.G.; Simagina, V.I.; Komova, O.V. Role of the electronic state of rhodium in sodium borohydride hydrolysis. *J. Mol. Catal. A Chem.* **2014**, *390*, 125–132. [CrossRef]

104. Netskina, O.; Komova, O.; Mukha, S.; Simagina, V. Aqueous-alkaline NaBH4 solutions: The influence of hydride decomposition on catalytic properties of Co3O. *Catal. Commun.* **2016**, *85*, 9–12. [CrossRef]

105. Netskina, O.; Komova, O.; Simagina, V.; Odegova, G.; Prosvirin, I.; Bulavchenko, O. Aqueous-alkaline NaBH$_4$ solution: The influence of storage duration of solutions on reduction and activity of cobalt catalysts. *Renew. Energy* **2016**, *99*, 1073–1081. [CrossRef]

106. Netskina, O.V.; Pochtar, A.A.; Komova, O.V.; Simagina, V.I. Solid-State NaBH4 Composites as Hydrogen Generation Material: Effect of Thermal Treatment of a Catalyst Precursor on the Hydrogen Generation Rate. *Catalysts* **2020**, *10*, 201. [CrossRef]

107. Netskina, O.V.; Tayban, E.S.; Ozerova, A.M.; Komova, O.V.; Simagina, V.I. Solid-State NaBH4/Co Composite as Hydrogen Storage Material: Effect of the Pressing Pressure on Hydrogen Generation Rate. *Energies* **2019**, *12*, 1184. [CrossRef]

108. Netskina, O.; Tayban, E.; Prosvirin, I.; Komova, O.; Simagina, V. Hydrogen storage systems based on solid-state NaBH4/Co composite: Effect of catalyst precursor on hydrogen generation rate. *Renew. Energy* **2020**, *151*, 278–285. [CrossRef]

109. Oh, T.H.; Gang, B.G.; Kim, H.; Kwon, S. Sodium borohydride hydrogen generator using Co-P/Ni foam catalysts for 200 W proton exchange membrane fuel cell system. *Energy* **2015**, *90*, 1163–1170. [CrossRef]

110. Okumus, E.; San, F.G.B.; Okur, O.; Turk, B.E.; Cengelci, E.; Kilic, M.; Karadağ, Ç.; Cavdar, M.; Turkmen, A.; Yazici, M.S. Development of boron-based hydrogen and fuel cell system for small unmanned aerial vehicle. *Int. J. Hydrogen Energy* **2017**, *42*, 2691–2697. [CrossRef]

111. Park, D.; Kim, T. Electroless Plated Co-Ni-P-B/Ni Foam Catalyst for Hydrogen Generation from Sodium Borohydride. *J. Nanosci. Nanotechnol.* **2016**, *16*, 1740–1743. [CrossRef]

112. Patil, K.N.; Prasad, D.; Bhanushali, J.T.; Kim, H.; Atar, A.B.; Nagaraja, B.M.; Jadhav, A.H. Sustainable Hydrogen Generation by Catalytic Hydrolysis of NaBH4 Using Tailored Nanostructured Urchin-like CuCo2O4 Spinel Catalyst. *Catal. Lett.* **2020**, *150*, 586–604. [CrossRef]

113. Pornea, A.M.; Abebe, M.W.; Kim, H. Ternary NiCoP urchin like 3D nanostructure supported on nickel foam as a catalyst for hydrogen generation of alkaline NaBH4. *Chem. Phys.* **2019**, *516*, 152–159. [CrossRef]

114. Prasad, D.; Patil, K.N.; Sandhya, N.; Chaitra, C.; Bhanushali, J.T.; Samal, A.K.; Keri, R.S.; Jadhav, A.H.; Nagaraja, B.M. Highly efficient hydrogen production by hydrolysis of NaBH4 using eminently competent recyclable Fe$_2$O$_3$ decorated oxidized MWCNTs robust catalyst. *Appl. Surf. Sci.* **2019**, *489*, 538–551. [CrossRef]

115. Retnamma, R.; Novais, A.; Rangel, C.M.; Yu, L.; Matthews, M.A. Kinetic modeling of self-hydrolysis of aqueous NaBH4 solutions by model-based isoconversional method. *Int. J. Hydrogen Energy* **2014**, *39*, 6567–6576. [CrossRef]

116. Rivarolo, M.; Improta, O.; Magistri, L.; Panizza, M.; Barbucci, A. Thermo-economic analysis of a hydrogen production system by sodium borohydride (NaBH4). *Int. J. Hydrogen Energy* **2018**, *43*, 1606–1614. [CrossRef]

117. Şahin, Ö.; Izgi, M.S.; Onat, E.; Saka, C. Influence of the using of methanol instead of water in the preparation of Co-B-TiO2 catalyst for hydrogen production by NaBH$_4$ hydrolysis and plasma treatment effect on the Co-B-TiO2 catalyst. *Int. J. Hydrogen Energy* **2016**, *41*, 2539–2546. [CrossRef]

118. Şahin, Ö.; Kılınç, D.; Saka, C. Hydrogen generation from hydrolysis of sodium borohydride with a novel palladium metal complex catalyst. *J. Energy Inst.* **2016**, *89*, 182–189. [CrossRef]

119. Şahin, Ö.; Kılınç, D.; Saka, C. Bimetallic Co-Ni based complex catalyst for hydrogen production by catalytic hydrolysis of sodium borohydride with an alternative approach. *J. Energy Inst.* **2016**, *89*, 617–626. [CrossRef]
120. Sahiner, N.; Yasar, A.O. H2 generation from NaBH4 and NH3BH3 using metal catalysts prepared within p(VI) capsule particles. *Fuel Process. Technol.* **2014**, *125*, 148–154. [CrossRef]
121. Sahiner, N.; Yasar, A.O.; Aktaş, N. An alternative to metal catalysts: Poly(4-vinyl pyridine)-based polymeric ionic liquid catalyst for H2 generation from hydrolysis and methanolysis of NaBH4. *Int. J. Hydrogen Energy* **2016**, *41*, 20562–20572. [CrossRef]
122. Saka, C.; Eygi, M.S.; Balbay, A. CoB doped acid modified zeolite catalyst for enhanced hydrogen release from sodium borohydride hydrolysis. *Int. J. Hydrogen Energy* **2020**, *45*, 15086–15099. [CrossRef]
123. Santra, S.; Das, D.; Das, N.S.; Nanda, K.K. An efficient on-board metal-free nanocatalyst for controlled room temperature hydrogen production. *Chem. Sci.* **2017**, *8*, 2994–3001. [CrossRef]
124. Selvitepe, N.; Balbay, A.; Saka, C. Optimisation of sepiolite clay with phosphoric acid treatment as support material for CoB catalyst and application to produce hydrogen from the NaBH4 hydrolysis. *Int. J. Hydrogen Energy* **2019**, *44*, 16387–16399. [CrossRef]
125. Semiz, L.; Abdullayeva, N.; Sankir, M. Nanoporous Pt and Ru catalysts by chemical dealloying of Pt-Al and Ru-Al alloys for ultrafast hydrogen generation. *J. Alloys Compd.* **2018**, *744*, 110–115. [CrossRef]
126. Shavi, R.; Jadhav, A.H.; Lee, K.; Gil Seo, J. Sulfonated Nanolayers of H+-Montmorillonite as an Efficient Acidic Catalyst for Hydrogen Generation from Hydrolysis of Sodium Borohydride. *J. Nanosci. Nanotechnol.* **2016**, *16*, 10980–10985. [CrossRef]
127. Shen, J.; Chen, W.; Lv, G.; Yang, Z.; Yan, J.; Liu, X.; Dai, Z. Hydrolysis of NH3BH3 and NaBH4 by graphene quantum dots-transition metal nanoparticles for highly effective hydrogen evolution. *Int. J. Hydrogen Energy* **2021**, *46*, 796–805. [CrossRef]
128. Shen, X.; Wang, Q.; Wu, Q.; Guo, S.; Zhang, Z.; Sun, Z.; Liu, B.; Wang, Z.; Zhao, B.; Ding, W. CoB supported on Ag-activated TiO2 as a highly active catalyst for hydrolysis of alkaline NaBH4 solution. *Energy* **2015**, *90*, 464–474. [CrossRef]
129. Shi, L.; Chen, Z.; Jian, Z.; Guo, F.; Gao, C. Carbon nanotubes-promoted Co-B catalysts for rapid hydrogen generation via NaBH4 hydrolysis. *Int. J. Hydrogen Energy* **2019**, *44*, 19868–19877. [CrossRef]
130. Shi, L.; Xie, W.; Jian, Z.; Liao, X.; Wang, Y. Graphene modified Co-B catalysts for rapid hydrogen production from NaBH4 hydrolysis. *Int. J. Hydrogen Energy* **2019**, *44*, 17954–17962. [CrossRef]
131. Shu, H.; Lu, L.; Zhu, S.; Liu, M.; Zhu, Y.; Ni, J.; Ruan, Z.; Liu, Y. Ultra small cobalt nanoparticles supported on MCM41: One-pot synthesis and catalytic hydrogen production from alkaline borohydride. *Catal. Commun.* **2019**, *118*, 30–34. [CrossRef]
132. Singh, P.K.; Das, T. Generation of hydrogen from NaBH4 solution using metal-boride (CoB, FeB, NiB) catalysts. *Int. J. Hydrogen Energy* **2017**, *42*, 29360–29369. [CrossRef]
133. Soltani, M.; Zabihi, M. Hydrogen generation by catalytic hydrolysis of sodium borohydride using the nano-bimetallic catalysts supported on the core-shell magnetic nanocomposite of activated carbon. *Int. J. Hydrogen Energy* **2020**, *45*, 12331–12346. [CrossRef]
134. Sousa, T.; Rangel, C.M. A dynamic two phase flow model for a pilot scale sodium borohydride hydrogen generation reactor. *Int. J. Hydrogen Energy* **2014**, *39*, 5291–5300. [CrossRef]
135. Tamboli, A.; Chaugule, A.A.; Sheikh, F.A.; Chung, W.-J.; Kim, H. Synthesis and application of CeO2-NiO loaded TiO2 nanofiber as novel catalyst for hydrogen production from sodium borohydride hydrolysis. *Energy* **2015**, *89*, 568–575. [CrossRef]
136. Tamboli, A.H.; Gosavi, S.; Terashima, C.; Fujishima, A.; Pawar, A.A.; Kim, H. Synthesis of cerium and nickel doped titanium nanofibers for hydrolysis of sodium borohydride. *Chemosphere* **2018**, *202*, 669–676. [CrossRef]
137. Tamboli, A.H.; Jadhav, A.; Chung, W.-J.; Kim, H. Structurally modified cerium doped hydrotalcite-like precursor as efficient catalysts for hydrogen production from sodium borohydride hydrolysis. *Energy* **2015**, *93*, 955–962. [CrossRef]
138. Tang, M.; Huang, G.; Gao, C.; Li, X.; Qiu, H. Co nanoparticles supported 3D structure for catalytic H2 production. *Mater. Chem. Phys.* **2017**, *191*, 6–12. [CrossRef]
139. Tang, M.; Xia, F.; Gao, C.; Qiu, H. Preparation of magnetically recyclable CuFe2O4/RGO for catalytic hydrolysis of sodium borohydride. *Int. J. Hydrogen Energy* **2016**, *41*, 13058–13068. [CrossRef]
140. Tomboc, G.R.M.; Tamboli, A.; Kim, H. Synthesis of Co3O4 macrocubes catalyst using novel chitosan/urea template for hydrogen generation from sodium borohydride. *Energy* **2017**, *121*, 238–245. [CrossRef]
141. Tuan, D.D.; Lin, K.-Y.A. ZIF-67-derived Co3O4 rhombic dodecahedron as an efficient non-noble-metal catalyst for hydrogen generation from borohydride hydrolysis. *J. Taiwan Inst. Chem. Eng.* **2018**, *91*, 274–280. [CrossRef]
142. Tuan, D.D.; Lin, K.-Y. Ruthenium supported on ZIF-67 as an enhanced catalyst for hydrogen generation from hydrolysis of sodium borohydride. *Chem. Eng. J.* **2018**, *351*, 48–55. [CrossRef]
143. Uzundurukan, A.; Devrim, Y. Hydrogen generation from sodium borohydride hydrolysis by multi-walled carbon nanotube supported platinum catalyst: A kinetic study. *Int. J. Hydrogen Energy* **2019**, *44*, 17586–17594. [CrossRef]
144. Wang, F.-C.; Fang, W.-H. The development of a PEMFC hybrid power electric vehicle with automatic sodium borohydride hydrogen generation. *Int. J. Hydrogen Energy* **2017**, *42*, 10376–10389. [CrossRef]
145. Wang, J.; Ke, D.; Li, Y.; Zhang, H.; Wang, C.; Zhao, X.; Yuan, Y.; Han, S. Efficient hydrolysis of alkaline sodium borohydride catalyzed by cobalt nanoparticles supported on three–dimensional graphene oxide. *Mater. Res. Bull.* **2017**, *95*, 204–210. [CrossRef]
146. Wang, L.; Liu, Y.; Ashraf, S.; Jiang, J.; Han, G.; Gao, J.; Wu, X.; Li, B. Pitaya pulp structural cobalt-carbon composite for efficient hydrogen generation from borohydride hydrolysis. *J. Alloys Compd.* **2019**, *808*, 151774. [CrossRef]
147. Wang, L.; Li, Z.; Liu, X.; Zhang, P.; Xie, G. Hydrogen generation from alkaline NaBH 4 solution using electroless-deposited Co-W-P supported on γ-Al2O3. *Int. J. Hydrogen Energy* **2015**, *40*, 7965–7973. [CrossRef]

148. Wang, L.; Li, Z.; Zhang, P.; Wang, G.; Xie, G. Hydrogen generation from alkaline NaBH4 solution using Co-Ni-Mo-P/γ-Al₂O₃ catalysts. *Int. J. Hydrogen Energy* **2016**, *41*, 1468–1476. [CrossRef]

149. Wang, L.; Li, Z.; Zhang, Y.; Zhang, T.; Xie, G. Hydrogen generation from alkaline NaBH4 solution using electroless-deposited Co-Ni-W-P/γ-Al₂O₃ as catalysts. *J. Alloys Compd.* **2017**, *702*, 649–658. [CrossRef]

150. Wang, L.; Zhong, M.; Li, J.; Zhao, X.; Hao, W.; Guo, Y. Highly efficient ferromagnetic Co-B-O catalyst for hydrogen generation. *Int. J. Hydrogen Energy* **2018**, *43*, 17164–17171. [CrossRef]

151. Wang, M.; Ouyang, L.; Liu, J.; Wang, H.; Zhu, M. Hydrogen generation from sodium borohydride hydrolysis accelerated by zinc chloride without catalyst: A kinetic study. *J. Alloys Compd.* **2017**, *717*, 48–54. [CrossRef]

152. Wang, W.; Zhao, Y.; Chen, D.; Wang, X.; Peng, X.; Tian, J. Promoted Mo incorporated Co-Ru-B catalyst for fast hydrolysis of NaBH 4 in alkaline solutions. *Int. J. Hydrogen Energy* **2014**, *39*, 16202–16211. [CrossRef]

153. Wang, X.; Zhao, Y.; Peng, X.; Jing, C.; Hu, W.; Tian, S.; Tian, J. In Situ synthesis of cobalt-based tri-metallic nanosheets as highly efficient catalysts for sodium borohydride hydrolysis. *Int. J. Hydrogen Energy* **2016**, *41*, 219–226. [CrossRef]

154. Wang, X.; Sun, S.; Huang, Z.; Zhang, H.; Zhang, S. Preparation and catalytic activity of PVP-protected Au/Ni bimetallic nanoparticles for hydrogen generation from hydrolysis of basic NaBH4 solution. *Int. J. Hydrogen Energy* **2014**, *39*, 905–916. [CrossRef]

155. Wang, X.; Liao, J.; Li, H.; Wang, H.; Wang, R. Solid-state-reaction synthesis of cotton-like CoB alloy at room temperature as a catalyst for hydrogen generation. *J. Colloid Interface Sci.* **2016**, *475*, 149–153. [CrossRef] [PubMed]

156. Wang, X.; Liao, J.; Li, H.; Wang, H.; Wang, R. Preparation of pompon-like Co-B nanoalloy by a room-temperature solid-state-reaction as a catalyst for hydrolysis of borohydride solution. *Int. J. Hydrogen Energy* **2017**, *42*, 6646–6656. [CrossRef]

157. Wang, Y.; Li, G.; Wu, S.; Wei, Y.; Meng, W.; Xie, Y.; Cui, Y.; Lian, X.; Chen, Y.; Zhang, X. Hydrogen generation from alkaline NaBH4 solution using nanostructured Co-Ni-P catalysts. *Int. J. Hydrogen Energy* **2017**, *42*, 16529–16537. [CrossRef]

158. Wang, Y.; Li, T.; Bai, S.; Qi, K.; Cao, Z.; Zhang, K.; Wu, S.; Wang, D. Catalytic hydrolysis of sodium borohydride via nanostructured cobalt–boron catalysts. *Int. J. Hydrogen Energy* **2016**, *41*, 276–284. [CrossRef]

159. Wang, Y.; Lu, Y.; Wang, D.; Wu, S.; Cao, Z.; Zhang, K.; Liu, H.; Xin, S. Hydrogen generation from hydrolysis of sodium borohydride using nanostructured NiB catalysts. *Int. J. Hydrogen Energy* **2016**, *41*, 16077–16086. [CrossRef]

160. Wang, Y.; Shen, Y.; Qi, K.; Cao, Z.; Zhang, K.; Wu, S. Nanostructured cobalt-phosphorous catalysts for hydrogen generation from hydrolysis of sodium borohydride solution. *Renew. Energy* **2016**, *89*, 285–294. [CrossRef]

161. Wang, Y.; Zou, K.; Zhang, D.; Cao, Z.; Zhang, K.; Xie, Y.; Zhou, G.; Li, G.; Bai, S. Cobalt-copper-boron nanoparticles as catalysts for the efficient hydrolysis of alkaline sodium borohydride solution. *Int. J. Hydrogen Energy* **2020**, *45*, 9845–9853. [CrossRef]

162. Wei, L.; Dong, X.; Ma, M.; Lu, Y.; Wang, D.; Zhang, S.; Zhao, D.; Wang, Q. Co3O4 hollow fiber: An efficient catalyst precursor for hydrolysis of sodium borohydride to generate hydrogen. *Int. J. Hydrogen Energy* **2018**, *43*, 1529–1533. [CrossRef]

163. Wei, L.; Dong, X.-L.; Yang, Y.-M.; Shi, Q.-Y.; Lu, Y.-H.; Liu, H.-Y.; Yu, Y.-N.; Zhang, M.-H.; Qi, M.; Wang, Q. Co-O-P composite nanocatalysts for hydrogen generation from the hydrolysis of alkaline sodium borohydride solution. *Int. J. Hydrogen Energy* **2020**, *45*, 10745–10753. [CrossRef]

164. Wei, Y.; Huang, X.; Wang, J.; Yu, H.; Zhao, X.; Cheng, D. Synthesis of bifunctional non-noble monolithic catalyst Co-W-P/carbon cloth for sodium borohydride hydrolysis and reduction of 4-nitrophenol. *Int. J. Hydrogen Energy* **2017**, *42*, 25860–25868. [CrossRef]

165. Wei, Y.; Meng, W.; Wang, Y.; Gao, Y.; Qi, K.; Zhang, K. Fast hydrogen generation from NaBH 4 hydrolysis catalyzed by nanostructured Co-Ni-B catalysts. *Int. J. Hydrogen Energy* **2017**, *42*, 6072–6079. [CrossRef]

166. Wei, Y.; Wang, Y.; Wei, L.; Zhao, X.; Zhou, X.; Liu, H. Highly efficient and reactivated electrocatalyst of ruthenium electrodeposited on nickel foam for hydrogen evolution from NaBH4 alkaline solution. *Int. J. Hydrogen Energy* **2018**, *43*, 592–600. [CrossRef]

167. Wu, C.; Guo, J.; Zhang, J.; Zhao, Y.; Tian, J.; Isimjan, T.T.; Yang, X. Palladium nanoclusters decorated partially decomposed porous ZIF-67 polyhedron with ultrahigh catalytic activity and stability on hydrogen generation. *Renew. Energy* **2019**, *136*, 1064–1070. [CrossRef]

168. Wu, Z.; Mao, X.; Zi, Q.; Zhang, R.; Dou, T.; Yip, A.C.K. Mechanism and kinetics of sodium borohydride hydrolysis over crystalline nickel and nickel bordie and amorphous nickel-boron nanoparticles. *J. Power Source* **2014**, *268*, 596–603. [CrossRef]

169. Xiang, C.; Jiang, D.; She, Z.; Zou, Y.; Chu, H.; Qiu, S.; Zhang, H.; Xu, F.; Tang, C.; Sun, L. Hydrogen generation by hydrolysis of alkaline sodium borohydride using a cobalt–zinc–boron/graphene nanocomposite treated with sodium hydroxide. *Int. J. Hydrogen Energy* **2015**, *40*, 4111–4118. [CrossRef]

170. Xie, L.; Wang, K.; Du, G.; Asiri, A.M.; Sun, X. 3D hierarchical CuO/Co₃O₄ core-shell nanowire array on copper foam for on-demand hydrogen generation from alkaline NaBH 4 solution. *RSC Adv.* **2016**, *6*, 88846–88850. [CrossRef]

171. Xin, Y.; Wang, Z.; Jiang, Y. Kinetic study of NaBH4 catalytic hydrolysis using supported NiCo₂O₄. *Mater. Res. Express* **2019**, *6*, 125530. [CrossRef]

172. Xu, D.; Zhang, X.; Zhao, X.; Dai, P.; Wang, C.; Gao, J.; Liu, X. Stability and kinetic studies of MOF-derived carbon-confined ultrafine Co catalyst for sodium borohydride hydrolysis. *Int. J. Energy Res.* **2019**, *43*, 3702–3710. [CrossRef]

173. Xu, Y.; Chen, J.; Wu, C.; Chen, Y.; Li, J.; Li, Z. Hydrogen generation from hydrolysis of NaBH4 and NH3BH3 composite promoted by AlCl₃. *Int. J. Hydrogen Energy* **2016**, *41*, 16344–16351. [CrossRef]

174. Yang, L.; Huang, X.; Zhang, J.; Dong, H. Protonated Poly(ethylene imine)-Coated Silica Nanoparticles for Promoting Hydrogen Generation from the Hydrolysis of Sodium Borohydride. *ChemPlusChem* **2020**, *85*, 399–404. [CrossRef] [PubMed]

175. Yu, L.; Matthews, M.A. A reactor model for hydrogen generation from sodium borohydride and water vapor. *Int. J. Hydrogen Energy* **2014**, *39*, 3830–3836. [CrossRef]

176. Yu, L.; Pellechia, P.; Matthews, M.A. Kinetic models of concentrated NaBH4 hydrolysis. *Int. J. Hydrogen Energy* **2014**, *39*, 442–448. [CrossRef]

177. Abdelhamid, H.N. Hierarchical porous ZIF-8 for hydrogen production via the hydrolysis of sodium borohydride. *Dalton Trans.* **2020**, *49*, 4416–4424. [CrossRef]

178. Yue, C.; Yang, P.; Wang, J.; Zhao, X.; Wang, Y.; Yang, L. Facile synthesis and characterization of nano-Pd loaded NiCo microfibers as stable catalysts for hydrogen generation from sodium borohydride. *Chem. Phys. Lett.* **2020**, *743*, 137170. [CrossRef]

179. Zabielaitė, A.; Balčiūnaitė, A.; Stalnionienė, I.; Lichušina, S.; Šimkūnaitė, D.; Vaičiūnienė, J.; Šimkūnaitė-Stanynienė, B.; Selskis, A.; Tamašauskaitė-Tamašiūnaitė, L.; Norkus, E. Fiber-shaped Co modified with Au and Pt crystallites for enhanced hydrogen generation from sodium borohydride. *Int. J. Hydrogen Energy* **2018**, *43*, 23310–23318. [CrossRef]

180. Zhang, H.; Feng, X.; Cheng, L.; Hou, X.; Li, Y.; Han, S. Non-noble Co anchored on nanoporous graphene oxide, as an efficient and long-life catalyst for hydrogen generation from sodium borohydride. *Colloids Surfaces A Physicochem. Eng. Asp.* **2019**, *563*, 112–119. [CrossRef]

181. Zhangab, H.; Xuc, G.; Zhangab, L.; Wangb, W.; Miaob, W.; Chenb, K.; Chengb, L.; Lib, Y.; Hanab, S. Ultrafine cobalt nanoparticles supported on carbon nanospheres for hydrolysis of sodium borohydride. *Renew. Energy* **2020**, *162*, 345–354. [CrossRef]

182. Zhangab, H.; Zhangab, L.; Rodríguez-Pérez, I.A.; Miaob, W.; Chenb, K.; Wangb, W.; Lib, Y.; Hanab, S. Carbon nanospheres supported bimetallic Pt-Co as an efficient catalyst for NaBH4 hydrolysis. *Appl. Surf. Sci.* **2021**, *540*, 148296. [CrossRef]

183. Zhang, J.; Hao, J.; Ma, Q.; Li, C.; Liu, Y.; Li, B.; Liu, Z. Polyvinylpyrrolidone stabilized-Ru nanoclusters loaded onto reduced graphene oxide as high active catalyst for hydrogen evolution. *J. Nanoparticle Res.* **2017**, *19*, 227. [CrossRef]

184. Zhang, J.; Lin, F.; Yang, L.; Dong, H. Highly dispersed Ru/Co catalyst with enhanced activity for catalyzing NaBH4 hydrolysis in alkaline solutions. *Chin. Chem. Lett.* **2020**, *31*, 2512–2515. [CrossRef]

185. Zhang, J.; Lin, F.; Yang, L.; He, Z.; Huang, X.; Zhang, D.; Dong, H. Ultrasmall Ru nanoparticles supported on chitin nanofibers for hydrogen production from NaBH4 hydrolysis. *Chin. Chem. Lett.* **2020**, *31*, 2019–2022. [CrossRef]

186. Zhang, X.; Zhang, Q.; Xu, B.; Liu, X.; Zhang, K.; Fan, G.; Jiang, W. Efficient Hydrogen Generation from the NaBH4 Hydrolysis by Cobalt-Based Catalysts: Positive Roles of Sulfur-Containing Salts. *ACS Appl. Mater. Interfaces* **2020**, *12*, 9376–9386. [CrossRef]

187. Zhang, X.; Sun, X.; Xu, D.; Tao, X.; Dai, P.; Guo, Q.; Liu, X. Synthesis of MOF-derived Co@C composites and application for efficient hydrolysis of sodium borohydride. *Appl. Surf. Sci.* **2019**, *469*, 764–769. [CrossRef]

188. Abdelhamid, H.N. UiO-66 as a catalyst for hydrogen production via the hydrolysis of sodium borohydride. *Dalton Trans.* **2020**, *49*, 10851–10857. [CrossRef]

189. Zhang, X.; Cheng, Y.; Li, C.; Guo, Q.; Meng, X. Catalytic hydrolysis of alkaline sodium borohydride solution for hydrogen evolution in a micro-scale fluidized bed reactor. *Int. J. Energy Res.* **2020**, *44*, 6758–6766. [CrossRef]

190. Zhao, L.; Li, Q.; Su, Y.; Yue, Q.; Gao, B. A novel Enteromorpha based hydrogel for copper and nickel nanoparticle preparation and their use in hydrogen production as catalysts. *Int. J. Hydrogen Energy* **2017**, *42*, 6746–6756. [CrossRef]

191. Zhou, S.; Yang, Y.; Zhang, W.; Rao, X.; Yan, P.; Isimjan, T.T.; Yang, X. Structure-regulated Ru particles decorated P-vacancy-rich CoP as a highly active and durable catalyst for NaBH4 hydrolysis. *J. Colloid Interface Sci.* **2021**, *591*, 221–228. [CrossRef]

192. Zhou, Y.; Fang, C.; Fang, Y.; Zhu, F.; Liu, H.; Ge, H. Hydrogen generation mechanism of BH4− spontaneous hydrolysis: A sight from ab initio calculation. *Int. J. Hydrogen Energy* **2016**, *41*, 22668–22676. [CrossRef]

193. Zhuang, D.-W.; Dai, H.-B.; Zhong, Y.-J.; Sun, L.-X.; Wang, P. A new reactivation method towards deactivation of honeycomb ceramic monolith supported cobalt-molybdenum-boron catalyst in hydrolysis of sodium borohydride. *Int. J. Hydrogen Energy* **2015**, *40*, 9373–9381. [CrossRef]

194. Zou, Y.; Gao, Y.; Huang, P.; Xiang, C.; Chu, H.; Qiu, S.; Yan, E.; Xu, F.; Sun, L. Effects of the Preparation Solvent on the Catalytic Properties of Cobalt–Boron Alloy for the Hydrolysis of Alkaline Sodium Borohydride. *Metals* **2017**, *7*, 365. [CrossRef]

195. Zou, Y.; Yin, Y.; Gao, Y.; Xiang, C.; Chu, H.; Qiu, S.; Yan, E.; Xu, F.; Sun, L. Chitosan-mediated Co-Ce-B nanoparticles for catalyzing the hydrolysis of sodium borohydride. *Int. J. Hydrogen Energy* **2018**, *43*, 4912–4921. [CrossRef]

196. Abu-Zied, B.M.; Alamry, K.A. Green synthesis of 3D hierarchical nanostructured Co3O4/carbon catalysts for the application in sodium borohydride hydrolysis. *J. Alloys Compd.* **2019**, *798*, 820–831. [CrossRef]

197. Ai, L.; Gao, X.; Jiang, J. In situ synthesis of cobalt stabilized on macroscopic biopolymer hydrogel as economical and recyclable catalyst for hydrogen generation from sodium borohydride hydrolysis. *J. Power Source* **2014**, *257*, 213–220. [CrossRef]

198. Akbayrak, S.; Özkar, S. Inverse relation between the catalytic activity and catalyst concentration for the ruthenium(0) nanoparticles supported on xonotlite nanowire in hydrogen generation from the hydrolysis of sodium borohydride. *J. Mol. Catal. A Chem.* **2016**, *424*, 254–260. [CrossRef]

199. Al-Thabaiti, S.A.; Khan, Z.; Malik, M.A. Bimetallic Ag-Ni nanoparticles as an effective catalyst for hydrogen generation from hydrolysis of sodium borohydride. *Int. J. Hydrogen Energy* **2019**, *44*, 16452–16466. [CrossRef]

200. Ali, F.; Khan, S.B.; Asiri, A.M. Enhanced H2 generation from NaBH4 hydrolysis and methanolysis by cellulose micro-fibrous cottons as metal templated catalyst. *Int. J. Hydrogen Energy* **2018**, *43*, 6539–6550. [CrossRef]

201. Aman, D.; Alkahlawy, A.; Zaki, T. Hydrolysis of NaBH4 using ZVI/Fe2(MoO4)3 nanocatalyst. *Int. J. Hydrogen Energy* **2018**, *43*, 18289–18295. [CrossRef]

202. Aydin, M.; Hasimoglu, A.; Ozdemir, O.K. Kinetic properties of Cobalt-Titanium-Boride (Co-Ti-B) catalysts for sodium borohydride hydrolysis reaction. *Int. J. Hydrogen Energy* **2016**, *41*, 239–248. [CrossRef]
203. Balbay, A.; Saka, C. Effect of phosphoric acid addition on the hydrogen production from hydrolysis of NaBH4 with Cu based catalyst. *Energy Sources Part A Recover. Util. Environ. Eff.* **2018**, *40*, 794–804. [CrossRef]
204. Balkanli, E.; Figen, H.E. Sodium borohydride hydrolysis by using ceramic foam supported bimetallic and trimetallic catalysts. *Int. J. Hydrogen Energy* **2019**, *44*, 9959–9969. [CrossRef]
205. Bandal, H.; Jadhav, A.; Kim, H. Cobalt impregnated magnetite-multiwalled carbon nanotube nanocomposite as magnetically separable efficient catalyst for hydrogen generation by NaBH 4 hydrolysis. *J. Alloys Compd.* **2017**, *699*, 1057–1067. [CrossRef]
206. Baydaroglu, F.; Ozdemir, E.; Hasimoglu, A. An effective synthesis route for improving the catalytic activity of carbon-supported Co-B catalyst for hydrogen generation through hydrolysis of NaBH4. *Int. J. Hydrogen Energy* **2014**, *39*, 1516–1522. [CrossRef]
207. Baye, A.F.; Abebe, M.W.; Appiah-Ntiamoah, R.; Kim, H. Engineered iron-carbon-cobalt (Fe3O4@C-Co) core-shell composite with synergistic catalytic properties towards hydrogen generation via NaBH4 hydrolysis. *J. Colloid Interface Sci.* **2019**, *543*, 273–284. [CrossRef]
208. Bekirogullari, M. Hydrogen production from sodium borohydride by ZnCl2 treated defatted spent coffee ground catalyst. *Int. J. Hydrogen Energy* **2020**, *45*, 9733–9743. [CrossRef]
209. Boran, A.; Erkan, S.; Eroglu, I. Hydrogen generation from solid state NaBH4 by using FeCl3 catalyst for portable proton exchange membrane fuel cell applications. *Int. J. Hydrogen Energy* **2019**, *44*, 18915–18926. [CrossRef]
210. 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]
211. Bozkurt, G.; Özer, A.; Yurtcan, A.B. Development of effective catalysts for hydrogen generation from sodium borohydride: Ru, Pt, Pd nanoparticles supported on Co_3O_4. *Energy* **2019**, *180*, 702–713. [CrossRef]
212. Cai, H.; Lu, P.; Dong, J. Robust nickel-polymer nanocomposite particles for hydrogen generation from sodium borohydride. *Fuel* **2016**, *166*, 297–301. [CrossRef]
213. Ceyhan, A.A.; Edebali, S.; Fangaj, E. A study on hydrogen generation from NaBH4 solution using Co-loaded resin catalysts. *Int. J. Hydrogen Energy* **2020**, *45*, 34761–34772. [CrossRef]
214. Chen, B.; Chen, S.; Bandal, H.A.; Appiah-Ntiamoah, R.; Jadhav, A.R.; Kim, H. Cobalt nanoparticles supported on magnetic core-shell structured carbon as a highly efficient catalyst for hydrogen generation from $NaBH_4$ hydrolysis. *Int. J. Hydrogen Energy* **2018**, *43*, 9296–9306. [CrossRef]
215. Chen, Y.; Jin, H. Fabrication of amorphous Co-Cr-B and catalytic sodium borohydride hydrolysis for hydrogen generation. *J. Mater. Res.* **2020**, *35*, 281–288. [CrossRef]
216. Chinnappan, A.; Jadhav, A.H.; Puguan, J.M.C.; Appiah-Ntiamoah, R.; Kim, H. Fabrication of ionic liquid/polymer nanoscale networks by electrospinning and chemical cross-linking and their application in hydrogen generation from the hydrolysis of $NaBH_4$. *Energy* **2015**, *79*, 482–488. [CrossRef]
217. Chinnappan, A.; Puguan, J.M.C.; Chung, W.-J.; Kim, H. Hydrogen generation from the hydrolysis of sodium borohydride using chemically modified multiwalled carbon nanotubes with pyridinium based ionic liquid and decorated with highly dispersed Mn nanoparticles. *J. Power Source* **2015**, *293*, 429–436. [CrossRef]
218. Chou, C.-C.; Hsieh, C.-H.; Chen, B.-H. Hydrogen generation from catalytic hydrolysis of sodium borohydride using bimetallic Ni–Co nanoparticles on reduced graphene oxide as catalysts. *Energy* **2015**, *90*, 1973–1982. [CrossRef]
219. Filiz, B.C.; Figen, A.K. The Molecular-Kinetic Approach to Hydrolysis of Boron Hydrides for Hydrogen Production. *Kinet. Catal.* **2019**, *60*, 37–43. [CrossRef]
220. Filiz, B.C.; Figen, A.K. Hydrogen production from sodium borohydride originated compounds: Fabrication of electrospun nano-crystalline Co_3O_4 catalyst and its activity. *Int. J. Hydrogen Energy* **2019**, *44*, 9883–9895. [CrossRef]
221. Filiz, B.C.; Figen, A.K. Insight into the role of solvents in enhancing hydrogen production: Ru-Co nanoparticles catalyzed sodium borohydride dehydrogenation. *Int. J. Hydrogen Energy* **2019**, *44*, 28471–28482. [CrossRef]
222. Cui, L.; Sun, X.; Xu, Y.; Yang, W.; Liu, J. Cobalt Carbonate Hydroxide Nanowire Array on Ti Mesh: An Efficient and Robust 3D Catalyst for On-Demand Hydrogen Generation from Alkaline NaBH4 Solution. *Chem. A Eur. J.* **2016**, *22*, 14831–14835. [CrossRef]
223. Cui, Z.; Guo, Y.; Ma, J. In situ synthesis of graphene supported Co-Sn-B alloy as an efficient catalyst for hydrogen generation from sodium borohydride hydrolysis. *Int. J. Hydrogen Energy* **2016**, *41*, 1592–1599. [CrossRef]
224. Dai, P.; Zhao, X.; Xu, D.; Wang, C.; Tao, X.; Liu, X.; Gao, J. Preparation, characterization, and properties of Pt/Al_2O_3/cordierite monolith catalyst for hydrogen generation from hydrolysis of sodium borohydride in a flow reactor. *Int. J. Hydrogen Energy* **2019**, *44*, 28463–28470. [CrossRef]
225. Demirci, S.; Sahiner, N. Superior reusability of metal catalysts prepared within poly(ethylene imine) microgels for H2 production from NaBH4 hydrolysis. *Fuel Process. Technol.* **2014**, *127*, 88–96. [CrossRef]
226. Demirci, U.B.; Miele, P. Reaction mechanisms of the hydrolysis of sodium borohydride: A discussion focusing on cobalt-based catalysts. *Comptes Rendus Chim.* **2014**, *17*, 707–716. [CrossRef]
227. Deonikar, V.; Rathod, P.V.; Pornea, A.M.; Puguan, J.M.C.; Park, K.; Kim, H. Hydrogen generation from catalytic hydrolysis of sodium borohydride by a Cu and Mo promoted Co catalyst. *J. Ind. Eng. Chem.* **2020**, *86*, 167–177. [CrossRef]

228. Didehban, A.; Zabihi, M.; Babajani, N. Preparation of the efficient nano-bimetallic cobalt-nickel catalysts supported on the various magnetic substrates for hydrogen generation from hydrolysis of sodium borohydride in alkaline solutions. *Polyhedron* **2020**, *180*, 114405. [CrossRef]

229. Didehban, A.; Zabihi, M.; Shahrouzi, J.R. Experimental studies on the catalytic behavior of alloy and core-shell supported Co-Ni bimetallic nano-catalysts for hydrogen generation by hydrolysis of sodium borohydride. *Int. J. Hydrogen Energy* **2018**, *43*, 20645–20660. [CrossRef]

230. Ding, C.; Gao, Z.; Wang, J.; Ma, L.; Shangguan, J.; Yuan, Q.; Zhao, M.; Zhang, K. The coralline cobalt oxides compound of multiple valence states deriving from flower-like layered double hydroxide for efficient hydrogen generation from hydrolysis of $NaBH_4$. *Int. J. Hydrogen Energy* **2021**, *46*, 2390–2404. [CrossRef]

231. Ding, J.; Li, Q.; Su, Y.; Yue, Q.; Gao, B.; Zhou, W. Preparation and catalytic activity of wheat straw cellulose based hydrogel-nanometal composites for hydrogen generation from $NaBH_4$ hydrolysis. *Int. J. Hydrogen Energy* **2018**, *43*, 9978–9987. [CrossRef]

232. Dou, S.; Zhang, W.; Yang, Y.; Zhou, S.; Rao, X.; Yan, P.; Isimjan, T.T.; Yang, X. Shaggy-like Ru-clusters decorated core-shell metal-organic framework-derived $CoOx@NPC$ as high-efficiency catalyst for $NaBH_4$ hydrolysis. *Int. J. Hydrogen Energy* **2021**, *46*, 7772–7781. [CrossRef]

233. Duman, S.; Kaya, B.; Caf, F.; Enez, B.; Fincan, S.A. Innovative hydrogen release from sodium borohydride hydrolysis using biocatalyst-like Fe_2O_3 nanoparticles impregnated on Bacillus simplex bacteria. *Int. J. Hydrogen Energy* **2021**, *46*, 15410–15430. [CrossRef]

234. Duman, S.; Özkar, S. Ceria supported manganese(0) nanoparticle catalysts for hydrogen generation from the hydrolysis of sodium borohydride. *Int. J. Hydrogen Energy* **2018**, *43*, 15262–15274. [CrossRef]

235. Durano, M.M.; Tamboli, A.; Kim, H. Cobalt oxide synthesized using urea precipitation method as catalyst for the hydrolysis of sodium borohydride. *Colloids Surfaces A Physicochem. Eng. Asp.* **2017**, *520*, 355–360. [CrossRef]

236. Fangaj, E.; Ali, A.A.; Güngör, F.; Bektaş, S.; Ceyhan, A.A. The use of metallurgical waste sludge as a catalyst in hydrogen production from sodium borohydride. *Int. J. Hydrogen Energy* **2020**, *45*, 13322–13329. [CrossRef]

237. Fiorenza, R.; Scirè, S.; Venezia, A. Carbon supported bimetallic Ru-Co catalysts for H2 production through $NaBH_4$ and NH3 BH3 hydrolysis. *Int. J. Energy Res.* **2018**, *42*, 1183–1195. [CrossRef]

238. Gao, Z.; Ding, C.; Wang, J.; Ding, G.; Xue, Y.; Zhang, Y.; Zhang, K.; Liu, P.; Gao, X. Cobalt nanoparticles packaged into nitrogen-doped porous carbon derived from metal-organic framework nanocrystals for hydrogen production by hydrolysis of sodium borohydride. *Int. J. Hydrogen Energy* **2019**, *44*, 8365–8375. [CrossRef]

239. Guo, J.; Hou, Y.; Li, B. Facile synthesis of a hollow Ni–Fe–B nanochain and its enhanced catalytic activity for hydrogen generation from $NaBH_4$ hydrolysis. *RSC Adv.* **2018**, *8*, 25873–25880. [CrossRef]

240. Guo, J.; Hou, Y.; Li, B.; Liu, Y. Novel Ni-Co-B hollow nanospheres promote hydrogen generation from the hydrolysis of sodium borohydride. *Int. J. Hydrogen Energy* **2018**, *43*, 15245–15254. [CrossRef]

241. Guo, J.; Wang, B.; Yanga, D.; Wana, Z.; Yana, P.; Tiana, J.; Isimjan, T.T.; Yanga, X. Rugae-like $Ni2P$-CoP nanoarrays as a bi-functional catalyst for hydrogen generation: $NaBH_4$ hydrolysis and water reduction. *Appl. Catal. B Environ.* **2020**, *265*, 118584. [CrossRef]

242. Guo, J.; Wu, C.; Zhang, J.; Yan, P.; Tian, J.; Shen, X.; Isimjan, T.T.; Yang, X. Hierarchically structured rugae-like $RuP3$-CoP arrays as robust catalysts synergistically promoting hydrogen generation. *J. Mater. Chem. A* **2019**, *7*, 8865–8872. [CrossRef]

243. Guo, S.; Wu, Q.; Sun, J.; Chen, T.; Feng, M.; Wang, Q.; Wang, Z.; Zhao, B.; Ding, W. Highly stable and controllable CoB/Ni-foam catalysts for hydrogen generation from alkaline $NaBH_4$ solution. *Int. J. Hydrogen Energy* **2017**, *42*, 21063–21072. [CrossRef]

244. Guo, Y.; Qian, J.; Iqbal, A.; Zhang, L.; Liu, W.; Qin, W. Pd nanoparticles immobilized on magnetic carbon dots@Fe_3O_4 nanocubes as a synergistic catalyst for hydrogen generation. *Int. J. Hydrogen Energy* **2017**, *42*, 15167–15177. [CrossRef]

245. Hansu, T.A.; Caglar, A.; Sahin, O.; Kivrak, H. Hydrolysis and electrooxidation of sodium borohydride on novel CNT supported CoBi fuel cell catalyst. *Mater. Chem. Phys.* **2020**, *239*, 122031. [CrossRef]

246. Hostert, L.; Neiva, E.G.C.; Zarbin, A.J.G.; Orth, E.S. Nanocatalysts for hydrogen production from borohydride hydrolysis: Graphene-derived thin films with Ag- and Ni-based nanoparticles. *J. Mater. Chem. A* **2018**, *6*, 22226–22233. [CrossRef]

247. Hsieh, C.P.; Ho, C.Y.; Hsu, L.C.; Chang, Y.-J. Synergistic effect on hydrolytic sodium borohydride adding waste Al for hydrogen generation. *Int. J. Hydrogen Energy* **2020**, *45*, 10334–10341. [CrossRef]

248. Huang, X.; Wu, D.; Cheng, D. Porous $Co2P$ nanowires as high efficient bifunctional catalysts for 4-nitrophenol reduction and sodium borohydride hydrolysis. *J. Colloid Interface Sci.* **2017**, *507*, 429–436. [CrossRef]

249. Huff, C.; Dushatinski, T.; Abdel-Fattah, T.M. Gold nanoparticle/multi-walled carbon nanotube composite as novel catalyst for hydrogen evolution reactions. *Int. J. Hydrogen Energy* **2017**, *42*, 18985–18990. [CrossRef]

250. Inokawa, H.; Driss, H.; Trovela, F.; Miyaoka, H.; Ichikawa, T.; Kojima, Y.; Zaman, S.F.; Al-Zahrani, A.; Alhamed, Y.; Petrov, L. Catalytic hydrolysis of sodium borohydride on Co catalysts. *Int. J. Energy Res.* **2016**, *40*, 2078–2090. [CrossRef]

251. Irum, M.; Zaheer, M.; Friedrich, M.; Kempe, R. Mesoporous silica nanosphere supported platinum nanoparticles (Pt@MSN): One-pot synthesis and catalytic hydrogen generation. *RSC Adv.* **2016**, *6*, 10438–10441. [CrossRef]

252. Izgi, M.S.; Şahin, Ö.; Saka, C. Hydrogen production from $NaBH_4$ using Co-Cu-B catalysts prepared in methanol: Effect of plasma treatment. *Int. J. Hydrogen Energy* **2016**, *41*, 1600–1608. [CrossRef]

253. Kao, H.-Y.; Lin, C.-C.; Hung, C.-J.; Hu, C.-C. Kinetics of hydrogen generation on $NaBH_4$ powders using cobalt catalysts. *J. Taiwan Inst. Chem. Eng.* **2018**, *87*, 123–130. [CrossRef]

254. Kassem, A.A.; Abdelhamid, H.N.; Fouad, D.M.; Ibrahim, S.A. Metal-organic frameworks (MOFs) and MOFs-derived CuO@C for hydrogen generation from sodium borohydride. *Int. J. Hydrogen Energy* **2019**, *44*, 31230–31238. [CrossRef]

255. Ke, D.; Tao, Y.; Li, Y.; Zhao, X.; Zhang, L.; Wang, J.; Han, S. Kinetics study on hydrolytic dehydrogenation of alkaline sodium borohydride catalyzed by Mo-modified Co–B nanoparticles. *Int. J. Hydrogen Energy* **2015**, *40*, 7308–7317. [CrossRef]

256. Kibar, M.E.; Engintepe, E.; Özdemir, E.; Kaplan, Ö.; Çelik, C.; Akın, A.N. Effect of morphology of activated carbon supports for cobalt boride catalysts on the hydrolysis reaction of sodium borohydride. *Int. J. Chem. Kinet.* **2018**, *50*, 839–845. [CrossRef]

257. Kilinc, D.; Sahin, O. Highly active and stable CeO$_2$ supported nickel-complex catalyst in hydrogen generation. *Int. J. Hydrogen Energy* **2021**, *46*, 499–507. [CrossRef]

258. Kim, C.; Lee, S.S.; Li, W.; Fortner, J.D. Towards optimizing cobalt based metal oxide nanocrystals for hydrogen generation via NaBH$_4$ hydrolysis. *Appl. Catal. A Gen.* **2020**, *589*, 117303. [CrossRef]

259. Kim, H.; Oh, T.H.; Kwon, S. Simple catalyst bed sizing of a NaBH$_4$ hydrogen generator with fast startup for small unmanned aerial vehicles. *Int. J. Hydrogen Energy* **2016**, *41*, 1018–1026. [CrossRef]

260. Kılınç, D.; Şahin, Ö. Synthesis of polymer supported Ni (II)-Schiff Base complex and its usage as a catalyst in sodium borohydride hydrolysis. *Int. J. Hydrogen Energy* **2018**, *43*, 10717–10727. [CrossRef]

261. Kılınç, D.; Şahin, Ö. Al$_2$O$_3$ based Co-Schiff Base complex catalyst in hydrogen generation. *Int. J. Hydrogen Energy* **2019**, *44*, 28391–28401. [CrossRef]

262. Kılınç, D.; Şahin, Ö. Effective TiO$_2$ supported Cu-Complex catalyst in NaBH$_4$ hydrolysis reaction to hydrogen generation. *Int. J. Hydrogen Energy* **2019**, *44*, 18858–18865. [CrossRef]

263. Kılınç, D.; Şahin, Ö.; Saka, C. Salicylaldimine-Ni complex supported on Al$_2$O$_3$: Highly efficient catalyst for hydrogen production from hydrolysis of sodium borohydride. *Int. J. Hydrogen Energy* **2018**, *43*, 251–261. [CrossRef]

264. Klindtworth, E.; Delidovich, I.; Palkovits, R. Borohydride in ionic liquids for tailored hydrogen release. *Int. J. Hydrogen Energy* **2018**, *43*, 20772–20782. [CrossRef]

265. Kwon, S.-M.; Kim, M.J.; Kang, S.; Kim, T. Development of a high-storage-density hydrogen generator using solid-state NaBH$_4$ as a hydrogen source for unmanned aerial vehicles. *Appl. Energy* **2019**, *251*, 113331. [CrossRef]

266. Lale, A.; Wasan, A.; Kumar, R.; Miele, P.; Demirci, U.B.; Bernard, S. Organosilicon polymer-derived mesoporous 3D silicon carbide, carbonitride and nitride structures as platinum supports for hydrogen generation by hydrolysis of sodium borohydride. *Int. J. Hydrogen Energy* **2016**, *41*, 15477–15488. [CrossRef]

267. Lee, J.; Shin, H.; Choi, K.S.; Lee, J.; Choi, J.-Y.; Yu, H.K. Carbon layer supported nickel catalyst for sodium borohydride (NaBH$_4$) dehydrogenation. *Int. J. Hydrogen Energy* **2019**, *44*, 2943–2950. [CrossRef]

268. Lee, Y.-J.; Lee, Y.-S.; A Shin, H.; Jo, Y.S.; Jeong, H.; Sohn, H.; Yoon, C.W.; Kim, Y.; Kim, K.-B.; Nam, S.W. Surface area enhancement of nickel foam by low-temperature chemical alloying/dealloying and its application for sodium borohydride hydrolysis. *J. Alloys Compd.* **2020**, *843*, 155759. [CrossRef]

269. Li, H.-Y.; Chen, Y.-T.; Lu, M.-T.; Lai, Y.-H.; Yang, J.-T. Design and testing of a novel catalytic reactor to generate hydrogen. *Int. J. Hydrogen Energy* **2014**, *886*, 1–10. [CrossRef]

270. Li, J.; Hong, X.; Wang, Y.; Luo, Y.; Huang, P.; Li, B.; Zhang, K.; Zou, Y.; Sun, L.; Xu, F.; et al. Encapsulated cobalt nanoparticles as a recoverable catalyst for the hydrolysis of sodium borohydride. *Energy Storage Mater.* **2020**, *27*, 187–197. [CrossRef]

271. Li, K.; Ma, M.; Xie, L.; Yao, Y.; Kong, R.; Du, G.; Asiri, A.M.; Sun, X. Monolithically integrated NiCoP nanosheet array on Ti mesh: An efficient and reusable catalyst in NaBH$_4$ alkaline media toward on-demand hydrogen generation. *Int. J. Hydrogen Energy* **2017**, *42*, 19028–19034. [CrossRef]

272. Li, Q.; Wang, F.; Zhou, X.; Chen, J.; Tang, C.; Zhang, L. Synergistical photo-thermal-catalysis of Zn$_2$GeO$_4$:xFe^{3+} for H2 evolution in NaBH$_4$ hydrolysis reaction. *Catal. Commun.* **2021**, *156*, 106321. [CrossRef]

273. Li, Q.; Yang, W.; Li, F.; Cui, A.; Hong, J. Preparation of CoB/ZIF-8 supported catalyst by single step reduction and its activity in hydrogen production. *Int. J. Hydrog. Energy* **2018**, *43*, 271–282. [CrossRef]

274. Aakko-Saksa, P.T.; Cook, C.; Kiviaho, J.; Repo, T. Liquid organic hydrogen carriers for transportation and storing of renewable energy—Review and discussion. *J. Power Source* **2018**, *396*, 803–823. [CrossRef]

275. Dai, H.-B.; Gao, L.-L.; Liang, Y.; Kang, X.-D.; Wang, P. Promoted hydrogen generation from ammonia borane aqueous solution using cobalt–molybdenum–boron/nickel foam catalyst. *J. Power Source* **2010**, *195*, 307–312. [CrossRef]

276. Shen, Y.; Yang, X.; Sun, T.; Jia, J. Innovative Desulfurization Process of Coal Water Slurry under Atmospheric Condition via Sodium Metaborate Electroreduction in the Isolated Slot. *Energy Fuels* **2011**, *25*, 5007–5014. [CrossRef]

277. Shen, Y.; Sun, T.; Jia, J. A novel desulphurization process of coal water slurry via sodium metaborate electroreduction in the alkaline system. *Fuel* **2012**, *96*, 250–256. [CrossRef]

278. Shu, C.; Sun, T.; Jia, J.; Lou, Z. A novel desulfurization process of gasoline via sodium metaborate electroreduction with pulse voltage using a boron-doped diamond thin film electrode. *Fuel* **2013**, *113*, 187–195. [CrossRef]

279. Shu, C.; Lai, F.; Zhu, F.; Luo, D. Optimal extractive and reductive desulfurization process using sodium borohydride in situ generated via sodium metaborate electroreduction in ionic liquid. *Chem. Eng. Process. Process. Intensif.* **2020**, *150*, 107869. [CrossRef]

280. Liu, C.-H.; Chen, B.-H. The Concept about the Regeneration of Spent Borohydrides and Used Catalysts from Green Electricity. *Materials* **2015**, *8*, 3456–3466. [CrossRef]

281. Varin, R.; Jang, M.; Czujko, T.; Wronski, Z. The effect of ball milling under hydrogen and argon on the desorption properties of MgH2 covered with a layer of Mg(OH)2. *J. Alloys Compd.* **2010**, *493*, L29–L32. [CrossRef]
282. Zhu, Q.-Y.; Zhu, C.-G.; Wang, F.-W.; Wei, Y.-J. Preparation of Sodium Borohydride by Copper Electrolysis. *Asian J. Chem.* **2013**, *25*, 7749–7752. [CrossRef]