

Review

Review on Magnesium Hydride and Sodium Borohydride Hydrolysis for Hydrogen Production

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Abstract: Metal hydrides such as MgH₂ and NaBH₄ are among the materials for with the highest potential solid-state hydrogen storage. However, unlike gas and liquid storage, a dehydrogenation process has to be done prior to hydrogen utilization. In this context, the hydrolysis method is one of the possible methods to extract or generate hydrogen from the materials. However, problems like the MgH₂ passivation layer, high cost and sluggish self-hydrolysis of NaBH₄ are the known limiting factors for this process, but they can be overcome with the help of catalysts. In this work, selected studies have been reviewed on the performance of catalysts like chloride, oxide, fluoride, platinum, ruthenium, cobalt and nickel-based on the MgH₂ and NaBH₄ system. These studies show a significant enhancement in the amount of hydrogen released as compared to the hydrolysis of the pure MgH₂ and NaBH₄. Therefore, the addition of catalysts is proven as one of the options in improving hydrogen generation via the hydrolysis of MgH₂ and NaBH₄.

Keywords: hydrogen production; hydride hydrolysis; magnesium hydride; sodium borohydride; catalyst



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1. Introduction

A crucial component of a sustainable development community is the possible creation, preservation, and generation of new renewable, ecologically friendly energies, especially given the rapid use of energy sources [1]. Sources of energy including coal, oil, and gas, on the other hand, continue to rise in price, resulting in the urgent need for renewable energy sources [2]. Thereupon, hydrogen has been considered to be among the most suitable replacements to fossil fuels over the last ten years as a clean and energy carrier resulting from high energy requirement and intensified environmental degradation [3]. Moreover, hydrogen's chemical energy per unit mass (142 MJ/kg) is almost three times more than any other fuel (for example, hydrocarbons' chemical energy per unit mass itself is 47 MJ/kg) [4]. Hydrogen also produces water as its by-product from the combustion process which is environmentally-safe [5].

Hydrogen can be stored in gas, liquid and solid form. However, the high working pressure (70 MPa) for gaseous-state hydrogen storage and low temperature requirements (−253 °C) for liquid-state hydrogen storage had restrained their applications. Likewise, because hydrogen must be stored at 253 °C, it loses a huge proportion of energy (up to

40%), making it ineffective for long-term hydrogen storage. Solid-state hydrogen storage has some benefits over gaseous and liquid hydrogen storage. With substantial pressure and temperature requirements, the storage method offers a larger energy capacity. Besides that, unlike hydrogen storage in gas and liquid, hydrogen stored in solid need to undergo an extraction process so that the hydrogen can be utilized.

However, the global-scale utilization of hydrogen as a major energy source has been restricted by many issues starting from its production. Although hydrogen is inexhaustible and the richest element in the universe, it is normally bound to other elements to form compounds like hydrocarbon fuels, water and other organic forms. Owing to this characteristic, hydrogen needs to be extracted or to be produced prior to its utilization. However, up to this point, hydrogen production is coming from fossil fuels like natural gas, oil, naphtha and coal. Meanwhile, green hydrogen generation methods such as photocatalysis [6], biomass [7] and water electrolysis [7] have been studied. In recent years, more and more attention has been paid to hydrogen generation by hydrolysis of metal hydrides for their high theoretical hydrogen yield [8–10].

As stated by Brack et al. [5], hydrogen production via metal hydrides consists of two methods which are thermolysis and hydrolysis. The hydrogen is produced by heating for thermolysis and reaction with water for hydrolysis. Hydrolysis is more appealing for MgH_2 and $NaBH_4$ due to the spontaneous and exothermic process that can be improved with the help of a catalyst. Also, they can hydrolyze at a low temperature such as room temperature [11,12].

To date, the hydrolysis of metal hydrides is widely studied. This includes the hydrolysis of MgH_2 and $NaBH_4$. Both the overall amount of generated hydrogen and the kinetic parameters in the hydrolysis process are highly influenced by the type of hydride, active surface area, pH value and temperature of water [13–17]. Besides that, high cost of electrical energy usage is a significant constraint even when hydrogen can be readily produced by electrolysis from water [18]. Even so, with the process of hydrolysis, it is plausible to generate hydrogen by disintegrating metal hydrides at ambient temperature in an aqueous solution. Also, the hydrolysis process happens naturally at a temperature lower than the electrolysis process.

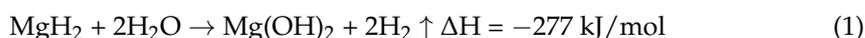
This article reviewed the hydrolysis of metal hydrides focusing on MgH_2 and $NaBH_4$ with the aid of catalysts such as chloride, oxide, fluoride, platinum, ruthenium, cobalt and nickel-based catalysts. The aim is to classify the types of catalysts and its effect that have been studied by other researchers on the hydrolysis of MgH_2 and $NaBH_4$.

2. Influence of Catalysts on the Hydrogen Production of MgH_2

This section focused on MgH_2 hydrolysis and the utilization of several catalysts to enhance the hydrolysis process by previous researchers.

2.1. Why MgH_2

Recently, several researchers have shifted their focus to hydrolysis of MgH_2 as MgH_2 has so far been considered to be among the most effective metal hydrides for hydrolysis. Although it has a lower capacity for hydrogen storage (7.6 wt.%), as compared to $NaBH_4$ and NH_3BH_3 , but it is relatively low cost [19]. When stoichiometric water is taken into account, it has been reported that the hydrogen yield of the hydrolysis reaction of MgH_2 is 6.4 wt.% [20]. Furthermore, due to MgH_2 's strong reducibility, when it interacts chemically with water at room temperature, as depicted in Equation (1), the hydrogen production can reach to 15.2% wt.% if the weight of water is not evaluated, making it particularly ideal for the fuel cell in terms of supplying hydrogen [13,21–24].



Equivalently, the by-product from MgH_2 hydrolysis is insufficiently water-soluble, thus hydrolysis promptly stops when a passive layer of magnesium hydroxide forms on the surface of unreacted MgH_2 [14]. The passive magnesium hydroxide layer blocks

hydrolysis by reducing the kinetics of MgH_2 due to its high pH value which is 10.44 [25]. After only 1 min of hydrolysis, the pH of the solution has increased to the point where Mg^{2+} solubility is minimal [20]. The maximum conversion of MgH_2 in direct hydrolysis cannot be surpassed 30% in 1 h, according to prior research, which is insufficient for practical implementation [16,25–27]. Therefore, several methods have been used to extract the passivation layer and boost MgH_2 hydrolysis effects which include alloying, ball milling, modifying the aqueous solution and many others [11]. Because of the increased specific surface area, ball milling leads in a significant increase in the reactivity of MgH_2 , but the milling time should not surpass one hour because this will induce particle agglomeration and the hydrolysis properties of the resulting materials will deteriorate [28]. Similarly, the introduction of structural defects and the development of nanocrystalline structures are advantageous to MgH_2 hydrolysis [29]. The example of set-up apparatus to study MgH_2 hydrolysis by Chen et al. [30] was as in Figure 1.

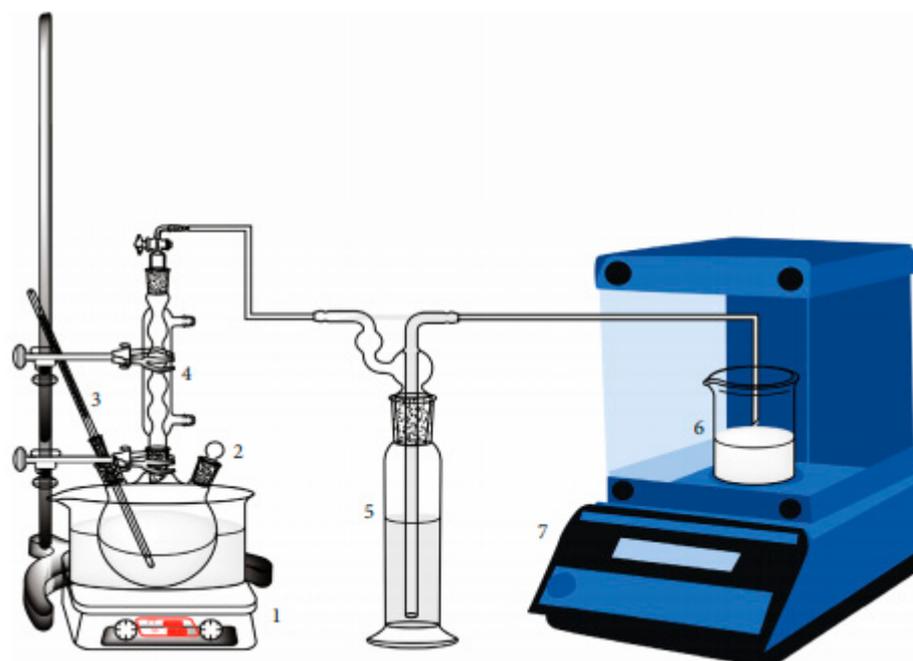


Figure 1. The set-up apparatus to study MgH_2 hydrolysis ((1) water bath, (2) 250 mL three-necked flask, (3) thermometer, (4) condenser, (5) gas washing bottle (6) beaker (7) analytical balance) (source: [30]).

However, optimum milling time needs to be studied as reported by Grosjean et al. [16] where they found that the 0.5 h of milling time was the best compared to 3 and 10 h of milling for the Mg and MgH_2 hydrolysis. In addition, Bacha et al. [31,32] reported that Mg alloy that milled for more than 2 h with and without AlCl_3 will have lower hydrolysis performance as compared to 5 and 10 h of milling time due to powder oxidation and homogeneity of the defect distribution.

Furthermore, hydrolysis at higher temperatures will increase the hydride hydrolysis. Previous researchers such as in [11,14,33,34] have shown and reported the significance of temperature on the hydrolysis performance of MgH_2 . Higher temperatures significantly boost the hydrogen yield for the hydrolysis process in terms of kinetics and capacity.

2.2. Chloride-Based Catalysts

Chloride salts are considered as a potential catalytic material in hydrolysis. One of the reasons is because Cl^- can destabilize or disintegrate the passivation layer of magnesium hydroxide by a pit corrosion process [11]. Figure 2 highlights the function of chloride ions in the hydrolysis process. According to Tegel et al. [13], it is evident that the pH

of the reaction mixture and the reaction's overall yield are only positively influenced by additives that contain anions from powerful Brønsted acids, such as Cl^- . The fact that hydride acts as a base and raises the reaction's pH can be used to explain this observation. As a result, magnesium hydride rapidly develops strong passivation layers that stop any further reaction.

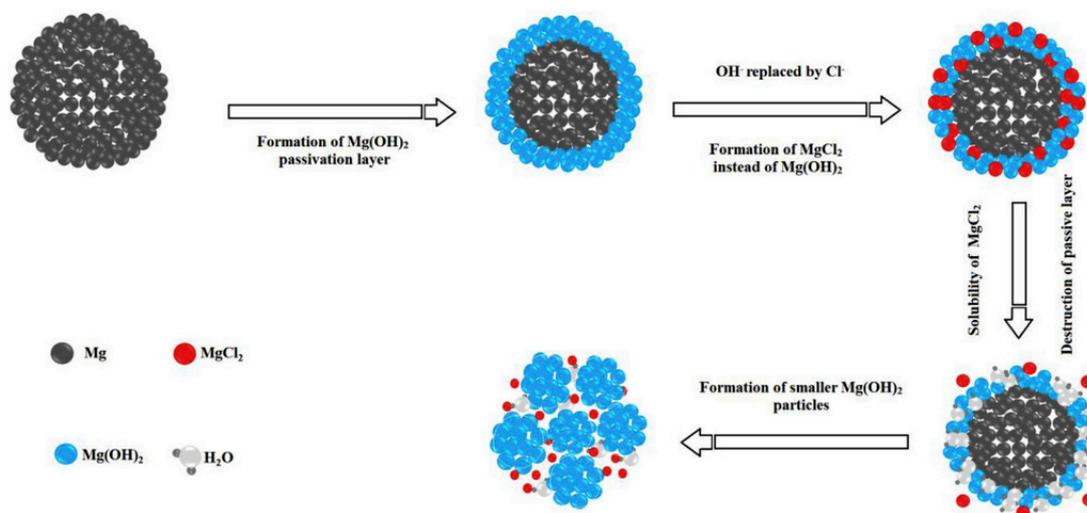


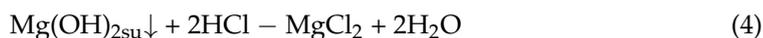
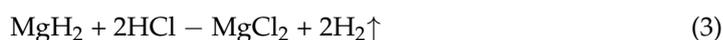
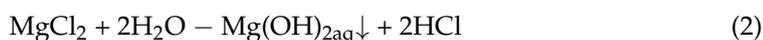
Figure 2. The role of chloride ions in the hydrolysis reaction mechanism. Reprinted with permission from Ref. [35]. 1976, Elsevier Science & Technology Journals.

Gan et al. [11] studied hydrolysis of MgH_2 catalyzed with 0.1 M and 0.5 M AlCl_3 from 5 °C to 30 °C. From the result, for both 0.1 M and 0.5 M of AlCl_3 , the hydrogen yield was the highest at 30 °C. For comparison, at 10, 20 and 30 min, the amount of hydrogen yield for 0.1 M of AlCl_3 was 805 mL/g, 1004 mL/g and 1061 mL/g. In contrast, for the 0.5 M of AlCl_3 , at a similar time frame, the amount of hydrogen yield was 1487 mL/g, 1683 mL/g and 1700 mL/g, for the 10, 20 and 30 min, respectively. Meanwhile, for the activation energy, the reported values were 35.68 kJ/mol (0.1 M AlCl_3) and 21.64 kJ/mol (0.5 M AlCl_3). Korablov et al. [36] suggested the $\text{MgH}_2 + 5 \text{ wt.}\% \text{ AlCl}_3$ sample as an effective hydrogen generating material due to the efficient hydrogen production of 557 mL/g and a conversion rate of 30.3% within 10 min of hydrolysis.

Into the bargain, Huang et al. [14] reported the effect of 0.5 wt.% and 4.5 wt.% of NH_4Cl from 20 °C to 90 °C. From their work, they found that at 90 °C, the amount of hydrogen yield was 1000 mL/g (10 min), 1100 mL/g (20 min) and 1154 mL/g (30 min) for 0.5 wt.% of NH_4Cl . As for the 4.5 wt.% of NH_4Cl , under a similar time and a much lower temperature (60 °C), the amount of hydrogen yield was 1604 mL/g (10 min) and constant (1660 mL/g) from 20 min to 30 min. The reported activation energy was 50.858 kJ/mol for 0.5 wt.% of NH_4Cl and 30.373 kJ/mol for 4.5 wt.% of NH_4Cl . A vast improvement of activation energy was observed when the catalyst was added which the value decreased from 58.058 kJ/mol.

Moreover, Li et al. [37] investigated the effect of 3%, 5% and 10% of NaCl , MgCl_2 and NH_4Cl at 25 °C. Based on their result, NH_4Cl showed the best performance with the highest hydrogen yield while NaCl recorded the lowest value of hydrogen yield. The amount of hydrogen yield for 3% of NH_4Cl was 581 mL/g (10 min), 761 mL/g (20 min) and 872 mL/g (30 min). Next, for 3% of NaCl , the recorded value for hydrogen yield was 413 mL/g (10 min), 540 mL/g (20 min) and 620 mL/g (30 min). Based on the best result obtained in this research, it can be seen that 10% of NH_4Cl greatly improves the hydrolysis performance of MgH_2 with the hydrogen yield of 916 mL/g (10 min), 1105 mL/g (20 min) and 1208 mL/g (30 min). On top of that, NH_4Cl also recorded the highest conversion rate in 60 min (85.69%) as compared to both NaCl (64.64%) and MgCl_2 (68.95%).

Besides that, Zhou et al. [25] disclosed the outcome of MgH_2 -0.5 M MgCl_2 and MgH_2 - H_2O systems. According to their result, at 30 °C, the amount of hydrogen yield for H_2O was measured as 257 mL/g (10 min), 291 mL/g (20 min) and 318 mL/g (30 min). Under similar temperature, with the use of 0.5 M MgCl_2 as a catalyst, the amount of hydrogen yield for 10, 20 and 30 min was 1431 mL/g, 1580 mL/g and 1621 mL/g respectively. This demonstrated that the initial result of 0.5 M MgCl_2 was nearly five times better than H_2O . In addition, the value of conversion rate for 0.5 M MgCl_2 was marked at 96% in just 30 min which is higher than H_2O (20%). When MgCl_2 was added to the mixture, the pH value decreased in conformance with Equation (2), promoting the decomposition of $\text{Mg(OH)}_{2\text{su}}$ and $\text{Mg(OH)}_{2\text{aq}}$ ($\text{Mg(OH)}_{2\text{su}}$ and $\text{Mg(OH)}_{2\text{aq}}$ referred to Mg(OH)_2 developed on the surface of MgH_2 and that formed in the solution, respectively). When $\text{Mg(OH)}_{2\text{su}}$ dissolves, a fresh surface of MgH_2 was exposed to the solution and reacts with water and HCl in accordance with Equation (3). As a result, every mole of MgH_2 that reacted produced two moles of hydrogen. According to Equation (4), once the $\text{Mg(OH)}_{2\text{su}}$ passive film had developed and had slowed the release of hydrogen, HCl would then dissolve the passive layer. To maintain the solution's low pH, Mg^{2+} from $\text{Mg(OH)}_{2\text{su}}$ and MgH_2 simultaneously replaces Mg^{2+} used in the formation of $\text{Mg(OH)}_{2\text{aq}}$.



In line with Berezovets et al. [38], hydrolysis performance improved as the relative quantity of MgCl_2 increased, with the best results coming from the stoichiometric ratio $\text{MgH}_2 + 0.7\text{MgCl}_2$ ($\text{MgCl}_2/\text{MgH}_2$ weight ratio of 12.75/100). This resulted in a 1025 mL (H_2)/g MgH_2 hydrogen production. Maximum hydrogen production reached 89% of theoretical hydrogen generation capacity within 150 min of starting the hydrolysis, with 35% of hydrogen released in the first 10 min and a hydrogen generation rate of 800 mL/min/g MgH_2 .

The latest research done by Zhou et al. [39] centralized on the hydrolysis of MgH_2 with the addition of 10 wt.% of CoCl_2 . Based on their research, they found that the interaction of MgH_2 with deionized water exhibited unfavourable kinetics, yielding only 377 mL/g of hydrogen after 60 min and 30 °C, whereas adding acid chloride improved the hydrolysis performance greatly. Under the same conditions, a 3 h milled MgH_2 doped with 10 wt.% of CoCl_2 produced 1481.7 mL/g of hydrogen and initiated the value of activation energy to be 17.59 kJ/mol. The activation energy reported by Coşkuner Filiz [10] was 20 kJ/mol alongside the ideal concentration of catalyst was found to be 6.25 wt.% CoCl_2 , with the quickest hydrogen generation rate of 18.55 mL/min/g and full conversion of MgH_2 to Mg(OH)_2 .

2.3. Oxide-Based Catalysts

As proclaimed by Awad et al. [35], only MgO has been investigated in the reaction of hydrolysis even though many other metal oxides were already tested as catalysts in the reaction of hydrogen sorption for Mg or MgH_2 . In spite of that, the high reactivity of MgH_2 with water leads to an increment in the rate of hydrogen yield due to the presence of numerous defects and clean surfaces in conjunction with the decreasing size of particles throughout the milled process of the MgH_2 - MgO system [40].

Kojima et al. [26] researched the reaction of hydrolysis for MgH_2 catalyzed by 50 mg of Pt-LiCoCO₂ and 2 wt.% of acetic acid at 20 °C. By referring to their result, for $\text{MgH}_2 + 2$ wt.% of acetic acid, the reported percentage of hydrogen yield was 60% (10 min), 68% (20 min) and 72% (30 min). Comparatively, $\text{MgH}_2 + 50$ mg of Pt-LiCoCO₂ + 2 wt.% of acetic acid showed the best kinetic performance with the percentage of hydrogen yield 84% (10 min), 90% (20 min) and 96% (30 min). This validated that the use of Pt-LiCoCO₂ as a catalyst helped

in increasing the hydrogen yield percentage up to more than 20%. In addition, in 60 min, almost 100% of hydrogen was generated when the system was catalyzed by Pt-LiCoCO₂.

In addition, research done by Awad et al. [35] fixated on the effectiveness of carbons, transition metals and oxides such as 10 wt.% of Nb₂O₅ and V₂O₅ as catalysts. The effect of 10 wt.% of Nb₂O₅ and V₂O₅, ball-milled from 1 h to 5 h at 25 °C was studied. As stated from their result, 10 wt.% of Nb₂O₅, ball milled for 1 h, exhibited the percentage of hydrogen yield 96% in 10 min and 100% in both 20 and 30 min. In comparison, the exhibited percentage of hydrogen yield for 10 wt.% of V₂O₅ was 80% (10 min), 96% (20 min) and 100% (30 min) under the same condition. This confirmed that Nb₂O₅ was more effective as a catalyst and it also owned an activation energy of 31.46 kJ/mol.

The impacts of graphite (C) and Fe₂O₃ on the kinetics of MgH₂ hydrolysis were explored by Yang et al. [41]. When compared to pure MgH₂, they found that both MgH₂ + C and MgH₂ + C + Fe₂O₃ samples performed better in terms of hydrolysis reaction rate and hydrogen conversion rate. The MgH₂ + C + Fe₂O₃ sample had the highest hydrolytic yield rate and conversion rate of all of them. The 30 min conversion rate of MgH₂ + C + Fe₂O₃ sample at 80 °C is 9.8% greater than that of the MgH₂ + C sample, and 42.6% greater than that of pure MgH₂. The hydrolysis activation energy of pure MgH₂ was also discovered to be 55.57 kJ/mol. The introduction of C and Fe₂O₃ to MgH₂ + C and MgH₂ + C + Fe₂O₃ samples reduced the activation energy values to 43.40 kJ/mol and 36.92 kJ/mol, correspondingly.

Recently, Xie et al. [42] investigated the systems of MgH₂ doped with 10% of Nb₂O₅ and 10% of CeO₂. On the hydrolysis performance of MgH₂, Nb₂O₅ is discovered to have superior facilitating effects than CeO₂. Within 60 min and in the temperature of 20 °C, MgH₂ doped with 10% of Nb₂O₅ and 10% of CeO₂ generated 705 mL/g and 474 mL/g of hydrogen in distilled water, respectively. In a 5% of MgCl₂ solution, the sample of MgH₂ doped with 10% of Nb₂O₅ generated 1222 mL/g of hydrogen, equating to a conversion rate of 74.6%. This proved that the addition of MgCl₂ to water can also improve the kinetics and conversion rate of the hydrolysis reaction. Nevertheless, in MgCl₂ solution, an air-exposed MgH₂ doped with 10% of Nb₂O₅ sample barely generated any hydrogen. Meanwhile, after 24 h of air exposure, the sample of MgH₂ doped with 10% of CeO₂ could generate 250 mL/g of hydrogen. This is because CeO₂ can alter oxidation resistance.

In the same year, Naseem et al. [43] studied the Mo and B₂O₃ catalysts for the co-hydrolysis of Al and MgH₂. In the 1 M AlCl₃ solution at ambient temperature, the Al₁₂Mg₁₇-1.5 wt.% Mo and Al₁₂Mg₁₇-3.5 wt.% B₂O₃ composites yielded 1341.6 mL/g and 1304 mL/g of hydrogen. Moreover, the greatest hydrogen yield was reached when both Mo and B₂O₃ were included as additions, with 1420.2 mL/g of hydrogen released in the 1 M AlCl₃ solution at ambient temperature. After 2 h of milling in 0.1, 0.5, and 1 M AlCl₃ solutions, the hydrolysis of Al₁₂Mg₁₇-1.5 wt.% Mo-3.5 wt.% B₂O₃ yielded evident activation energies of 16.4, 13.3, and 9.4 kJ/mol, correspondingly. Additionally, the H₃BO₃ that was produced from the interaction with water caused a concentration of H⁺ ions to increase, further shattering the layers of MgAl₂O₄ and Mg(OH)₂. This procedure increased the number of new surfaces available for the subsequent hydrolysis reaction, which also improved the hydrolysis kinetics.

2.4. Fluoride-Based Catalyst

In consonance with Mao et al. [33], fluorides are also anticipated as being efficient catalysts to stimulate the reaction of hydrolysis by considering the fact that the properties of fluorides are close to those of chlorides and bromides. On top of that, the hydrogen absorption and resistance of oxidation will significantly improve due to the development of the fluoride layer on top of the magnesium particles. Nonetheless, a limited amount of research projects have been published on the fluorides' catalytic performances for the hydrolysis of MgH₂.

Correspondingly, the hydrolysis of MgH₂ catalyzed by 10 wt.% of VF₃, NiF₂, LaF₃ and CeF₃ from 20 °C to 50 °C was studied by Mao et al. [33]. Based on their study, for 10 wt.% of VF₃, NiF₂, LaF₃ and CeF₃, the highest hydrogen yield was detected at 50 °C. Meanwhile,

10 wt.% of VF_3 showed the fastest hydrolysis kinetic with the amount of hydrogen yield 1491 mL/g (5 min), 1534 mL/g (10 min) and 1550 mL/g (15 min). This contrasts with 10 wt.% of NiF_2 which showed the slowest hydrolysis kinetic with the amount of hydrogen yield 1136 mL/g (5 min), 1173 mL/g (10 min) and 1179 mL/g (15 min). In the meantime, the values of activation energy for 10 wt.% of VF_3 and NiF_2 were recorded as 95.56 kJ/mol and 88.61 kJ/mol respectively.

2.5. Other Catalysts

The milled MgH_2 with the addition of catalyst brings benefits including the synergies among nanostructuring and catalyst supports, allowing the synthesis of numerous products with greater potential for hydrogen yield [44]. There are many other types of catalyst which were found to be effective for the hydrolysis of MgH_2 . For instance, since Ge was viewed as an efficient catalyst for ammonia borane, so Ge was presumed to be effective in MgH_2 [44].

Research done by Adeniran et al. [44] focused on the use of Ge (5–20 wt.%) as a catalyst for hydrolysis of MgH_2 in 30% concentration of citric acid and acetic acid from 30 °C to 50 °C. According to their work, at 30 °C, for 5 wt.% of Ge in 30% citric acid, the amount of hydrogen yield was 700 mL/g (10 s), 1100 mL/g (20 s) and 1350 mL/g (30 s). Also at 30 °C, for 5 wt.% of Ge in 30% acetic acid, the amount of hydrogen yield was 1000 mL/g (10 s), 1300 mL/g (20 s) and 1360 mL/g (30 s). This proved that the hydrolysis kinetic for 5 wt.% of Ge in 30% acetic acid was faster than in 30% acetic acid.

Other than that, Ma et al. [45] have carried out an investigation on the hydrolysis of MgH_2 - LiNH_2 (Lithium Amide) system with different ratios of MgH_2 to LiNH_2 (1:1, 2:1, 4:1, 8:1, 16:1 and 32:1) from 0 °C to 40 °C. Based on their work, at 25 °C, the 4 MgH_2 - LiNH_2 system exhibited the highest kinetic performance with the amount of hydrogen yield 950 mL/g (10 min), 970 mL/g (20 min) and 1000 mL/g (30 min). Under the same temperature, the 32 MgH_2 - LiNH_2 system appeared as the lowest kinetic performance with the amount of hydrogen yield 620 mL/g (10 min), 690 mL/g (20 min) and 700 mL/g (30 min). Simultaneously, the listed activation energy for 4 MgH_2 - LiNH_2 and 32 MgH_2 - LiNH_2 systems was 16.0 kJ/mol and 52.5 kJ/mol respectively.

A study on the hydrolysis of MgH_2 catalyzed by different concentrations of citric acid (0.005 mol dm^{-3} , 0.01 mol dm^{-3} , 0.02 mol dm^{-3} , 0.05 mol dm^{-3} and 0.1 mol dm^{-3}) at 25 °C was done by Hiraki et al. [46]. From their result, 0.1 mol dm^{-3} of citric acid owned an outstanding kinetic performance with the amount of hydrogen yield 1700 mL/g from 10 min to 30 min. In comparison, 0.005 mol dm^{-3} of citric acid showed poor kinetic performance with the amount of hydrogen yield 400 mL/g from 10 min to 30 min. This showed that the amount of hydrogen yield for 0.1 mol dm^{-3} of citric acid has reached up to 3 times better than 0.005 mol dm^{-3} of citric acid. Concurrently, the reported rates of conversion were 99% (0.1 mol dm^{-3} of citric acid) and 20% (0.005 mol dm^{-3} of citric acid).

Next, the effectiveness of 10 at% of Ni at 25 °C in pure water and 1 M KCl was observed by Grosjean et al. [16]. Firstly, for 10 at% of Ni in pure water, the percentage of hydrogen conversion yield was 20% (10 min), 23% (20 min) and 25% (30 min). In contrast, the percentage of hydrogen conversion yield for 10 at% of Ni in 1 M KCl was 26% (10 min), 30% (20 min) and 34% (30 min). This verified that the percentage of hydrogen conversion yield for 10 at% of Ni in 1 M KCl showed an increase of more than 5% when compared to 10 at% of Ni in pure water.

Liu et al. [34] investigated the effect of 10 wt.%, 20 wt.% and 30 wt.% of Ca in the MgH_2 system from 25 °C to 70 °C. Based on their work, it was found that the best hydrolysis kinetic was recorded at 70 °C. Along with that, at 70 °C, the best hydrolysis kinetic was obtained from 30 wt.% of Ca with the amount of hydrogen yield 1150 mL/g (10 min), 1250 mL/g (20 min) and 1350 mL/g (30 min). Meanwhile, poor hydrolysis kinetic was obtained from 10 wt.% of Ca with the amount of hydrogen yield 800 mL/g (10 min), 1050 mL/g (20 min) and 1200 mL/g (30 min) at the same temperature. As for the activation energy, 30 wt.% of Ca recorded the lowest value (8.3 kJ/mol) while 10 wt.% of Ca recorded the highest value (21.1 kJ/mol).

3. Influence of Catalysts on the Hydrogen Production of NaBH₄

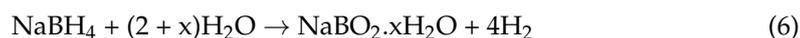
Section 3 introduces the hydrolysis of NaBH₄ and the implementation of different types of catalysts to improve the NaBH₄ hydrolysis done by previous researchers.

3.1. Why NaBH₄

In 2007, the US Department of Energy recommended a no-go on NaBH₄ hydrolysis [47]. However, the no-go recommendation is only for the on-board systems due to the high “net system” cost in order to regenerate sodium borate (NaBO₂) back to NaBH₄ fuel. In addition, the water-driven NaBH₄ was seen as impossible to meet the capacity performance targets for 2010 [48]. However, due to NaBH₄'s high hydrogen storage capacity, non-combustible and exemplary constancy of its alkaline solution, it is regarded as a possible choice for the generation of hydrogen through hydrolysis [49] and stands as a promising hydrogen carrier for the on-demand power supply [47]. In addition, studies on the economic potential NaBH₄ regeneration process were extensively done by researchers [8,9,47,50,51]. Ideally, the hydrolysis reaction of NaBH₄ is given as [8]:



However, since the hydrolysis of NaBH₄ only happen with the introduction of water, the actual the hydrolysis reaction of NaBH₄ in water is given by [8]:



where x , which might have a value of 2 or 4 depending on the reaction circumstances, is the excess hydration factor [52].

Producing hydrogen by hydrolyzing sodium borohydride is not without issues. The amount of water needed is a significant problem. The stoichiometric chemical reaction is shown as in equation 1, however in reality, at least four molar equivalents of water are needed for every mole of NaBH₄. This is happened due to two factors; (i) sodium metaborate (NaBO₂) hydrates very quick and (ii) low solubility of NaBH₄ (55 g for every 100 g of H₂O at 25 °C) [53].

Based on NaBH₄'s low effective gravimetric hydrogen storage capacity, high cost, and ineffectiveness for recycling its hydrolysis by-product (NaBO₂), the United States DOE recommended against using it [54]. In the interim, the process of NaBH₄ hydrolysis progresses smoothly at room temperature and is an exothermic reaction and in order to stimulate this reaction, it is essential to include acid or a relevant metal catalyst [12]. This is because NaBH₄'s self-hydrolysis without any catalyst is very sluggish [3,55,56].

3.2. Platinum-Based Catalysts

In line with Zhang et al. [57], the outlandish cost and minimal availability cause Pt difficult to be considered for a wide range of applications even though many existing works consistently show the notable reaction of Pt in catalyzing NaBH₄ hydrolysis. Thus, to attain bimetallic catalysts through the inclusion of non-costly metals is an enticing approach that will substantially lower the cost, retaining only minor costly metal products. It will also generate efficacy among the distinct metals that can help in increasing the catalytic performance. Table 1 shows several previous latest studies for the hydrolysis of NaBH₄ which used Pt as a catalyst.

3.3. Ruthenium-Based Catalysts

Ru has been perceived as a compelling catalyst not only for its impeccable catalytic performance but also due to its low cost contrasted to several other noble metals [65]. Conversely, Ru's deficiency and expensive price are the obstructions on the path to industrial purposes [66]. Accordingly, further improvement in the catalytic efficiency of Ru for hydrolysis of NaBH₄ is indispensable which leads to Ru being extensively studied. Thus, Table 2 displays prior studies for NaBH₄ hydrolysis with the use of Ru as a catalyst.

Table 1. Previous latest studies on the hydrogen yield rate due to the effect of platinum on NaBH₄ hydrolysis.

Catalysts	H ₂ Yield Rate	Temperature (°C)	Activation Energy (kJ/mol)	Year	Reference
PtCo _{fiber} /Cu	3700 mL/min.g _{cat}	30–70	62.60	2018	[58]
Pt-Co ₃ O ₄	23,916 mL/min.g _{cat}	25–55	43.52	2019	[59]
Pt/MWCNT	159 mmol/min.g _{cat}	27–67	27.00	2019	[60]
Pt/Al ₂ O ₃ /cordierite	53 mL/min	autothermal	-	2019	[61]
PdPt	372.52 mL/min.g _{cat}	20–35	13.93	2021	[62]
Ag-Pt	294.78 mL/min.g _{cat}	20–35	25.61	2022	[63]
N@Pt-Ag	367.01 mL/min.g _{cat}	20–35	16.02	2022	[64]

Table 2. Previous latest studies on the hydrogen yield rate due to the effect of ruthenium on NaBH₄ hydrolysis.

Catalysts	H ₂ Yield Rate	Temperature (°C)	Activation Energy (kJ/mol)	Year	Reference
Ru/ZIF	22,400 mL/min.g _{cat}	30–60	39.00	2018	[65]
Ru-Co ₃ O ₄	20,628 mL/min.g _{cat}	25–55	28.26	2019	[59]
RuMo/CNT	82,758.43 mL/min.g _{cat}	20–50	35.11	2020	[67]
Ru/CoO _x @NPC	8019.5 mL/min.g _{cat}	25–45	59.30	2021	[68]
Ru _{9.8} /r-CoP	9783.3 mL/min.g _{cat}	25–45	45.30	2021	[69]
Ru/NH ₂ -magadiite	36,515 ± 500 mL/min.g _{Ru}	5–20	54.50	2021	[70]
Ru/Co	19.67 mL/min	30–60	30.18	2021	[71]
RuW/MWCNT	198,397.2 mL/min.g _{cat}	20–50	16.32	2022	[72]
Ru-TiO ₂ -Ti ₃ C ₂	434,500 mL/min.g _{Ru}	30–60	50.96	2022	[73]
Ru complex	299,220 mL/min.g _{cat}	20–50	25.80	2022	[74]

Annotation: Ru complex = fabricated via 5-Amino-2,4-dichlorophenol-3,5-diterbutylsilylaldimine ligand and RuCl₃-H₂O salt.

3.4. Cobalt-Based Catalysts

Noble metals are costly and hard to come by. Therefore, it is extremely desirable to adopt catalyst systems based on the less expensive transition metals. One of the most popular active metals and a transition metal catalyst, Co, exhibits superior catalytic activity to other transition metal catalysts when used to hydrolyze NaBH₄ [75–77]. In comparison to Co catalysts made with Co(NO₃)₂, Co(CH₃COO), and CoSO₄, those made with CoCl₂ as a precursor have the highest catalytic activity [78–80]. Co-B was given significant recognition for its superior catalytic behaviour, reasonable price and convenient method of preparation [81]. Next, by dissolving the particles into an acceptable support material, the catalytic performance of Co-B can be optimized [82]. Table 3 presents previous works done when Co was used as a catalyst for NaBH₄ hydrolysis.

3.5. Nickel-Based Catalysts

It is essential to look at the lower-priced alternatives like Ni since the price of cobalt, which is in high demand in the creation of lithium-ion batteries, is rising [93]. Although Ni does not directly involved in the hydrogen generation reaction, it greatly improves the efficiency of the process [94]. Furthermore, because of the shift in electronic states of the active metals, it has been discovered that combining Ni with a metalloid atom (such as B or P) will boost the catalytic activity [95]. Table 4 exhibits previous works resulting from using Ni as a catalyst for NaBH₄ hydrolysis.

Table 3. Previous latest studies on the hydrogen yield rate due to the effect of cobalt on NaBH₄ hydrolysis.

Catalysts	H ₂ Yield Rate	Temperature (°C)	Activation Energy (kJ/mol)	Year	Reference
Co/Ti ₄ N ₅ T _x	526 mL/min.g _{cat}	30–60	44.23	2021	[83]
Co@150PC	11,086.4 mL/min.g _{Co}	15–55	31.25	2021	[84]
Co-Cr-B/NG	2231.7 mL/min.g _{cat}	15–45	38.41	2022	[85]
Co/CuO–NiO–Al ₂ O ₃	6460 mL/min.g _{cat}	25–55	31.59	2022	[86]
Co ⁰ hollow microspheres	1560 mL/min.g _{cat}	25–40	55.5 ± 1.9	2022	[87]
Co–W–B/PPy	13,470 mL/min.g _{cat}	20–35	49.18	2022	[88]
Co/Co _x O _y Nanofilm	4067 mL/min.g _{cat}	30–45	43.19	2022	[89]
Co@C-462-145	5392 mL/min.g _{Co}	25–40	32.70	2022	[90]
Co _{0.45} W _{0.55}	1770 mL/min.g _{cat}	0–35	55.56	2022	[91]
Co/HTNT	1750 mL/min.g _{Co}	20–50	29.68	2022	[92]

Annotation: Co@C-462-145 = 462 µL of ammonia, 145 °C of hydrothermal temperature, Co/HTNT = immobilized Co on the surface of titanate nanotubes and Co@150PC = Co nanoparticles supported on bagasse-derived porous carbon.

Table 4. Previous latest studies on the hydrogen yield rate due to the effect of nickel on NaBH₄ hydrolysis.

Catalysts	H ₂ Yield Rate	Temperature (°C)	Activation Energy (kJ/mol)	Year	Reference
Ni	22,500 mL/min.g	10–60	46.60	2019	[96]
Ni–Zn	430 mL/min.g	25	-	2019	[97]
Ni ₅ P ₄ /Fe	175 mL/min.g	30	53.41	2019	[98]
Pine-needle-like NiCo ₂ O ₄	1904.76 mL/min.g	25–55	47.69	2020	[99]
Network-like NiCo ₂ O ₄	2251.14 mL/min.g	25–55	52.21	2020	[99]
Ball-cactus-like NiCo ₂ O ₄	6219 mL/min.g	25–55	55.79	2020	[99]
Dandelion-like NiCo ₂ O ₄	3125 mL/min.g	25–55	63.44	2020	[99]
Ni/TiO ₂	110.87 mL/min.g _{cat}	20–60	25.11	2021	[100]
NiB25	8970 mL/min.g _{cat}	65	48.05	2021	[101]
Nickel (II) complex/CeO ₂	43.392 mL/min.g _{cat}	20–50	20.58	2021	[102]
Ni/Dolomite	88.16 mL/min.g _{cat}	30–60	38.33	2022	[103]

Annotation: NiB25 = with the addition of 25 µL Triton.

4. Conclusions

In conclusion, metal hydrides like MgH₂ and NaBH₄ can be used to store hydrogen via the solid-state form. Consequently, the hydrolysis method is one of the methods accustomed to release the stored hydrogen. However, problems like the MgH₂ passivation layer, high cost and sluggish self-hydrolysis of NaBH₄ are the known limiting factors that can be overcome with the help of catalysts. Based on selected studies reviewed in this article, catalysts like chloride, oxide, fluoride, platinum, ruthenium, cobalt and nickel-based are proven to be significant to enhance the amount of hydrogen released as compared to non-catalyzed MgH₂ and NaBH₄ system.

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