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HYDROGEN GENERATION BY HYDROLYSIS OF MgH_2

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Magnesium hydride MgH_2 is a hydrogen-rich compound which generates significant amount of hydrogen by a hydrolysis process – its chemical interaction with water or with aqueous solutions. This process is of great interest for on-site hydrogen generation aimed at use of H_2 as a fuel for PEM fuel cells. The present paper is a review of the recent reference publications on the topic which also presents the results of the own research. Increase of the rates of H_2 release and a completeness of transformation of MgH_2 are two important goals which can be reached by: optimizing size of the powders of MgH_2 by ball milling; using catalysers added to MgH_2 and to the aqueous solutions; increasing the temperature of interaction. The effect of these parameters on the extent of conversion and the rates of hydrogen evolution are analysed in detail and the best systems to reach the efficient hydrolysis performance are identified. The mechanism of catalytic hydrolysis was proposed while further improvements of the hydrolysis process are required and need further studies of this important topic.

Keywords: *hydrogen, magnesium hydride, composites, hydrolysis, hydrogen energy.*

Introduction. Magnesium hydride (MgH_2) if formed by inexpensive and abundant on Earth magnesium metal and has a high theoretical hydrogen storage capacity of 7.6 wt.% H. Hydrogen can be obtained by hydrolysis of MgH_2 and it provides double as much H_2 as compared to Mg according to the reaction: $Mg + 2H_2O = Mg(OH)_2 + 2H_2$. The weight yield of the released hydrogen is 6.4% when water is accounted in the calculations and it even increases to 15.2% if the water produced by oxidation of H_2 in the fuel cell is collected and used for the hydrolysis reaction. Importantly, this reaction has an advantage of producing eco-friendly $Mg(OH)_2$. When using MgH_2, the hydrolysis reaction quickly stops due to the formation of a compact layer of magnesium hydroxide on the surface of the reacting material. To increase the yield of the hydrolysis process, several methods have been proposed [1–23]. The main techniques included ball milling, alloying, modification of the composition of the hydrolysis solution, introduction of catalysts. In present paper, we aim at summarizing the recent advances in the studies of hydrolysis of MgH_2-based materials.

Materials and experimental methods. Using the designed in-house experimental setup (see Fig. 1), we studied the evolution of hydrogen during the reaction of magnesium hydride with aqueous solutions. The hydrolysis reactor consisted of a 250 cc reaction flask with five openings where the powder, water and additives were mixed. The flask was placed into a water bath and the temperature was maintained constant during the reaction. A thermometer and a sensor of a pH meter were immersed into the reactor to control the conditions of the reaction. Reactions were performed under Ar atmosphere and the produced gas was passed through a flowmeter Sierra 100. We used commercially available MgH_2 as well as magnesium hydride synthesized in our lab by a reaction of Mg metal with H_2.

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In the reference data, commercial MgH_2 (95%, Goldschmidt) [1, 3–5], 95%, Sigma-Aldrich Inc. [2, 14–16, 19], and laboratory produced by direct hydrogenation MgH_2 [6, 7, 11] or synthesized by using hydriding combustion synthesis (HCS) when utilizing $Mg_{99}Ni_1$ [12, 20, 22] as a source of Mg metal, were studied.

Ball milling. The influence of ball milling on the morphology and size of MgH_2 powders as related to its interaction with water was considered in a number of publications [1, 3, 4, 7, 15, 19]. In was concluded that mechanical preactivation increased the reactivity of MgH_2 (Table 1).

Table 1. Parameters of materials and hydrogen generation yield

Origin of MgH_2	Milling time	Specific surface MgH_2, m^2/g	Hydrogen yield (% / mL H_2/g) at time *t*	Literature
Goldschmidt	0 h	1.2	9 % (1 h)	[1]
Goldschmidt	10 h	9.7	18% (1 h)	[1]
As-prepared	5 min	5.4	22% (40 min)	[7]
As-prepared	1 h	2.8	18% (40 min)	[7]
As-prepared / 10% C	5 min	14	26% (40 min)	[7]
As-prepared / 10% C	1 h	27	62% (40 min)	[7]
Sigma-Aldrich	3 h	–	– / 395 (5 min)	[15]
Sigma-Aldrich	2 h	–	– / 422 (50 min)	[19]
Sigma-Aldrich	5 h	–	34% / 584 (50 min)	[19]

According to [1], hydrolysis of MgH_2 stopped after just about 1 min. Measurements of the pH of the solution showed that it reached 10.5 in the first few minutes of hydrolysis. From the potential–pH equilibrium diagram, the concentration of the soluble species of Mg^{2+} was only 10^{-4} M at pH 10.5. Therefore, after only 1 min of hydrolysis, the pH of the solution became high enough to reduce the solubility of Mg^{2+} to a negligible level. This may explain the sudden stop of the initial burst of the reaction, as the formation of insoluble magnesium hydroxide at the surface of the grains will prevent the water solution from reaching unreacted MgH_2.

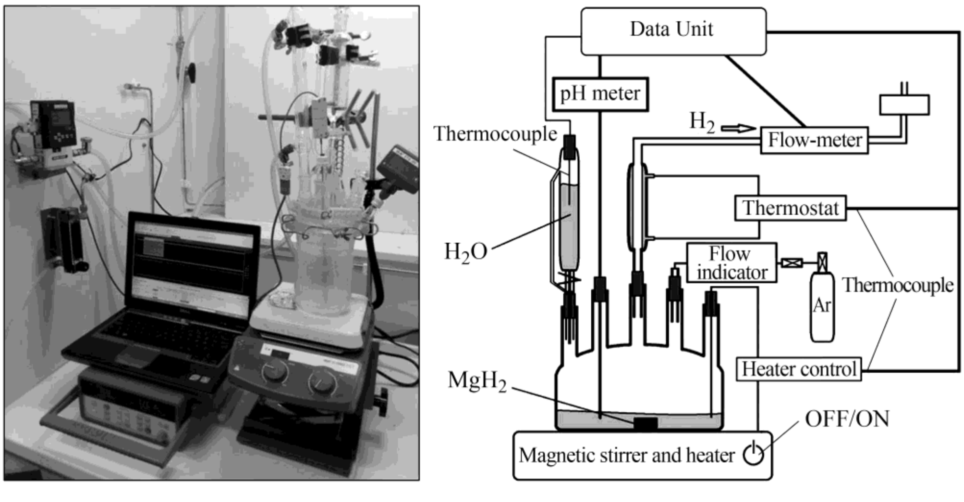

Fig. 1. Experimental setup used to quantify hydrogen generation rates and yields.

The ball-milling method can effectively increase the reaction rate and yield of hydrogen generation (Fig. 2*a*). This phenomenon could be ascribed to the fact that the ball milling process refines the particle and grain sizes, and increases the specific surface area. In addition, the introduction of structural defects and formation of nanocrystalline structures are also beneficial for the MgH_2 hydrolysis [7]. Although the ball milling improves the hydrolysis properties of MgH_2-based materials, the hydrolysis reaction of MgH_2 was still interrupted because of the formation of a passivation layer of magnesium hydroxide.

According to [3], the highest reactivity is obtained for a 30 min milled MgH_2, which shows a conversion yield of 26% as compared to 9% for the unmilled MgH_2 powder. The specific surface area of 30 min milled powder displays a maximum of 12.2 m^2/g. Further milling reduces the specific surface area due to the particles agglomeration. The specific surface area of 7.8 m^2/g and conversion yield of 16% were observed for 10 h milled MgH_2 powder. From extrapolation of the fitting curve of conversion yield of MgH_2 powders vs their effective surface area, a yield of 100% might be reached for MgH_2 powder having an effective surface area of 23 m^2/g [4].

From the additives enhancing the efficiency of the mechanochemical treatment of magnesium hydride, carbonaceous materials are particularly interesting. The reaction of the MgH_2–graphite composites with water was studied in [7], and some data are displayed in Fig. 2*b*, showing increase of H_2 yield caused by the addition of graphite.

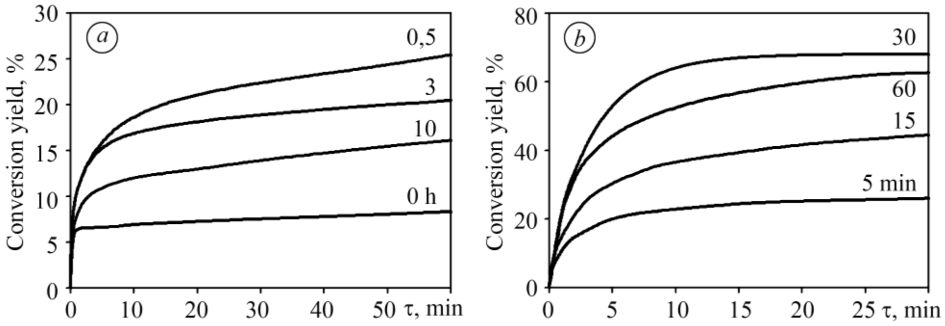

Fig. 2. Time dependences of hydrogen generation rates for the milled MgH_2 (*a*) and MgH_2 containing 10 wt.% graphite (*b*) in pure water.

Effect of salts. The studies of the salt additives on the hydrolysis kinetics of magnesium hydride were performed as related to the content of the additives. In particular, the following solutions of salts [3, 4, 6] or acidic salts and MgH_2 [6, 9] and MgH_2/salt composites [5, 18, 20] hydrolyzed using distilled/tap/sea water (Table 2) were studied. Among the salts, chlorides were in focus [3–6, 12, 15, 18, 20, 23]. The mechanism of hydrolysis of MgH_2 directly depends on the pH of the formed solution [9]. Hydrolysis of MgH_2 with acidic salt solutions gives a maximum conversion and shows a high hydrogen release rate [6, 9]. Increase of the salt content (but to a certain limiting value) in solution or composite leads to the increase of hydrogen yield. Addition of nickel as a catalytic additive to pure magnesium hydride does not result in a noticeable effect on the yield of the hydrolysis process, while having magnesium in the material shows a competitive with MgH_2 performance. Nickel exhibits low electrochemical potential of hydrogen evolution and is a suitable cathode material that induces a strong galvanic corrosion of magnesium. Thus, the use of composite materials containing Mg–Ni composites will increase the yield of H_2 and improves the kinetics of the hydrolysis reaction.

The influence of the composition of the selected ammonium salts and their concentration in aqueous solutions on the hydrolysis of magnesium hydride were studied in [6, 15]. The presence of even a small amount of NH_4Cl (0.5% solution) considerably promotes the hydrolysis [6]: the amount of hydrogen released in 5 min exceeds the amount of hydrogen released within 24 h during the hydrolysis process in a pure water (60 and 57%, respectively). As the concentration of ammonium chloride increases from

0.5 to 7.5%, the hydrolysis rate increases and the conversion in the latter case becomes significantly higher (92% in 5 min). In this solution, the extent of hydrolysis achieved within 24 h (α_{24}) is also the highest (95.4%). Further increase of the concentration of NH_4Cl solution leads to some decrease in the hydrolysis rate and α_{24}. The $(NH_4)_2SO_4$ showed approximately the same effect on the hydrolysis rate. The hydrolysis in the presence of $(NH_4)HSO_4$ proceeds faster and in a more profound extent than in the presence of the neutral ammonium salts. The HSO_4^- anion neutralizes the hydroxyl ion produced in the hydrolysis and thus it promotes the hydrolysis process. Indeed, a complete hydrolysis (100%) with $(NH_4)HSO_4$ was observed after less than 30 min.

Table 2. Hydrogen generation yields with different salt additives

Materials	Solution	Hydrogen yield (% / mL H_2/g) after *t*	Literature
30 min milled MgH_2	1 M KCl	37 / 656 (1 h)	[4]
30 min milled MgH_2 / 10% Ni	1 M KCl	39 / 564 (1 h)	[4]
30 min milled MgH_2 / 3 M $MgCl_2$	H_2O	61 / 964 (1 h)	[5]
30 min milled MgH_2 / 10 M $MgCl_2$	H_2O	75 / – (1 h)	[5]
MgH_2 / 4% Fe / 4% V_2O_5	7.5% NH_4Cl	92 / – (5 min)	[6]
MgH_2 / 4% Fe / 4% V2O5	7.5% $(NH_4)HSO_4$	100 / – (20 min)	[6]
HCS MgH_2 / 1% Ni	0.5 M $MgCl_2$	96 / 1635 (30 min)	[12]
Sigma-Aldrich MgH_2	27.1 % NH_4Cl	99 / 1711 (10 min)	[15]
3 h milled MgH_2	0.05 M $MgCl_2$	– / 1137 (1.5 h)	[15]
1 h milled MgH_2 / 0.024 M $MgCl_2$	H_2O	85/– (1 h)	[18]
1 h milled MgH_2 / 0.024 M $ZrCl_4$	H_2O	94/– (1 h)	[18]
5 h milled MgH_2 / 5% $MgCl_2$	H_2O	68 / 1094 (1 h)	[20]
5 h milled MgH_2 / 10% NH_4Cl	H_2O	86 / 1311 (1 h)	[20]

The hydrolysis reaction of MgH_2 in aqueous solution of magnesium chloride was studied in [12, 15, 23]. It can be noticed that in the presence of $MgCl_2$ the hydrogen yield is higher than that for pure water (Fig. 3*a*). According to [12] and [15], the hydrogen yield was 1635 ml/g and 1137 ml/g in 0.5 M $MgCl_2$ and in 0.05 M $MgCl_2$ after 50 and 90 min, respectively. However, the effect of chlorine ions on the process of crystallization of magnesium hydroxide at the surface of MgH_2 is not completely understood even though they clearly affect the extent of the hydrolysis.

Various hydrolysis reactions between MgH_2/salt composites and distilled water are described in [5, 18, 20]. The composites were prepared by milling the MgH_2 with a certain amount of salt under argon for up to 10 h. The influence of the milling time and the concentration of salt in the $MgH_2/MgCl_2$ composites was studied in [5]. Milling magnesium hydride with salts always led to a several times increase in the specific surface area, but this increase appears to be nonproportional to the milling time. A clear correlation between the hydrogen yields and the values of the specific surface area was not observed. The authors noted that the exothermic dissolution of magnesium chloride may also affect the conversion rate and extent of MgH_2. As a reference point, a conversion yield as high as 81% was obtained when using MgH_2–10 mol% $MgCl_2$ composite milled for 10 h.

The influence of the nature of the cations contained in the chloride salts and the amount of the salts was studied in [20]. The composites MgH_2/NaCl, $MgH_2/MgCl_2$ and MgH_2/NH_4Cl were prepared with 3; 5 and 10% salt and MgH_2 synthesized by HCS

(Fig. 3*b*). Hydrogen yield increased with increasing the salt content in the sequence NaCl – $MgCl_2$ – NH_4Cl. The NH_4Cl has the strongest effect on the kinetics of the hydrolysis process as compared to two other chlorides. At room temperature, MgH_2–10% NH_4Cl composite exhibited the best performance with the hydrogen generation yield of 1311 mL/g and a conversion rate of 85.69% in 60 min.

The effect of the nature of the cation on the hydrolysis of MgH_2/salt composites was studied in more detail in [18], where several chlorides including NaCl, $ZnCl_2$, $AlCl_3$, $ScCl_3$, $FeCl_3$, $TiCl_3$, $MgCl_2$, and $ZrCl_4$ were used (Fig. 4*a*).

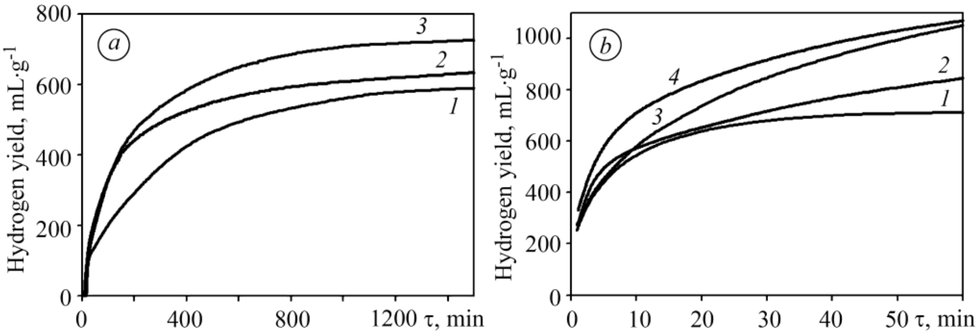

Fig. 3. Hydrogen generation curves from the hydrolysis of MgH_2 with different additions of $MgCl_2$ (*a*: *1* – 4 wt.% $MgCl_2$; *2* – 11.5 wt.% $MgCl_2$; *3* – 21 wt.% $MgCl_2$) [23] and additions of different chlorides (*b*: *1* – MgH_2; *2* – MgH_2+3% NaCl; *3* – MgH_2+3% $MgCl_2$; *4* – MgH_2+3% NH_4Cl) [20].

A series of time-dependent diagrams are built showing a development of a degree of conversion of MgH_2 and pH of the reaction mixture. Among the above mentioned composites containing 0.024 mol equivalents of all additives, the smallest effect on the hydrolysis is observed when using the sodium chloride and the largest effect happens for zirconium chloride. All other salts show an intermediate impact on the kinetics of hydrolysis and hydrogen yield. It can be noticed, that the salts with higher oxidation states of the cations are more efficient in facilitating the hydrolysis. The degree of conversion in all cases is inversely related to the pH of the solution, and it was therefore the lowest for $ZrCl_4$ with pH = 9.8. It was proposed that such behaviour is related to the following activation mechanisms.

A. Formation of a poorly soluble hydroxide of additive metal formed by hydrolysis according to $[M(OH)_n]^{z+} + H_2O \rightarrow [M(OH)_{n+1}]^{(z-1)+} + H^+$ or $MCl_n + nH_2O \rightarrow$ $\rightarrow M(OH)_n\downarrow + nHCl$. This process dynamically buffers the reaction solution and lowers its pH at the initial stage of the process, which improves both the reaction kinetics and the yield of hydrogen.

B. Formation of metal hydroxides induces the predominant formation of a stable (crystalline) $Mg(OH)_2$ or co-precipitation products based on $Mg(OH)_2{\cdot}M(OH)_n{\cdot}H_2O$ or, in the case of $MgCl_2$, $MgCl_2{\cdot}3MgO{\cdot}11H_2O$. Such products are less soluble than $Mg(OH)_2$, and the pH of the solutions decreases. Furthermore, the formation of stable crystalline $Mg(OH)_2$ takes place because of a decrease in the nucleation rate and an increase in the crystal growth rate.

The effect of the anions was studied by replacing the chlorides with bromides using the salts of sodium, magnesium and zirconium. Bromides behave similar to chlorides as a reduction of the pH was also observed. Hydrogen yield (86% and 99% after 1 h by using $MgBr_2$ and $ZrBr_4$ as additives) was not significantly different between two salts, but the bromides showed a faster reaction kinetics. Furthermore, it should be noted that zirconium bromide acts as the best activator of the hydrolysis reaction among all tested salts.

Our studies of the effect of metal forming a chloride on the hydrolysis reaction showed an increase in the yield of the reaction with increasing concentration of Cl^-.

The hydrolysis of magnesium hydride was performed with the additions of metal chlorides with a cation valence from 1 to 4 ($NaCl$ / $MgCl_2$ / $AlCl_3$ / $ZrCl_4$). Conversion rate of the reaction appeared to be directly related to the concentration of chlorine anions. The cations can also affect the behaviour. Selected metal chlorides (except of NaCl) act as Lewis acids and decrease the pH of the solution during their dissolution; this increases a degree of conversion [23].

We believe that the described assumptions concerning the probable mechanism of activation of the hydrolysis of MgH_2 in the presence of metal chlorides may be complemented by the hypothesis of the formation of a buffer system "$Mg(OH)_2 + MgCl_2$" at the late stages of transformation. This assumption is supported by a very good correlation ($R^2 = 0.997$) between the experimental pH values [18] and the calculated ($pH_{(calc)}$) using the equation $pH = 14 - pK_{Mg(OH)_2} + \log [Mg(OH)_2]/[MgCl_2]$ (Fig. 4*b*).

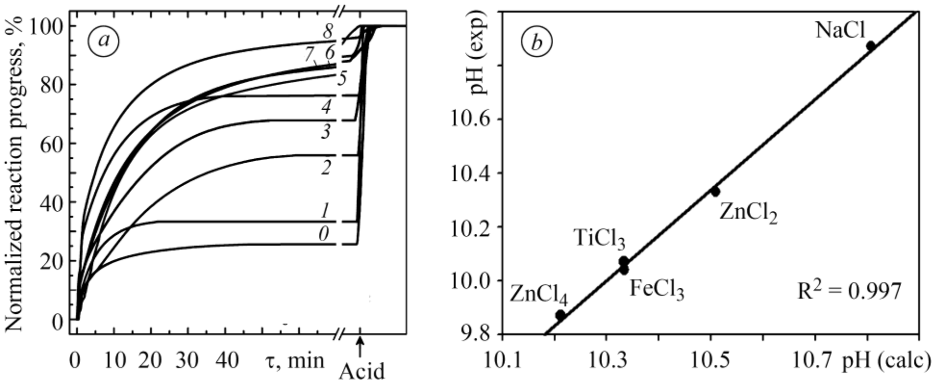

Fig. 4. Time-dependent hydrogen generation curves for the reaction of MgH_2 with solutions of various chlorides (*a*: *0* – none; *1* – NaCl; *2* – $ZnCl_2$; *3* – $AlCl_3$; *4* – $ScCl_3$; *5* – $FeCl_3$; *6* – $TiCl_3$; *7* – $MgCl_2$; *8* – $ZrCl_4$) and the relationship between the experimental [18] and the calculated pH values in the studied solutions (*b*).

Effect of acids. The study of the effect of acids on the hydrolysis of magnesium hydride was studied in [2, 11, 13, 14, 21, 23]. At room temperature the acids result in a significant increase of the conversion of MgH_2 during the hydrolysis reaction, even with no catalysts involved or absence of the activation treatment of MgH_2 (Table 3). Significant amounts of hydrogen can be obtained using inorganic acids [14], organic acids, for example, acetic acid with a platinum catalyst [2] or when heating the reaction mixtures [21] in laboratory experiments; however, a commercial application of acids appears to meet the drawbacks being both expensive and not practically viable due to a significant corrosion of the reactor interior in acidic solutions. Thus, considerable attention is recently focused on the studies of the effect of citric acid (2-hydroxypropane-1,2,3-tricarboxylic acid, $C_6H_8O_7$) on the reaction with magnesium hydride [11, 13]. It should be noted that in a dilute citric acid solution beside the hydrolysis reaction, a direct interaction between MgH_2 and $C_6H_8O_7$ or the formation of salt due to a reaction of the acid with magnesium hydroxide occur.

The choice of the most effective acid as an accelerator for the MgH_2 hydrolysis reactions by using analysis of a chemical equilibrium conditions was performed in [11]. The proposed approach allows us to calculate the effect of weak organic acids on the concentration of magnesium ions after the hydrolysis. The authors suggested to use citric acid or EDTA as efficient buffering agents. The experimental results from Fig. 5*a* show a clear dependence between the hydrogen yield and the concentration of the citric acid. As expected, the conversion extent was rather low (only 13%) in distilled water after 30 min, since the passive $Mg(OH)_2$ layer was formed at the surface of the unreacted MgH_2. Hydrogen release considerably increased when using a relatively dilute solution of citric acid. Both the hydrogen generation rates and the conversion yields increased when applying higher concentrations of citric acid solutions. At low concentration (0.01 mol/l), the reaction proceeded to 40% after 30 min. The reaction in 0.1 mol/l citric acid went to 99% of completion after 30 min, which is 7.7 times higher yield as compared to distilled water. It should be noted that in the described process citric acid acts as a proton donor only. This conclusion is based on the analysis of the reference data and also on our own results (Fig. 5*b*) [23]. The experimental and calculated values of the conversion yield and the pH of the solutions after the completed reaction when using an excess of citric acid well agree with each other (Table 4).

Table 3. Hydrogen generation yield with different acids

Materials	Solution	Hydrogen yield (% / mL H_2/g) after t	Literature
Aldrich MgH_2 (50 mg)	5 g 2 wt.% CH_3COOH + 10 mg Pt – $LiCoO_2$	97 / – (1 h)	[2]
As-prepared MgH_2	0.1 M $C_3H_5O(COOH)_3$	99 / >1600 (30 min)	[11]
MgH_2 (0.36 M)	0.92 M $C_3H_5O(COOH)_3$	100 / – (1 h)	[13]
Aldrich MgH_2	HCl (pH = 1)	100 / – (100 s)	[14]
Aldrich MgH_2 milled 3 h	HCl (pH = 2)	55 / – (25 min)	[14]
Rockwood MgH_2 (1.2 g)	50 wt. % CH_3COOH	– / 15 (5 min)	[21]

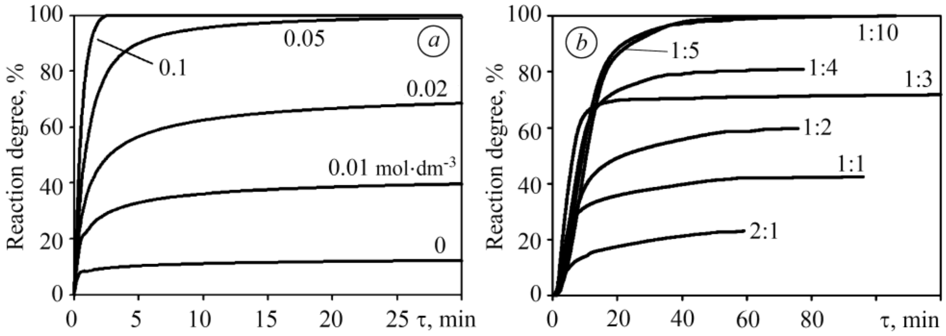

Fig. 5. Time-dependent yield of hydrogen gas at different concentrations of citric acid when using aqueous solutions (mol/dm^3) (*a*) [11] and composites (weight ratio MgH_2/citric acid) (*b*) [23].

Table 4. Relationship between the conversion yield and pH of the solutions at different contents of citric acid

Composition $MgH_2/C_6H_8O_7$, wt.%	Yield for MgH_2(exp), %	Yield for MgH_2(calc), %	pH(exp)	pH(calc)[*]
1/0	16	–	–	–
2/1	12	10	–	–
1/2	56	59	–	–
1/4	81	81	–	–
1/5	100	100	3.9	3.6
1/10	100	100	4.83	4.98

[*] pH is calculated by using equation for buffering solution pH = *p*K + log[BA]/[HA], where [HA] i [BA] – concentrations of citric acid and its corresponding salt.

MgH_2 / metal hydride composites. Increase of the rates of hydrolysis reaction is observed when using the mixtures of MgH_2 with calcium hydride (Table 5). The latter was added to the mixture or was formed during the milling with MgH_2 [1, 10]. The phase-structural composition and hydrolysis reaction of ball-milled MgH_2–Ca and MgH_2–CaH_2 mixtures where studied as a function of milling time and components ratio [1]. The formed by milling nanocomposites show a faster hydrolysis reaction as well as a higher hydrogen yield as compared to the conventional polycrystalline materials. This improvement is due to the formation of calcium hydride upon the milling and the formation of a mixture of fine powders MgH_2+CaH_2 after an extensive milling. When using the milled mixture MgH_2–20.3 mol% CaH_2, the reaction yield reaches 80% after 30 min of hydrolysis. Figure 6 presents the effect of Ca content in 10 h ball-milled MgH_2–Ca nanocomposites. As calcium content increases, both the rate of hydrolysis and the yield of hydrogen significantly increase. It can be seen, that the shapes of the time-dependent curves of the reaction completion vary depending on the composition. These changes probably reflect the fact that hydrolysis reaction has various stages with a variable contribution of different stage components to the complex overall process, as the milled composites comprise of β-MgH_2, γ-MgH_2, CaH_2, Mg and Ca. There is no strong relationship between the size of the powders and specific surface areas of the materials in the composites and the yield of hydrolysis reaction. Interestingly, specific surface area of the milled composites decreases (from 9.7 to 3.4 m^2/g) with increasing calcium content. This takes place because of a high ductility of calcium which acts as a binding component.

Table 5. Hydrogen generation yield when using different additives

Materials	Solution	Hydrogen yield (% / mL H_2/g) after t	Literature
Milled 10 h MgH_2 / 20.3 mol % CaH_2	H_2O	80 / – (30 min)	[1]
Milled 1 h MgH_2 / 10 mol % CaH_2	H_2O	95 / 1389 (1 h)	[10]
Milled 4 h 5 MgH_2 / LaH_3	H_2O	– / 1195 (80 min)	[15]
Milled 2 h 4 MgH_2 / $LiNH_2$	H_2O	73 / 1016 (50 min)	[19]

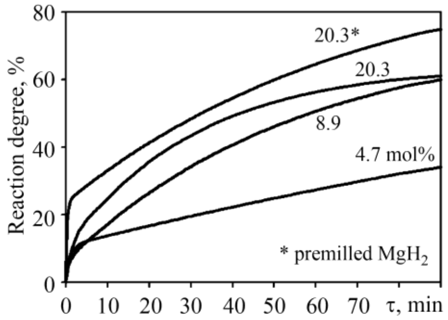

Fig. 6. Time-dependent curves of hydrogen release during hydrolysis of the milled MgH_2+X mol% Ca nanocomposites.

The hydrogenated $Mg_{17}Al_{12}$ alloy was used to produce hydrogen by hydrolysis in [10]. Hydrogenation and hydrolysis reactions can be described by the following paths; $Mg_{17}Al_{12} + 17H_2 = 17MgH_2 + 12Al$ and $17MgH_2 + 12Al + 70H_2O = 17Mg(OH)_2 + 12Al(OH)_3 + 52H_2$. However, the hydrolysis reaction of MHA without additives was rapidly interrupted because of the formation of a passive layer on the surface of the particles. As expected, addition of CaH_2 by using the ball-milling appears to be an efficient way to improve the yield of the hydrolysis when using the mixtures [10]. As calcium hydride very actively reacts with water, showing a considerable exothermic effect, this results in a local heating at points of contact of CaH_2 with magnesium hydride, which facilitates the hydrolysis process. The best effect was observed for the $Mg_{17}Al_{12}$ + 10 wt.% CaH_2 mixture ball-milled for 1 h, which produced 1389 ml H_2/g at 70 ºC after 1 h of hydrolysis in pure water (hydrogen yield was 94.8%).

The formation of microgalvanic pairs, when using transition elements during the hydrolysis, is advantageous and promotes achieving a higher hydrogen yield [15, 17]. According to [15], the use of the milled composites in the reaction of hydrolysis with REM hydrides results in a more active hydrolysis process. Addition of nickel to these composites has also a positive effect on the hydrogen yield. Indeed, the MgH_2 / LaH_3 / Ni composite exhibits the highest hydrogen generation rate of 120 ml/g·min in the first 5 min as compared to MgH_2 / LaH_3 composite providing 95 ml/g·min.

The hydrogen generation curves of ball-milled MgH_2 and LaH_3 mixed in a variable atomic ratio are shown in Fig. 7*a*. The MgH_2/LaH_3 composites with the atomic ratio of 3:1 and 8.5:1 can generate 706.7 mL/g of H_2 in 40 min and 473.0 mL/g of H_2 in 60 min, respectively. The highest observed hydrolysis yield equals to 1195 mL/g of H_2 in 80 min and belongs to the composite with the optimal mole ratio of 5:1 [15]. Investigations of other multicomponent hydride compositions showed that the composite formed in the H–Mg_3Mm system exhibited a higher yield of hydrolysis reaction together with the fastest hydrolysis rate, and produced 828 ml/g H_2 for 15 min and 1097 ml/g of H_2 for 36 h of the hydrolysis process, respectively.

The MgH_2/LaH_3/Ni composite obtained by hydrogenation of La_2Mg_{17}/Ni during the milling at a pressure of 7 MPa H_2 showed the best results [17]. It released 1208 ml/g of hydrogen during 40 min at room temperature and showed a reduced activation energy of the hydrolysis process of 52.9 kJ/mol. This is because of the milling and because of the catalytic influence of LaH_3 and Ni.

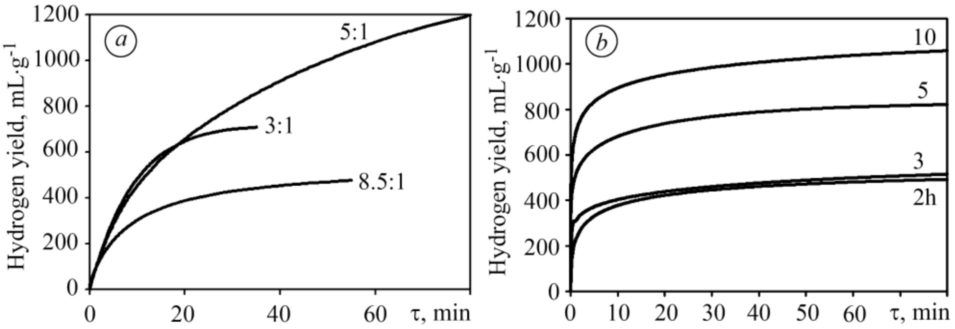

Fig. 7. Hydrogen generation curves of the atomic ratio MgH_2–LaH_3 (*a*) and $16MgH_2$–$LiNH_2$ (*b*) composites.

The air-stable $MgH_2/LiNH_2$ composites were another system investigated in the hydrolysis reaction (Table 4) in [19]. Here, $LiNH_2$ greatly enhances the rate of such reaction of MgH_2 hydrolysis. The composition $4MgH_2$-$LiNH_2$ milled for 5 h generates 887.2 ml/g of hydrogen in just one minute and 1016 ml/g of hydrogen in the next 50 min. The $LiOH·H_2O$ and NH_4OH phases which are formed as hydrolysis products during the interaction of $LiNH_2$ with water may prevent formation of the passivation layer of $Mg(OH)_2$ at the surface and supply enough channels for the hydrolysis of MgH_2. Effect of the ball milling was also studied by the authors for the $16MgH_2$–$LiNH_2$ composite. The results indicate that the hydrolysis process facilitates with the increasing milling time (Fig. 7*b*). The highest hydrolysis rate and hydrogen generation yield were obtained for the sample milled for 10 h. Its specific hydrogen yield reached 823.8 mL/g within the first 5 min and 1058.5 mL/g in 80 min.

Effect of temperature. Increase of the hydrolysis temperature, as expected, leads to an increase in both reaction rates and hydrogen yields [8, 13, 16, 17, 19, 22]. Evaluation of the apparent activation energy (E_a) of the hydrolysis reactions calculated using the Arrhenius equation and based on the analysis of the kinetic curves of hydrogen generation at different temperatures showed that different additives were able to significantly decrease the E_a (see Table 6).

Table 6. Calculated activation energies for the selected materials studied in the hydrolysis systems

Materials	Solution	E_a (exp)	Literature
Sigma Aldrich MgH_2	H_2O	58.06 kJ/mol	[16]
Sigma Aldrich MgH_2	0.5 wt. % NH_4Cl	50.86 kJ/mol	[16]
Sigma Aldrich MgH_2	4.5 wt. % NH_4Cl	30.37 kJ/mol	[16]
La_2Mg_{17}/Ni = 1/0.1 mol / H_2	H_2O	52.9 kJ/mol	[17]
Milled $32MgH_2 – 1LiNH_2$	H_2O	52.5 kJ/mol	[19]
Milled $8MgH_2 – 1LiNH_2$	H_2O	22.0 kJ/mol	[19]
Milled $2MgH_2 – 1LiNH_2$	H_2O	14.9 kJ/mol	[19]
MgH_2 (HCS)	0.1 M $AlCl_3$	34.68 kJ/mol	[22]
MgH_2 (HCS)	0.5 M $AlCl_3$	21.64 kJ/mol	[22]

CONCLUSIONS

The hydrogen generation by hydrolysis of MgH_2 or MgH_2-based composites containing additives can be improved by high-energy ball milling, by adding catalysts, salts and acids, or at elevated temperatures. Ball milling process results in a remarkable increase of the reactivity of MgH_2 due to the increasing specific surface area. However, the milling time should not exceed more than one hour, as the particle agglomeration would take place and obtained materials would show worsening of the hydrolysis properties.

Hydrolysis of the MgH_2 strongly depends on pH of the used aqueous solutions. Decrease of the pH significantly speeds up the kinetics of interaction and increases the yield of the liberated hydrogen, thus use of the acids or acidic salts for hydrogen generation shows a positive influence. Environment friendly and inexpensive citric acid shows the best effect. The addition of salts shows an advantageous effect on the hydrolysis reaction. Salts are inexpensive, easy-to-use materials, and even in small amounts they cause high rates of hydrogen evolution and significant reaction yields. Among the salts, the ones containing divalent or higher valent cations ($MgCl_2$, $FeCl_3$, $AlCl_3$, $ZrCl_4$, $ZrBr_4$) show the most distinct effect on the reaction kinetics and yield of the MgH_2 hydrolysis process. Despite of a clear influence on the pH of the aqueous solution, which is related to the reaction kinetics and yield, the role of salts is not completely understood. Further studies of the effect of salts and the mechanisms of their influence on the hydrolysis of MgH_2 are required.

РЕЗЮМЕ. Гідрид магнію MgH_2 – це сполука з високим вмістом водню, яка утворює значну його кількість під час гідролізу – хімічної взаємодії з водою або водними розчинами. Цей процес особливо цікавий для автономного вироблення водню як палива для низькотемпературних паливних елементів. У цій праці подано огляд останніх публікацій з цієї теми, а також результати власних експериментів. Вказано на важливість підвищити швидкість виділення H_2 та повноту конверсії MgH_2. Для цього слід оптимізувати розмір порошків MgH_2 шляхом кульового помелу; використати каталізатори, додані до MgH_2, та водні розчини; підвищити температуру взаємодії. Вплив цих чинників на ступінь конверсії та швидкість виділення водню детально проаналізовано та визначено системи для досягнення ефективних показників реакції. Запропоновано механізм каталітичного впливу, а для вдосконалення показників гідролізу потрібні подальші дослідження.

Ключові слова: *водень, гідрид магнію, композити, гідроліз, воднева енергетика.*

РЕЗЮМЕ. Гидрид магния MgH_2 – это соединение с высоким содержанием водорода, которое образует значительное его количество при гидролизе – химическом взаимодействии с водой или водными растворами. Этот процесс представляет особенный интерес для автономной выработки водорода для низкотемпературных топливных элементов. В работе приведены обзор последних публикаций по этой теме, а также результаты собственного исследования. Вывялена необходимость повышения скорости выделения H_2 и полноты конверсии MgH_2. Для этого следует оптимизировать размер порошков MgH_2 путем шарового помола; использовать катализаторы, приложенные к MgH_2, или водные растворы; повысить температуру взаимодействия. Влияние этих факторов на степень конверсии и скорость выделения водорода детально проанализированы и определены наиболее приемлемые системы для достижения эффективных показателей реакции. Предложен механизм каталитического воздействия, а для совершенствования показателей гидролиза необходимы дальнейшие исследования.

Ключевые слова: *водород, гидрид магния, композиты, гидролиз, водородная энергетика.*

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