DOI 10.1007/s11003-020-00390-5

Materials Science, Vol. 56, No. 1, July, 2020 (Ukrainian Original Vol. 56, No. 1, January–February, 2020)

HYDROGEN GENERATION BY THE HYDROLYSIS OF MgH_2

Yu. V. Verbovytskyy,[1,2] **V. V. Berezovets,**[1] **A. R. Kytsya,**[1]
I. Yu. Zavaliy,[1] **and V. A. Yartys**[3]

UDC 546.3-19′11

Magnesium hydride (MgH_2) is a hydrogen-rich compound generating significant amounts of hydrogen in the process of hydrolysis, i.e., in the course of its chemical interaction with water or with aqueous solutions. This process is of great interest for the on-site hydrogen generation aimed at application of H_2 as a fuel for PEM fuel cells. We propose a review of recent reference publications in the field and also present the results of our own research. The increase of the rates of H_2 release and the completeness of transformation of MgH_2 are two important goals, which can be attained by optimizing the size of the powders of MgH_2 by ball milling, by using catalysts added to MgH_2 and to aqueous solutions, and by increasing the interaction temperature. The effect of these parameters on the degree of conversion and the rates of hydrogen evolution are analyzed in detail and the best systems to reach the efficient hydrolysis performance are identified. The mechanism of catalytic hydrolysis is proposed, while further improvements of the process of hydrolysis are required and additional studies of this important topic are needed.

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

Introduction

Magnesium hydride (MgH_2) is obtained from magnesium, which is an inexpensive metal abundant on the Earth and characterized by a high theoretical hydrogen storage capacity of 7.6 wt.% H. Hydrogen can be obtained as a result of hydrolysis of MgH_2, which gives double as much H_2 as compared with Mg according to the reaction:

$$Mg + 2H_2O = Mg(OH)_2 + 2H_2 .$$

The weight yield of released hydrogen is 6.4% when water is taken into account in calculations and even increases up to 15.2% if the water produced by the oxidation of H_2 in a fuel cell is collected and used for hydrolysis. It is worth noting that this reaction has an advantage of producing eco-friendly $Mg(OH)_2$. When using MgH_2, the reaction of hydrolysis is rapidly terminated due to the formation of a compact layer of magnesium hydroxide on the surface of the reacting material. Several methods were proposed to increase the yield of hydrolysis [1–23]. The main techniques used for this purpose included ball milling, alloying, modification of the composition of solutions used for hydrolysis, and introduction of catalysts. In the present paper, our aim is to summarize recent advances in the investigations of hydrolysis of MgH_2-based materials.

---

[1] Karpenko Physicomechanical Institute, Ukrainian National Academy of Sciences, Lviv, Ukraine.

[2] Corresponding author; e-mail: xintermetallics@gmail.com.

[3] Institute for Energy and Technology, Kjeller, Norway.

Published in Fizyko-Khimichna Mekhanika Materialiv, Vol. 56, No. 1, pp. 9–20, January–February, 2020. Original article submitted September 10, 2019.

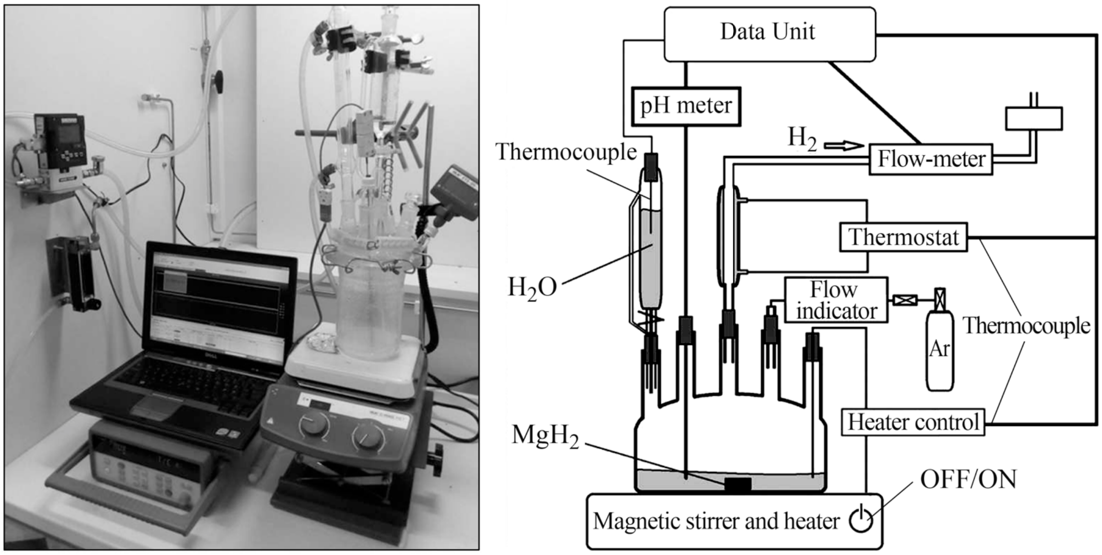

Fig. 1. Experimental installation used to quantify the rates of hydrogen generation and yields.

Materials and Experimental Procedures

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 aimed at mixing powder, water, and additives. The flask was placed in a water bath and the temperature was kept constant during the reaction. A thermometer and a sensor of the pH meter were immersed in the reactor to control the conditions of the reaction. Reactions were performed in an Ar atmosphere, and the produced gas was passing through a Sierra-100 flowmeter. We used both commercially available MgH_2 and magnesium hydride synthesized in our lab as a result of the reaction of metal Mg with H_2.

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

Ball Milling

The influence of ball milling on the morphology and sizes of MgH_2 powders as related to its interaction with water was considered in numerous publications [1, 3, 4, 7, 15, 19]. As a result, a conclusion was made that mechanical preliminary activation increases the reactivity of MgH_2 (Table 1).

According to [1], the process of hydrolysis of MgH_2 terminated after just 1 min. The measurements of the pH value of the solution showed that it reached 10.5 for the first few minutes of hydrolysis. According to the potential–pH equilibrium diagram, the concentration of the soluble species of Mg^{2+} was only 10^{-4} M for pH 10.5. Therefore, after only 1 min of hydrolysis, the pH value of the solution becomes sufficiently high 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 on the surfaces of grains prevents the penetration of a water solution to unreacted MgH_2.

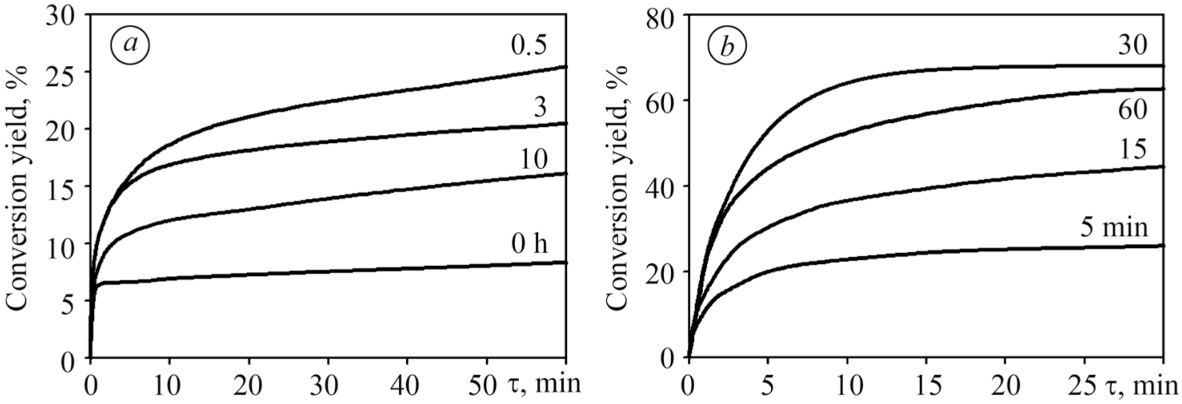

Fig. 2. Time dependences of hydrogen generation rates for milled MgH_2 (a) and MgH_2 containing 10 wt.% graphite (b) in pure water.

Table 1
Parameters of Materials and Hydrogen Generation Yield

Origin of MgH_2	Milling time	Specific surface MgH_2, m^2/g	Hydrogen yield (%/mliter 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]

The ball-milling method may effectively increase the reaction rate and the yield of hydrogen generation (Fig. 2a). This phenomenon could be explained by 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 the formation of nanocrystalline structures are also beneficial for the hydrolysis of MgH_2 [7]. Although the ball milling improves the hydrolysis properties of MgH_2-based materials, the hydrolysis of MgH_2 was still interrupted due to the formation of a passivation layer of magnesium hydroxide.

According to [3], the highest reactivity is attained 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 a powder milled for 30 min displays a maximum of $12.2\ m^2/g$. Further milling reduces the specific surface area due to

Table 2
Hydrogen Generation Yields for Different Salt Additives

Materials	Solution	Hydrogen yield (%/mliter H_2/g) after t	Reference
MgH_2 milled for 30 min	1 M KCl	37/656 (1 h)	[4]
MgH_2/10% Ni milled for 30 min	1 M KCl	39/564 (1 h)	[4]
MgH_2/3 M $MgCl_2$ milled for 30 min	H_2O	61/964 (1 h)	[5]
MgH_2/10 M $MgCl_2$ milled for 30 min	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% V_2O_5	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]
MgH_2 milled for 3 h	0.05 M $MgCl_2$	–/1137 (1.5 h)	[15]
MgH_2/0.024 M $MgCl_2$ milled for 1 h	H_2O	85/– (1 h)	[18]
MgH_2/0.024 M $ZrCl_4$ milled for 1 h	H_2O	94/– (1 h)	[18]
MgH_2/5% $MgCl_2$ milled for 5 h	H_2O	68/1094 (1 h)	[20]
MgH_2/10% NH_4Cl milled for 5 h	H_2O	86/1311 (1 h)	[20]

the particles agglomeration. A specific surface area of 7.8 m^2/g and a conversion yield of 16% were observed for the 10 h-milled MgH_2 powder. From the 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 the MgH_2 powder with an effective surface area of 23 m^2/g [4].

Note that carbonaceous materials are of especial interest as additives enhancing the efficiency of the mechanochemical treatment of magnesium hydride. The reaction of the MgH_2–graphite composites with water was studied in [7], and some data are displayed in Fig. 2b. These data show an increase in the H_2 yield caused by the addition of graphite.

Effect of Salts

The studies of the effect salt additives on the kinetics of hydrolysis of magnesium hydride were performed depending on the contents of 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 by using distilled/tap/sea water (Table 2)

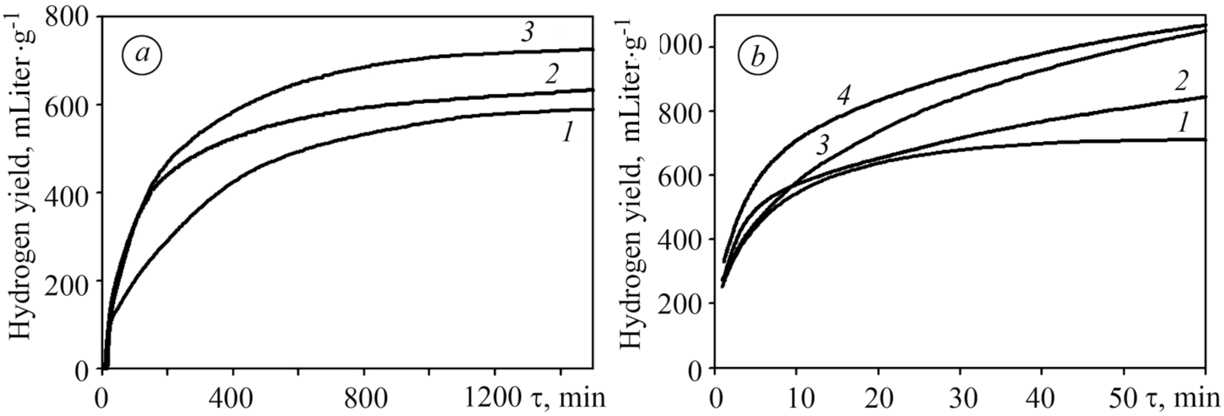

Fig. 3. Hydrogen generation curves from the hydrolysis of MgH_2 with various additions of $MgCl_2$ [(a): (1) 4 wt.% $MgCl_2$; (2) 11.5 wt.% $MgCl_2$; (3) 21 wt.% $MgCl_2$] [23] and additions of different chlorides [(b): (1) MgH_2; (2) MgH_2 + 3% NaCl; (3) MgH_2 + 3% $MgCl_2$; (4) MgH_2 + 3% NH_4Cl] [20].

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 value of the formed solution [9]. The hydrolysis of MgH_2 with acidic salt solutions gives a maximum conversion and shows a high hydrogen release rate [6, 9]. The increase in the salt content (up to a certain limiting value) in a solution or composite leads to an increase in hydrogen yield. The addition of nickel as a catalytic additive to pure magnesium hydride does not have a noticeable effect on the yield of the hydrolysis process, while the presence of magnesium in the material reveals a performance competitive with MgH_2. 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 increases the yield of H_2 and improves the kinetics of the hydrolysis reaction.

The influence of the compositions of selected ammonium salts and their concentrations in aqueous solutions on the hydrolysis of magnesium hydride was studied in [6, 15]. The presence even of small amounts of NH_4Cl (0.5% solution) noticeably accelerates the process of hydrolysis [6]: the amount of hydrogen released for 5 min exceeds the amount of hydrogen released for 24 h in the case of hydrolysis running in pure water (60 and 57%, respectively). As the concentration of ammonium chloride increases from 0.5 to 7.5%, the hydrolysis rate becomes higher and the degree of conversion (in the second case) also becomes much higher (92% for 5 min). In this solution, the degree of hydrolysis attained for 24 h (α_{24}) also takes the highest values (95.4%). A subsequent increase in the concentration of NH_4Cl solution leads to a decrease both in the hydrolysis rate and in α_{24}. The $(NH_4)_2SO_4$ revealed almost the same effect on the hydrolysis rate. The hydrolysis in the presence of $(NH_4)HSO_4$ runs faster and to a more profound extent than in the presence of the neutral ammonium salts. The HSO_4^- anions neutralize hydroxyl ions produced in the course of hydrolysis and, thus, promote the hydrolysis process. Indeed, the complete hydrolysis (100%) with $(NH_4)HSO_4$ was observed after less than 30 min.

The reaction of hydrolysis of MgH_2 in aqueous solutions of magnesium chloride was studied in [12, 15, 23]. It is worth noting that, in the presence of $MgCl_2$, the hydrogen yield is higher than in pure water (Fig. 3a). According to [12] and [15], the hydrogen yield was equal to 1635 mliter/g and 1137 mliter/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 on the surface of MgH_2 is not completely clear, even despite the fact that these ions definitely affect the degree of hydrolysis.

Various hydrolysis reactions between MgH_2/salt composites and distilled water were described in [5, 18, 20]. The composites were prepared by milling MgH_2 with a certain amount of salt in argon for up to 10 h. The effects

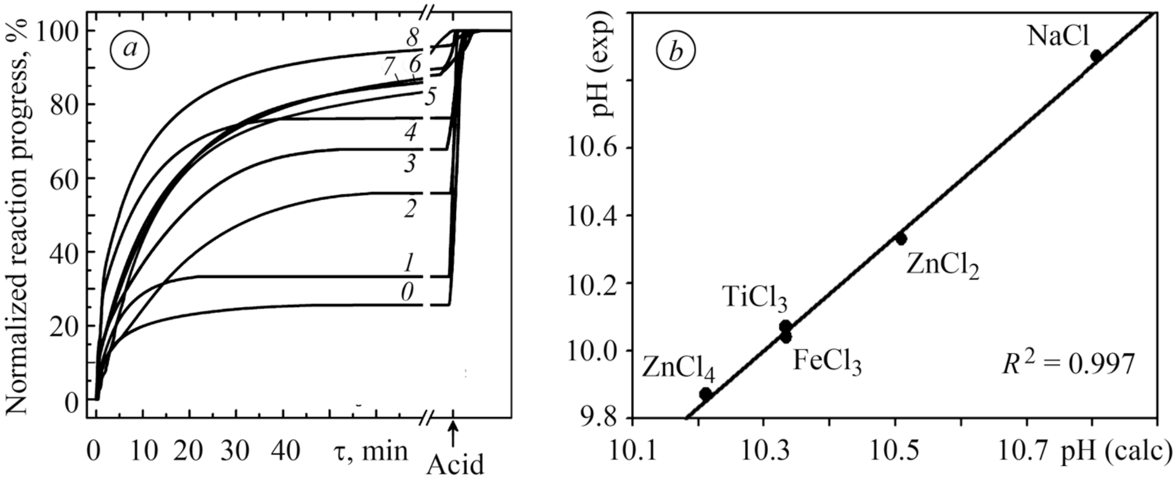

Fig. 4. Time dependences of hydrogen generation for the reaction of MgH_2 with solutions of various chlorides [(a): (0) none; (1) NaCl; (2) $ZnCl_2$; (3) $AlCl_3$; (4) $ScCl_3$; (5) $FeCl_3$; (6) $TiCl_3$; (7) $MgCl_2$; (8) $ZrCl_4$] and the relationship between the experimental [18] and the calculated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

of the duration of milling and the concentration of salt in $MgH_2/MgCl_2$ composites were studied in [5]. The procedure of milling magnesium hydride with salts always leads to a severalfold increase in the specific surface area. However, the indicated increase appears to be not proportional to the duration of milling.

A clear correlation between the yields of hydrogen and the values of specific surface area was not observed. The authors indicated that the exothermic dissolution of magnesium chloride may also affect the rate of conversion and the extent of MgH_2. As a reference point, the level of conversion yield as high as 81% was obtained by using the MgH_2–10 mole% $MgCl_2$ composite milled for 10 h.

The influence of the nature of cations contained in chloride salts and the amount of salts was studied in [20]. The MgH_2/NaCl, $MgH_2/MgCl_2$ and MgH_2/NH_4Cl composites were prepared with 3, 5, and 10% of salt and MgH_2 synthesized by HCS (Fig. 3b). Hydrogen yield increases with the increase in the salt content in the following sequence: NaCl–$MgCl_2$–NH_4Cl. The NH_4Cl has the strongest effect on the kinetics of the process of hydrolysis as compared wit the other two chlorides. At room temperature, the MgH_2–10% NH_4Cl composite exhibits the best performance with a hydrogen generation yield of 1311 mliter/g and a conversion rate of 85.69% for 60 min.

The effect of the nature of cations 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. 4a).

Several time-dependent diagrams are constructed and reveal the development both of the degree of conversion of MgH_2 and of the pH value of the reaction mixture. Among the above-mentioned composites containing 0.024 mole-equivalent of all additives, the weakest effect on hydrolysis is observed when using sodium chloride, while the strongest effect is recorded for zirconium chloride. All other salts exert intermediate effects on the kinetics of hydrolysis and hydrogen yield. It can be seen that the salts with higher oxidation states of the cations are more efficient in facilitating hydrolysis. In all cases, the degree of conversion is inversely related to the pH value of the solution and, therefore, the lowest value was obtained for $ZrCl_4$ with pH = 9.8. It was assumed that the behavior of this type is related to the following activation mechanisms:

A. The formation of poorly soluble hydroxides of additive metals obtained as a result of hydrolysis according to the reaction

$$[M(OH)_n]^{z+} + H_2O \rightarrow [M(OH)_{n+1}]^{(z-1)+} + H^+$$

or

$$MCl_n + nH_2O \rightarrow M(OH)_n\downarrow + nHCl.$$

This process dynamically buffers the reaction solution and lowers its pH value in the initial stage of the process, which improves both the kinetics of the reaction and hydrogen yield.

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

The effect of anions was studied by replacing chlorides with bromides in sodium, magnesium and zirconium salts. The behavior of bromides is similar to the behavior of chlorides as a decrease in the pH value is also observed. The hydrogen yield (86% and 99% obtained after 1 h by using $MgBr_2$ and $ZrBr_4$ as additives, respectively) was not significantly different for the analyzed two salts but bromides exhibited faster reaction kinetics. Furthermore, it should be emphasized that zirconium bromide acts as the best activator of the hydrolysis reaction among all tested salts.

Our studies of the effect of metals that form chlorides on the hydrolysis reaction show an increase in the reaction yield as the concentration of Cl^- increases. The hydrolysis of magnesium hydride was performed with additions of metal chlorides with cations whose valence varies from 1 to 4 ($NaCl/MgCl_2/AlCl_3/ZrCl_4$). The conversion rate of the reaction appears to be directly related to the concentration of chlorine anions. The cations can also affect the behavior. Selected metal chlorides (except NaCl) act as Lewis acids and decrease the pH value of the solution during their dissolution; this increases the degree of conversion [23].

We believe that the outlined assumptions concerning the possible mechanism of activation of the hydrolysis of MgH_2 in the presence of metal chlorides can be complemented by the hypothesis of formation of a "$Mg(OH)_2$ + $MgCl_2$" buffer system in the late stages of transformation. This assumption is supported by a very good correlation ($R^2 = 0.997$) between the experimental [18] and calculated ($pH_{(calc)}$) pH values described by the following equation (see Fig. 4b):

$$pH = 14 - pK_{Mg(OH)_2} + \log [Mg(OH)_2]/[MgCl_2].$$

Effect of Acids

The effect of acids on the hydrolysis of magnesium hydride was studied in [2, 11, 13, 14, 21, 23]. At room temperature, the action of acids results in a significant increase in the conversion of MgH_2 in the course of the hydrolysis reaction, even without catalysts or in the absence of the activation treatment of MgH_2 (Table 3). Significant amounts of hydrogen can be obtained either by using inorganic [14] or organic acids, e.g., acetic acid with a platinum catalyst [2], or by heating reaction mixtures [21] in the laboratory experiments. However, the commercial application of acids appears to meet drawbacks being both expensive and not practically viable due to the presence of significant corrosion of the reactor interior in acidic solutions. Thus, considerable attention

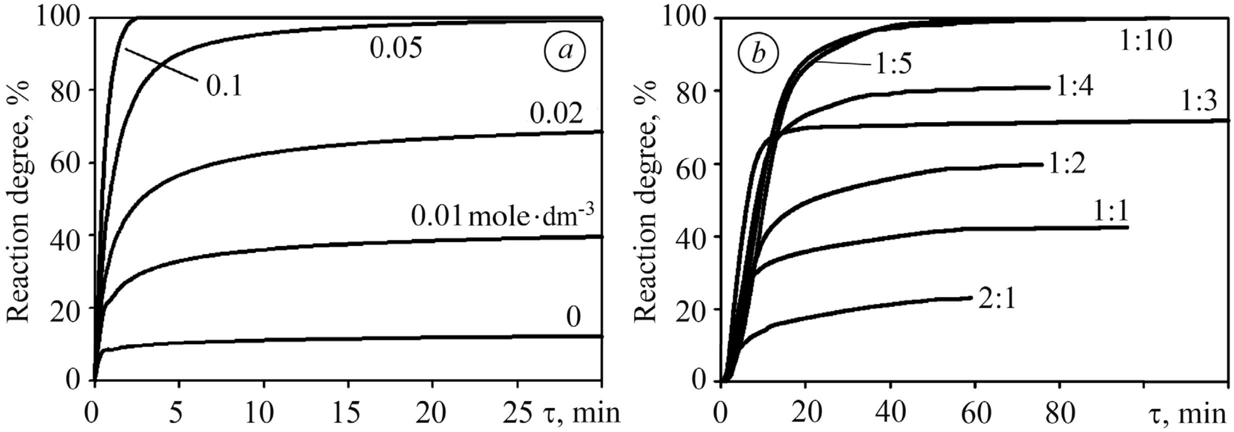

Fig. 5. Time-dependent yield of gaseous hydrogen for different concentrations of citric acid in aqueous solutions (mole/dm^3) (a) [11] and in composites (weight ratio MgH_2/citric acid) (b) [23].

Table 3
Hydrogen Generation Yield for Different Acids

Materials	Solution	Hydrogen yield (%/mliter H_2/g) after *t*	References
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 sec)	[14]
Aldrich MgH_2 milled for 3 h	HCl (pH = 2)	55/ – (25 min)	[14]
Rockwood MgH_2 (1.2 g)	50 wt. % CH_3COOH	–/15 (5 min)	[21]

is now focused on the investigation 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 solution of citric acid, parallel with the hydrolysis reaction, we observe either the direct interaction between MgH_2 and $C_6H_8O_7$ or the formation of salt as a result of the reaction of acid with magnesium hydroxide.

The choice of the most effective acid (as an accelerator of the MgH_2 hydrolysis reactions) was performed, by using the analysis of chemical equilibrium conditions, in [11]. The proposed approach allows us to calculate the effect of weak organic acids on the concentration of magnesium ions after hydrolysis. The authors suggested to use citric acid or EDTA as efficient buffering agents. The experimental results presented in Fig. 5a show

Table 4
Relationship Between the Conversion Yield and the pH Values of Solutions for 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]
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

Comments: 1. The pH values are found from the following equation for a buffering solution:

$$\mathrm{pH} = pK + \log[BA]/[HA],$$

where [HA] and [BA] are the concentrations of citric acid and its corresponding salt.

a clear dependence of the hydrogen yield on the concentration of citric acid. As expected, the degree of conversion was rather low (only 13%) in distilled water after 30 min because the passive $Mg(OH)_2$ layer was formed on the surface of the unreacted MgH_2. Hydrogen release considerably increases if we use a relatively dilute solution of citric acid. Both the rates of hydrogen generation and conversion yields increase for higher concentrations of the solutions of citric acid. For a low concentration (0.01 mole/liter), the reaction proceeded to 40% after 30 min. The reaction in a 0.1 mole/liter citric acid runs up to 99% of completion after 30 min, which means that the yield is 7.7 times higher than in distilled water. Note that, in the described process, citric acid acts only as a proton donor. This conclusion is based on the analysis of the reference data and also on our own results (Fig. 5b) [23]. The experimental and computed values of the conversion yield and the pH values of the solutions after the completed reaction obtained by using an excess of citric acid are in good agreement with each other (Table 4).

MgH_2/Metal Hydride Composites

The increase in the rates of hydrolysis reactions is observed if we use the mixtures of MgH_2 with calcium hydride (Table 5). Calcium hydride was either added to the mixture or formed as a result of milling with MgH_2 [1, 10]. The phase-structural compositions and the hydrolysis reactions for ball-milled MgH_2–Ca and MgH_2–CaH_2 mixtures were studied as a function of the duration of milling and the ratio of the components [1]. The nanocomposites formed by milling show a faster hydrolysis reaction, as well as a higher hydrogen yield as compared with the conventional polycrystalline materials.

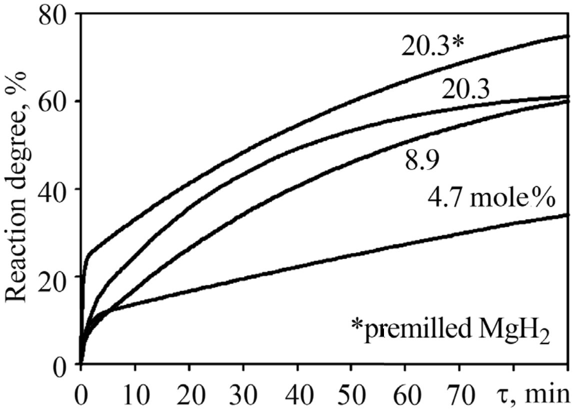

Fig. 6. Time-dependent curves of hydrogen release in the course of hydrolysis of MgH_2 + X mole% Ca milled nanocomposites.

Table 5

Hydrogen Generation Yields Obtained by Using Different Additives

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

This improvement is explained by the formation of calcium hydride as a result of milling and the formation of a MgH_2 + CaH_2 mixture of fine powders after extensive milling. When using the MgH_2–20.3 mole % CaH_2 milled mixture, the reaction yield becomes as high as 80% after 30 min of hydrolysis. In Fig. 6, we illustrate the effect of the Ca content in MgH_2–Ca nanocomposites ball milled for 10 h. As the calcium content increases, both the hydrolysis rate and hydrogen yield significantly increase. It can be seen that the shapes of the time-dependent curves of completion of the reaction vary depending on the composition. These changes probably reflect the fact that the hydrolysis reaction has various stages with variable contributions of different stage components to the complex overall process, as the milled composites comprise β-MgH_2, γ-MgH_2, CaH_2, Mg, and Ca. There is no strong relationship between the sizes of powders and the specific surface areas of the materials in the composites and the yield of the hydrolysis reaction. It is of interest that the specific surface area of the milled composites decreases (from 9.7 to 3.4 m^2/g) as the calcium content increases. This takes place due to the high ductility of calcium, which acts as a binding component.

The hydrogenated $Mg_{17}Al_{12}$ alloy was used to produce hydrogen as a result of hydrolysis in [10]. The hydrogenation and hydrolysis reactions can be described by the following paths:

$$Mg_{17}Al_{12} + 17H_2 = 17MgH_2 + 12Al$$

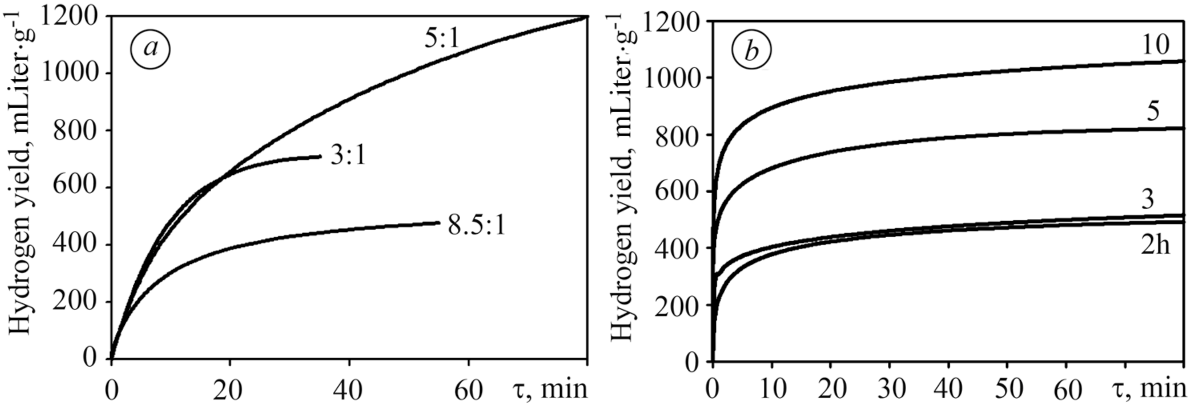

Fig. 7. Hydrogen generation curves for the composites with atomic ratios MgH_2–LaH_3 (a) and $16MgH_2$–$LiNH_2$ (b).

and

$$17MgH_2 + 12Al + 70H_2O = 17Mg(OH)_2 + 12Al(OH)_3 + 52H_2.$$

However, the reaction of hydrolysis of MHA without additives was rapidly interrupted as a result of the formation of a passive layer on the surfaces of the particles. As expected, the addition of CaH_2 with the help of ball milling appears to be an efficient way to improve the yield of hydrolysis when using the mixtures [10]. As calcium hydride very actively reacts with water and shows a considerable exothermic effect, this results in a local heating at the points of contact of CaH_2 with magnesium hydride, which facilitates the process of hydrolysis. The best effect was observed for the $Mg_{17}Al_{12}$ + 10 wt.% CaH_2 mixture ball milled for 1 h, which produced 1389 mliter H_2/g at 70°C after 1 h of hydrolysis in pure water (with a hydrogen yield of 94.8%).

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

The hydrogen generation curves of ball-milled MgH_2 and LaH_3 mixed in variable atomic ratios are shown in Fig. 7a. The MgH_2/LaH_3 composites with atomic ratios of 3:1 and 8.5:1 may generate 706.7 mliter/g of H_2 for 40 min and 473.0 mliter/g of H_2 for 60 min, respectively.

The highest observed hydrolysis yield is equal to 1195 mliter/g of H_2 for 80 min and belongs to the composite with the optimal mole ratio of 5:1 [15]. The investigations of the other multicomponent hydride compositions show that the composite formed in the H–Mg_3Mm system exhibits a higher yield of the hydrolysis reaction together with the highest hydrolysis rate and produces 828 mliter/g H_2 for 15 min and 1097 mliter/g of H_2 for 36 h of the hydrolysis process, respectively.

The $MgH_2/LaH_3/Ni$ composite obtained as a result of hydrogenation of La_2Mg_{17}/Ni in the course of milling under a pressure of 7 MPa H_2 showed the best results [17]. It released 1208 mliter/g of hydrogen for 40 min at room temperature and showed a reduced activation energy of the process of hydrolysis equal to 52.9 kJ/mole. This is explained by milling and by the catalytic influence of LaH_3 and Ni.

Another system investigated in the hydrolysis reactions was formed by the air-stable $MgH_2/LiNH_2$ composites (Table 4) [19]. In this case, $LiNH_2$ greatly enhances the rate of the reaction of MgH_2 hydrolysis.

Table 6
Calculated Activation Energies for Some Materials Studied in the Hydrolysis Systems

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

The $4MgH_2$-$LiNH_2$ composition milled for 5 h generates 887.2 mliter/g of hydrogen for the first minute of the process and 1016 mliter/g of hydrogen for the next 50 min. The $LiOH \cdot H_2O$ and NH_4OH phases formed as the products of hydrolysis during the interaction of $LiNH_2$ with water may prevent the formation of a passivation layer of $Mg(OH)_2$ on the surface and supply sufficiently many channels for the hydrolysis of MgH_2. The effect of ball milling was also studied by the authors for the $16MgH_2$–$LiNH_2$ composite. The accumulated results indicate that the process of hydrolysis is facilitated as the duration of milling increases (Fig. 7b). The highest hydrolysis rate and hydrogen generation yield were obtained for the sample milled for 10 h. Its specific hydrogen yield reached 823.8 mliter/g within the first 5 min and 1058.5 mliter/g for a period of 80 min.

Effect of Temperature

As expected, the elevation of the hydrolysis temperature leads to an increase both in the reaction rates and in the hydrogen yields [8, 13, 16, 17, 19, 22]. The evaluation of the apparent activation energy (E_a) of hydrolysis reactions computed according to the Arrhenius equation and based on the analysis of the kinetic curves of hydrogen generation at different temperatures shows that various additives may significantly decrease the values of E_a (see Table 6).

CONCLUSIONS

The process of hydrogen generation by the 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. The process of ball milling results in a remarkable increase in the reactivity of MgH_2 due to the increase in the specific surface area. However, the duration of milling should not exceed one hour because this would lead to the agglomeration of particles and the obtained materials would exhibit worsening of their hydrolysis properties.

The hydrolysis of MgH_2 strongly depends on the pH values of the applied aqueous solutions. A decrease in the pH value significantly speeds up the kinetics of interaction and increases the yield of released hydrogen. Hence, the application of acids or acidic salts for hydrogen generation shows a positive effect. The environment friendly and inexpensive citric acid shows the best effect. The addition of salts has an advantageous effect on the hydrolysis reaction. Salts are low-cost and easy-to-use materials. Moreover, even small amounts of salts may cause high rates of hydrogen evolution and significant reaction yields. Among various salts, we can mention the salts containing divalent cations (or cations with higher valence), such as $MgCl_2$, $FeCl_3$, $AlCl_3$, $ZrCl_4$, and $ZrBr_4$, as exhibiting the most pronounced effect on the reaction kinetics and the yield of the MgH_2 hydrolysis process. Despite a clear influence on the pH value of the aqueous solution, which affects the reaction kinetics and yield, the role of salts is not completely clear. Thus, additional investigations of the effect of salts and the mechanisms of their influence on the hydrolysis of MgH_2 are required.

Acknowledgements. The present work was financially supported by the NATO SPS Program (Project G5233 “Portable Energy Supply”).

REFERENCES

1. J.-P. Tessier, P. Palau, J. Huot, R. Schulz, and D. Guaya, “Hydrogen production and crystal structure of ball-milled MgH_2–Ca and MgH_2–CaH_2 mixtures,” *J. Alloys Comp.,* **376**, 180–185 (2004).
2. Y. Kojima, K.-I. Suzuki, and Y. Kawai, “Hydrogen generation by hydrolysis reaction of magnesium hydride,” *J. Mat. Sci.,* **39**, 2227–2229 (2004).
3. M.-H. Grosjean, M. Zidoune, and L. Roué, “Hydrogen production from highly corroding Mg-based materials elaborated by ball milling,” *J. Alloys Comp.,* **404**, 712–715 (2005).
4. M.-H. Grosjean, M. Zidoune, L. Roué, and J.-Y. Huot , “Hydrogen production via hydrolysis reaction from ball-milled Mg-based materials,” *Int. J. Hydrogen Energy,* **31**, 109–119 (2006).
5. M.-H. Grosjean and L. Roué, “Hydrolysis of Mg–salt and MgH_2–salt mixtures prepared by ball milling for hydrogen production,” *J. Alloys Comp.,* **416**, 296–302 (2006).
6. V. D. Makhaev, L. A. Petrova, and B. P. Tarasov, “Hydrolysis of magnesium hydride in the presence of ammonium salts,” *Rus. J. Inorg. Chem.,* **53**, No. 6, 858–860 (2008).
7. R. V. Lukashev, N. A. Yakovleva, S. N. Klyamkin, and B. P. Tarasov, “Effect of mechanical activation on the reaction of magnesium hydride with water,” *Rus. J. Inorg. Chem.,* **53**, No. 3, 343–349 (2008).
8. H. Uesugi, T. Sugiyama, I. Nakatsugawa, and T. Ito, “Production of hydrogen storage material MgH_2 and its application,” *J. Jap. Inst. Light Met.,* **60**, No. 11, 615–618 (2010).
9. S. D. Kushch, N. S. Kuyunko, R. S. Nazarov, and B. P. Tarasov, “Hydrogen-generating compositions based on magnesium,” *Int. J. Hydrogen Energy,* **36**, 1321–1325 (2011).
10. Y. Xiao, C. Wu, H. Wu, and Y. Chen, “Hydrogen generation by CaH_2-induced hydrolysis of $Mg_{17}Al_{12}$ hydride,” *Int. J. Hydrogen Energy,* **36**, 15698–15703 (2011).
11. T. Hiraki, S. Hiroi, T. Akashi, N. Okinaka, and T. Akiyama, “Chemical equilibrium analysis for hydrolysis of magnesium hydride to generate hydrogen,” *Int. J. Hydrogen Energy,* **37**, 12114–12119 (2012).
12. Z. Zhao, Y. Zhu, and L. Li, “Efficient catalysis by $MgCl_2$ in hydrogen generation via hydrolysis of Mg-based hydride prepared by hydriding combustion synthesis,” *Chem. Comm.,* **48**, 5509–5511 (2012).
13. C.-H. Chao and T.-C. Jen, “Reaction of magnesium hydride with water to produce hydrogen,” *Applied Mech. Mat.,* **302**, 151–157 (2013).
14. T. Tayeh, A.S. Awad, M. Nakhl, M. Zakhour, J.-F. Silvain, and J.-L. Bobet, “Production of hydrogen from magnesium hydrides hydrolysis,” *Int. J. Hydrogen Energy,* **39**, 3109–3117 (2014).
15. L. Ouyang, M. Ma, M. Huang, R. Duan, H. Wang, L. Sun, and M. Zhu, “Enhanced hydrogen generation properties of MgH_2-based hydrides by breaking the magnesium hydroxide passivation layer,” *Energies,* **8**, 4237–4252 (2015).
16. M. Huang, L. Ouyang, H. Wang, J. Liu, and M. Zhu, “Hydrogen generation by hydrolysis of MgH_2 and enhanced kinetics performance of ammonium chloride introducing,” *Int. J. Hydrogen Energy,* **40**, 6145–6150 (2015).

17. H. Zhong, H. Wang, J. W. Liu, D. L. Sun, F. Fang, Q. A. Zhang, L. Z. Ouyang, and M. Zhu, “Enhanced hydrolysis properties and energy efficiency of MgH_2-base hydrides,” *J. Alloys Comp.,* **680**, 419–426 (2016).
18. M. Tegel, S. Schöne, B. Kieback, and L. Röntzsch, “An efficient hydrolysis of MgH_2-based materials,” *Int. J. Hydrogen Energy,* **42**, 2167–2176 (2017).
19. M. Ma, L. Ouyang, J. Liu, H. Wang, H. Shao, and M. Zhu, “Air-stable hydrogen generation materials and enhanced hydrolysis performance of MgH_2–$LiNH_2$ composites,” *J. Power Sources,* **359**, 427–434 (2017).
20. S. Li, D. Gan, Y. Zhu, Y. Liu, G. Zhang, and L. Li, “Influence of chloride salts on hydrogen generation via hydrolysis of MgH_2 prepared by hydriding combustion synthesis and mechanical milling,” *Trans. Nonferrous Met. Soc. China,* **27**, 562–568 (2017).
21. J. A. Adeniran, E. T. Akinlabi, H.-S. Chen, R. Fono-Tamo, and T.-C. Jen, “Organic acid-catalyzed hydrolysis of magnesium hydride for generation of hydrogen in a batch system hydrogen reactor,” in: *Proc. of the World Congr. on Engineering and Computer Science (October 25–27, 2017, San Francisco, USA),* Vol. II, WCECS 2017, October 25–27, San Francisco, USA (2017).
22. D. Gan, Y. Liu, J. Zhang, Y. Zhang, C. Cao, Y. Zhu, and L. Li, “Kinetic performance of hydrogen generation enhanced by $AlCl_3$ via hydrolysis of MgH_2 prepared by hydriding combustion synthesis,” *Int. J. Hydrogen Energy,* **43**, 10232–10239 (2018).
23. V. V. Berezovets, Yu. V. Verbovytskyy, I. Yu. Zavaliy, and V. A. Yartys, "Mg-based materials for application in hydrogen supply systems,” in: *Proc. of the HighMatTech.–2019 Conf.* (*October 28–30, 2019, Kyiv, Ukraine)* Kyiv, Ukraine (2019).