



Research Article

The Usage of Mg - Metal Chlorides in Hydrogen Generation

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ABSTRACT: The reaction of metals with water is one of the hydrogen generation methods. Mg stands out as a viable alternative when compared to other metals for producing hydrogen. However, the emergence of $Mg(OH)_2$, which interrupts hydrogen production in its reaction with water, has led to the search for new methods to improve the hydrogen production process. For this reason, in our study, chloride salts ($CoCl_2$ and $AlCl_3$) have been used to improve hydrogen generation. The composites have been prepared with the addition of different chlorides ($AlCl_3$ and $CoCl_2$) into Mg with ball milling. $AlCl_3$ and $CoCl_2$ have been used separately and together while forming Mg-metal composite powder. Powder mixtures have been grounded by a planetary ball mill at different times (2 and 4 hours). Deformations, which are thought to contribute positively to the reaction, have been obtained on the metal surface with ball milling. The microscopic images of the powder mixtures have been analyzed by SEM. In addition, distilled water, acetic acid and citric acid have been used in our study to observe the effects of hydrogen production. When distilled water has been used with powder mixtures in the hydrogen generation experiments, a minimal amount of hydrogen gas output has been observed. It has been observed that the use of acetic acid or citric acid solutions significantly enhances the amount of hydrogen formed. 4 hours milled Mg- 10wt% $CoCl_2$ composite has the best hydrolysis properties for all experiments with its 138 ml of hydrogen generation at 30°C in 30 ml, 2 M citric acid solution.

Keywords: Mg, Hydrogen production, Mg- metal chloride composites, Ball milling.

1. INTRODUCTION

Environmental pollution that occurs while producing and consuming energy is an important issue. The negative effects of these issues threaten our future. The energy demand is rising with the increasing population, technology, and standard of living in the world [1]. For the time being, this energy demand is mostly provided by fossil fuels [2]. However, the use of conventional fossil fuels causes vigorously pollution of the environment [3]. So, the decline of the non-renewable energy reserves has accelerated the search for alternative and renewable energy sources [4].

Hydrogen has attracted great attention in recent years due to its high energy carrier potential and environmentally friendly end product [5]. Hydrogen is a carrier of energy. The chemical energy releases from two hydrogen bonds as a result of combustion and only water forms as a by-product. The energy content of hydrogen (120 MJ/ kg) is quite high compared to gasoline (44 MJ/ kg) [6]. Today, the use of hydrogen as a fuel is rising day by day. The vehicles that may be operated with hydrogen fuel cells are almost three times more efficient than gasoline-

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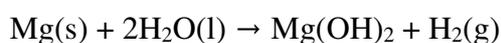
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powered engines [7]. It is expected that hydrogen fuel cells will be used widely in the future and therefore environmental pollution will be lowered.

Hydrogen can be produced by different methods such as steam reforming of hydrocarbons, electrolysis of water, gasification of heavy oil, coal or biomass [8]. However, the manufacturing of hydrogen by fossil fuels is ineffectual and unsustainable applications which cause releasing of pollutants and harmful gases such as NO_x , SO_x , etc. and also increase CO_2 emissions [9]. The significant point is the use of clean and inexpensive energy sources while obtaining hydrogen [10]. For this purpose, many scientific types of research focus on hydrogen generation by using metals [4, 11], metal hydrides [12] and their alloys [13].

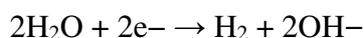
Most of the laboratory studies have been used active metals such as Mg [5, 8], Al [4], Li [14, 15], borohydrides such as NaBH_4 [16] and metal hydrides such as LiAlH_4 [17], etc. In particular, Al and Mg were preferred in most of the studies because of their high activity and low toxicity [4, 5, 8, 18].

Hydrogen can be obtained as a result of the following reaction between solid magnesium with water:

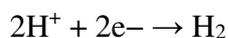


Mg based systems provide high H_2 yield in the presence of water and activator. H_2 conversion from aqueous solutions is based on the cathodic/anodic reaction of H^+ or H_2 molecules in H_2O and a highly interactive material [10,19]:

Cathodic reactions:



and/or

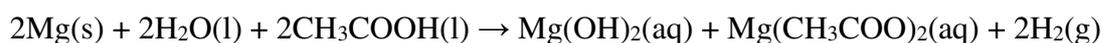


Anodic reactions:



It was observed that the reaction rate increased in a highly corrosive environment. In various scientific studies, it has been stated that acids [8, 10, 20], saline solutions [8, 14, 19, 21] and seawater [18] are used by the researchers to improve the hydrogen yield.

Organic acids such as citric acid ($\text{C}_6\text{H}_8\text{O}_7$, molar mass: 192.124 g/mole) and acetic acid (CH_3COOH , molar mass: 60.052 g/mole) have been reported as accelerate the rate of hydrogen production [22]. The following equation shows the hydrolysis reaction with using acetic acid and citric acid:



Acetic acid and citric acid have been preferred because they are easily accessible, promote hydrogen production, do not produce toxic end products, do not harm to the health and environment while using in the experiments [20]. End of the reactions between Mg and acetic acid solution forms $\text{Mg(CH}_3\text{COO)}_2$ (magnesium acetate) which can be used food additive in industrial processes [23]. The reaction between Mg and citric acid solution results in the $\text{C}_6\text{H}_8\text{MgO}_7$ (magnesium citrate) salt [24]. This substance is used as an additive in the pharmaceutical and food industry.

Mg [11], MgH_2 [12], Mg_2Si [13], various Magnesium Borohydrides such as $Mg(BH_4)_2 \cdot 2NH_3$ [17], $Mg(BH_4)_2$ [5], Mg nanopowder [25] and waste Mg shavings [8] are used as the source of hydrogen production with Mg.

Researchers have submitted some physical and chemical procedures for improving hydrogen generation such as ball milling [14, 21, 26-28], using carbon materials [29], usage of catalyst [30], arc plasma method [25], two-step water splitting method [31], etc.

However, the most effective methods for generating hydrogen are ball milling which has been performed on various metals such as Mg and Al and their hydrides and composites for hydrogen generation by hydrolysis [8, 26].

In our study, for optimizing the hydrogen generation, the effects of the ball milling method, the use of the metal chlorides ($CoCl_2$ and $AlCl_3$) which forms composite with Mg at various grinding times (2 and 4 hours), the content of the solutions in which the experiments took place were investigated. The initial experiments were carried out at $60^\circ C$ using 30 ml of distilled water, 0.24 g of powder and a magnetic stirrer. To observe the effect of the acid solutions on the $Mg(OH)_2$ layer which disrupted the reaction, experiments were also carried out with stirring, using 30 ml of 1 M and 2 M acetic acid and citric acid solutions and using 0.12 g of composite powders at $30^\circ C$. The effects of the acid solution type and varying milling time on hydrogen production have been investigated. Characterization of composite materials was carried out by SEM (Carl Zeiss 300VP) analysis. The results were compared with each other.

2. MATERIALS AND METHOD

2.1. Materials

Mg was purchased from Merck with 99% purity. The components, $AlCl_3$ (99.99% Merck), $CoCl_2$ (98%, Merck) have been milled with Mg. Distilled water has been used for hydrolysis experiments, preparing solutions and diluting acetic acid. In the first experiments, distilled water has been used for hydrolysis. Acetic acid (100% purity, Merck) and citric acid monohydrate (8.7% water include was purchased from Weifang Ensign Industry Co.) have been used for creating an acidic medium.

2.2. Method

2.2.1. Preparation of powder mixtures

The effect of using different metal chlorides on hydrogen production has been observed in the experiments. In addition, the effect of changing the weight percentages of chlorides in Mg composite and changing the milling times have been investigated. The metal chlorides used in the preparation of the composites, the weight percentages of the chlorides in the composites and the milling times have been represented in Table 1.

Table 1. The contents and the milling times of Mg-metal composites.

Mg amount in the composite (wt%)	Metal chloride amount in the composite (wt%)	The metal chloride content of the composite	Milling time (h)
90	10	CoCl ₂	2
95	5	CoCl ₂	2
90	5 + 5	CoCl ₂ + AlCl ₃	2
95	2.5 + 2.5	CoCl ₂ + AlCl ₃	2
90	10	CoCl ₂	4
95	5	CoCl ₂	4
90	5 + 5	CoCl ₂ + AlCl ₃	4
95	2.5 + 2.5	CoCl ₂ + AlCl ₃	4

2.2.2. Preparing composites by ball milling

The composites have been used to compare the results using different grinding durations and amounts of salts on hydrogen production. Stainless steel vials and balls have been used in the milling process. The balls were about 200 grams and the powder-to-ball mass ratio was 1:20. The maximum milling time was 4 hours. Longer grinding times have not been preferred for energy and time-saving. For the milling process, ECO planetary ball miller (200 rpm, 25 Hertz) has been used.

2.2.3. Performing the experiments

For the experiments, a three-necked (250 ml), round bottom glass reactor has been used. The reactor has been placed into a magnetic stirrer heater (Figure 1). The connection of the reactor and a glass measuring cylinder (250 ml) that was suspended by inverting in a half-full beaker, has been made using a 400 mm long 8 mm inner diameter pipe. Hydrogen formed in the reactor, which passed through the pipe and cooled with water at room temperature, has been collected in the measuring cylinder. Hydrogen production has been recorded with the help of the measuring cylinder. The water displacement procedure has been used for measuring the amount of produced hydrogen.

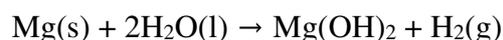
The experiments have been carried out in distilled water, 1 M and 2 M citric acid and acetic acid solutions, respectively. Each test has been repeated at least twice, and the margin error has been accepted as $<\pm 5\%$ in the experiments. Each hydrogen generation experiment has been observed for one hour.



Figure 1. Experimental setup

3. RESULTS AND DISCUSSION

It is well known that the reaction between Mg and water causes hydrogen generation [26]:



In our study gas output has not been observed when distilled water and other solutions have been used with non-milling Mg to obtain hydrogen. The biggest handicap of this reaction is that the formed hydroxide layer discontinues the reaction. To eliminate this formed hydroxide layer, different weights of metal chlorides have been used together with Mg. The ball milling method has been preferred to create Mg- metal chloride composites. The formed Mg-metal chloride composites have been reacted with distilled water, and acidic (acetic acid and citric acid) solutions to observe hydrogen production. The effects of the ball milling in the production of hydrogen, the use of metal chlorides and the interaction of Mg-metal chloride composite materials with different solutions have been studied also in the Master's Thesis [27].

It is widely recognized that the repeated grinding process in ball-milling changes microstructure, distribution of the components and formation. It is submitted that combining these defects may support also metal corrosion. The effects of the ball-milling process on powder mixtures have been observed with the help of SEM images (Carl Zeiss 300VP). The original material was Mg powder (Figure 2) which had a relatively smooth surface, which after milling, became irregular and exhibited breakdown in the powder surface. In the literature studies, it is seen that the milling of Mg with solid salts is very effective for improving the hydrolysis reactivities. The salt additive is generally reported to act as a process control agent in the milling process which increases the specific surface area of Mg powder [11, 14, 19, 29].

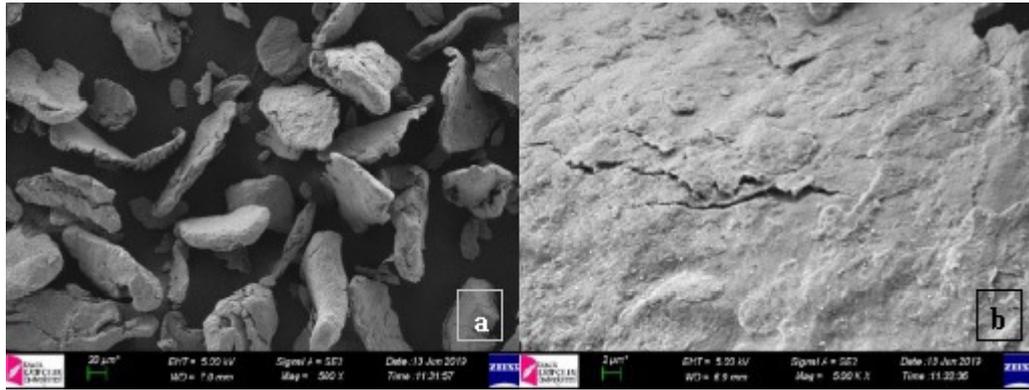


Figure 2. SEM images of Mg powder without milling a) and b) with different magnifications.

The ball-milling time is a very important parameter that affects hydrogen generation. Various changes have been observed with increasing milling time in the composite material subjected to milling. One of the most important of these changes is the slow reduction of the powder mixture which causes an increase in the surface area. It has been considered that 2 hours of milling caused a noticeable increase in the surface area of the powder (Figure 3).

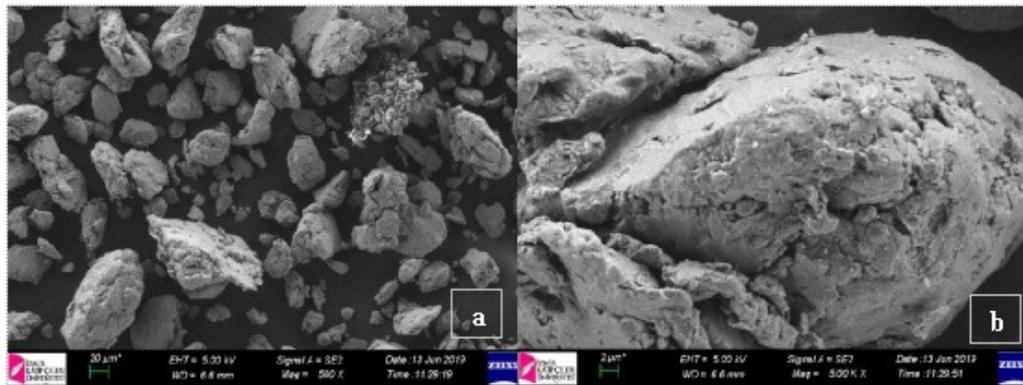


Figure 3. SEM images of 10wt% CoCl_2 – 90wt% Mg composite with 2h milling time, a) and b) with different magnifications

Another change is that the milling process causes deformations on the surface of the material, thereby increasing the formation of fresh surfaces. Increased surface deformation can be observed in 4 hours milled 10wt% CoCl_2 - 90wt% Mg composite (Figure 4), compared to 2 hours milled same powder and unmilled Mg powder.

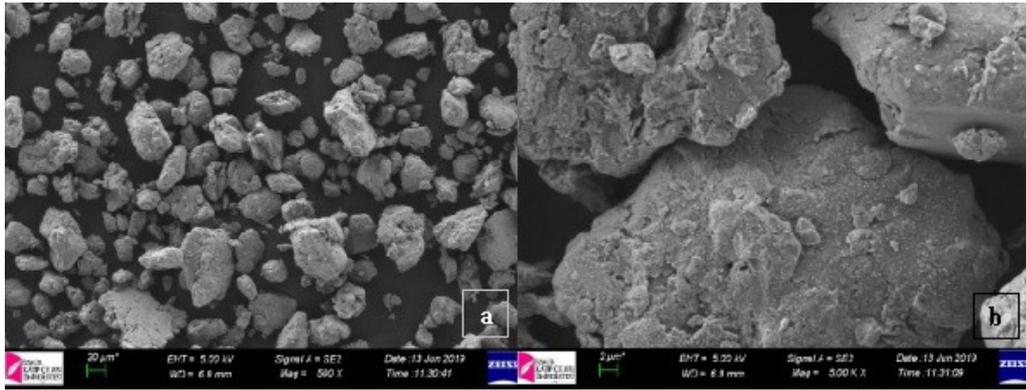


Figure 4. SEM images of 10wt% CoCl₂ – 90wt% Mg composite with 4h milling time, a) and b) with different magnifications

It can also be concluded that metal chloride salts are held onto the surface of Mg powder during milling (Figure 5). Prolonged milling of Mg-containing powders may result in cold welding and agglomeration of the particles, as opposed to reducing the particle size [21, 26]. For this reason and to save energy, milling times 2 and 4 hours have been selected, longer milling times have not been preferred.

The weight percentage of metal chloride in Mg-metal chloride composite is the other important parameter. Although the cold welding predominated on ductile Mg, the addition of chlorides such as CoCl₂, and AlCl₃ have favored the fracturing of Mg during the milling process (Figure 5). It may be concluded that adding chloride to the composite and increasing the weight percentage of chloride in the composite may effectively improve the hydrolysis kinetics.

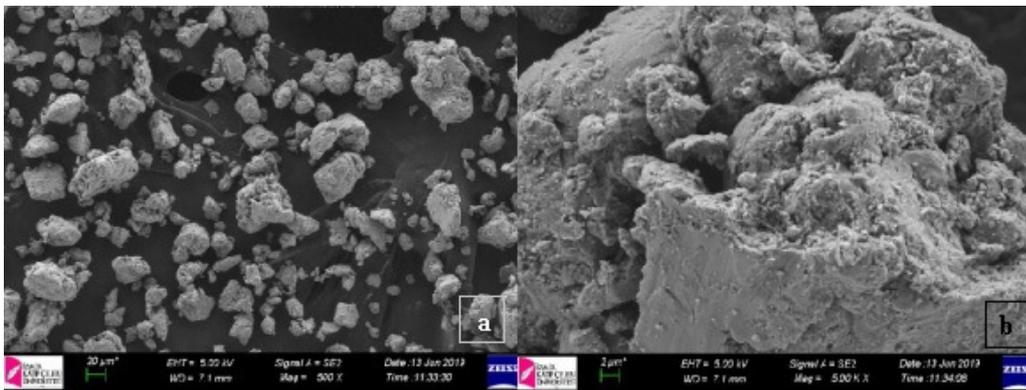
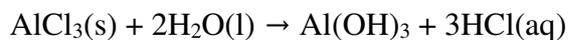


Figure 5. SEM images of 5wt% CoCl₂ – 5wt% AlCl₃ – 90wt% Mg composite with 4h milling time, a) and b) with different magnifications

AlCl₃ is often used for the preparation of aluminum hydroxide and may react with water as the following [14]:

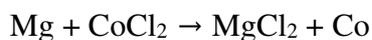


223.85 kJ/mol heat releases during AlCl_3 dissolution. Liu et al. (2012) stated that the H^+ ions from the generated HCl may dissolve $\text{Mg}(\text{OH})_2$ layer formed from the reaction, thus increasing the fresh Mg surfaces revealed. So, the large amount of releasing heat and the generating HCl from AlCl_3 dissolution may improve the hydrolysis reaction [14].

In the study of Liu et al.(2013), 3 mol% AlCl_3 has been added to the Mg powder and the mixture has been milled for 6 hours. 50 mg powder and 10 ml distilled water has been used. The best result in that study has been recorded as approximately 455.9 ml. min/(g Mg). In our study, different milling times and percentage amounts have been used in the experimental study.

Also, a replacement reaction may occur during the ball milling process between Mg and metal chlorides. After the replacement reaction, the hydrolysis properties of Mg-metal chloride composites may be improved with the electronegativity of the metal element in the chlorides which possibly created a more effectual micro galvanic cell with Mg [11, 26].

Sun et al. (2014) have mentioned that the replacement reaction between Mg and CoCl_2 may occur during the milling process [11]:



Increasing the CoCl_2 content of the powder mixture may pioneer a remarkable improvement in hydrogen generation.

In the study of Sun et al.(2014), the different weight percentage of CoCl_2 (2, 4, 6, 8, 10 wt %) has been added to the Mg powder and the mixture has been milled for 1 hour. 1 g powder has been used. Powder: Water ratio has been informed as 1:40. The best result in the study has been recorded as 558.6 ml. min/(g Mg). It may be noted that the results are given in terms of Hydrogen Generation Rate (ml. min/(g Mg)). In our study, the results have been given in terms of the amount of Hydrogen Generation (ml). Different amounts of powder and the milling times have been used in our experimental studies.

There are many studies in the literature on hydrogen production using Mg-chloride powders. Creating Mg-chloride composites with the ball milling method has made quite noticeable contributions to hydrogen production. In their work, Liu et al. have contributed to the literature by using CoCl_2 , and Sun et al. with using AlCl_3 . In our study, the effect of using chlorides separately on hydrogen generation has been given. In addition, we have used also the combination of CoCl_2 and AlCl_3 salts to observe their effects on hydrogen production in our study. In addition, the reactions of Mg-chloride composites with organic acids and hydrogen recovery have been detailed.

The highest hydrogen formation in 30 ml distilled water at 60°C using the Mg composite containing 5wt% CoCl_2 + 5wt% AlCl_3 (4 hours milled) has been recorded as 78 ml. The use of these two metal chlorides in the Mg composite may have a synergistic effect. Another remarkable result with 4 hours milled Mg + 10wt% CoCl_2 has been recorded as 68 ml of hydrogen gas. Increasing the milling time from 2 hours to 4 hours has been supported by the increase in the amount of hydrogen obtained. Besides, it has been observed that composite powders containing 5wt% CoCl_2 alone and 2.5wt% CoCl_2 + 2.5wt% AlCl_3 with 2 hours milling time were not as effective as the powders containing 10wt% chlorides for all milling times (Figure 6).

Since chloride ions have a catalytic effect, it may have removed the fresh hydroxide layer formed from the surface of Mg. They may also have a preventive effect on the formation of the new hydroxide layer. In this case, more water molecules may reach the surface, so more hydrogen may be obtained.

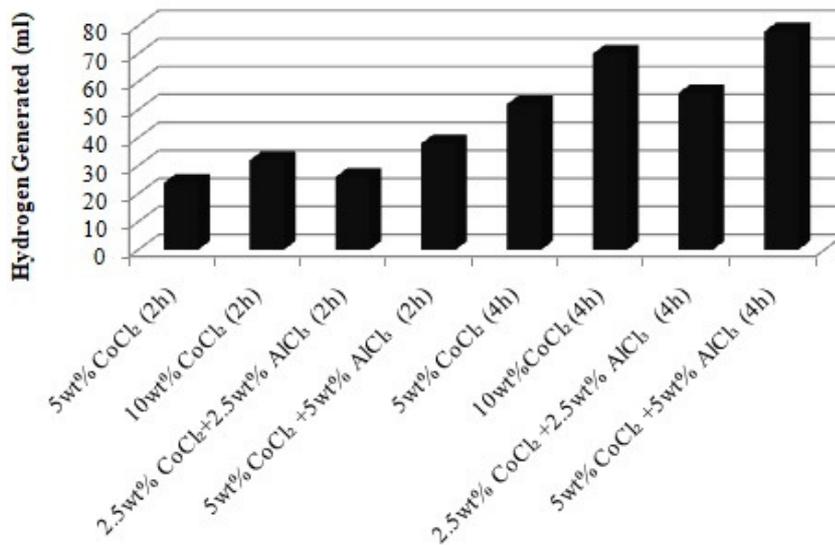


Figure 6. Hydrogen generation with 0.24 g of powder and 30 ml distilled water at 60°C.

Acidic solutions have been also used to observe the influence on the hydrogen generation process in this study. Acetic acid and citric acid have been used for creating the acidic medium. To produce H₂, the transition of H⁺ ions into the medium should be procured. Therefore, the hydrolysis reaction with using Mg interrupts quickly and requires an activator. Acids such as metals and chlorides can also be preferred as activators [20]. The use of two different acid solutions (acetic and citric acid) has been acted as an activator in the hydrolysis medium. When 30 ml, 1 M acid solutions (acetic and citric acid) have been used at even 30°C, it has been observed that using acid solutions enhanced the hydrogen generation tremendously.

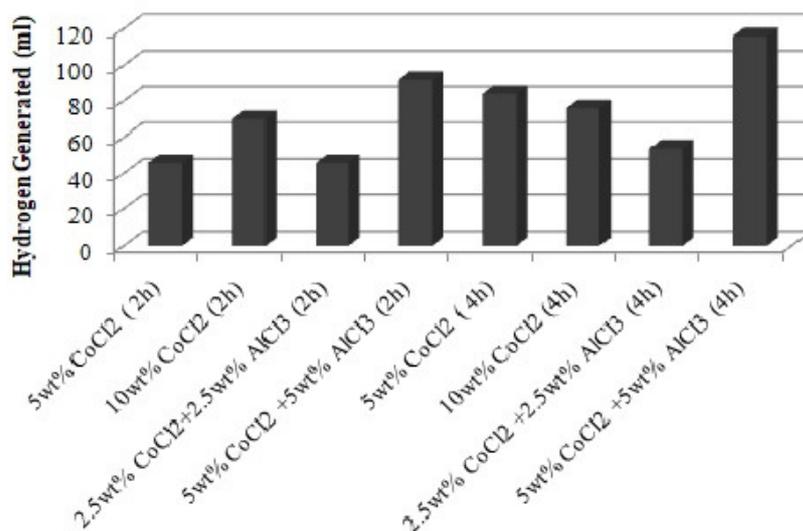


Figure 7. Hydrogen generation with 0.12 g of powders and 30 ml, 1 M acetic acid solution.

The increase in weight percent of CoCl_2 in the Mg-metal chloride composite may cause a significant improvement in the generation of hydrogen. Also, it may be seen that the combination of AlCl_3 and CoCl_2 in Mg-metal chloride composites enhances the hydrolysis properties. Adjusting the total chloride to 10wt% may improve hydrogen production as may be seen from the results. 4 hours milled 0.12 g of Mg- 5wt% CoCl_2 - 5wt% AlCl_3 composite has the best hydrolysis properties with its 116 ml of hydrogen generation for 1 M acetic acid solution (Figure 7).

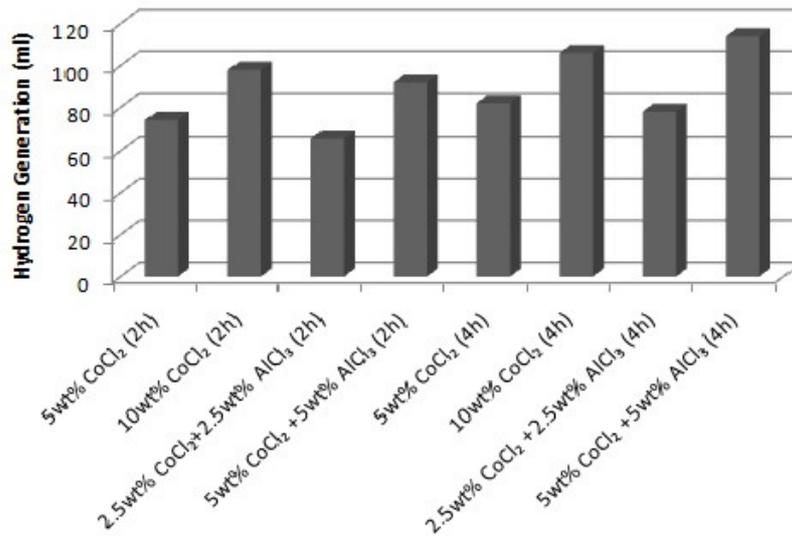


Figure 8. Hydrogen generation with 0.12 g of powder and 30 ml, 1 M citric acid solution.

The presence of an acid in the solution may be supported the continuation of the hydrolysis reaction. Acid concentration has an important role in the hydrogen production process when used with Mg-metal chloride composite. It has been noted that when using CoCl_2 in samples containing 5wt% metal chloride, the maximum hydrogen gas has been released as 82 ml. It may be possible to conclude that the use of 10wt% metal chloride significantly improves the hydrolysis properties. The positive effect of using 5wt% CoCl_2 and 5wt% AlCl_3 together has been reflected in the results. The hydrogen production of this composite structure with a milling time of 4 hours has been enrolled as 114 ml (Figure 8).

The organic acids compared to distilled water may be promising candidates for their contribution to the hydrogen production process. When the concentrations of acetic acid and citric acid solutions have been adjusted to 2 M and the experiments have been repeated to understand the effect of acid concentration on hydrogen production, the obtained results were quite remarkable. Whenever the results of the experiments using 2 M acetic acid solution have been examined, the effect of Mg-metal chloride composite containing the combination of 5wt% CoCl_2 and 5wt% AlCl_3 on hydrogen generation can become preminent. Hydrogen generation has been achieved more than 100 ml in both milling times for this combination (Figure 9).

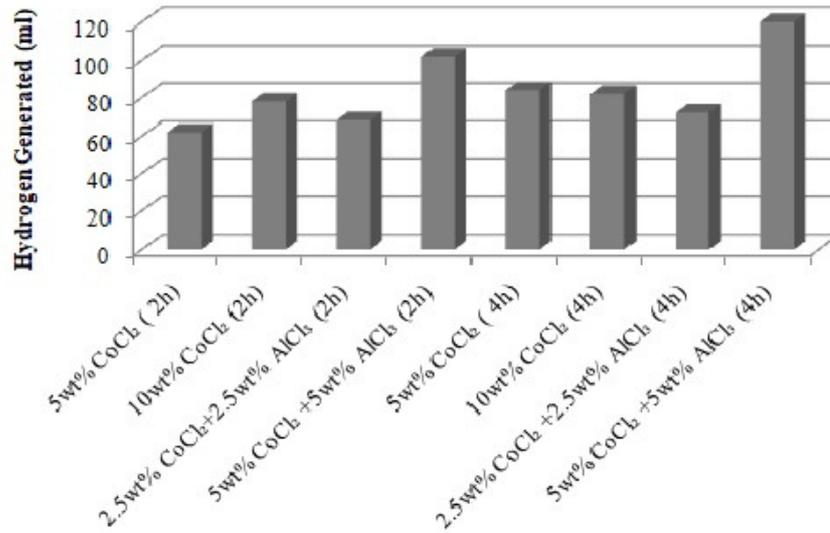


Figure 9. Hydrogen generation with 0.12 g of powder and 30 ml, 2 M acetic acid solution.

As can be seen in Figure 10, the best result obtained with a citric acid concentration of 2 M and Mg-metal chloride composite containing 10wt% CoCl₂ has been recorded as 138 ml. When the same experiments have been carried out in 1 M citric acid solution, 106 ml of hydrogen evolution has been observed (Figure 8). Another remarkable result has been noted as 134 ml hydrogen production during experiments involving the 5wt% CoCl₂ and 5wt% AlCl₃ duo with 4 hours milling time. It may be also supported by these results that the increase in milling time increases hydrogen production. When the composite containing 10wt% CoCl₂ with a milling time of 4 hours has been used, 12 ml more hydrogen has been obtained than the same composite with 2 hours milling time. Whenever the results have been compared, it has been seen that doubling the organic acid concentration has been contributed to the increase in the amount of hydrogen obtained.

It may be understood that samples containing only 5wt% metal chloride in total have not been efficient in hydrogen production processes. But they may be supportive data to create comparisons. It may be noted that citric acid solution takes a more active role. The increase in weight percentages of metal chlorides in Mg-metal chloride composites and the use of CoCl₂ and AlCl₃ together provided remarkable results in terms of the efficiency of the process.

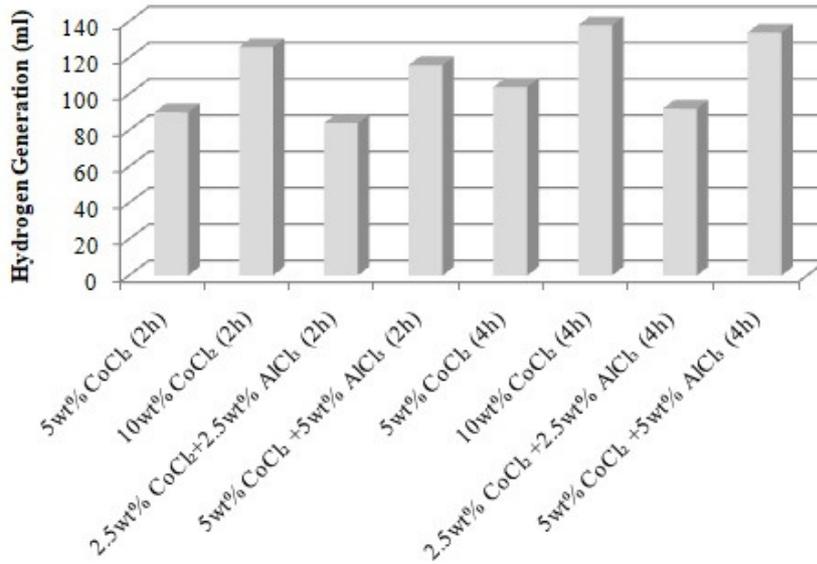


Figure 10. Hydrogen generation with 0.12 g of powder and 30 ml, 2 M citric acid solution.

4. CONCLUSIONS

To use Mg more effectively in H₂ production, surface properties should be improved. For this purpose, in our study, the preparation of Mg-metal chloride composite has been carried out by ball milling. To make the hydrolysis medium more conductive, acetic acid and citric acid solutions (1 and 2 M) have been used and the effect on hydrogen gas production has been investigated. It may be appropriate to use environmentally friendly acetic acid and citric acid as a catalyst with Mg-metal composites in the hydrogen generation reaction. In addition, the use of acetic acid and citric acid may further reduce the cost of hydrogen production. The results showed that CoCl₂ and AlCl₃ addition increased the reactivity and hydrogen generation amounts. Also, the use of CoCl₂ and AlCl₃ together improved the hydrogen generation rates and performances. Mg-metal chlorides are very promising for hydrogen production applications.

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