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Study on hydrogen generation from the hydrolysis of a ball milled aluminum/calcium hydride composite

Yongan Liu,^a Xinhua Wang,^{*ab} Haizhen Liu,^a Zhaohui Dong,^a Shouquan Li,^a Hongwei Ge^a and Mi Yan^{*a}

Metal Al was ball milled with CaH₂ to improve its hydrolysis properties. The effects of reaction temperature and milling conditions on the hydrogen generation performances of Al are investigated. A higher temperature has been shown to be beneficial for the hydrolysis of Al–CaH₂ composites. With increasing the added amount of CaH₂ and milling time, the grain size of Al is decreased and the protective oxide film on the surface of the Al powder is damaged. The hydrolysis of CaH₂ helps to open up the structure of Al grains and provide OH[−] to enhance the corrosion of Al. As a result, the hydrogen production of Al powder has been greatly optimized, and the addition of CaH₂ proves to be more effective than the addition of some other hydrides. The yield and maximum hydrogen generation rate (mHGR) of an Al-10 mol% CaH₂ mixture milled for 15 h are 97.8% and 2074.3 mL min^{−1} g^{−1}, respectively.

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1. Introduction

Nowadays, the energy crisis and air pollution arising from burning fossil fuels are becoming more and more serious,¹ and scientists are forced to find new forms of energy. Hydrogen has been considered to be the best energy carrier because of its light weight, high caloric value and environmentally friendly byproduct.² Hydrogen fuel cells are believed to be an ideal alternative to traditional fuels in the future because of their clean combustion and zero greenhouse gas emissions.³ Cheng *et al.*⁴ claim that hydrogen and its application in fuel cells is an important energy storage method as it allows energy to be carried in a chemical form instead of using traditional fossil fuels. Finding a proper technique to produce hydrogen is a challenging issue now. Traditionally, hydrogen is produced through direct decomposition or partial oxidation of hydrocarbon compounds⁵ as well as through steam reforming of hydrocarbons.⁶ However, considerable quantities of CO and other contaminative by-products will also be generated during these processes, which could cause catalyst poisoning in proton exchange membrane fuel cells.⁷

Recently, producing hydrogen through hydrolysis of metal Al has attracted much attention because of its low cost, abundance in the earth's crust and relatively high theoretical hydrogen capacity. 1 g of Al can produce 1.36 L of H₂, and the by-product,

Al(OH)₃, can be recycled to produce Al through the Hall–Héroult process.⁸ The gravimetric capacity is 11.1 wt%, which is formulated on a material base without considering the mass of water. This is different from DOE (Department of Energy, USA) which uses a tank system based concept for calculating the energy density values.⁹ However, it is usually difficult to make the Al–H₂O reaction proceed due to the protective oxide film covering on the surface of metal Al and the dense hydroxide by-product generated during the hydrolysis. In order to activate Al and improve its hydrolysis properties, much work has been carried out. The corrosion of Al in alkaline solution has been widely studied.^{10–12} Soler *et al.*¹³ found that compared with NaOH, the addition of NaAlO₂ showed higher maximum rates and hydrogen generation yields. Complete reaction could be reached using NaAlO₂ concentrations higher than 0.65 M. By doping with particular metals, such as Ga, In, Bi and Sn, to form amalgamated aluminum also proves to be an effective method to activate Al.^{14–17} Ball milling is an effective method to activate materials and has been widely used in hydrogen storage materials,^{18–20} but the hydrolysis properties can also be improved by ball milling. Ilyukhina *et al.*²¹ milled aluminum with different amounts of gallium and found that the addition of a small amount of gallium (2–3 wt%) allowed for a high reaction rate and a nearly 100% hydrogen yield at 60 °C. Besides, Al surface modification by milling metal Al with different oxides also improves its hydrolysis properties.^{22,23} Deng *et al.*²⁴ used different modification agents, γ-Al₂O₃, α-Al₂O₃, and TiO₂ to modify the Al particle surface and it turned out that the γ-Al₂O₃ doped sample had a short induction time and reacted with water completely. Salt addition² is another simple way to raise the hydrogen yield. Alinejad *et al.*²⁵ milled Al with NaCl, and this

^aState Key Laboratory of Silicon Materials, School of Materials Science and Engineering, Zhejiang University, Hangzhou, 31007, China. E-mail: xinhwang@zju.edu.cn; mse_yanmi@zju.edu.cn; Fax: +86-571-8795-2716; Tel: +86-571-8795-2716

^bKey Laboratory of Novel Materials for Information Technology of Zhejiang Province, Zhejiang University, Hangzhou 310027, China

composite could reach a hydrogen yield of 100% within 40 min when the salt to aluminum molar ratio was set at 1.5. What's more, Fan *et al.*^{3,26} examined the effects of metal Li addition on the hydrolysis of Al. The optimized Al–Bi–Li alloy could release 1340 mL H₂ at 298 K with 100% efficiency with a hydrogen generation rate of 998 mL min⁻¹. However, alkaline solutions could corrode the reactor, and the addition of Ga, In, Al₂O₃, salts, Bi *etc.*, doesn't generate hydrogen, reducing the hydrogen production per gram of composite. The cost is also increased by the addition of some expensive metals, such as Ga and In.

Soler *et al.*⁸ discovered a synergistic effect existing between Al and NaBH₄ that favored the hydrolysis of both Al and NaBH₄. However, due to its high cost, limited solubility, necessity of expensive catalysts, *etc.*, NaBH₄ has recently been banned from on-board hydrogen production.²⁷ We choose another chemical hydride, CaH₂, to investigate its effects on Al hydrolysis. Different from Soler's work, the Al–CaH₂ composites are treated by high energy ball milling and Al here acts as the main fuel. The aim is to establish a new way to generate hydrogen through Al hydrolysis, which could be applied as a hydrogen source for portable devices.

2. Experimental

Al (Sinopharm Chemical Reagent Co., Ltd, 99.0%, 100–200 mesh), LiBH₄ (Acros Organics, 95%), CaH₂ (Sigma Aldrich, 95%), MgH₂ and NaBH₄ (Alfa Aesar, 98%) were used as received. Samples were weighed and mounted into stainless pots to be milled using a planetary QM-3SP4 ball miller. The ball-to-powder ratio was fixed at 25 : 1. All sample handling was performed in a glove box with a recirculation system.

The hydrogen generation experiment setup was similar to what was depicted in Zhao's work.²⁸ Reagents were added into a 250 mL glass reactor to react with 10 mL of tap water. A water bath was employed to maintain a constant temperature. The produced hydrogen was passed through a spiral condenser and a desiccant (CaCl₂) to remove moisture. Then the flow was measured by a flow meter (ADM 2000) which was connected to a computer to record the data. Each test was repeated at least twice to make sure that the experiment was capable of giving reproducible results, and the precision of the measurement was estimated to be 5%. The flow meter showed some background flow (about 0.08 mL min⁻¹) even when connected with nothing; this phenomena existed in every other flow meter and couldn't be eliminated. In order to get precise data for the hydrogen volume, the background flow was measured without sample addition under the same conditions and subtracted from the hydrogen volume measured. The final data was then converted to that under the standard conditions (273 K, 1 atm) using the ideal gas equation. As the data recorded by the flow meter was the instantaneous value that was presented as the hydrogen generation (HG) rate curves in the following figures, the integral of these curves would show the volume of hydrogen generated. The hydrogen yield (%) was calculated as this volume over the theoretical value assuming that the hydrolysis was carried out completely. The maximum hydrogen generation rate (mHGR) was defined as the largest volume of

hydrogen generated per minute per gram of composite, which was read directly from the data recorded by the flow meter. Hydrogen generation curves within the first hour were presented and discussed in this work.

An X-ray diffractometer (X'Pert PRO) with Cu K α radiation was used to analyze the phases of the milled sample and hydrolysis by-product. A scanning electron microscopy (SEM) system (SIRON) equipped with an INCA energy dispersive X-ray spectroscope (EDS) was used to carry out the microstructure study. The specific surface area of the powders was measured by N₂ adsorption (multipoint BET) using an ASIC-2 analyzer. The samples were degassed for 12 h at 200 °C to remove any moisture or adsorbed contaminants.

3. Results and discussion

3.1 Effects of temperature

Fig. 1 shows the effects of temperature on the hydrogen generation of an Al-10 mol% CaH₂ mixture milled for 6 h. Apparently, the hydrolysis of Al is highly sensitive to temperature, which was also found in previous works.^{29,30} The hydrolysis becomes quicker with a higher yield when the initial temperature is raised. As can be seen in Fig. 1, the reaction is very slow at 25 °C, and becomes faster with increasing temperature, ending up with a high hydrogen production at 75 °C. The hydrogen yield is 10.9% at 25 °C, 34.6% at 45 °C, 74.9% at 60 °C and 91.6% at 75 °C, respectively. What's more, the reaction taking place at 75 °C also shows the highest mHGR of about 1294.2 mL min⁻¹ g⁻¹. A higher temperature is beneficial for the diffusion of species such as OH⁻, which improves the hydrolysis kinetics. More importantly, as pointed out by Dupiano *et al.*,²³ temperature can change the permeability of the oxide film on the surface of Al. The film that is protective at low temperatures could be permeable at high temperatures. Since the sample shows the best performance at 75 °C, the following experiments were all carried out at this temperature unless specified.

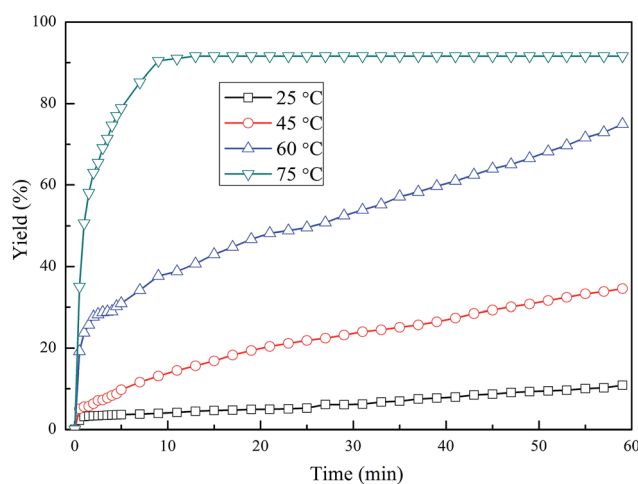


Fig. 1 Hydrogen generation curves of an Al-10 mol% CaH₂ mixture milled for 6 h at different temperatures.

3.2 Effects of CaH₂ content

Fig. 2 shows the hydrogen generation (HG) rate (top) and yield (bottom) of Al milled with different amounts of CaH₂ for 6 h. As can be seen in the picture, the hydrolysis performances of Al can be improved by milling with CaH₂. The hydrogen yield increases with the increasing amount of CaH₂. A marked improvement can be observed when 10 mol% CaH₂ is added. The yield of Al-1 mol% CaH₂ is about 31.4%, which increases to nearly 96.9% for the Al-15 mol% CaH₂ mixture. The HG rate curves show a similar trend, with the sample with 15 mol% CaH₂ added having the highest mHGR of 2034.3 mL min⁻¹ g⁻¹. There might be two reasons for the improvement of Al hydrolysis by milling with CaH₂: firstly, CaH₂, with its brittle characteristic, can serve as a cutter during the milling process, preventing the agglomeration of Al powder, and reducing the grain size of the Al particles. As a result, the reactivity of the Al particles can be improved. Secondly, CaH₂ is easier to hydrolyze than Al,³¹ which helps to open up the structure of Al and provides numerous passages for water to permeate and react with the freshly exposed Al.

Fig. 3 shows the SEM images of Al milled with different amounts of CaH₂ for 6 h. The shape of the Al particles is round and smooth when 1 mol% CaH₂ (a) is added. Then it changes to fractured platelets when the added amount of CaH₂ is increased, implying the breakage of the oxide film on the

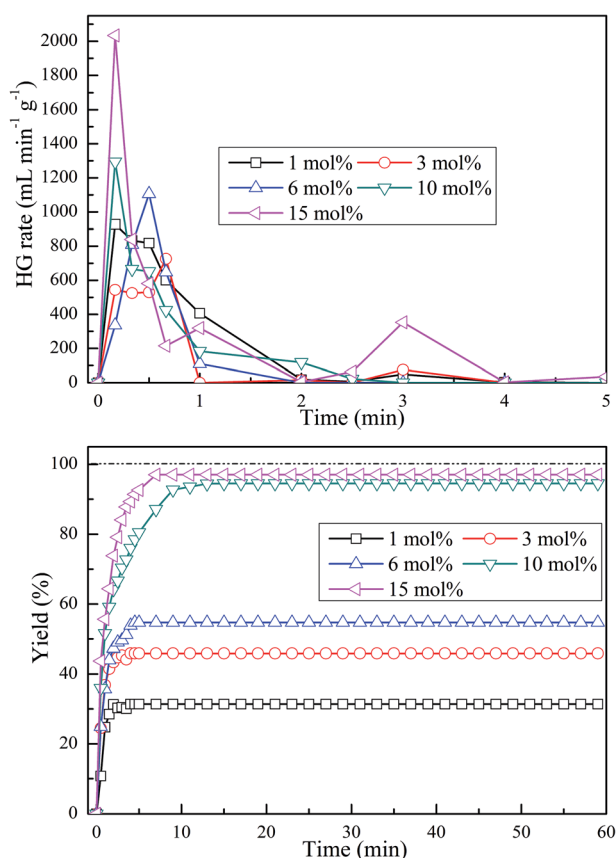


Fig. 2 HG rate (top) and hydrogen yield of Al milled with different amounts of CaH₂ for 6 h.

surface of the Al powder. Finally, much smaller particles can be observed in the Al-15 mol% CaH₂ mixture (e). To make it clear, the specific surface area of these samples were measured and plotted against the hydrogen yield, as shown in Fig. 4. The specific surface area of the samples with a small amount of added CaH₂ is very small and can hardly be detected. With more addition of CaH₂, the surface area increases, meanwhile the hydrogen yield increases as well. This observation is consistent with the claim stated above. The decreased particle size leads to the increase of the specific surface area and many defects are generated, which work together to promote the hydrolysis properties of the Al powder.

3.3 Effects of milling time

Fig. 5 shows the HG rate (top) and yield (bottom) of Al-10 mol% CaH₂ milled for different numbers of hours. An addition amount of 10 mol% is chosen on the basis of the results shown in Fig. 2 where more CaH₂ addition shows limited improvement. As can be seen in Fig. 4, hydrogen production increases with milling time. A mixture milled for 1 h already shows a high yield of about 84.2%, and this value is further raised to 97.8% when the mixture is milled for 15 h. The improvement is limited when the milling time is more than 6 h. As for the HG rate, though the 10 h milled mixture has the highest mHGR of about 2194.3 mL min⁻¹ g⁻¹, the 15 h milled one seems to have a higher average HG rate. As mentioned above, ball milling can change the sample's microstructure, redistribute the constituents and induce severe plastic deformation and defects, which contribute to the activation of metals.^{15,32} What's more, with

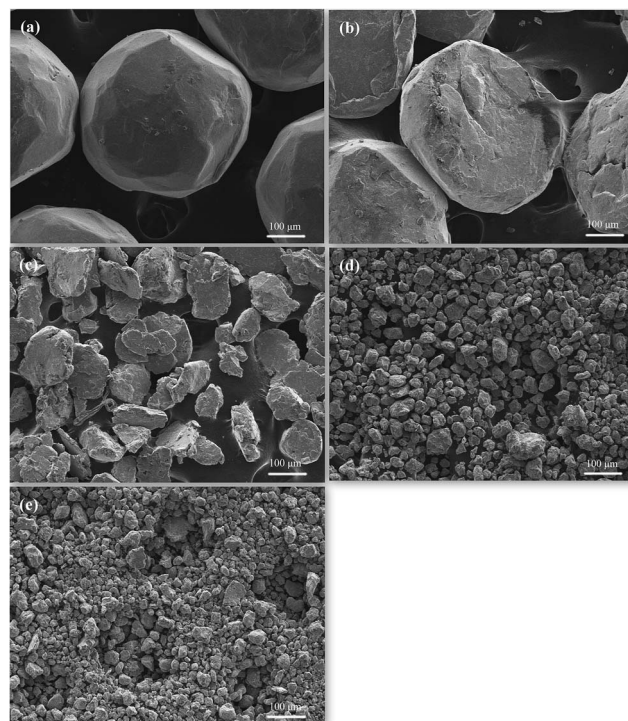


Fig. 3 SEM images of Al milled with 1 mol% (a), 3 mol% (b), 6 mol% (c), 10 mol% (d) and 15 mol% (e) CaH₂ for 6 h.

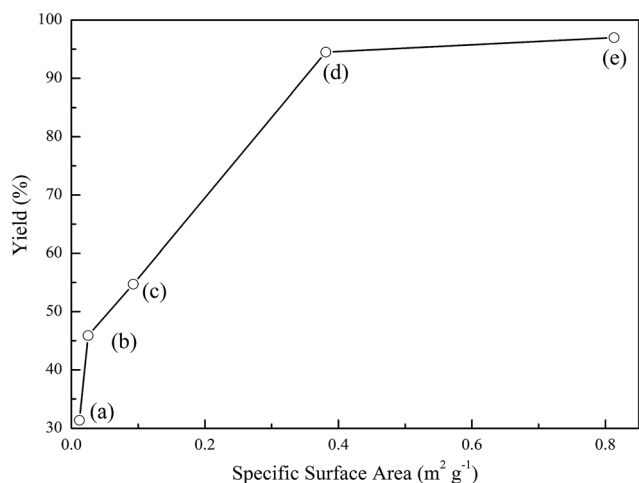


Fig. 4 Relationship of hydrogen yield and the specific surface area of Al milled with 1 mol% (a), 3 mol% (b), 6 mol% (c), 10 mol% (d) and 15 mol% (e) CaH₂ for 6 h.

CaH₂ as the cutter, these effects can be enhanced during long-time ball milling. As a result, the grain size of the Al particles is reduced and numerous defects are generated, which lead to a higher hydrogen yield.

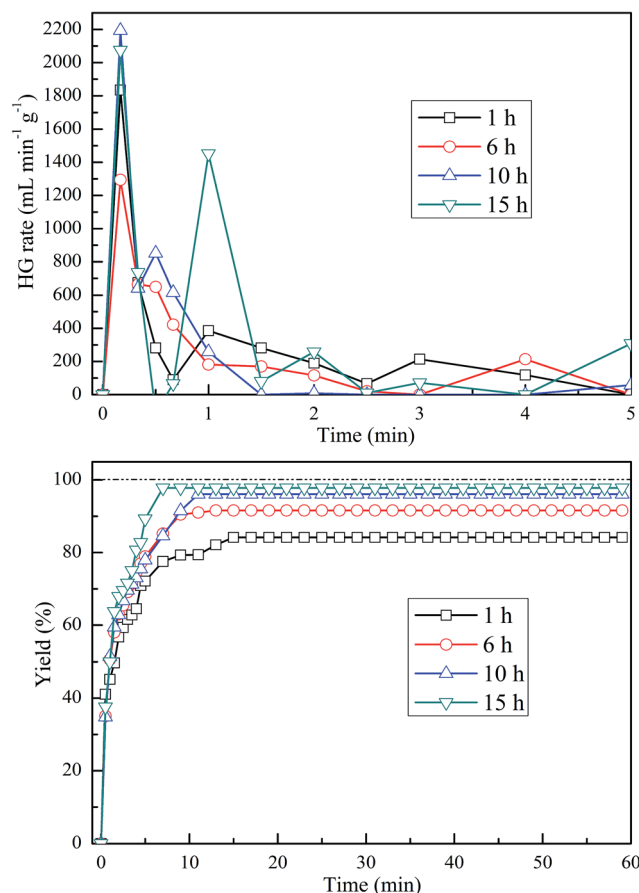


Fig. 5 HG rate (top) and hydrogen yield of Al-10 mol% CaH₂ milled for different numbers of hours.

Fig. 6 shows the SEM images of Al-10 mol% CaH₂ milled for different numbers of hours. It can be seen that the shape of the Al particles change from big solid grains (1 h) to small fractured platelets (6 h) and finally to smaller particles (15 h). In the case of the Al-CaH₂ mixture discussed in this work, increasing the milling time does reduce the grain size of Al and promotes its hydrolysis properties. Fig. 7 shows the EDS mapping of Al-10 mol% CaH₂ milled for 15 h. It's clear that CaH₂ has been uniformly distributed into the Al grains after the long ball milling process. The relationship of hydrogen yield and the specific surface area of the samples above are shown in Fig. 8. Apparently, samples subjected to a longer milling time have a bigger specific surface area and a higher hydrogen yield, which is consistent with the SEM observations.

3.4 Hydrolysis by-product

Fig. 9 shows the XRD patterns of the Al-10 mol% CaH₂ mixture milled for 15 h (a) and its hydrolysis by-product (b). The mixture milled for 15 h mainly contains Al and CaH₂, and no other peaks can be observed, indicating that no chemical reactions between Al and CaH₂ took place during the milling process. After the mixture is submerged into water to release hydrogen, the peaks of Al are greatly weakened. The hydrolysis by-product mainly contains Al(OH)₃, which might cover the small amount of Ca(OH)₂ generated from the hydrolysis of CaH₂, making it undetectable. The results of the XRD suggest the high hydrogen yield of the Al-10 mol% CaH₂ mixture milled for 15 h, which is shown in Fig. 5. Fig. 10 shows the EDS mapping of the by-product of Al-10 mol% CaH₂ milled for 15 h. As can be seen in the SEM image, the surface of this hydrolysis by-product is porous and many petal-like structures can be noticed. A similar structure is also found in previous work³³ and is claimed to be formed by the breaking of H₂ bubbles at the interface of Al and the dense oxide.¹ The mapping also shows O signal which is as strong as that of Al, indicating the existence of a large amount of oxide. Ca can also be detected but with a much weaker signal and a scattered distribution.

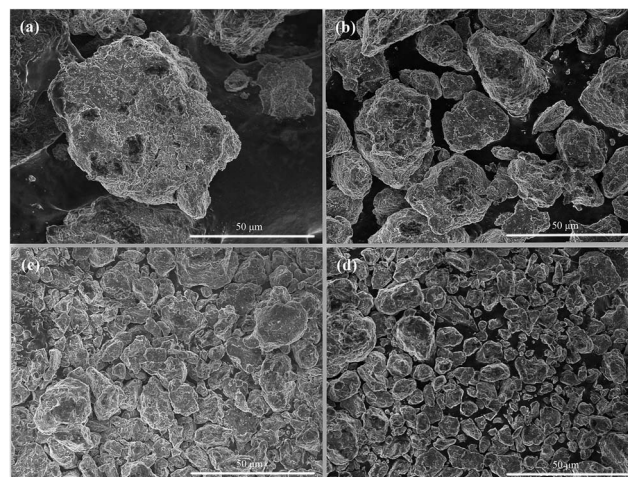


Fig. 6 SEM images of Al-10 mol% CaH₂ milled for 1 h (a), 6 h (b), 10 h (c) and 15 h (d).

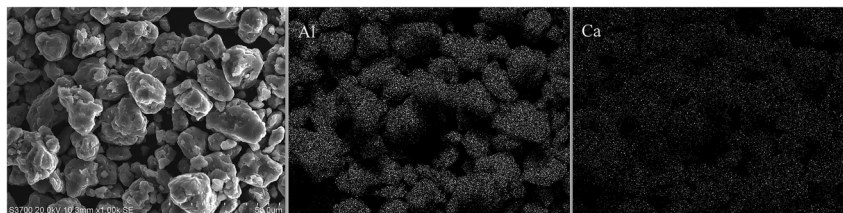


Fig. 7 SEM images and EDS mapping of Al-10 mol% CaH₂ milled for 15 h.

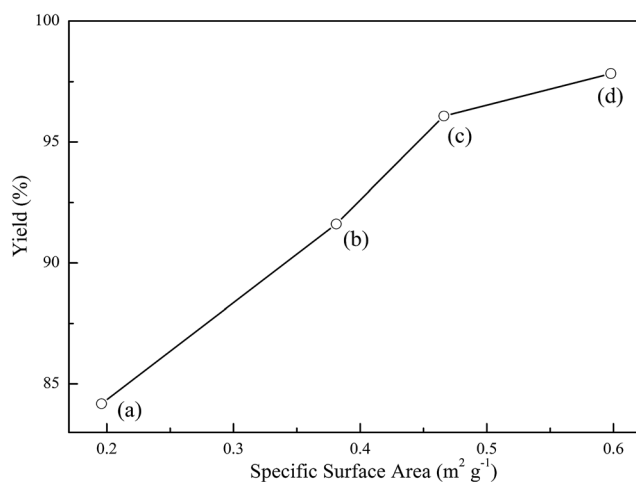


Fig. 8 Relationship of hydrogen yield and the specific surface area of Al-10 mol% CaH₂ milled for 1 h (a), 6 h (b), 10 h (c) and 15 h (d).

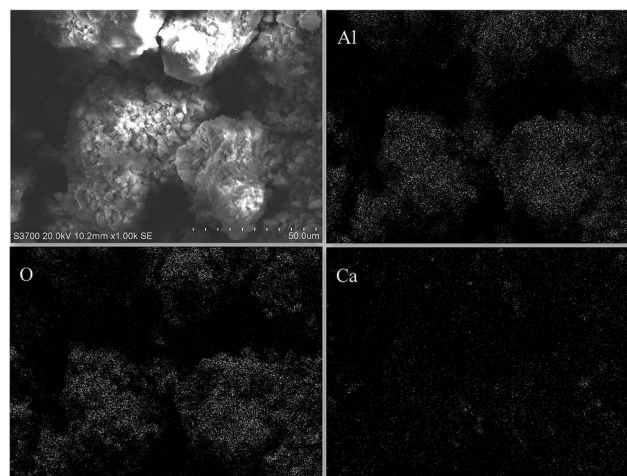


Fig. 10 SEM image and EDS mapping of the by-product of Al-10 mol% CaH₂ milled for 15 h.

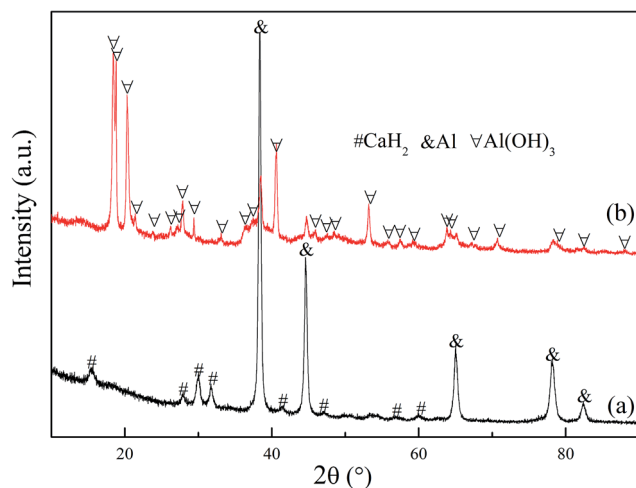


Fig. 9 XRD patterns of Al-10 mol% CaH₂ milled for 15 h and the corresponding hydrolysis by-product.

3.5 Comparison with addition of other hydrides

Fig. 11 shows the hydrogen generation curves of Al milled with 10 mol% of different hydrides for 6 h. Among the hydrides tested, CaH₂ shows the best performance with a hydrogen yield of about 91.6%, and MgH₂ has the least activation effect with a hydrogen yield of about 57.8%. Although it has been reported that a synergistic effect exists between Al and NaBH₄,^{8,26} CaH₂

seems to have a better influence on improving the hydrolysis properties of Al. The differences might result from the fact that the samples in this work are prepared by high energy ball milling and the addition amount of the hydrides is much smaller. What's more, the sample with LiBH₄ addition has the highest mHGR of about 1734.3 mL min⁻¹ g⁻¹, suggesting the high reactivity of this mixture at the initial stage. However, the continuity is not very good and the reaction stops quickly with a relatively low yield of about 74.9%. This mixture is also promising if some measures can be taken to improve its hydrolysis continuity.

Fig. 12 shows the SEM images of the samples stated above. It can be seen from the picture that the grain size of the Al-CaH₂ mixture (a) is finer than that of other samples. The shape of the ball milled Al-LiBH₄ (b) mixture is platelet and similar to that of Al-NaBH₄ (c). It is bigger solid grains when Al is milled with MgH₂ (d) which accounts for its low hydrogen yield shown in Fig. 11. Though the grain size is very important for the optimized hydrolysis of the 6 h milled Al-10 mol% CaH₂ mixture, the chemical effect of the hydride cannot be ignored as well. The Al-LiBH₄ mixture has the highest mHGR, showing that LiBH₄ is actually more chemically active than CaH₂.

3.6 Preliminary mechanism

Due to the nm-thin passive film of the oxide layer that covers the surface of Al, it is hard to corrode Al at room temperature (RT),

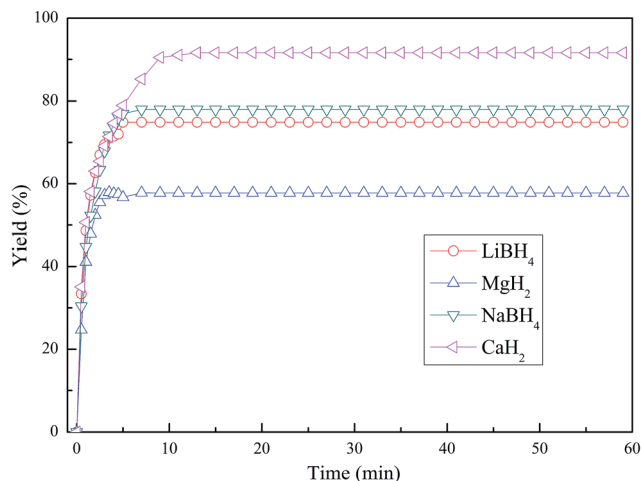


Fig. 11 Hydrogen generation curves of Al milled with 10 mol% of different hydrides for 6 h.

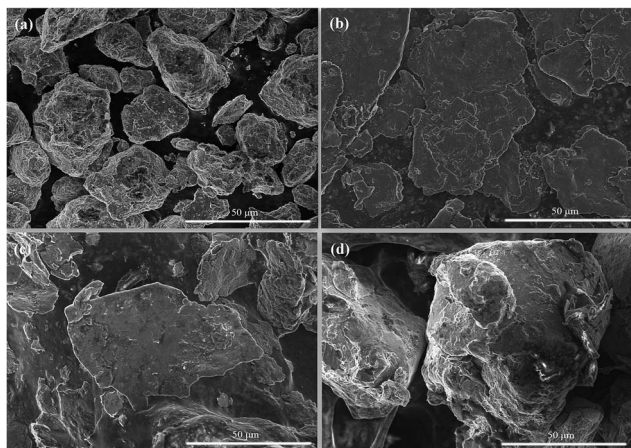


Fig. 12 SEM images of Al milled with 10 mol% of different hydrides for 6 h, CaH₂ (a), LiBH₄ (b), NaBH₄ (c) and MgH₂ (d).

and the yield of pure Al powder is only 6.5% at 55 °C.³⁴ However, hydrogen generation can be improved when Al is ball milled with CaH₂; as shown in Fig. 1, the Al–CaH₂ mixture reaches a yield of 10.9% at RT. With an elevated temperature, the hydrogen production is further improved due to the modification of the permeability of the protective film as stated above. However, temperature is not the sole element affecting the hydrolysis of Al because the yield of pure Al is low even at high temperatures.³⁴ The possible synergistic effects between Al and CaH₂ are also important, as Vajo *et al.* found in their research that chemical hydride AH₂ can be destabilized if combined with an alloying species B.³⁵ In other words, the main reasons for the improvement observed in this work can be generalized into two aspects; the first part is about the milling process. As stated above, ball milling is beneficial for reducing the grain size, generating defects, and damaging the protective oxide film, which activates metal Al. However, the good ductility of Al may counteract these beneficial effects through agglomeration.

CaH₂ is added as a cutter to ensure that Al can be sufficiently activated during the milling process. CaH₂ proves to be a good additive which renders the grain size of Al reduced with an increase in its addition amount and milling time. The second part concerns the hydrolysis process. As CaH₂ is easier to hydrolyze than Al, the hydrolysis of CaH₂ could help to open up the structure of the Al and provide numerous passages for water to penetrate through and react with freshly exposed Al. The heat released by the reaction between CaH₂ and water can also promote the kinetics locally and help initiate the hydrolysis of Al. What's more, the dissolution of CaH₂ supplies OH[−] and improves the solution's alkalinity which is favorable for the corrosion of Al. Besides, as found in previous work,³⁶ Al(OH)₃ or Ca(OH)₂ in the solution could act as crystallization nuclei and transfer the newly formed Al(OH)₃ from the surface of Al to these existing nuclei. As a result of the above elements, Al powder is well activated and the passivation of the Al surface is greatly alleviated, which leads to the optimized hydrogen generation performances of the Al–CaH₂ mixture.

4. Conclusions

In this work, the hydrolysis of Al is greatly improved by ball milling with CaH₂. Temperature proves to be an important factor affecting the reactivity of Al, because a higher temperature can make the dense oxide film permeable, and 75 °C is chosen as the default experimental temperature in this work. Milling conditions, such as CaH₂ content and milling time are important factors contributing to the optimization of the Al–H₂O reaction by decreasing the grain size of the Al particles and increasing their reactivity. The addition of CaH₂ is very important because CaH₂ can serve as a cutter during the milling process, initiating the overall hydrolysis and providing a local alkaline environment. The hydrogen yield increases with the increasing CaH₂ content and milling time. The Al–10 mol% CaH₂ mixture milled for 15 h reaches a yield of about 97.8% with the mHGR at 2074.3 mL min^{−1} g^{−1}. In summary, a novel hydrogen production material has been discovered in this work, which could be applied as the hydrogen source for portable devices.

Acknowledgements

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