The use of silicon oxide extracted from rice husk ash as catalyst in magnesium hydrides (MgH₂) prepared by mechanical alloying method

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Abstract. MgH₂ is one of the most promising material for hydrogen storage application, since it is reversible and able to store hydrogen in large amounts of 7.6wt%. However, to be applied as a hydrogen absorber material, this material still has a deficiency, its kinetic reaction is still very slow and its operational temperature is still high. In this study, nickel and silicon oxide catalysts were used to reduce the operational temperature of MgH₂. The silicon oxide used in this study was extracted from rice husks ash. The composition of MgH₂ + SiO₂ 5wt% + Ni 10wt% was prepared by mechanical alloying technique, by varying milling time 0, 1, 5, 10 and 15 hours. XRD results indicate a decrease in particle size with longer milling time. MgH₂ was obtained as the main phase followed by Ni and SiO₂. SEM results showed that the longer milling time, the more particle size is homogeneous. Furthermore, thermal investigation using DSC showed that the desorption temperature obtained was in the range of values of 334.62 ℃ to 347.85 ℃. The addition of 5 wt% SiO₂ and 10 wt% Ni have improved sorption temperature and kinetic of MgH₂.

1. Introduction

MgH₂ has been considered as one of the most promising candidate as hydrogen storage material, because it has high hydrogen storage capacity, abundance in deposit, low cost and environmentally friendly. MgH₂ has high thermodynamic stability. This characteristic lead to a high temperature operation (>350 ℃) which is not good for hydrogen storage application. Another drawback of MgH₂ is its slow reaction kinetics and difficult activation. An ideal hydrogen storage material should cost-affordable, high hydrogen storage capacity, mild operation temperature, easy to absorb and de-absorb hydrogen, and long life span [1]. Some effort have been carried out to improve the properties of MgH₂. Reducing the particle size and doping it with different kinds of catalysts [2,3] can partially eliminated the drawbacks of MgH₂ as hydrogen storage material. Nano scaling by using ball milling is one of effective method in optimizing the thermodynamics and kinetics of MgH₂, because it can increase fresh surface, decreased diffusion distance for hydrogen, intimate contract between reactants, and condensed atom in the grain boundaries.

The effectiveness of metal oxide type silica (SiO₂) as catalyst for hydrogen storage have been investigated by Norton et al [4], Jalil et al [5,6] and Mustanir et al [7]. Jalil et al reported the progress of using 1 wt%, 3 wt% and 5 wt% nano-silica (SiO₂), extracted from local rice husk ash [5] and local beach sand [6], to improve the thermodynamics and kinetics of magnesium hydrides. Mustanir et al have added 2 wt% SiO₂ to MgH₂. It was found that nano-silica reduce the hydrogen
desorption temperature of MgH$_2$, but desorption time is still high when the 5 wt% variation of catalyst was applied.

Furthermore, it has been reported that small amount of metals catalysts in nanometre scale can improve the kinetics of MgH$_2$ [8-16]. In this study we have used Ni and silica (SiO$_2$) which was extracted from rice husks ash (RHA) as catalyst in MgH$_2$. The sample was prepared by intensive mechanical milling, using a planetary high energy ball milling technique. Using this doubles catalyst is an effort to improve sorption and kinetics properties of MgH$_2$.

2. Experimental Details

MgH$_2$ (99.99%, size 50 µm) and Ni (99.99%, size 50 µm) powder were purchase from Sigma Aldrich. RHA was collected from a local milling factory in Blang Bintang, Aceh Besar. The solution of hydrochloric acid (HCl) and ammonium hydroxide (NH$_4$OH), as well as aquadest were used for silica (SiO$_2$) extraction.

Then, the MgH$_2$ was catalysed with 5 wt% SiO$_2$ and 10 wt% Ni and prepared using a high-energy milling technique. The mixing process of the sample using planetary ball milling (Fritsch, P6) with a ball to powder ratio (BPR) of 10:1 and a speed of 350 rpm for 0 h, 1 h, 5 h, 10 h and 15 h. The composition phase of the samples was determined by using x-ray diffraction (XRD; Shimadzu D6000, Cu-Kα radiation λ = 1.54060 Å). Morphological structures and thermal properties were observed by scanning electron microscopy (SEM; Philips, XL30) and Differential scanning calorimetric (DSC; Shimadzu, D50).

3. Results and Discussions

XRD patterns showed that the main phase was dominated by MgH$_2$. The smaller intensity of the patterns was influenced by longer milling time (Figure 1). It showed that milling process have changed crystallite size of the sample. The calculation of crystallite size is summarized in the Table 1. Table 1 revealed that the crystal size is getting smaller when the milling time was extended, except for milling time about 15 h. There are the agglomeration phenomena during the milling process at the sample. This agglomeration occur due to the puncture and pressure given by the balls against the powder which cause the particle joint each other, and it part of mechanical alloying process. This agglomeration reduce surface area of magnesium contact with hydrogen, therefore it can reduce the sorption properties of MgH$_2$ [6].

![Figure 1. XRD patterns of MgH$_2$ + 5 wt% SiO$_2$ + 10 wt% Ni](image)

Figure 1. XRD patterns of MgH$_2$ + 5 wt% SiO$_2$ + 10 wt% Ni
Table 1. Crystallite sized of MgH$_2$ + 5 wt% SiO$_2$ + 10 wt% Ni in each variation of milling time

| Milling time | Fasa  | 2θ   | FWHM  | Crystallite size (nm) |
|--------------|-------|------|-------|-----------------------|
| 0 h          | MgH$_2$ | 27,9052 | 0,14660 | 58,94414               |
| 1 h          | MgH$_2$ | 27,9369 | 0,16470 | 52,46997               |
| 5 h          | MgH$_2$ | 27,8628 | 0,34200 | 25,26438               |
| 10 h         | MgH$_2$ | 27,8798 | 0,48470 | 17,82697               |
| 15 h         | MgH$_2$ | 44,4884 | 0,41390 | 21,89068               |

Thermal observation, which was analyzed with DSC, is shown in Figure 2, and the resume can be seen in Table 2. We can observe that desorption temperature did not change significantly when crystallite size getting smaller, but desorption time is shorter (Table 2). Addition 5 wt % SiO$_2$, extracted from RHA, has improved the desorption temperature of pure MgH$_2$ that was in range of 409 °C. Meanwhile, 10 wt% Ni has improved desorption time of MgH$_2$, because of catalytic effect of Ni [10].

![Figure 2](image_url)  
**Figure 2.** The DSC Result of MgH$_2$ + 5 wt% SiO$_2$ + 10 wt% Ni with 0 h, 1 h, 5 h, 10 h, and 15 h milling time.

Table 2. The resume of DSC result

| Milling time (hours) | Desorption temperature (°C) | Desorption time (minutes) |
|----------------------|-----------------------------|---------------------------|
| 0                    | 334,62                      | 5,8                       |
| 1                    | 339,34                      | 5,9                       |
| 5                    | 348,83                      | 5                         |
| 10                   | 347,30                      | 4,7                       |
| 15                   | 347,83                      | 4,1                       |
SEM image (Figure 3) showed that the longer milling time, the more particle size is homogeneous, and the particle size decrease with extending of milling time. However, the sample that milling for 15 h were agglomerated. These results agree with XRD result.

![SEM Images](image)

Figure 3. SEM Image for the samples: (a) unmilling, (b) 1 h milling, (c) 5 h milling, (d) 10 h milling, (e) 15 h milling.

4. Conclusions

MgH₂ with double catalyst was successfully prepared using a high-energy ball milling technique. As a result, the addition of 5 wt% SiO₂ and 10 wt% Ni have improved sorption temperature and kinetic of MgH₂. The addition of SiO₂ in the sample have decreased desorption temperature, meanwhile, the Ni catalyst decreased the desorption time. The Extending of milling time decrease crystallite size and increase the surface area and defect concentration.

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References

[1] Wang Ying and Wang Yijing 2017 Recent Advances in Additive-Enhanced Magnesium Hydrides for Hydrogen Storage Progress in Natural Science: Materials International 27, pp. 41-49.

[2] Sabitu S T and Goudy A J 2012 Dehidrogenation Kinetics and Modelling Studies of MgH₂
Enhanced by Transition Metal Oxide Catalysts Using Constant Pressure Thermodynamic Driving Force, *Open Access Metal*, ISSN 2075-4701, www.mdpi.com/journal/metal/

[3] Wang H, Zhang J, Liu J W, Ouyang L Z and Zhu M 2013 Improving Hydrogen Storage Properties of MgH₂ by addition of Alkali Hydroxide, *Hydrogen Energy*, **38**, pp. 10932 – 10938.

[4] Norton M G, Milica Nanospring: A Novel Nanostructured Material for Hydrogen Storage *Proc. Clean Technology Conference*, Houston

[5] Jalil Z, Rahwanto A, Mulana Farid and Mustanir 2016 Desorption Temperature Characteristic of Mg-based Hydrides catalyzed by Nano-SiO₂ prepared by high energy ball Milling *International Journal of Technology* **8**, pp. 1301-1306.

[6] Jalil Z, Rahwanto A, Sofyan H, Usman M and Handoko E 2018 The Use of Silica from beach sand as catalyst in Magnesium Based Hydrides for Hydrogen Storage Materials, *IOP Conf. Series: Earth and Environmental Science* **105** 012093

[7] Mustanir, Nur S, Jalil Z and Fauzi 2011 Pengaruh Sisipan Katalis SiO₂ dalam MgH₂ yang disintesis melalui Rute Mechanical Alloying, *Jurnal Sains MIPA* **17** pp 43-47

[8] Mustanir, Rahwanto A and Jalil Z 2010 Hydrogen Sorption Behaviour of MgH₂- 1 mol% Ni prepared by Reactive Ball Milling, *International Journal of Material Science* **5** pp 173-179

[9] Zhang Q, Zang L, Yike H, Gao P, Jiao L, Yuan H and Wang Y 2017 Improve Hidrogen Storage Properties of MgH₂ with Ni-based Compound *Hydrogen Energy* **42** pp 24247-24255

[10] Ranjar A, Guo Z P, Yu X B, Attard D, Calka A and Liu H K 2009 Effects of SiC nanoparticles with and without Ni on the hydrogen storage properties of MgH₂ *International of Hydrogen Energy* **xxx** pp. 1-6.

[11] Jalil Z, Rahwanto A, Akhyar H, Razali R and Handoko E 2018 MgH₂-SiC Based Hydrogen Storage Material Prepared by Reactive mechanical alloying method *IOP Conf. Series: Earth and Environmental Science* **105** 012098

[12] Kwak YJ, Lee SH, Mumm DR and Song MY 2015 Development of a Mg-based Hydrogen Storage Material by Addition of Ni and NBF₅ Via Milling Under Hydrogen *Hydrogen Energy* **40** pp 11908-11916

[13] Z Jalil, A Rahwanto, E Handoko, Mustanir, 2017 *AIP Conference Proceedings* 1826 (1), 020002

[14] Z Jalil, A Rahwanto, Mustanir, Akhyar, E. Handoko, 2017 *AIP Conference Proceedings* 1862, 030023

[15] Z Jalil, A Rahwanto, E Handoko 2018 Effect of nanostructure Ni on the sorption properties of mechanical milled MgH₂, *MATEC Web of Conferences* **197**, 02014

[16] Z Jalil, A Rahwanto, I Ismail, H Sofyan, E Handoko, The use of nano-silicon carbide and nickel as catalyst in magnesium hydrides (MgH₂) for hydrogen storage material application, *Mater. Res. Express* **5** (2018) 064002