Effect of Milling Time on The Desorption Temperature of MgH\textsubscript{2}-10wt\% Fe\textsubscript{3}O\textsubscript{4} for Hydrogen Storage Materials Application

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Abstract. The effect of milling time on the desorption temperature of hydrogen storage material MgH\textsubscript{2}-Fe\textsubscript{3}O\textsubscript{4} has been carried out. This study aims to determine the effect of milling time variation and the effect of adding Fe3O4 catalyst on the characterization of MgH\textsubscript{2}. Milling time variation using mechanical alloying technique, with milling time given for 10 hours, 20 hours, 30 hours with a ball ratio of 10:1 and a speed of 350 rpm. MgH\textsubscript{2}-10wt\% Fe3O4 was characterized using XRD and DSC. The results showed the phases of MgH\textsubscript{2}, MgO, and Fe3O4. The crystal grain size of MgH\textsubscript{2} decreased from 11.81 nm to 8.35 nm. Variation of ownership time and the addition of Fe3O4 catalyst can reduce the desorption time from 377\degree C to 369\degree C.

1. Introduction
Hydrogen is an alternative energy that can be used as a substitute for fossil fuels whose availability is dwindling. Hydrogen was chosen because it has the advantages of high abundance, reproducibility, and zero-pollutant or environmentally friendly emissions during combustion [1] The advantages of hydrogen have prompted researchers to use hydrogen as a substitute fuel for transportation. Hydrogen can be used as a substitute for fuel (fuel cell) by converting energy into electricity, a fuel cell is an electrochemical device that converts chemical energy into electrical energy [2].

Fuel cell-based fuels are often used in the automotive industry in motor vehicles. However, when applied, it still inhibits the hydrogen storage system (hydrogen storage). Hydrogen storage consists of three types of storage, namely in the form of gas, liquid, and solid. In this study, hydrogen storage is used in solid form. This is because hydrogen in solid form is better able to store or absorb hydrogen in large quantities, is lighter and at a more economical price. Light metal elements that have the ability to absorb hydrogen in large quantities are magnesium (Mg). Magnesium was chosen because it has the ability to absorb hydrogen in large amounts (7.6 weight%). However, magnesium has a weakness, namely the temperature required for desorption is very high (> 300 \degree C) and the time required is quite long. The World Energy Agency (IEA) is able to absorb 5wt % hydrogen at a temperature of 100 \degree C and the desorption time is less than 1 hour.

The weakness of MgH\textsubscript{2} can be minimized by adding a catalyst, the catalyst that is commonly used is Fe\textsubscript{3}O\textsubscript{4}. The addition of Fe\textsubscript{3}O\textsubscript{4} catalyst can reduce the desorption temperature from 310\degree C to 200\degree C [3]. The addition of Fe\textsubscript{3}O\textsubscript{4} catalyst can keep the desorption temperature lower [4]. Jalil \textit{et al.} [5] Tried to add Ni catalyst, the results obtained changed the crystalline nature of MgH\textsubscript{2}, namely a widening of the diffraction peak and it could reduce the desorption temperature peak. Variations in milling time can also affect the crystal grain size and widen the diffraction peaks of MgH\textsubscript{2} [6-9]. In this study, we present the results of adding Fe\textsubscript{3}O\textsubscript{4} catalyst and produced by variations in milling time using mechanical alloying method.
2. Method
The materials used were magnesium hydride (Sigma Aldrich, Germany 99.9%) and Fe3O4 powder (Sigma Aldrich, Germany 99.9%). The mechanical alloying process was then carried out with a planetary ball mill machine (Fritsch, P6). The ratio of the weight of the ball and the powder used is 10:1. The composition of the weight used is 2 grams with a composition of 10wt% Fe3O4. Then the milling time was varied from 10 hours, 20 hours, and 30 hours with a milling speed of 350 rpm. Identification of the phase composition present in the material was carried out using X-Ray diffraction (XRD) Shimadzu D6000, Cu-Kα with \(\lambda = 1.54060\). Furthermore, the thermal properties of hydrogen desorption were tested using the Shimadzu D50 Differential Scanning Calorimetry (DSC). The data obtained from the XRD test results were calculated by calculating the crystal size of the identified material, using the Scherrer method.

3. Results and Discussion
The X-ray diffraction pattern with variations in milling time is shown in Figure 1, where the detected phases are MgH2, Fe3O4, and a small peak MgO. The MgH2 phase appears at angles of \(2\theta = 38.05^\circ, 37.94^\circ, 37.93^\circ, 52.46^\circ, \) and \(44.65^\circ\), while the Fe3O4 phase appears at angles of \(2\theta = 16.7018^\circ \) and \(35.46^\circ\). The MgO phase appears in samples that have been milled, this is influenced by outside air contamination during sample preparation. The MgO phase is considered as an impurity because it can affect the desorption properties of hydrogen [8,10].

Figure 1. Shows the X-ray diffraction pattern after milling time variations of 10 hours, 20 hours, and 30 hours, it is seen that there is an increase in the intensity value and peak widening. The widening of the peaks indicates that the crystal size reduction process occurs, resulting in an increase in the material surface of grain volume ratio. Therefore, hydrogen will easily interact and absorb in the MgH2 material [5,7,11]. The Fe3O4 phase becomes a minor phase due to the peak of the pattern that appears at a very low intensity. This proves that Fe3O4 which acts as a catalyst, but does not participate in the reaction in MgH2. So that Fe3O4 is expected to accelerate the hydrogen desorption process as needed.

![Figure 1. XRD pattern of MgH2-10wt%Fe3O4 material with variations in milling time.](image_url)

The results of the calculation of the crystal size of MgH2–10wt% Fe3O4 are shown in Table 1, where the calculation results for each MgH2 phase field with milling time variations since 10, 20, and 30 hours. From the calculation results show that the longer the milling time, the smaller the crystal grain size [12]. This shows that the mechanical alloying process is quite effective in reducing the grain size of the MgH2-10wt% Fe3O4 material. The smaller crystal grain size is influenced by the presence of a balanced collision between
the milling balls with the sample and the vial wall in the milling process [13]. The smaller crystal size is also influenced by the occurrence of peak widening which is influenced by the X-ray reflected field [14].

Table 1. Crystal Size of the MgH₂ phase with variations in milling time

| Nr. | MgH₂–10wt% Fe₃O₄ | θ (°) | FWHM   | Crystal size (nm) |
|-----|------------------|-------|--------|-------------------|
| 1   | 0 hour           | 19.0257 | 0.75050 | 11.81             |
| 2   | 10 hours         | 18.9664 | 0.86640 | 10.22             |
| 3   | 20 hours         | 18.9735 | 1.02960 | 8.61              |
| 4   | 30 hours         | 18.9720 | 1.06150 | 8.35              |

In Figure 2, information is obtained that the peak desorption temperature of the MgH₂ material before milling is at a temperature of 377 °C. After milling for 10 hours, 20 hours, and 30 hours there was a significant decrease in temperature as shown in Table 2. The decrease in desorption temperature was still very large, namely 369 with the release of hydrogen of 1.463 mg in 426 seconds. This is due to the presence of impurities during the sample preparation process. The decrease in desorption temperature is influenced by the role of the Fe₃O₄ catalyst [15]. Based on XRD testing, the crystal size of MgH₂ has shown nanocrystals size, so that the hydrogen diffusion process was occurring and can be released [16,18]. The addition of Fe₃O₄ proves that according to the desorption temperature, the crystal size of MgH₂ is getting smaller. Thus, improving thermal properties and maintaining hydrogen storage capacity [19,20].

Figure 2. DSC curve of MgH₂–10wt% Fe₃O₄ with variations in milling time.
Table 2. DSC results on MgH2–10wt% Fe3O4 with variations in milling time

| Nr. | Milling Time | Temperature (°C) |
|-----|--------------|------------------|
| 1   | 0 hour       | 377              |
| 2   | 10 hours     | 372              |
| 3   | 20 hours     | 370              |
| 4   | 30 hours     | 369              |

4. Conclusion
Based on the results of the study, it was found that variations in milling time can affect the crystalline of MgH2 and an increase in intensity and peak widening occurs. So that the reduction of the crystal grain size resulted in a decrease in the crystal size from 11.81 nm to 8.35 nm with the longer milling time. The addition of Fe3O4 catalyst and variations in milling time can also reduce the desorption temperature from 377 °C to 369 °C.

Acknowledgement
After completing this research, the author would like to thank the Material and Energy Laboratory FMIPA, the Chemical Engineering Laboratory of Syiah Kuala University, Banda Aceh and the Geology Laboratory in Bandung in supporting the structural and thermal properties measurements.

References
[1] Wang Y and Wang Y 2017 Recent Advances in Additive-Enhanced Magnesium Hydrides for Hydrogen Storage Progress in Natural Science: Materials International 27, pp. 41-49.
[2] Hanada N, Ichikawa T, Fujii H 2005 Catalytic effect of nanoparticle 3d-transition metals in hydrogen storage properties in magnesium hydride MgH2 prepared by mechanical milling, J Phys Chem B, 109 (15) 7188–7194.
[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, International Journal of Hydrogen Energy, pp. 38 10932–10938.
[4] Sabitu S T and Goudy A J 2012 Dehydrogenation Kinetics and Modelling Studies of MgH2 Enhanced by Transition Metal Oxide Catalysts Using Constant Pressure Thermodynamic Driving Force, Open Access Metal, ISSN 2075-4701
[5] Jalil Z, Rahwanto A, Handoko E 2018 Effect of nanostructure Ni on the sorption properties of mechanical milled MgH2, MATEC, Web of Conferences, pp. 197 02014
[6] Jalil Z, Rahwanto A, Ismail I, Sofyan H, Handoko E 2018 The use of nano-silicon carbide and nickel as catalyst in magnesium hydrides (MgH2) for hydrogen storage material application, Mater. Res. Express, pp. 5 064002
[7] Malahayati, Ismail, Mursal, Jalil Z 2018 The use of silicon oxide extracted from rice husk ash as catalyst in magnesium hydrides (MgH2) prepared by mechanical alloying method, J. Phys.: Conf. Ser., pp. 1120 012061
[8] Rahwanto A, Jalil Z, Akhyar, Handoko E 2020 IOP Conf. Series: Materials Science and Engineering, pp. 931 012012
[9] Sharbati M and Kashani-Bozorg S F 2012 Acta Physica Polonica A, pp. 121 211-213
[10] Zhang Q, Zang L, Yike H, Gao P, Jiao L, Yuan H and Wang Y 2017 Improve Hydrogen Storage Properties of MgH2 with Ni-based Compound, International Journal of Hydrogen Energy, pp. 42 24247-24255
[11] 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, pp. 105 012093

[12] Ranjbar 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, pp. 34 7263-7268.

[13] 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, pp. 105 012098

[14] 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. International Journal of Hydrogen Energy 40 11908-11916

[15] Li-Shuai X, Jin-Shan L, Tie-bang Z, Hong-Chao, K 2017 Role of milling time and Ni content on dehydrogenation behavior of MgH2/Ni composite Trans. Nonferrous Met. Soc. China 27 569–577

[16] Wang H, Zhang S F, Liu J W, Ouyang, L Z, Zhu M 2012 The MgH2 dehydrogenation property improvement was attributed to the nanosized effect of mesoporous silica. Materials Chemistry and Physics 136 146-150

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

[18] Ismail I, Aini Q, Zulfalina, Jalil Z, Fadzullah S H S M 2018 Journal of Physics: Conf. Series 1120 012014

[19] Malahayati M, Yufita Z, Ismail I, Mursal M, Idroes R, Jalil Z 2021 Hydrogen Desorption Properties of MgH2 + 10 weight% SiO2 + 5 weight% Ni Prepared by Planetary Ball Mill, Bulletin of Chemical Reaction Engineering & Catalysis, pp. 16 (2) 280-285

[20] Rahwanto A, Ismail I, Nuralita N, Mustanir, Jalil Z 2021 Nanoscale Ni as a catalyst in MgH2 for hydrogen storage material, Journal of Physics: Conference Series, 1882(1)