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DESORPTION TEMPERATURE CHARACTERISTIC OF Mg-BASED HYDRIDES CATALYZED BY NANO-SiO_2 PREPARED BY HIGH ENERGY BALL MILLING

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ABSTRACT

Magnesium-based hydrogen storage alloy is one of the most attractive hydrogen storage materials for fuel cell-powered vehicle application. However, a high desorption temperature and slow kinetics limit its practical application. Extensive efforts are required to overcome these problems, one of which is inserting a metal oxide catalyst. In this work, we reported the current progress of using nano-silica (SiO_2) as a catalyst to improve the thermodynamics and kinetics of magnesium hydride (MgH_2). Nano-SiO_2 was extracted from local rice husk ash (RHA) using the co-precipitation method. Then, the MgH_2 was catalyzed with a small amount of nano-SiO_2 (1 wt%, 3 wt%, and 5 wt%) and prepared using a high-energy milling technique. The microstructure and hydrogen desorption performance were studied using x-ray diffraction (XRD), scanning electron microscopy (SEM), and differential scanning calorimetry (DSC). The results of the XRD test showed that the milling process over 5 h reduced the material to a nanometer scale. Then, SEM images showed that the powders were agglomerated after 5 h of milling. Furthermore, it was also found that nano-SiO_2 reduced the hydrogen desorption temperature of MgH_2 to 338°C in 14.75 min when the 5 wt% variation of the catalyst was applied.

Keywords: Catalyst; Hydrogen storage; Magnesium hydride; Milling; Rice husk ash; Silica

1. INTRODUCTION

One of the limitations of fuel cells for automotive application is hydrogen storage systems. Among the three types of storage systems (gas, liquid, and solid), the technique repository for solid storage is actively being studied by researchers. A solid storage method is used when hydrogen is in the form of gas, as it cannot be stored in a high-pressure tube (700 bar (3.0 MJ/L)) for security reasons. Meanwhile, if hydrogen is stored in a liquid form, the temperature should remain stable at -253°C (8 MJ/L). Both of the above techniques have not been adequate from a security viewpoint (Schlapbach & Zuttel, 2001). Therefore, integrated research to identify a superior absorbing material is currently being conducted intensively.

Several types of materials (generally light-metal metal element) are believed to have the ability to absorb large amounts of hydrogen. One of these is magnesium (Mg), which is considered a

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potential candidate for a hydrogen storage material. Magnesium, theoretically, has the ability to absorb large quantities of hydrogen (7.6 wt%). This amount exceeds the maximum limit of the International Energy Agency (IEA) target, i.e. amounting to 5 wt% and able to work at temperatures below 100°C (Zuttel et al., 2008).

However, a high working temperature, slow reaction kinetics, and a difficult activation limit the practical application of Mg-based hydrides. Many efforts have been put forth to improve sorption properties and reaction kinetics, such as element substitution (metal or metal oxides) as a catalyst on a nanometer scale and modification of the ball milling technique (Liang, 2004; Oelerich et al., 2001a; Varin et al., 2007). Furthermore, the grain size of the materials is reduced to the nanoscale using the mechanical alloying technique to form a composite material, and a specific catalyst is added, such as metals or metal oxides (Oelerich et al., 2001b; Zaluska et al., 1999; Ichikawa et al., 2005).

Recently, Norton et al. (2009) have reported on the effectiveness of a metal oxide type of silica (SiO_2) that can be used as a material for hydrogen storage. In this study, we have produced natural silica (SiO_2), which was extracted from rice husk ash (RHA) and was catalyzed in MgH_2. The sample was prepared using a planetary high-energy ball milling technique to improve the properties of the reaction kinetics of magnesium-based hydrogen storage materials.

2. MATERIALS AND METHOD

The main material (MgH_2, 99.99%, size 50 µm) was purchased from Sigma Aldrich, and the RHA was collected from a local milling factory in Blang Bintang, Aceh Besar. Hydrochloric acid (HCL) and ammonium hydroxide (NH_4OH) solutions, as well as aquadest were used for silica extraction. At the early stage of the silica extraction process, the RHA was dissolved with HCL and stirred with a magnetic stirrer at 700°C until a solution was formed. The solution was then filtered with a filter paper, deposited with NH_4OH, and subsequently washed with aquadest. The precipitated silica was washed and then dried with an oven at a temperature of 70°C for 5 h.

The next process was the mixing of MgH_2 with SiO_2 (1 wt%, 3 wt%, and 5 wt%) using planetary ball milling (Fritsch, P6) with a ball to powder ratio (BPR) of 10:1 and a speed of 400 rpm for 5 h. A small amount of the samples was transferred to other containers for every variation of SiO_2 for further characterization. To determine the composition phase, x-ray diffraction was applied to the samples (XRD; Shimadzu D6000, Cu-Kα radiation λ = 1.54060 Å). A morphological observation was obtained by scanning electron microscopy (SEM; Philips, XL30). Furthermore, thermal properties were observed by differential scanning calorimetry (DSC; Shimadzu, D50).

3. RESULTS AND DISCUSSION

Based on the XRD observations (Figure 1), no changes were indicated among the three variations of SiO_2. The XRD pattern in Figure 1 shows that almost a third of the curve has the same diffraction pattern due to milling for the same period of 5 h, with the only variations being to the amount of silica (SiO_2).

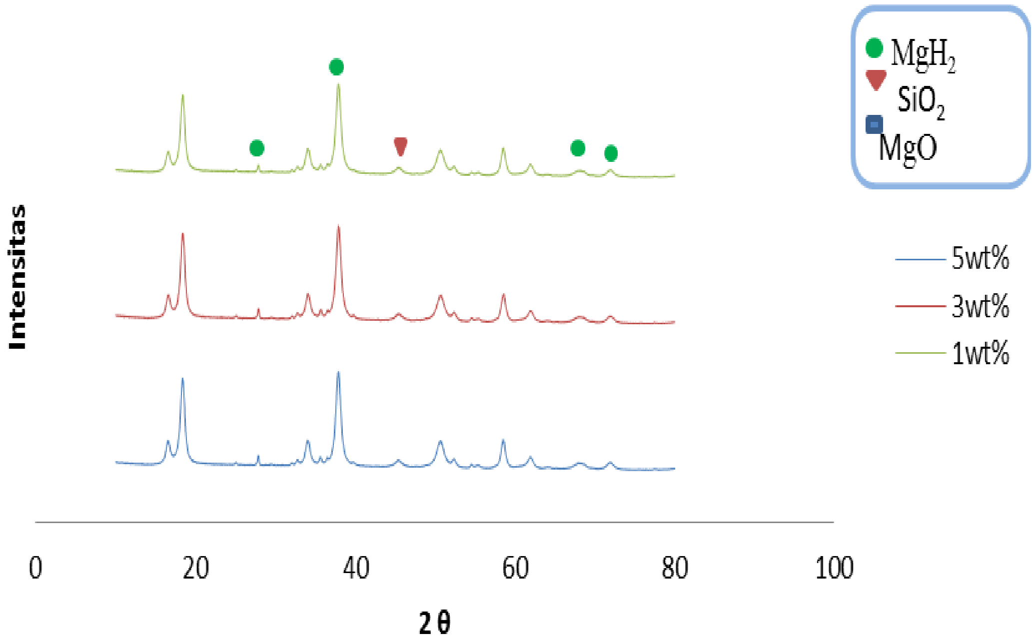

Figure 1 XRD patterns of MgH_2-$xSiO_2$ (x = 1, 3, and 5 wt%)

Silica (SiO_2), in this research, works as a catalyst and is only used in a small amounts. A catalyst serves to accelerate the reaction, but it does not enter react. As shown in the pictures, the SiO_2 phase emerged because the reaction did not participate in the SiO_2 MgH_2, it is characterized by the occurrence of phase changes not SiO_2. The diffraction pattern can be calculated from the size of the sample using the Scherrer method (Barreto et al., 2013),

$$D = (0.9\lambda)/B \cos \theta \qquad (1)$$

where;

D : crystallite size (Å)
λ : wavelength (λ = 1.54060 Å)
θ : the Bragg angle
B : line broadening at half the maximum intensity, FWHM (rad)

The results of the calculation of the size of the crystals are summarized in Table 1 as a result of the calculations for each field phase of MgH_2+wt% SiO_2. As shown in the table, there are no changes in the Bragg angle (2θ).

Table 1 Crystallite size of MgH_2 + SiO_2 in each variation of the SiO_2

Sample	Measurement Parameters		
	FWHM	2θ	Crystallite size (nm)
1 wt% SiO_2	0.76260	37.8439	106.42
3 wt% SiO_2	0.76480	37.8712	106.18
5 wt% SiO_2	0.75360	37.8890	104.99

It was shown that as more of the SiO_2 catalyst was added to MgH_2, the crystallite size began to decrease, but the change was not significant. As evident in the table, when 1 wt% SiO_2 was added, the crystallite size of MgH_2 was 106.42 nm; when 3 wt% SiO_2 was added, the crystallite size was 106.18 nm; and when 5 wt% SiO_2 was added, the crystallite size reached 104.99 nm.

The SEM micrographs (Figure 2) show a secondary electron image of powders that were intensively milled in the planetary mill for 5 h. The surface of the powder is irregular due to fracturing during the milling process. This is consistent with the structural analysis by XRD of the 5-h-milled powder. From the SEM data, it was also shown that the powders were agglomerated. The surface of the powder is irregular due to fracturing during the milling process.

In order to reduce the agglomeration, especially for ductile materials, a process control agent (PCA) during milling could be added to inhibit particle agglomeration (Suryanarayana, 2001). A wide range of PCAs (can be solids, liquids, or gases) has been used in practice at a level of about 1–5 wt% of the total powder charge. The PCAs, like stearic acid, hexane, methanol, ethanol, graphite and salts are commonly used during milling process.

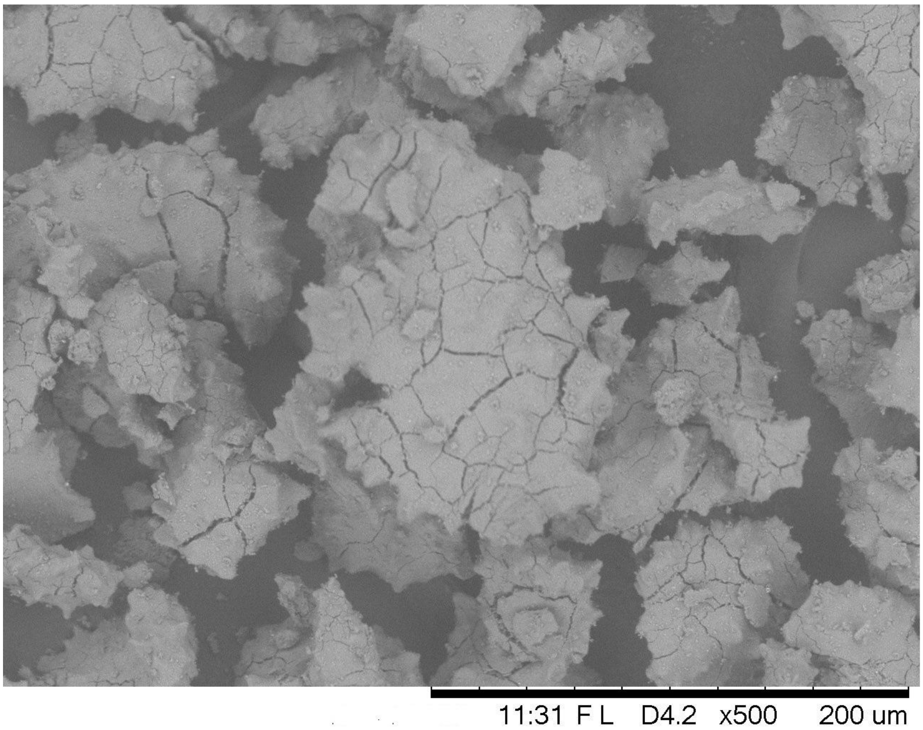

Figure 2 SEM images of MgH_2 + 5 wt% SiO_2

Furthermore, from the thermal observation, the desorption temperature of MgH_2 + SiO_2, which was analyzed with DSC, is shown in Figures 3 and 4.

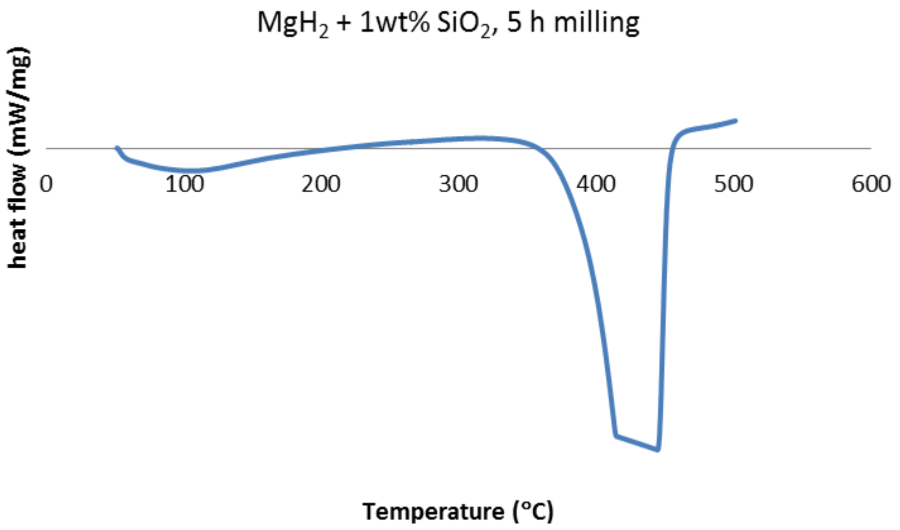

Figure 3 The DSC result of MgH_2 + 1 wt% SiO_2 after 5 hours of milling

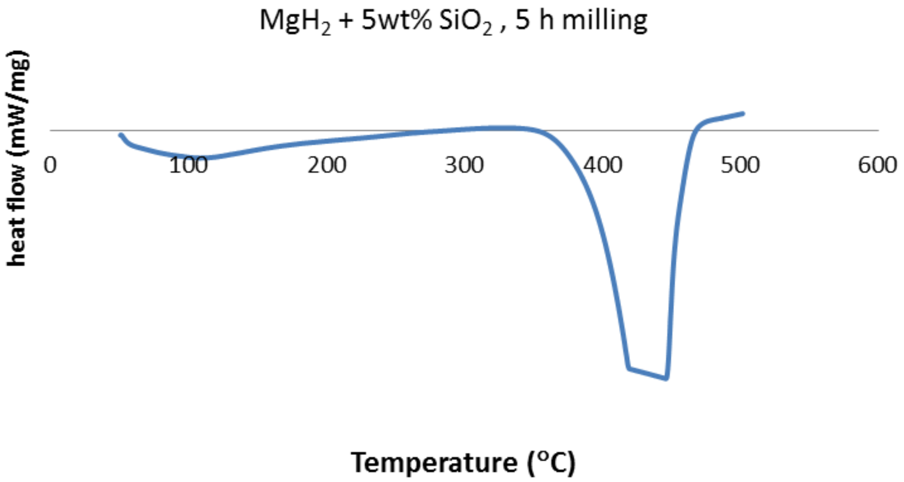

Figure 4 The DSC results of MgH_2 + 5 wt% SiO_2 after 5 h of milling

The DSC test results in Figure 3 show that with MgH_2 + 1 wt% SiO_2, after 5 h of milling, the desorption temperature reached 340.27°C within 14.83 min. In Figure 4, the desorption temperature reached 338.72°C within 14.75 min. In this case, the addition of a catalyst showed a decrease in the desorption temperature.

Compared to previous work (Mustanir et al., 2011), this research has shown an improvement in certain characteristics with the addition of a small amount of an SiO_2 catalyst, especially to desorption time. As pure MgH_2 takes 60 min for desorption, with an SiO_2 catalyst (1 wt% and 5 wt%) and after milling for 5 h, the desorption time is reduced (see Table 2).

Table 2 Results of thermal observation with DSC for variations of SiO_2

Nr	SiO_2 variation (wt%)	Temperature (°C)	Time (min)
1	1	340.27	14.83
2	5	338.72	14.75

If referring to previous research, with the 2 wt% SiO_2 catalyst, after 12 h of milling, a desorption temperature of 350°C was reached within 57.29 min (Mustanir et al., 2011).

Referring to the data of the International Energy Agency (IEA), the obtained temperature in this investigation is still far from reaching the target—i.e., a hydrogen storage system capable of storing at least 5 wt% in operational temperatures under 100°C and with a desorption time of under 60 min (Zuttel et al., 2008).

4. CONCLUSION

Nano-SiO_2 was successfully extracted from local RHA using the co-precipitation method. Then, MgH_2 was catalyzed with a small amount of nano-SiO_2 (1 wt%, 3 wt%, and 5 wt%) and was successfully prepared using a high-energy ball milling technique. As the results of the XRD test show, milling for over 5 h reduced the material to the nanometer scale. SEM images showed that the powders were agglomerated. Furthermore, it was also found that the nano-SiO_2 reduced the hydrogen desorption temperature of pure MgH_2 to 338°C within 14.75 min using the 5 wt% variation of the catalyst.

5. ACKNOWLEDGEMENT

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