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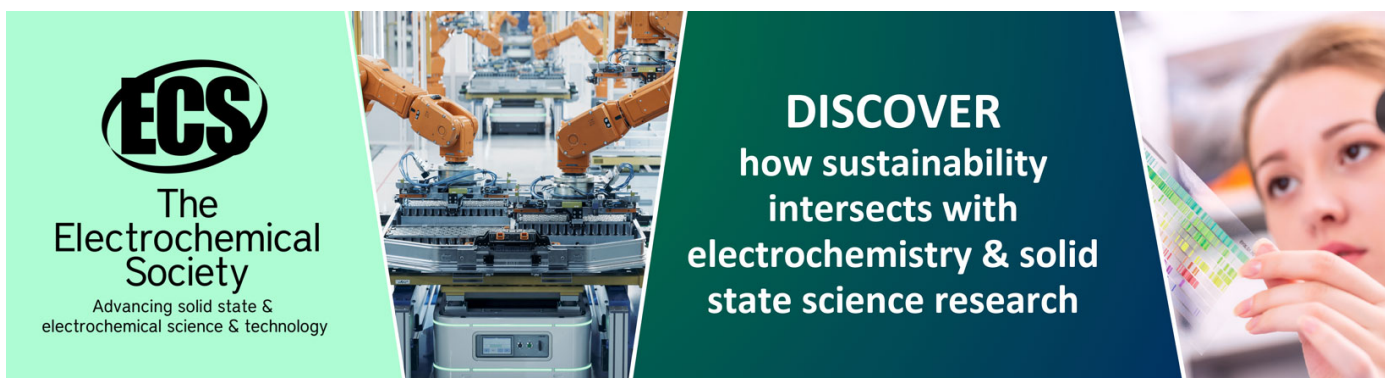
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The use of Silica from beach sand as catalyst in Magnesium based hydrides for Hydrogen storage materials

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Abstract. Magnesium (Mg) as one of the potential candidate material for absorbing hydrogen, because theoretically has the ability to absorb large quantities of hydrogen 7,6 wt%. However, the kinetic reaction of Mg is very slow. Its takes 60 minutes to adsorb hydrogen with the operating temperature (adsorb/desorb) high of 350°C. Therefore, in this study discusses the hydrogen storage materials based on MgH₂-SiO₂. The purpose of this study to improve desorption temperature of hydrogen storage system based on MgH₂. The main material is MgH₂ combined with inserting SiO₂ catalyst was successfully extracted from quartz sand with coprecipitation method. As for the material preparation process is done with the technique of mechanical alloying. Milling MgH₂+SiO₂ samples using a ball milling for 5 hours, with the ratio of ball to powder 10:1 and a speed of 400 rpm. By variation of the catalyst insertion of 1 wt%, 3 wt%, and 5 wt% of SiO₂. The results of XRD measurement known that the sample was reduced to scale nanocrystal. Phase arising from the result of XRD observation are MgH₂ phase as the main phase, and SiO₂ phase as a minor phase. DSC testing results show that the lowest desorption temperature obtained on the sample with the addition of inserts weight of the catalyst 5 wt% SiO₂ has milling for 5 hours which is equal 307,11°C.

1. Introduction

Magnesium-based hydrogen storage alloy is one of the most attractive hydrogen storage materials for fuel cell powered vehicle application. But, high desorption temperature, slow kinetics, however, limits its practical application. Several types of material (generally light-metal metal element) is believed to have the ability to absorb large amounts of hydrogen.

One of these is magnesium (Mg), which is considered a potential candidate for the hydrogen storage material. Magnesium, theoretically, have the ability to absorb large quantities of hydrogen (7.6 wt%). This amount exceeds the maximum limit of International Energy Agency (IEA) targeted i.e. amounting to 5 wt% and able to work at temperature below 100°C [2].

However, high working temperature, slow reaction kinetics and difficult activation limit the practical application of Mg-based hydrides. Some effort has been done to improve the properties of



Mg-based hydrides. For example the reduction of grain size of materials up to the nanoscale using the mechanical alloying technique, forming a composite material, and adding a specific catalyst, such as metals and metal oxides [3-5].

Furthermore, Norton *et al* [6] have been reported on the effectiveness of metal oxide type of silica (SiO_2) that can be used as material for hydrogen storage. In this study, we have used the natural silica (SiO_2) which was extracted from natural beach sand and catalyzed in MgH_2 . The sample was prepared using a planetary high energy ball milling technique, as an effort to improve the properties of 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 quartz sand was collected from Calang Beach in Aceh Jaya District. Then, hydrochloric acid (HCL) and ammonium hydroxide (NH_4OH) solution and aquadest were used for silica extraction. Then, the extraction process of silica was done, which at the early stage of beach sand dissolved with HCL, and stirred with magnetic stirrer at 700°C until the solution is formed. The solution is then filtered with a filter paper. The solution is then 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 hours. The next process was the mixing of MgH_2 with SiO_2 (1wt%, 3wt% and 5wt%) using a planetary ball milling (Fritsch, P6) with ball to powder ratio (BPR) is 10:1 at a speed of 400 rpm for 5 hours. A small amount of samples were transferred into other containers in every variation of SiO_2 for further characterization. In order to find out the composition phase, the samples were carried out using XRD (Shimadzu D6000, Cu-K α radiation $\lambda = 1.54060 \text{ \AA}$). Morphological observation was obtained by SEM (Philips, XL30). Furthermore, the thermal properties was observed by DSC (Shimadzu, D50).

3. Results and Discussion

Before the extraction process using coprecipitation method, this quartz sand has been characterized by XRF. The chemical composition as stated in Table 1 below.

Table 1. XRF results of Calang natural beach sand

No.	Compound	Concentration (%)
1	SiO_2	88.78
2	CaO	3.7
3	Fe_2O_3	2.21
4	SrO	2.12
5	Al_2O_3	1.2
6	MoO_3	1.2
7	Yb_2O_3	0.25
8	TiO_2	0.24
9	NiO	0.15
10	BaO	0.09
11	MnO	0.078
12	CuO	0.056

From table 1 it can be seen that the compounds contained in quartz sand such as SiO_2 (%), CaO (%), Fe_2O_3 (%) and others. However, the highest percentage of SiO_2 compound content was 88.78% while the lowest percentage was CuO of 0.056%.

The extraction process of quartz sand is carried out to obtain high purity silica using coprecipitation method. Corrosive methods include extraction methods of inorganic compounds such as quartz sand, which can be extracted using low temperature. This extraction process will bring down a solute down to the desired sediment. In this method, treatment has been done. One of the initial treatments was to

immerse the quartz sand in HCl 2M solution for 24 hours. With the soaking treatment of the HCl 2M solution, it was able to reduce the impurities in sand before proceeding in the extraction process.

Then, based on observations by XRD (figure 1), indicated that there are no changes from the 3 variations of SiO₂. X-ray diffraction pattern in figure 1 shows that almost a third of the curve have the same diffraction pattern due to milling in the same time of 5 hours, only in variations on the insertion of silica (SiO₂).

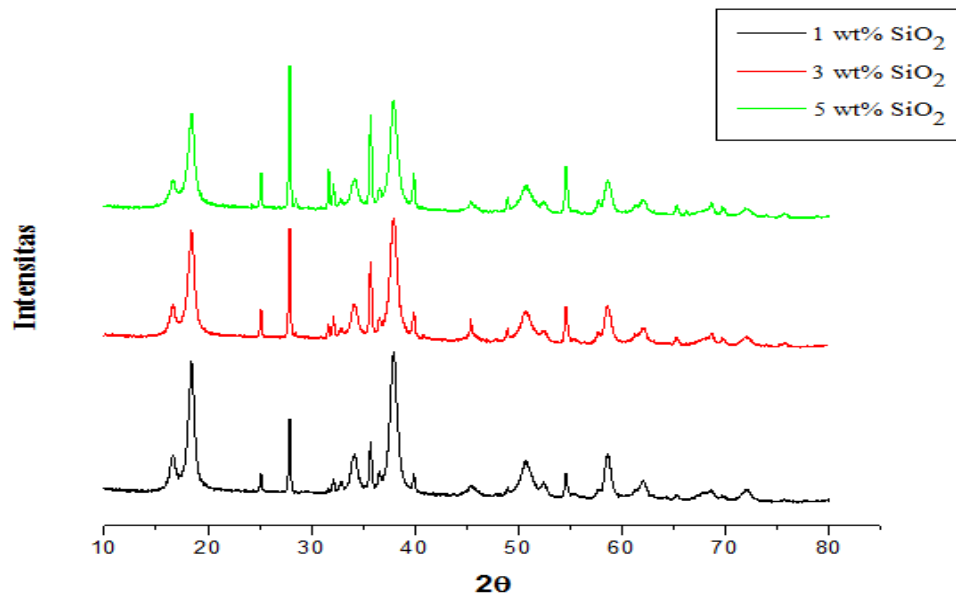


Figure 1. XRD pattern of the sample MgH₂-SiO₂

From the XRD result we can calculate the crystallite size in order to check whether the particle already decrease or not. Diffraction pattern can be calculated from the size of the sample using the Scherrer method [7],

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

where :

D : Crystallite size (Å)

λ : Wavelength ($\lambda = 1.54060$ 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 is summarized in Table 2 is a result of calculations for each field phase MgH₂ + wt% SiO₂.

Table 2. Crystallite size of MgH₂ + SiO₂ in each variation of the SiO₂.

Catalyst	Crystalline Plane (hkl)	Parameter		
		2θ (°)	FWHM (°)	Crystallite size (nm)
1 wt%	0 2 1	37,9130	0,82480	10,75
3 wt%	0 2 1	37,9143	0,85420	10,38
5 wt%	1 1 0	27,8840	0,18540	46,60

In table 2 it can be seen that with the addition of catalysts the crystal size is getting smaller. The size of the crystals on the addition of the variation of the catalyst weight may change with the same milling time due to silica (SiO_2) as a catalyst having a hardening effect that will accelerate the process of breaking MgH_2 powder. Although SiO_2 is only used in very small quantities. This indicates that the grain size is smaller as the addition of the catalyst.

However, it does not apply to the addition of catalyst 5 wt% SiO_2 . There is the agglomeration phenomena during the milling process. This agglomeration occurs due to the puncture and pressure given by the balls against the powder which causes the particles to join each other. Agglomeration is part of the mechanical alloying process. However, this excessive agglomeration can reduce the adsorption and desorption properties as it reduces the surface area of magnesium contact with hydrogen.

Thermal testing using the Differential Scanning Calometry (DSC) tool, to see changes in temperature and time function in a sample that occurs during the heating process. Thermal testing using DSC was carried out for a MgH_2 - SiO_2 sample which has been milled for 5 hours with variation of SiO_2 catalysts of 1, 3, and 5 wt% can be seen in Figure 2.

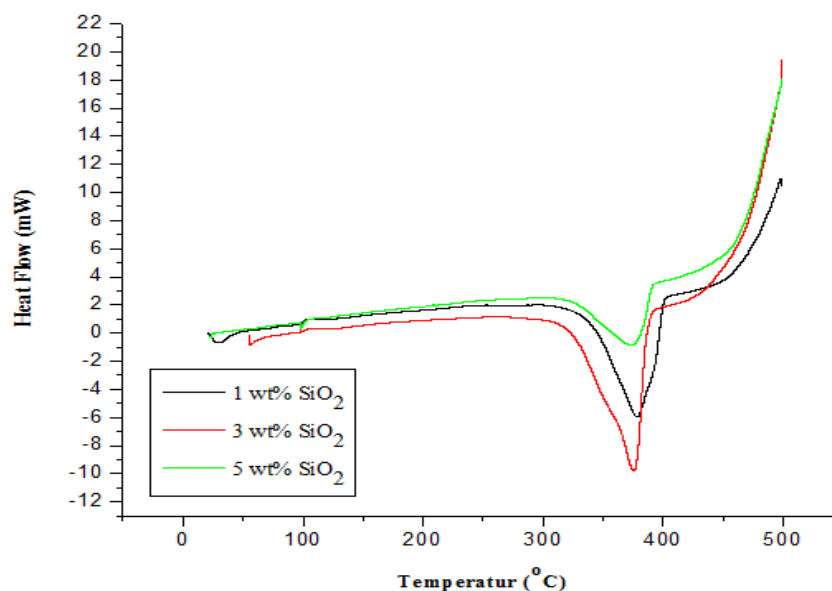


Figure 2. DSC of MgH_2 - wt% SiO_2 curve on the variation of catalyst for 5 hours of milling time.

Table 3. DSC results of MgH_2 with variation of SiO_2

No	Samples	Milling time (hours)	T_{onset} ($^{\circ}\text{C}$)
1	MgH_2 + 1 wt % SiO_2	5	321,85
2	MgH_2 + 3 wt % SiO_2	5	313,86
3	MgH_2 + 5 wt % SiO_2	5	307,11

Based on figure 2. indicates that when the sample was added 1 wt% and 3 wt% SiO_2 the peak of the chart was sharp, it indicates that the reaction process when the hydrogen heating was released slower than MgH_2 . Whereas the addition of SiO_2 catalysts as much as 5 wt% indicates that the peak of the chart is seen more shallow means that the reaction process when heated is so fast. This proves that

the SiO₂ catalyst insertion has an effect on the MgH₂ desorption temperature. SiO₂ as a catalyst has an important role that can lower the activation energy of a reaction so it can accelerate the reaction.

Compared to previous research results with 2 wt% SiO₂ milling insertion, desorption temperature was at 350⁰ C for 57.29 minutes [8]. Therefore, this research has improved certain characteristics of MgH₂ with the addition of SiO₂ catalyst, which was extracted from beach sand. The characteristic that can be improved is the temperature of the desorption and its timing. With the addition of small amount of catalysts [9,10], in this case as 1, 3, and 5 wt% SiO₂, has been able to lower the desorption temperature and its desorption time is shorter. This result corresponds to the pure MgH₂ before the addition of catalysts were in the range of 409⁰ C and when given a catalyst, the desorption temperature tended to decrease.

4. Conclusion

The natural crystalline type catalyst of SiO₂ was successfully produced from local beach sand and milled with MgH₂. This work has improved certain characteristics of MgH₂ with the addition of natural SiO₂ catalyst. The characteristic that can be improved is the temperature of the desorption and its timing. With the addition of small amount of catalysts as 1, 3, and 5 wt% SiO₂, has been able to lower the desorption temperature and its desorption time is shorter.

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