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Research Article

Hydrogen Desorption Properties of MgH_2 + 10 wt% SiO_2 + 5 wt% Ni Prepared by Planetary Ball Milling

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Abstract

MgH_2 is a very hopeful material for application as hydrogen storage material in the solid form. This is due to its reversibility and its ability to store large amounts of hydrogen, which is 7.6 wt%. However, this material still has weaknesses, namely high operating temperature and slow kinetic reactions. Various attempts have been made to overcome this weakness, including downsizing and adding catalyst. In this study, double catalyst was used, namely natural silica extracted from rice husk ash and nickel nano powder, with a composition of MgH_2 + 10 wt% SiO_2 + 5 wt% Ni. The purpose of this research was to study the effect of downsizing and using these catalysts to the thermodynamic and kinetic properties of the hydrogen storage material MgH_2. Samples were prepared by using High Energy Ball Milling (HEBM), with variations in milling time of 1, 5, 10, and 15 hours. The X-ray Diffraction (XRD) pattern showed the presence of an impurity phase in the samples milled for 10 and 15 hours. It also showed a reduction in grain size with increasing milling time. However, agglomeration has occurred in the samples milled for 15 hours. From the Scanning Electron Microscope (SEM) results can be seen that the sample with longer milling time, were homogeneously distribute. Thermal investigation showed that the lowest desorption temperature was achieved in samples with milling time of 5 and 10 hours, namely 287 °C and 288 °C. This study shows that natural silica catalyst plays a role in improving the thermodynamic characteristics of MgH_2, while Ni plays a role in improving the kinetic characteristics of MgH_2.

Keywords: hydrogen storage material; planetary ball milling; natural silica; rice husk ash

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1. Introduction

Hydrogen is a promising alternative energy source because it is renewable. Hydrogen is also classified as a light material with high energy density and its combustion does not produce harmful substances, so it is environmentally friendly. There are many sources of hydrogen in nature, like water (H_2O), biological and bio-inspired, solar wind hydro, nuclear or solar chemical cycles and fossil fuel reforming. Converting hydrogen into electrical energy can be done with the help of a fuel cell. One of the uses

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of fuel cells today is in the automotive industry. Hydrogen must be stored in a right storage media in order to be used efficiently. MgH_2 is considered as an appropriate medium for storing hydrogen. Because it has high hydrogen capacity (7.6 wt%), light weight, low cost and abundance in deposit. Unfortunately, this material has limitations for its application as a hydrogen storage, namely its operating temperature is still high and reaction rate is still slow (high activation energy).

Several modifications can be made to recover this deficiency. Various materials have been used as catalysts in the MgH_2, including transition metal compound [1], Ni-based compound [2], Ti-based alloy [3] and natural material diatomite (Diatomite as sedimentary rock, mainly formed from SiO_2, Fe_3O_4, and Al_2O_3) [4]. The catalytic mechanism of the catalyst on the MgH_2 varies greatly depending on the type of catalyst. It involves the formation of an intermediate phase to complete the nanostructures and prevent agglomeration [5].

Various studies have shown that among all the transition metals, nickel is an excellent (de)hydrogenation catalyst, and has been the mostly adopted catalysts for the MgH_2. It accelerates the absorption and desorption of hydrogen by adsorbing and dissociating hydrogen molecules into adsorbed atomic species and vice versa [6]. It has been reported that adding small amount of nickel (Ni) nanometre sized can recover the reaction rate or kinetic of the MgH_2 [7–13]. Meanwhile, the effectiveness of natural silica (SiO_2), extracted from beach sand, as catalyst in hydrogen storage have been examined by Jalil *et al.* [14]. It was reported that nanosize natural silica decrease the hydrogen desorption temperature of the MgH_2.

Decreasing the particle size and adding a suitable catalyst are two things that many researchers have suggested [1,15–19]. According to Li *et al*. [19] and Luo *et al*.[20], downsizing and adding catalyst only have an effect on improving kinetic characteristics and have no effect on their thermodynamic characteristics at particle sizes above 5 nm. However, it was shown that downsizing and adding natural silica catalyst were able to reduce desorption temperature (T_{onset}) of the MgH_2 even though the particle size was above 5 nm [14]. Furthermore, among all the transition metals that have been studied in recent years, nickel is the most widely used catalyst in the MgH_2 [21]. Therefore, in this study, a dual catalyst, namely natural silica and nickel, was used with a composition of the MgH_2 + 10 wt% SiO_2 + 5 wt% Ni. Double catalysts have been used in several study of the MgH_2 to find out the excellent synergistic catalytic mechanism [12,22–24]. However, as far as the author searches, research using a similar catalyst and composition has never been carried out by other researchers. The research is an exploration effort towards an efficient catalyst type for the MgH_2 to improve the hydrogen storage characteristics of the material. Because even the same type of catalyst can show different effects on MgH_2/Mg depending on the morphology and structure, and both can be optimized with the help of nanotechnology [17], namely reducing the grain size to a nanometer scale. Reducing the grain size will increase the ratio of surface area to grain volume [20], which is useful to the diffusion and occupation of H atoms [25]. The purpose of this research was to study the effect of using a dual catalyst, namely natural silica extracted from rice husk ash and nickel nano powder with a composition of MgH_2 + 10 wt% SiO_2 + 5 wt% Ni. Besides that, the effect of particle size on the hydrogen storage characteristics of the MgH_2 material was also observed.

The samples were prepared by a mechanical grinding method, using High Energy Ball Milling (HEBM). The HEBM can refine the particles size of the sample, raise the volume fraction of grain boundaries and increase the surface area. HEBM technic was chosen because it is easy to operate and allows controlling the particle size on a wide scale, from micro to nanosizes.

2. Materials and Methods

Pure MgH_2 powder (purity 99.9%, particle size 50 μm, Aldrich), Ni (99.9%, size 50 μm, Aldrich) and natural silica (SiO_2) were used as starting material. Natural silica was synthesized from rice husk ash (RHA) that was collected from a local milling factory in Blang Bintang, Aceh Besar. The synthesis process was obtained by co-precipitation method. It begins with washing the rice husk ash to clean it from dirt, followed by drying it in the sun until it is completely dry. Furthermore, 1.5% KOH solution was added and then heated. The next step is filtering the solution and adding HCl solution and then leaving it for 24 hours. The gel formed is then washed with distilled water in a vacuum pump and then filtered. The results of the filtering are then heated at a temperature of 110 °C to form a powder of SiO_2.

MgH_2 was catalysed with 10 wt% SiO_2 and 5 wt% Ni and prepared by intensive mechanical grinding. Planetary ball milling (Fritsch, P6) was used in the mixing process of the sample,

with a ball to powder ratio (BPR) of 10:1. The speed of disc revolution was 350 rpm for 1, 5, 10, and 15 hours. The composition phase of the samples was determined by using x-ray diffraction apparatus (XRD; Shimadzu D6000, Cu-Kα radiation (λ=1.54060 Å). Scanning electron microscopy (SEM; Philips, XL30) was used to observe morphological structures of the samples. Meanwhile thermal properties was observed by Thermo Gravimetric Analysis (TGA) and Differential scanning calorimetric (DSC; Shimadzu, D50).

3. Results and Discussion

Figure 1 show X-Ray Diffraction (XRD) pattern of MgH_2 + 10 wt% SiO_2 + 5 wt% Ni after milling for 1, 5, 10, and 15 hours. In samples milled for 1 and 5 hours, the highest peak is the MgH_2 phase, while in samples milled 10 and 15 hours the peak of SiO_2 and Mg $(OD)_2$ began to appear. The XRD pattern also shows that the size of crystal get smaller as the milling time increases, except for the samples that were milled for 15 hours. Long milling times have led to agglomeration of these samples. The decrease in particle size can be seen from the broadening of the peaks that occur on the XRD graph shown in Figure 1, and can be calculated using Scherer method [26]. The calculation results are displayed in the second column of Table 1.

Figure 2 present thermal observations analysed by Differential Scanning Calorimetry (DSC) at different milling time. The hydrogen desorption process was analyzed from data obtained from the DSC test. The onset temperature (T_{onset}) represents the temperature of hydrogen desorption from the MgH_2 material [27]. The value of desorption time and desorption temperature of the sample can be seen in Table 1, in the fourth and sixth columns, respectively. It can be understood that milling time affects the desorption temperature and desorption time of the sample. However, there is no clear relationship between crystal size and characteristic of hydrogen storage, such as temperature and desorption time. The optimum results occurred in samples that were milled for 5 hours. This sample has a lower desorption temperature and takes a shorter time to release more hydrogen than the other sample.

Comparison of the particle size, kinetic (desorption time) and thermodynamics (desorption time) characteristics with our previous studies [28], showed in the Table 1. The composition used in our previous research is MgH_2 + 5 wt% SiO_2 + 10 wt% Ni (A), while the

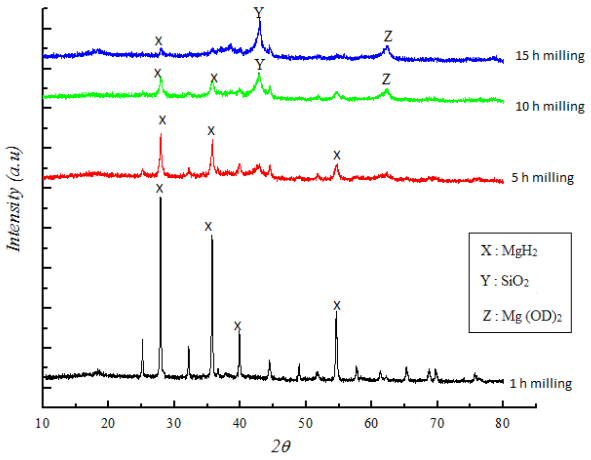

Figure 1. Phase composition of samples for milling time of 1, 5, 10, and 15 hours.

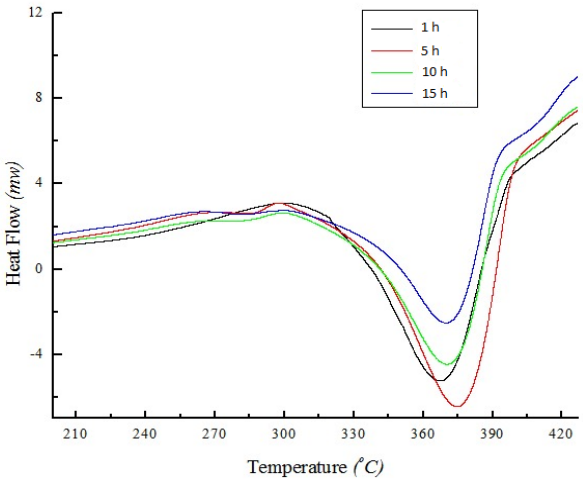

Figure 2. Hydrogen desorption profile of MgH_2 + 10 wt% SiO_2 + 5wt% Ni.

Table 1. Comparison of data with previous research.

Particle Size (nm)		Desorption Time (minutes)		Desorption Temperature (°C)	
A	B	A	B	A	B
52.47	52.02	5.9	8.31	339	308
25.26	27.18	5	7.87	349	287
27.83	8.46	5.7	8.3	347	288
21.89	11.43	4.1	8.7	348	294

composition used in this study is MgH_2 + 10 wt% SiO_2 + 5 wt% Ni (B). From the data displayed in Table 1, it can be seen that the samples with the percentage by weight of nickel is larger the kinetic characteristics of the samples have improved, while the thermodynamic characteristics do not increase. Furthermore, in samples with a greater percentage by weight of SiO_2, the thermodynamic characteristics were improved especially in samples milled for 5 and 10 hours. This shows that the Ni catalyst plays a more important role in increasing the kinetic characteristics, in this case desorption time, while SiO_2 plays a more important role in increasing the thermodynamic characteristics, in this case the desorption temperature, of the hydrogen storage material MgH_2. These results also indicate that the particle size affects the kinetic and thermodynamic characteristics of MgH_2.

Hydrogen interacts with metals in atomic form, not in molecular form. The hydrogen atoms occupy the main metal lattice as interstitial atoms. The process of inserting a hydrogen atom into Mg metal begins with the absorption and separation of hydrogen atoms on the Mg surface, followed by diffusion and the formation of hydride formations.

Ni catalyst can accelerate the separation of hydrogen molecules into hydrogen atoms (dissociation) and vice versa fuse hydrogen atoms into hydrogen molecules (recombination) [12], so that the addition of Ni catalysts in the sample is expected to accelerate the process of adsorption and desorption of hydrogen. While silica which has hard properties is expected to be able to assist in the refining process of grain size and prevent agglomeration of MgH_2 crystals during the milling process.

The surface structure of the sample can be seen from the SEM image as shown in Figure 3, 4, 5, and 6. There is a reduction in grain size with increasing milling time, except for samples with a milling time of 15 hours which shows agglomeration. The Mg-based materials which have a nanostructure will have a larger

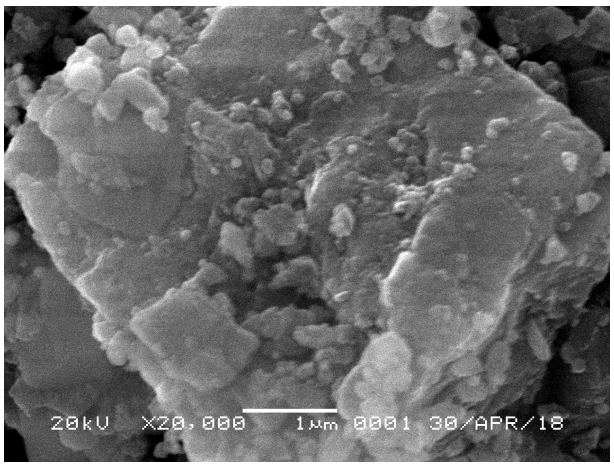

Figure 3. SEM image for the sample with 1 h milling time.

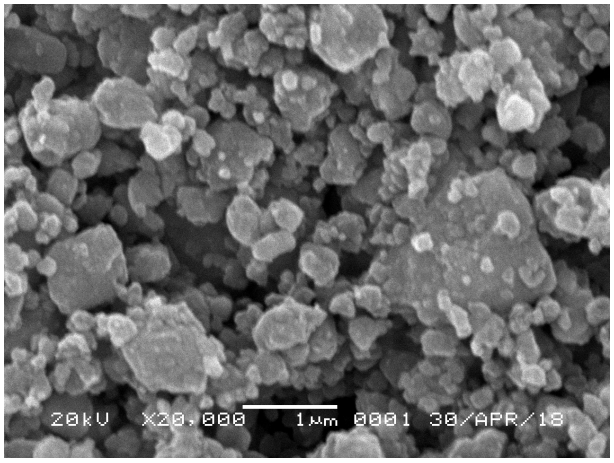

Figure 4. SEM image for the sample with 5 h milling time.

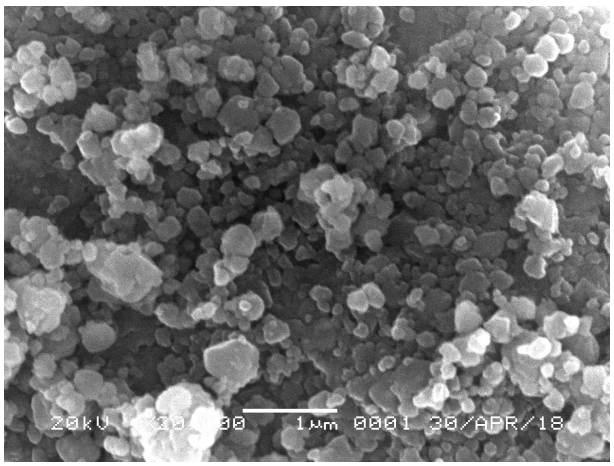

Figure 5. SEM image for the sample with 10 h milling time.

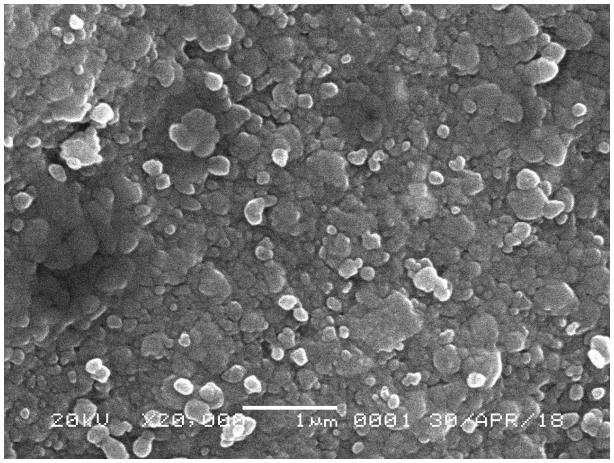

Figure 6. SEM image for the sample with 15 h milling time.

contact area for the hydrogen reaction. The diffusion distance during the hydrogen absorption reaction is also smaller so as to increase the kinetic and thermodynamic of the MgH_2 [15].

According to Yartis *et al.* [5] the catalytic effect of a catalyst is not only determined by the type of catalyst with a certain catalytic mechanism, but also related to the size and distribution of the catalyst in the samples, which is determined by the preparation process, and can be seen from the SEM image of the sample. In addition, the stability of the catalyst structure in the de/hydrogenation cycle is also an important factor to consider.

4. Conclusions

The addition of double catalysts from natural silica and Ni is able to recover the hydrogen storage characteristic of the MgH_2 material. This means that silica synthesized from rice husk ash has a good prospect for application as a catalyst in hydrogen storage material MgH_2. The role of the silica catalyst is to improve the thermodynamic characteristics of the MgH_2, while the Ni catalyst plays a role in improving its kinetic characteristics. The results also showed that the milling treatment could produce the MgH_2 material in nanometer sizes. However, it should also be noted that long milling times can reduce the performance of the MgH_2 as a hydrogen storage material due to agglomeration and the appearance of impurity phases.

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