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The Effect of Natural Silica from Rice Husk Ash and Nickel as a Catalyst on the Hydrogen Storage Properties of MgH_2

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ABSTRACT

The characteristics of MgH_2 as a hydrogen storage material in this study were observed by varying the composition of the catalyst. The added catalyst was a dual catalyst, namely nickel and natural silica extracted from rice husk ash with a composition of MgH_2 + 10 wt% SiO_2 + 10 wt% Ni (Sample A), then MgH_2 + 5 wt% SiO_2 + 10 wt% Ni (Sample B) , and MgH_2 + 10 wt% SiO_2 + 5 wt% Ni (sample C). The samples were prepared using the high energy ball milling (HEBM). The results showed that the natural silica extracted from rice husk ash (hereafter called "RHA") can be used as a catalyst in MgH_2. Then, simultaneous use of nickel with silica as dual catalyst has shown the improvement in the hydrogen storage characteristics such as temperature and desorption time. The results of this study also indicate that the composition of the catalyst affects the particle size, although the time and milling treatment are the same. Furthermore, the particle size affects the characteristics of MgH_2 as a hydrogen storage material. Apart from particle size, there are other parameters that influence the characteristics of MgH_2, which appear during the sample preparation process such as impurity and agglomeration phases, all of which are closely related to the composition and type of catalyst used and the milling treatment applied to the sample. The 10 hours milling time used in this study has succeeded in reducing the sample to nano size. The Mg-based materials which have a nanostructure will have a larger contact area for the hydrogen reaction. The diffusion distance during the hydrogen absorption reaction also becomes smaller so as to improve the kinetic and thermodynamic characteristics of MgH_2.

Keywords: hydrogen storage, natural silica, rice husk ash, high energy ball milling, desorption temperature

INTRODUCTION

Hydrogen is an important source of energy, and a candidate for replacing fossil fuels, because hydrogen has the potential to be a clean, reliable and affordable energy source. The main advantage of this fuel is that the combustion product is in the form of water so that it does not pollute the environment unlike the CO and CO_2 produced from fossil fuels.

Hydrogen can be stored in a solid storage form by inserting it between the atoms of other compounds. Hydrogen atoms penetrate into the inner layer of the metal, then spread out and finally occupy a certain position on the metal lattice. The hydrogen which is embedded in the metal will form a solid solution. The temperature at which hydrogen atoms insert into the metal is called the adsorption temperature. Meanwhile, the temperature at which the H atoms recombine to form hydrogen molecules is known as the desorption temperature.

Certain metals begin absorbing hydrogen in a solid solution state or also called α-phase, a state where hydrogen atoms begin to insert into the metal. When the pressure and hydrogen concentration are increased, the position of the hydrogen atoms is more properly arranged in the metal lattice (localized) and nucleation appears accompanied by the formation of hydrides. This state is referred to as β-phase (Varin et al., 2006).

In non-metallic materials, hydrogen is stored in porous materials such as carbon in the form of nanotubes. Even though the operating temperature is low, the hydrogen storage capacity of this material is relative small (Sudibandriyo et al., 2015). Nasruddin et al. (2016) found the optimum adsorption capacity of open-ended single-walled carbon nanotubes equal to 1.75 wt% at a temperature of 233 K and a pressure of 10 MPa. Numerous metallic types are believed to be capable of absorbing large amounts of hydrogen and have the potential to store hydrogen. MgH_2 is a metal that has prospects as a storage material for hydrogen because it is able to absorb large amounts of hydrogen, which is 7.6 wt%. This value is higher than the determined limit agreed by the world energy agency of 5 wt%. Besides that, the nature of Mg which is light, easy to obtain and the price is affordable is also another consideration for world researchers currently investigating MgH_2 as a hydrogen storage material. However, the MgH_2 material has several disadvantages to be widely applied as a hydrogen storage material, namely its high operating temperature (> 350° C) and its slow chemical reaction.

Several studies have shown that adding a catalyst and refining the particle size to the nanometres scale can improve the hydrogen storage properties of the MgH_2 material (Hong & Song, 2018; Hou et al., 2013; Khodaparast & Rajabi, 2015; Li et al., 2018; Malahayati, Nurmalita, et al., 2021; Malahayati, Yufita, et al., 2021; Yartys et al., 2019). Kinetic improvement still exists when the particle size of MgH_2 is below 50 nm (Kou et al., 2013). Jalil et al. (2016) informed that by 1 wt%, 3 wt% and 5 wt% nano-silica (SiO_2), extracted from local RHA and similar to the silica from local beach sand (Jalil et al., 2018), the thermodynamics and kinetics of magnesium hydrides can develop. In addition, it has been described that a small quantity of metal catalysts, in particular Ni, can increase the hydrogen characteristic of magnesium hydrides in nanometer scale (Berlouis et al., 2001; Jalil et al., 2017; Jalil et al., 2018; Khan et al., 2018; Kwak et al., 2015; Mustanir & Jalil, 2009; Rahwanto et al., 2021; Ranjbar et al., 2009; Zeng et al., 2020; Zhang et al., 2017; Zhang et al., 2017). The positive effect of improving certain characteristics of the hydrogen storage material can be attended by a reduction in other characteristics, relevant to the hydrogen storage material (Yartys et al., 2019). Therefore, research is currently focused on the exploration of additional efficient elements, especially multi-functional materials, namely materials that can simultaneously improve the thermodynamics and kinetics of MgH_2.

The research related to the use of multi-functional material (double catalysts) in hydrogen storage materials has been carried out by numerous researchers (Chen et al., 2019; Rahwanto et al., 2020; Rajabpour et al., 2016; Ranjbar et al., 2009). However, the use of Ni catalysts and natural silica with the composition as in this paper has not been reported thus far. The use of double catalysts with the suitable composition is expected to improve the kinetic and thermodynamic characteristics of the MgH_2 material.

In this work, pure nickel (Ni) and natural silica (SiO_2) which was extracted from RHA, have been used as a catalyst in MgH_2. The composition of catalysts used in this study was varied as follows: MgH_2 + 10 wt% SiO_2 + 10 wt% Ni (Sample A); then MgH_2 + 5 wt% SiO_2 + 10 wt% Ni (Sample B); and MgH_2 + 10 wt% SiO_2 + 5 wt% Ni (sample C). Sample preparation was carried out using a planetary ball milling equipment through a milling time of 10 hours.

MATERIALS AND METHOD

Pure MgH_2 (99.99%, size 50 μm) and Ni (99.99%, size 90 nm) powder were used in this study. Natural silica was obtained from the extraction of RHA using co-precipitation method, as published elsewhere (Malahayati et al., 2018). The samples were milled for 10 hours with the following composition: (A) MgH_2 + 10 wt% SiO_2 + 10 wt% Ni); (B) MgH_2 + 5 wt% SiO_2 + 10 wt% Ni; (C) MgH_2 + 10 wt% SiO_2 + 5 wt% Ni. The samples were then mixed and milled using a planetary ball mill (Fritsch, P6) through a ball to powder ratio (BPR) of 10:1 and a speed of 350 rpm. The composition phase of the samples was obtained by using x-ray diffraction (XRD; Shimadzu D6000, Cu-Kα radiation λ = 1.54060 A). Morphological structures and thermal properties were detected by scanning electron microscopy

(SEM; Philips, XL30) Thermogravimetic Analyzer (TGA) and Differential Scanning Calorimetric (DSC; Shimadzu, D50).

RESULTS AND DISCUSSION

Figure 1 shows the XRD pattern of MgH_2 + 10 wt% SiO_2 +10 wt% Ni, MgH_2 + 5 wt% SiO_2 +10 wt% Ni and MgH_2 + 10 wt% SiO_2 + 5 wt% Ni. It was shown that the impurity phase appears in sample A. This sample also has a narrow peak width. Meanwhile, samples B and C have a wide peak width. This means that sample A has a larger crystallites size than sample B and C. The crystallites size were calculated by the Scherer method (Patternson, 1939) and the summary results can be seen in Table 1.

The crystallites size affects the thermal properties of the sample as shown in the DSC (Figure 2) and TGA (Figure 3) curves. The reduction in crystallites size causes a decrease in the desorption temperature. The desorption temperatures of samples A, B, and C were 356.37° C, 286.66° C and 288.23° C, respectively.

Furthermore, the results of the thermal analysis carried out through DSC and TGA are presented in Figures 2 and 3. The DSC curve shows that the variations in the composition of the catalyst have an effect on the desorption temperature. Meanwhile, the TGA curve shows the influence of catalyst composition on desorption time and mass loss. Thermal investigation through DSC and TGA provides the data as shown in Table 2.

Microstructure observations are shown in Figure 4, 5 and 6. Sample A (Fig. 4) with a composition of MgH_2 + 10 wt% SiO_2 + 10 wt% Ni, appears to have the largest particle size, followed by sample B (Fig. 5) with a composition of MgH_2 + 5 wt% SiO_2 + 10 wt% Ni, and sample C (Fig. 6) with a composition of MgH2 + 10 wt% SiO2 + 5 wt% Ni. This data is consistent with the results shown by XRD.

The phase, thermal and microstructure investigations in this study have consistently shown the effect of the catalyst composition on the characteristics of the hydrogen storage material MgH_2. Sample A (MgH_2 + 10 wt% SiO_2 + 10 wt% Ni) have a high desorption temperature, but it only takes 6.67 minutes to release 11% of the mass of hydrogen. This means that the kinetic characteristics of the sample A were successfully improved, even though the improvement in their thermodynamic characteristics was not significant. The impurity layer that appears in sample A adheres to the particle surface which is also the grain boundary plane. These impurities can block the penetration and diffusion pathways of hydrogen into the bulk, destroying the intersection between the grain boundary plane and the particle surface, which is the penetration and diffusion pathway of hydrogen into the bulk (Varin et al., 2009). The appearance of impurity is caused by the nature of MgH_2 which is easily oxidized through oxygen and air (Sadhasivam et al., 2017)

The sample with a higher weight percent Ni (MgH_2 + 5 wt% SiO_2 + 10 wt% Ni) or sample B showed the lowest desorption temperature among

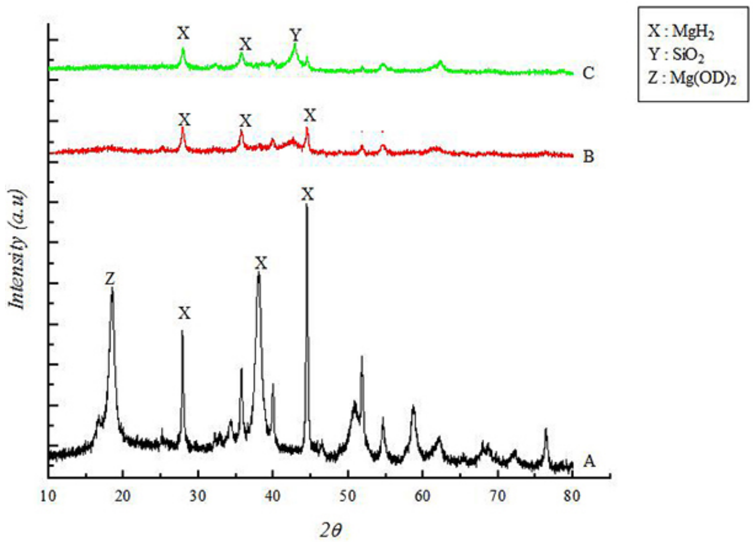

Figure 1. XRD pattern of MgH_2 + 10 wt% SiO_2 +10 wt% Ni (A), MgH_2 + 5 wt% SiO_2 +10 wt% Ni (B) and MgH_2 + 10 wt% SiO_2 +5 wt% Ni (C).

Table 1. The result of calculating the crystal size

Sample code	2θ	FWHM	Crystal size
A (composition 1)	44.4436	0.25940	34.92
B (composition 2)	27.8798	0.48470	17.83
C (composition 3)	42.732	1.06400	8.46

Table 2. The TGA and DSC results for different composition.

Sample	Desorption temperature (°C)	Desorption time (min)	Lost mass of hydrogen (%)
A	356.37	6.67	11
B	286.66	11.37	6.4
C	288.23	8.3	5.7

the three samples. However, it took 11.37 minutes to remove 6.4% hydrogen. Sample C (MgH_2 + 10 wt% SiO_2 + 5 wt% Ni) has the smallest particle size among the three samples. This is due to the high percentage of silica in this sample. Silica as a catalyst has a hardening effect that will accelerate the process of breaking MgH_2 powder (Jalil, Rahwanto, Sofyan, et al., 2018). The small particle size will increase the kinetic of hydrogen absorption and desorption (Li et al., 2018). The desorption temperature of this sample is also relatively low, and it took 8.3 minutes to release 5.7% mass of hydrogen. The optimum condition was achieved by sample C, because in this sample, the thermodynamic and kinetic were significantly improved compared to other samples.

The results of this study indicate that the natural silica catalyst combined with pure nickel in the right composition can improve the characteristics of the hydrogen storage material MgH_2. It also showed that the composition of the catalyst affects the particle size of the sample, even though the time and milling treatment are the same. It appears that the particle size affects the characteristics of MgH_2 as a hydrogen storage material. However, there is no visible trend or in other words it cannot be directly related because there are other factors that influence such as sample homogeneity, agglomeration and the appearance of impurity phases. The appearance of these three factors is influenced by the composition and type of catalyst used, in addition to the milling time and several other things.

The 10 hours milling time used in this study has succeeded in reducing the sample to nano size. The Mg-based materials which have a nanostructure will have a larger contact area for the hydrogen reaction. The diffusion distance during the hydrogen absorption reaction also becomes smaller so that it can increase the kinetic and thermodynamic value of MgH_2 (Luo et al., 2019)

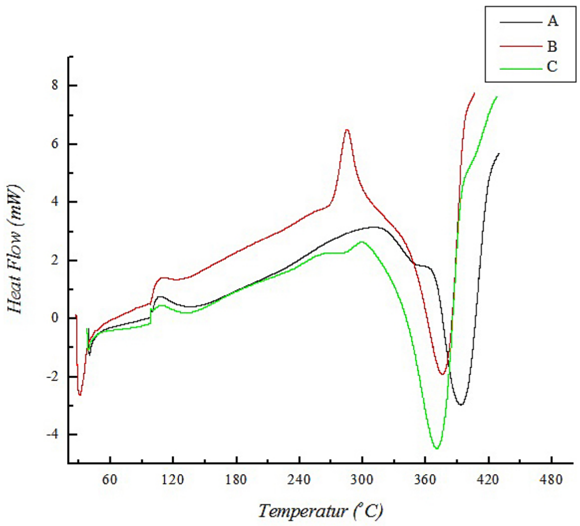

Figure 2. DSC result of the samples with different catalyst compositions

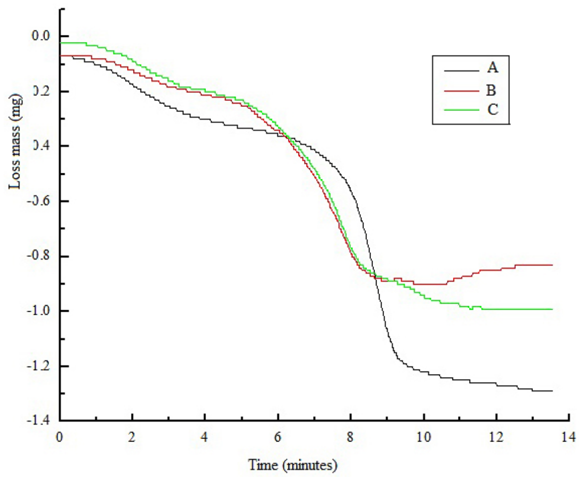

Figure 3. TGA curves of the samples with different catalyst composition

CONCLUSIONS

The obtained results showed that the natural silica extracted from rice husk ash can be used as a catalyst in hydrogen storage material MgH_2. Its use with nickel has shown improved hydrogen storage characteristics such as temperature and desorption time. Sample B with a composition of MgH_2 + 5 wt% SiO_2 + 10 wt% Ni has the lowest desorption temperature, but the highest desorption time among the three samples. In turn, sample A with a composition of MgH_2 + 10 wt%

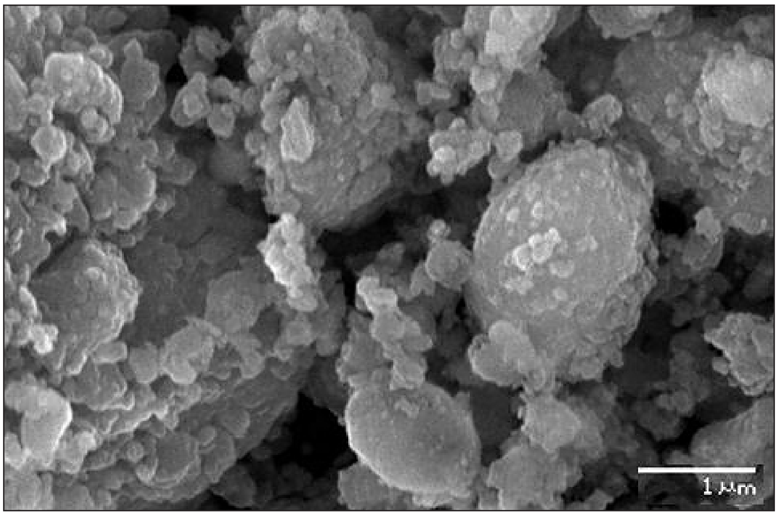

Figure 4. SEM Image of MgH_2 + 10 wt% SiO_2 + 10 wt% Ni

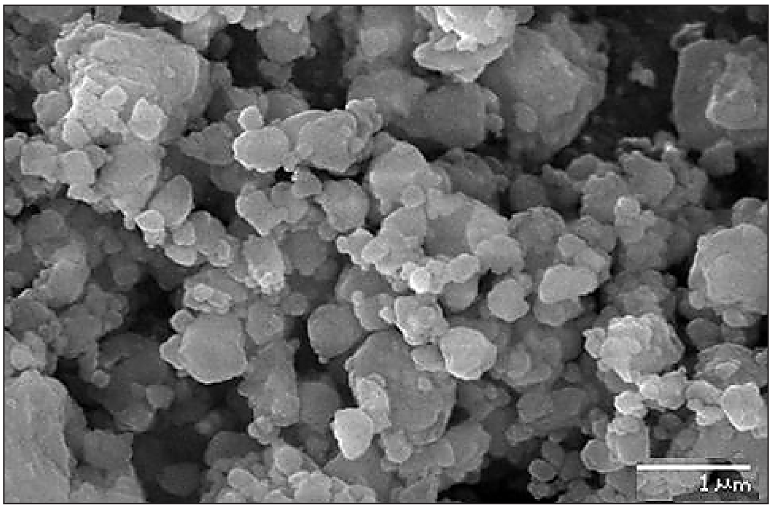

Figure 5. SEM Image of MgH2 + 5 wt% SiO2 + 10 wt% Ni

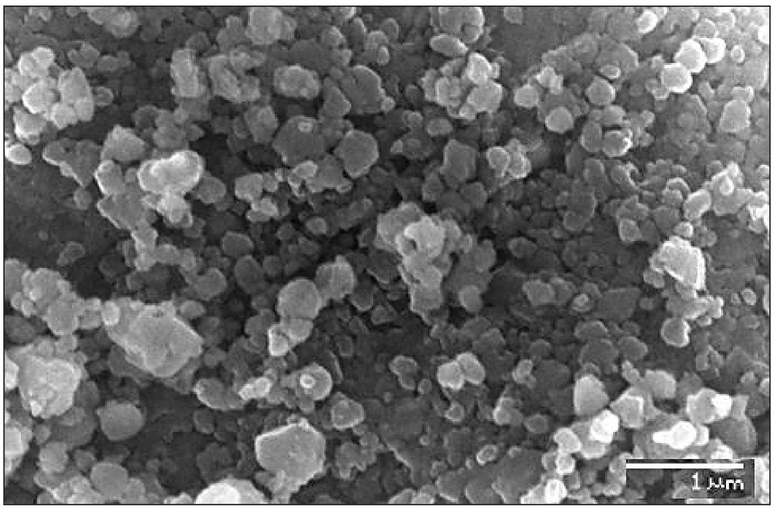

Figure 6. SEM Image of MgH2 + 10 wt% SiO2 + 5 wt% Ni

SiO_2 + 10 wt% Ni has the highest desorption temperature, but desorption time is the lowest among the three samples. For better results, further exploration of the catalyst composition and milling time is required.

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