Desorption properties of mechanically milled MgH$_2$ with double catalysts Ni and SiC

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Abstract. The study of the MgH$_2$ double-catalyzed Ni and SiC based storage system has been done. The objective of this study is to improve the hydrogen desorption temperature and hydrogen desorption capacity. The material preparation was done through mechanical alloying technique. In this method, the milling of the material was carried out within 5 hours, 10 hours and 15 hours, with the ratio of the ball to the powder was and the speed of 350 rpm with the catalyst insertion catalyst by 5 wt% and 10 wt% SiC. Results from XRD measurements revealed that the sample was successfully reduced to a nanocrystal scale. The phase emerging from the XRD observation is the phase MgH$_2$ as the main phase and followed by Ni and SiC phase as the minor phase. From the observation with SEM showing irregular particle shape, the particle size in the sample is not homogeneous because of the agglomeration effect and cold welding that causes the particle size to look large. The hydrogen release capacity was obtained in the samples which were milled for 10 hours at the weight of 5 wt% Ni-SiC catalyst with the release of 2.6 wt%. Based on observation with thermogravimetric analyzer (TGA), the lowest temperature was obtained in the samples which were milled 10 hours with catalyst 5 wt% SiC, which was 365 °C.

1. Introduction
Theoretically, magnesium (Mg) can absorb hydrogen in large quantities (7.6 wt%). This number exceeds the maximum limit targeted by the World Energy Agency of 5 wt% and the absorption/desorption temperature ≤100 °C [1]. Also, Mg is an easy to obtain, affordable light element for research in today's world. But Mg has a drawback, its kinetic reaction is very slow, to absorb the hydrogen takes at least 60 minutes, then its operating temperature is very high (300°C). As to the limits set by the IEA, a material must be able to absorb hydrogen at temperatures below 100°C and in a short time [2-4].

Research on magnesium alloys has been done by several researchers with various methods of manufacture and various alloying elements. Ranjbar et al [6] have conducted a study that SiC particles are evenly dispersed in the MgH$_2$ matrix, hydrogen absorption/desorption kinetics after inserting a small amount of SiC (5wt%), which can absorb 6.3 wt% hydrogen in a very short time (5 minutes) at 350 ° C.
The study of double catalyzed MgH$_2$ material on Ni and SiO$_2$ with SiO$_2$ 3 wt%, 5 wt%, 10 wt%, and 15 wt% catalysts using reactive ball milling technique on thermal testing using DSC showed that the lowest H$_2$ desorption process among four variations of catalyst that is at 15 wt% happened at temperature 361 °C [7-8]. From these results, the temperature obtained has decreased. But the temperature is still very high to be applied to the automotive industry, so it needs to do further research using the same material but with a nano-catalyst [9-14]. Very recently, Jalil et al. [15] introduced a double nano-catalyst to improve the characteristics of magnesium hydrides for hydrogen storage material application. In this work, we report the using of dual-catalysts Ni and SiC simultaneously in magnesium hydrides (MgH$_2$) prepared by high energy planetary ball milling.

2. Materials and method
The materials used were MgH$_2$ 99.99% in purity, 50 μm in size, both from Sigma Aldrich. Then, Ni (with 99% purity and 50 nm particle size) and silicon carbide (SiC), both purchased from Hongwu Nano. The three ingredients are mixed and then divided into two parts, namely MgH$_2$ + Ni + 5 wt% SiC; and MgH$_2$ + Ni + 10 wt% SiC are milling with time variation for 5 hours, 10 hours and 15 hours. The sphere and material ratio is 10:1 with a sample weight of 1 g at 350 rpm for each sample. A small sample is transferred for characterization. Samples were characterized by X-ray diffraction (XRD) (Cu-Kα radiation with λ = 1.54060 Å) to determine the phase that appeared. The morphology of the samples was obtained by using SEM (JEOL JSM-5310LV) and the thermal properties of hydrogen desorption were observed using Thermogravimetric Analyzer (TGA).

3. Results and discussion
The identification on MgH$_2$ + Ni + SiC sample using X-Ray Diffractometer (Shimadzu D6000) from sample with catalyst variation of SiC (5 wt% and 10 wt%) and have been milled for 5 hours, 10 hours and 15 hours, produces X-ray diffraction patterns (Fig. 1 and 2). Then, to know the phase contained in the sample, the comparison of the experimental data with the standard data using the database of files issued by the Joint Committee for Powder Diffraction Standard (JCPDS) has been done.

![Figure 1. XRD profile on MgH$_2$ + Ni + SiC material with catalyst variation 5 wt% SiC.](image-url)
In the diffraction pattern shown, it is clear that the MgH$_2$ phase appears as the main phase at an angle of 37.9°. The MgH$_2$ phase is also seen appearing at an angle of 2θ = 16.6°, the Ni phase appearing at an angle of 2θ = 35.6°, and followed by the SiC phase that appears at peaks of 2θ = 58.6°, and 31.1°. However, during the weighing and removal process from the sample site to the milling container, the material is contaminated with air so that the emergence of Mg(OD)$_2$ at an angle of 2θ = 50.7° and 18.4° as an impurities that may affect the process of hydrogen desorption temperature, likewise seen in Figure 2 it is clear that the phase MgH$_2$ appears as the main phase at an angle of 37.7°. The MgH$_2$ phase is also seen appearing at an angle of 2θ = 16.6°, the Ni phase appearing at an angle of 2θ = 35.6°, and followed by the SiC phase that appears at peaks of 2θ = 58.6°, and 31.1°. However, during the weighing and removal process from the sample site to the milling container, the material is contaminated with air so that the emergence of Mg(OD)$_2$ phase at an angle of 2θ = 50.7° and 18.8°.

Ni and SiC in this study worked as a catalyst and were used only in very small amounts. The catalyst serves to speed up the reaction but does not react, as shown in Figure 1. The emergence of Ni and SiC phases is caused because Ni and SiC do not participate in react in MgH$_2$, this is indicated by no change of phase of Ni and SiC. The emergence of Mg(OD)$_2$ phase in the XRD test results is due to the process of weighing the sample and moving from the sample to the milling container, the material is contaminated with the outside air causing the oxygen to enter the material.

The peak widening distribution in Figure 1 shown from the FWHM value in each sample did not show any significant change, meaning that the difference of FWHM value in each sample is very small, causing the diffraction pattern to look the same. In the sample with 5 wt% Ni catalyst insertion with SiC (5 and 10 wt%) catalyst variations and 5, 10 and 15 hour milling time. The FWHM value shows the peak width of the diffraction pattern. From the XRD diffraction pattern, it can be concluded that the increasing catalyst wt% SiC FWHM value and the resulting smaller crystal size means the diffraction peak and the crystalline size decreases with increasing catalyst from 5wt% to 10 wt% SiC and inversely proportional to milling time, milling time is larger the FWHM value and grain size. The widening of the peaks indicates that the MgH$_2$ phase crystallinity has occurred. In the previous study, the decrease in crystal size can decrease the temperature of onset and temperature. Smaller crystal sizes will form larger surface areas when compared to larger crystal sizes. This results in hydrogen making recombination easier.
Ranjar et al [6] mentioned that in addition to the reactive milling process, the role of silicon carbide (SiC) can accelerate grain refinement. Because SiC has the hard properties which are generally carbide metals. With a fine grain size, the hydrogen will more easily enter the hydrogen atomic grid and the more hydrogen capacity absorbed. Furthermore, as reported in [6] that the milling process in the atmosphere of hydrogen, either with pure Mg or MgH$_2$ has been able to reduce the size of the ductile Mg grains. One more thing, it is believed that the hardness of the carbide element in SiC is also capable of reducing the grain size to cause the MgH$_2$ surface area to become larger. With the widening of this surface area will ultimately have a positive effect on the desorption properties of MgH$_2$.

The result of surface morphology with SEM obtained information that the dimension of sampling grains with time 10 hours is smaller than the dimension of sampling grain with 5 hours. The results as shown in Figure 3 and 4.

However, as previously reported [6] the milling process is believed that the hardness of the Ni element can reduce grain size to cause the MgH$_2$ surface area to become larger. With the widening of this surface area will ultimately have a positive effect on the properties of MgH$_2$ absorption and desorption. However, the number of Ni catalysts in MgH$_2$ should be limited, because if more Ni doping will cause negative effects such as low absorbed hydrogen capacity, slow reaction kinetics and can also block the diffusion process of H$_2$.

Gravimetric testing is required to see the hydrogen release capacity of the double catalyzed-MgH$_2$ sample. In Fig. 4. showed the desorption characteristic of MgH$_2$ + Ni + 5wt% SiC with 10 hours of the milling process. It was shown that MgH$_2$ + Ni + 5wt% SiC material with 10 hours of milling process was able to hydrogen as much as 1.2 wt% in 16 minutes at the T onset 365 °C. It can be explained that smaller particle sizes will result in a large contact surface area between the samples and the hydrogen, resulting in the hydrogen chamber entering the sample particles larger and consequently the hydrogen absorption rate increases [14]. Despite the reaction relatively fast (in 16 minutes), the hydrogen release is still high (desorption/T onset at 365 °C). Dai et al. [19] have studied that the dehydrogenation improvement of Ni doped MgH$_2$ system is expectable due to the formation of thermodynamically less stable Mg$_2$NiH$_4$ phase. It was found that desorption property is improved by surface distortion & formation of second phase.
Figure 5. TGA profile of MgH$_2$ + Ni + 5wt% SiC milled for 10 hours.

Based on observation with TGA, the lowest temperature was obtained in the samples which were milled 10 hours with catalyst 5 wt% SiC, which was 365 °C. Goudarziafshar et al. [16] has studied that the effect of Ni atom doped on SiC nanocage on the molecular adsorption of hydrogen for practical hydrogen storage. It is important that the substituted Ni atom is capable of adsorbing two hydrogen molecules at room temperature. The effect of nanostructure catalyst was also studied as one of the important role in the improvement of magnesium hydrides as solid hydrogen storage [17]. El-Khatabi et al [18] have investigated that double substitution will effect to the reduction of heat of desorption and preserve the optimum gravimetric capacity. It was also reported that the co-doping have desorption temperatures within the optimum range and therefore suitable for the practical applications.

4. Conclusion
The study on the use of double catalysts Ni and SiC on the desorption of MgH$_2$ for solid hydrogen storage material with variation of wt% SiC has been successfully done. It can be concluded that MgH$_2$ catalyzed with Ni and wt% SiC variations in small amounts (5 wt% and 10 wt%) synthesized by high energy planetary ball milling technique of 350 rpm was successful, and the desorption properties of MgH$_2$ material can be improved. SEM analysis shows that Ni and SiC can act well as a catalyst. TGA profile inform that the desorption temperature was obtained at 365 °C for 5 wt% SiC. However, despite the fast reaction of double catalyzed on MgH$_2$ kinetic, the desorption temperature is still high for the application.

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