

Hydrogen Uptake Enhancement by the Use of a Magnesium Hydride and Carbon Nanotubes Mixture

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Studies show that the carbon nanotubes (CNTs) serve as hydrogen diffusion channels, when used with magnesium hydride. The hydrogen sorption study, of a MgH₂ and 5wt% of multiwalled carbon nanotubes mixture, was the main purpose of this work. The samples were analyzed by means of X-ray diffraction (XRD) and also studied in a differential scanning calorimeter (DSC). The carbon nanotubes, that were ball milled during 20 min to the MgH₂, were observed in the scanning electron microscopy (SEM) images. The mixture of MgH₂-CNT turned out to enhance the hydrogen sorption when compared to pure MgH₂ and in 5 min it desorbed around 5 wt% of hydrogen, at 350°C and 0.1 bar.

Keywords: *hydrogen storage, carbon nanotubes, ball milling, magnesium hydride.*

1. Introduction

Nanomaterials have been thoroughly studied regarding energy storage in the past years^{1,2}

When it comes to studying these nanomaterials with magnesium, some recent and interesting results were obtained in the past decade, especially with carbon nanotubes^{3,4,5}. Magnesium is chosen because of its low cost and abundance. However, the use of magnesium for hydrogen storage presents some limitations such as slow kinetics and high operation temperatures. A nanomaterial such as carbon nanotube (CNT) is milled to magnesium to help overcome those limitations aforementioned⁶⁻¹¹. Researchers agree that carbon nanotubes can act as a catalyst enhancing hydrogen uptake but the sorption mechanism is still not fully understood⁸. The type of CNT chosen for this work was the multi-walled carbon nanotube (MWCNT) and magnesium hydride (MgH₂) was used to be milled to the catalyst. The comparison of the results found in this work with others performed previously that use other types of materials^{13,14} that have a one-dimensional morphology could help shed a light on the mechanism involved in the hydrogen sorption.

2. Experimental

Multi-walled carbon nanotubes (MWCNTs), with diameters ranging from 5 to 60 nm and lengths ranging from 5 to 30 mm, were supplied by CT Nanotubos (Federal University of Minas Gerais). This material has 95% purity

and controlled size distribution. Magnesium hydride (MgH₂) was supplied by Sigma-Aldrich and submitted to ball milling with tungsten carbide balls under H₂ atmosphere for 24 hours at 300 rpm using a Fritsch P-6 planetary mill. After that, the MgH₂ was milled for 20 minutes more with 5 wt. (%) of carbon nanotube. The samples were handled in a glove box under argon atmosphere. The MgH₂-CNT morphology was analyzed by using scanning electron microscopy (SEM-JEOL JSM 6460LV). X-ray diffraction analysis were performed in a Bruker- G8 Discovery equipment. A differential scanning calorimeter (DSC- Setaram) was used to investigate the hydride phase stability under argon atmosphere. The kinetics tests were performed by an automatic Sievert's type apparatus designed by PCT-Pro 2000. The hydrogen absorption and desorption measurements were performed at 20 bar and 0.1 bar of hydrogen pressure, respectively, at 300 and 350 °C.

3. Results and Discussion

The scanning microscopy (SEM) micrograph, Fig. 1, shows an agglomerate of small particles with size ranging from nanometers to micrometers. The multi-walled carbon nanotubes (MWCNT) combined to magnesium hydride MgH₂ can be seen. Since ball milling can be detrimental to some catalysts such as carbon nanotubes¹², it was performed for only 20 min. Although a thorough investigation on ball milling conditions is still needed, for the present research, the fact that the MWCNT appear as their original morphology on the SEM image is an interesting finding.

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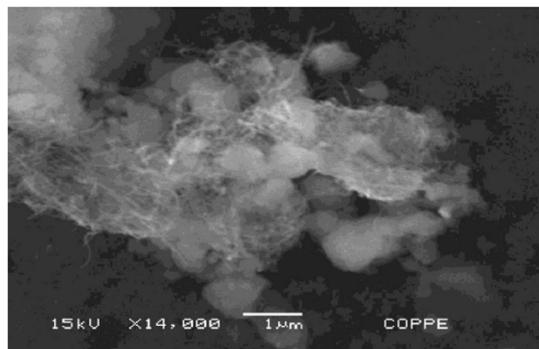


Figure 1. SEM image of MgH₂ milled with 5 wt% MWCNT for 20 min

In Fig. 2b, the β and γ peaks for MgH₂ due to grinding are shown for the MgH₂ milled with 5 wt % MWCNT pattern. The MWCNTs peaks were not detected because of their low abundance. The DSC result shown in Fig. 3 were obtained at a heating rate of 10 °C min⁻¹, for MgH₂ milled for 24 hours¹⁴ and after being milled for 20 min with MWCNT catalyst. The curve shows two endothermic peaks which correspond to the β and γ MgH₂ phases, which were seen previously in the XRD patterns (Fig. 2). The hydride decomposition temperature is 370 °C. This temperature is lower than the values obtained for pure MgH₂ between 400 and 450 °C^{13,14} because of the presence of the catalyst.

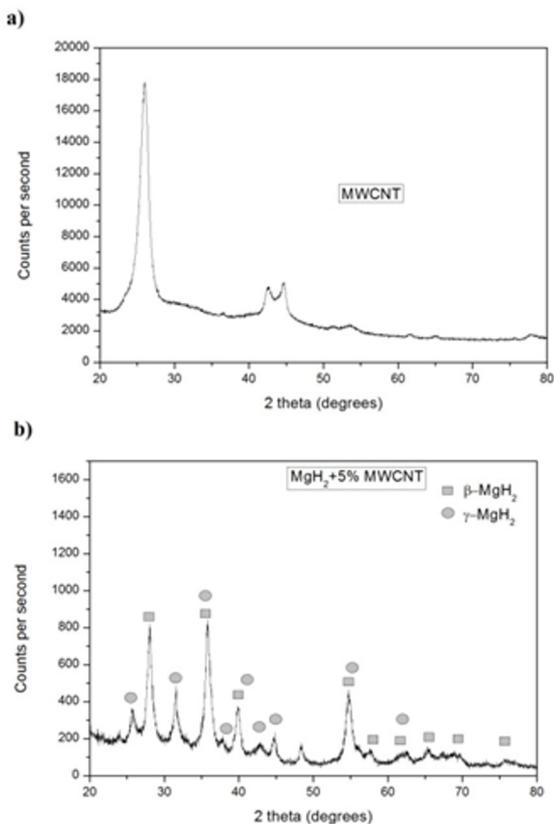


Figure 2. XRD patterns of multi-walled carbon nanotubes and MgH₂ milled for 20 min with MWCNT Only

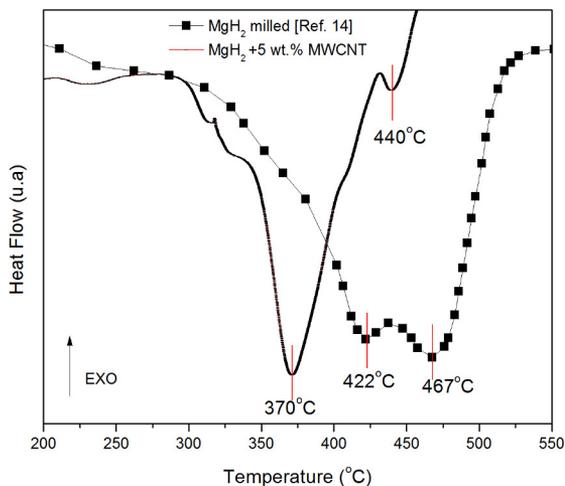


Figure 3. The DSC curves (heating rate 10 °C/min) for the sample MgH₂ + 5 wt% MWCNT and MgH₂ milled for 24 hours.

The absorption/desorption kinetic curves are shown in Fig. 4a and Fig.4b, respectively. The absorption kinetic results do not show a significant change on the hydrogen uptake when varying the temperature from 300 °C to 350 °C, Fig.4a. The absorption results are in accordance to the ones obtained in the literature for Mg-5wt% MWCNT, at 300 °C, since the hydrogen uptake was almost 4.0 wt% at 2 min¹⁰. However, the pressure used in the kinetic tests were higher than those used in the present work.

The plateau was attained in 2.5 min, at 350 °C, for MgH₂+5wt% MWCNT and the maximum hydrogen uptake was around 5wt%, Fig.4b at 350 °C, 0.1 bar.

Previous work performed with MgH₂ milled with one-dimensional (1-D) niobium based catalysts, and other work with TiO₂ based 1D nanomaterial^{13,14} are shown in Figure 5 along with the one obtained in the present work for MWCNT. The experimental conditions were the same to prepare the sample and the temperature used to conduct the kinetic tests was 350 °C. The difference between the amount of absorbed and desorbed hydrogen is the result of an already expected experimental error. The hydrogen uptake value obtained for these samples with MgH₂ are between 5.0 and 6.0 wt%. Besides the catalytic properties of those three types of materials, it seems as if the one-dimensional morphology facilitates the hydrogen diffusion. The effects of using different carbon materials on MgH₂ decomposition was studied and carbon nanotubes showed better results than graphite and activated carbon that do not have a 1-D morphology and therefore contributes to interpret these findings⁶.

Other studies also investigated the results of the addition of MWCNT to MgH₂^{15,16}. The conditions of ball milling, temperature and pressure are determining factors for the kinetics and absorption capacity of the composite material. Lototsky et. al.¹⁵ observed a high capacity of 6 to 7 % of MgH₂ + MWCNT (1 to 5 %) during high energy reactive ball milling (HRBM). These values were reached after a long grinding time and under more energetic conditions

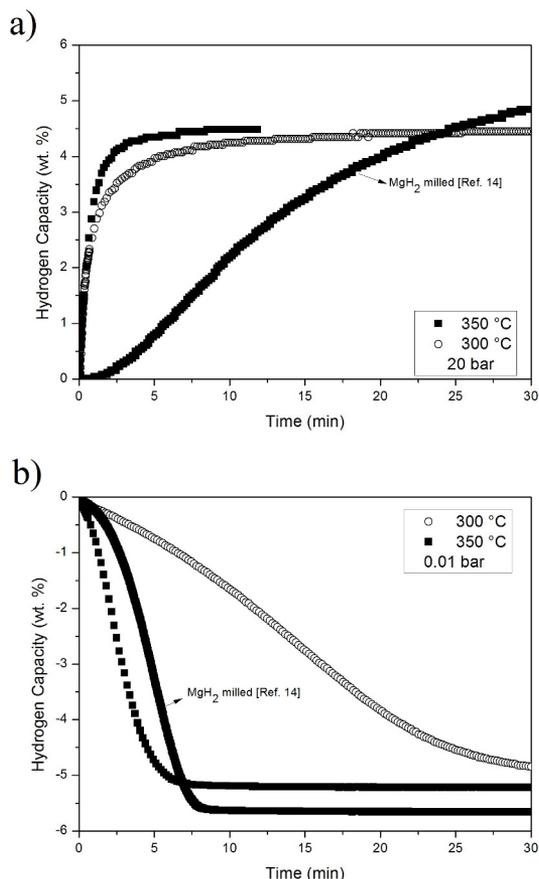


Figure 4. Hydrogen absorption (a) and desorption curves (b) of MgH_2 milled for 24 hours and $\text{MgH}_2 + 5 \text{ wt. \% MWCNT}$

(ball-to-powder mass ratio of 40:1) with a pressure of 30 bar. For the mixture of MgH_2 with 1 % MWCNT the HRBM time was 6h and 1.5 h for 5 % MWCNT.

Another study carried out by Verón et. al.¹⁶ verified the effect of the co-addition of Co + MWCNT to the MgH_2 also processed in high energy conditions with very long milling time of about 50 h. In this case, in addition to the evident destruction of the nanotubes, the MgH_2 became nanocrystalline, which significantly improved the absorption capacity of hydrogen (about 6.5%). The concomitant addition of Co to MWCNT promoted a further refinement of the mixture.

The comparison with these works indicates that the mixture of $\text{MgH}_2 + \text{MWCNT}$ is quite promising to be used as a catalyst even in cases where the milling time is long, although the milling conditions are different.

Figure 5 shows the best results of hydrogen capacity obtained for MgH_2 milled with 5%wt. of different catalysts but using the same conditions employed in the present work. The results of niobium oxide, niobate and titanate, both with a one-dimensional structure are obtained from references 13 and 14. The fastest kinetic results were attained for the $\text{MgH}_2 - \text{MWCNT}$ system. However, the hydrogen uptake was around 2% wt lower than $\text{MgH}_2 - \text{niobate}$ for both hydrogen absorption and desorption results.

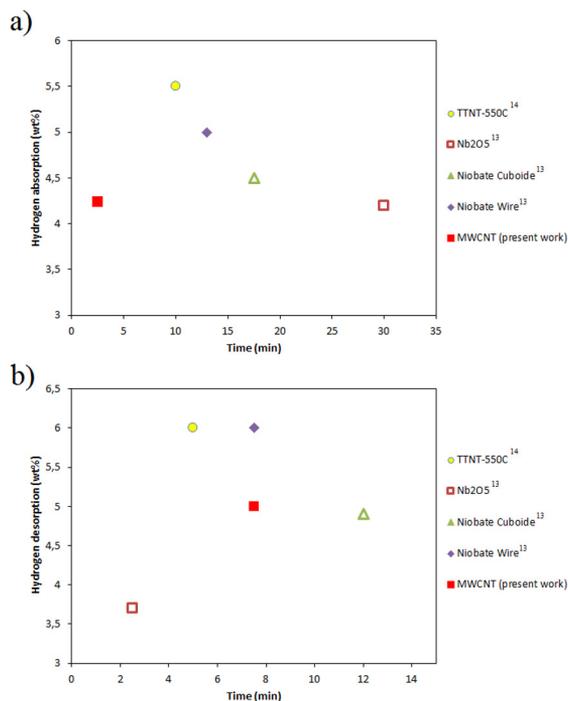


Figure 5. Comparison between the absorption (a) and desorption (b) of hydrogen obtained with 5wt.% of different materials milled with magnesium hydride at 350 C

The effect of using carbon materials with different structures on MgH_2 decomposition was studied and the carbon nanotubes showed better results than graphite and activated carbon. So the ones that do not have a 1-D morphology showed the worst results and therefore contributes to interpret these findings mentioned previously⁶. Besides the catalytic properties of those materials, it seems as if the one-dimensional morphology facilitates the hydrogen diffusion.

4. Final Considerations

The observed effect of $\text{MgH}_2 + \text{MWCNT}$ was more effective than other types of carbon-based catalysts. This can be attributed to the morphology and distribution of MWCNT catalysts. However, further studies to elucidate this effect are underway in our research.

5. Conclusions

Multi-walled carbon nanotubes (MWCNT) were used as catalysts to enhance hydrogen sorption and were milled only for 20 min with pre-milled MgH_2 . The kinetics tests carried out with $\text{MgH}_2 + 5 \text{ wt. \% MWCNT}$, showed a fast kinetics when comparing to other one-dimensional (1-D) catalysts studied previously and this result can help to emphasize the importance of the catalysts morphology acting as diffusion channels in hydrogen sorption process.

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7. References

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