

# The Effects of Mechanical Milling and Nb-Based Additives on the Kinetics Sorption Properties of 2LiBH<sub>4</sub>-MgH<sub>2</sub>

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**Abstract** – In this work, the effects of ball milling with different catalysts (including NbF<sub>5</sub> and Nb<sub>2</sub>O<sub>5</sub>) on the hydrogen storage properties of 2LiBH<sub>4</sub>-MgH<sub>2</sub> system were investigated. The increase of ball-milling time (from 5 min to 24 h) can reduce the crystallites size of MgH<sub>2</sub> from 74 nm to 14 nm and decrease the dehydrogenation temperature of MgH<sub>2</sub> from 390°C to 345°C. Among Nb-based catalysts, sample with NbF<sub>5</sub> shows slightly better sorption kinetics than the one with Nb<sub>2</sub>O<sub>5</sub>, it can store reversibly about 9 wt.% of H<sub>2</sub> in 24 h at 350°C, whereas more than 60 h are needed with Nb<sub>2</sub>O<sub>5</sub>. This indicates that NbF<sub>5</sub> is superior to Nb<sub>2</sub>O<sub>5</sub> for improving the sorption kinetics of 2LiBH<sub>4</sub>-MgH<sub>2</sub> system.

**Index Terms** – Ball milling, Catalysts, Hydrogen storage, Magnesium hydride.

## INTRODUCTION

One of the most promising metal hydrides as hydrogen storage material is magnesium hydride (MgH<sub>2</sub>). MgH<sub>2</sub> has very good properties for hydrogen storage, such as high gravimetric (7.6 wt.%) and volumetric hydrogen capacity (110 g/l) [1]. However, MgH<sub>2</sub> requires a high temperature of 350-400°C for dehydrogenation with slow kinetics and high desorption enthalpy ( $\Delta H=78 \text{ kJ}\cdot\text{mol}^{-1} \text{ H}_2$ ). Therefore, several strategies have been proposed for solving these issues, one of them is the use of reactant destabilization, such as LiBH<sub>4</sub> to form Reactive Hydride Composites (RHCs), LiBH<sub>4</sub>-MgH<sub>2</sub>, which has been proven to be effective to reduce the reaction enthalpy by 32 kJ mol<sup>-1</sup> H<sub>2</sub> in comparison with pure MgH<sub>2</sub> [2].

Although the reaction enthalpy is lowered, dehydrogenation and rehydrogenation processes still occur at high temperatures with slow kinetics. In this present work, we investigated the effect of mechanical milling and addition of transition-metal-based catalysts (such as NbF<sub>5</sub> and Nb<sub>2</sub>O<sub>5</sub>) on the kinetics rate of hydrogenation-dehydrogenation of 2LiBH<sub>4</sub>-MgH<sub>2</sub> system.

## MATERIALS AND METHODS

The starting materials of MgH<sub>2</sub> (98%), NbF<sub>5</sub> (99%), and Nb<sub>2</sub>O<sub>5</sub> (99.9985%), were purchased from Alfa-Aesar. LiBH<sub>4</sub> (95%) was purchased from Acros-Organic. The handlings of all materials were performed in a glove box under a purified argon atmosphere.

One gram of 2LiBH<sub>4</sub>-MgH<sub>2</sub> composite material was mechanically milled with a ball-to-powder weight ratio of 48:1 using a planetary ball-miller Retsch PM 100 with a rotation speed rate of 600 rpm. Different ball milling times were used in this research: 5 min, 1 h, 3 h, 24 h, 36 h, and 72 h. After milling, all the samples were characterized by XRD and DSC. X-ray Powder Diffraction (XRD) experiments were performed using a Bruker D8 Advance diffractometer with Co K $\alpha$  radiation ( $\lambda_1 = 1.788970 \text{ \AA}$ ,  $\lambda_2 = 1.792850 \text{ \AA}$ ) equipped with a PSD-VANTEC-1 detector. DSC was performed using a Netzch 204 F1 calorimeter with a heating rate of 10 K/min from 25°C to 500°C under a constant flow of argon in sealed aluminum crucibles.

We have also examined the effects of catalysts addition. NbF<sub>5</sub> and Nb<sub>2</sub>O<sub>5</sub> were added to one gram of the 2LiBH<sub>4</sub>-MgH<sub>2</sub> material by 72 h ball-milling with different loadings: 5 wt.% and 10 wt.% for NbF<sub>5</sub>; and 10 wt.% for Nb<sub>2</sub>O<sub>5</sub>. To be able to conclude about the most efficient catalyst (i.e. the one leading to the best kinetic rates), we have recorded the absorption-desorption kinetics curves for all samples at different temperatures: 250°C, 300°C, and 350°C. Typically, absorption was performed under a pressure of about 50 bars, whereas desorption was conducted with pressure always kept below 0.5 bar using a Hy-Energy PCT-Pro 2000 volumetric apparatus.

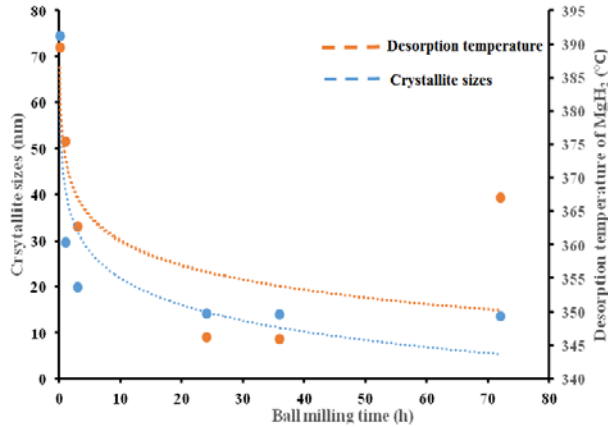
## RESULTS AND DISCUSSION

The effect of ball-milling time on the hydrogen storage properties of 2LiBH<sub>4</sub>-MgH<sub>2</sub> system can be seen in Figure 1. The crystallite size of MgH<sub>2</sub> and desorption temperature of MgH<sub>2</sub> were collected respectively from XRD data using the Scherrer equation and from DSC curves. We can clearly see that the increase of ball milling time (5 min to 24 h) leads to a strong decrease of MgH<sub>2</sub> crystallites size from 74.4 nm to 14 nm and reduces the desorption temperature of MgH<sub>2</sub> from 390°C to 345°C. The reduction of crystallites size allows a shortening of

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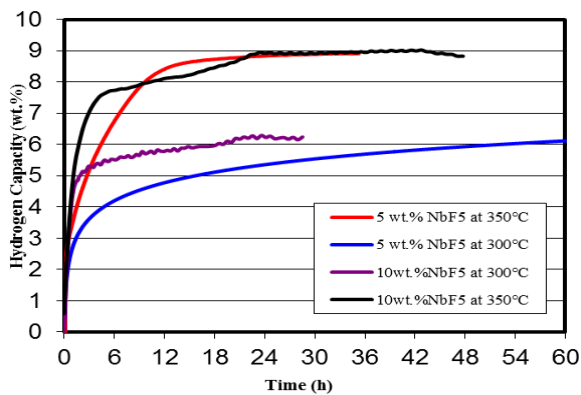
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the hydrogen diffusion distance into the solids, therefore leads to a faster hydrogen release. However, with a ball-milling time of 72 h, the desorption temperature of  $\text{MgH}_2$  is higher with a peak at  $367^\circ\text{C}$ . This could be related to a strong agglomeration of the crystallites as proposed by Yuan et al [3].



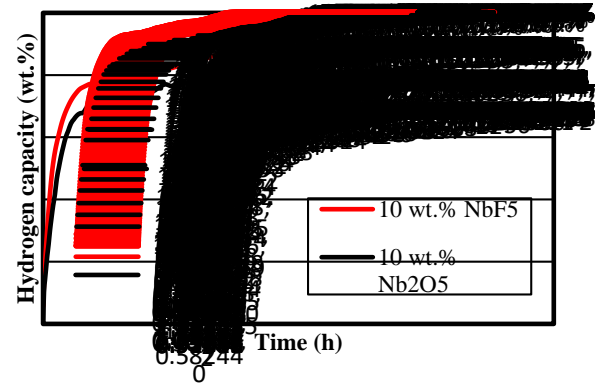
**Figure 1.** Correlation between ball-milling time,  $\text{MgH}_2$  crystallites sizes and desorption temperature of  $\text{MgH}_2$ .

The addition of Nb-based catalysts into the  $2\text{LiBH}_4\text{-MgH}_2$  system has been done in order to improve its hydrogen sorption properties. In Figure 2, the absorption kinetics for both 5 wt.% and 10 wt.%  $\text{NbF}_5$  loadings are very similar highlighting the fact that a large amount of  $\text{NbF}_5$  is not needed to get fast kinetics. Obviously, the sorption kinetics are faster at  $350^\circ\text{C}$  than those at  $300^\circ\text{C}$  with about 9 wt.% of hydrogen reversibly stored within 24 h.



**Figure 2.** Kinetic curves of absorption of 72 h ball-milled  $\text{LiBH}_4\text{-MgH}_2$  +5wt.% or 10 wt.%  $\text{NbF}_5$ .

Under the conditions used, the sample doped with  $\text{NbF}_5$  shows slightly better adsorption kinetics than  $\text{Nb}_2\text{O}_5$  (cf. Figure 3). The  $\text{NbF}_5$ -catalyzed mixture absorbs about 9 wt.% of  $\text{H}_2$  in 24 h, whereas the  $\text{Nb}_2\text{O}_5$ -catalyzed mixture takes more than 60 h. This indicates that  $\text{NbF}_5$  is a little bit superior to  $\text{Nb}_2\text{O}_5$  for improving the kinetics of  $2\text{LiBH}_4\text{-MgH}_2$  system.



**Figure 3.** Kinetic curves of absorption of 72 h ball milled  $2\text{LiBH}_4\text{-MgH}_2$  +10 wt.%  $\text{NbF}_5$  or 10 wt.%  $\text{Nb}_2\text{O}_5$  at  $350^\circ\text{C}$ .

#### REFERENCES

- [1] House, Stephen D, et al., "Effect of ball-milling duration and dehydrogenation on the morphology, microstructure and catalyst dispersion in Ni-catalyzed  $\text{MgH}_2$  hydrogen storage materials". *Acta Materialia*, vol. 86, pp 55-68, 2015.
- [2] Vajo, John.J, et al., "Reversible storage of hydrogen in destabilized  $\text{LiBH}_4$ ". *The Journal of Physical Chemistry Letters* vol. 109, pp 3719-3722, 2005.
- [3] Yuan, Huajun, et al., "Hydriding behavior of magnesium-based hydrogen storage alloy modified by mechanical ball-milling". *Materials Chemistry and Physics* vol. 83, pp 340-344, 2004.