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A study of the $LiNH_2$–MgH_2 system for solid state hydrogen storage

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Abstract

The influence of different high energy milling times and of the addition of catalysts such as Nb_2O_5, $TiCl_3$ and graphite on the hydrogen absorption/desorption (A/D) kinetics of a mixture of $2LiNH_2 + 1.1MgH_2$ has been studied in the temperature range 220–240 °C. It is found that a prolonged milling time is effective in improving the A/D kinetics, irrespective the presence or not of any kind of tested additive. The enthalpy of decomposition reaction results to be about 40.4 kJ/mol, as derived from van't Hoff plot using the values of the plateau pressures measured in desorption mode. This thermodynamic parameter fits well with the current literature data.

1. Introduction

The use of a solid material to store hydrogen seems to be a valid alternative to the more traditional storage techniques as high pressure vessels and special cryostats. To this purpose, metal hydrides, intermetallic compounds, zeolites and carbon based structures have been widely studied in the recent years. Currently the attention of several research groups has been addressed to new types of materials, in particular complex hydrides as alanates, borohydrides, amides, which seem very promising due to their interesting characteristics.

It has been found that it is often convenient to study mixtures of such compounds (e.g. amides plus hydrides) in order to obtain more favourable thermodynamic conditions of the hydrogen A/D processes than the single compounds. For example Chen et al. [1] observed that ball milled mixtures of $LiNH_2$ and LiH begin to desorb hydrogen at temperatures as low as 150 °C and complete hydrogen desorption ends to about 400 °C. The decomposition reactions are:

$$LiNH_2 + 2LiH \leftrightarrow Li_2NH + LiH + H_2 \leftrightarrow Li_3N + 2H_2. \qquad (1)$$

The authors explained the process assuming that the hydrogen molecule is formed by the close contact of positive $H^{\delta+}$ and negative $H^{\delta-}$ hydrogen ions carried by the amide and the hydride, respectively. A hydrogen amount of 6.5 wt.% was released during the first step, while a total theoretical reversible hydrogen amount of 10.4 wt.% could be obtained from both reactions. Despite the high content of hydrogen released during the first step of reaction (1) and of relatively low desorption temperature, the plateau pressure in desorption mode at 280 °C was only 0.1 MPa. Hence, further destabilisation of the mixed system $LiNH_2 + LiH$ is required in order to use it practically. Orimo et al. [2] suggested that in the $LiNH_2$ crystal the bonding between Li^+ cation and $[NH_2]^-$ anion has ionic character and in consequence partial substitution of Li by Mg (more electronegative element than Li) would decrease the interaction of Li^+ with $[NH_2]^-$ leading to destabilisation. The predicted thermodynamic behaviour was first observed separately by Luo [3] and Xiong et al. [4]. The correct interpretation of the process was achieved by Yang et al. [5] who found that starting from the ball milled mixture by means of a heat treatment at high hydrogen pressure the

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following reaction of activation occurs:

$$2LiNH_2 + MgH_2 \rightarrow Mg(NH_2)_2 + 2LiH. \quad (2)$$

The obtained mixed products can be used to reversibly release and absorb hydrogen, according to the reaction:

$$Mg(NH_2)_2 + 2LiH \leftrightarrow Li_2Mg(NH)_2 + 2H_2. \quad (3)$$

The theoretical hydrogen capacity of the material is 5.6 wt.%, with an operating temperature around 200 °C. The great potentiality of this material lies in the fact that the desorption enthalpy is within the interval from 34 to 41.6 kJ/mol H_2 [3,5,7,8]. This allows to obtain plateau pressures higher than 0.1 MPa at temperatures lower than 100 °C. A limit consists in the kinetic properties; in particular for a complete hydrogen absorption a time of 3–4 h is required at 220 °C [5]. Up to now the absorption kinetics of this material has not been studied in detail and a study to relate the milling time of the mixture with the rate of hydrogen absorption/desorption (A/D) is not yet available. Aim of this work is to test the effectiveness of the presence of additives and of a prolonged milling time in improving the kinetics of hydrogen A/D processes.

2. Experimental details

Samples of 2.5 g were obtained mixing powders of $LiNH_2$ (Sigma–Aldrich, 95% purity) and MgH_2 (Th. Goldschmidt GmbH, 95% MgH_2 + 5% Mg) in the stoichiometric ratio 2:1.1. Small amounts of Nb_2O_5, $TiCl_3$ and graphite were added to the powders for testing their effectiveness as catalysts. The samples were ball milled in a SPEX 8000M mill in argon atmosphere using stainless steel spheres with a BPR of 10:1. The milling times were 2, 12, 24 and 48 h and every sample was labelled accordingly. The milling process was carried out alternating 5 min of milling and 5 min of stop in order to avoid an excessive heating of the powders inside the vial. All the procedure of the powder handling before and after milling were carried out inside a glove box in argon atmosphere.

The thermodynamic and kinetic properties of hydrogen storage of samples were measured by means of a Sievert's volumetric apparatus supplied by Advanced Materials Co.

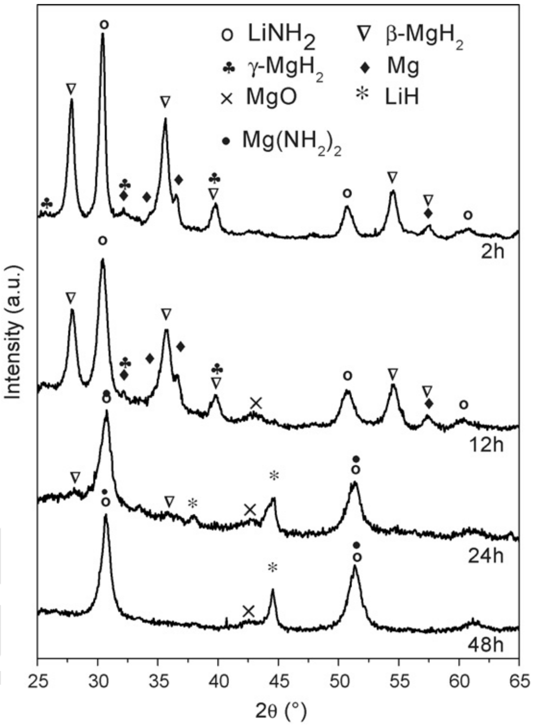

Fig. 1. XRD patterns of $2LiNH_2 + 1.1MgH_2$ samples milled for the times indicated.

The microstructure of the samples was analysed by means of Rietveld refinement (using the software MAUD) of XRD patterns obtained using a Philips PW1820/00 diffractometer with Cu Kα radiation. The XRD measurements were carried out on samples prepared into the glove box by protected them with a thin kapton film (8 μm). The diffraction peaks originated by kapton film are within 10–20° 2θ, far from the sample region of interest.

The milled samples were activated by means of a 18–20 h heat treatment at 220–230 °C in hydrogen high pressure (11–12 MPa), following the procedure suggested by Yang et al. [5].

Table 1
Results of Rietveld analysis of studied samples

Sample	As milled		Rehydrogenated	
	Phases	Crystallite size (nm)	Phases	Crystallite size (nm)
Milled 2 h	$LiNH_2$ tetragonal β-MgH_2 tetragonal γ-MgH_2 orthorhombic Mg hexagonal	31 ± 4 22 ± 3 15 ± 4 –	$Mg(NH_2)_2$ tetragonal LiH cubic MgO cubic	38 ± 4 130 ± 10 –
Milled 12 h	$LiNH_2$ tetragonal β-MgH_2 tetragonal γ-MgH_2 orthorhombic Mg hexagonal MgO cubic	18 ± 3 13 ± 2 23 ± 5 – –	$Mg(NH_2)_2$ tetragonal LiH cubic MgO cubic	30 ± 5 110 ± 15 –
Milled 24 h	LiH cubic $LiNH_2$ tetragonal $Mg(NH_2)_2$ tetragonal MgO cubic	70 ± 15 17 ± 3 20 ± 7 –	$Mg(NH_2)_2$ tetragonal LiH cubic MgO cubic	16 ± 2 110 ± 10 –
Milled 48 h	LiH cubic $LiNH_2$ tetragonal $Mg(NH_2)_2$ tetragonal MgO cubic	80 ± 20 15 ± 3 15 ± 6 –	$Mg(NH_2)_2$ tetragonal LiH cubic MgO cubic	15 ± 2 60 ± 7 –

3. Results and discussion

The XRD patterns of 2, 12, 24 and 48 h as milled samples are shown in Fig. 1. The crystallite size, as obtained from Rietveld analysis of all samples, is reported in Table 1 for all recognised phases, except for metallic Mg and MgO, present in a too small amount for quantitative determinations.

After a milling time of 2 h is possible to recognize two main phases: $LiNH_2$, β-MgH_2 and a small amount of metastable γ-MgH_2 and metallic Mg. Metallic Mg is already present in the provided commercial MgH_2 and probably derives also from the partial decomposition of the hydride during the milling process. The average crystallite size is less than 25 nm for β-MgH_2 and γ-MgH_2 and less than 35 nm for $LiNH_2$.

The XRD patterns of 2 and 12 h as milled samples are similar, as can be seen in Fig. 1, meaning that the phases within the two samples are the same, and differ only in the peak broadening due to the smaller crystallite size of 12 h sample. This is quantitatively confirmed by the results of Rietveld analysis reported in Table 1: after milling for 12 h the average crystallite size is less than 25 nm for all the phases. Particularly for $LiNH_2$ and β-MgH_2 the average crystallite size decreases more than 40% with respect to 2 h sample.

When the milling time exceeds 12 h, the characteristic peaks related to β-MgH_2 and γ-MgH_2 disappear, while those of the $LiNH_2$ remain and the peaks related to LiH appear. This suggests that a certain quantity of the starting mixture has reacted to form $Mg(NH_2)_2$ and LiH according to reaction (2). Anyway, it is difficult to establish the real presence of $Mg(NH_2)_2$, because the peaks of this phase are overlapped with those of $LiNH_2$. However, the Rietveld refinement worked better including this phase in the calculation. The presence of $Mg(NH_2)_2$ and LiH can be justified by the fact that during milling the local temperature of the powders could raise remarkably. The fact that the peaks related to $LiNH_2$ are still present in the XRD pattern suggests that also β-MgH_2 must be present in the sample, even if the characteristic peaks are not observable. A possible explanation is a crystal degradation together with a very fine dispersion of the remaining MgH_2 into the 24 and 48 h samples due to the prolonged milling time. A small amount of MgO (less than 1–2 vol.%) can be observed in the XRD patterns of 24 and 48 h milled samples, probably due to oxidation of Mg during milling by traces of oxygen inside the vial. $LiNH_2$ is the only phase displayed in all the XRD patterns of as milled samples and it is possible to notice from Table 1 that the average crystallite size decreases by increasing milling time.

The XRD patterns of rehydrogenated samples are shown in Fig. 2. The phases present in these samples are $Mg(NH_2)_2$ and a small amount of MgO. Also in this case (see Table 1) it is possible to note that the average crystallite size of $Mg(NH_2)_2$ and LiH decreases with milling time. Moreover, in 2, 12 and 24 h samples the average crystallite size of LiH is quite larger compared to $Mg(NH_2)_2$, while in 48 h sample they are close. In particular, the crystallite size related to $Mg(NH_2)_2$ decreases by more than 50% going from 2–12 h samples to 24–48 h samples. Concerning LiH, the crystallite size decreases remarkably only after 48 h of milling.

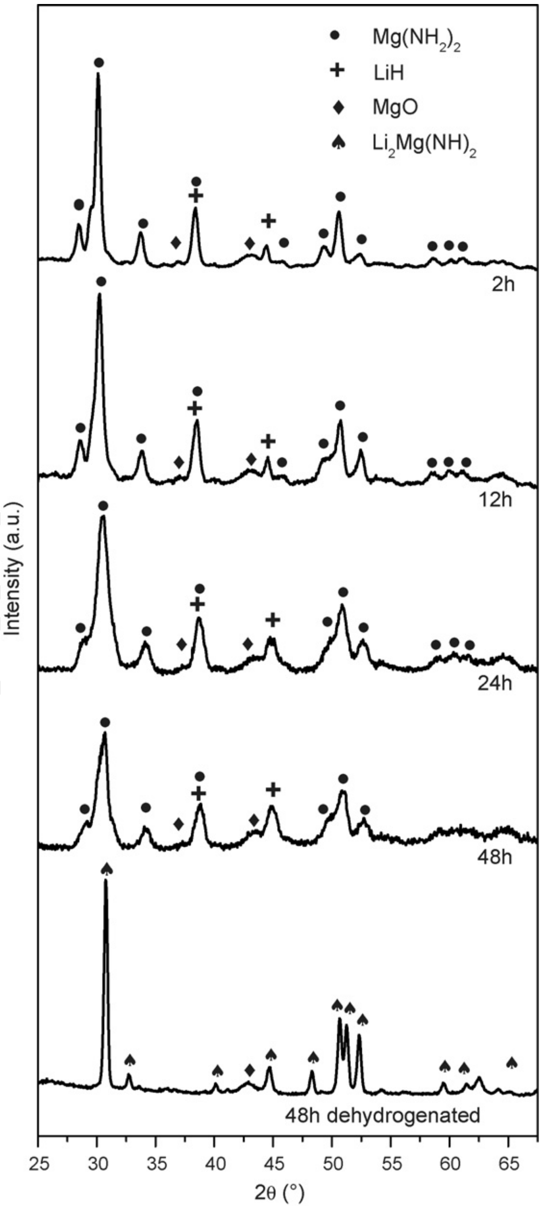

Fig. 2. XRD patterns of rehydrogenated samples; for comparison also the pattern of 48 h milled dehydrogenated sample is reported.

The XRD pattern related to 48 h milled dehydrogenated sample is shown in Fig. 2 and is very similar to that reported in the literature [5,6,9]. The dehydrogenated material is composed essentially by a mixed Li and Mg imide ($Li_2Mg(NH)_2$), whose structure has been recently resolved by Rijssenbeek et al. [9] by means of neutron diffraction. The crystal structure of this phase belongs to the orthorombic system at room temperature and can be described as a supercell of the high temperature cubic form of Li_2NH. The Li and Mg atoms are randomly distributed over two crystallographic sites (4b) and (8c). The Rietveld analysis of the XRD profile carried out using the structure suggested by Rijssenbeek et al. [9] (space group *Iba*2) gave the following cell

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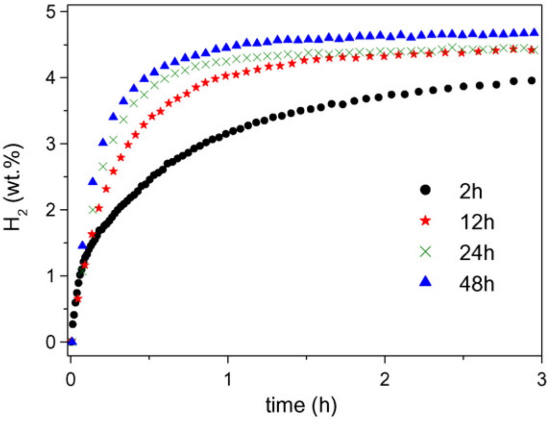

Fig. 3. Absorption kinetics of 2, 12, 24 and 48 h samples at 220 °C and 9 MPa of H_2.

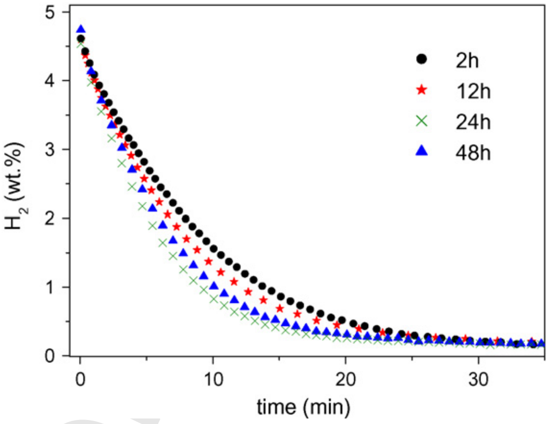

Fig. 4. Desorption kinetics of 2, 12, 24 and 48 h samples at 220 °C and 0.25 MPa of H_2.

parameters:

$$a = (9.781 \pm 0.003)\text{Å}\,, \qquad b = (4.990 \pm 0.003)\text{Å}\,,$$
$$c = (5.195 \pm 0.003)\text{Å}\,,$$

in agreement with their results.

The A/D kinetics has been studied at 220 °C for all samples in order to investigate the effect of milling time. It has been found that none of the additive tested has a significant effect on the kinetics, then only the results obtained with samples free of additives are shown in the following. In Fig. 3 (left) the absorption kinetics at 220 °C and a starting hydrogen pressure of 9 MPa is shown for all samples. Sample milled 48 h displays the maximum measured hydrogen capacity, 4.7 wt.%. It is possible to observe that the hydrogen absorption kinetics of studied samples is improved by increasing the milling time. While 60 min and more than 3 h are necessary to 12 and 2 h samples, respectively, in order to absorb 4.0 wt.% of H_2 (about 85% of the maximum hydrogen capacity), 24 h sample needs 40 min in order to absorb the same amount. Samples milled for 24 and 48 h have, approximately, the same kinetics: the small difference is due to the higher hydrogen capacity of 48h sample (4.7 wt.% H_2 against 4.5).

Desorption kinetics, shown in Fig. 3 (right) results considerably faster than absorption and less sensitive to milling time: faster for 12 h sample than for 2 h sample, while for 24 and 48 h samples is almost the same.

Chen et al. [10] reported that the reversibility of this system is dominated by a local interaction between $Mg(NH_2)_2$ and LiH. The samples milled for a longer time (24 and 48 h) are characterized by lower crystallite size and more homogeneous inter-dispersion of the phases; this assures a higher contact surface by which $Mg(NH_2)_2$ and LiH can interact. The higher capacity of 48 h sample should be justified by a finer and homogeneous dispersion of MgH_2 inside the starting mixture. This fact assures that MgH_2 is closely in contact with $LiNH_2$ during the activation reaction, in order to convert a greater quantity of material according to reaction (2).

The better desorption kinetics of 24 and 48 h samples can be directly connected to the average crystallite size of $Mg(NH_2)_2$ and LiH hydrogenated phases, that are remarkably smaller in comparison with 2 and 12 h samples: in particular, the decrease is more than 50% for $Mg(NH_2)_2$. A smaller crystallite size reduces the average diffusion paths of hydrogen during desorption.

This peculiarity of hydrogenated state ($Mg(NH_2)_2$ and LiH) probably leads, after the release of hydrogen, to the nucleation of a dehydrogenated phase characterized by a microstructure that enhances the absorption kinetics. Moreover, a prolonged milling leads to a higher concentration of structural defects that can represent preferential nucleation sites characterized by lower activation energy for the hydrogenated phases.

The thermodynamic characterisation of the system has been carried out measuring pressure–composition isotherms (PCI) at 225, 231, 235 and 242 °C for 12 h sample (see Figs. 4 and 5), showing a reversible capacity of 4.6 wt.% H_2, according to the kinetics measurements. The isotherms exhibit two plateaus which may correspond, in agreement with Luo and Sickafoose [6], to the following reactions:

$$Li_2MgN_2H_2 + 0.6H_2 \leftrightarrow Li_2MgN_2H_{3.2} \quad (0 < \text{wt.\%}H_2 < 1.5) \qquad (4)$$

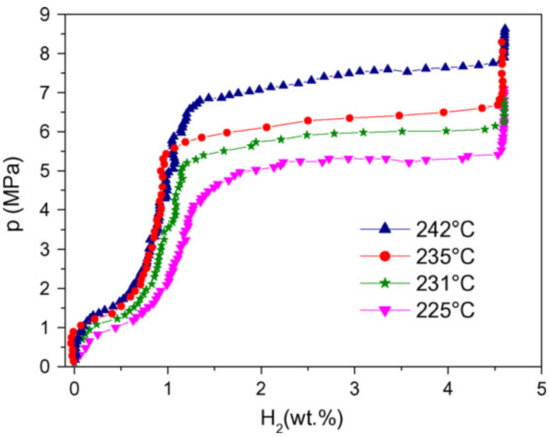

Fig. 5. Desorption pressure composition isotherms at 225, 231, 235 and 242 °C for 12 h sample.

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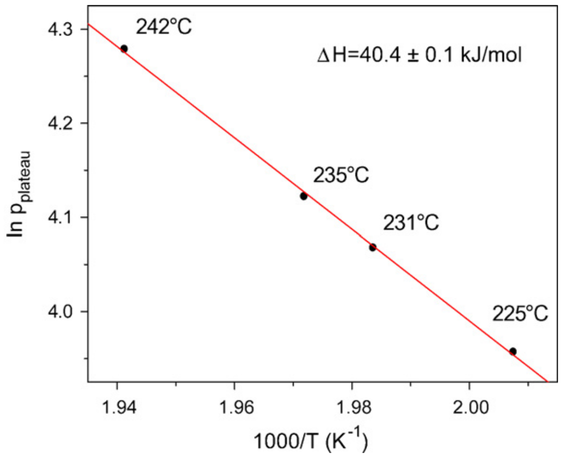

Fig. 6. Van't Hoff plot for the Li–Mg–N–H system.

$$Li_2MgN_2H_{3.2} + 1.4H_2 \leftrightarrow Mg(NH_2)_2 + 2LiH \quad (1.5 < wt.\%H_2 < 5.1) \qquad (5)$$

From the PCI plateau pressures and the corresponding temperatures a van't Hoff plot of Fig. 6 has been built up in order to evaluate the reaction desorption enthalpy, which results to be 40.4 kJ/mol H_2, in agreement with the literature data [3,5,7,8].

4. Conclusions

The effectiveness of prolonged milling on absorption/desorption kinetics of the Li–Mg–N–H system has been studied. A milling time of 24 h (or longer) gives a better kinetics compared to 2 and 12 h milled samples. The improvement is higher in absorption mode, where the system shows worse kinetics than desorption. The sample milled for 48 h shows an higher hydrogen capacity with respect to the other samples. In this case, the prolonged milling leads to a reciprocal better dispersion of $LiNH_2$ and MgH_2 which leads to a more efficient activation of the material. The kinetics improvement is due to the reduced average crystallite size, which gives rise to increase of surface to bulk ratio, enhancing the solid–solid reactivity and shortening the hydrogen diffusion paths.

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