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Kinetic improvement on the CaH_2 -catalyzed $\text{Mg}(\text{NH}_2)_2$ + 2LiH system

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ABSTRACT:

In the present work we focused on the catalytic effect of CaH_2 on the dehydrogenation process of the $\text{Mg}(\text{NH}_2)_2\text{-2LiH}$ system. The synthesis, hydrogen storage properties and energy barriers were investigated by X-ray diffraction (XRD), temperature-programmed desorption (TPD) and differential scanning calorimetry (DSC). The TPD measurements proved that desorption of the $\text{Mg}(\text{NH}_2)_2\text{-2LiH}$ system milled with 0.08 mol of CaH_2 started at temperature of 78 °C, lower if compared with the 125 °C observed in the pristine material. Furthermore, Kissinger analysis revealed that CaH_2 acted as a catalyst to decrease the activation energy of the dehydrogenation step from a value of 135 kJ/mol for the pristine material, to 105 kJ/mol when CaH_2 was dispersed into the mixture.

KEYWORDS: Hydrogen absorbing materials; Gas-solid reactions; Catalysis; Kinetics; Thermal analysis; X-ray diffraction

1 INTRODUCTION:

In the last decade the amide-hydride systems have been object of intense studies as solid-state hydrogen storage materials, thanks to their very promising thermodynamic properties particularly attractive for onboard-application on light-duty vehicles [1]. In this framework pioneering study was performed by Chen et al. which discovered that the $\text{LiNH}_2\text{-2LiH}$ system desorbed hydrogen at very low temperature (150°C) with respect to the singular materials. The authors supposed that driving force for the desorption mechanism could be ascribed to the difference, in terms of partial charge, between the $\text{H}^{\delta+}$ and $\text{H}^{\delta-}$ of the amide and hydride species, respectively [2]. Further thermodynamic improvements were obtained by partially replacing Li with Mg, which acts destabilizing the N-H bond and then decreasing the desorption enthalpy up to 40 kJ/mol [3, 4]. Among the class of materials Mg-Li-N-H, $2\text{LiNH}_2\text{-MgH}_2$ and $\text{Mg}(\text{NH}_2)_2\text{-2LiH}$ systems resulted the most studied: they, in fact, can desorb

hydrogen under moderate conditions ($< 150\text{ }^{\circ}\text{C}$) forming the ternary imide $\text{Li}_2\text{Mg}(\text{NH})_2$. An other interesting aspect was also represented by the opportunity to re-hydrogenate Li/Mg-imide with the formation of the Mg-based amide phase, instead of Li-, as illustrated by the following reaction:



Although the theoretical thermodynamic properties of the Li-Mg-N-H system matched the working conditions required for PEMFC, several kinetic constrains limit its practical application [1]. To this regard, in order to improve the kinetic performance of the $\text{LiNH}_2\text{-LiH}$ system, several strategies have been proposed in the recent past, as the particle size reduction by high-energy ball milling and addition of metal catalysts [5-9]. T. Durojaiye et al., demonstrated that the addition of KH to the $2\text{LiNH}_2\text{-MgH}_2$ system, decreased the desorption temperature with respect to the undoped system (75.3°C vs 109°) while keeping similar gravimetric capacity of 5 wt. % [8]. Encouraging results were also obtained by using RbH as a catalyst in the initial mixture: although the activation energy estimated of 87 kJ/mol resulted comparable with the data obtained for the KH-doped system, RbH-system was characterized by a desorption kinetic 60 times than pristine material and twice than the KH-system [9].

Potassium hydride was also used as additive in the $\text{Mg}(\text{NH}_2)_2\text{-2LiH}$ mixture. Wang et al., proved that the system milled with 3% mol of KH, released hydrogen $50\text{ }^{\circ}\text{C}$ below the undoped material without emission of NH_3 up to $200\text{ }^{\circ}\text{C}$ [10]. In addition, the doped system was able to absorb the 75% of hydrogen in 12 minutes at $143\text{ }^{\circ}\text{C}$ and under 30 bar of H_2 , with respect to the 20 hours necessary for the raw sample. A recent study conducted on the $\text{Mg}(\text{NH}_2)_2\text{-2LiH-}n\text{KH}$ system (where n ranging from 0.01 to 0.15) has demonstrated that an increasing of the concentration of KH contributes significantly to optimize the kinetic performance of the system [11]. In the best performing material, KH allowed to reversibly store the 5.2 wt. % of hydrogen with a T onset of $70\text{ }^{\circ}\text{C}$ and $50\text{ }^{\circ}\text{C}$ for the dehydrogenation and hydrogenation processes, respectively, and minimizing the release of ammonia.

Most recently, Chen and coauthors investigated the nature of the kinetic barrier in the decomposition of $\text{Mg}(\text{NH}_2)_2\text{-2LiH}$ with also the purpose of clarifying the crucial role played by KH in the catalysis of

the reaction [12]. They stated that KH reacts, in a first step, with $\text{Mg}(\text{NH}_2)_2$ forming $\text{K}_2\text{Mg}(\text{NH}_2)_4$ which combined rapidly with LiH to produce fresh KH. The dehydrogenation step involved also $\text{KLi}_3(\text{NH}_2)_4$ which significant influences, together with the other two K-rich phases, the kinetic performance of the catalyzed reaction. Along this point, also the impact of different K-based catalysts, including KF, KCl, KBr and KI, were recently tested in order to elucidate the effect of the anions, with important improvement for the KF-doped mixture [13]

The formation of the mixed amide phases seems to be the key for enhancing the hydrogen storage kinetics of the $\text{Mg}(\text{NH}_2)_2\text{-2LiH}$ composite, in the light of the fact that the introduction of a second cation further destabilizes the N-H bonding. Along this direction, Ca could represent a promising alternative, because, being more electronegative than K (1 vs 0.82), it should promote the destabilization in the N-H bonding. In addition, as reported by Y. Liu and coauthors, CaH_2 and $\text{Mg}(\text{NH}_2)_2$ can react and form an imide phase, $\text{CaMg}(\text{NH})_2$ [14].

In this work, the effect of CaH_2 on the kinetic desorption of the $\text{Mg}(\text{NH}_2)_2\text{-2LiH}$ system, was reported. The calcium-doped $\text{Mg}(\text{NH}_2)_2\text{-2LiH}$ systems were prepared by ball milling and their structural and dehydrogenation properties were evaluated by X-ray diffraction (XRD) and temperature-programmed desorption (TPD), respectively. The activation energies of the doped and undoped samples were estimated by differential scanning calorimetry applying the Kissinger's plot.

2 EXPERIMENTAL DETAILS

Commercial powders of LiH (95% purity) and CaH_2 (98% purity) were purchased from Sigma-Aldrich and Alfa Aesar, respectively. Magnesium amide, $\text{Mg}(\text{NH}_2)_2$, was synthesized in our own laboratory by reacting MgH_2 power (98%, Alfa Aesar) with 8 bar of ammonia (gas) at about 250°C. In particular, 4 g of MgH_2 were activated by high-energy ball milling for 24h (two ball of 7 g each one) using a Spex Mix/Mill machine working at 875 rpm. For each synthesis, 0.660 g of pre-milled MgH_2 were introduced into a Parr reactor and then annealed from room temperature to 250°C under ammonia

atmosphere (8 bar). The system was kept at 250°C for 48 h in order to guarantee the complete conversion. The mixture of Mg(NH₂)₂ and LiH at a molar ratio of 1:2 was processed by ball-milling for 1 h on Spex Mix/Mill machine rotating at 875 rpm. The Mg(NH₂)₂-2LiH-0.08CaH₂ system was then prepared by milling CaH₂ and Mg(NH₂)₂-2LiH system for further 15 minutes.

Structural and microstructural properties of the milled powders were characterized by means of Rigaku X-ray Diffractometer (XRD) with a Bragg–Brentano geometry using Cu K α radiation ($\lambda = 1.54178 \text{ \AA}$) and a graphite monochromator in the diffracted beam. The powders were located in an air-sensitive sample holder equipped by an airtight hood of Kapton foil specifically designed for materials that might degrade in the presence of oxygen and then sealed in the glove box. The microstructural parameters were evaluated by fitting the full XRPD patterns using MAUD (Materials Analysis Using Diffraction), a Rietveld refinement software [15]. Calorimetric measurement was performed on the as-milled powders by using a high-pressure cell in a Sensys DSC (Setaram) charged with ~50 mg of powder under Ar atmosphere (1 bar). Hydrogen desorption properties was performed by a Sievert-type apparatus, PCT-pro 2000 (Setaram), heating the sample from room temperature to 220 °C at 2 °C/min under static vacuum.

3 RESULTS AND DISCUSSION

The synthesis of Mg(NH₂)₂ was successfully demonstrated by X-ray diffraction as reported in Fig. 1. The processed powders consist of nanocrystalline Mg(NH₂)₂ (98.5 wt. %) with crystallite size of 260 Å, and MgH₂ (0.8 wt. %) and MgO (0.7 wt. %) in traces, as reported in Table. 1.

In the post-1h milled mixture, the peaks of Mg(NH₂)₂ (71.5 wt.%) and LiH (20.5 %) can be unambiguously identified and compared with previous data [16]. Peak broadening and the reduction in intensity of the diffraction peaks are associated to the refinement in crystallite size and lattice internal micro-strain as a direct consequence of the milling processing (see table 1). Therefore, at the end of the mechanical treatment the formation of an intimate mixture between nanocrystalline LiH and Mg(NH₂)₂, can be supposed.

The system was then doped with CaH₂ (0.08 mol) through a further ball-milling of 15 minutes in order to preserve the microstructure of the mixture and, at the same time, to allow a good intermixing between the additive and the composite. To evaluate the effect of CaH₂ kinetic, TPD of the samples with and without CaH₂, were measured and compared in Fig. 2.

The manometric analysis of the two samples reveals a similar dehydrogenation behavior: both the mixtures release hydrogen in a single step. For the initial mixture (blue curve), the desorption step starts at ca. 128 °C with a total release of about 3.98 wt. % recorded at the end of the heat treatment. 62.0 % of total hydrogen is released at 125 °C. Interesting, the doped system (green curve) starts desorbing at very low temperature of 78 °C, with a favorable kinetic with respect to the undoped mixture. It, in fact, releases the 67.5 % of total hydrogen at 125 °C and a total amount of 4.01 wt. % under 220 °C.

In the light of the fact that the kinetics enhancement can be related to the energy barriers, the activation energy is calculated using DSC analysis in order to quantify the influence of CaH₂ on the desorption kinetic of the Mg(NH₂)₂-2LiH composite. Fig. 3 shows DSC traces at different heating rates for the neat Mg(NH₂)₂ + 2LiH and the Mg(NH₂)₂ + 2LiH+ 0.08 CaH₂ mixture.

Broad endothermic peak associated to the reaction $\text{Mg}(\text{NH}_2)_2\text{-}2\text{LiH} \rightarrow \text{Li}_2\text{Mg}(\text{NH})_2 + 2\text{H}_2$, is recorded for both the systems and their onset shift to higher temperature values when the heating rate increases from 2 to 10 °C/ min.

As reported by the TDS measurements (Fig. 2), the onset decomposition of the sample mixed with CaH₂ (Fig. 2a, dark line), shifts to lower temperature with respect to the pristine composite (Fig. 2b, dark line). On the other hand, although a similar trend, the release of gas takes place at higher temperatures for both the processes (150°C vs 78 °C and 175 °C vs 125 °C) probably due to the back pressure of 1 bar Ar used for the DSC experiments.

The activation energy, E_a, for the hydrogen desorption was calculated by the Kissinger approach using the following equation [17]:

$$\frac{d \ln \left(\frac{\beta}{T_m^2} \right)}{d \left(\frac{1}{T_m} \right)} = - \frac{E_a}{R} \quad \text{eq. 1}$$

Where β is the heating rate, T_m the peak temperature in the DSC curve and R the gas constant. Kissinger analysis was applied to endothermic peak as shown in Fig. 4 for the undoped and doped systems.

The apparent activation energy estimated from Kissinger's plot for $\text{Mg}(\text{NH}_2)_2 - 2\text{LiH}$ (Fig. 4 a) in the undoped system is found to be 135 kJ/mol, comparable with the value of 127 kJ/mol obtained by Gao et al. [16]. The value of E_a obtained for the pristine material decreases to 105 kJ/mol when CaH_2 is introduced into the $\text{Mg}(\text{NH}_2)_2 - 2\text{LiH}$ mixture (Fig. 4 b) confirming its active role in enhancing the kinetic performance of this system.

These reported findings represent the first tentative, by our knowledge, to provide a quantitative evidences for decreased kinetic barriers during the dehydrogenation of the $\text{Mg}(\text{NH}_2)_2 - 2\text{LiH}$ mixture using CaH_2 as dopant. Further effort will be addressed to elucidate the effect of CaH_2 content on the dehydrogenation behavior of the $\text{Mg}(\text{NH}_2)_2 - 2\text{LiH}$ system and to identify the intermediates involved in the process.

4 CONCLUSIONS

In this work we investigated the effect of calcium hydride on the dehydrogenation properties of the $\text{Mg}(\text{NH}_2)_2 - 2\text{LiH}$ system. It was demonstrated that a good intermixing of the starting reagents can be achieved after 1 h of mechanical treatment by high-energy ball milling. During the dehydrogenation process, the TDS measurements reported that the desorption in the $\text{Mg}(\text{NH}_2)_2 - 2\text{LiH} - 0.08 \text{CaH}_2$ system were shifted to low interesting temperature of 78 °C compared with the 128 °C required for the neat $\text{Mg}(\text{NH}_2)_2 - 2\text{LiH}$. The reaction kinetic was improved by the addition of CaH_2 as also established by the Kissinger analysis applied to the broad endothermic event recorded during the DSC analysis

conducted at different heating rates. Kissinger's plots evidenced that the activation energy of the dehydrogenation of $\text{Mg}(\text{NH}_2)_2 - 2\text{LiH}$ was decreased from 135 kJ/mol, for the pristine material, to 105 kJ/mol when CaH_2 is introduced into the mixture. These results confirm the important role that the CaH_2 could play to further enhance the hydrogenation kinetic process of the $\text{Mg}(\text{NH}_2)_2 - 2\text{LiH}$ system in order to definitely overcome the kinetic barrier which limit the application of this promising system.

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FIGURE CAPTIONS:

Figure 1. XRD patterns of the as-synthesized $\text{Mg}(\text{NH}_2)_2$ and the $\text{Mg}(\text{NH}_2)_2/2\text{LiH}$ system milled for 1h. $\text{Cu K}\alpha = 1.54184 \text{ \AA}$

Figure 2. A Temperature programmed desorption of the undoped (blue curve) and doped (green curve) systems. The sample was gradually heated from room temperature to 220 °C with a heating rate of 2 °C/min under static vacuum.

Figure 3. DSC traces of a) $\text{Mg}(\text{NH}_2)_2 + 2\text{LiH}$ and b) $\text{Mg}(\text{NH}_2)_2 + 2\text{LiH} + 0.08 \text{ CaH}_2$ composites at different heating rates.

Figure 4. Kissinger's plots of the $\text{Mg}(\text{NH}_2)_2 - 2\text{LiH}$ (a) and b) $\text{Mg}(\text{NH}_2)_2 - 2\text{LiH} - 0.08\text{CaH}_2$

Table 1. Phase abundance and microstructural parameters of the as-prepared $\text{Mg}(\text{NH}_2)_2$ and $\text{Mg}(\text{NH}_2)_2 + 2\text{LiH}$ system.

FIGURES

Figure 1

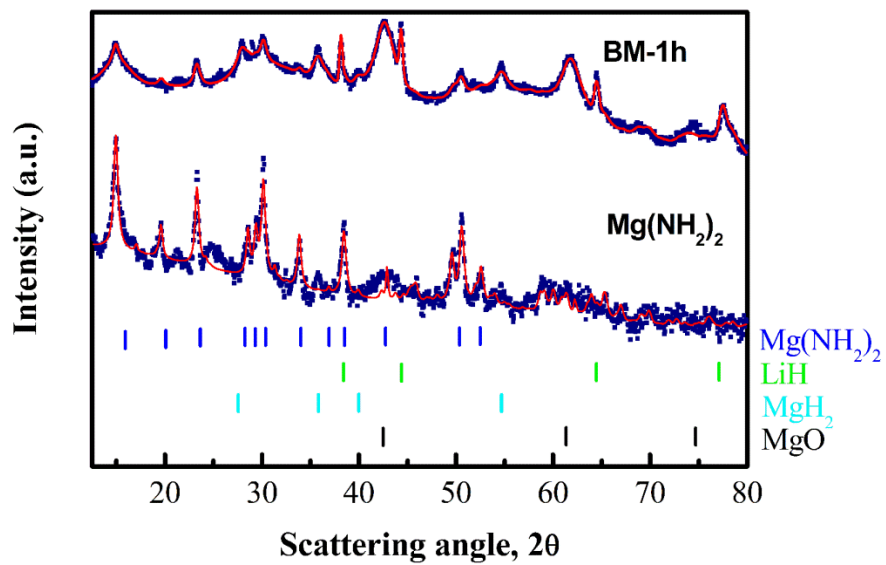


Figure 2

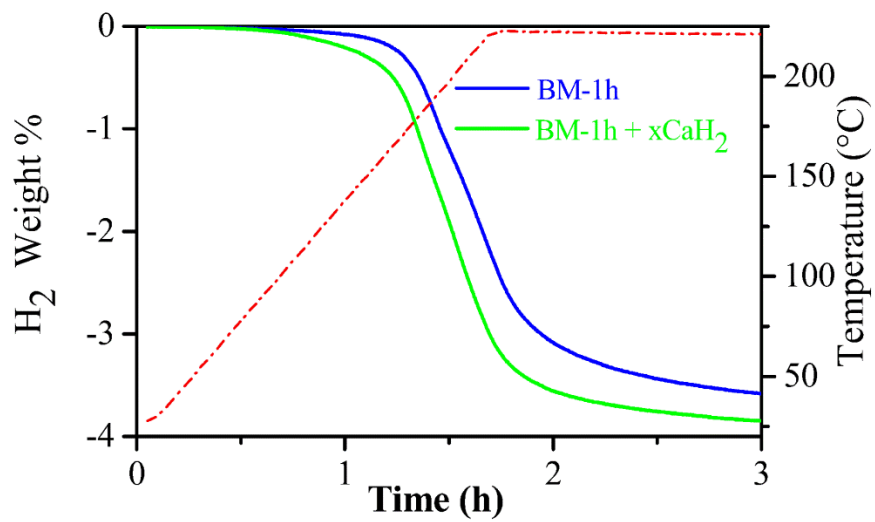


Figure 3

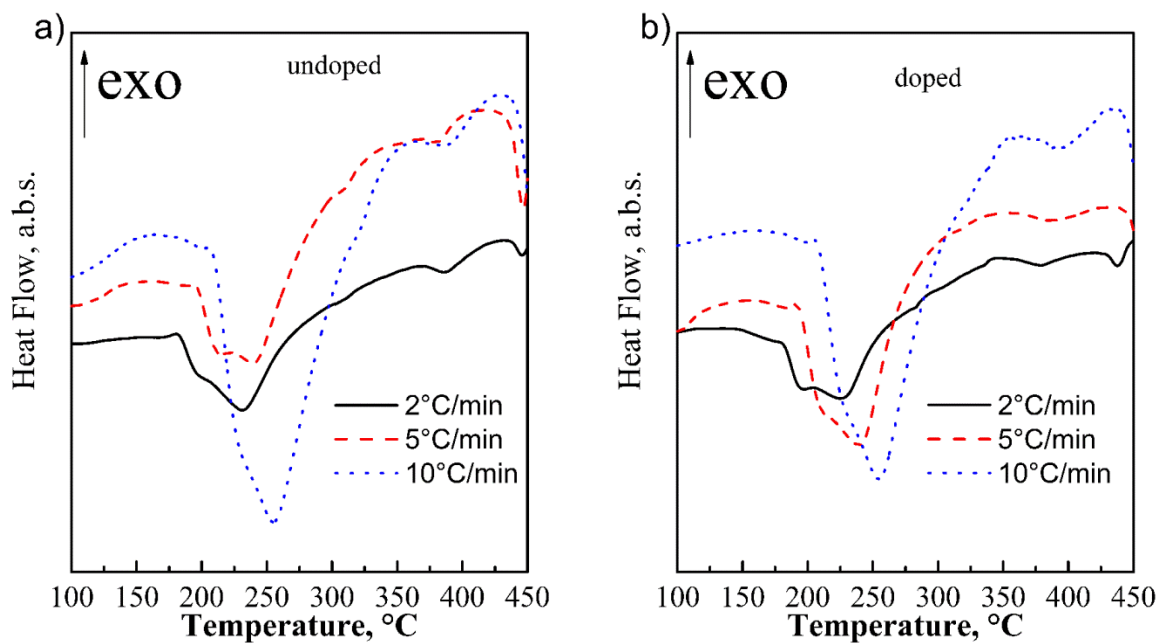


Figure 4

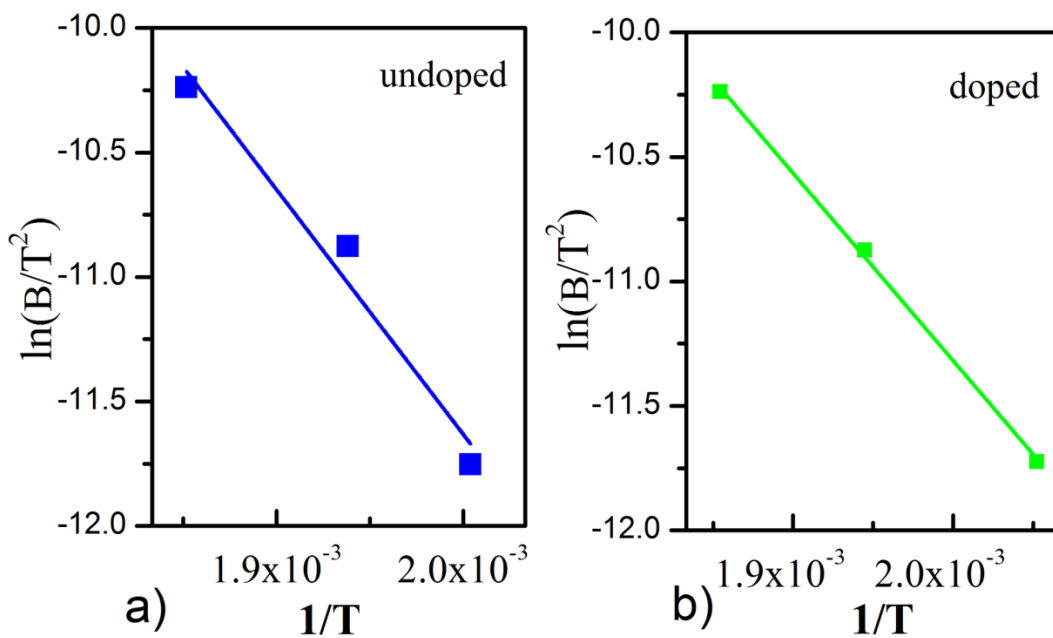


Table 1

<i>Samples</i>	<i>wt. %</i>	<i>a, Å</i>	<i>c, Å</i>	<i>Crystallite size, Å</i>	<i>Microstrain</i>
Mg(NH₂)₂ as-prepared					
Mg(NH ₂) ₂	98.5	10.40	20.05	260	2.4*10 ⁻⁵
MgO	0.8	4.21		150	6.0 *10 ⁻⁴
MgH ₂	0.7	4.48	3.03	931	3.0*10 ⁻³
Mg(NH₂)₂+2LiH 1h BM					
Mg(NH ₂) ₂	71.5	10.36	20.14	145	9.583*10 ⁻⁴
LiH	20.5	4.086		465	2.65*10 ⁻⁵
MgO	8.0	4.24		60	3.4*10 ⁻³

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