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Design of a Nanometric AlTi Additive for MgB₂ Based Reactive Hydride Composites with Superior Kinetic Properties

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ABSTRACT

Solid-state hydride compounds are a promising option for efficient and safe hydrogen storage systems. Lithium reactive hydride composite system $2\text{LiBH}_4+\text{MgH}_2/2\text{LiH}+\text{MgB}_2$ (Li-RHC) has been widely investigated owing to its high theoretical hydrogen storage capacity and low calculated reaction enthalpy (11.5 wt.% H_2 and 45.9 kJ/mol H_2). In this paper, a thorough investigation into the effect of the formation of nano TiAl alloys on the hydrogen storage properties of the Li-RHC is presented. The additive $3\text{TiCl}_3.\text{AlCl}_3$ is used as nanoparticle precursor. For the investigated temperatures and hydrogen pressures, the addition of ~ 5 wt. % of $3\text{TiCl}_3.\text{AlCl}_3$ leads to hydrogenation/dehydrogenation times of only 30 min and to a reversible hydrogen storage capacity of 9.5 wt.%. The material containing $3\text{TiCl}_3.\text{AlCl}_3$ possesses superior hydrogen storage properties in terms of rates and stable hydrogen capacity during several hydrogenation/dehydrogenation cycles. These enhancements are attributed to an *in situ* nanostructure and hexagonal AlTi_3 phase observed by HR-TEM. This phase acts in a twofold manner, first promoting the nucleation of MgB_2 upon dehydrogenation and second suppressing the formation of $\text{Li}_2\text{B}_{12}\text{H}_{12}$ upon hydrogenation/dehydrogenation cycling.

1. INTRODUCTION

Hydrogen is widely recognized as a promising energy carrier for a clean and environmental friendly energy. Nowadays, hydrogen is commonly stored in liquid or compressed gas form¹⁻³. However, both storage methods are neither safe nor cost efficient. Hydrogen can also be stored in solid state: this is the safest solution to store it since mainly the pressure and temperature conditions are milder than those required for the compressed and cryogenic hydrogen storage methods, respectively. Because of their high volumetric hydrogen storage capacities, light metal complex hydrides are considered potential storage candidates for hydrogen driven applications^{4,5}. Among the complex metal hydrides, LiBH₄ possesses one of the highest gravimetric and volumetric hydrogen storage capacities (18.5 wt.% H₂ and 121 kg H₂/m³, respectively)⁶⁻⁸. However, the dehydrogenation of LiBH₄ takes place only at relatively high temperatures (over 400 °C) and its decomposition products (i.e. LiH, B, Li₂B₁₂H₁₂) are too stable to reversibly form LiBH₄ under moderate temperature and hydrogen pressure⁹⁻¹⁴. Barkhordarian *et al.*¹⁵ and Vajo *et al.*¹⁶ independently reported on the possibility to obtain fully reversible metal borohydrides based hydrogen storage systems. Owing to its theoretical hydrogen storage capacity and calculated reaction enthalpy (11.5 wt.% H₂ and 45.9 kJ/mol H₂), the 2LiBH₄+MgH₂/2LiH+MgB₂ (Li-RHC) system is regarded as one of the most prominent candidates for hydrogen storage. However, the dehydrogenation and hydrogenation processes of this composite system take place only at relative elevated temperatures (over 350 °C) due to kinetic constraints. Under dynamic conditions the dehydrogenation reaction occurs in a steps reaction: 2LiBH_{4(l)} + MgH_{2(s)} → Mg_(s) + 2LiBH_{4(l)} + H_{2(g)} → 2LiH_(s) + MgB_{2(s)} + 4H_{2(g)}¹⁷. Additionally, as also observed in other RHC systems¹⁸⁻²², the Li-RHC system reacts *via* different pathways depending on the temperature and pressure conditions and requires an appropriate hydrogen overpressure during the dynamic

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3 dehydrogenation process to assure the reversibility of the hydrogen uptake-release process^{23,24}. In
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5 the last decade, several studies have been conducted to investigate the effect of transition metal
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7 (TM) based additives (e.g. Ti containing additives, Zr containing additives, V containing
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9 additives, Sc_2O_3 , Nb_2O_5 , NbF_5 and Ce containing additives) on the
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11 dehydrogenation/hydrogenation reaction rates of $2\text{LiBH}_4+\text{MgH}_2$. In addition, some attempts to
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13 improve the reaction kinetics of $2\text{LiBH}_4+\text{MgH}_2$ by doping it with metallic Al were also taken²⁵⁻
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15 ³⁴. Among the transition metal additives, the Li-RHC doped with 5 mol % TiCl_3 shows markedly
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17 improved kinetic behavior. Bösenberg *et al.*²⁵ reported that the addition of TM or TM-
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19 compounds improve the kinetic behavior of Li-RHC by forming transition metal borides that
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21 provide heterogeneous nucleation sites for the formation of MgB_2 upon desorption .
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26 In the present work, the effects of the *in situ* formation of nano AlTi alloys on the hydrogen
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28 storage properties of the Li-RHC system are thoroughly investigated. For comparison purposes,
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30 the hydrogenation and dehydrogenation properties of the Li-RHC+ $3\text{TiCl}_3.\text{AlCl}_3$ system are
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32 compared with the ones of the pristine Li-RHC and Li-RHC+ TiCl_3 systems. The
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34 dehydrogenation and hydrogenation kinetic behavior are evaluated by volumetric and
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36 calorimetric techniques. The hydride systems are further characterized by means of *in situ*
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38 synchrotron powder X-ray diffraction, Magic Angle Spinning Solid-state Nuclear Magnetic
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40 Resonance, High resolution Transmission Electron Microscopy and Anomalous Small-Angle X-
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42 ray Scattering methods.
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46 **2. EXPERIMENTAL SECTION**

47 **2.1. Sample preparation**

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49 The raw materials were purchased in powder form from commercial suppliers without further
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51 modification: Lithium borohydride (LiBH_4 , 95 % purity, Sigma Aldrich), magnesium hydride
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(MgH₂, 98 % purity, Alfa Aesar), lithium hydride (LiH, 95 % purity, Sigma Aldrich), magnesium boride (MgB₂, 99 % purity, Alfa Aesar), titanium (III) chloride (TiCl₃, 99.999% purity, Alfa Aesar) and aluminum (III) chloride-titanium (III) chloride (3TiCl₃.AlCl₃, ~ 76-78% TiCl₃ purity, Fisher Scientific). The 2LiBH₄+MgH₂ (Li-RHC_a) and 2LiH+MgB₂ (Li-RHC_d) systems were mixed in several different ratios with TiCl₃ and 3TiCl₃.AlCl₃ (Li-RHC_a +xA and Li-RHC_d +xA, x= from 0.3125 to 2.5 mol %; A= TiCl₃ or 3TiCl₃.AlCl₃). In order to obtain a homogeneous dispersion of the additives into the main hydride phases, all the materials were mechanically milled in a 8000M Mixer/Mill[®] High-Energy Ball Mill for 400 min using stainless steel vial and grinding medium in a ball-to-powder ratio of 20:1. Since the hydrogen storage capacity of the systems is sensibly affected by the amount of Cl⁻ contained in the additives, the quantity of added TiCl₃ was calculated to match the one of the Cl⁻ contained in 3TiCl₃.AlCl₃. Therefore, all prepared materials are designated with respect to the amount of Cl⁻ in the additives as indicated in Table 1. All material handling was carried out in MBraun Unilab glove boxes with oxygen and moisture controlled atmosphere (< 10 ppm of O₂ and H₂O) to prevent oxidation of the samples.

Table 1. Prepared Hydride Mixtures 2LiBH₄ + MgH₂ and 2LiH + MgB₂ doped with TiCl₃ and 3TiCl₃.AlCl₃

No.	Materials (The amount of additive is expressed in mol %)	Mol % of added Cl ⁻	Designation
1	2LiBH ₄ + MgH ₂	-	Li-RHC _a
2	2LiBH ₄ + MgH ₂ + 2.5 mol % TiCl ₃	7.50	Li-RHC _a +7.5 TiCl ₃
3	2LiBH ₄ + MgH ₂ + 0.625 mol % (3TiCl ₃ .AlCl ₃)	7.50	Li-RHC _a +7.5 (3TiCl ₃ .AlCl ₃)

4	$2\text{LiBH}_4 + \text{MgH}_2 + 0.9375 \text{ mol } \% (3\text{TiCl}_3 \cdot \text{AlCl}_3)$	11.2	Li-RHC _a +11.2 (3TiCl ₃ .AlCl ₃)
5	$2\text{LiBH}_4 + \text{MgH}_2 + 1.25 \text{ mol } \% (3\text{TiCl}_3 \cdot \text{AlCl}_3)$	15.0	Li-RHC _a +15 (3TiCl ₃ .AlCl ₃)
6	$2\text{LiBH}_4 + \text{MgH}_2 + 2.5 \text{ mol } \% (3\text{TiCl}_3 \cdot \text{AlCl}_3)$	30.0	Li-RHC _a +30 (3TiCl ₃ .AlCl ₃)
7	$2\text{LiH} + \text{MgB}_2 + 2.5 \text{ mol } \% \text{TiCl}_3$	7.50	Li-RHC _d + 7.5 TiCl ₃
8	$2\text{LiH} + \text{MgB}_2 + 0.3125 \text{ mol } \% (3\text{TiCl}_3 \cdot \text{AlCl}_3)$	3.70	Li-RHC _d +3.7 (3TiCl ₃ .AlCl ₃)
9	$2\text{LiH} + \text{MgB}_2 + 0.625 \text{ mol } \% (3\text{TiCl}_3 \cdot \text{AlCl}_3)$	7.50	Li-RHC _d +7.5 (3TiCl ₃ .AlCl ₃)
10	$2\text{LiH} + \text{MgB}_2 + 2.5 \text{ mol } \% (3\text{TiCl}_3 \cdot \text{AlCl}_3)$	30.0	Li-RHC _d +30 (3TiCl ₃ .AlCl ₃)

2.2. Sample characterization

2.2.1. Volumetric measurements

De-/hydrogenation measurements and hydrogen kinetic behavior of the materials were performed using a custom-built volumetric Sieverts type apparatus. The first dehydrogenation of some samples was measured from room temperature up to 400 °C with a temperature ramp of 3 °C/min under 3 bar of H₂. Hydrogenation-dehydrogenation cycling measurements for all the materials were performed 3 bar hydrogen overpressure at 400 °C for the dehydrogenation and 50 bar at 350 °C for the hydrogenation. The hydrogen kinetic behavior was also evaluated *via* isothermal measurements at 360 °C, 370 °C, 380 °C, 390 °C and 400 °C under 50 bar and 3 bar of hydrogen for hydrogenation and dehydrogenation, respectively. The hydrogenation/dehydrogenation measurements lasted until the plateau was met the criteria: Δw_t (%) = 0.0002 and Δt (min) = 1. For hydrogenation and dehydrogenation processes the activation

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3 energies (E_a) were calculated by fitting of the kinetic curves with proper solid-gas models to
4 obtain the kinetic rate constant (k) and by plotting $\ln(k)$ vs. $1/T$ (T = temperature).
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7 8 **2.2.2. Coupled Sieverts with differential scanning calorimetry**

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10 Coupled Sieverts-DSC measurements were carried out by using a high-pressure calorimeter
11 (Sensys DSC, Setaram) coupled to a Sieverts-type apparatus (PCTPro-2000, Setaram & Hy-
12 Energy). The high-pressure cell of the calorimeter was loaded with ~ 13 -50 mg of the powder
13 sample. The dehydrogenation was performed by heating the sample from room temperature up to
14 450 °C with a heating rate of 5 °C/min under 3 bar H_2 back pressure and the hydrogenation was
15 carried out with a heating rate of 5 °C/min from room temperature to 350 °C under 50 bar H_2 .
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17 The calorimetric profiles were evaluated by the Calisto software to obtain the peak temperatures.
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20 21 **2.2.3. Synchrotron powder X-Ray diffraction (SR-PXD)**

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23 *Ex situ* PXD measurements were performed on Bruker D8 Discover in Bragg-Brentano
24 geometry laboratory device equipped with a copper source ($\lambda = 1.54184$ Å) and general area
25 detector³⁵.
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29 *In situ* SR-PXD was carried out at the beamline I711 at Max-lab II (Lund, Sweden, $\lambda =$
30 0.9938 Å), the measurement time was chosen to be 30 or 60 s for fixed exposure time mode and
31 varied between 50 and 100 s for dose mode. All PXD data was referred to the magnitude of the
32 scattering vector $q = 4\pi \sin \theta / \lambda$ where λ is the X-ray wavelength and 2θ is the scattering angle.
33
34 The diffracted intensity was measured by a Mar-165 CCD detector. The sample (0.5 mg–2 mg)
35 was airtight encapsulated in a sapphire capillary and then mounted into an in house developed *in*
36 *situ* cell, which is able to control heating temperatures and operating pressures^{36,37}. The 2D
37 diffraction patterns were azimuthally averaged and reduced to 1D diffractograms by using
38 FIT2D program³⁸.
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2.2.4. Magic angle spinning solid-state nuclear magnetic resonance (MAS NMR)

¹¹B MAS NMR spectra of the materials were obtained on a Varian Direct-Drive VNMRs-600 spectrometer (14.1 T) using a custom-built CP/MAS NMR probe for rotors with a diameter of 4 mm. The experiments were performed at room temperature using airtight end-capped zirconia rotors packed with the samples in an argon-filled glovebox (O₂ and H₂O levels were monitored to be below 10 ppm). A spinning speed of $\nu_R = 12.0$ kHz, a 0.5 μ s excitation pulse for a ¹¹B rf field strength of $\gamma B_1/2\pi \approx 60$ kHz, and a 10 s relaxation delay was employed for each experiment.

2.2.5. High resolution transmission electron microscopy (HR-TEM)

HR-TEM images were obtained on a FEI Titan 80-300 microscope operating at 300 kV. The samples for TEM were prepared by dispersing a small amount of powder on a commercial silicon nitride membrane grid inside a glove box and then directly introducing the specimen into the microscope. The samples were exposed to air for a very short time. TEM image processing was done with the following programs: Digital Micrograph (License n^o. 90294175), i-TEM (License n^o. A2382500) and JEMs (License n^o. IEb59yBDfUMh).

2.2.6. Energy dispersive spectroscopy (EDS)

EDS measurements were performed using a FEI Talos (S)TEM running at 200 kV. The specimen was prepared by suspension of the sample powder in dry cyclohexane and ultrasonication for 5 min, then one drop was placed on the copper grid and left to dry. Then the sample grid was mounted on the TEM sample holder and inserted for measurement. The data were collected using the ChemiSTEM technology from FEI with an X-FEG electron source and a High Angle Annular Dark Field (HAADF) detector setup.

2.2.7. Small-angle X-ray scattering (ASAXS)

The Ti-ASAXS measurements were performed at the FCM beamline of the PTB installed at the synchrotron radiation facility BESSY II (HZB, Berlin, Germany)³⁹. The beamline was combined with the HZB ASAXS instrument⁴⁰. The four-crystal monochromator has an energy resolution of $\Delta E/E \sim 1 \times 10^{-4}$, using the Si (111) crystals⁴¹. An in vacuum version of a Pilatus 1M detector was used to record the scattering pattern⁴². All measurements were performed at two sample-to-detector distances (0.8 m and 3.70 m) to cover the maximum experimentally accessible q -range. Here, q is the magnitude of the scattering vector: $q = 4\pi \sin \theta / \lambda$, where λ is the wavelength of the radiation and θ is half of the scattering angle. In order to separate the resonant scattering of Ti-containing nanostructures, all measurements were carried out below the K absorption edge of titanium⁴³. All selected energies E_i with their corresponding anomalous dispersion factors are listed in ESI Table S1⁴⁴. The samples were mounted on molybdenum sample holder sheets of 0.2 mm thickness with a circular hole of 5 mm in diameter. The samples were supported and sealed within Kapton tape on each side of the sample holder to avoid any change in oxidation state of the samples. They were mounted inside a glovebox. All ASAXS measurements were integrated and corrected for detector responsivity and sample transmission. For each measurement a sample of Ag-behenate powder was measured as a standard for the q -axis in order to merge the curves measured at two different distances. Additionally, a glassy carbon standard was measured for all samples to convert the measured intensities to an absolute scale. The anomalous scattering contribution caused by the Ti containing structures was separated by using the method described in Haas *et al.*⁴⁵. The curves for the scattered intensity $I(q, E_i)$ were fitted simultaneously for all energies, assuming spherical particles, according to:

$$I(q, E_i) = \Delta\rho^2(E_i) \int N(r)\Psi^2(r, q)dr + Kq^{-x} + B(E_i) \quad (1)$$

where $\Delta\rho(E_i)$ is the electron density difference between particles and matrix, $N(r)$ the particle size distribution, r the particle radius and $\psi(r, q)$ the form factor for spherical particles. The term

Kq^{-x} summarizes scattering contributions from larger constituents, while $B(E_i)$ describes the energy-dependent background (fluorescence and resonant-Raman scattering) and the scattering originating from surface roughness and large scale correlations of the powder. The form factor for spheres was given by:

$$\Psi(r, q) = \frac{4}{3} \pi r^3 \frac{\sin(qr) - qr \cos(qr)}{(qr)^3} \quad (2)$$

To account for the polydispersity of Ti-containing particles in the hydride matrix, a normalized log-normal distribution was assumed:

$$N(r) = \frac{1}{\sqrt{2\pi\sigma} r} \exp\left[-\frac{\ln(r/R)^2}{2\sigma^2}\right] \quad (3)$$

with σ being the standard deviation of the distribution and R the mean radius. For the fitting procedure of the volume-weighted size distribution, the program SASfit has been used⁴⁶.

2.3. Thermodynamic calculations

To determine the nature of the Al and Ti containing species, thermodynamic calculations were carried out using the HSC Chemistry software⁴⁷. The calculations were done based on the reactivity of the Li-RHC_d/Li-RHC_a with 3TiCl₃.AlCl₃, respectively, under different temperature and pressure conditions. The most favorable reactions were identified through a combination of Gibbs minimization equilibrium with selected solid and gas species. The obtained results represent ideal phase equilibrium compositions useful to predict possible reaction mechanisms between the Li-RHC_d/Li-RHC_a matrix and the additive involving solid products and gaseous species such as B₂H₆, B_xH_y (x= 5 to 12, y = 5 to 14) and B_xH_yCl_z (x= 1, y = 1 and 2, z = 1 and 2). For all the calculations the solid orthorhombic LiBH₄ (Pnma) was taken into account. Al-Ti alloys as well as MB₂ (M = Ti and Al) were considered as possible products. Li₂B₁₂H₁₂ was not taken into account owing to the lack of available physicochemical data.

3. RESULTS

3.1. Volumetric and calorimetric investigations

The influence of the amounts of the additive on the first non-isothermal dehydrogenation behavior as well as on the kinetic rates of the undoped and doped Li-RHC_a mixtures have been investigated in a volumetric Sieverts apparatus (Fig. 1). In Fig. 1A the effect of two different additives (TiCl₃ and 3TiCl₃.AlCl₃) in the Li-RHC_a system are compared. The dehydrogenation reactions of all samples occur in two consecutive steps. The first step corresponds to the dehydrogenation of MgH₂ to Mg and releases approximately 2.8 wt.% of hydrogen. In the second step, the reaction between Mg and LiBH₄ to form MgB₂ and LiH takes place with the release of about 8.5 wt.% of H₂¹⁷. In the case of the undoped Li-RHC_a (Fig. 1A(a), B(a)), a long incubation period of about 10 hours is observed between the two dehydrogenation steps. This long interval between the two reaction steps is considerably reduced for the case of Li-RHC_a+7.5TiCl₃ and Li-RHC_a+7.5(3TiCl₃.AlCl₃), as can be seen in Fig. 1A(b) and (c). From the literature, it is well known that the addition of TiCl₃ to Li-RHC notably enhances its kinetic behavior^{16,31,48}. However, for future use of such a material in mobile applications, TiCl₃ cost (~ 80 USD/g) is a major constraint for the design of a solid-state hydrogen storage reservoir⁴⁹. For these reasons, a Ti based cost efficient additive composed of 3TiCl₃.AlCl₃ (~ 0.50 USD/g) is here utilized⁵⁰. Fig. 1B shows clearly that the increase in the molar amount of the cost effective 3TiCl₃.AlCl₃ additive from 7.5 to 30 mol % of added Cl⁻ avoids the described incubation period. However, as a consequence of the increased amount of the 3TiCl₃.AlCl₃ additive, the hydrogen capacity considerably decreases from about 10 wt.% to 8 wt.% H₂.

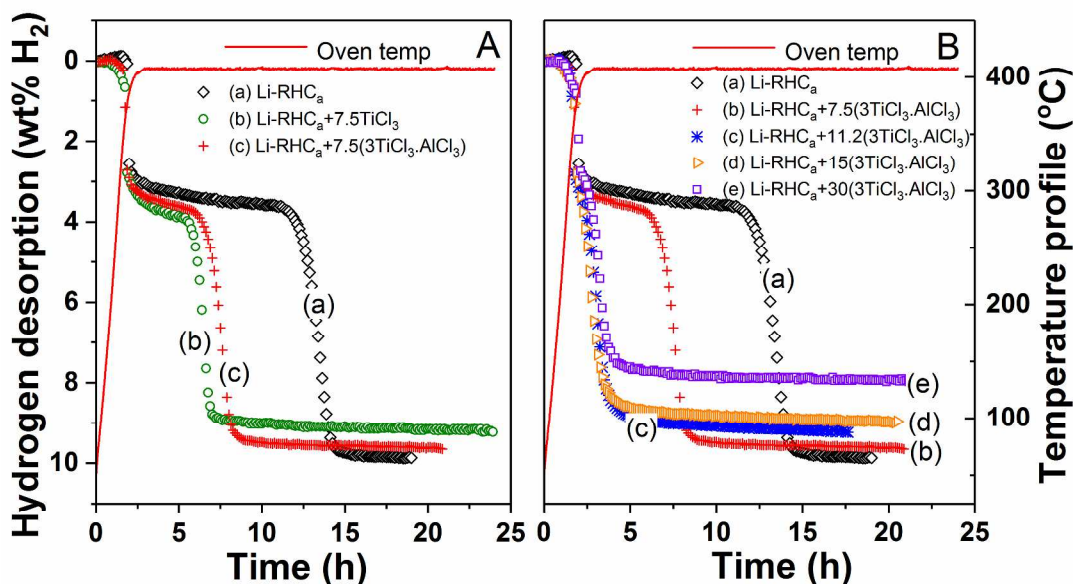


Figure 1. First dehydrogenation reaction of the Li-RHC_a composite systems measured from RT to 400°C, heating rate 3 °C/min, under P_{H₂}= 3 bar. **A** (a) undoped Li-RHC_a; (b) Li-RHC_a+7.5TiCl₃, (c) Li-RHC_a+7.5(3TiCl₃.AlCl₃). **B** (a) undoped Li-RHC_a, (b) Li-RHC_a+7.5(3TiCl₃.AlCl₃), (c) Li-RHC_a+11.2(3TiCl₃.AlCl₃), (d) Li-RHC_a+15(3TiCl₃.AlCl₃), (e) Li-RHC_a+30(3TiCl₃.AlCl₃).

Several samples composed of Li-RHC_a and Li-RHC_d plus different contents of 3TiCl₃.AlCl₃ and TiCl₃ additives have been cycled 20 times (ESI Fig. S1). Fig. 2 summarizes the evolution of the hydrogen capacity for the tested compositions. The addition of both additives (TiCl₃ and 3TiCl₃.AlCl₃) has a clear beneficial effect on the hydrogen storage capacity of the Li-RHC_d (Fig. 2B) rather than on Li-RHC_a (Fig. 2A, ESI Table S2). The Li-RHC_d+7.5(3TiCl₃.AlCl₃) material possesses the highest hydrogen capacity, i.e. around 9.5 wt.% H₂, and a stable cycling behavior, i.e. the loss of capacity is smaller than 1 wt.%. The reduced capacity over the cycling period for most of the Li-RHC_a compositions is above 1 wt.% (Fig. 2A(a)-(c), ESI Table S2), except for the system with large amount of additive (Fig. 2A(d), ESI Table S2). In contrast, when starting from

the desorbed state (Li-RHC_d) with 7.5TiCl₃, 7.5 and 30(3TiCl₃.AlCl₃) exhibit a drop of capacity below 1 wt.% (Fig. 2B(a), (c), (d), ESI Table S2). The Li-RHC_d+3.7(3TiCl₃.AlCl₃), instead, shows the largest decrease of capacity (> 2 wt.%) upon cycling (Fig. 2B(b), ESI Table S2). Fig. 2A and 2B also show that hydrogen capacity is not always in correlation with the amount of additive, i.e. some compositions with lower amount of additive exhibit decreased hydrogen capacities (Fig. 2A(b) and Fig 2B(b)). In addition, the material Li-RHC_d+3.7(3TiCl₃.AlCl₃) exhibits a fast deterioration of the reversible hydrogen capacity. These facts can be attributed to the non-homogenous distribution of the additive all over the base material (Li-RHC).

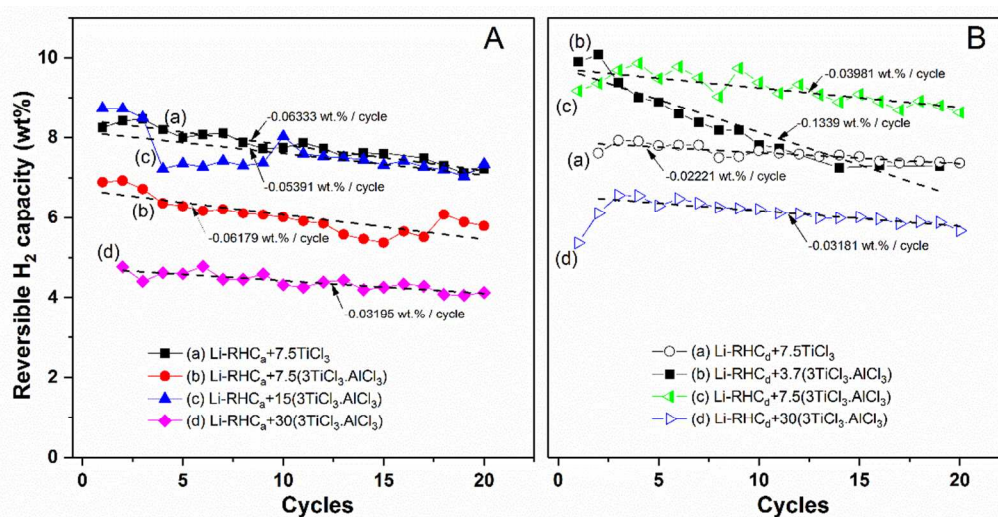


Figure 2. Reversible hydrogen storage capacities versus number of cycles based on the desorption curves. Cycling process preformed at 350 °C and 400 °C under 50 bar and 3 bar of H₂ for the hydrogenation and dehydrogenation, respectively. **A** sample prepared in the hydrogenated state (Li-RHC_a). **B** sample prepared in the dehydrogenated state (Li-RHC_d).

Fig. 3 shows the time required to reach 95% of the total hydrogen storage capacity during hydrogenation and dehydrogenation. In the case of the TiCl₃ additive, Li-RHC_a+7.5TiCl₃ presents better hydrogenation-dehydrogenation kinetic performance than Li-RHC_d+7.5TiCl₃ (ESI Table S2). As seen in Fig. 3A(a) and B(a), the material Li-RHC_a+7.5(3TiCl₃.AlCl₃) exhibits

the slowest kinetic performance. However, the Li-RHC_d+7.5(3TiCl₃.AlCl₃) material possesses the shortest hydrogenation-dehydrogenation times (~ 30 min). A further increment of the amount of 3TiCl₃.AlCl₃ does not lead to faster kinetic behavior.

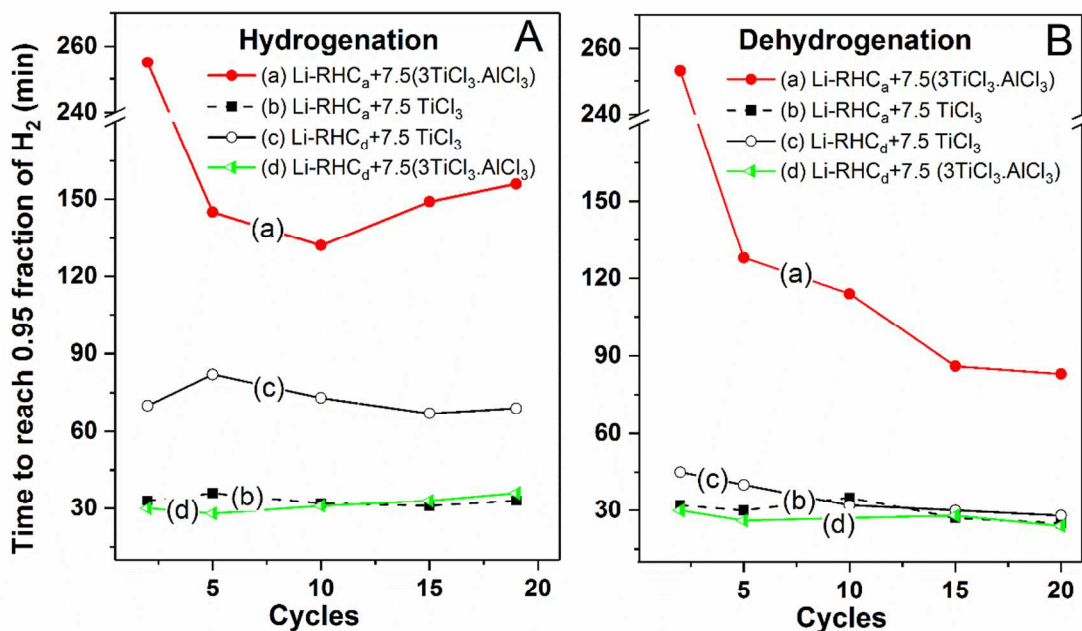


Figure 3. Time to reach 95% of the maximum hydrogen content versus the number of cycles: **A** hydrogenation from the 2nd to the 19th cycle and **B** dehydrogenation from 2nd to 20th cycle. The cycling process is performed at 350 °C and 400 °C, under 50 bar and 3 bar of H₂ for the hydrogenation and dehydrogenation, respectively. The hydrogen fraction was determined from the normalization of the kinetic curves taking as a reference the actual hydrogen capacity.

Calorimetric measurements coupled with Sieverts apparatus for Li-RHC_d, Li-RHC_d+7.5TiCl₃ and Li-RHC_d+7.5(3TiCl₃.AlCl₃) (ESI Fig. S2) show endothermic events related to the LiBH₄ phase transition (event I), LiBH₄ melting (event II) and hydrogen release (events III and IV)^{51,52}. Events (I and II) are slightly shifted toward lower temperatures in the doped materials. Events III and IV are associated to the dehydrogenation reaction of MgH₂ and LiBH₄ e with simultaneous

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3 formation of MgB_2 , respectively^{17,52}. These endothermic events related to the hydrogen release
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5 are in agreement with the coupled Sieverts measurements in the range of temperatures between
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7 330 °C and 450 °C. The dehydrogenation temperature of MgH_2 is roughly 20 °C lower in the
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9 doped hydrogenated materials $\text{Li-RHC}_d+7.5(3\text{TiCl}_3.\text{AlCl}_3)$ and $\text{Li-RHC}_d+7.5\text{TiCl}_3$ (ESI Fig.
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11 S2(b) and (c)) in comparison to the undoped hydrogenated Li-RHC_d (ESI Fig. S2(a)). The onset
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13 temperature for the decomposition of LiBH_4 in the doped materials is at about 390 °C whereas
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15 that for the undoped material is at around 440 °C. From the volumetric curves, it is clear that the
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17 dehydrogenation processes for the doped materials are almost completed (ESI Fig. S2(e) and (f))
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19 when reaching the final temperature of 450 °C. However, for the undoped material the second
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21 step of the dehydrogenation barely starts at 450 °C with a release of hydrogen of just 3.0 wt.%
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23 (ESI Fig. S2(d)).
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28 **3.2. Characterization of the crystalline and non-crystalline phases: *ex situ*, *in situ* PXD** 29 30 **and ^{11}B MAS-NMR measurements**

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33 The $\text{Li-RHC}_d+7.5(3\text{TiCl}_3.\text{AlCl}_3)$ material has the best performance in terms of hydrogen
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35 storage capacity, kinetic behavior and stability upon cycling (Fig. 2 and 3, ESI Table S2). In
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37 addition, it presents enhanced thermal properties in comparison with the undoped material (ESI
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39 Fig. S2). Hence, the material containing $7.5(3\text{TiCl}_3.\text{AlCl}_3)$ has been characterized and compared
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41 with the doped TiCl_3 material with the same amount of Cl (7.5TiCl_3). Fig. 4 shows the *ex situ*
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43 PXD (A) diffraction patterns and ^{11}B MAS NMR spectra (B) of the $\text{Li-RHC}_d+7.5(3\text{TiCl}_3.\text{AlCl}_3)$
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45 and $\text{Li-RHC}_d+7.5\text{TiCl}_3$ after milling and cycling. The patterns of the $\text{Li-RHC}_d+7.5(3\text{TiCl}_3.\text{AlCl}_3)$
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47 and $\text{Li-RHC}_d+7.5\text{TiCl}_3$ after milling (Fig. 4A(a), 4A(c)) exhibit reflections of MgB_2 , LiH and
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49 LiCl. After 20 cycles, the samples in dehydrogenated states (Fig. 4A(b) and (d)) show the
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51 presence of the phases found after milling and free Mg (always present in the as received MgB_2).
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3 *In situ* PXD measurement during heating, hydrogenation, dehydrogenation and cooling for the
4 Li-RHC_d+7.5(3TiCl₃.AlCl₃) sample after previous 20 cycles has been performed (ESI Fig. S3).
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8 At room temperature and during heating up to 350 °C, MgB₂, LiH, LiCl and elemental Mg are
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10 found. Upon hydrogenation at 350 °C under 50 bar H₂, the disappearance of residual Mg and
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12 MgB₂ are followed by the formation of MgH₂. At these temperatures, LiBH₄ is not observed
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14 because it is in its molten state. At the end of the isothermal period at 50 bar H₂ pressure, the
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16 reflections of unreacted MgB₂ are still visible. However, the LiCl peaks are not visible anymore.
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19 After decreasing the pressure to 5 bar H₂ and increasing the temperature up to 400 °C, Mg and
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21 then MgB₂ reflections appear^{17,24}. During the cooling period, the reappearance of the LiCl at
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23 275 °C is noticed. In the case of the material prepared in hydrogenated state (i.e. Li-
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25 RHC_a+7.5(3TiCl₃.AlCl₃) and Li-RHC_a+7.5TiCl₃), both the *ex situ* and *in situ* PXD (ESI Fig. S4
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27 and S5) show similar behavior as the material prepared starting from the dehydrogenated state
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29 (Li-RHC_d). The *ex situ* PXD of the material after milling (ESI Fig. S4) exhibits the presence of
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31 LiBH₄, MgH₂ and LiCl, while after 20 cycles the material in desorbed state shows the presence
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33 MgB₂, LiH, LiCl and free Mg. Moreover, the *in situ* PXD for the dehydrogenation mechanism
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35 starting from as-milled Li-RHC_a+7.5(3TiCl₃.AlCl₃) is similar to the one described above for the
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37 Li-RHC_d+7.5(3TiCl₃.AlCl₃) after 20 cycles (ESI Fig. S5). Interestingly, the presence of the
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39 additives, i.e. TiCl₃, 3TiCl₃.AlCl₃, and crystalline Ti and Al containing phases, are not detected
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41 by PXD (Fig. 4A, ESI Fig. S3-S5).
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47 ¹¹B MAS NMR spectra of the milled and the cycled Li-RHC_d+7.5(3TiCl₃.AlCl₃) and Li-
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49 RHC_d+7.5TiCl₃ materials are shown in Fig. 4B. The spectra of the ball milled samples (Fig. 4B
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51 (a) and 4B (c)) are nearly identical and are dominated by the central-transition resonances from
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53 MgB₂ with the centerband resonance at 100.3 ppm. In addition, the analysis of central transition
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intensities of the spectra show a low-intensity centerband resonance is observed at 5.2 ppm, which constitutes 8.4 % and 5.1 % of the total ^{11}B NMR intensity for the as-milled $\text{Li-RHC}_d+7.5(3\text{TiCl}_3.\text{AlCl}_3)$ and $\text{Li-RHC}_d+7.5\text{TiCl}_3$ materials, respectively.

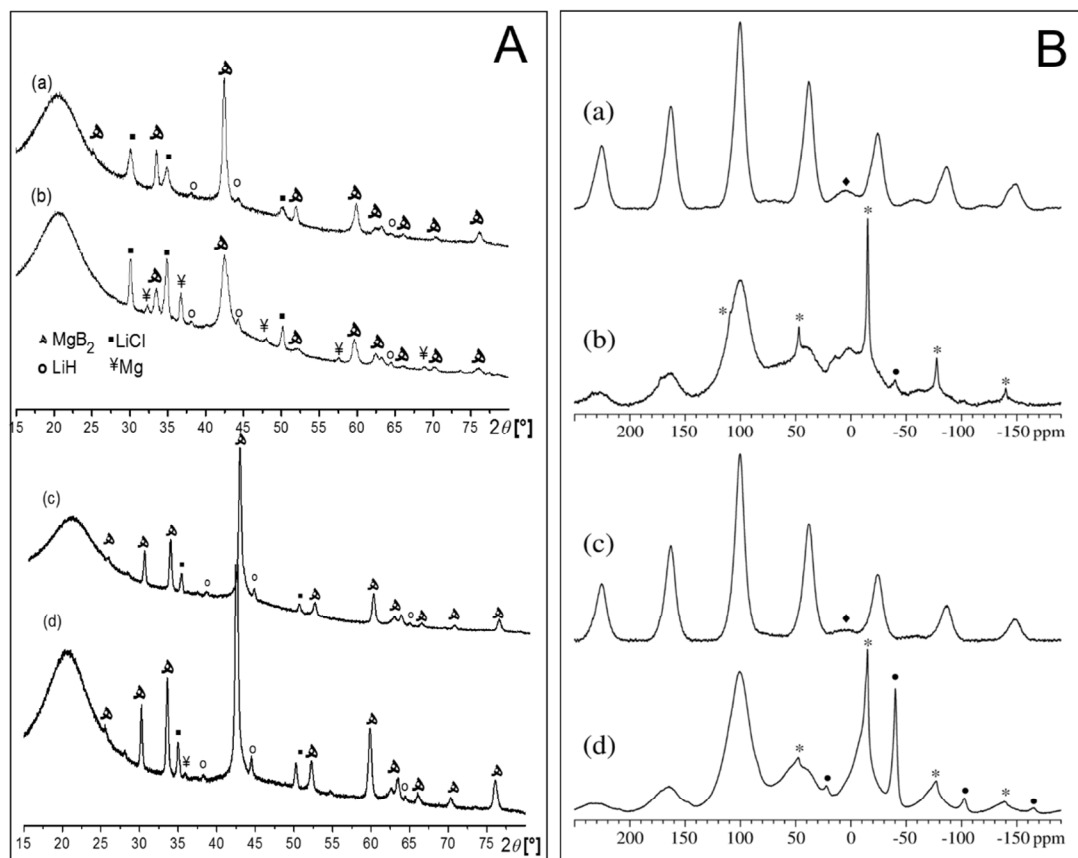


Figure 4. A *Ex situ* PXD and B ^{11}B MAS NMR spectra (14.1 T, $\nu\text{R} = 12.0$ kHz) of the doped samples prepared in the dehydrogenated state: (a) $\text{Li-RHC}_d+7.5(3\text{TiCl}_3.\text{AlCl}_3)$ after milling, (b) $\text{Li-RHC}_d+7.5(3\text{TiCl}_3.\text{AlCl}_3)$ after the 20th cycle, (c) $\text{Li-RHC}_d+7.5\text{TiCl}_3$ after milling and (d) $\text{Li-RHC}_d+7.5\text{TiCl}_3$ after the 20th cycle. The diamonds (♦) indicate the 5.2 ppm centerband, observed for the two ball-milled samples, whereas centerband and spinning sideband resonances from $\text{Li}_2\text{B}_{12}\text{H}_{12}$ and LiBH_4 are indicated by asterisks (*) and solid circles (●), respectively.

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5 The ^{11}B NMR spectra of the cycled materials (Fig. 4B (b) and 4B (d)) are more complicated
6 because of overlapping resonances (centerbands and spinning sidebands) of the boron-containing
7 phases. In addition to MgB_2 , which is still the dominate phase in both cycled materials,
8 resonances from unreacted $\text{Li}_2\text{B}_{12}\text{H}_{12}$ at -15.2 ppm and LiBH_4 at -40.5 ppm are also observed.
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10 For the $\text{Li-RHC}_d+7.5(3\text{TiCl}_3.\text{AlCl}_3)$ material (Fig. 4B (b)), two additional centerbands appear at
11 2.4 ppm and 15.9 ppm, which could not be assigned to any specific phase and are thus, denoted
12 unknown phases, UP(1) and UP(2), respectively. The 2.4 ppm peak might potentially originate
13 from AlB_2 , following an earlier ^{11}B NMR spectrum obtained for this phase at identical
14 conditions. A deconvolution of the central transition region for the cycled Li-
15 $\text{RHC}_d+7.5(3\text{TiCl}_3.\text{AlCl}_3)$ material, including centerbands and spinning sidebands, gives the
16 following relative ^{11}B NMR intensities for the individual phases: 63.0 % MgB_2 , 12.2 %
17 $\text{Li}_2\text{B}_{12}\text{H}_{12}$, 0.6 % LiBH_4 , 20.9 % UP(1) and 3.3 % UP(2). The UP(1) and UP(2) resonances are
18 not identified for the cycled $\text{Li-RHC}_d+7.5\text{TiCl}_3$ material (Fig. 4B (d)), which on the contrary
19 includes a new resonance at approx. -6.3 ppm (UP(3)). This resonance is clearly visible as a
20 high-frequency shoulder to the narrow centerband resonance from $\text{Li}_2\text{B}_{12}\text{H}_{12}$ at -15.2 ppm, which
21 gives a strong contribution to the spinning sidebands at 50 ppm, -30 ppm, and -135 ppm. A
22 simulation of this spectrum results in the relative intensities: 59.2 % MgB_2 , 7.1 % $\text{Li}_2\text{B}_{12}\text{H}_{12}$,
23 6.5 % LiBH_4 , and 27.3 % UP(3). A resonance from TiB_2 at -4.9 ppm is expected for all cycled
24 samples. However, this signal is not observed in the NMR spectra.
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49 **3.3. Nanostructure and distribution of the Ti-rich phase: ASAXS measurement**

50 The volume weighted size distributions of the Ti rich nanosized particles obtained by ASAXS
51 measurements for the as-milled and cycled Li-RCH_d plus TiCl_3 and $(3\text{TiCl}_3.\text{AlCl}_3)$ samples are
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3 shown in Fig. 5. Li-RHC_d+7.5TiCl₃ in the as-milled state has been measured as a reference
4 sample and the resulting ASAXS curves are shown in ESI Fig. S6, exemplarily. At q -values
5 around 1 nm⁻¹ the curves show a clear resonant scattering structure. At very high q -values above
6 about 2.5 nm⁻¹, incoherent and inelastic scattering contributions limit the further decrease of the
7 scattered intensity. In the lower q -region the curves become off-resonant and follow a power law
8 behavior. The exponent of the power-law amounts to 3.6, implying mass fractals with dense bulk
9 and rough surfaces. Fig. 5 shows that the as-milled Li-RHC_d+7.5TiCl₃ and Li-
10 RHC_d+7.5(3TiCl₃.AlCl₃) mainly differ in their polydispersity. The normalized standard
11 deviation of the size distribution for as-milled Li-RHC_d+7.5TiCl₃ is 0.38 whereas the
12 corresponding value for the as-milled Li-RHC_d+7.5(3TiCl₃.AlCl₃) amounts to 0.57, which is
13 around 33 % larger. The mean radius for as-milled Li-RHC_d+7.5TiCl₃ is around 3.6 nm while
14 this value is about 32 % (5.3 nm) larger for the as-milled Li-RHC_d+7.5(3TiCl₃.AlCl₃). For the
15 Li-RHC_d+7.5(3TiCl₃.AlCl₃) material after 20th cycles, the mean nanoparticle radius after 20
16 cycles decreases to about 3.5 nm. Increasing the amount of the 3TiCl₃.AlCl₃ additive does not
17 change significantly the size distribution as seen for Li-RHC_d+30(3TiCl₃.AlCl₃).
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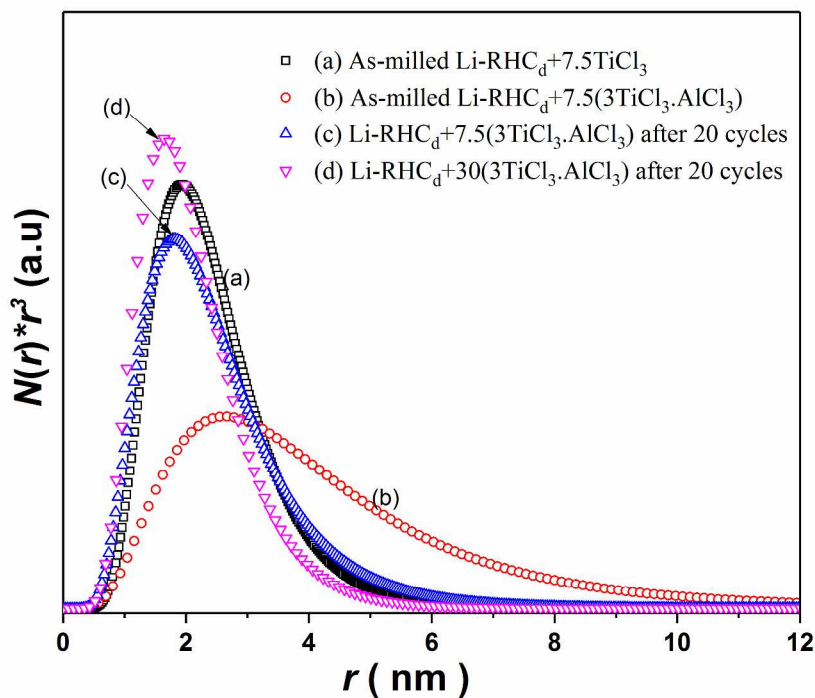


Figure 5. Volume weighted size distributions of Ti rich - nanosized particles obtained by ASAXS for (a) as-milled $\text{Li-RHC}_d+7.5\text{TiCl}_3$, (b) as-milled $\text{Li-RHC}_d+7.5(3\text{TiCl}_3.\text{AlCl}_3)$, (c) $\text{Li-RHC}_d+7.5(3\text{TiCl}_3.\text{AlCl}_3)$ after 20 cycles, (d) $\text{Li-RHC}_d+30(3\text{TiCl}_3.\text{AlCl}_3)$ after 20 cycles.

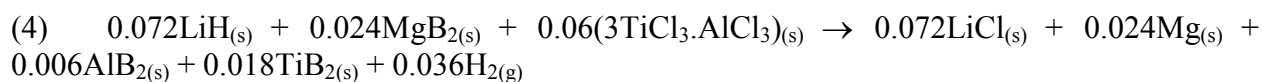
4. DISCUSSION

Hydrogen storage properties of Li-RHC have been notably improved by the addition of $3\text{TiCl}_3.\text{AlCl}_3$ (section 3.1). It has been shown that the $\text{Li-RHC}_d+7.5(3\text{TiCl}_3.\text{AlCl}_3)$ material exhibits the best performance upon cycling with a stable capacity of about 9.5 wt. % H_2 and reduced hydrogenation and dehydrogenation times of about 30 min. The characterization of the crystalline and non-crystalline phases in the $\text{Li-RHC}_d+7.5(3\text{TiCl}_3.\text{AlCl}_3)$ after milling and cycling has been performed via *ex situ* and *in situ* PXD (Fig. 4A, ESI Fig. S3-S5) and ^{11}B MAS NMR (Fig. 4B), respectively. ASAXS results (Fig. 5) show that Ti rich nanosized particles are dispersed in the sample. Therefore, to shed light on the nature of the additive within the hydride system and to understand the reasons laying behind the observed beneficial effect on the

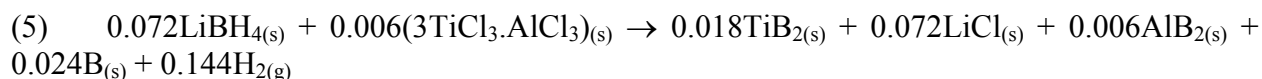
material's hydrogenation/dehydrogenation properties, the collected results are herein discussed in detail.

4.1. Phase equilibrium compositions: Thermodynamic calculations

In order to infer the crystalline and amorphous phases obtained by the interaction of Li-RHC and $3\text{TiCl}_3\cdot\text{AlCl}_3$, phase composition equilibrium calculations based on the Gibbs free energy minimization have been carried out with the HSC Chemistry software⁴⁷. Taking into account the experimental results obtained from the characterizations of the materials (Fig. 4A and B, ESI Fig. S3-S5), the calculations for $\text{Li-RHC}_d+7.5(3\text{TiCl}_3\cdot\text{AlCl}_3)$ and $\text{Li-RHC}_a+7.5(3\text{TiCl}_3\cdot\text{AlCl}_3)$ materials under different conditions such as mechanical milling (MM), first hydrogenation and first dehydrogenation have been performed. In several works²⁵⁻³⁴, it has been proposed the formation of transition metal borides from the interaction between the Li-RHC material and transition metal based compounds. For the Li-RHC doped with $3\text{TiCl}_3\cdot\text{AlCl}_3$ (ESI Table S3), the calculations show that the formation of TiB_2 and AlB_2 upon milling is thermodynamically feasible for both the dehydrogenated (Li-RHC_d) and hydrogenated (Li-RHC_a) states as shown in reaction (4) and (5), respectively. These boride species remain stable upon cycling (ESI Table S3).



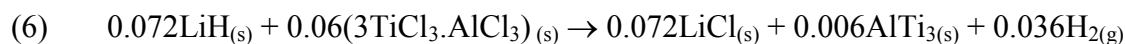
$$\Delta G_{1\text{bar}, 25^\circ\text{C}} = -10.9 \text{ kJ}$$



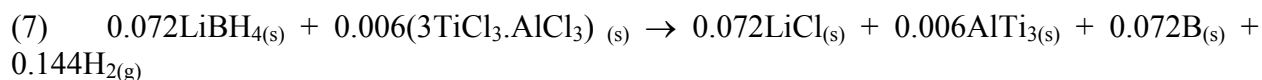
$$\Delta G_{1\text{bar}, 25^\circ\text{C}} = -4.4 \text{ kJ}$$

Instead, if we consider the possible formation of Al-Ti alloys (ESI Table S4), the phase composition equilibrium calculations hint at the formation of the AlTi_3 alloy during milling as

described in reactions (6) and (7) for the Li-RHC_d and Li-RHC_a, respectively. The calculations also suggest that this AlTi₃ alloy remains stable upon cycle once formed (ESI Table S3).



$$\Delta G_{1\text{bar}, 25^\circ\text{C}} = -7.6 \text{ kJ}$$



$$\Delta G_{1\text{bar}, 25^\circ\text{C}} = -3.5 \text{ kJ}$$

The formation of titanium boride species (TiB₂ and AlB₂) is thermodynamically more favorable than the formation of the AlTi₃ alloy. Nonetheless, the characterization of the materials evidences certain discrepancy with the formation of the transition metal boride species (Fig. 4, ESI Fig. S3-S5). In the case of Li-RHC_d+7.5(3TiCl₃.AlCl₃) and Li-RHC_a+7.5(3TiCl₃.AlCl₃), the diffraction patterns after milling do not show the presence of free Mg as proposed in reaction (4), unless this phase is not detected due to its low amount (Fig. 4A(a) and Fig. S4 A(a)). Additionally, the NMR spectrum of the Li-RHC_d+7.5(3TiCl₃.AlCl₃) material after cycling does not evidence clearly the presence of any transition metal boride species (Fig. 4 B (b)). On the contrary, the formation of the AlTi₃ alloy after milling and after cycling appears to be likely (Fig. 4A(a), (b) and 4B(a) and (b)) since neither the presence of free Mg nor the formation of transition metal boride species are included in reactions (6) and (7). Therefore, the formation of TiB₂ and AlB₂ might be kinetically restricted, so that the formation of the AlTi₃ alloy takes place.

4.2. Nature of the nanosized additive: HR-TEM

Experimental results indicate that the additive (3TiCl₃.AlCl₃) interacts with Li-RHC (Fig. 4) and provides the *in situ* formation of nanostructured Ti-rich phase distributed on the MgB₂ particles (ESI Fig. S7). The phase equilibrium thermodynamic calculations suggest that the

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3 nanosized Ti-rich phase is composed of Al and Ti, specifically AlTi_3 alloy. Therefore, to verify
4 the nature of the nanosized Ti-rich phase, HR-TEM observations combined with the analysis of
5 the fast Fourier transformation analysis (FFT) and simulations of the electron diffraction pattern
6 (DP) in Zone Axis (ZA) condition have been performed on several particles. Fig. 6 shows the
7 HR-TEM micrographs and their respective analysis (FFT and simulated DP). The presence of
8 nanosized particles of hexagonal AlTi_3 and cubic AlTi_2 is observed in the material after milling
9 (Fig. 6A). Upon cycling (Fig. 6B and C), hexagonal AlTi_3 and cubic AlTi_2 are still seen and the
10 appearance of cubic AlTi_3 is noticed. The same Al-Ti alloys as for the Li-
11 $\text{RHC}_a+7.5(3\text{TiCl}_3.\text{AlCl}_3)$ are also observed (ESI Fig. S8). It is important to point out that the
12 most frequently identified nanoparticles belong to the hexagonal AlTi_3 phase. Moreover, Mg-Al
13 alloys, Mg-Al-B compounds as well as TiB_2 and AlB_2 have not been identified *via* HR-TEM.
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28 These HR-TEM observations confirm the formation of nanosized AlTi alloys, mainly the
29 hexagonal AlTi_3 , as predicted with the equilibrium thermodynamic calculations as shown in
30 reaction (6) and (7), and in ESI Table S3 and S4. This is in concordance with the PXD analysis
31 (Fig. 4A(a) and (b)) since no Al-Ti crystalline phase has been detected. NMR spectra (Fig. 4B)
32 show the presence of a peak that might belongs to AlB_2 (UP1) and of another peak which cannot
33 be attributed to any boron containing species (UP2). Considering the HR-TEM observation, it is
34 possible to discard AlB_2 as a potentially or at least dominantly formed phase. Regarding the size
35 of the Al-Ti alloys nanoparticles, it is possible to see in Fig. 6 that the sizes of the hexagonal
36 AlTi_3 after milling and cycling are in the range of 1 to 10 nm and 1 to 5 nm, respectively. These
37 findings are in good agreement with the SAXS results (Fig. 5).
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51 **4.3. Effect of the $3\text{TiCl}_3.\text{AlCl}_3$ additive on Li-RHC**

52 **4.3.1. Interfacial energy minimization: d-value mismatch**

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3 In the previous section, the *in situ* formation of AlTi alloys (Section 4.2) has been verified by
4 HR-TEM observation. It has been reported that phases with similar crystal structure as MgB₂ can
5 act as heterogeneous nucleation sites for its formation²⁵. Several transition metal borides such as
6 TiB₂, NbB₂ and VB₂ are able to provide coherent interfaces to enhance the heterogeneous
7 nucleation and growth of hexagonal MgB₂^{25-32,53}. There are three necessary requirements for an
8 effective heterogeneous nucleation: the most important is a low interfacial energy between the
9 nucleation agent and the nucleate new phase (MgB₂), the second is sufficiently high amount of
10 the nucleation agent and the third is the homogenous distribution of the nucleation agent^{25,54,55}. A
11 sufficient condition for interfacial energy minimization is a minimized lattice mismatch in
12 consecutive atom rows across an interface. To achieve the minimized lattice mismatch condition,
13 the inter-planar spaces (d-value) between the closed-packed planes of the nucleation agent and
14 the MgB₂ should be lower than the critical d-value mismatch of 6 %⁵⁴. In our case, no
15 transition-metal boride species have been detected as a product of the interaction between Li-
16 RHC material and the 3TiCl₃.AlCl₃ additive (Fig. 4 and Fig. 6). For this reason and considering
17 that the AlTi alloys can potentially act as an effective heterogeneous nucleation center for MgB₂,
18 their d-value mismatches have been calculated. These parameters have been determined from
19 the diffraction cards of the AlTi alloys determined via HR-TEM (Fig. 6): hexagonal-AlTi₃ (ICSD
20 191189), cubic-AlTi₃ (ICSD 189695) and cubic-AlTi₂ (ICSD 189696). The d-value mismatch
21 for the closed-packed planes between the AlTi alloys and MgB₂ are: MgB₂{1011}//hexagonal-
22 AlTi₃{2021} = 3.3 %; MgB₂{1010}//cubic-TiAl₃{2020} = 31.9 % and MgB₂{1010}//cubic-
23 TiAl₂{2020} = 35.0 %. As seen, the hexagonal AlTi₃ phase, the most frequent identified phase,
24 shows a suitable d-value mismatch well below 6 %. Thus, it fulfils the first above-mentioned
25 requirement for an efficient heterogeneous nucleation of MgB₂. Moreover, based on the observed
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kinetic improvement of the $\text{Li-RHC}_d+7.5(3\text{TiCl}_3.\text{AlCl}_3)$ (Fig. 3) and according to the ASAXS (Fig. 5), EDS in STEM-HAADF mode (ESI Fig. S7) and HR-TEM results (Fig. 6), the *in situ* formed nanosized hexagonal- AlTi_3 phase covers the second and third requirement since the proper amount of its nanoparticles is well distributed and upon cycling is located on the formed MgB_2 to assure an enhanced heterogeneous nucleation of new MgB_2 seeds.

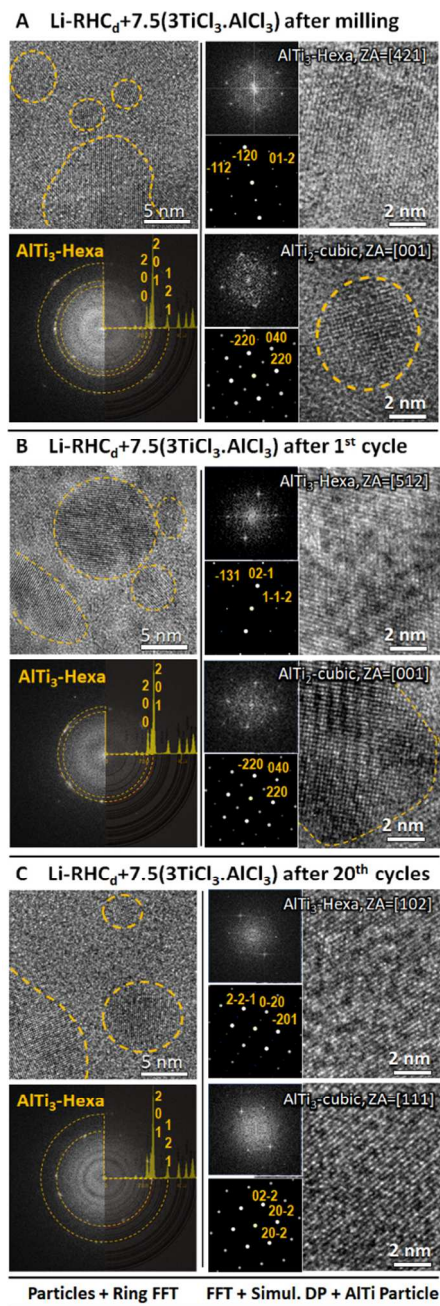
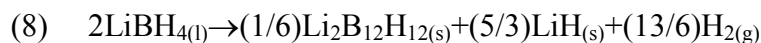


Figure 6. HR-TEM characterization of the nanosized AlTi alloys in Li-RHC_d+7.5(3TiCl₃.AlCl₃) material **A** after milling, **B** after 1st cycle (sample in dehydrogenated state) and **C** after 20th cycle (sample in dehydrogenated state). FFT was calculated in each region and compared to simulated diffraction patterns (DPs) in the adequate orientation; the width of the FFT and corresponding simulations is 18 nm⁻¹. Structure cards: hexagonal AlTi₃ ICSD 191189, cubic AlTi₃ ICSD 189695, cubic AlTi₂ ICSD 189696.

4.3.2. First dehydrogenation of Li-RHC_a: effects on the incubation period

It has been already reported that the reaction pathways of Li-RHC depend on the temperature and hydrogen pressure conditions²⁴. LiBH₄ and MgH₂ individually decompose and do not form MgB₂ under 1 bar of H₂ overpressure in the temperature range from 400 to 450 °C, hindering the reversibility of Li-RHC^{14,24}. The dehydrogenation of Li-RHC proceeds in three steps when it is carried out in the pressure range from 3 to 5 bar of H₂: (1) fast decomposition of MgH₂, (2) incubation period with a small hydrogen release and (3) reaction between free Mg and LiBH₄ to form MgB₂ and LiH. The incubation period is attributed to the reaction (8), which leads to the individual reaction of LiBH₄ into Li₂B₁₂H₁₂ and not to the LiBH₄ decomposition to LiH, B and H₂ (reaction (9)) because of the thermodynamic stability of the reactions, i.e. 56 kJ/mol H₂ and 75 kJ/mol H₂, respectively^{14,56-58}:



As proposed in the literature about LiBH₄ + YH₃^{59,60} and 2LiBH₄ + MgH₂⁵⁷, reaction (8) may not proceed by the intermediate formation of gaseous di-borane (B₂H₆)^{61,62} since the gas overpressure kinetically suppresses its formation. It has been proposed that the sluggish kinetic behavior of the first dehydrogenation of Li-RHC is associated with the formation of Li₂B₁₂H₁₂

(reaction (8)) as an intermediate phase which blocks the direct contact between LiBH_4 and Mg^{14} . It has been found that at 450 °C under 10 bar of H_2 overpressure, the formation of $\text{Li}_2\text{B}_{12}\text{H}_{12}$ is avoided because the equilibrium pressure of reaction (8) is below 10 bar ($\sim 9 \text{ bar}^{10}$), enhancing the dehydrogenation kinetic behavior compared to that at lower overpressure conditions⁵⁷. ^{11}B MAS NMR spectra of as-purchased LiBH_4 , pristine Li-RHC_a and $\text{Li-RHC}_a+15(3\text{TiCl}_3.\text{AlCl}_3)$ materials after milling and partially dehydrogenated are shown in Fig. 7. The pressure conditions selected for the partially dehydrogenated samples are the reported equilibrium pressures for the reaction between Mg and LiBH_4 to form MgB_2 and LiH (3 bar H_2 at 350 °C and 8 bar H_2 at 400 °C)^{63,64}.

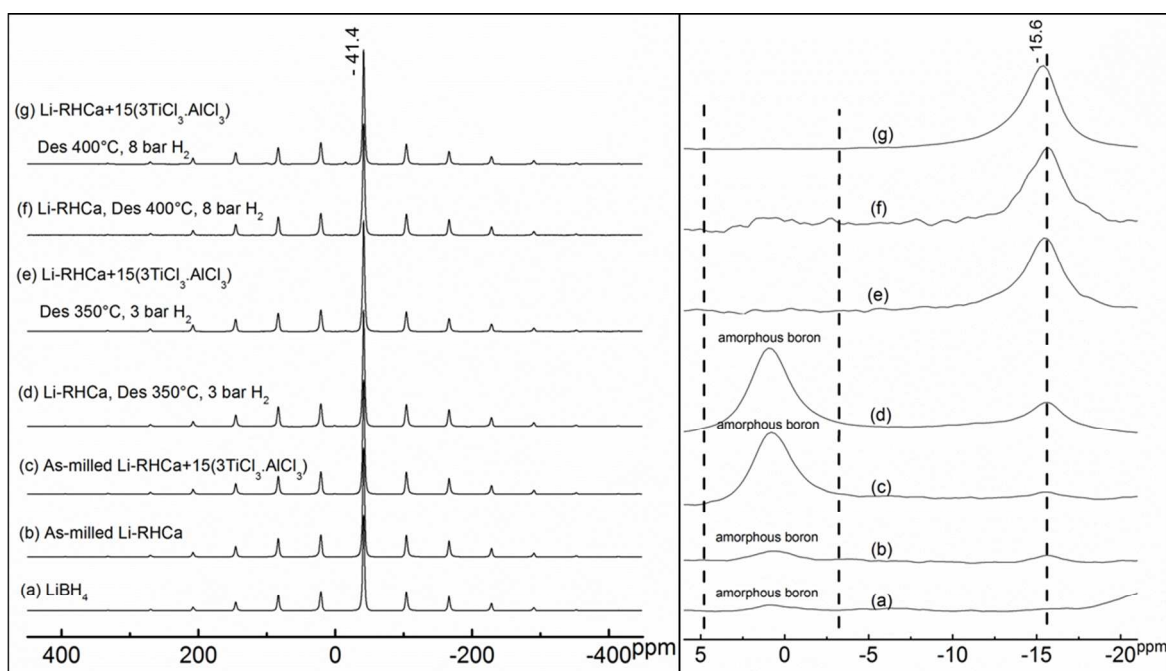


Figure 7. **A** NMR spectra of the (a) as-purchased LiBH_4 , (b) as-milled Li-RHC_a , (c) as-milled $\text{Li-RHC}_a+15(3\text{TiCl}_3.\text{AlCl}_3)$, (d) Li-RHC_a partially dehydrogenated at 350 °C under 3 bar of H_2 , (e) $\text{Li-RHC}_a+15(3\text{TiCl}_3.\text{AlCl}_3)$ partially dehydrogenated at 350 °C under 3 bar of H_2 , (f) Li-RHC_a partially dehydrogenated at 400 °C under 8 bar of H_2 , (g) $\text{Li-RHC}_a+15(3\text{TiCl}_3.\text{AlCl}_3)$ partially dehydrogenated at 400 °C under 8 bar of H_2 . **B** Zoom of **A** between -20 to 5 ppm to

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3 highlight the peaks belonging to $\text{Li}_2\text{B}_{12}\text{H}_{12}$ at about -15 ppm and amorphous boron between –
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5 2.5 ppm and 5 ppm.
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8 Under these conditions, the equilibrium pressures of the reaction (8) (~ 1.5 bar H_2 at 350°C
9 and ~ 4 bar H_2 at 400°C) and reaction (9) (~ 0.5 bar H_2 at 350°C and ~ 1.5 bar H_2 at 400°C) are
10 below to the selected experimental pressures and hence reactions (8) and (9) can be
11 avoided^{10,14,57,58}. It is important to mention that the partially dehydrogenated samples have been
12 taken from the reactor after the dehydrogenation of MgH_2 and after leaving the sample a while
13 where no hydrogen release has been noticed.
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22 The as-purchased LiBH_4 , as-milled Li-RHC_a and as-milled $\text{Li-RHC}_a+15(3\text{TiCl}_3.\text{AlCl}_3)$
23 samples (Fig. 7A(a)-(c)) show strong signals of LiBH_4 at -41.4 ppm and broad peaks originating
24 from amorphous boron. As seen in Fig. 7 B(a), as-purchased LiBH_4 contains just amorphous
25 boron (besides LiBH_4). After milling (Fig. 7 B(b)), the as-milled Li-RHC_a also shows small and
26 broad peaks that belong to $\text{Li}_2\text{B}_{12}\text{H}_{12}$. The addition of $3\text{TiCl}_3.\text{AlCl}_3$ during milling makes
27 possible the formation of a larger amount of boron (Fig. 7 B(c) bigger area of the free boron
28 peak) as a result of the formation of the AlTi alloys (mainly AlTi_3), which is in agreement with
29 the predicted reaction (7) and the experimental results (ESI Fig. S4, S5 and Fig. 6). Therefore,
30 this suggests that the energy transmitted by the grinding medium to the powder during milling is
31 enough to promote two reactions. The first possible reaction is the decomposition of a small
32 amount of LiBH_4 to free boron and $\text{Li}_2\text{B}_{12}\text{H}_{12}$ via two parallel reactions (reactions (8) and (9)).
33
34 The second one is the reaction of the free boron contained in the as-purchased LiBH_4 with LiH
35 stemming from the decomposition of LiBH_4 (as indicated in reaction (9)) to form $\text{Li}_2\text{B}_{12}\text{H}_{12}$ and
36 more free boron. In the case of the as-milled Li-RHC_a after the partial dehydrogenation (Fig. 7
37 (d) and (f)), the presence of free boron (Fig. 7B(d)) and $\text{Li}_2\text{B}_{12}\text{H}_{12}$ is evident (Fig. 7 B(d) and (f)).
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3 Experimental results show that during the first non-isothermal dehydrogenation of the as-milled
4 Li-RHC_a the incubation period does not always last the same time (ESI Fig. S9). It implies that
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6 the incubation period related to the formation of Li₂B₁₂H₁₂ is highly dependent on the nature of
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8 the starting material and the amounts of boron and Li₂B₁₂H₁₂ generated during milling which
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10 seems not to be homogenously distributed in the material. For as-milled Li-
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12 RHC_a+15(3TiCl₃.AlCl₃) after partial dehydrogenation (Fig. 7 B(e) and (g)), just the presence of
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14 Li₂B₁₂H₁₂ is noticed. Ohba *et al.*¹⁰ has calculated that the decomposition of Li₂B₁₂H₁₂ towards
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16 LiH and free B presents a high enthalpy value of 125 kJ/mol H₂. Caputo *et al.*¹² based on first-
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18 principles calculations has reported that the decomposition of LiBH₄ can proceed *via* different
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20 pathways and proposed that the Li₂B₁₂H₁₂ is a product and not an intermediate phase because of
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22 its high stability. Pitt *et al.*⁶⁵ has experimentally confirmed that under vacuum or H₂ overpressure
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24 conditions anhydrous Li₂B₁₂H₁₂ begins to decompose after 250 °C to a substoichiometric
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26 Li₂B₁₂H_{12-x} composition dependent on the amount of hydrogen released. Recently, White *et al.*⁶⁶
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28 has shown that Li₂B₁₂H₁₂ can be converted into metal borides or borides species under harsh
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30 temperature and pressure conditions, e.g. the reaction between Li₂B₁₂H₁₂ and MgH₂ can form
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32 MgB₂ and LiH above 500 °C upon dehydrogenation in vacuum.

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34 As mentioned above, the used temperature and hydrogen pressure conditions for the
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36 preparation of the samples for the NMR measurements (Fig. 7 (d)-(g)) are over the equilibrium
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38 pressures of reaction (8) and (9). In this regard and owing to the high stability of Li₂B₁₂H₁₂, it is
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40 possible to suggest that the small amount of formed Li₂B₁₂H₁₂ upon dehydrogenation can come
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42 from the reaction between LiH, generated during the formation of MgB₂, and the free boron
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44 contained in the as-purchased material and the one generated during the milling process. This
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46 analysis allows a thorough interpretation of the results shown in Fig. 1. For the first non-
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3 isothermal dehydrogenation of Li-RHC_a at 400 °C under 3 bar of overpressure (Fig. 1 A(a)), the
4 incubation period starts at about 400 °C. At these conditions, the equilibrium pressure of reaction
5 (8) is about 4 bar and thus the reaction pathway can undergo to the slow formation of Li₂B₁₂H₁₂
6 and LiH with an insignificant hydrogen release. Moreover, the free boron, already contained in
7 the as-purchased LiBH₄ material and then generated during milling, might react with the already
8 formed LiH to produce more Li₂B₁₂H₁₂, which finally remains stable. The presence of Li₂B₁₂H₁₂
9 precludes the contact between free Mg and LiBH₄ and the fast formation of MgB₂. This process
10 might retard the third step of the dehydrogenation (i.e. the reaction of LiBH₄ with Mg to form
11 MgB₂) until a minimum amount of MgB₂ seeds are formed. In the case of the Li-
12 RHC_a+x(3TiCl₃.AlCl₃) (x = 7.5, 11, 15 and 30) (Fig. 1B), during milling the formation of
13 nanosized AlTi₃ alloy (reaction (7)) produces free boron and Li₂B₁₂H₁₂ as by-products (Fig. 7
14 B(c)). Upon non-isothermal dehydrogenation (Fig. 1B(b)-(e)), a reduced incubation period (Li-
15 RHC_a+7.5(3TiCl₃.AlCl₃)) or the direct fast LiBH₄ decomposition (Li-RHC_a+11, 15,
16 30(3TiCl₃.AlCl₃)) after the MgH₂ dehydrogenation are seen at about 400 °C under 3 bar H₂ of
17 overpressure. The reaction (8) is partially or totally avoided. It is possible to infer that upon the
18 first dehydrogenation the formation of stable Li₂B₁₂H₁₂ occurs as described for the as-milled Li-
19 RHC_a. However, the well-distributed *in situ* formed nanosized AlTi₃ alloy acts as an efficient
20 heterogeneous nucleation agent for the rapid formation of MgB₂ seeds (as shown in Section
21 4.3.1). In spite of the small amount of stable and irreversible Li₂B₁₂H₁₂, the availability of
22 efficient heterogeneous nucleation sites improves the Mg-LiBH₄ contact and avoids the further
23 generation of Li₂B₁₂H₁₂ by accelerating the formation of MgB₂. It is important to point out that
24 in Fig. 2 and 3 the Li-RHC_a shows lower reversible hydrogen capacity and slightly higher
25 deterioration rates than Li-RHC_d upon cycling. This fact may account for the presence of
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3 amorphous boron in as-received LiBH_4 and to the further formation of stable $\text{Li}_2\text{B}_{12}\text{H}_{12}$ during
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6 milling.

7 **4.3.3. Rate limiting step and hydrogenation-dehydrogenation activation energy**

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10 In order to elucidate if the notable kinetic enhancement (Fig. 3 and Fig. S1) of the Li-
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12 $\text{RHC}_d+7.5(3\text{TiCl}_3.\text{AlCl}_3)$ material is related to a change in the rate-limiting step and/or a
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14 decrease in the hydrogenation-dehydrogenation activation energy, gas-solid models have been
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16 applied.
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19 Fig. 8A shows the hydrogenation kinetic curves of the second cycle at 390 °C and their
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21 respective model fittings for the Li- $\text{RHC}_d+7.5(3\text{TiCl}_3.\text{AlCl}_3)$ and Li- RHC_d materials. It is
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23 observed that the presence of the *in situ* formed AlTi alloys clearly increases the hydrogen
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25 uptake rate. In order to identify the proper rate limiting step mechanism for the hydrogenation
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27 process, the Sharp's and Jone's method has been applied: plotting the experimental value of
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29 $(t/t_{0.5})_{\text{experimental}}$ versus the theoretical ones $(t/t_{0.5})_{\text{theoretical}}$ (ESI Fig. S10)^{67,68}. On the one hand, for
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31 all the hydrogenation curves of Li- RHC_d material in the range of temperature between 360 °C
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33 and 400 °C, the Johnson-Mehl-Avrami (JMA) reaction model with $n=1$ (one dimensional
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35 interface-controlled reaction) is the most suitable one⁶⁹. On the other hand, for the Li-
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37 $\text{RHC}_d+7.5(3\text{TiCl}_3.\text{AlCl}_3)$ material in the same range of temperature, the three-dimensional
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39 contracting volume reaction model (R3, three dimensional interface-controlled reaction) fits
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41 better⁷⁰. Both models have been found as rate limiting steps in previous publications^{25,64,71} (ESI
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43 Fig. S10). All hydrogenation curves show good fitting agreements with a correlation coefficient
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45 R^2 near 1 (Fig. 8A, ESI Fig. S11 kinetic curves fitting and fitting parameters for all the
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47 hydrogenation curves). *In-situ* SR-PXD measurements have shown that the hydrogenation
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49 process of the pure Li-RHC is a single step reaction which involves the formation of MgH_2 and
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3 LiBH₄ from MgB₂ and LiH^{17,24} and the same behavior has been observed in the *in situ* SR-PXD
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5 measurement carried out in this work (ESI Fig. S3). Fig. 8 (B and C) presents the hydrogenation
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7 activation energies (E_a) for the single step hydrogen uptake. As seen there, the hydrogenation E_a
8
9 is reduced by about 60 kJ/mol H₂ due to the presence of the additive (Li-RHC_d = 184±6 kJ/mol
10
11 H₂ and Li-RHC_d+7.5(3TiCl₃.AlCl₃) = 124±6 kJ/mol H₂). The markedly improvement in the
12
13 hydrogenation kinetic behavior can be attributed to two main factors: first, the reduced particle
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15 size of MgB₂ down to about 300 nm (ESI Fig. S7A) that leads to a faster MgB₂ consumption;
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17 second, the homogenous distribution of the nanosized particles of AlTi alloys located on the
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19 MgB₂ that prevents the agglomeration, generates more active surface for the hydrogen-material
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21 interaction and enables the faster three dimensional interface movement.
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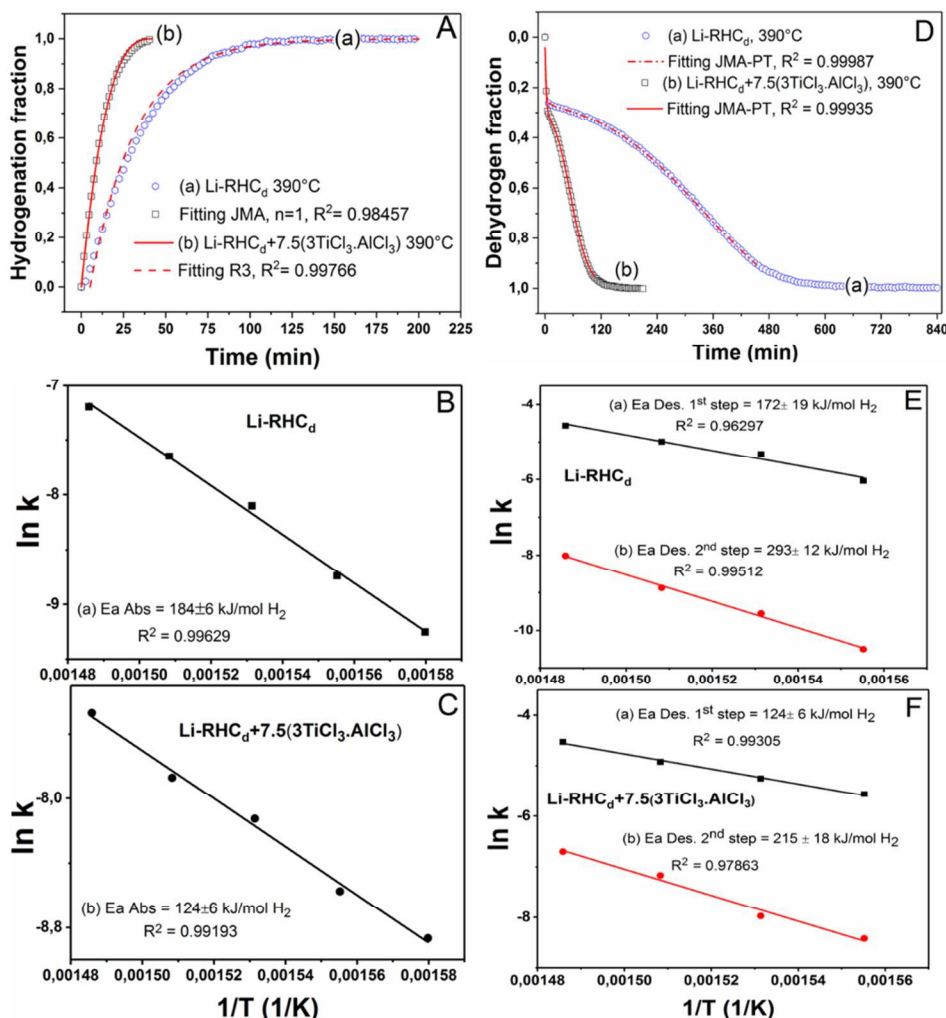


Figure 8. Kinetic behavior for Li-RHC_d and Li-RHC_d+7.5(3TiCl₃.AlCl₃): **A** Hydrogenation and **D** Dehydrogenation kinetic curves of the 2nd cycle and model fitting. **B** and **C** Hydrogenation activation energy. **E** and **F** Dehydrogenation activation energy.

In Fig. 8D a comparison between the dehydrogenation kinetic curves of Li-RHC_d and Li-RHC_d+7.5(3TiCl₃.AlCl₃) at 390 °C clearly shows that the doping improves notably the material's kinetic behavior. For the kinetic modelling of the dehydrogenation curves a novel approach proposed by Puzkiel *et al.*⁶⁴ has been applied, consisting in the combination of two kinetic models, i.e. the JMA model for the first step (MgH₂ decomposition) and the modified Prout-Topkins (PT) model for the second step (reaction between Mg and LiBH₄ to give LiH,

MgB₂ and H₂ release)^{70,72}. The fitting employing the combined model⁶⁴ to the dehydrogenation curves of Li-RHC_d and Li-RHC_d+7.5(3TiCl₃.AlCl₃) between 370 °C and 400 °C under 3 bar of H₂ shows good agreement with correlation coefficient R² of about 1 (Fig. 8D, ESI Fig. S12). During the first step of the dehydrogenation, the MgH₂ decomposition is limited by a MgH₂/Mg interface-controlled mechanism along a one-dimensional dislocation line (JMA with n ~ 1)⁷³. Fig. 8 (E and F) exhibits the dehydrogenation E_a for Li-RHC_d and Li-RHC_d+7.5(3TiCl₃.AlCl₃) corresponding to the first and second step. In the case of MgH₂ decomposition (Fig. 8E(a) and F(a)), E_a is decreased from 172±19 kJ/mol H₂ for Li-RHC_d to 124±6 kJ/mol H₂ for Li-RHC_d+7.5(3TiCl₃.AlCl₃). These results suggest that the reaction kinetics of the first step of the dehydrogenation process for Li-RHC_d is enhanced by the presence of the nanosized AlTi alloy, which has been already seen for pure MgH₂⁷³. Fig.8 E(b) and F(b) show the dehydrogenation E_a belonging to the second step for Li-RHC_d and Li-RHC_d+7.5(3TiCl₃.AlCl₃), respectively. The dehydrogenation E_a for Li-RHC_d+7.5(3TiCl₃.AlCl₃) is lower than that for Li-RHC_d, i.e. 215±18 kJ/mol H₂ and 293±12 kJ/mol H₂, respectively. This is in agreement with the fitted autocatalytic (PT) model, in which the involvement of products as reactive phases is considered⁷⁰. As explained in a previous section (4.3.1), the interaction of 3TiCl₃.AlCl₃ with the Li-RHC material produces *in situ* nanosized AlTi alloys. Hexagonal AlTi₃ is the most abundant nanosized AlTi phase. This phase presents excellent properties to promote the fast growth of MgB₂ nuclei and it is very well distributed. Therefore, the dehydrogenation E_a of the second step is markedly reduced due to the availability of well-distributed hexagonal AlTi₃ nanoparticles acting as effective nucleation centers and allowing the fast formation of MgB₂ on their surfaces.

5. CONCLUSIONS

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3 In this work, the effect of the formation of nano TiAl alloys on the hydrogenation storage
4 properties of the $2\text{LiBH}_4+\text{MgH}_2/2\text{LiH}+\text{MgB}_2$ system has been investigated in detail. The
5 samples have been prepared in both hydrogenated and dehydrogenated states adding either
6 $3\text{TiCl}_3\cdot\text{AlCl}_3$ or TiCl_3 . The hydrogenation/dehydrogenation rates of the doped composite systems
7 show a significant enhancement compared to the pristine material. The $7.5(3\text{TiCl}_3\cdot\text{AlCl}_3)$ doped
8 Li-RHC_d exhibits the best performance among the investigated systems. In fact, for this material
9 the hydrogenation-dehydrogenation times are about 30 minutes and the reversible hydrogen
10 storage capacity is about 9.5 wt.%. These values are stable through 20
11 hydrogenation/dehydrogenation cycles. Moreover, in comparison to the pristine material, the
12 activation energy for the hydrogenation of the Li-RHC_d+ $7.5(3\text{TiCl}_3\cdot\text{AlCl}_3)$ is significantly
13 reduced by 60 kJ/mol H₂. The dehydrogenation activation energies of the first and the second
14 steps are also considerably decreased by about 50 kJ/mol H₂ and 80 kJ/mol H₂, respectively. This
15 shows that the addition of $3\text{TiCl}_3\cdot\text{AlCl}_3$ has a strong effect on the Li-RHC system and a
16 beneficial effect by avoiding the further generation of $\text{Li}_2\text{B}_{12}\text{H}_{12}$. It has been found that the
17 nanosized AlTi alloys are formed *in situ* as a result of the interaction between the $3\text{TiCl}_3\cdot\text{AlCl}_3$
18 additive and Li-RHC upon milling. Among the observed AlTi alloys, the nanosized hexagonal
19 AlTi_3 is the most abundant species. These AlTi nanoparticles are stable upon
20 hydrogenation/dehydrogenation cycling. The enhanced hydrogenation kinetic behavior is
21 attributed to the nanosized AlTi alloys which facilitates the reduction of the particle size of
22 MgB_2 down to about 300 nm leading to a faster MgB_2 consumption, preventing the MgB_2
23 agglomeration, generating more active surface for the hydrogen-material interaction and making
24 possible the faster three dimensional interface movements. Upon dehydrogenation, nanosized
25 AlTi alloys also account for the improvement during the first and second dehydrogenation steps.
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3 The decomposition of MgH_2 during the first step is catalyzed by the presence of these well-
4 distributed nanosized AlTi alloys. Furthermore, the kinetic behavior during second
5 dehydrogenation step is improved by the presence of *in situ* formed nanosized and hexagonal
6 AlTi₃, which acts as an effective heterogeneous nucleation site for MgB₂ nuclei and precludes
7 the additional formation of Li₂B₁₂H₁₂. This novel catalytic mechanism opens a potential for an
8 economical and efficient design of hydrogen storage materials.
9

17 ASSOCIATED CONTENT

19 **Supporting Information.** Hydrogenation-dehydrogenation curves during 20 cycles of tested
20 materials, coupled Sieverts-DSC measurements of the undoped and doped Li-RHC samples, *in*
21 *situ* SR-PXD data of a full sorption process of the Li-RHC_d+7.5(3TiCl₃.AlCl₃) sample, *ex situ*
22 PXD of the doped samples prepared in the hydrogenated state Li-RHC_a+7.5(3TiCl₃.AlCl₃) after
23 milling and after cycling, *in situ* SR-PXD data of the desorption reaction measured for the
24 sample Li-RHC_a+7.5(3TiCl₃.AlCl₃) after milling, ASAXS curves of the as-milled Li-
25 RHC_d+7.5TiCl₃ sample, thermodynamic data parameters for thermodynamic calculations,
26 EDS/STEM mode of Li-RHC_d+7.5(3TiCl₃.AlCl₃) after milling and after cycling, HR-TEM
27 micrographs of Li-RHC_d+7.5(3TiCl₃.AlCl₃), first non-isothermal dehydrogenation of as-milled
28 Li-RHC_a, $(t/t_{0.5})_{\text{experimental}}$ vs. $(t/t_{0.5})_{\text{theoretical}}$ plots for Li-RHC_d and Li-RHC_d+7.5(3TiCl₃.AlCl₃),
29 Li-RHC_d and Li-RHC_d+7.5(3TiCl₃.AlCl₃) hydrogenation and dehydrogenation curves fitted in
30 the range of temperature between 360 °C and 400 °C.
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All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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TOC Graphic

