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Bill, Rachel; Reed, Daniel; Book, David; Anderson, Paul

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## Accepted Manuscript

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**Effect of the calcium halides,  $\text{CaCl}_2$  and  $\text{CaBr}_2$ , on hydrogen desorption in  
the Li–Mg–N–H system**

Rachel F. Bill <sup>a</sup>, Daniel Reed <sup>b</sup>, David Book <sup>b</sup>, Paul A. Anderson <sup>a,\*</sup>

<sup>a</sup> School of Chemistry, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK

<sup>b</sup> School of Metallurgy and Materials, University of Birmingham, Edgbaston, Birmingham

B15 2TT, UK

\*Corresponding author: Tel: +44 (0) 121 414 4447, Fax: +44 (0) 121 414 4403, Email:  
p.a.anderson@bham.ac.uk (P. A. Anderson)

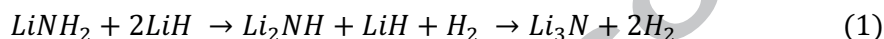
**Abstract**

Calcium-halide-doped lithium amide–magnesium hydride samples were prepared both by hand-grinding and ball-milling  $2\text{LiNH}_2\text{--MgH}_2\text{--}x\text{CaX}_2$  ( $x = 0, 0.1, \text{ and } 0.15$ ;  $X = \text{Cl or Br}$ ). The addition of calcium halides reduced the hydrogen desorption temperature in all samples. The ball-milled undoped sample ( $2\text{LiNH}_2\text{--MgH}_2$ ) began to desorb hydrogen at around  $125^\circ\text{C}$  and peaked at  $170^\circ\text{C}$ . Hydrogen desorption from the  $0.15$  mol  $\text{CaCl}_2$ -containing sample began  $ca$   $30^\circ\text{C}$  lower than that of the undoped sample and peaked at  $150^\circ\text{C}$ . Both the onset and peak temperatures of the  $\text{CaBr}_2$  sample ( $x = 0.15$ ) were reduced by  $15^\circ\text{C}$  compared to the chloride. Kissinger's method was used to calculate the effective activation energy ( $E_a$ ) for the systems:  $E_a$  for the  $0.15$  mol  $\text{CaCl}_2$ -containing sample was found to be  $91.8 \text{ kJ mol}^{-1}$  and the value for the  $0.15$  mol  $\text{CaBr}_2$ -containing sample was  $78.8 \text{ kJ mol}^{-1}$ .

**Keywords:** hydrogen storage, lithium amide ( $\text{LiNH}_2$ ), magnesium hydride ( $\text{MgH}_2$ ), temperature-programmed desorption, kinetics, calcium halides

## 1. Introduction

Numerous complex hydrides of light metals and combinations of light and transition metal hydrides have been investigated [1-5]. Since research by Chen *et al.* [6] revealed that a reaction between lithium amide and lithium hydride (equation 1) could desorb *ca* 10.3 wt% H<sub>2</sub> in a two-step process [6], materials based around the Li–N–H system and including amide (NH<sub>2</sub><sup>-</sup>) anions, have become popular candidates for lightweight solid-state hydrogen storage systems.



Following this work, the Li–Mg–N–H system has been widely studied by many groups [7-14], with efforts now concentrated on its improvement as a hydrogen store and, in particular, low temperature hydrogen cycling.

Li *et al.* [12, 15] investigated the benefits of adding Ca(BH<sub>4</sub>)<sub>2</sub> (10–30 mol%) to the Li–Mg–N–H system. Through the introduction of calcium borohydride it was proposed that simultaneous kinetic and thermodynamic improvements are made due to the presence of BH<sub>4</sub><sup>-</sup> [16] and Ca<sup>2+</sup> [17] ions, respectively. It was concluded that optimum performance was achieved by adding 10 mol% Ca(BH<sub>4</sub>)<sub>2</sub>. The *in situ* identification of the fast lithium ion conductor Li<sub>4</sub>BH<sub>4</sub>(NH<sub>2</sub>)<sub>3</sub> [18], as a key intermediate in the desorption process was especially interesting. It has previously been reported that the addition of halides may produce a kinetic improvement in a system by improving lithium ion mobility [19]. An isostructural equivalent to Li<sub>4</sub>BH<sub>4</sub>(NH<sub>2</sub>)<sub>3</sub> is Li<sub>4</sub>(NH<sub>2</sub>)<sub>3</sub>Cl, which has been found to possess improved ion mobility when compared to LiNH<sub>2</sub>. A similar bromide phase Li<sub>7</sub>(NH<sub>2</sub>)<sub>6</sub>Br and magnesium-doped analogues have also been reported [19], and the effect of lithium halides on the Li–Mg–N–H system continues to attract attention [20, 21]. In this paper we discuss the effects on hydrogen desorption of the addition of various amounts of CaCl<sub>2</sub> and CaBr<sub>2</sub> in comparison to the undoped system.

## 2. Experimental

### 2.1 Preparation

The  $2\text{LiNH}_2\text{-MgH}_2\text{-}x\text{CaX}_2$  ( $x = 0, 0.1, \text{ and } 0.15$ ;  $X = \text{Cl or Br}$ ) samples were prepared by hand-grinding (HG) or ball-milling (BM) commercially available lithium amide (Sigma–Aldrich, 95%) and magnesium hydride (Alfa–Aesar, 98%) with either anhydrous  $\text{CaCl}_2$  (Sigma–Aldrich, >96%) or anhydrous  $\text{CaBr}_2$  (Alfa–Aesar, 99.5%) in the desired molar ratio. All sample storage and handling was conducted in an argon-atmosphere glovebox. Hand-grinding was carried out with a porcelain pestle and mortar for 10 minutes. Ball-milling was performed in a 250 ml stainless steel milling-pot in a Retsch PM400 Planetary Ball Mill at 300 rpm for 24h with a ball to sample ratio of 40:1. To prevent temperature rise in the milling vessel, 2 minutes of milling was followed by a 2 minute pause.

### 2.2 Powder X-ray Diffraction

Powder X-ray Diffraction (XRD) data were collected on a Bruker D8 Advance Diffractometer operating in transmission geometry with a  $\text{Cu K}_{\alpha 1}$  radiation source ( $\lambda = 1.5406 \text{ \AA}$ ). To protect them from the atmosphere during measurement, samples were sealed between two pieces of amorphous tape.

### 2.3 Thermal desorption analysis

Temperature-programmed desorption data were collected on a home-built system described previously [22], which was coupled to a mass spectrometer (HPR-20, Hiden Analytical) for *in situ* monitoring of gas release (TPD–MS). Samples of ~100 mg were heated in quartz tubes at a ramp rate of  $2^\circ\text{C min}^{-1}$  to  $400^\circ\text{C}$  in argon (1.5 bar,  $100 \text{ ml min}^{-1}$ ) and maintained at temperature for 1 hour before cooling to room temperature. Thermogravimetric analysis (TGA) experiments were performed on a Netzsch 209 TGA with the outlet coupled to a mass spectrometer (HPR-20, Hiden Analytical). The TGA was located in a flowing argon glovebox and was also connected to the mass spectrometer (TGA–MS). Samples of approximately 10

mg were loaded into an alumina crucible and heated at  $2^{\circ}\text{C min}^{-1}$  to  $400^{\circ}\text{C}$  in argon (1.5 bar,  $100\text{ ml min}^{-1}$ ) and then cooled.

### 3. Results and Discussion

#### 3.1 Hydrogen desorption from hand-ground samples

Figs. 1a & b show the TPD–MS profiles of the  $2\text{LiNH}_2\text{--MgH}_2\text{--}x\text{CaX}_2$  ( $X = \text{Cl}$  and  $\text{Br}$ , respectively) HG samples. The undoped sample desorbed both hydrogen and ammonia; the former started at  $340^{\circ}\text{C}$  and peaked at  $\sim 375^{\circ}\text{C}$  with hydrogen release continuing after the main peak. The addition of  $\text{CaCl}_2$  reduced the peak hydrogen desorption temperature and the amount of ammonia released (Fig. 1a). The lowest peak temperature observed for the  $\text{CaCl}_2$ -doped samples was at  $310^{\circ}\text{C}$  for  $x = 0.15$ , a reduction of *ca*  $65^{\circ}\text{C}$  compared to the undoped sample.

The behaviour of  $\text{CaBr}_2$ -doped samples was also examined by TPD–MS (Fig. 1b). Similarly to the  $\text{CaCl}_2$ -doped samples, a reduction in temperature of the hydrogen peak and suppression of ammonia release also occurred compared to the undoped sample. The hydrogen peak for  $x = 0.15$  was seen at  $275^{\circ}\text{C}$ , a further decline of  $35^{\circ}\text{C}$  compared to the analogous chloride-doped sample and  $100^{\circ}\text{C}$  lower than the undoped sample. The samples doped with calcium bromide also displayed a second hydrogen desorption peak at similar temperatures to the main peak of the undoped sample. The addition of more  $\text{CaCl}_2$  or  $\text{CaBr}_2$  ( $x > 0.15$ ) did not reduce the desorption temperatures but increased the amount of ammonia released.

#### 3.2 Hydrogen desorption from ball-milled samples

When samples were ball-milled, the resulting as-prepared materials were different when compared to as prepared hand-ground samples. The BM samples were analysed using powder XRD (Fig. 2) and several phases were identified including  $\text{LiCl}$ ,  $\text{CaH}_2$ ,  $\text{LiH}$ ,  $\text{MgH}_2$ ,

and an amide phase. Due to the broad peaks characteristic of the powder XRD patterns of ball-milled samples it was not possible to determine whether it was lithium or calcium amide. The observation of multiple new phases in the BM sample indicated that metathesis reactions probably occurred during ball-milling.

TGA of the ball-milled samples in Fig 3a shows good agreement with the corresponding mass spectrometry profiles in Figure 3b. At temperatures below 300°C the undoped sample lost *ca* 4.6 wt%, this can be ascribed solely to hydrogen, consistent with the TGA–MS in Fig 3b. Upon the addition of both calcium halides, the desorption process was split into two distinct ranges, the first complete around 230°C. As expected, when the heavier calcium and halide ions were included the desorption capacities for the first step were lower, with approximately 3.3 (4.5) wt% and 3.0 (3.9) wt% observed from the 0.15 mol CaCl<sub>2</sub>- and CaBr<sub>2</sub>-doped samples. The amounts above correspond to 73% and 77%, respectively, of the hydrogen theoretically available in the amide–imide reaction step from the calcium-halide-containing samples (figures in brackets), significantly less than can theoretically be released in the amide–imide step of the undoped sample (5.6 wt%).

Figure 3b shows the TGA–MS profiles observed from the ball-milled samples. The undoped BM sample, began to desorb hydrogen at around 125°C and peaked at 170°C. The onset hydrogen desorption temperature for the 2LiNH<sub>2</sub>–MgH<sub>2</sub>–0.15CaCl<sub>2</sub> BM sample was reduced by *ca* 30°C and peaked at 150°C. Both the onset and peak temperatures of the comparable CaBr<sub>2</sub>-doped sample (*x* = 0.15) were reduced by 15°C, compared to the chloride-doped analogue, with the bromide-doped sample peaking at 135°C. There is a clear difference between the hydrogen mass spectrometry profiles for the chloride- and bromide-doped samples shown in Fig 3b. These results compare to a lowest peak temperature of 150°C observed for 2LiNH<sub>2</sub>–MgH<sub>2</sub>–0.3Ca(BH<sub>4</sub>)<sub>2</sub> [15].

The addition of calcium halides reduces the temperature for both the decomposition of the amide and imide compounds allowing a greater total mass loss compared to the undoped



sample. However, the total mass loss from the bromide-doped sample (7.2 wt%) was greater than the theoretical hydrogen capacity of the CaBr<sub>2</sub>-doped sample (5.9 wt%), which indicates that additional gases were evolved. As bromine is much heavier than the other atoms present, this could be accounted for by a relatively small amount of bromine loss, which would be difficult to detect. Experiments are underway to investigate this.

### 3.3 Kinetic measurements

The activation energies ( $E_a$ ) for hydrogen desorption from the 0.15 mol CaX<sub>2</sub>-doped samples were estimated by Kissinger's method [23] via equation 2 below:

$$\ln\left(\frac{\beta}{T_m^2}\right) = -\frac{E_a}{RT_m} \quad (2)$$

where  $\beta$  is the heating rate,  $T_m$  is the peak temperature and  $R$  is the molar gas constant.

Here  $T_m$  was determined from TGA–MS profiles recorded under flowing argon (1.5 bar, 100 ml min<sup>-1</sup>) at heating rates of 1, 2, 5, 10 and 15°C min<sup>-1</sup>. As shown in Fig. 4, the expected linear relationship was observed for all samples. The estimated activation energy of dehydrogenation of the undoped sample was 104.2 kJ mol<sup>-1</sup>, whereas the estimated  $E_a$  values for the 0.15 mol CaCl<sub>2</sub>-doped BM and 0.15 mol CaBr<sub>2</sub>-doped BM samples were found to be 91.8 and 78.8 kJ mol<sup>-1</sup>, respectively. These values compare to an activation energy of 101 kJ mol<sup>-1</sup> for 2LiNH<sub>2</sub>–MgH<sub>2</sub>–0.3Ca(BH<sub>4</sub>)<sub>2</sub> reported by Li *et al.* [15].

## 4. Conclusions

The hydrogen desorption properties of 2LiNH<sub>2</sub>–MgH<sub>2</sub>–*x*CaX<sub>2</sub> ( $x = 0, 0.1, 0.15$ , and X = Cl and Br) samples have been investigated through TPD–MS, TGA–MS and the activation energies estimated by Kissinger's method. During initial ball-milling, metathesis reactions occurred leading to the formation of several products that may aid the dehydrogenation

process. In both halide-doped samples the lowest dehydrogenation peak temperature was observed when  $x = 0.15$ . The  $2\text{LiNH}_2\text{-MgH}_2\text{-}0.15\text{CaBr}_2$  sample showed the lowest peak desorption temperature with a calculated activation energy of  $78.8 \text{ kJ mol}^{-1}$ .

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## REFERENCES

- [1] S. Orimo, Y. Nakamori, J.R. Eliseo, A. Züttel, C.M. Jensen, Complex hydrides for hydrogen storage, *Chem. Rev.*, 107 (2007) 4111-4132.
- [2] P. Chen, Z. Xiong, G. Wu, Y. Liu, J. Hu, W. Luo, Metal-N-H systems for the hydrogen storage, *Scripta Mater.*, 56 (2007) 817-822.
- [3] M.B. Ley, L.H. Jepsen, Y.-S. Lee, Y.W. Cho, J.M.B. von Colbe, M. Dornheim, M. Rokni, J.O. Jensen, M. Sloth, Y. Filinchuk, J.E. Jorgensen, F. Besenbacher, T.R. Jensen, Complex hydrides for hydrogen storage - new perspectives, *Mater. Today*, 17 (2014) 122-128.
- [4] L.H. Jepsen, M.B. Ley, Y.-S. Lee, Y.W. Cho, M. Dornheim, J.O. Jensen, Y. Filinchuk, J.E. Jorgensen, F. Besenbacher, T.R. Jensen, Boron-nitrogen based hydrides and reactive composites for hydrogen storage, *Mater. Today*, 17 (2014) 129-135.
- [5] H.J. Cao, Y. Zhang, J.H. Wang, Z.T. Xiong, G.T. Wu, P. Chen, Materials design and modification on amide-based composites for hydrogen storage, *Prog. Nat. Sci-Mat. Int.*, 22 (2012) 550-560.
- [6] P. Chen, Z.T. Xiong, J.Z. Luo, J.Y. Lin, K.L. Tan, Interaction between lithium amide and lithium hydride, *J. Phys. Chem. B*, 107 (2003) 10967-10970.
- [7] Y. Nakamori, G. Kitahara, K. Miwa, N. Ohba, T. Noritake, S. Towata, S. Orimo, Hydrogen storage properties of Li-Mg-N-H systems, *J. Alloys Compd.*, 404 (2005) 396-398.
- [8] H. Leng, T. Ichikawa, H. Fujii, Hydrogen storage properties of Li-Mg-N-H systems with different ratios of LiH/Mg(NH<sub>2</sub>)<sub>2</sub>, *J. Phys. Chem. B*, 110 (2006) 12964-12968.
- [9] M. Aoki, T. Noritake, Y. Nakamori, S. Towata, S. Orimo, Dehydrogenating and rehydrogenating properties of Mg(NH<sub>2</sub>)<sub>2</sub>-LiH systems, *J. Alloys Compd.*, 446 (2007) 328-331.
- [10] T. Noritake, M. Aoki, M. Matsumoto, K. Miwa, S. Towata, H.W. Li, S. Orimo, Crystal structure change in the dehydrogenation process of the Li-Mg-N-H system, *J. Alloys Compd.*, 509 (2011) 7553-7558.
- [11] H. Pan, S. Shi, Y. Liu, B. Li, Y. Yang, M. Gao, Improved hydrogen storage kinetics of the Li-Mg-N-H system by addition of Mg(BH<sub>4</sub>)<sub>2</sub>, *Dalton Trans.*, 42 (2013) 3802-3811.
- [12] B. Li, Y.F. Liu, J. Gu, M.X. Gao, H.G. Pan, Synergetic Effects of In Situ Formed CaH<sub>2</sub> and LiBH<sub>4</sub> on Hydrogen Storage Properties of the Li-Mg-N-H System, *Chem.-Asian J.*, 8 (2013) 374-384.
- [13] C. Li, Y.F. Liu, Y.P. Pang, Y.J. Gu, M.X. Gao, H.G. Pan, Compositional effects on the hydrogen storage properties of Mg(NH<sub>2</sub>)<sub>2</sub>-2LiH-xKH and the activity of KH during dehydrogenation reactions, *Dalton Trans.*, 43 (2014) 2369-2377.
- [14] D. Pottmaier, F. Dolci, M. Orlova, G. Vaughan, M. Fichtner, W. Lohstroh, M. Baricco, Hydrogen release and structural transformations in LiNH<sub>2</sub>-MgH<sub>2</sub> systems, *J. Alloys Compd.*, 509 (2010) S719-S723.
- [15] B. Li, Y.F. Liu, J. Gu, Y.J. Gu, M.X. Gao, H.G. Pan, Mechanistic investigations on significantly improved hydrogen storage performance of the Ca(BH<sub>4</sub>)<sub>2</sub>-added 2LiNH<sub>2</sub>/MgH<sub>2</sub> system, *Int. J. Hydrogen Energy*, 38 (2013) 5030-5038.
- [16] C. Liang, Y. Liu, Y. Jiang, Z. Wei, M. Gao, H. Pan, Q. Wang, Local defects enhanced dehydrogenation kinetics of the NaBH<sub>4</sub>-added Li-Mg-N-H system, *PCCP*, 13 (2011) 314-321.
- [17] Y. Liu, J. Hu, Z. Xiong, G. Wu, P. Chen, K. Murata, K. Sakata, Investigations on hydrogen desorption from the mixture of Mg(NH<sub>2</sub>)<sub>2</sub> and CaH<sub>2</sub>, *J. Alloys Compd.*, 432 (2007) 298-302.
- [18] M. Matsuo, A. Remhof, P. Martelli, R. Caputo, M. Ernst, Y. Miura, T. Sato, H. Oguchi, H. Maekawa, H. Takamura, A. Borgschulte, A. Züttel, S. Orimo, Complex Hydrides with BH<sub>4</sub><sup>-</sup> and NH<sub>2</sub><sup>-</sup> Anions as New Lithium Fast-Ion Conductors, *J. Am. Chem. Soc.*, 131 (2009) 16389-16391.
- [19] P.A. Anderson, P.A. Chater, D.R. Hewett, P.R. Slater, Hydrogen storage and ionic mobility in amide-halide systems, *Faraday Discuss.*, 151 (2011) 271-284.
- [20] B. Li, Y.F. Liu, C. Li, M.X. Gao, H.G. Pan, In situ formation of lithium fast-ion conductors and improved hydrogen desorption properties of the LiNH<sub>2</sub>-MgH<sub>2</sub> system with the addition of lithium halides, *J. Mat. Chem. A*, 2 (2014) 3155-3162.

[21] H. Cao, G. Wu, Y. Zhang, Z. Xiong, J. Qiu, P. Chen, Effective thermodynamic alteration to  $\text{Mg}(\text{NH}_2)_2\text{-LiH}$  system: achieving near ambient-temperature hydrogen storage, *J. Mat. Chem. A*, 2 (2014) 15816-15822.

[22] P.A. Chater, P.A. Anderson, J.W. Prendergast, A. Walton, V.S.J. Mann, D. Book, W.I.F. David, S.R. Johnson, P.P. Edwards, Synthesis and characterization of amide-borohydrides: New complex light hydrides for potential hydrogen storage, *J. Alloys Compd.*, 446 (2007) 350-354.

[23] H.E. Kissinger, Reaction kinetics in differential thermal analysis, *Anal. Chem.*, 29 (1957) 1702-1706.

#### FIGURE CAPTIONS

**Figure 1:** TPD-MS of hand-ground (a)  $2\text{LiNH}_2\text{-MgH}_2\text{-xCaCl}_2$  samples and (b)  $2\text{LiNH}_2\text{-MgH}_2\text{-xCaBr}_2$  samples heated at  $2^\circ\text{C min}^{-1}$  under 1.5 bar flowing argon at  $100\text{ ml min}^{-1}$ .

**Figure 2:** Powder XRD of the as-prepared ball-milled and hand-ground  $2\text{LiNH}_2\text{-MgH}_2\text{-0.15CaCl}_2$  samples.

**Figure 3:** (a) TGA traces (b) TGA-MS of evolved gases for the halide-doped samples from ball-milled  $2\text{LiNH}_2\text{-MgH}_2\text{-0.15CaX}_2$  samples heated at  $2^\circ\text{C min}^{-1}$  under 1.5 bar flowing argon at  $100\text{ ml min}^{-1}$ .

**Figure 4:** Kissinger plot of the ball-milled  $2\text{LiNH}_2\text{-MgH}_2\text{-0.15CaX}_2$  samples heated at variable heating rates under 1.5 bar flowing argon at  $100\text{ ml min}^{-1}$ .

Fig 1

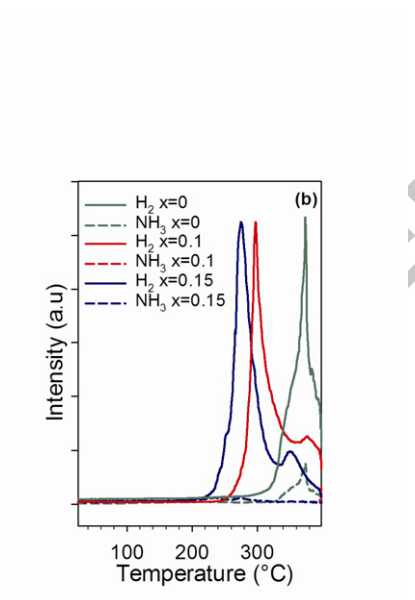
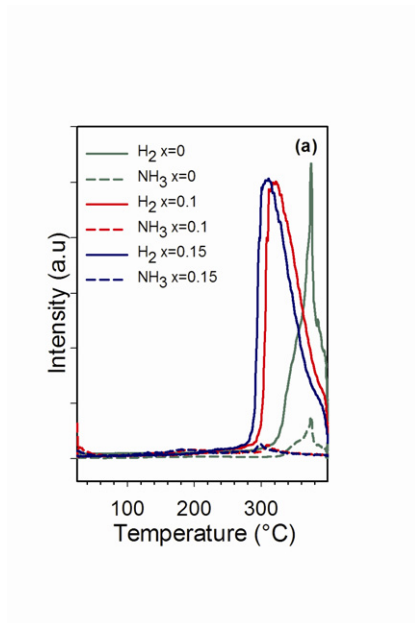


Fig 2

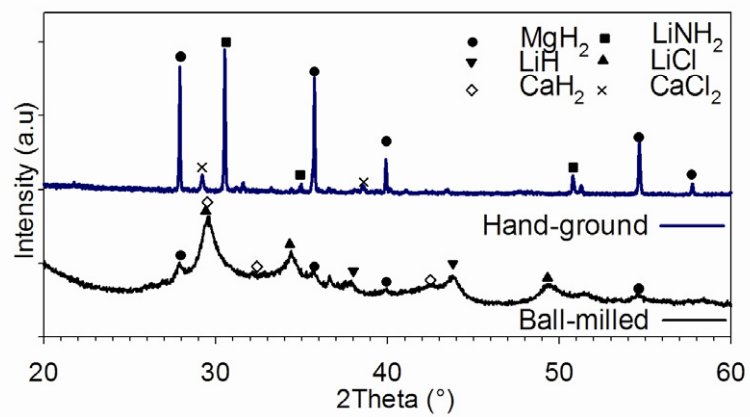


Fig 3

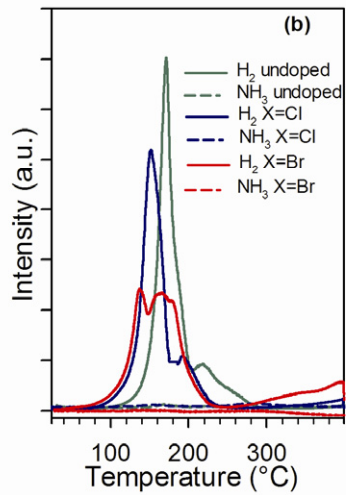
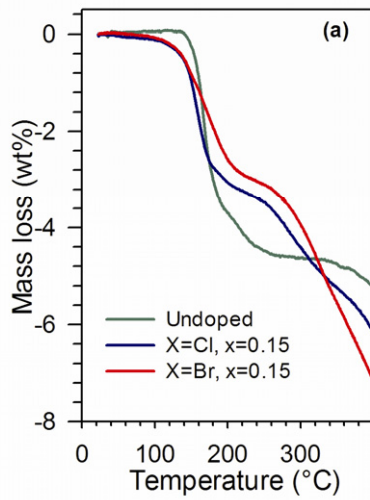
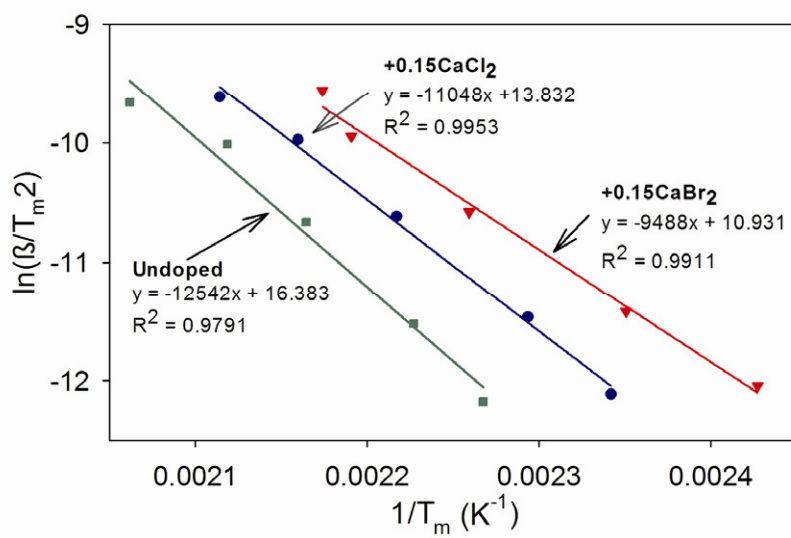




Fig 4



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**HIGHLIGHTS**

Studied H<sub>2</sub> desorption from 2LiNH<sub>2</sub>-MgH<sub>2</sub>-xCaX<sub>2</sub> (x = 0, 0.1, 0.15; X = Cl, Br) samples

Addition of calcium halides reduced the desorption temperature in all samples

Peak H<sub>2</sub> release was around 150°C lower in ball-milled than in hand-ground samples

The 2LiNH<sub>2</sub>-MgH<sub>2</sub>-0.15CaBr<sub>2</sub> sample showed the lowest peak desorption temperature

CaBr<sub>2</sub> reduced the activation energy to 78.8 kJ mol<sup>-1</sup>, 24% less than the undoped sample