Supplementary Information

## Dual borohydride(Li and Na borohydride) catalyst/additive together with intermetallic FeTi for optimization of hydrogen sorption characteristics of Mg(NH$_2$)$_2$/2LiH

Vivek Shukla[a], Ashish Bhatnagar[a], Sweta Singh[a,b], PK Soni[a], Satish K Verma[a], TP Yadav[a], MA Shaz[a], ON Srivastava[a]

[a]*Hydrogen Energy Centre, Department of Physics, Banaras Hindu University, Varanasi-221005, India*

[b]*Department of Physics, School of physical and material sciences, Mahatma Gandhi Central University Bihar, 845401,India.*

*Corresponding author: email: heponsphy.bhu@gmail.com, Tel: +91 0542 2368468
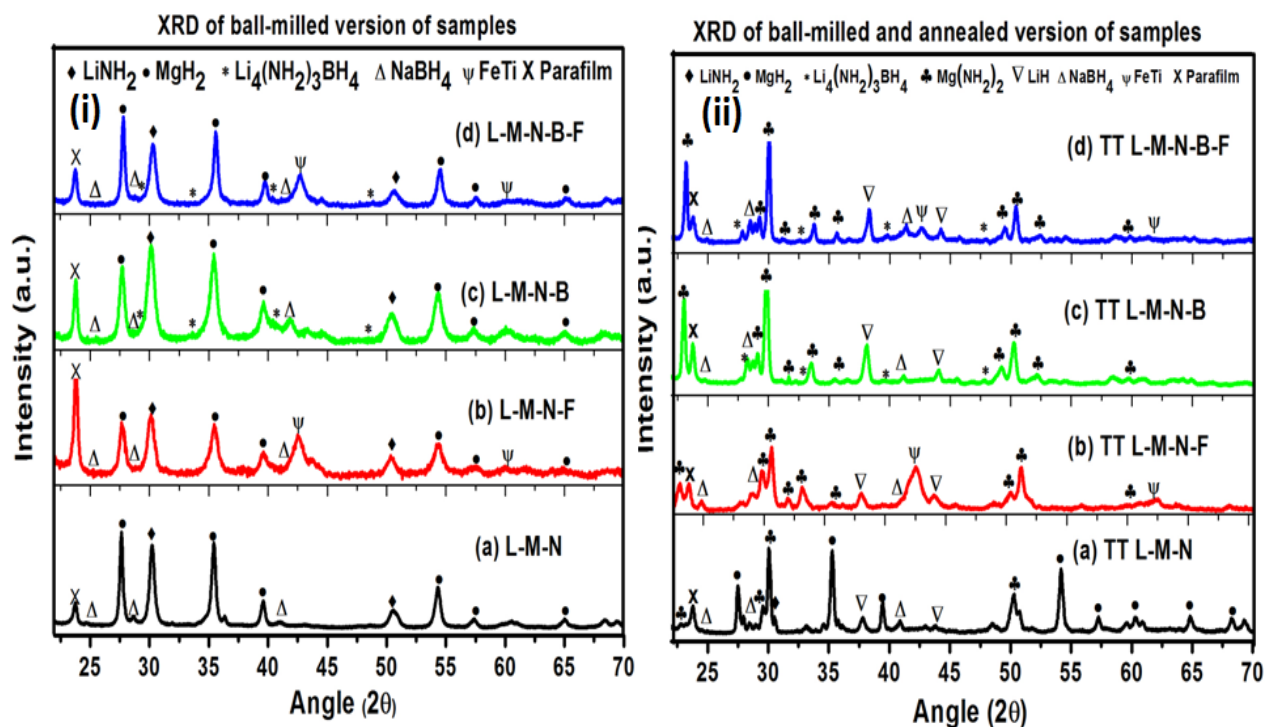
Figure S1 XRD of 30 hrs ball-milled version of samples (a) L-M-N (b) L-M-N-F (c) L-M-N-B (d) L-M-N-B-F **(ii)** XRD of 30 hrs ball-milled and annealed version of samples (a) TT L-M-N (b) TT L-M-N-F (c) TT L-M-N-B (d)TT L-M-N-B-F.
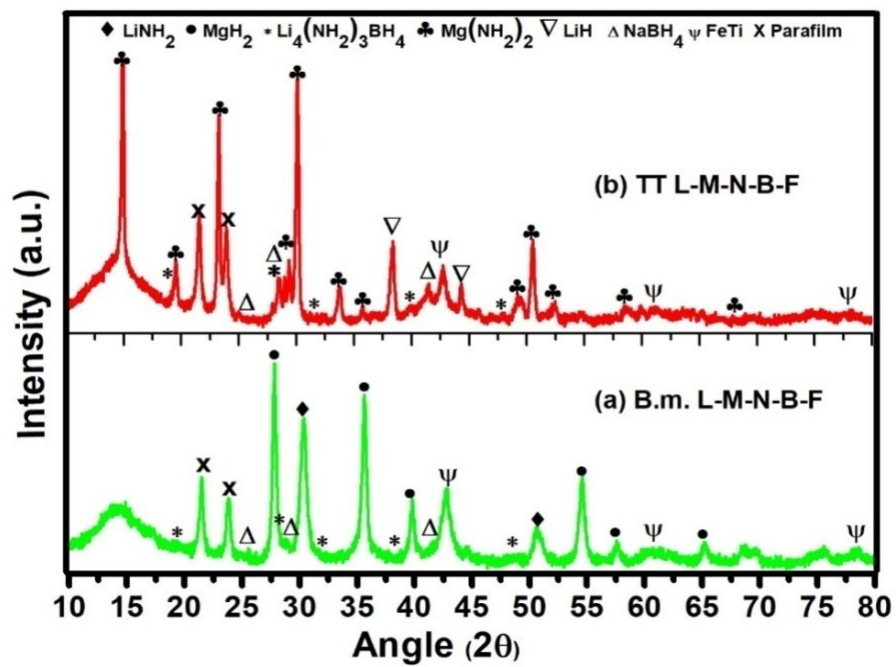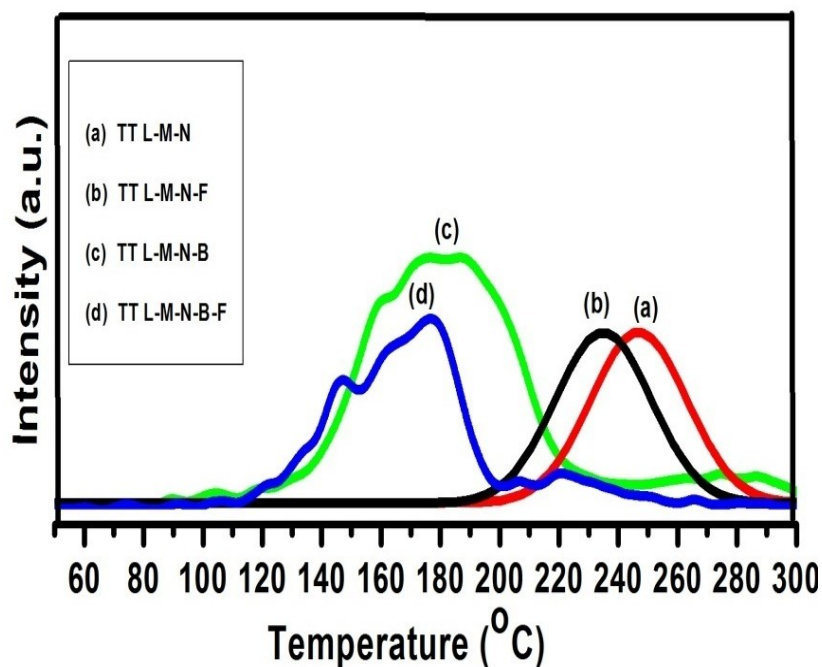
**Figure S2** XRD of ball milled (L-M-N-B-F) and annealed version (TT L-M-N-B-F) of samples.

S-1 TPD of different samples has been performed up to 350°C. Figure S3 shows the non-isothermal dehydrogenation (peak intensity vs. temperature) of the sample. Figure S3(a-d) show the peak desorption temperature of (a)TT L-M-N (b)TT L-M-N-F (c)TT L-M-B-N (d)TT L-M-N-B-F sample respectively. The peak desorption temperature of TT L-M-N, TT L-M-N-F, TT L-M-B-N and TT L-M-N-B-F composite has been found to be 249°C, 234°C, 186°C, and 174°C respectively. Thus peak desorption temperature of TT L-M-N-B-F has been found to be lowered by 75°C, 60°C, 12°C as compared to TT L-M-N, TT L-M-N-F and TT L-M-B-N respectively. As observed in the particle size distribution curve (Figure 9(a-b)), there are distribution of particles form 0.2 μm to 20 μm for TT L-M-N-B and from 0.1μm to 10μm for TT L-M-N-B-F. Because of this different desorption peaks are expected due to varied particle sizes. These peaks can't be attributed to different reaction pathways. However, the temperature at which maximum hydrogen is desorbed from the sample is mentioned as peak desorption temperature.


Figure S3 TPD curves (peak intensity vs temperature) of ball milled and annealed version of samples (a) L-M-N (b) L-M-N-F (c) L-M-N-B (d) L-M-N-B-F
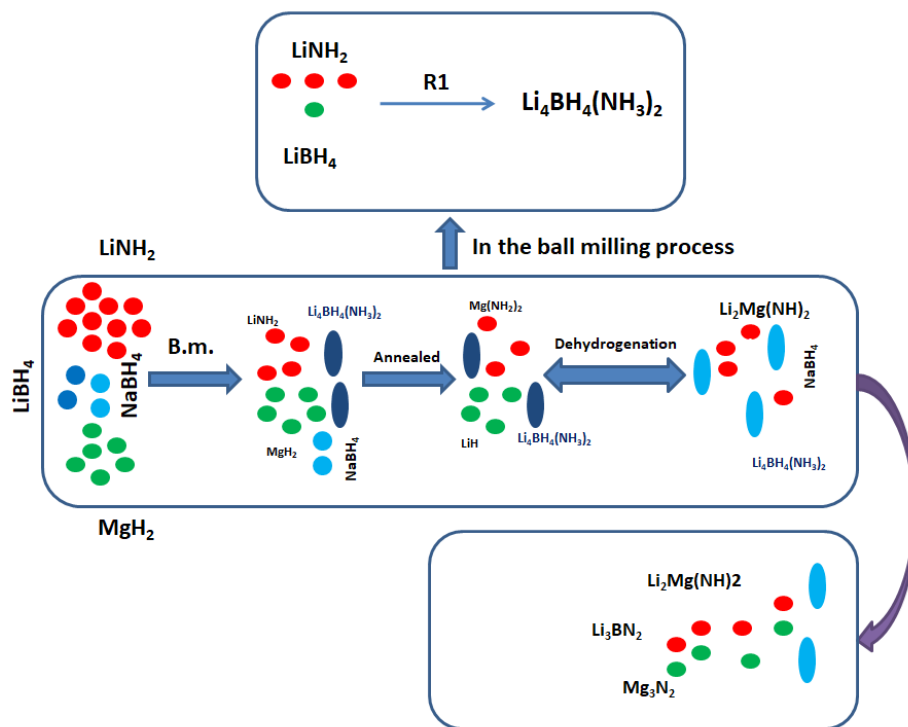
Figure S4 Schematic diagram at different step of temperature point for TT L-M-N-B
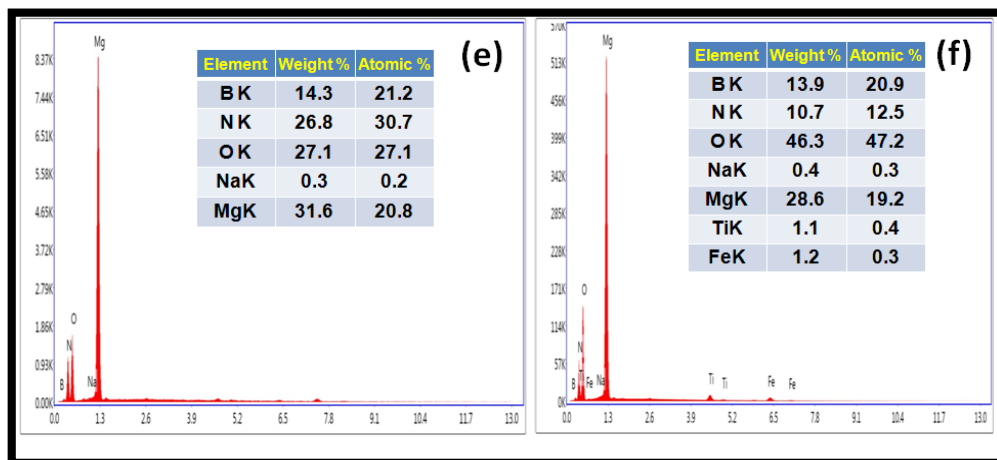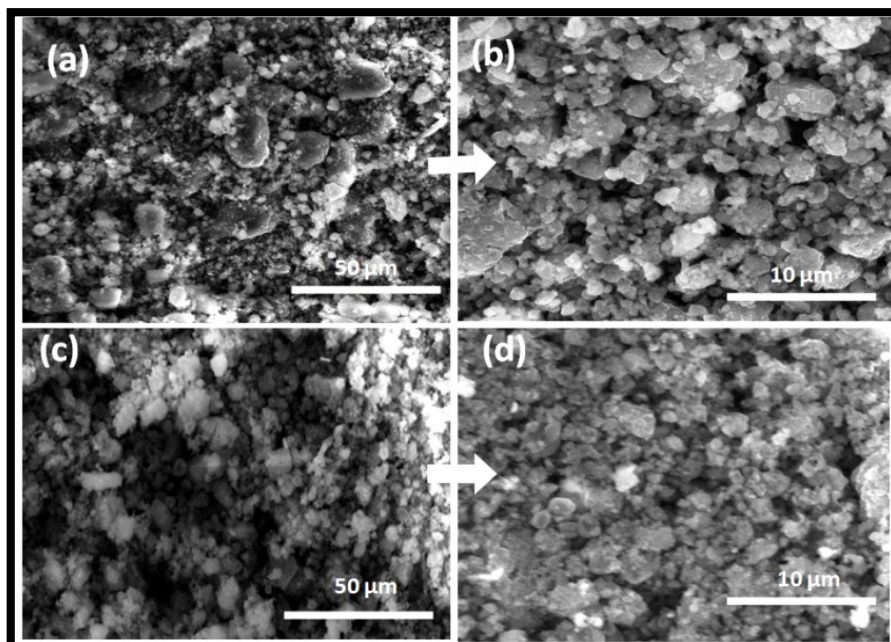
Figure S5 Scanning Electron Micrograph of L-M-N-B mixture with and without catalyst (a) L-M-N-B (b)TT L-M-N-B (c) L-M-N-B-F (d) 1^{st}absorption of L-M-N-B-F (e) EDX spectrum of TT L-M-N-B (f) EDX spectrum after the cycling of TT L-M-N-B-F.
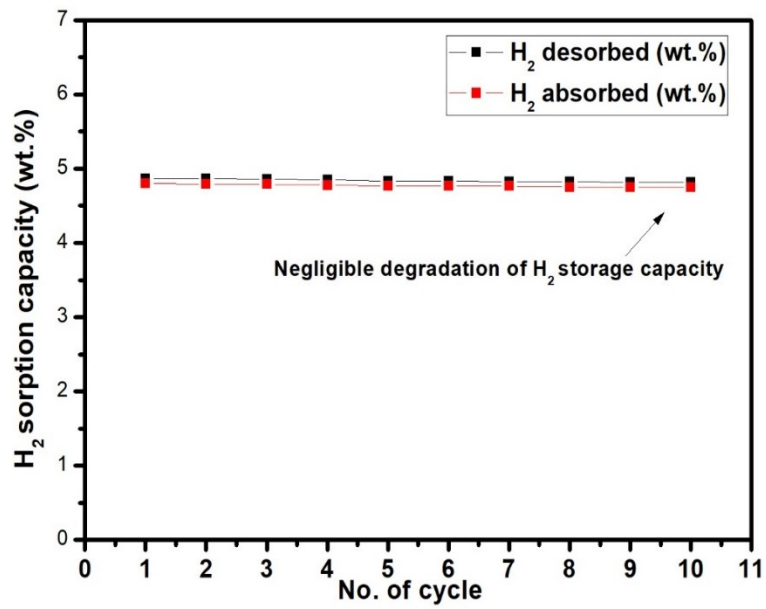
Figure S6 Storage capacities on hydrogen sorption cycling at 170ºC of TT L-M-N-B-F sample
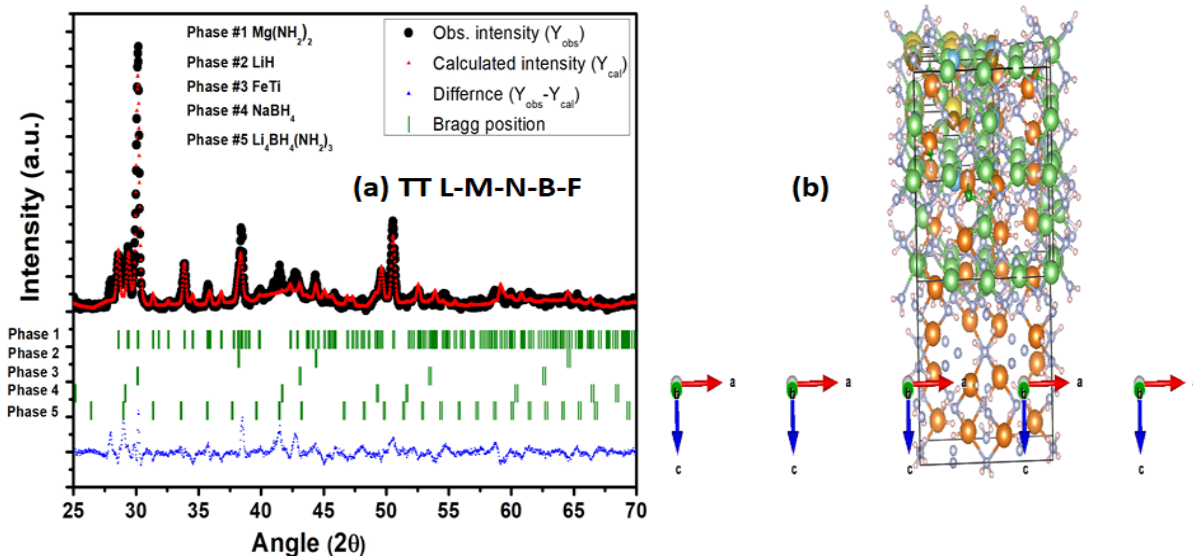
Figure S7 Rietveld refinement fits for TT L-M-N-B-F by FullProf Suite software. Dots indicate experimentally observed data while Rietveld calculated data are shown by overlapping continuous line. The difference curve is shown by a lower continuous line. The vertical bars indicate the Bragg peak positions. (d) Ball and Stick model for the structure of $Mg(NH_2)_2$-2LiH-$(Li_4(BH_4)(NH_2)_3$-FeTi).

S 2 Details of parameter used in refinement

1-Mg(NH₂)₂: Cell Parameters $a = 10.3909$ $b = 10.3909$ $c = 20.0873$

alpha =90.000 beta = 90.000 gamma = 90.000

2-LiH: Cell parameters $a = 4.0829$ $b = 4.0829$ $c = 4.0829$
alpha = 90.000 beta = 90.000 gamma = 90.000

3- FeTi: Cell parameters: $a = 2.9677$ $b = 2.9677$ $c = 2.9677$

alpha =90.000   beta =90.000 gamma =90.000

4-NaBH₄: Cell parameters: $a = 6.1319$ $b = 6.1319$ $c = 6.1319$

alpha =90.000 beta =90.000 gamma =90.000

5-Li$_4$BH$_4$(NH$_2$)$_3$: Cell parameters: a =10.6750 b =10.6750 c =10.6750

alpha =90.000 beta = 90.000 gamma =90.000

BRAGG R-Factors and weight fractions for TT L-M-B-N-F sample for different phases

Phase: 1

=> Bragg R-factor: 28.4   Vol: 2168.838(0.000)   Fract(%): 74.96(0.89)

=> Rf-factor= 25.0   ATZ: 2251.423   Brindley: 1.0000

Phase: 2

=> Bragg R-factor: 34.1   Vol: 68.063(0.000)   Fract(%): 23.06(0.17)

=> Rf-factor= 19.4   ATZ: 73257.703   Brindley: 1.0000

Phase: 3

=> Bragg R-factor: 24.7   Vol: 26.138 (0.000)   Fract(%):   1.84(0.26)

=> Rf-factor= 18.4   ATZ: 77874.672   Brindley: 1.0000

Phase: 4

=> Bragg R-factor: 82.9   Vol: 230.562 (0.000)   Fract(%):   0.10(0.00)

=> Rf-factor= 47.6   ATZ: 238957.062   Brindley: 1.0000

Phase: 5

=> Bragg R-factor: 93.2   Vol: 1216.479 (0.000)   Fract(%):   0.03(0.00)

=> Rf-factor= 74.2   ATZ: 1192.118   Brindley: 1.0000

S 3 BRAGG R-Factors and weight fractions for TT L-M-B-N-F sample at 100ºC
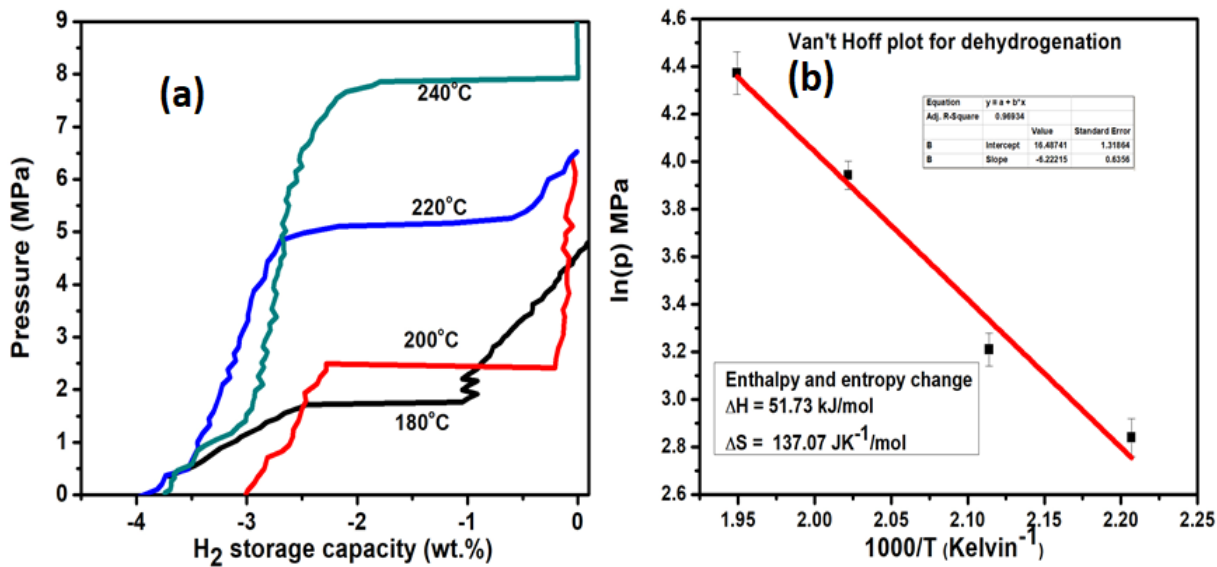
Pattern # 1
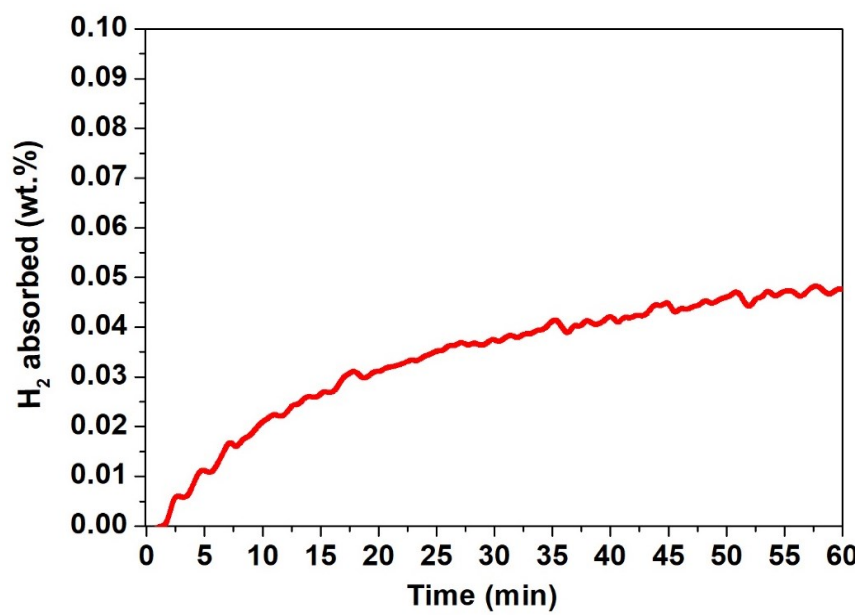
Phase:1 Fract(%): 73.87 Phase: 2 Fract (%): 22.98

Phase:3 Fract (%): 1.83   Phase: 4   Fract (%):   0.1

Phase:5 Fract(%):   1.22

Figure S8 (a) PCI desorption curves of LM ($2LiNH_2$-MgH_2) composite determined at different temperatures (b) van't Hoff plot for dehydrogenation of $2LiNH_2$-MgH_2.

Figure S9 Hydrogenation of FeTi at 200ºC and 7MPa H_2 pressure.