

Supplementary Materials

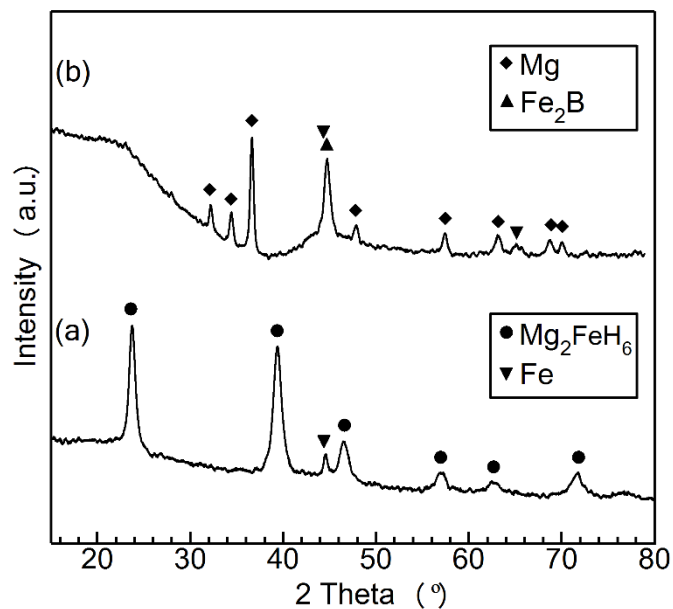


Figure S1. XRD profiles of $0.75\text{Mg}_2\text{FeD}_6 + 0.25\text{LiBH}_4$; (a) as-ball-milled and (b) after the TG measurement at 400 °C.

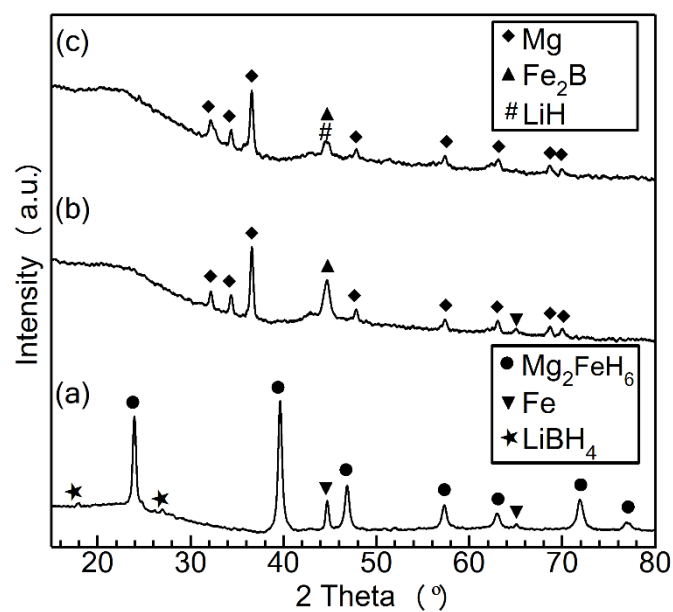


Figure S2. XRD profiles of $0.75\text{LiBH}_4 + 0.25\text{Mg}_2\text{FeD}_6$; (a) as-ball-milled, (b) stopped at 370 °C in the TG measurement and (c) stopped at 420 °C after the TG measurement.

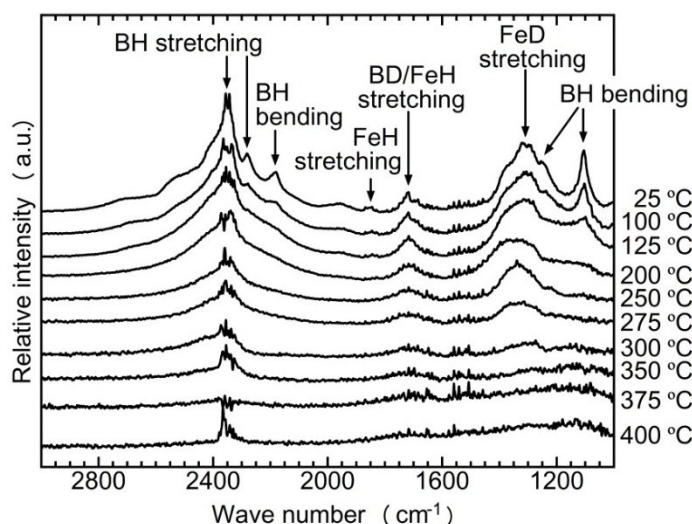


Figure S3. *In situ* IR spectra of $0.75\text{LiBH}_4 + 0.25\text{Mg}_2\text{FeD}_6$. Heating rate was $5\text{ }^\circ\text{C}/\text{min}$. The atmosphere in the sample holder was 0.1 MPa Ar without gas flow.

The *in situ* IR spectra of $0.75\text{LiBH}_4 + 0.25\text{Mg}_2\text{FeD}_6$ is shown in Figure S3. In the $25\text{ }^\circ\text{C}$ spectrum, the merged BD and FeH stretching peaks at around 1720 cm^{-1} indicate that H-D exchange occurred during ball milling. The splitting BH stretching peaks at $\nu \approx 2320\text{ cm}^{-1}$, 2290 cm^{-1} and 2190 cm^{-1} , and the BH bending peaks at $\nu = 1100\text{ cm}^{-1}$ and 1250 cm^{-1} suggest that isotopically pure $[\text{BH}_4]^-$ still existed. The peak at $\nu = 1310\text{ cm}^{-1}$ is assigned to be FeD stretching mode. During the heating process, the BH stretching peaks merged and broadened after $125\text{ }^\circ\text{C}$ because of H-D exchange promoted and phase transition of LiBH_4 occurred. The FeD stretching peak shifted to higher wavelength and broadened obviously when comparing to the situation of $x = 0.25$ because in this composition almost 5 D atoms in $[\text{FeD}_6]^{4-}$ were replaced by H. At $280\text{ }^\circ\text{C}$, all of the peaks faded as a result of the dehydriding reaction, consistent with the TG-MS measurements shown in Figure 3 in the text. The peaks disappeared and the spectrum did not change further at $400\text{ }^\circ\text{C}$, suggesting completion of the dehydriding reaction. The noise at $\nu \approx 2380\text{ cm}^{-1}$ was from the influence of CO_2 . Also the spectra became quiet noisy after $275\text{ }^\circ\text{C}$ because of the melting of LiBH_4 .