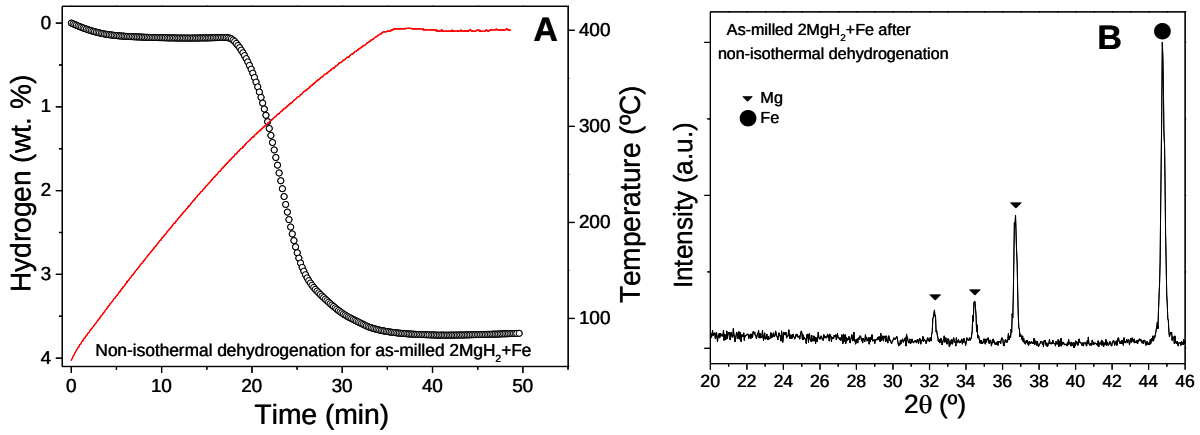

Figure S1. A First non-isothermal dehydrogenation for the as-milled 2MgH2-Fe at a heating ramp of 10 °C/min and 20 kPa and **B** XRD after dehydrogenation.

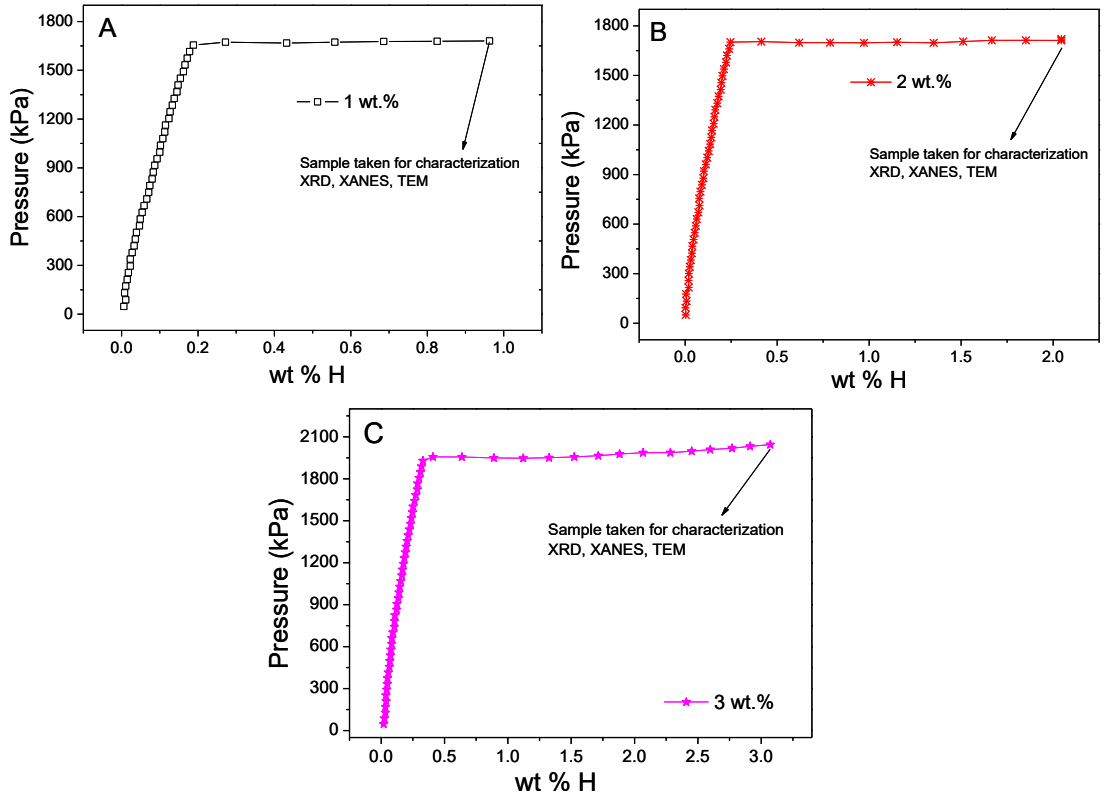

Figure S2. Hydrogenation PCIs at 400 °C for 2Mg:Fe (as-milled 2MgH2-Fe dehydrogenated as indicated in Figure S1) up to: **A** 1 wt %, **B** 2 wt % and **C** 3 wt % of hydrogen capacity.

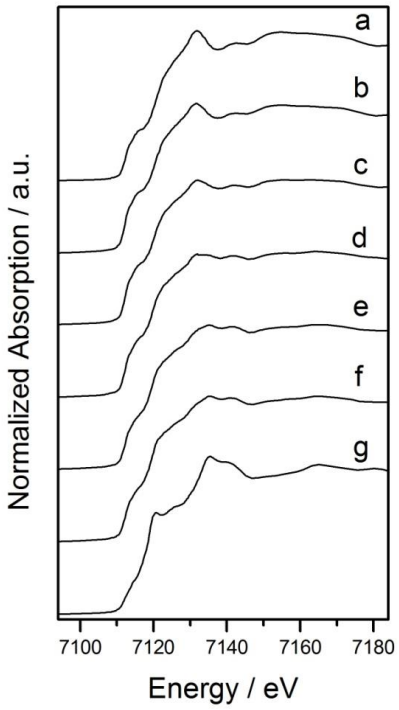

Figure S3. XANES spectra at the Fe K-edge of **a** metallic Fe, **b** as-milled $2MgH_2$+ Fe, samples hydrogenated in equilibrium conditions at 400 °C up to: **c** 1 wt % H_2, **d** 2 wt % H_2, **e** 3 wt % H_2, **f** Complete PCI at 400 °C and **g** Mg_2FeH_6 obtained after several thermal processes at high temperature and under high pressure from as-milled $2MgH_2$ + Fe.

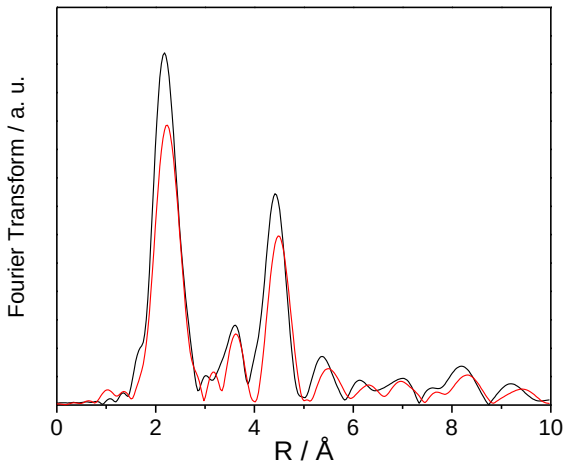

Figure S4. Comparison of the amplitude of the Fourier Transforms of the EXAFS oscillations of metallic Fe (black) and as-milled $2MgH_2$ + Fe (red).

Table S1. Results of the EXAFS fit for as-milled $2MgH_2$ + Fe.

Pair	N	R/Å	σ^2/Å^2
Fe-Fe	5.9(6)	2.46(1)	0.0044(8)
Fe-Fe	4.5(5)	2.85(1)	0.0044(8)

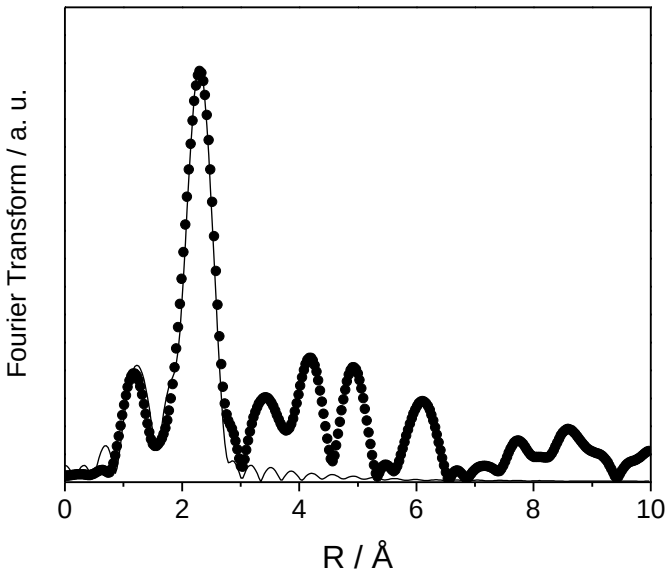

Figure S5. Fitting of the Fourier Transform of the EXAFS signal of as-milled $2MgH_2$ + Fe after several thermal processes (corresponding XANES spectrum Figure S3g). Black circles: experimental data. Solid line: fitting function.

Table S2. Results of the EXAFS fit for as-milled $2MgH_2$ + Fe after several thermal processes (XANES spectrum Figure S2g).

Pair	N	R/Å	σ^2/Å^2
Fe-H	5.5(8)	1.56(2)	0.002(1)
Fe-Mg	7.3(6)	2.73(2)	0.007(2)