Experimental procedure:

LiBH₄ with 95% purity was purchased from Acros. YH₃ was synthesized by the hydrogenation of yttrium (Acros, 99.9%, -40 mesh powder) at 350 °C and 9.0 MPa of hydrogen (99.9999 %) for 2 hours. The XRD pattern of the synthesized YH₃ powder shows that YH₃ is present as a main product together with a small amount of YH₂ and Y₂O₃ phase (Fig. S1). The yttrium oxide was formed due to the impurities of LiBH₄. 3 g of 4LiBH₄ + YH₃ composite was prepared using a planetary ball mill (Retsch PM200), sealed with a lid having a Viton O-ring at 650 rpm for 12 hours. Thirteen 12.7 mm diameter and twenty four 7.9 mm diameter Cr-steel balls were employed together with a 140 ml hardened steel bowl. The ball-to-powder weight ratio was 50:1. The whole process of sample mixing and loading was carried out inside an argon-filled glovebox (mBraun, UniLab), where oxygen and water vapor levels were kept below 1 ppm.

The dehydrogenation of the 4LiBH₄ + YH₃ composite under either hydrogen (99.9999 %) or argon (99.9999 %) back pressure was carried out using a Sievert-type volumetric apparatus. 0.3 g of the composite in a 110 ml reactor was dehydrogenated at 350 °C for 20 hours (heating rate = 30 °C/min), monitoring the pressure in the reactor.

High pressure differential scanning calorimetry (HP-DSC) measurements of the composite were performed in a Netzsch DSC 204 HP at 0.3, 0.4 and 0.5 MPa of 99.9999% hydrogen. 2 mg of the composite sample in an aluminum crucible was loaded into a chamber together with an empty reference aluminum crucible. The crucible was heated to 400 °C with a rate of 40 °C/min and then maintained at 400 °C for 200 minutes.

XRD measurements of the ball milled and dehydrogenated samples were performed using a Bruker D8 Advance X-ray diffractometer with Cu Kα radiation. In order to prevent air exposure of the samples, borosilicate capillary tubes were used during the measurements.

Raman spectroscopy was performed at room temperature using a Horiba Jobin-Yvon LabRam ARAMIS with a 514 nm Ar-ion laser. The samples were prepared by using a Sievert-type apparatus as described above. 0.3 g of the composite was dehydrogenated at 400 °C for an hour (heating rate = 30 °C/min) under static vacuum and various hydrogen and argon back pressures. Subsequently, the samples were cooled down to room temperature within a few minutes. During the measurements, the samples were inevitably exposed to air.
Supporting results:

**Fig. S1** XRD pattern of YH$_3$ synthesized at 350 °C for 2 hours under 9 MPa of hydrogen.
Fig. S2 XRD pattern of 4LiBH₄ + YH₃ composite prepared by ball milling.
Fig. S3 HP-DSC curves of 4LiBH₄ + YH₃ composite dehydrogenated under (a) 0.3, (b) 0.4 and (c) 0.5 MPa of hydrogen. The crucible was heated to 400 °C with a rate of 40 °C/min and then maintained at 400 °C for 200 minutes. The symbol triangle, star and arrows indicate the phase transformation of LiBH₄ (orthorhombic to hexagonal), melting of LiBH₄ and the dehydrogenation of LiBH₄+YH₃ composite, respectively.
**Fig. S4** XRD patterns of 4LiBH$_4$ + YH$_3$ composite dehydrogenated under (a) 0.1, (b) 0.2, (c) 0.5, (d) 0.7 and (e) 1.0 MPa of hydrogen.
Fig. S5 XRD patterns of 4LiBH₄ + YH₃ composite dehydrogenated under (a) 0.1, (b) 0.2, (c) 0.5, (d) 0.7 and (e) 1.0 MPa of argon.
Fig. S6 The amount of desorbed hydrogen of 4LiBH₄+YH₃ composite under (a) hydrogen and (b) argon back pressures.