Supplementary information:

Material preparation and characterization

Commercial $LiBH_4$ (95%, Acros), MgH_2 (99%, Alfa Aesar), Al (99.5%, Alfa Aesar), $LiAlH_4$ (97%, Alfa Aesar) and anhydrous $MgCl_2$ (99.9%, Alfa Aesar) powders were used as-received. $Mg(AlH_4)_2$ was synthesized by a mechano-chemically activated metathesis reaction of $LiAlH_4$ and $MgCl_2$ without solvent, namely,

$$2LiAlH_4 + MgCl_2 \rightarrow Mg(AlH_4)_2 + 2LiCl \quad (1)$$

Here the by-product LiCl was not further removed because it did not participate in any de-/rehydrogenation reaction, and thus has no contribution to the hydrogen amount de-/absorbed in the present work. The power mixtures of $6LiBH_4 + Mg(AlH_4)_2$, $2LiBH_4 + MgH_2$ and $2LiBH_4$ + Al were ball milled respectively under 0.5 MPa hydrogen atmosphere at a rotation speed of 400 rpm for only 2 h by using a QM-1SP planetary mill. Stainless steel vials (250 ml in volume) and balls (10 mm in diameter) were used. The ball to sample weight ratio was about 20:1. For keeping the sample from air-exposure, all sample handling was carried out in an Ar-filled glove box equipped with a purification system.

A carefully calibrated Sieverts-type apparatus was applied to determine the de-/rehydrogenation properties. Firstly, the hydrogen amount desorbed as a function of temperature was measured according to pressure rise at a heating rate of 3 K min^{-1}. The isothermal dehydrogenation kinetics was then measured against a background hydrogen pressure of 0.1 MPa. After full dehydrogenation, the isothermal rehydrogenation measurement was carried out with an initial hydrogen pressure of 3 MPa. The de-/absorbed hydrogen amounts were determined with respect to the total weight of the samples, except for

the $6LiBH_4$–$Mg(AlH_4)_2$ system where the weight of by-product LiCl was excluded.

To determine the phase components of the $6LiBH_4 + Mg(AlH_4)_2$ mixture after ball milling and isothermal de-/rehydrogenation at different temperatures, X-ray diffraction (XRD) measurement was performed using a Rigaku D/Max 2500VL/PC diffractometer with Cu Kα radiation at 50 kV and 200 mA. The XRD samples were loaded and sealed in a special holder that can keep the sample under argon atmosphere in the course of measurement. In addition, the element distribution of the dehydrogenated product was examined by an energy dispersive X-ray spectrometer (EDX) equipped to a Nova NanoSEM 430 scanning electron microscope (SEM).

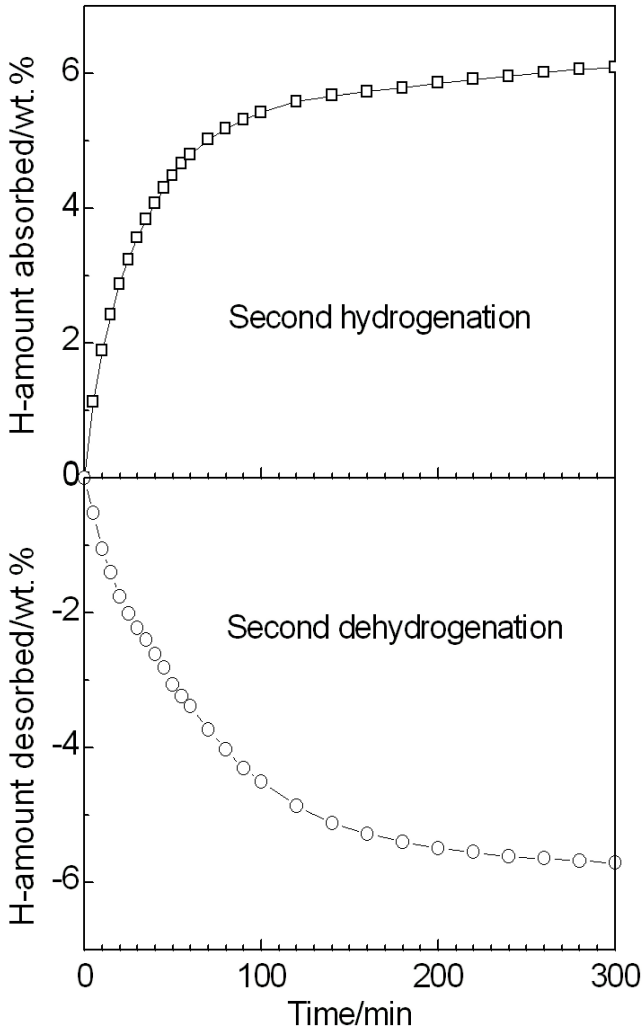

Fig. S1 Kinetic curves of the second dehydrogenation and hydrogenation at 673 K for the $6LiBH_4$–$Mg(AlH_4)_2$ system