**Supporting information**

Belonging to the manuscript

**Complex hydrides as multifunctional materials: characterisation and thermal decomposition of Na$_2$Mg$_2$NiH$_6$**

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**Additional experimental considerations**

**Thermal analysis of Na$_2$Mg$_2$NiH$_6$ shown in Fig. S3**

Temperature Programmed Desorption (TPD) experiments were carried out using a RGAPro residual gas analyser. The sample was heated from room temperature to 400 °C at a ramp rate of 2 °C/min. Hydrogen desorption was measured using a mass spectrometer by analysing the intensity of ions with the $m/z=2$ (H$_2$).

The differential scanning calorimetry (DSC) analysis was conducted simultaneously with thermogravimetric analysis (TGA) on a Mettler Toledo Star1 analyser. The powdered sample (~10 mg) was loaded into an alumina crucible of 70 μl volume and covered with alumina powder (~53 mg) to prevent the oxidation and hydrolysis during the quick transfer to the analyser and also to avoid a volatile foaming and flowing out of the crucible if the powder sample melted. An argon flow of 20 ml/min was set as a protection gas flow with a purge gas rate of 50 ml min$^{-1}$. The sample was heated up to 400 °C at a heating rate of 2 °C min$^{-1}$. 
Powder XRD analysis of Na$_2$Mg$_2$NiH$_6$ shown in Figs. S4 and S5

Powder X-ray diffraction (XRD) measurements were conducted using a PANalytical X’Pert-Pro using CuKa radiation inside a 0.7 mm borosilicate capillary. Data were collected using a X’Celerator X linear position sensitive detector within a 2θ range of 10 – 90° using 0.021 steps at 0.041/s with X-ray generator operating conditions of 45 kV and 40 mA. The XRD samples were loaded in an Ar glovebox to prevent oxygen/moisture contamination during data collection.

**Fig. S1.** Moles of crystalline phases calculated directly from quantitative Rietveld refinement of *in situ* SR-XRD data.
Fig. S2. DSC (a) and TPD-MS (b) analysis of Na$_2$Mg$_2$NiH$_6$. $\Delta T/\Delta t = 2$ °C/min.
**Fig. S3.** Multi peak fitting of the MS analysis of Na$_2$Mg$_2$NiH$_6$. Temperature of peak 0 = 278 °C, peak 1 = 300 °C, peak 2 = 350 °C.
**Fig. S4.** Room temperature XRD patterns of Na$_2$Mg$_2$NiH$_6$ performed after heating to (a) 260 °C and (b) 330 °C *in vacuo* before quenching. * = Na$_2$Mg$_2$NiH$_6$; ^ = Mg$_2$NiH$_{0.3}$; ! = NaH; + = MgNi$_2$. $\lambda$ = CuK$_\alpha$.

**Fig. S5.** PCI absorption measurement at 315°C of previously decomposed Na$_2$Mg$_2$NiH$_6$. 
**Fig. S6.** Room temperature XRD pattern of material after a PCI absorption measurement at 315 °C of previously decomposed Na₂Mg₂NiH₆. ~ = NaMgH₃; ! = NaH; + = MgNi₂. λ = CuKα.

**Fig. S7.** XRD pattern of hydrogenated material after four absorption and three desorption cycles starting from the desorbed state. * = Na₂Mg₂NiH₆; ~ = NaMgH₃; ! = NaH; + = MgNi₂. λ = CuKα. T_{des} = 395 °C and 0.2 bar H₂; T_{abs} = 315 °C and 60 bar H₂.
Fig. S8. (a) Absorption kinetics and (b) maximum hydrogen capacity of Na$_2$Mg$_2$NiH$_6$ for 30 cycles measured inside a Sieverts apparatus. $T_{des} = 400$ °C and 0.7 bar H$_2$; $T_{abs} = 400$ °C and 40 bar H$_2$. The blue circles (b) indicate the end pressure after the absorption step. The red triangles indicate the wt % H$_2$ absorbed in each cycle.