Supporting information

Belonging to the manuscript

Complex hydrides as multifunctional materials: characterisation and thermal decomposition of $Na_2Mg_2NiH_6$

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Additional experimental considerations

Thermal analysis of $Na_2Mg_2NiH_6$ 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 $Na_2Mg_2NiH_6$ 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.

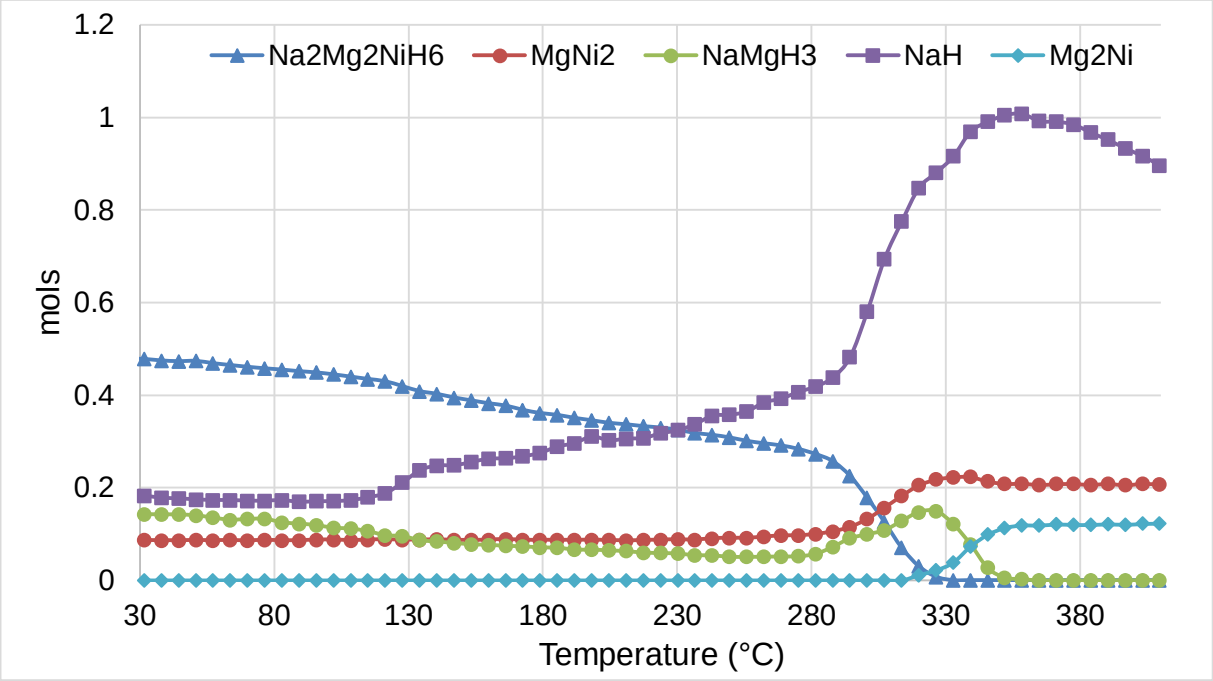

Fig. S1. Moles of crystalline phases calculated directly from quantitative Rietveld refinement of *in situ* SR-XRD data.

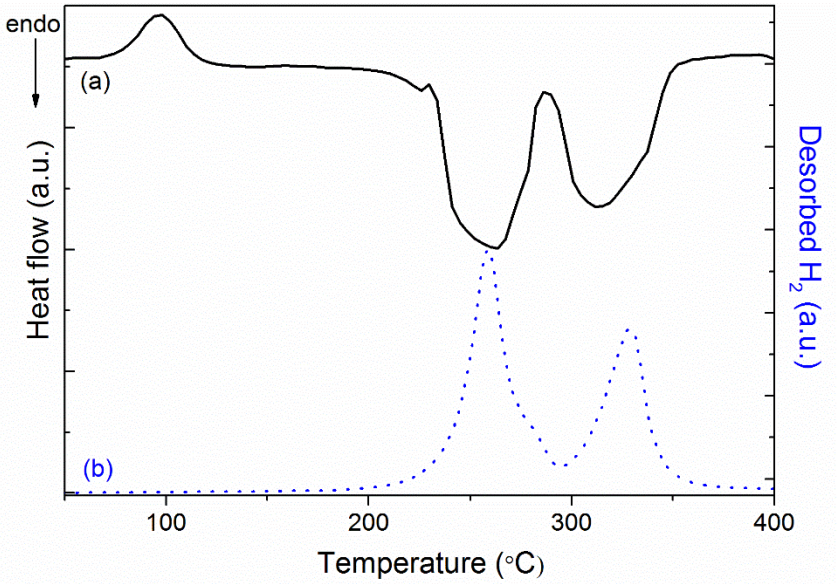

Fig. S2. DSC (a) and TPD-MS (b) analysis of $Na_2Mg_2NiH_6$. $\Delta T/\Delta t$ = 2 °C/min.

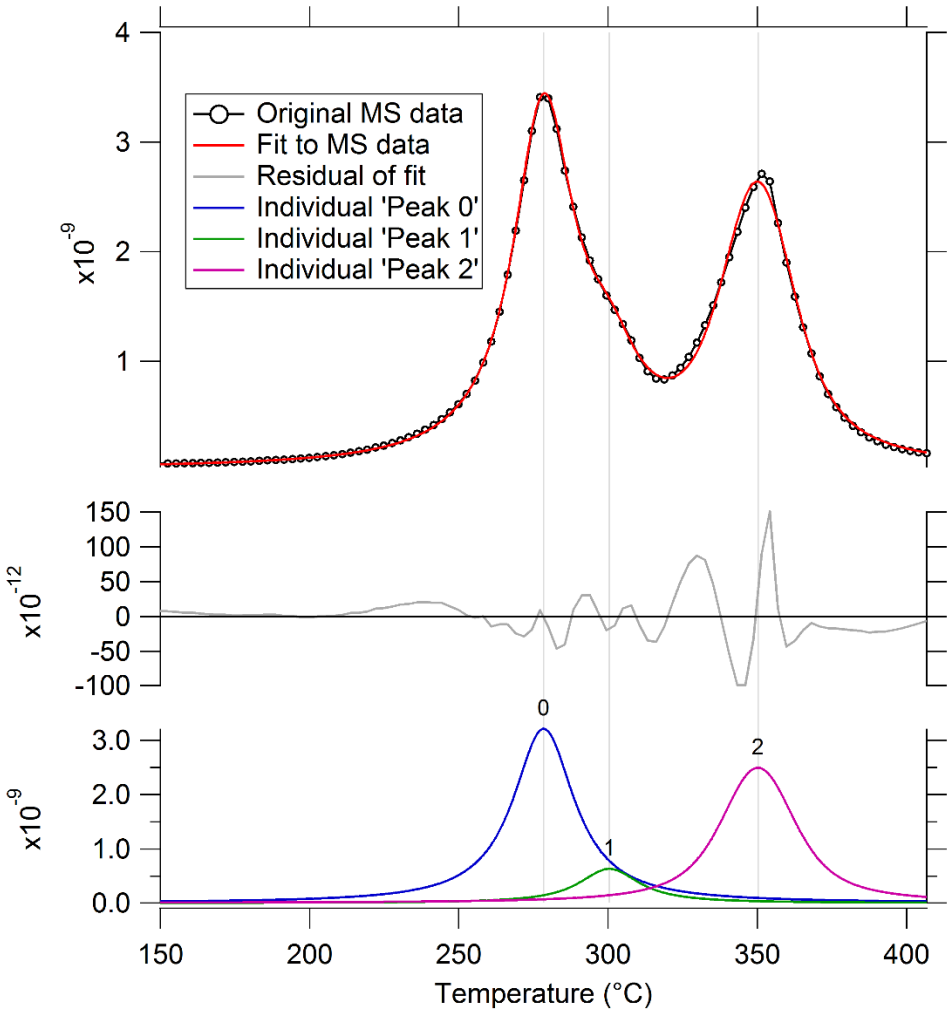

Fig. S3. Multi peak fitting of the MS analysis of $Na_2Mg_2NiH_6$. Temperature of peak 0 = 278 °C, peak 1 = 300 °C, peak 2 = 350 °C.

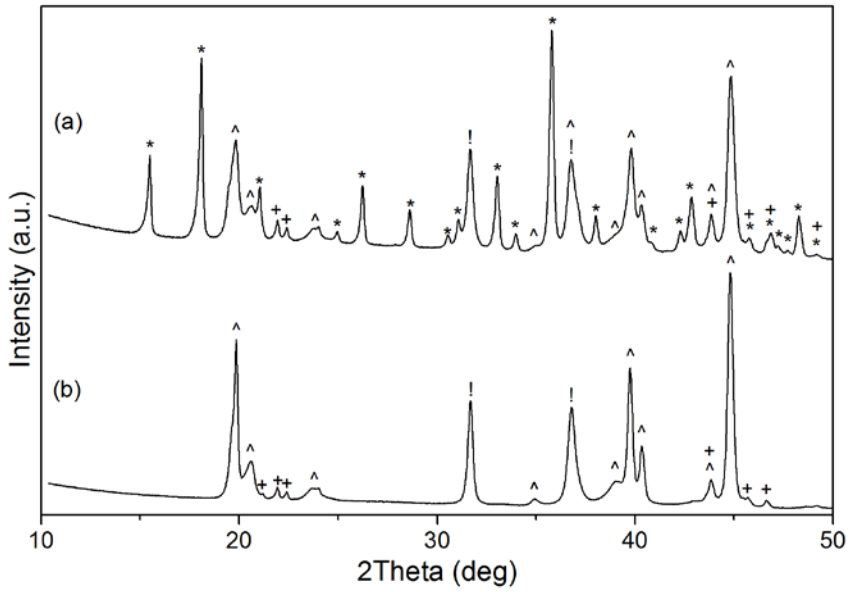

Fig. S4. Room temperature XRD patterns of $Na_2Mg_2NiH_6$ performed after heating to (a) 260 °C and (b) 330 °C *in vacuo* before quenching. * = $Na_2Mg_2NiH_6$; ^ = $Mg_2NiH_{0.3}$; ! = NaH; + = $MgNi_2$. λ = CuK_α.

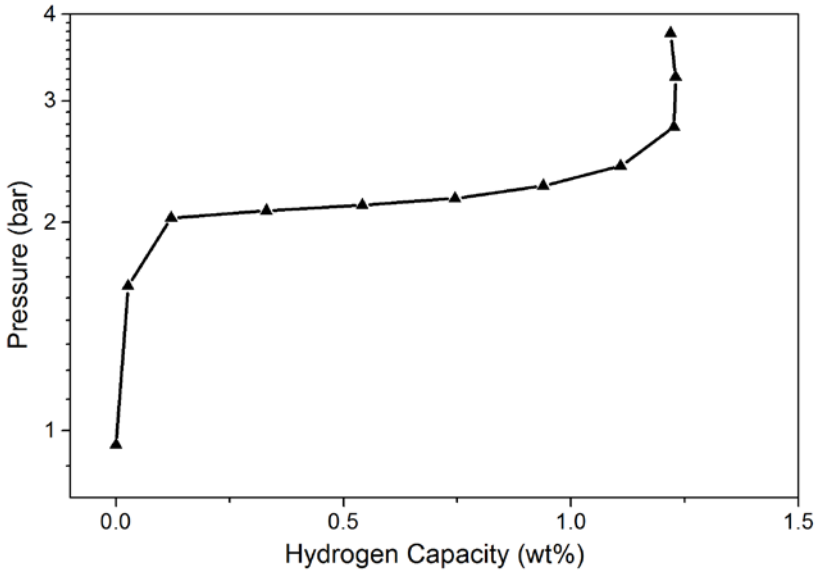

Fig. S5. PCI absorption measurement at 315°C of previously decomposed $Na_2Mg_2NiH_6$.

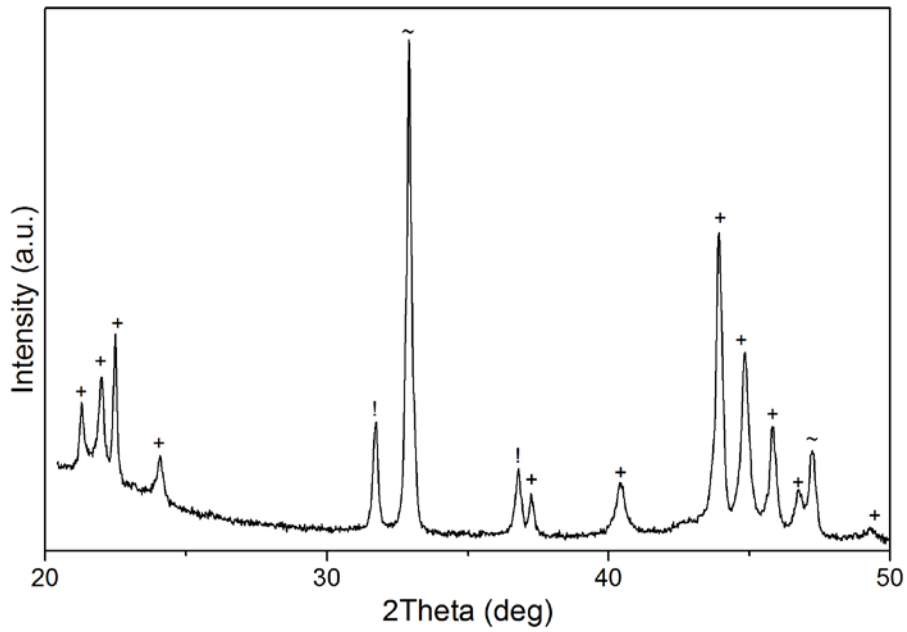

Fig. S6. Room temperature XRD pattern of material after a PCI absorption measurement at 315 °C of previously decomposed $Na_2Mg_2NiH_6$. ~ = $NaMgH_3$; ! = NaH; + = $MgNi_2$. λ = CuK_α.

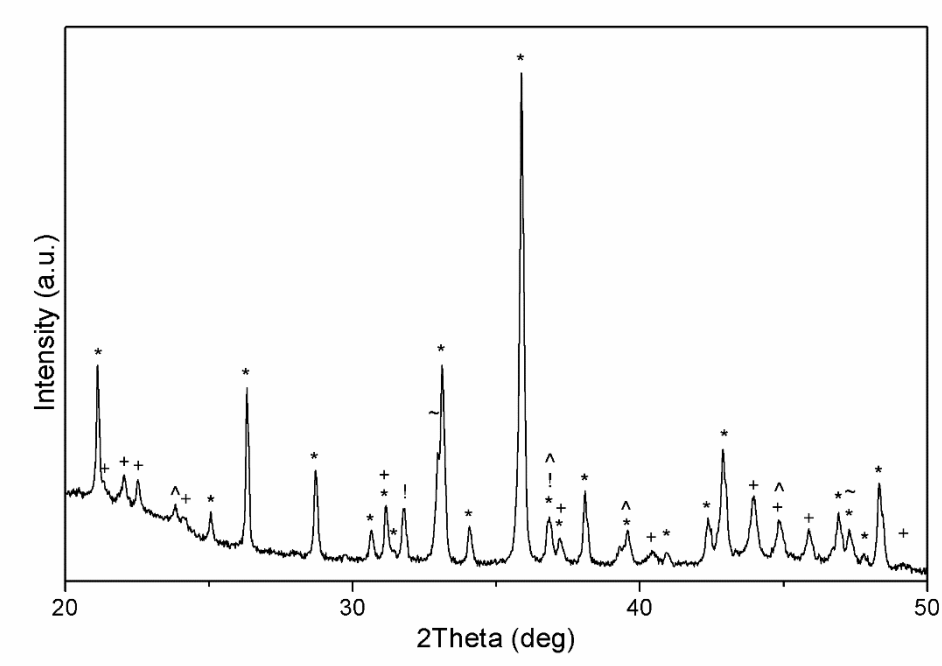

Fig. S7. XRD pattern of hydrogenated material after four absorption and three desorption cycles starting from the desorbed state. * = $Na_2Mg_2NiH_6$; ~ = $NaMgH_3$; ! = NaH; + = $MgNi_2$. λ = CuK_α. . T_{des} = 395 °C and 0.2 bar H_2; T_{abs}= 315 °C and 60 bar H_2.

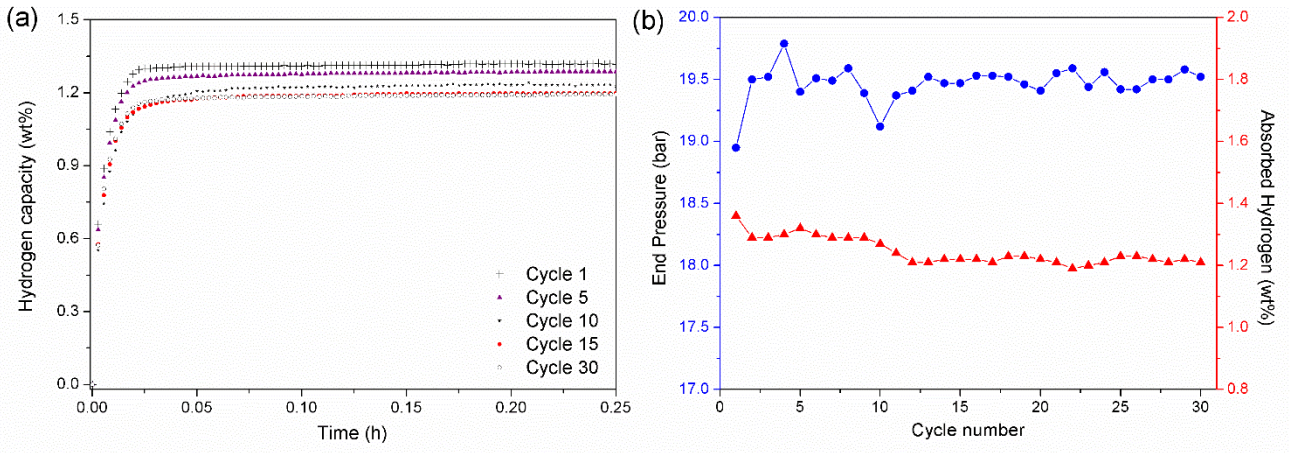

Fig. S8. (a) Absorption kinetics and (b) maximum hydrogen capacity of $Na_2Mg_2NiH_6$ for 30 cycles measured inside a Sieverts apparatus. T_{des} = 400 °C and 0.7 bar H_2; T_{abs}= 400 °C and 40 bar H_2. The blue circles (b) indicate the end pressure after the absorption step. The red triangles indicate the wt % H_2 absorbed in each cycle.