

Electronic Supplementary Information:

1. Material preparation and measurement

The source materials were obtained commercially, namely polycrystalline MgH_2 powder (98%, Alfa Aesar), Ge powder (99.999%, -100mesh, Alfa Aesar) and TiO_2 powder (P-25, Degussa AG, 80% anatase, 20% rutile.). All handling procedures and hand milling were conducted in an Argon glove box ($\text{O}_2 < 0.1\text{ppm}$, $\text{H}_2\text{O} < 0.1\text{ppm}$). Both MgH_2 and Ge powders were separately mechanically milled (Fritsch Pulverisette planetary ball mill) under Argon up to 4 and 2 hours respectively. 3 g mixtures of premilled MgH_2 / Ge with a 2:1 mass ratio either with or without catalyst precursor additions of 1 mol. % TiO_2 with respect to Mg_2Ge compound, were hand milled then mechanically milled together, under argon for different milling times up to 4 hrs. The milling pots were transferred to the glove box at regular intervals to remove samples for analysis.

Hydrogen decomposition kinetics and calorimetric measurements were recorded using thermal gravimetric analysis, TGA, (Netzsch TG 209 F1) and differential scanning calorimetry, DSC, (Netzsch DSC 204 HP) both at heating rate of $10^\circ\text{C min}^{-1}$ and an argon flow rate of 100 ml min^{-1} (DSC was also run under flowing H_2 at pressures up to 25 bar). Typically samples were 5-10 mg were loaded into a hermetically sealed aluminium pan in the glove box. The sample lid was pierced immediately before being loaded into the instrument to minimise air contamination. For powder X-ray diffraction, XRD, (Bruker D8 Adv) the powder samples were spread on a Si single crystal wafer and amorphous polymer tape was used to cover the surface of the powder to minimise contact with air during XRD measurements. Particle morphology and mixture homogeneity were analysed using scanning electron microscopy, SEM, and energy-dispersive X-ray spectroscopy, EDX, analysis (Philips XL 30). The samples were coated with carbon under Argon prior to loading into the SEM (Edwards coating system E306A) in order to improve the conductivity of the surface.

2. Results

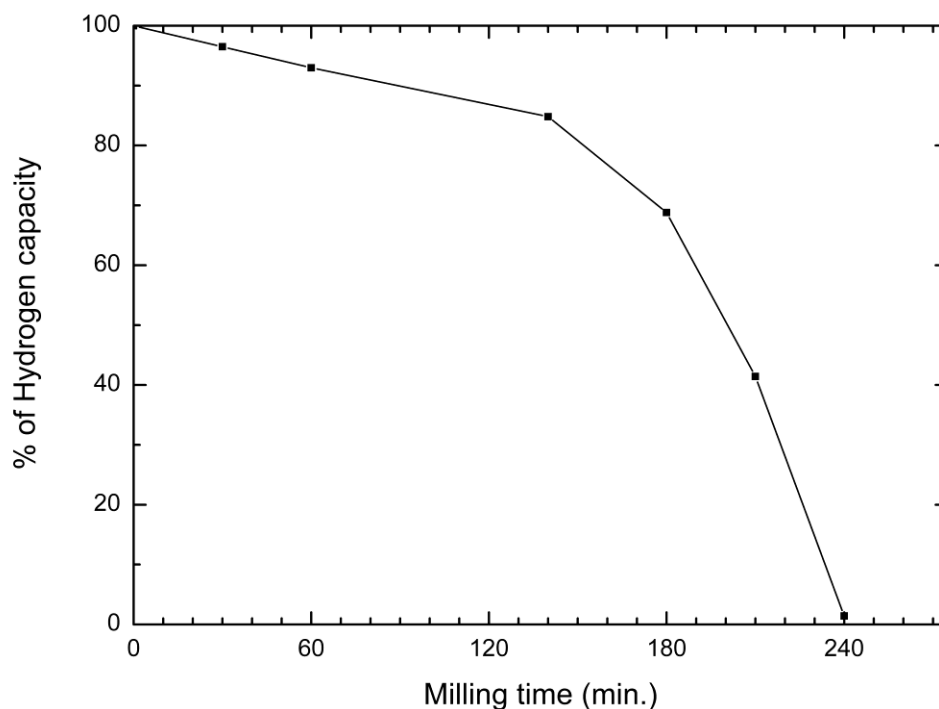


Figure S1. Hydrogen capacity of ball milled samples of MgH_2 / Ge in a 2:1 molar ratio, measured by TGA under an Ar carrier gas and heated to 585°C .

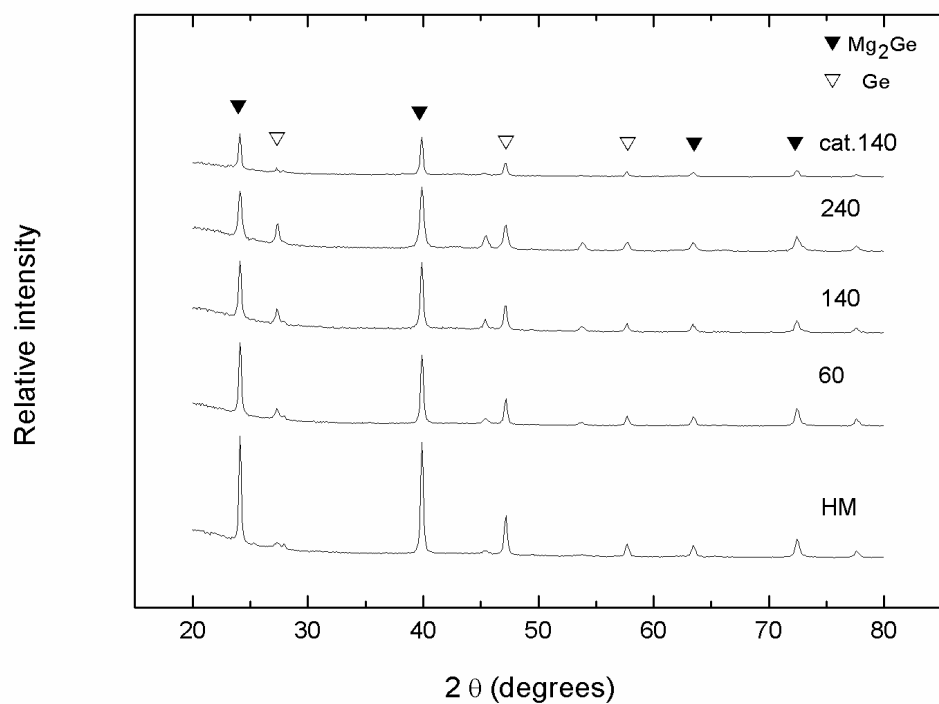


Figure S2. XRD of the dehydrogenation products for hand milled (HM) and ball milled samples of MgH₂ / Ge in a 2:1 molar ratio (milling time is given against each the plot and the catalysed sample is denoted by “cat.”). The samples were the end products from the DSC experiments.

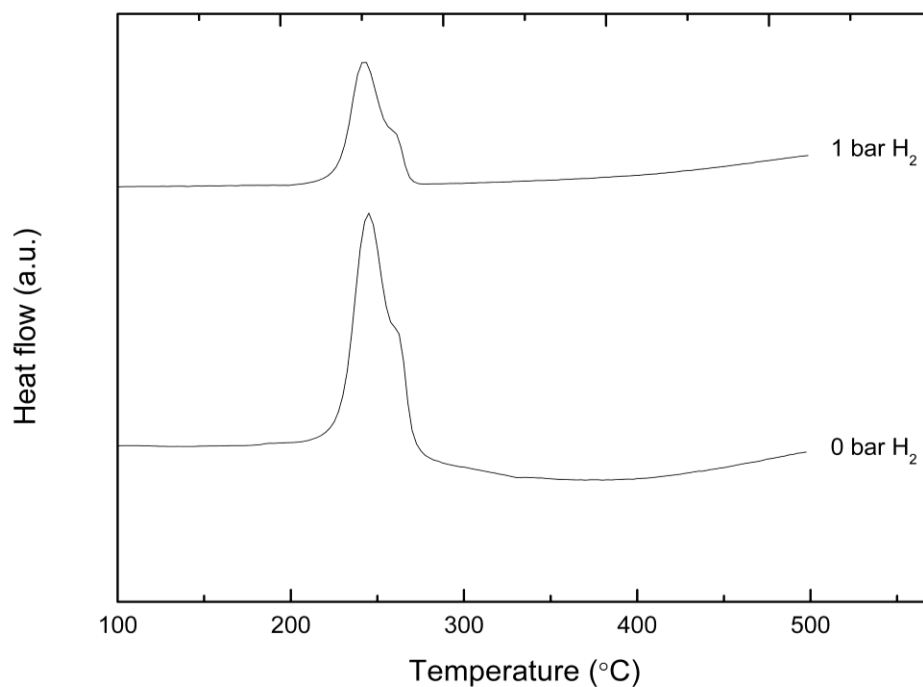


Figure S3. DSC of MgH₂ / Ge in a 2:1 molar ratio ball milled for 140 min, run under an Ar carrier gas (labelled as 0 bar H₂) and under H₂ as a carrier gas (labelled as 1 bar H₂).

Table S1. Comparison of major XRD reflections for the samples analyzed with literature data.

Phase	d- spacing (Å)		h k l
	Experimental values	Theoretical values	
MgH ₂ (tetragonal)	3.1940	3.1939	1 1 0
Ge (FCC)	3.2640	3.2660	1 1 1
Mg ₂ Ge (FCC)	3.6890	3.6863	1 1 1

Reference data:

- 1- MgH₂:** Ellinger, F.H., Holley, C.E., McInteer, B.B., Pavone, D., Potter, R.M., Staritzky, E., Zachariassen, W.H., J. Am. Chem. Soc., volume 77, page 2647 (1955)
Calculated from ICSD using POWD-12++ (1997)
- 2- Ge:** Swanson, Tatge., Natl. Bur. Stand. (U.S.), Circ. 539, volume I, page 18(1951)
- 3- Mg₂Ge:** Grosch, G.H., Range, K.-J., J. Alloys Compds., volume 235, page 250(1996)
Calculated from ICSD using POWD-12++ (1997)