

Electronic Supplementary Information

Material preparation and characterization:

Synthesis of the Ti₃C₂ catalyst

The Ti₃AlC₂ powder (98% purity, ≤ 30 μm; Beijing Wangyihutong Company, China) was immersed in hydrofluoric acid (≥ 40%; Sinopharm Chemical Reagent Co., Ltd, China) for 72 h at room temperature with stirring, and in a ratio of 1 g MAX powder to 10 mL HF. This was followed by cycles of washing with deionized water, centrifuge sedimentation (10 min at 10000 rpm per cycle) and decanting. When the pH value of the rinsed solution reached approximately 5, the solid was dried under vacuum at 100 °C for 20 h.

Preparation of MgH₂ and catalysed MgH₂ composites

Commercially available MgH₂ (98% purity; Alfa Aesar) was used as received without further purification. The MgH₂ - *x* wt% Ti₃C₂ composites, where *x* = 0, 1, 3, 5, 7 and 20, were prepared by ball milling the appropriate precursors under 50 bar hydrogen at a speed of 500 rpm for 24 h. The ball-to-powder weight ratio was about 75:1. To minimize temperature increases in the samples during ball milling, the mill was rotated for 0.3 h in one direction, paused for 0.1 h, and finally rotated in the reverse direction for 0.3 h. All samples were handled in a glove box (MBRAUN, Germany) filled with pure argon to prevent contamination from moisture and oxygen; the H₂O and O₂ concentrations were kept below 0.1 ppm.

Sample characterization

The phase structures of the samples were examined by powder X-ray diffraction (XRD). The XRD data were collected in a 2θ range of 5 to 90° with 0.05° step increments on an X'Pert Pro X-ray diffractometer (PANalytical, Netherlands) with Cu Kα radiation (40 kV, 40 mA). The powder samples were sealed in a custom designed container and covered with Scotch tape to prevent air and moisture contamination.

The morphologies of the samples were observed using scanning electron microscopy (SEM, Hitachi, S-4800) and transmission electron microscopy (TEM, FEI, Tecnai G2 F20 S-TWIN). The distribution of elemental Mg, Ti, C and F in the

samples was detected with an energy-dispersive X-ray spectrometer (EDS) attached to a Hitachi S-3400 scanning electron microscope.

X-Ray photoelectron spectroscopy (XPS) analyses were performed on an ESCALab 250 Xi spectrometer. The XPS spectra were recorded using a monochromatic Al K α X-ray source with a base pressure of 3.7×10^{-10} Torr. The XPS data were calibrated by using the adventitious C 1s signal at 284.8 eV as a reference and the peaks were fitted by XPSPEAK software.

A homemade Sieverts-type apparatus was used to quantitatively evaluate the hydrogen desorption/absorption behaviours. For each test, approximately 70 mg of sample was loaded into a stainless steel tube in a glove box filled with argon. For dehydrogenation, the sample was gradually heated to the desired temperature at an average rate of $2 \text{ }^\circ\text{C min}^{-1}$ under a primary vacuum ($\sim 10^{-3}$ Torr). During hydrogenation, an initial hydrogen pressure of 50 bar was applied to the dehydrogenated sample, and the temperature was gradually elevated at a constant rate of $1 \text{ }^\circ\text{C min}^{-1}$. For the isothermal examination, the sample was quickly heated to the pre-set temperature and kept there during the entire test.

Table. S1 Comparison of dehydrogenation/hydrogenation kinetics of MgH₂ with various Ti-based catalysts.

Samples	Dehydrogenation	Hydrogenation	Reference
MgH ₂ -5 wt% Ti ₃ C ₂	6.2 wt% - 1 min - 300 °C	6.1 wt% - 30 s - 150 °C	This work
MgH ₂ -10 wt% TiN@rGO	6.0 wt% - 18 min - 300 °C	-	S1
MgH ₂ -TiF ₃ -SWCNTs	6.3 wt% - 23 min - 300 °C	5.5 wt% - 20 min - 270 °C	S2
MgH ₂ -VTi-CNTs	6.0 wt% - 6 min - 300 °C	5.0 wt% - 30 s - 200 °C	S3
MgH ₂ -TiB ₂ -GNSs	6.5 wt% - 40 min - 300 °C	-	S4
MgH ₂ -0.1TiH ₂	-	4.8 wt% - 10 min - 300 °C	S5

Note: x wt% - y min - z °C represents x wt% hydrogen released/absorbed within y min at z °C.

[S1]Y. Wang, L. Li, C. H. An, Y. J. Wang, C. C. Chen, L. F. Jiao and H. T. Yuan, *Nanoscale*, 2014, **6**, 6684-6691.

[S2]R. R. Shahi, A. Bhatnagar, S. K. Pandey, V. Dixit and O. N. Srivastava, *Int. J. Hydrogen Energy*, 2014, **39**, 14255-14261.

[S3]X. D. Yao, C. Z. Wu, A. J. Du, J. Zou, Z. H. Zhu, P. Wang, H. M. Cheng, S. Smith and G. Q. Lu, *J. Am. Chem. Soc.*, 2007, **129**, 15650-15654.

[S4]G. Liu, Y. J. Wang, L. F. Jiao and H. T. Yuan, *Int. J. Hydrogen Energy*, 2014, **39**, 3822-3829.

[S5]H. Shao, M. Felderhoff and F. Schüth, *Int. J. Hydrogen Energy*, 2011, **36**, 10828-10833.

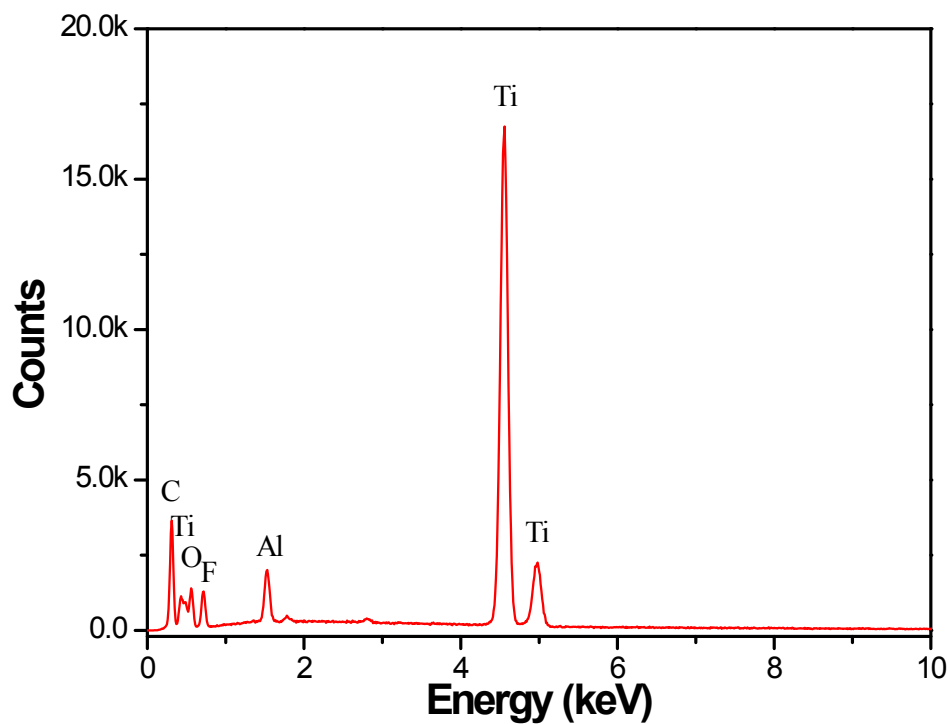


Fig. S1 EDS spectrum of the as-prepared Ti_3C_2 sample.

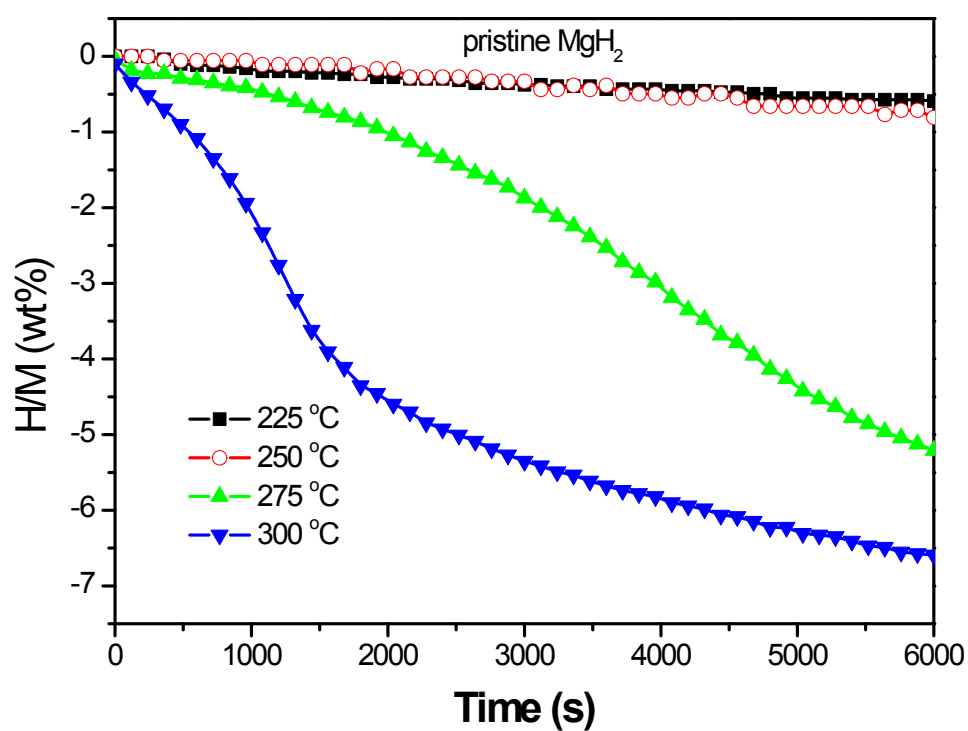


Fig. S2 Isothermal dehydrogenation curves of the pristine MgH_2 sample.

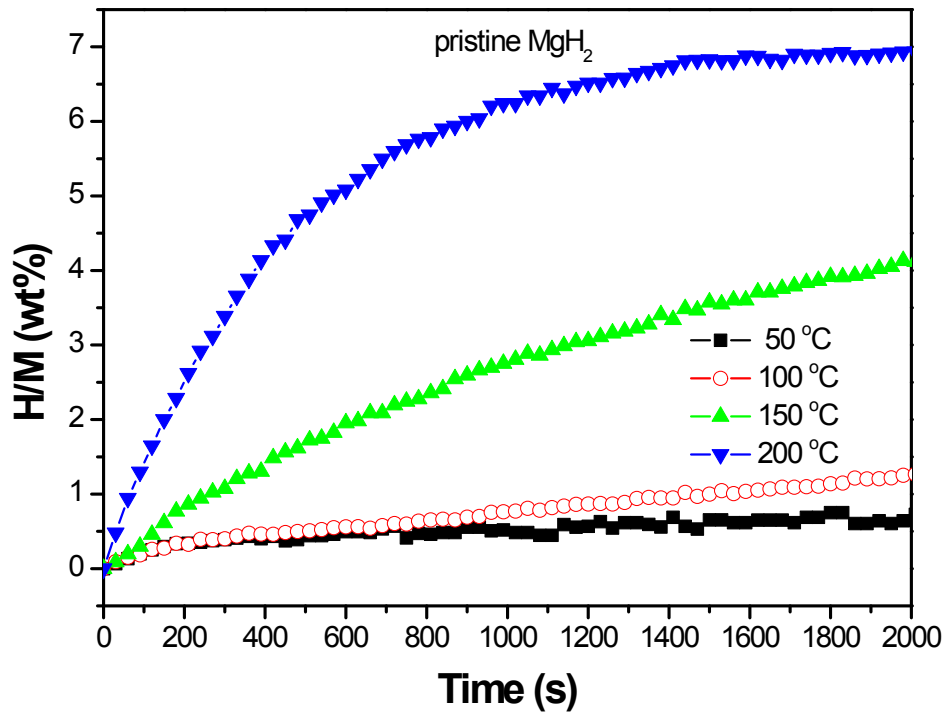


Fig. S3 Isothermal hydrogenation curves of the pristine MgH_2 sample under 50 bar hydrogen.

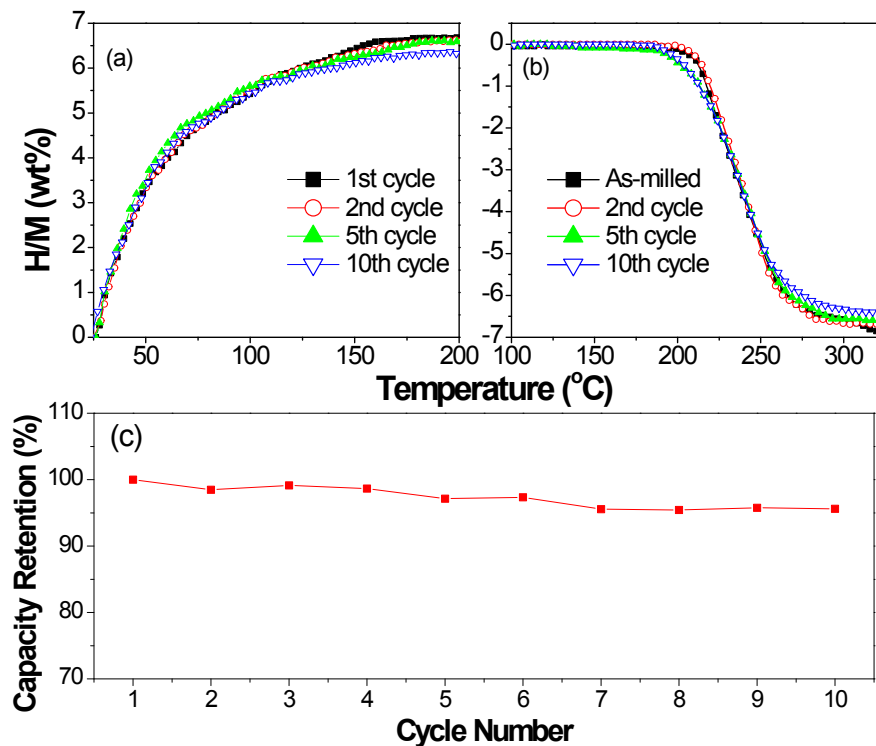


Fig. S4 Non-isothermal hydrogenation (a), dehydrogenation (b) and capacity retention (c) curves of the MgH_2 -5 wt% Ti_3C_2 sample as a function of cycle.

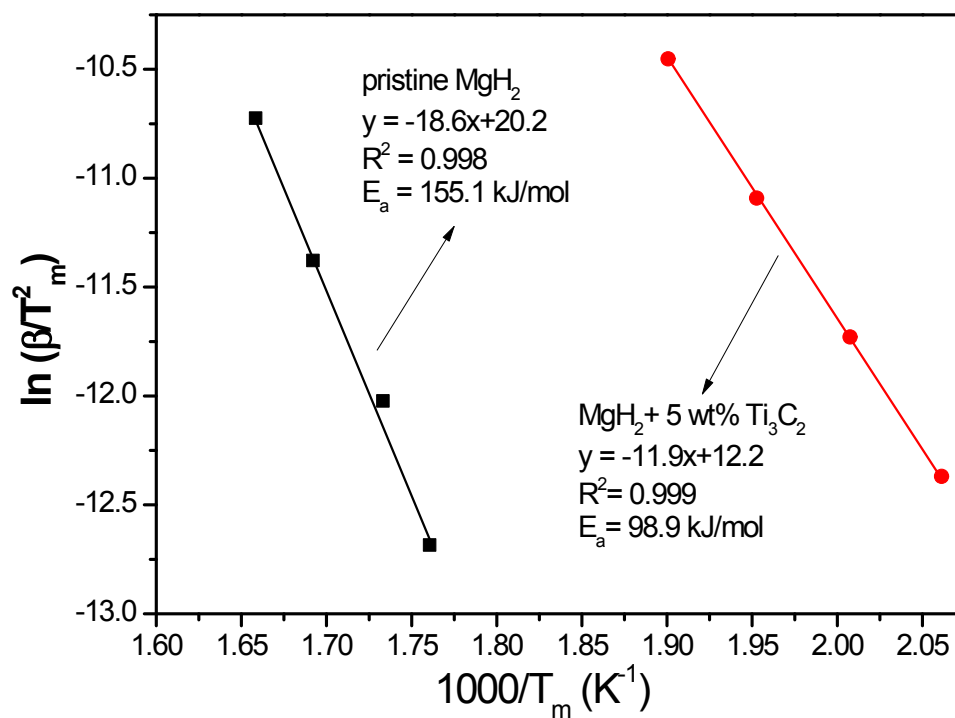


Fig. S5 Kissinger plots for pristine MgH₂ and MgH₂-5 wt% Ti₃C₂ samples.

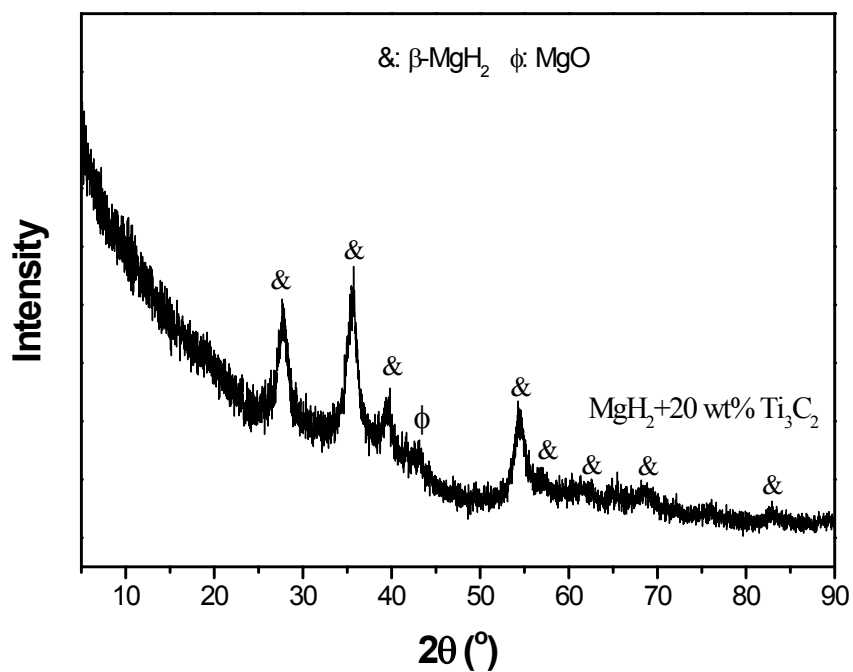


Fig. S6 XRD pattern of the as-milled MgH₂-20 wt% Ti₃C₂ sample.

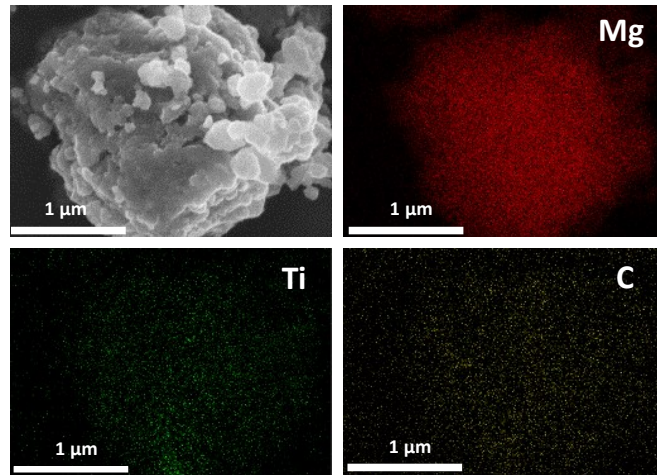


Fig. S7 SEM image and EDS mapping results of the MgH_2 -5 wt% Ti_3C_2 sample after dehydrogenation.

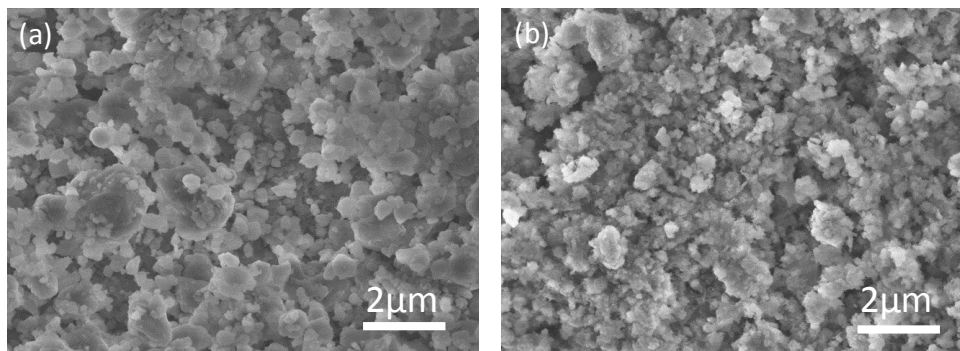


Fig. S8 SEM images of the Ti_3C_2 -doped samples: (a) as-milled and (b) after the 10th hydrogenation.