Supporting information

Understanding and unlocking the role of V in boosting reversible hydrogen storage

performance of MgH₂

Yang Meng^a, Jian Zhang^b, Shunlong Ju^a, Yaxiong Yang^c, Zhenglong Li^c, Fang Fang^a, Dalin Sun^a, Guanglin Xia^{a*}, Hongge Pan^c, and Xuebin Yu^{a*}

^aDepartment of Materials Science, Fudan University, Shanghai 200433, China E-mail: xiaguanglin@fudan.edu.cn, yuxuebin@fudan.edu.cn.

^bHunan Provincial Key Laboratory of Intelligent Manufacturing Technology for High-performance Mechanical Equipment, Changsha University of Science and Technology, Changsha, 410114, China

^cInstitute of Science and Technology for New Energy, Xi'an Technological University, Xi'an 710021, China

Experimental Section/Methods

Preparation of V_6O_{13} nanobelts

All reagents and solvents were commercially purchased and used without further purification. Typically, 476.2 mg ammonium metavanadate (NH₄VO₃, Aladdin, 99.95%) and 504.2 mg oxalic acid dihydrate (C₂H₂O₄·2H₂O, Aladdin, 99.98%) were dissolved in 20 mL deionized water with stirring, respectively. Then the ammonium metavanadate solution was slowly poured into the oxalic acid solution followed by ultrasonic concussion and stirring. After completed dissolution, the solution was transferred into a 100 mL stainless-steel autoclave with Teflon liner and heated at 180 °C for 8 h in a convection oven. The dark green products were collected by centrifugation after washing by deionized water and ethanol for several times. Then the products were dried at 70 °C for 12 h in a vacuum drying oven. V₆O₁₃ nanobelts were obtained by calcination at 450 °C in a tube furnace under argon for 8 h. For comparison, bulk V₆O₁₃ are purchased from Aladdin.

Preparation of MgH₂ with catalysts

To prepare MgH₂+x wt.% V₆O₁₃ nanobelts (x=3,5,10,15), V₆O₁₃ nanobelts were mixed with commercial MgH₂ (Alfa Aesar, 98%) by mechanically milling for 12 h under a H₂ pressure of 45 atm using a planetary ball mill (QM-1SP2, Nanjing) with the speed of 500 rpm. The ball-to-powder weight ratio was approximately 120:1. The ball milling process was set to pause for 5 min every 30 min of ball milling to prevent the temperature increasing. All the operations are handled in a glove box with high purity argon and the water and oxygen level are under 0.01 ppm to protect these samples. In addition, pure MgH₂ and MgH₂ with different additives were prepared by the same ball-milling process. It should be mentioned that the bulk catalysts were set to 10 wt.% for comparison. The obtained samples were labeled as ball-milled MgH₂, MgH₂+bulk V₆O₁₃, MgH₂+V₆O₁₃ nanobelts.

Hydrogen storage performance evaluation

The H₂ sorption and desorption tests were all evaluated by a home-built high-pressure gas sorption apparatus (HPSA), which had been carefully calibrated by adopting LaNi₅ as a reference sample in terms of hydrogen storage capacity and guaranteed an accuracy of $\pm 1\%$. The hydrogen capacity (wt.%) of all samples was calculated based on the total mass of whole system, including MgH₂ and catalysts. As ball-milled samples for each dehydrogenation test started with an initial pressure < 0.001 MPa. The heat rate of temperature-programmed desorption (TPD) test was 2 °C per minute. The isothermal test was handled by rapidly heating up to the target temperature followed by keeping the temperature constant. The hydrogenation test set a H₂ pressure of 50 atm with approximately 80 mg of samples.

Structural characterization

The crystalline structures of products were characterized by X-ray diffraction (XRD; D8 Advance, Bruker AXS) with Cu Ka radiation. To prevent any possible reactions between samples and air during the XRD measurement, the samples were covered by amorphous taped. The morphology and composition of samples were determined using an FE-SEM (JEOL 7500FA, Tokyo, Japan) and a TEM (JEOL 2011 F, Tokyo, Japan) coupled with an EDX spectrometer. Samples for TEM and SEM tests were first dispersed on Cu grids and conducting resin in the glove box, respectively, and then rapidly transferred into the chambers for testing within a few seconds. X-ray photoelectron spectroscopy (XPS) was carried out on a Perkin Elmer PHI 5000C ESCA system equipped with dual X-ray sources using an Mg K α anode and a hemispherical energy analyzer. The background pressure was maintained below 10⁻⁶ Pa during the measurements, and all measurements were made at a pass energy of 93.90 eV. All binding energies were calibrated with carbon (C *1s* = 284.8 eV).

Theoretical calculation

The calculations were performed based on the density functional theory (DFT) approach using DMol³ package.^{S1} The PBE exchange-correlation functional was adopted for GGA correction.^{S2} All-electron Kohn-Sham wave functions were expanded in a Double Numerical basis with Polarized orbital (DNP).^{S3} Sampling of irreducible wedge of Brillouin zone was performed with a regular Monkhorst-Pack grid of special *k*-points.^{S4} The convergences criteria of relaxation were 1.0×10^{-5} Ha, 0.002 Ha/Å and 0.005 Å for energy, gradient and atomic displacement, respectively. In order to evaluate the influence of V doping on the dehydrogenation and hydrogenation abilities of Mg-H system, the (2×2×2) MgH₂ supercell (Mg₁₆H₃₂) and (3×3) Mg(0001) surface models were constructed firstly, and then one central Mg atom in Mg₁₆H₃₂ supercell and one Mg atom on the top layer of Mg(0001) surface were replaced by one V atom, respectively, as shown in Figure S25.

The hydrogen desorption energies (E_{des}) of Mg₁₆H₃₂ and Mg₁₅VH₃₂ were calculated using Eqs. (1) and (2), respectively.

$$E_{des}(Mg_{16}H_{32}) = [16E_{tot}(Mg) + 16E_{tot}(H_2) - E_{tot}(Mg_{16}H_{32})]/16$$
(1)
$$E_{des}(Mg_{15}VH_{32}) = [15E_{tot}(Mg) + E_{tot}(V) + 16E_{tot}(H_2) - E_{tot}(Mg_{15}VH_{32})]/16$$
(2)

Where E_{tot} (Mg₁₆H₃₂) and E_{tot} (Mg₁₅VH₃₂) represent the total energies of Mg₁₆H₃₂ and Mg₁₅VH₃₂ supercells, respectively. E_{tot} (Mg) and E_{tot} (V) represent the single atomic energies of Mg and V in solid state, respectively. E_{tot} (H₂) represents the total energy of gaseous H₂ molecule.

The hydrogen removal energies (E_{rom}) of Mg₁₆H₃₂ and Mg₁₅VH₃₂ were calculated using Eqs. (3) and (4), respectively.

$$E_{\text{rom}}(\text{Mg}_{16}\text{H}_{32}\text{-}\text{H}) = 0.5E_{\text{tot}}(\text{H}_2) + E_{\text{tot}}(\text{Mg}_{16}\text{H}_{32}\text{-}\text{H}) - E_{\text{tot}}(\text{Mg}_{16}\text{H}_{32})$$
(3)
$$E_{\text{rom}}(\text{Mg}_{15}\text{V}\text{H}_{32}\text{-}\text{H}) = 0.5E_{\text{tot}}(\text{H}_2) + E_{\text{tot}}(\text{Mg}_{15}\text{V}\text{H}_{32}\text{-}\text{H}) - E_{\text{tot}}(\text{Mg}_{15}\text{V}\text{H}_{32})$$
(4)

Where $E_{tot}(Mg_{16}H_{32}-H)$ and $(Mg_{15}VH_{32}-H)$ represent the total energies of $Mg_{16}H_{32}$ and $Mg_{15}VH_{32}$ supercells with one H atom removal, respectively.

The hydrogen adsorption energies (E_{ads}) of H₂ molecule on clean Mg(0001) and V-doped Mg(0001) surface models were calculated using Eqs. (5) and (6), respectively.

$$E_{ads}(Mg(0001)+H_2) = E_{tot}(Mg(0001)+H_2) - E_{tot}(Mg(0001)-E_{tot}(H_2))$$
(5)

$$E_{ads}(Mg_V(0001)+H_2)=E_{tot}(Mg_V(0001)+H_2)-E_{tot}(Mg_V(0001)-E_{tot}(H_2))$$
(6)

Where $E_{tot}(Mg(0001)+H_2)$ and $E_{tot}(Mg_V(0001)+H_2)$ represent the total energies of clean and V-doped Mg(0001) surface models with one H₂ molecule adsorption, respectively. $E_{tot}(Mg(0001)$ and

 $E_{tot}(Mg_V(0001))$ represent the total energies of clean and V-doped Mg(0001) surface models, respectively.

To evaluate the influence of V doping on the hydrogenation kinetics, the transition states of H_2 dissociation on clean and V-doped Mg(0001) surface models were calculated by adopting NEB (nudged elastic band) method.^{S5}



Figure S1. XRD patterns of as-synthesized NH₄V₄O₁₀.



Figure S2. SEM images of as-synthesized $NH_4V_4O_{10}$ nanobelts.



Figure S3. SEM images of as-synthesized V_6O_{13} nanobelts.



Figure S4. TEM images of as-synthesized V_6O_{13} nanobelts.



Figure S5. HRTEM images of as-synthesized V_6O_{13} nanobelts.



Figure S6. SEM images of bulk V₆O₁₃.



Figure S7. XRD patterns of MgH_2 under the catalysis of V_6O_{13} nanobelts with various loading ratios.



Figure S8. SEM images of (a) ball-milled MgH_2 and (b) MgH_2 under the catalysis of V_6O_{13} nanobelts.



Figure S9. TEM images of MgH_2 catalyzed by V_6O_{13} nanobelts after ball-milling.



Figure S10. STEM and EDS elemental mapping images of Mg, V and O of MgH_2 under the catalysis of V_6O_{13} nanobelts after ball-milling.



Figure S11. TPD results of MgH_2 catalyzed by V_6O_{13} nanobelts with various loading ratios.



Figure S12. TPD curves of MgH₂ under the catalysis of V₆O₁₃ nanobelts with different heating rates.



Figure S13. The differential curves of the H₂ desorption of MgH₂ catalyzed by V₆O₁₃ nanobelts.



Figure S14. TPD curves of ball-milled MgH₂ with different heating rates.



Figure S15. The derivative curves of ball-milled MgH₂.



Figure S16. Kissinger's plots of MgH₂ with and without the catalysis of V_6O_{13} nanobelts.



Figure S17. Isothermal H₂ absorption curves of MgH_2 under the catalysis of V_6O_{13} nanobelts at 50 °C, with ball-milled MgH_2 catalyzed by bulk V_6O_{13} for comparison.



Figure S18. (a) PCI curves and (b) Van't Hoff plot of MgH₂ under the catalysis of V₆O₁₃ nanobelts.



Figure S19. STEM and EDS elemental mapping images of Mg, V, and O of MgH_2 catalyzed by V_6O_{13} nanobelts after 10th cycles.



Figure S20. High-resolution V 2p XPS spectra of MgH₂ under the catalysis of V₆O₁₃ nanobelts after ball milling.



Figure S21. TPD results of MgH_2 with the addition of metallic V powder and V_6O_{13} nanobelts, respectively.



Figure S22. DFT calculation of the length of Mg-H bonds under the catalysis of V and V_2O_3 , respectively, including pure MgH₂ for comparison.



Figure S23. Calculation models of MgH_2 (2×2×2) cells (a) without (*i.e.*, $Mg_{16}H_{32}$) and (b) with V doping (*i.e.*, $Mg_{15}VH_{32}$).



Figure S24. Calculated adsorption energy profiles for the H_2 adsorption of Mg (0001) and Mg (0001) doped with metallic V.



Figure S25. Calculated models for the H_2 dissociation energy barrier of Mg (0001) and Mg (0001) doped with metallic V, respectively.

Catalysts	The amount of	Peak	H ₂	
	catalysts	temperature	capacity	Refs.
	(wt.%)	(°C)	(wt.%)	
TiNb ₂ O ₇ nanoflakes	3	235	7.0	S6 ^{S6}
V ₂ O ₃ @C	9	248	6.8	S7 ^{S7}
V ₂ C Mxene	10	245	6.4	S8 ^{S8}
TiNb ₂ O ₇ porous-spheres	7	240	6.32	S9 ^{S9}
ZrH ₂ nanoparticles	10	238	6.42	S10 ^{S10}
3D fl-TiO ₂ @C	5	233	6.5	S11 ^{S11}
2D-NbTiC	9	230	6.8	S12 ^{S12}
2D-Nb ₄ C ₃ T _x	5	228	6.1	S13 ^{S13}
ZrO ₂ nanoparticles	10	223	6.5	S14 ^{S14}
V ₄ Nb ₁₈ O ₅₅ microspheres	10	220	6.0	S15 ^{S15}
V ₆ O ₁₃ nanobelts	3	221	7.25	This work

Table S1. Comparison of the onset and peak H₂ desorption temperature of different catalysts for MgH₂.

Reference

- S1. P. Hohenberg and W. Kohn, *Phys. Rev. B*, 1964, **136**, B864–B871.
- S2. J. P. Perdew, K. Burke and M. Ernzerhof, Phys. Rev. Lett., 1996, 77, 3865-3868.
- S3. B. Delley, J. Chem. Phys., 1991, 94, 7245-7250.
- S4. J. D. Pack and H. J. Monkhorst, *Phys. Rev. B*, 1977, 16, 1748-1749.
- S5. G. Henkelman, B. P. Uberuaga and H. Jonsson, J. Chem. Phys., 2000, 113, 9901-9904.
- S6. K. C. Xian, M. H. Wu, M. X. Gao, S. Wang, Z. L. Li, P. Y. Gao, Z. H. Yao, Y. F. Liu, W. P. Sun and H. G. Pan, *Small*, 2022, 18, 2107013.
- S7. Z. Y. Wang, Z. H. Ren, N. Jian, M. X. Gao, J. J. Hu, F. Du, H. G. Pan and Y. F. Liu, *J. Mater. Chem.* A, 2018, 6, 16177-16185.
- S8. C. L. Lu, H. Z. Liu, L. Xu, H. Luo, S. X. He, X. Q. Duan, X. T. Huang, X. H. Wang, Z. Q. Lan and J. Guo, *J. Magnes. Alloy.*, 2022, **10**, 1051-1065.
- S9. L. Zhang, K. Wang, Y. Liu, X. Zhang, J. Hu, M. Gao and H. Pan, *Nano Res.*, 2020, 14, 148-156.
- S10. M. Chen, Y. Wang, X. Xiao, Y. Lu, M. Zhang, J. Zheng and L. Chen, *Appl. Surf. Sci.*, 2021, 541, 148375.
- S11. M. Zhang, X. Xiao, B. Luo, M. Liu, M. Chen and L. Chen, J. Energy Chem., 2020, 46, 191-198.
- S12. Z. Y. Wang, X. L. Zhang, Z. H. Ren, Y. Liu, J. J. Hu, H. W. Li, M. X. Gao, H. G. Pan and Y. F. Liu, *J. Mater. Chem. A*, 2019, 7, 14244-14252.
- S13. Y. N. Liu, H. G. Gao, Y. F. Zhu, S. Y. Li, J. G. Zhang and L. Q. Li, *Appl. Surf. Sci.*, 2019, 493, 431-440.
- S14. X. Zhang, X. Zhang, L. Zhang, Z. Huang, F. Fang, J. Hu, Y. Yang, M. Gao, H. Pan and Y. Liu, Mater. Today Nano, 2022, 18, 100200.
- S15. Y. Meng, S. L. Ju, W. Chen, X. W. Chen, G. L. Xia, D. L. Sun and X. B. Yu, *Small Struct.*, 2022, 3, 2200119.