Supplementary Information

Insight into the effect of d-orbital electron rearrangements induced by Zr-H interaction: First-principles calculations

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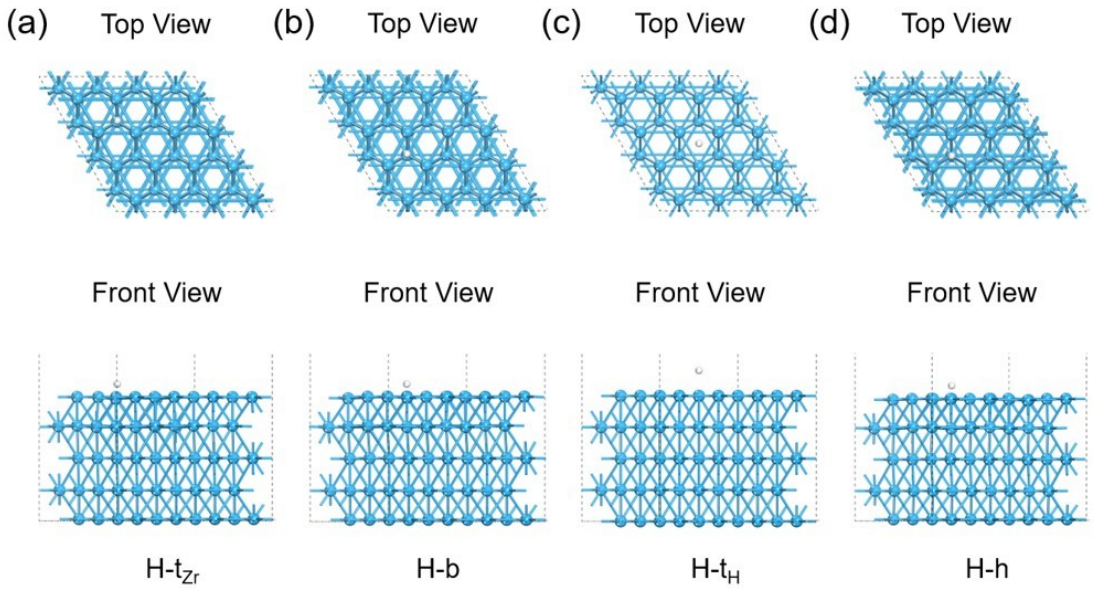

Figure S1. Top and front views of the final structure of H atom at various adsorption sites on the Zr(0 0 0 1) surface. (a) H-t_{Zr}; (b) H-b; (c) H-t_H; (d) H-h.

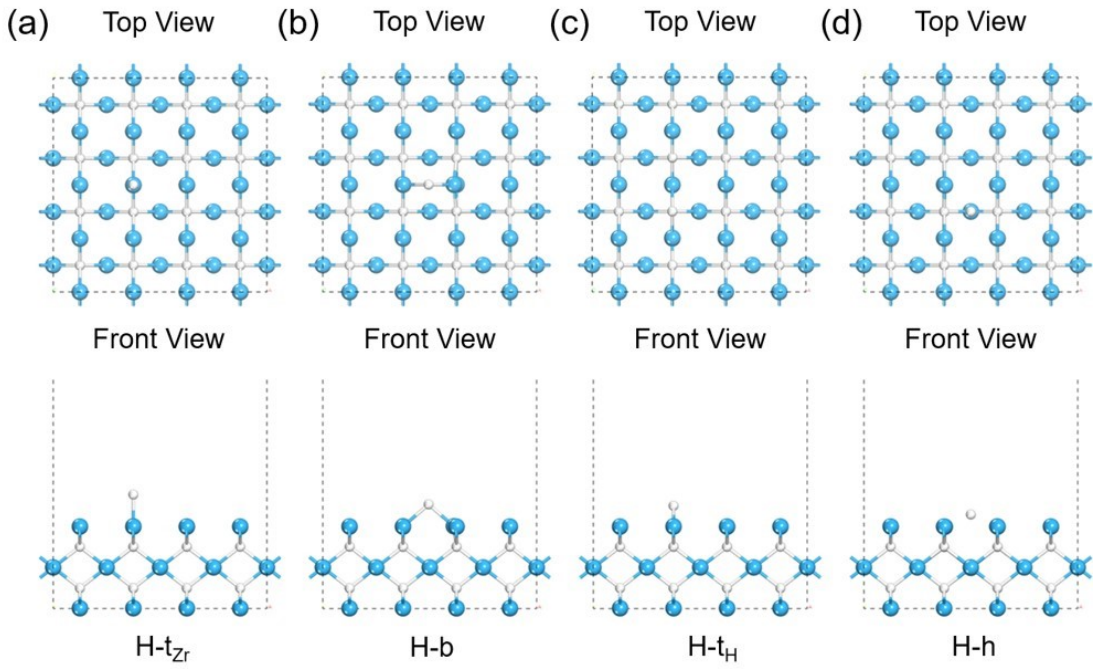

Figure S2. Top and front views of the final structure of H atom at various adsorption sites on the ZrH(0 0 1) surface. (a) H-t_{Zr}; (b) H-b; (c) H-t_H; (d) H-h.

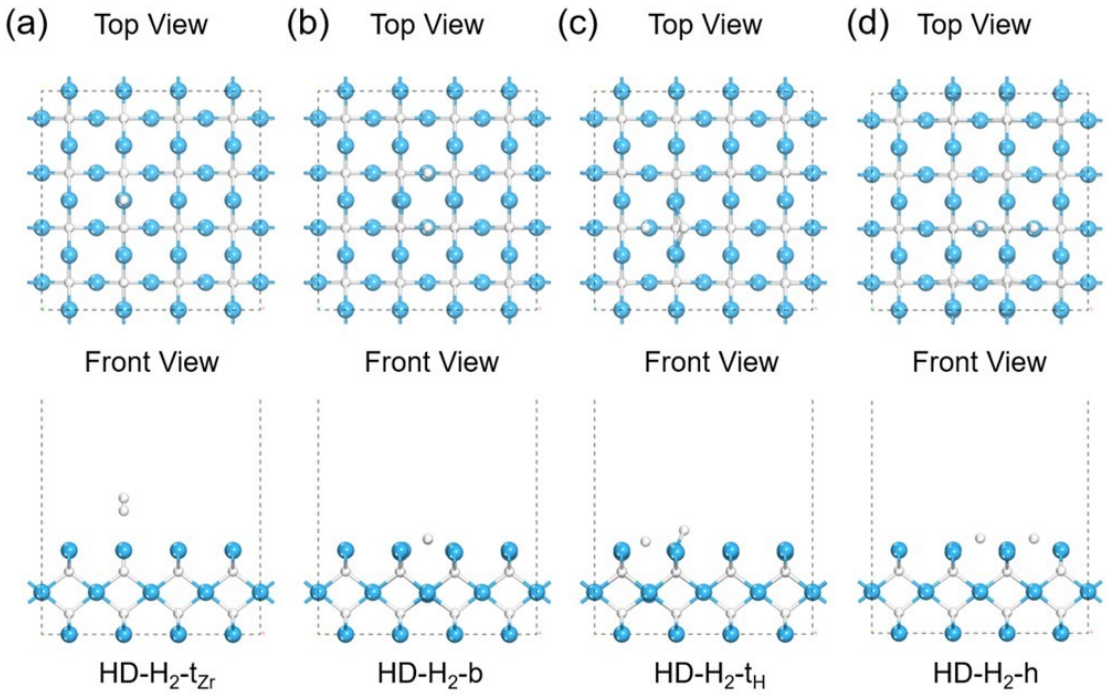

Figure S3. Top and front views of the final structure of HD-H_2 at various adsorption sites on the ZrH(0 0 1) surface. (a) HD-H_2-t_{Zr}; (b) HD-H_2-b; (c) HD-H_2-t_H; (d) HD-H_2-h.

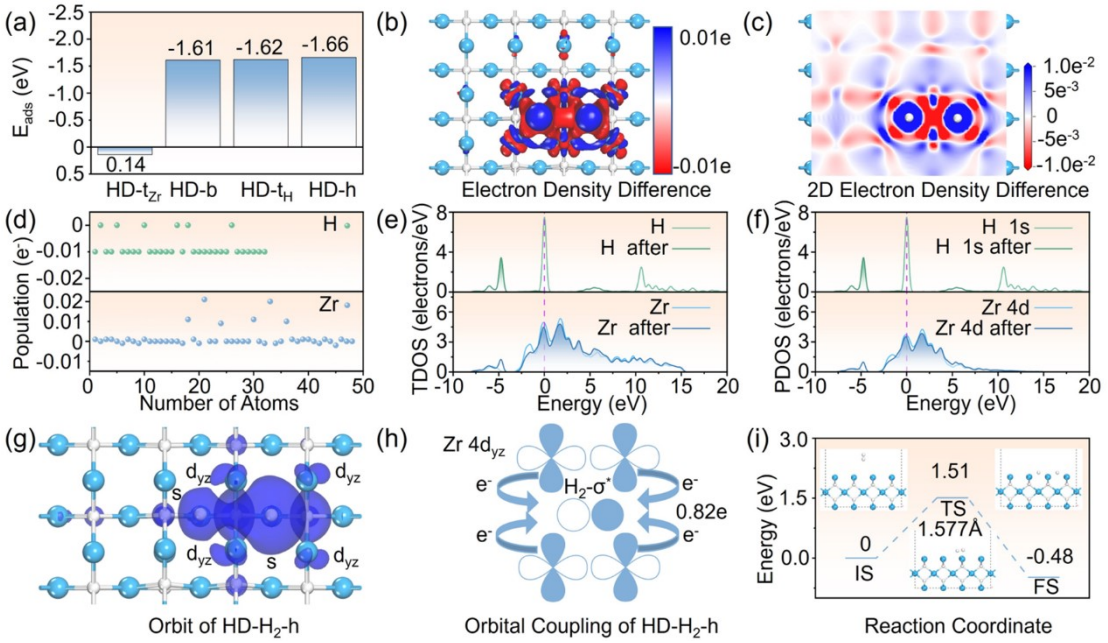

Figure S4. HD-H_2-h/ZrH(0 0 1). (a) Adsorption energy of HD-H_2 at different sites on the ZrH(0 0 1) surface; (b) Electron density difference of HD-H_2-h; (c) Two-dimensional electron density difference of HD-H_2-h; (d) The variation of Mulliken population of H and Zr atoms; (e) TDOS of HD-H_2-h; (f) PDOS of HD-H_2-h; (g) Orbit of HD-H_2-h; (h) Orbital Coupling of HD-H_2-h; (i) Reaction Coordinate.

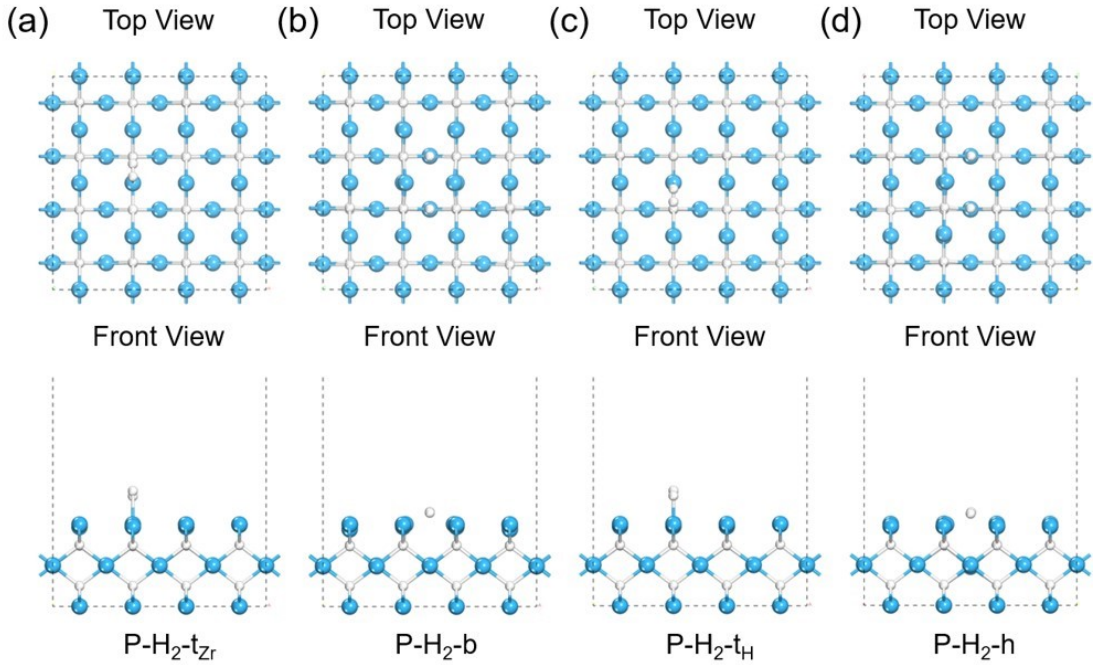

Figure S5. Top and front views of the final structure of P-H_2 at various adsorption sites on the ZrH(0 0 1) surface. (a) P-H_2-t_{Zr}; (b) P-H_2-b; (c) P-H_2-t_H; (d) P-H_2-h.

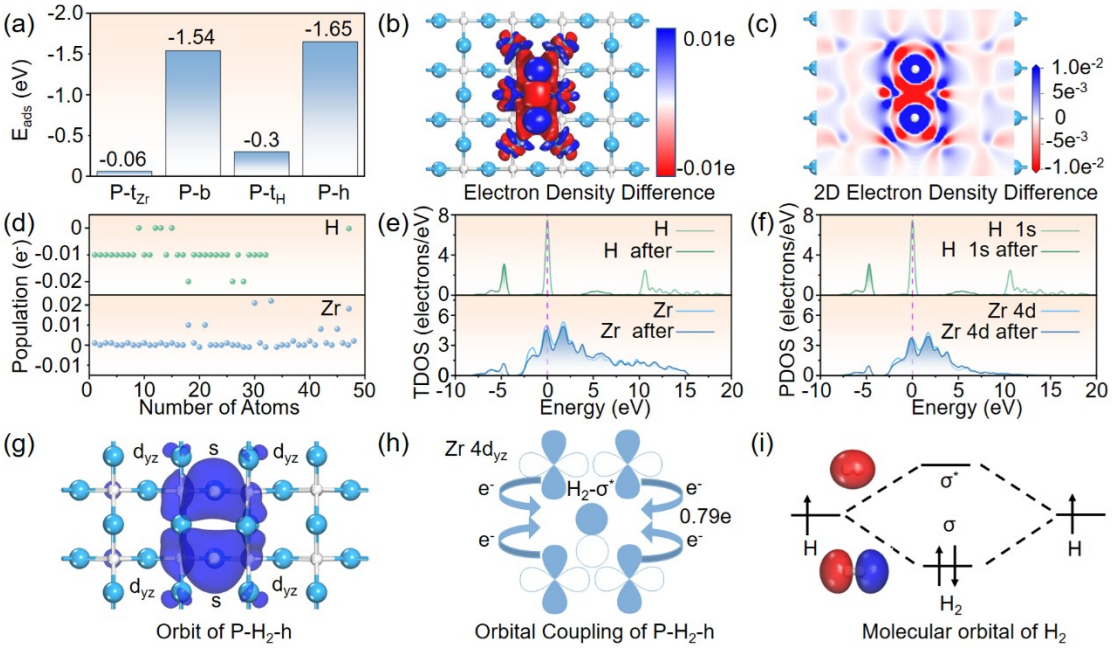

Figure S6. P-H_2-h/ZrH(0 0 1). (a) Adsorption energy of P-H_2 at different sites on the ZrH(0 0 1) surface; (b) Electron density difference of P-H_2-h; (c) Two-dimensional electron density difference of P-H_2-h; (d) The variation of Mulliken population of H and Zr atoms in P-H_2-h; (e) TDOS of P-H_2-h; (f) PDOS of P-H_2-h; (g) Orbit of P-H_2-h; (h) Orbital Coupling of P-H_2-h; (i) HOMO and LUMO of H_2.

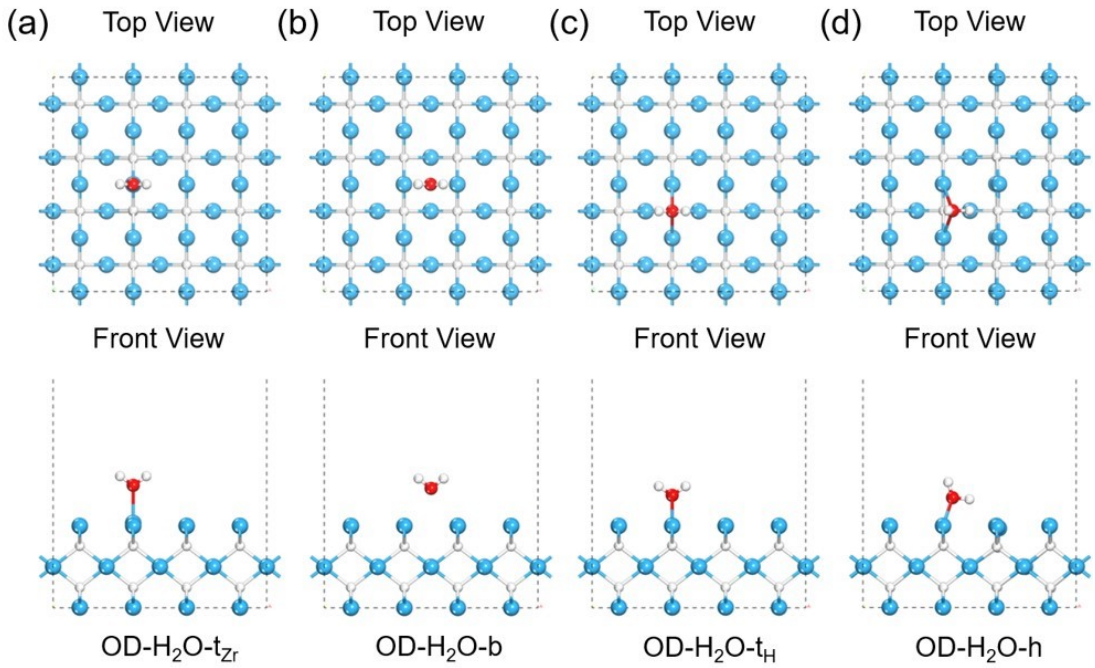

Figure S7. Top and front views of the final structure of OD-H_2O at various adsorption sites on the ZrH(0 0 1) surface. (a) OD-H_2O-t_{Zr}; (b) OD-H_2O-b; (c) OD-H_2O-t_H; (d) OD-H_2O-h.

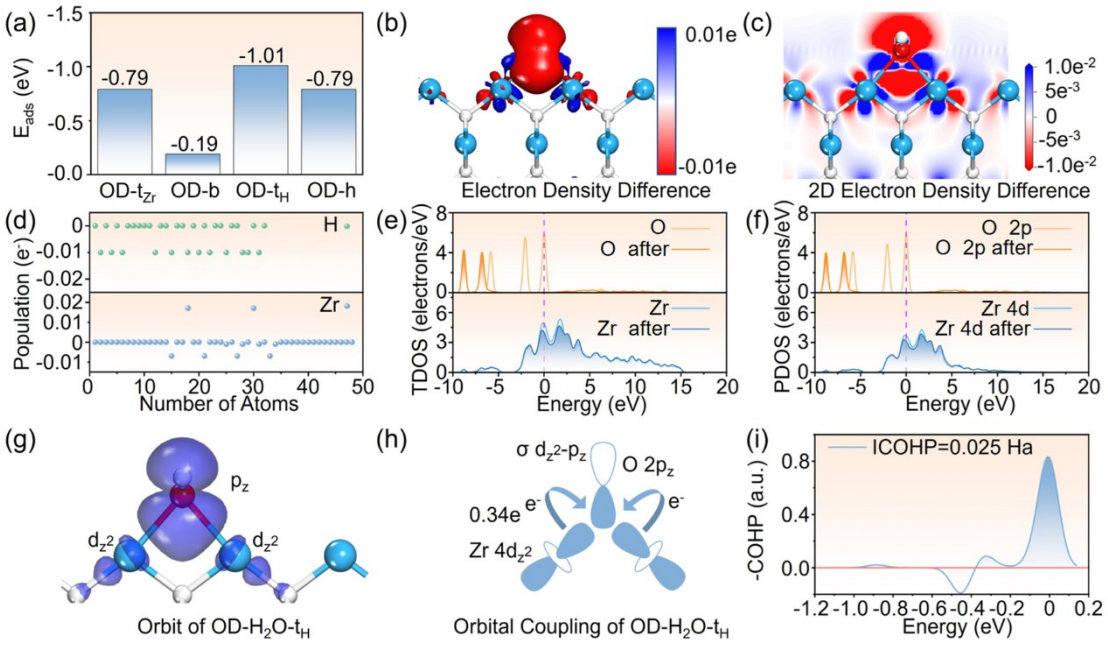

Figure S8. OD-H_2O-t_H/ZrH(0 0 1). (a) Adsorption energy of OD-H_2Oat different sites on the ZrH(0 0 1) surface; (b) Electron density difference of OD-H_2O-t_H; (c) Two-dimensional electron density difference of OD-H_2O-t_H; (d) The variation of Mulliken population of H and Zr atoms in OD-H_2O-h; (e) TDOS of OD-H_2O-t_H; (f) PDOS of OD-H_2O-t_H; (g) Orbit of OD-H_2O-t_H; (h) Orbital Coupling of OD-H_2O-t_H; (i) COHP of Zr-O bond.

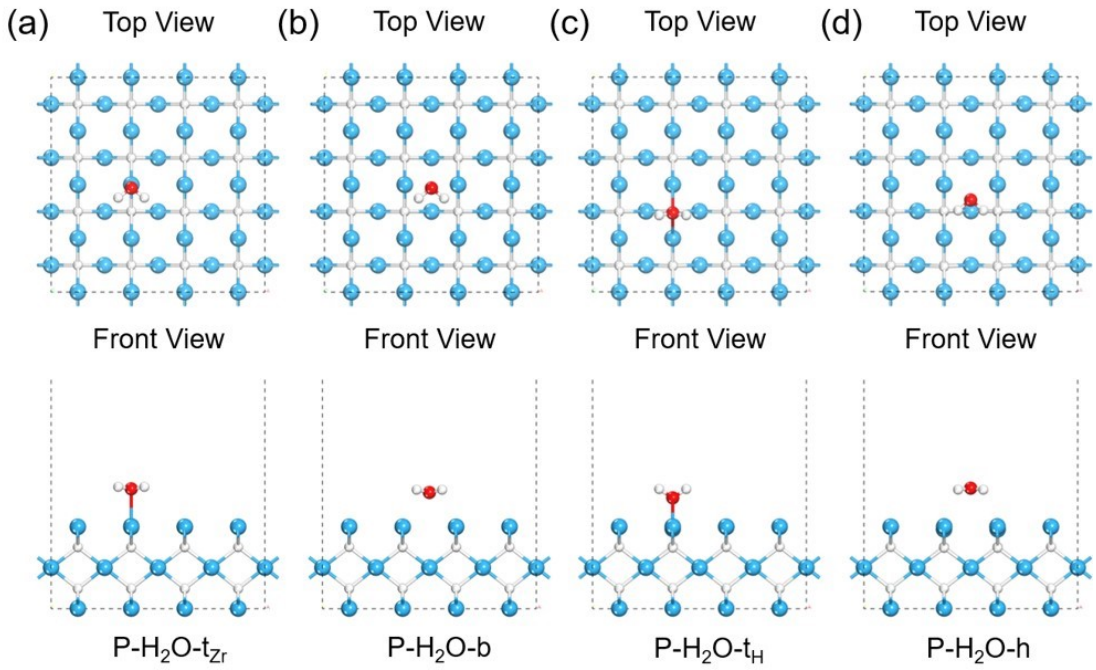

Figure S9. Top and front views of the final structure of P-H_2O at various adsorption sites on the ZrH(0 0 1) surface. (a) P-H_2O-t_{Zr}; (b) P-H_2O-b; (c) P-H_2O-t_H; (d) P-H_2O-h.

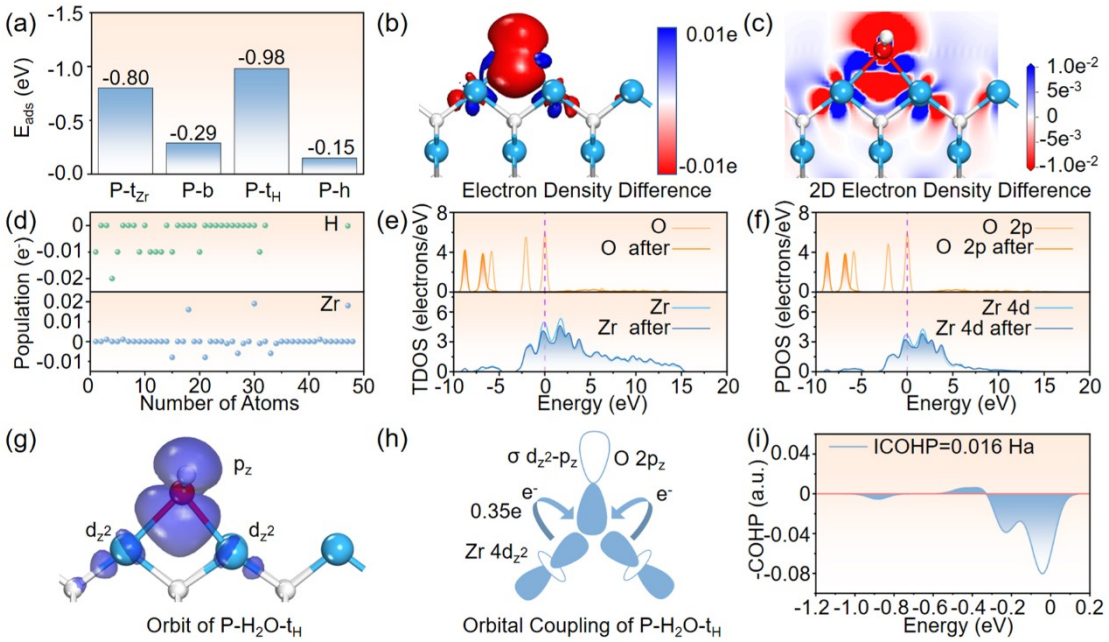

Figure S10. P-H_2O-t_H/ZrH(0 0 1). (a) Adsorption energy of P-H_2Oat different sites on the ZrH(0 0 1) surface; (b) Electron density difference of P-H_2O-h; (c) Two-dime0nsional electron density difference of P-H_2O-t_H; (d) The variation of Mulliken population of H and Zr atoms in P-H_2O-t_H; (e) TDOS of P-H_2O-t_H; (f) PDOS of P-H_2O-t_H; (g) Orbit of P-H_2O-t_H; (h) Orbital Coupling of P-H_2O-t_H; (i) COHP of Zr-O bond.

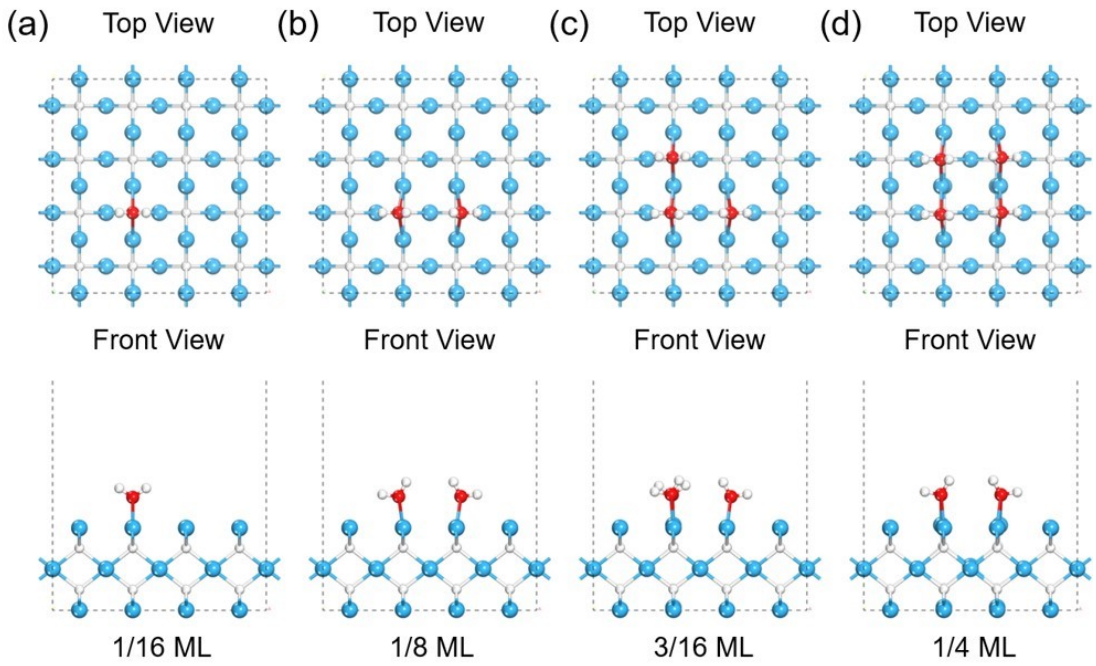

Figure S11. Top and front views of the final structure of H_2O adsorbed on the ZrH(0 0 1) surface at low coverage. (a) 1/16 ML; (b) 1/8 ML; (c) 3/16 ML; (d) 1/4 ML.

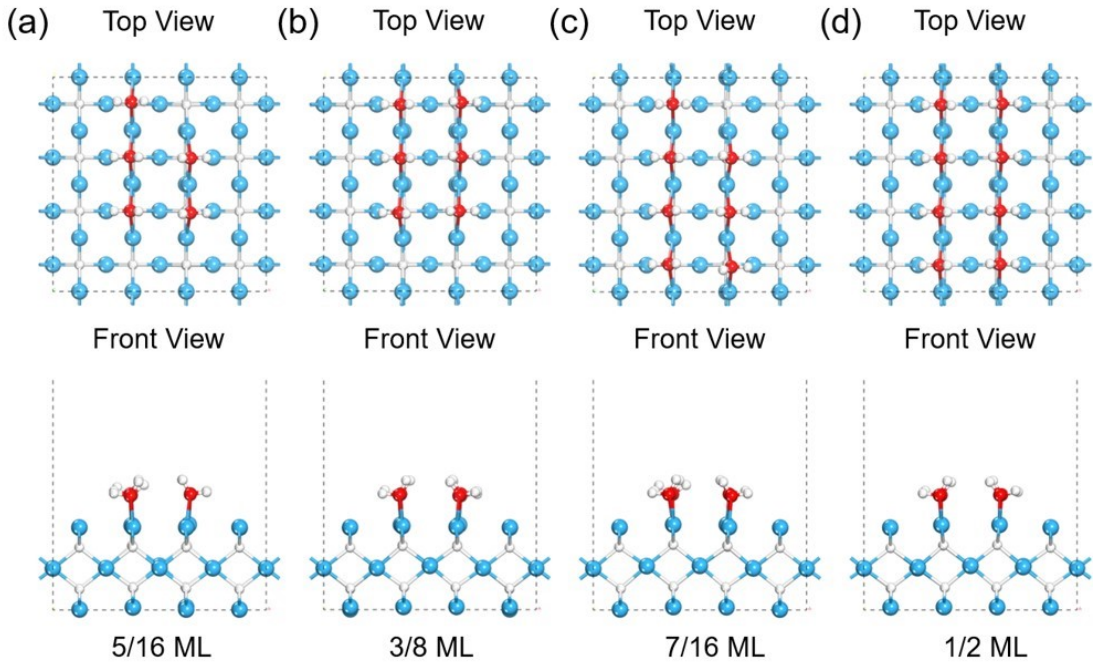

Figure S12. Top and front views of the final structure of H_2O adsorbed on the ZrH(0 0 1) surface at high coverage. (a) 5/16 ML; (b) 3/8 ML; (c) 7/16 ML; (d) 1/2 ML.

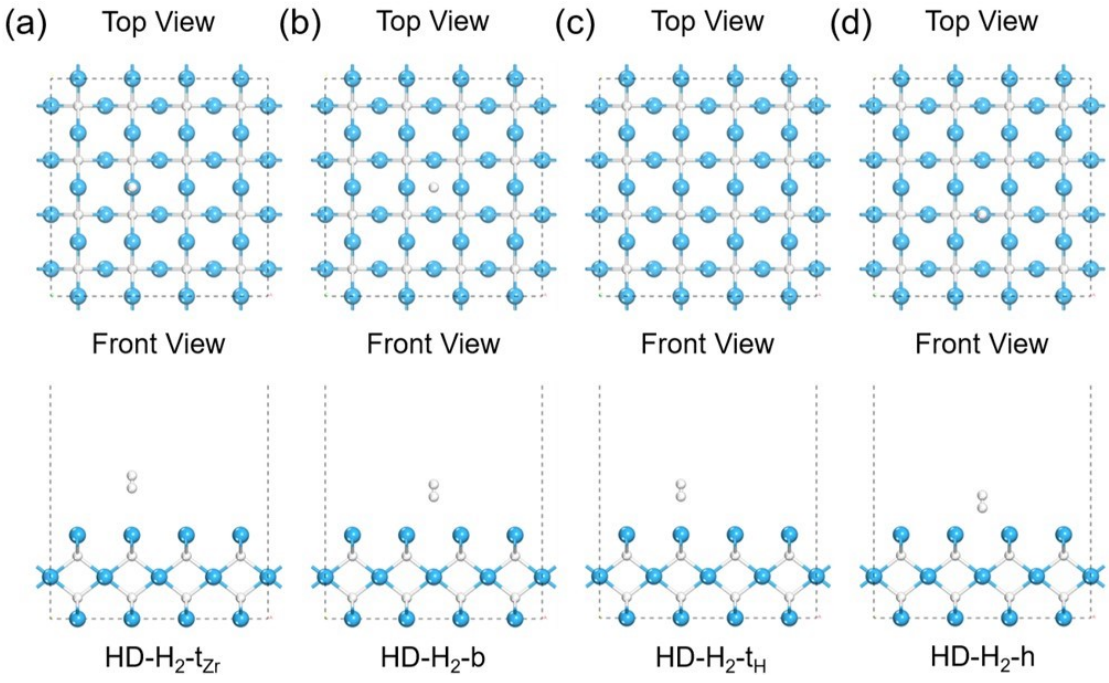

Figure S13. Top and front views of the initial structure of HD-H_2 at various adsorption sites on the ZrH(0 0 1) surface. (a) HD-H_2-t_{Zr}; (b) HD-H_2-b; (c) HD-H_2-t_H; (d) HD-H_2-h (Bule balls and white balls refer to Zr and H atoms, respectively).

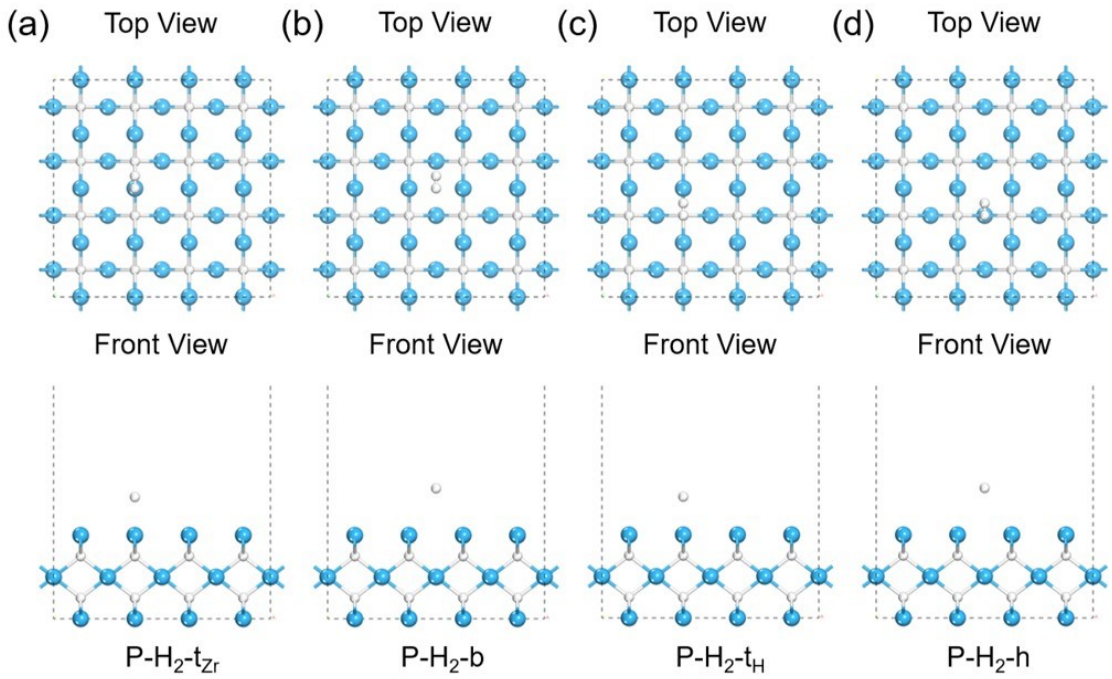

Figure S14. Top and front views of the initial structure of P-H_2 at various adsorption sites on the ZrH(0 0 1) surface. (a) P-H_2-t_{Zr}; (b) P-H_2-b; (c) P-H_2-t_H; (d) P-H_2-h.

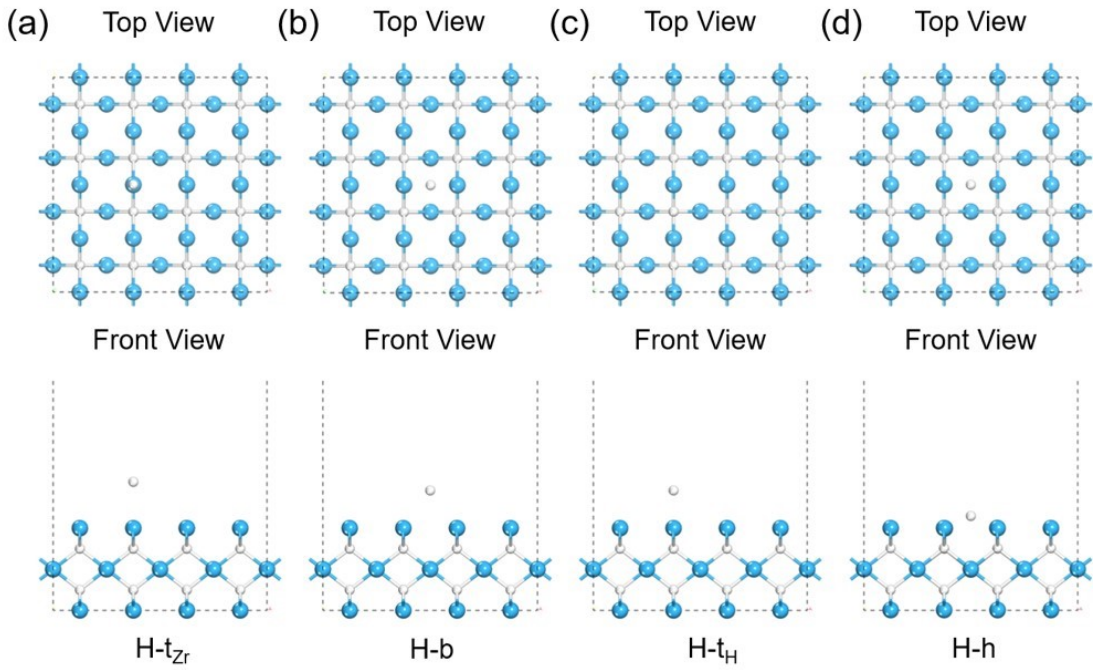

Figure S15. Top and front views of the initial structure of H atom at different adsorption sites on the ZrH(0 0 1) surface. (a) H-t_{Zr}; (b) H-b; (c) H-t_H; (d) H-h.

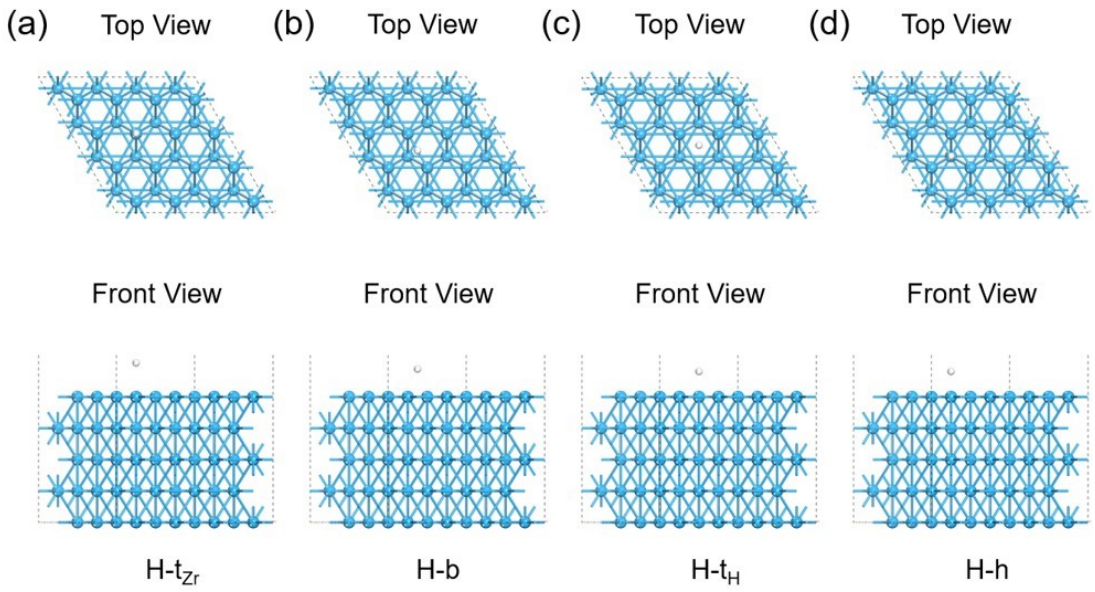

Figure S16. Top and front views of the initial structure of H atom at various adsorption sites on the Zr(0 0 0 1) surface. (a) H-t_{Zr}; (b) H-b; (c) H-t_H; (d) H-h.

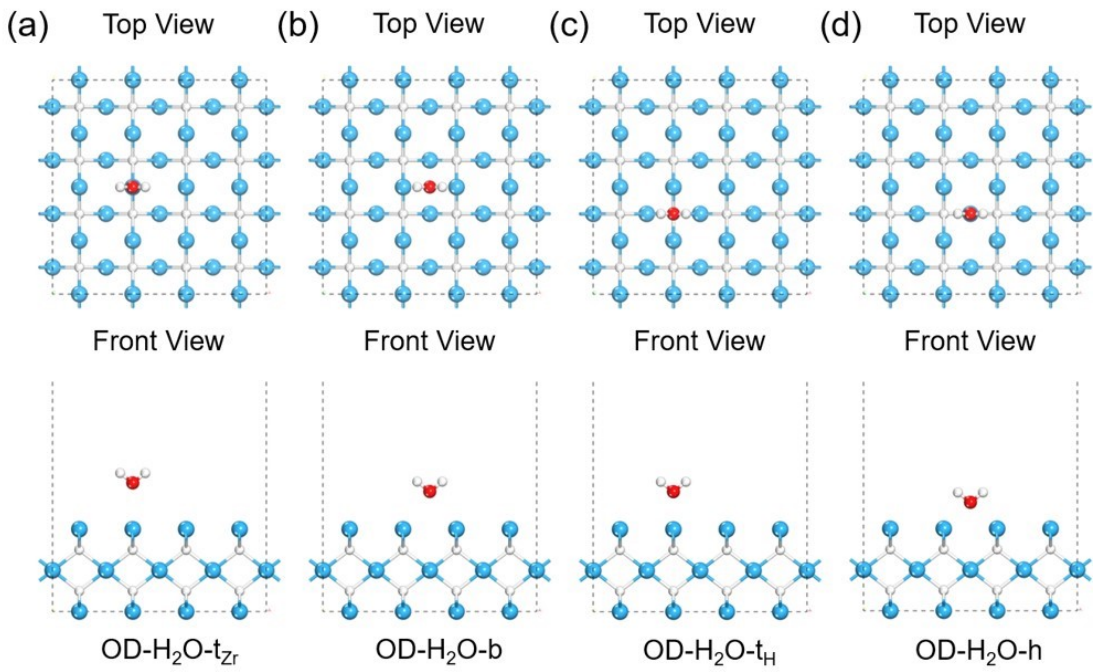

Figure S17. Top and front views of the initial structure of OD-H_2O at various adsorption sites on the ZrH(0 0 1) surface. (a) OD-H_2O-t_{Zr}; (b) OD-H_2O-b; (c) OD-H_2O-t_H; (d) OD-H_2O-h. (Red ball refer to O atom).

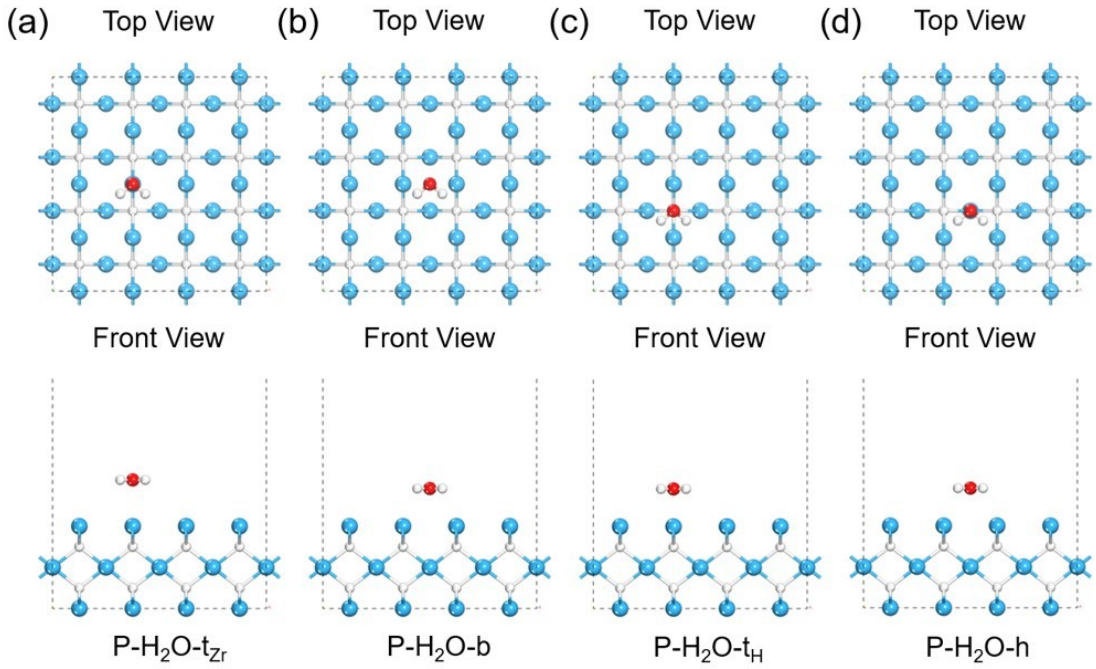

Figure S18. Top and front views of the initial structure of P-H_2O at various adsorption sites on the ZrH(0 0 1) surface. (a) P-H_2O-t_{Zr}; (b) P-H_2O-b; (c) P-H_2O-t_H; (d) P-H_2O-h.

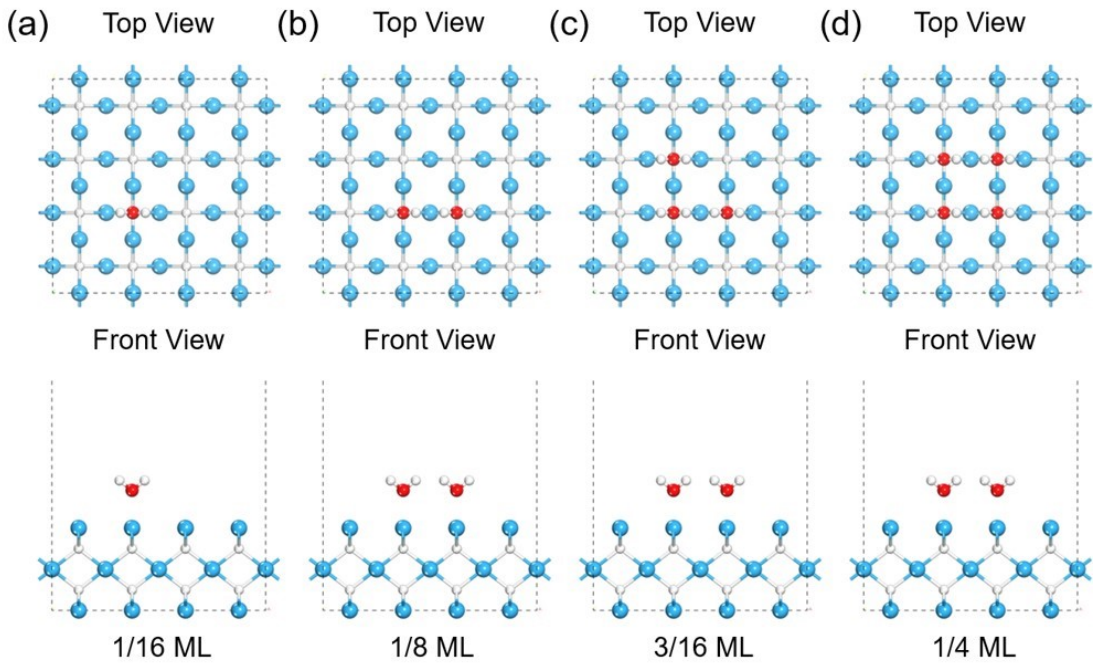

Figure S19. Top and front views of the initial structure of H_2O adsorbed on the ZrH(0 0 1) surface at low coverage. (a) 1/16 ML; (b) 1/8 ML; (c) 3/16 ML; (d) 1/4 ML.

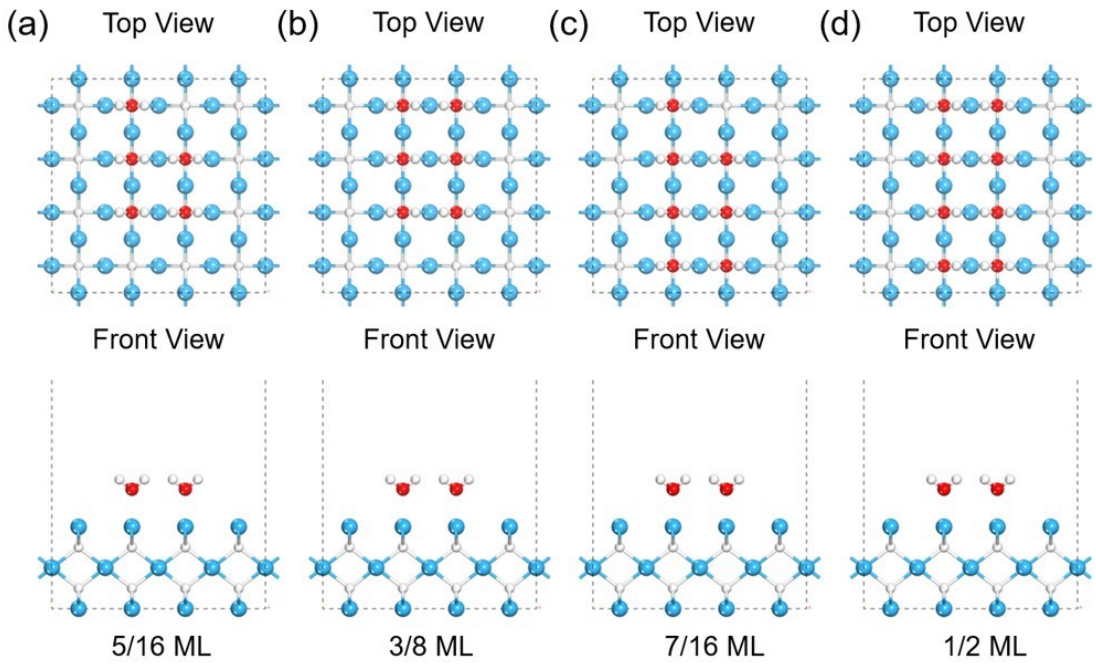

Figure S20. Top and front views of the initial structure of H_2O adsorbed on the ZrH(0 0 1) surface at high coverage. (a) 5/16 ML; (b) 3/8 ML; (c) 7/16 ML; (d) 1/2 ML.

Table S1. Parameters of ZrH cell before and after geometry.

Parameter		Cell parameters/Å		
		a/Å	c/Å	c/a
ZrH	original cell	3.236	5	1.545
	optimization	3.247	4.976	1.532
	Ref[1]	3.233	5.016	1.551

Table S2. Parameters of Zr cell before and after geometry.

Parameter		Cell parameters/Å		
		a/Å	c/Å	c/a
α-Zr	original cell	3.23	5.175	1.602
	optimization	3.231	5.17	1.602
	Ref[2]	3.24	5.18	1.599
	Ref[3]	3.236	5.165	1.596
	Ref[4]	3.233	5.146	1.593

Table S3. Surface energy of different surfaces of ZrH.

Surface	Surface Energy/eV
(1 0 0)	-0.15
(0 0 1)	-0.17
(1 1 0)	-0.17
(1 0 1)	-0.14

(1 1 1)	-0.17

Reference

1. X. Y. Zhu, D. Y. Lin, J. Fang, X. Y. Gao, Y. F. Zhao and H. F. Song, *Comput. Mater. Sci.*, 2018, **150**, 77-85.
2. S. X. Wang, P. Zhang, P. Zhang, J. Zhao and S. S. Li, *J. Nucl. Mater.*, 2012, **424**, 51-56.
3. Z. Xue, X. Y. Zhang, J. Q. Qin, M. Z. Ma and R. P. Liu, *J. Mater. Sci. Technol.*, 2020, **36**, 140-148.
4. Y. S. Zhao, J. Z. Zhang, C. Pantea, J. Qian, L. L. Daemen, P. A. Rigg, R. S. Hixson, G. T. Gray, Y. P. Yang, L. P. Wang, Y. B. Wang and T. Uchida, *Physical Review B*, 2005, **71**, 184119.