

Supporting Information

Correlation between Spin Effect and Catalytic Activity of Two Dimensional Metal Organic Frameworks for Oxygen Evolution Reaction

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Computational methods

All the simulations were explored based on density functional theory (DFT) using the Vienna *Ab initio* simulation package (VASP).^{1,2} The projector augmented wave (PAW)³ method and Perdew–Burke–Ernzerhof (PBE) functional within the generalized gradient approximation (GGA) for the exchange–correlation energy were considered.⁴ The wave functions of the simulated systems were expanded in a plane-wave basis with the energy cutoff as 420 eV, and the Monkhorst–Pack k -point mesh in the Brillouin zone was set to be $3 \times 3 \times 1$ and $11 \times 11 \times 1$ for the total energy and density of states calculations, respectively. The convergence criterion was set to be 0.01 eV·Å⁻¹ and 10⁻⁵ eV for force and energy of the studied system, respectively, within the conjugated gradient method for geometry optimization. DFT+U methods were applied to describe the localized 3d electron correlation of transition metals (TM) by taking the difference between the Coulomb U and exchange J parameter ($U_{\text{eff}} = U - J$) into account, with U_{eff} value of 4.0, 3.8, 4.4, 4.0, 4.0, and 4.0 eV⁵⁻⁹ for Fe, Co, Ni, Mn, Cr, and Ti atoms, respectively. To describe the effects of the long-range van der Waals interactions, a semiclassical dispersion correction scheme (DFT-D3) was used.¹⁰ The solvation treatment method of VASPsol, which well express the long-range electrostatic interaction and the average properties of the solvent were used. The vacuum layer is set to be 20 Å to avoid interaction between two neighboring images.

The formation energy (E_f) of monolayers was estimated according by

$$E_f = E_{M_3(\text{HAT})_2} - 2E_{\text{HAT}} - 3E_{\text{TM}}, \quad (\text{S1})$$

where $E_{M_3(\text{HAT})_2}$, E_{HAT} and E_{TM} are the total energy of the $M_3(\text{HAT})_2$ monolayer, HAT molecule, and central metal, respectively.

The d band center (ε_d) value can be given by:

$$\varepsilon_d = \frac{\int_{-\infty}^{+\infty} \rho(E)(E - E_f)dE}{\int_{-\infty}^{+\infty} (E - E_f)dE} \quad (\text{S2})$$

where $\rho(E)$ is the DOS projected on the d -states of the metal atoms and E_f is the Fermi

energy of the system.

The desorption energy (ΔE_{des}) of O_2 on the monolayer can be calculated by

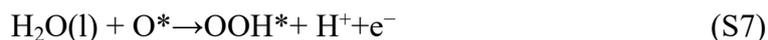
$$\Delta E_{\text{des}} = E_{\text{ads}} + E_{\text{sub}} - E_{\text{ads/sub}}, \quad (\text{S3})$$

where $E_{\text{ads/sub}}$ is the total energy of the $\text{M}_3(\text{HAT})_2$ monolayer with OO^* adsorption intermediates. E_{ads} and E_{sub} are the total energy of O_2 and the pristine $\text{M}_3(\text{HAT})_2$ substrate, respectively.

The overall OER process in the acid environment can be described as follows:



and the elementary reaction steps for the 4e^- pathway are shown below:



where the “*” denotes the active site of the catalyst. (l) and (g) refer to liquid and gas phase.

In the first step, a H_2O molecule is captured by the catalyst substrate “*”, followed by the release of a proton and an electron, leading to the formation of $^*\text{OH}$ (eq S5). Then, another proton and electron separate from $^*\text{OH}$, forming the $^*\text{O}$ intermediate (eq S6). In the third step, another H_2O molecules react with O^* to generate OOH^* , accompanied by the release of a proton and electron (eq S7). Finally, the O_2 molecules are generated from $^*\text{OOH}$, producing the final proton and electron (eq S8).

The thermochemistry of OER is interpreted by using the CHE model developed by Nørskov and co-workers to calculate the Gibbs reaction free energy,¹¹ which defines the free energy of $\text{H}^+ + \text{e}^-$ as that of $1/2\text{H}_2$ under standard conditions. For each step, the Gibbs free energy change (ΔG) is defined by the following equation:

$$\Delta G = \Delta E - T\Delta S + \Delta ZPE + \Delta G_U + \Delta G_{\text{pH}} \quad (\text{S9})$$

where ΔE , ΔZPE , and ΔS represent the total energy difference, zero-point energy change, and entropy change, respectively. The values for ΔZPE and ΔS were obtained from the vibrational frequency calculations, while the entropy of H_2 and H_2O can be

obtained directly from the standard thermodynamic database. T represents for the temperature and is taken as 298.15 K. ΔG_U is determined by the applied external potential U to the standard electrode and can be expressed as $\Delta G_U = -eU$. ΔG_{pH} represents the Gibbs free energy change correlated to the H^+ concentrations, which is determined by $\Delta G_{\text{pH}} = k_{\text{B}}T \times \ln 10 \times \text{pH}$, k_{B} refers to the Boltzmann constant and pH is assumed to be 0 in an acidic medium.

The Gibbs free energy changes of the four steps in eq S5–S8 are ΔG_1 , ΔG_2 , ΔG_3 , and ΔG_4 , respectively. The overpotential (η) is given by the following equations:

$$\eta = (\max [\Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4]/e) - 1.23\text{V} \quad (\text{S10})$$

Table S1 Lattice parameter (a , Å), pore size (D_M , Å), formation energy (E_f , eV), magnetic moments on M ion (M_m , μB) and system (M_{tot} , μB), the value of d -band center (ε_d) and charge transfer (q , $|e|$) of $M_3(\text{HAT})_2$ monolayer.

	Magnetic ground state	Lattice	D_M	E_f	M_m	M_{tot}	ε_d	Δq
$\text{Fe}_3(\text{HAT})_2$	spin	14.24	7.05	-7.59	3.66	10.31	-2.28	-0.86
	nonspin	13.75	6.87	-2.51	-	-	-0.61	-1.25
$\text{Co}_3(\text{HAT})_2$	spin	14.24	7.19	-3.37	2.37	6.53	-1.97	-0.74
	nonspin	13.82	6.91	-2.61	-	-	-1.17	-0.94
$\text{Ni}_3(\text{HAT})_2$	spin	14.09	7.05	-1.84	1.04	3.54	-1.69	-0.81
	nonspin	13.68	6.84	-0.41	-	-	-3.32	-0.56
$\text{Mn}_3(\text{HAT})_2$	spin	14.38	7.19	-10.12	4.58	12.00	-1.22	-1.04
	nonspin	13.75	6.87	-1.12	-	-	-0.20	-1.38
$\text{Cr}_3(\text{HAT})_2$	spin	14.19	7.09	-9.59	3.76	8.59	-0.03	-1.04
	nonspin	14.02	7.02	-0.04	-	-	0.48	-1.27
$\text{Ti}_3(\text{HAT})_2$	spin	14.28	7.14	-7.25	1.62	2.15	0.98	-1.48
	nonspin	14.25	7.12	-4.78	-	-	0.25	-1.33

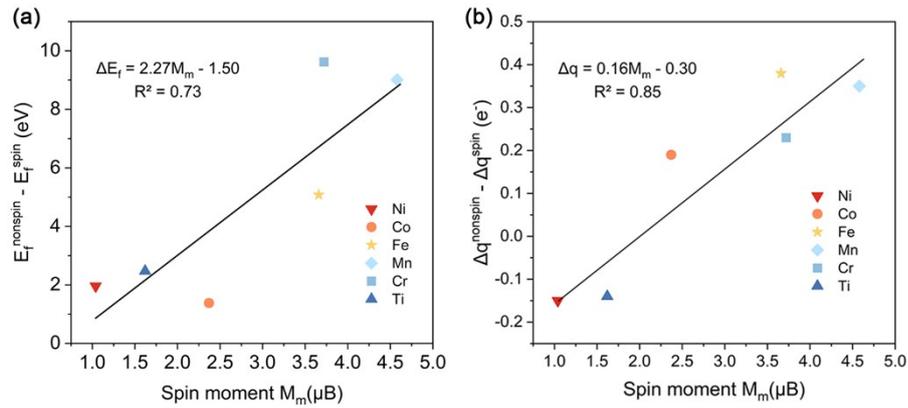


Fig. S1 Relations between spin moment and (a) formation energy difference (ΔE_f), (b) the charge transfer difference (Δq) from the metal atom to the coordinating atoms between spin-polarized and non-spin-polarized systems.

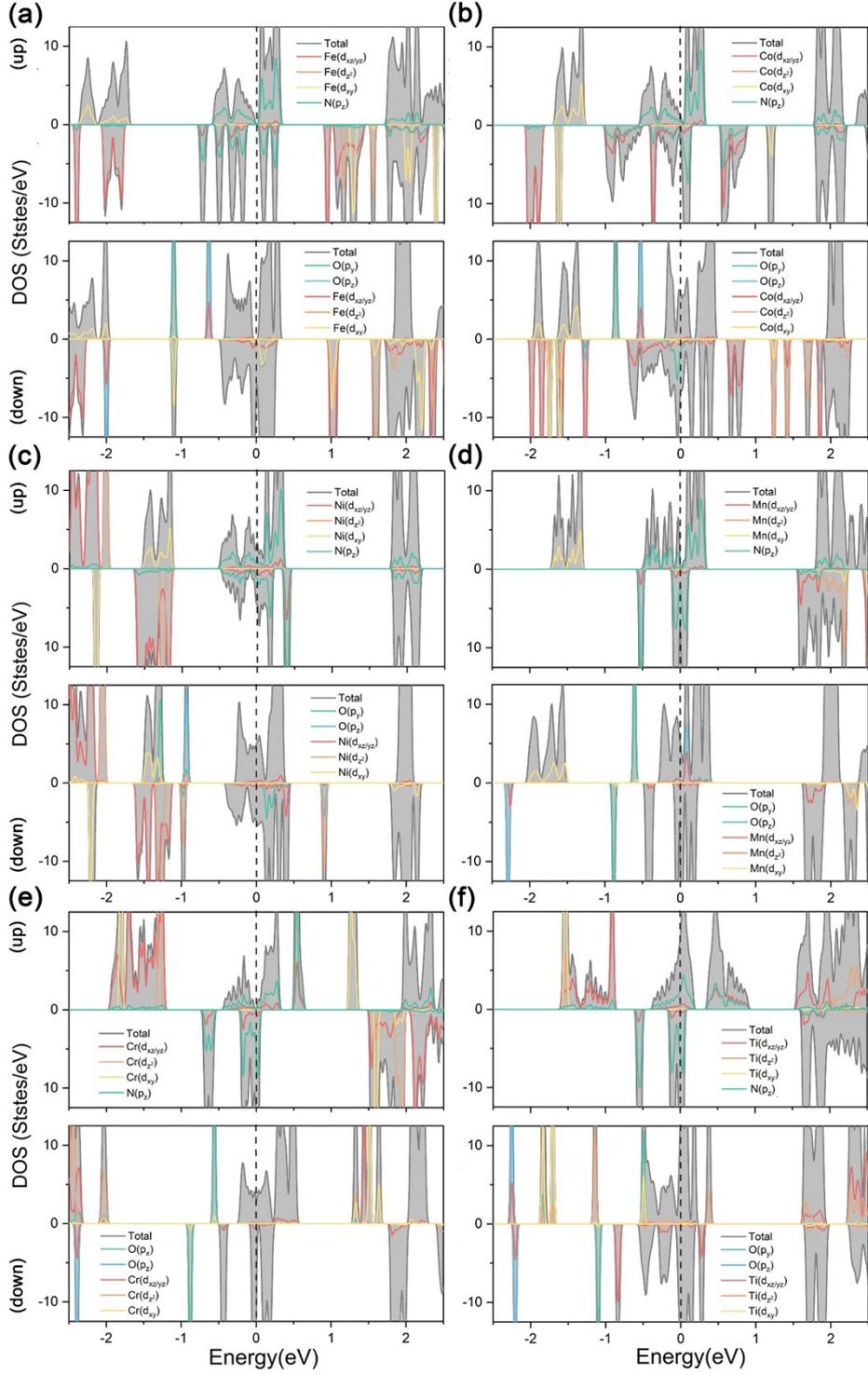


Fig. S2 The density of state (DOS) of the X and N atoms in the spin-polarized (a) $\text{Fe}_3(\text{HAT})_2$, (b) $\text{Co}_3(\text{HAT})_2$, (c) $\text{Ni}_3(\text{HAT})_2$, (d) $\text{Mn}_3(\text{HAT})_2$, (e) $\text{Cr}_3(\text{HAT})_2$, (f) $\text{Ti}_3(\text{HAT})_2$ monolayers, respectively. Spin-polarized $\text{M}_3(\text{HAT})_2$ and $\text{M}_3(\text{HAT})_2\text{-OO}$ are demonstrated above and below, respectively. The black dashed line at zero denotes the position of the Fermi level.

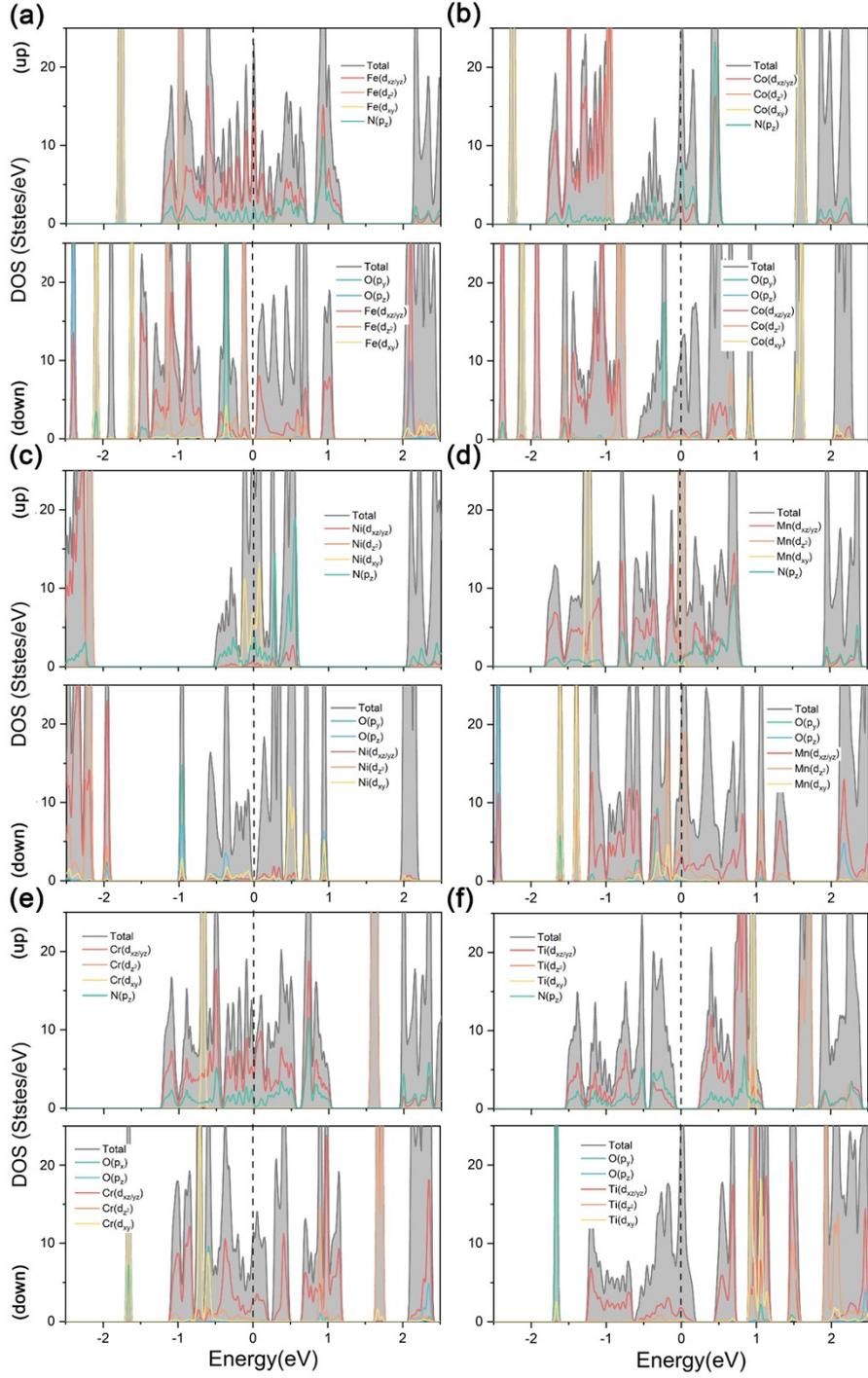


Fig. S3 The density of state (DOS) of the nonspin-polarized (a) $\text{Fe}_3(\text{HAT})_2$, (b) $\text{Co}_3(\text{HAT})_2$, (c) $\text{Ni}_3(\text{HAT})_2$, (d) $\text{Mn}_3(\text{HAT})_2$, (e) $\text{Cr}_3(\text{HAT})_2$, (f) $\text{Ti}_3(\text{HAT})_2$ monolayers, respectively. Nonspin-polarized $\text{M}_3(\text{HAT})_2$ and $\text{M}_3(\text{HAT})_2\text{-OO}$ are demonstrated above and below, respectively. The black dashed line at zero denotes the position of the Fermi level.

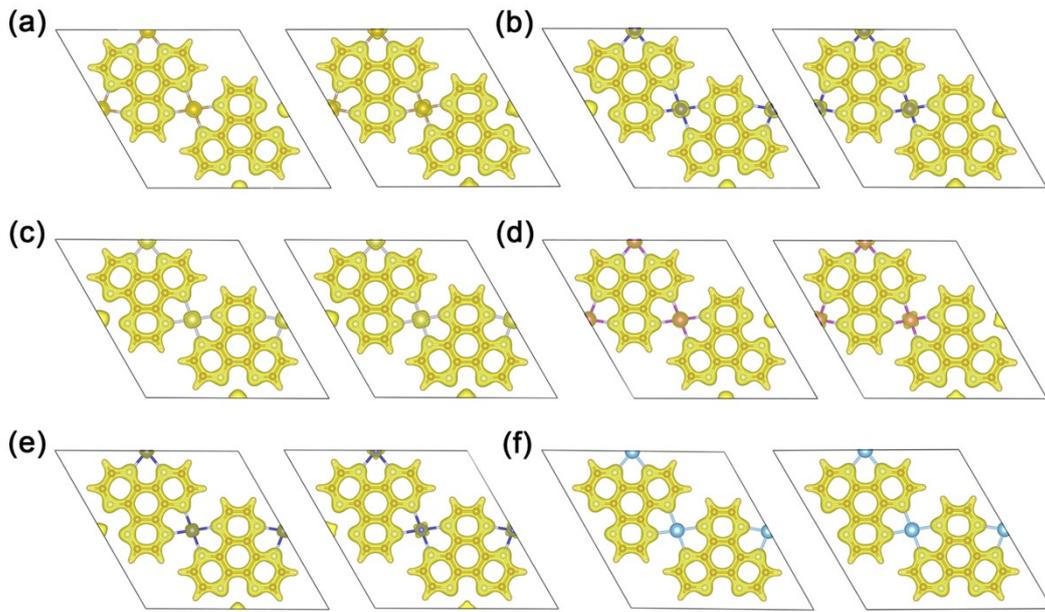


Fig. S4 The charge density distribution of (a) $\text{Fe}_3(\text{HAT})_2$, (b) $\text{Co}_3(\text{HAT})_2$, (c) $\text{Ni}_3(\text{HAT})_2$, (d) $\text{Mn}_3(\text{HAT})_2$, (e) $\text{Cr}_3(\text{HAT})_2$, (f) $\text{Ti}_3(\text{HAT})_2$ monolayers, respectively. Spin-polarized monolayers are on the left, and non-spin-polarized monolayers are on the right.

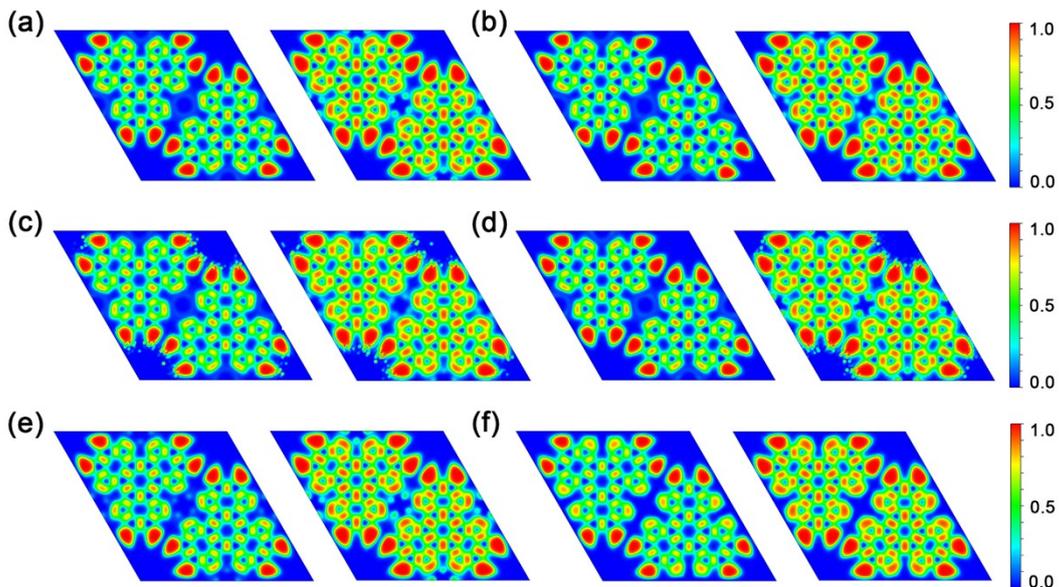


Fig. S5 ELF of (a) $\text{Fe}_3(\text{HAT})_2$, (b) $\text{Co}_3(\text{HAT})_2$, (c) $\text{Ni}_3(\text{HAT})_2$, (d) $\text{Mn}_3(\text{HAT})_2$, (e) $\text{Cr}_3(\text{HAT})_2$, (f) $\text{Ti}_3(\text{HAT})_2$ monolayers, respectively. Spin-polarized monolayers are on the left, and non-spin-polarized monolayers are on the right.

Table S2 Gibbs free energy change (ΔG) and overpotentials (η) of each elementary step for OER on $M_3(\text{HAT})_2$ monolayers

	Magnetic ground state	ΔG_1 (eV)	ΔG_2 (eV)	ΔG_3 (eV)	ΔG_4 (eV)	η (V)
$\text{Fe}_3(\text{HAT})_2$	spin	-0.74	1.61	1.63	2.43	1.20
	nonspin	-1.08	1.79	1.10	3.12	1.89
$\text{Co}_3(\text{HAT})_2$	spin	-0.26	1.22	1.83	2.14	0.91
	nonspin	0.26	1.35	1.57	1.76	0.53
$\text{Ni}_3(\text{HAT})_2$	spin	0.03	2.50	0.59	1.81	1.27
	nonspin	-0.44	1.30	1.65	2.42	1.19
$\text{Mn}_3(\text{HAT})_2$	spin	1.52	-0.61	3.84	0.18	2.61
	nonspin	-1.05	0.61	2.26	3.11	1.88
$\text{Cr}_3(\text{HAT})_2$	spin	0.06	1.41	1.68	1.77	0.54
	nonspin	-0.77	1.1	2.29	2.30	1.07
$\text{Ti}_3(\text{HAT})_2$	spin	-1.10	0.49	2.88	3.00	1.77
	nonspin	-1.40	0.04	3.13	3.14	1.91

Table S3 The spin moment, adsorption energy difference, variations of charge difference (after and before O₂ adsorption), the difference of charge transfer between non-spin-polarized M₃(HAT)₂ and spin-polarized M₃(HAT)₂ of O₂ adsorbed M₃(HAT)₂ systems.

	Ni ₃ (HAT) ₂	Co ₃ (HAT) ₂	Fe ₃ (HAT) ₂	Mn ₃ (HAT) ₂	Cr ₃ (HAT) ₂	Ti ₃ (HAT) ₂
ΔM_m (μB)	1.50	2.35	3.94	4.24	3.05	1.01
E_{OO}^{nonspin} (eV)	-1.94	-1.10	-2.80	-3.02	-2.85	-4.06
E_{OO}^{spin} (eV)	-1.30	-0.34	-1.82	-1.88	-1.77	-3.19
ΔE_{OO} (eV)	-0.64	-0.76	-0.98	-1.14	-1.08	-0.87
$\Delta q^{\text{nonspin}}$ (e^-)	0.03	-0.04	0.01	0.03	-0.07	-0.04
Δq^{spin} (e^-)	0.05	-0.04	-0.23	-0.08	-0.19	0.00
Δq (e^-)	-0.02	0.00	0.24	0.11	0.12	-0.04

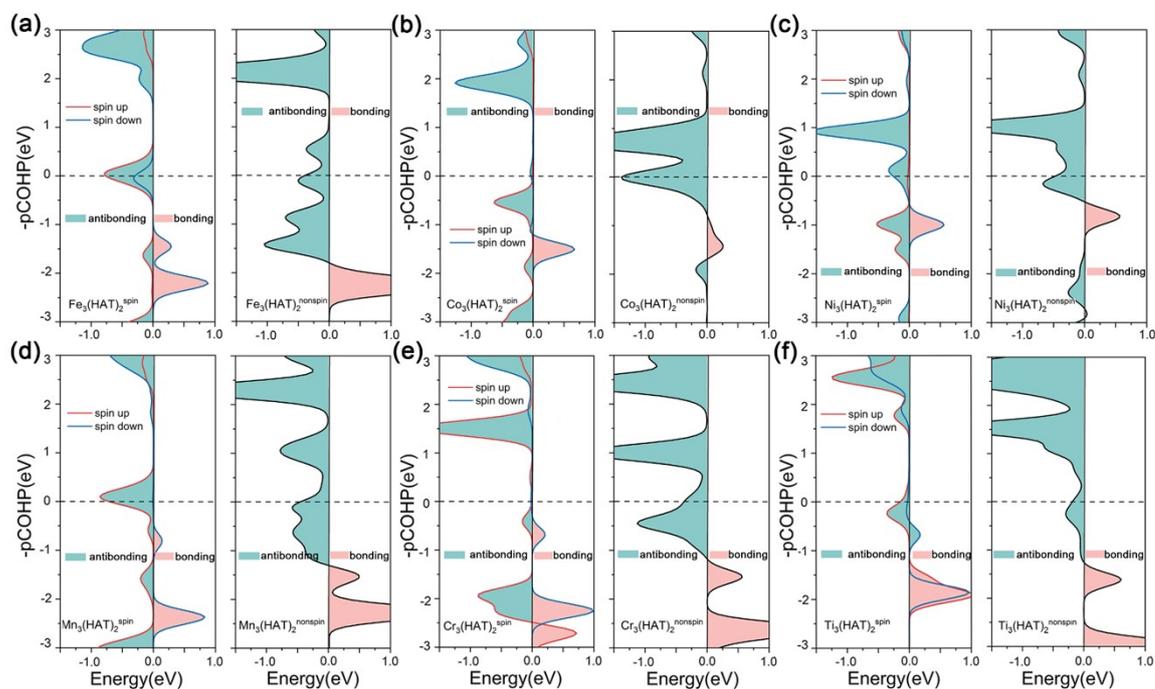


Fig. S6 The orbital contribution of pCOHP between M atoms (Fe, Co, Ni, Mn, Cr and Ti) and intermediates OO* on M₃(HAT)₂.

Table S4 The value of ICOHP between central metal atoms and the adsorption intermediate species OO*.

	Ni ₃ (HAT) ₂	Co ₃ (HAT) ₂	Fe ₃ (HAT) ₂	Mn ₃ (HAT) ₂	Cr ₃ (HAT) ₂	Ti ₃ (HAT) ₂
nospin	-2.63	-2.35	-2.35	-2.60	-3.18	-3.62
spin	-1.57	-1.31	-1.88	-1.91	-2.83	-3.10
Δ ICOHP	-1.06	-1.04	-0.47	-0.69	-0.35	-0.52

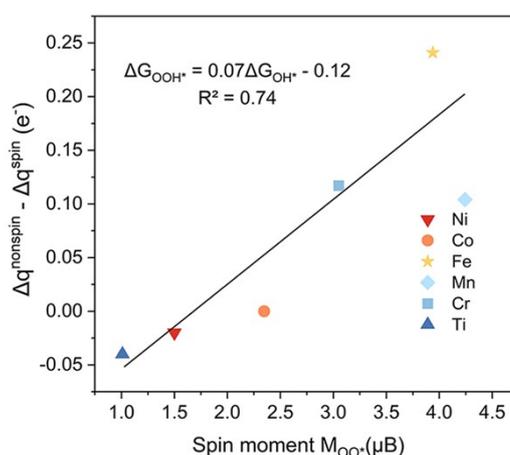


Fig. S7 Correlation between spin moment and the charge difference between M atom and O (Δq).

References

- 1 Kresse and Hafner, *Phy s. Rev. B: Condens. Matter*, 1993, **47**, 558-561.
- 2 Kresse and Furthmuller, *Phy s. Rev. B: Condens. Matter*, 1996, **54**, 11169-11186.
- 3 Blochl, *Phy s. Rev. B: Condens. Matter*, 1994, **50**, 17953-17979.
- 4 Perdew, Burke and Ernzerhof, *Phy s. Rev. Lett.*, 1996, **77**, 3865-3868.
- 5 M. Capdevila-Cortada, Z. Łodziana and N. López, *ACS Catal.*, 2016, **6**, 8370-8379.
- 6 J. Zhou and Q. Sun, *J. Am. Chem. Soc.*, 2011, **133**, 15113-15119.

- 7 M. Aykol and C. Wolverton, *Phys. Rev. B*, 2014, **90**, 115105.
- 8 L. Wang, T. Maxisch and G. Ceder, *Phys. Rev. B*, 2006, **73**, 195107.
- 9 J. Geng, R. Wu, H. Bai, I.-N. Chan, K. W. Ng, W. F. Ip and H. Pan, *Int. J. Hydrogen Energy*, 2022, **47**, 18725-18737.
- 10 S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104.
- 11 J. Rossmeisl, A. Logadottir and J. K. Nørskov, *Chem. Phys.*, 2005, **319**, 178-184.