Supplementary Information

Origin of adsorption trends in two-dimensional single-atom catalysts via d-state filling

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Table S1 Adsorption energies of atomic intermediates (H, C, N, O, Si, P, and S) on transition-metal dopants in N-doped graphene.

Dopant	H (k = 1)	C (k = 2)	N (k = 3)	O (k = 4)	Si (k = 2)	P (k = 3)	S (k = 4)
Sc (v_m = 3)	-3.074	-3.469	-4.202	-5.592	-2.254	-2.398	-3.155
Ti (v_m = 4)	-3.248	-4.216	-6.187	-8.184	-2.745	-3.328	-4.999
V (v_m = 5)	-2.897	-4.824	-7.388	-8.028	-2.729	-3.725	-4.787
Cr (v_m = 6)	-2.487	-4.662	-6.959	-6.317	-2.588	-3.370	-3.247
Mn (v_m = 7)	-2.396	-5.309	-6.522	-5.197	-2.994	-3.017	-2.610
Fe (v_m = 8)	-2.535	-5.608	-5.164	-4.784	-3.497	-2.690	-2.722
Co (v_m = 9)	-2.599	-3.729	-3.918	-3.394	-2.624	-2.163	-1.823
Ni (v_m = 10)	-1.128	-1.735	-2.326	-1.932	-1.181	-0.736	-0.497
Y (v_m = 3)	-2.914	-2.564	-3.946	-5.081	-2.162	-2.230	-2.944
Zr (v_m = 4)	-3.658	-4.250	-5.927	-8.136	-2.936	-3.387	-5.109
Nb (v_m = 5)	-3.496	-5.204	-7.869	-8.732	-3.396	-4.402	-5.546
Mo (v_m = 6)	-3.054	-6.359	-8.727	-8.661	-3.961	-5.138	-5.496
Tc (v_m = 7)	-3.195	-6.983	-8.805	-7.610	-4.564	-5.214	-4.812
Ru (v_m = 8)	-3.280	-7.126	-6.867	-5.462	-4.900	-4.179	-3.557
Rh (v_m = 9)	-2.930	-4.251	-4.069	-3.427	-3.133	-2.502	-2.071
Pd (v_m = 10)	-0.830	-1.446	-1.876	-1.375	-1.179	-0.494	-0.364
Hf (v_m = 4)	-3.851	-4.344	-5.859	-8.148	-2.554	-3.549	-5.237
Ta (v_m = 5)	-3.786	-5.253	-7.837	-8.911	-3.582	-4.625	-5.893
W (v_m = 6)	-3.705	-6.547	-8.921	-9.083	-4.324	-5.513	-6.042
Re (v_m = 7)	-3.523	-7.287	-9.089	-8.308	-5.040	-5.732	-5.529
Os (v_m = 8)	-3.310	-7.359	-7.605	-5.963	-5.168	-4.718	-3.913
Ir (v_m = 9)	-3.008	-5.022	-4.320	-3.667	-3.544	-2.691	-2.275
Pt (v_m = 10)	-1.089	-2.136	-1.902	-1.636	-1.410	-0.671	-0.590

Table S2 Adsorption energies of atomic intermediates (H, C, N, O, Si, P, and S) on transition-metal dopants in WS_2.

Dopant	H (k = 1)	C (k = 2)	N (k = 3)	O (k = 4)	Si (k = 2)	P (k = 3)	S (k = 4)
Sc (v_m = 3)	-3.081	-3.820	-5.774	-7.772	-2.458	-2.982	-5.457
Ti (v_m = 4)	-3.143	-4.319	-7.064	-8.044	-2.690	-3.993	-5.621
V (v_m = 5)	-2.731	-4.838	-7.178	-7.609	-2.579	-3.594	-5.337
Cr (v_m = 6)	-2.803	-5.121	-6.777	-6.532	-2.796	-3.428	-4.480
Mn (v_m = 7)	-2.975	-5.820	-7.053	-5.984	-3.410	-3.666	-4.551
Fe (v_m = 8)	-2.676	-5.948	-6.276	-5.451	-3.786	-3.603	-4.274
Co (v_m = 9)	-2.362	-5.237	-5.261	-5.105	-3.708	-3.299	-3.962
Ni (v_m = 10)	-2.076	-3.516	-3.832	-3.945	-2.780	-2.125	-3.244
Y (v_m = 3)	-3.047	-3.707	-5.606	-7.614	-2.418	-2.895	-5.409
Zr (v_m = 4)	-3.338	-4.689	-7.254	-8.302	-2.856	-3.698	-5.925
Nb (v_m = 5)	-3.289	-5.431	-7.999	-8.472	-3.388	-4.352	-6.080
Mo (v_m = 6)	-2.970	-6.410	-8.275	-8.405	-3.905	-4.748	-6.081
Tc (v_m = 7)	-2.929	-6.808	-8.372	-7.491	-4.209	-4.841	-5.541
Ru (v_m = 8)	-2.624	-6.969	-7.171	-5.876	-4.635	-4.316	-4.696
Rh (v_m = 9)	-2.523	-5.734	-5.220	-4.574	-4.081	-3.403	-3.717
Pd (v_m = 10)	-1.923	-3.325	-3.456	-3.031	-2.808	-1.909	-2.750
Hf (v_m = 4)	-3.408	-4.377	-6.683	-8.106	-2.719	-3.642	-5.925
Ta (v_m = 5)	-3.606	-5.402	-7.770	-8.843	-3.494	-4.548	-6.635
W (v_m = 6)	-3.599	-6.536	-8.543	-8.981	-4.182	-5.273	-6.812
Re (v_m = 7)	-3.512	-6.951	-8.682	-8.358	-4.574	-5.485	-6.517
Os (v_m = 8)	-3.239	-7.260	-8.069	-7.230	-5.073	-5.261	-5.907
Ir (v_m = 9)	-3.038	-6.660	-6.911	-5.624	-4.942	-4.806	-4.854
Pt (v_m = 10)	-2.781	-5.430	-4.817	-4.250	-4.428	-3.411	-3.893

Table S3 Adsorption energies of molecular intermediates (CO, NO, H_2O, NH_3, N_2, and NNH) on 4d transition-metal dopants in N-doped graphene.

Dopant	CO (k = 2)	NO (k = 3)	H_2O (k = 2)	NH_3 (k = 2)	N_2 (k = 2)	NNH (linear) (k = 3)	NNH (bent) (k = 1)
Y (v_m = 3)	-0.971	-2.278	-0.924	-1.058	-0.745	-1.977	–
Zr (v_m = 4)	-1.451	-3.085	-1.026	-1.205	-1.107	-2.898	–
Nb (v_m = 5)	-1.886	-3.631	-0.677	-1.035	-1.185	-3.307	–
Mo (v_m = 6)	-2.167	-4.062	-0.739	-1.180	-1.308	-3.550	–
Tc (v_m = 7)	-2.507	-4.149	-0.523	-1.081	-1.177	-3.546	–
Ru (v_m = 8)	-2.742	-3.020	-0.335	-1.105	-1.352	–	-2.393
Rh (v_m = 9)	-0.830	-0.566	-0.319	-0.271	0.099	–	-1.661
Pd (v_m = 10)	-0.077	-0.100	-0.221	-0.139	-0.074	–	-0.222

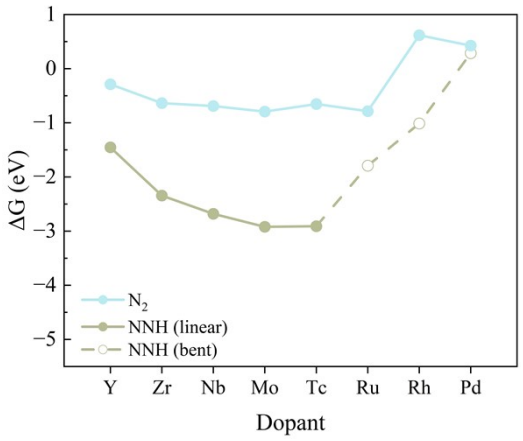

Fig. S1 Calculated Gibbs free energy (ΔG) of N_2 and NNH adsorption on the 4d dopant sites of N-doped graphene

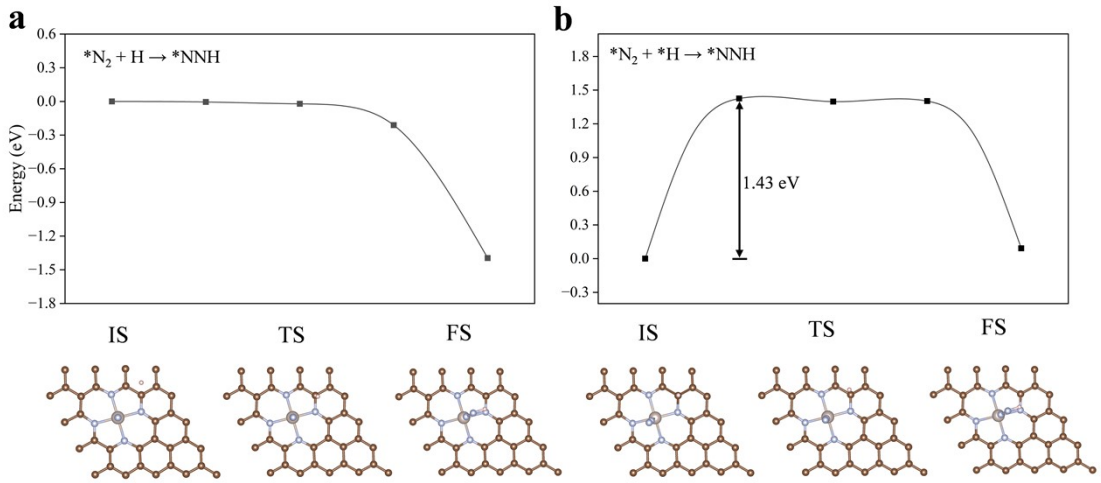

Fig. S2 Initial (IS), transition (TS), and final state (FS) configurations and the corresponding energy profiles for NNH formation. (a) Vacuum-assisted pathway, where N_2 reacts with a hydrogen species in the vacuum region; (b) Surface-mediated pathway involving an adsorbed hydrogen atom (*H) at the interfacial C-top site.

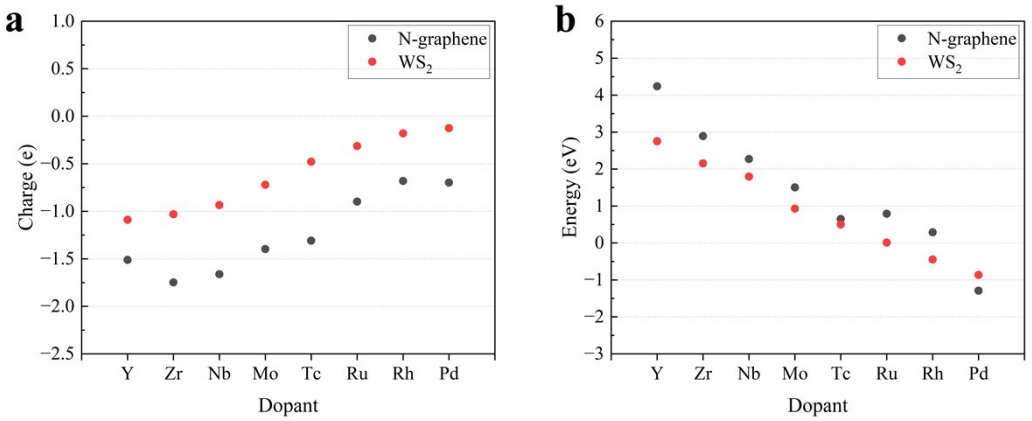

Fig. S3 (a) Comparison of Bader charges of 4d dopant metals on pristine N-doped graphene and WS_2, where negative and positive values indicate electron loss and gain, respectively; (b) d-band center positions of the 4d dopant metals on WS_2 and N-doped graphene.

To ensure the numerical reliability of our calculations, we performed systematic convergence tests using N adsorption on 4d transition metals anchored on N-doped graphene as a representative model system. We compared our standard parameters (400 eV cutoff, 3×3×1 k-point mesh) with more stringent settings (550 eV cutoff, 13×13×1 k-point mesh). As shown in Fig. S4, the calculated adsorption energies exhibit a maximum deviation of only 0.055 eV across the entire 4d series, and more importantly, the qualitative trend–essential to the 10-electron rule–remains perfectly consistent. Furthermore, a comparison of the projected density of states (PDOS) for the d-orbitals of Tc shows that the electronic structures are virtually identical under both parameter sets. These results confirm that a 400 eV cutoff and the chosen k-point sampling provide a well-balanced compromise between computational efficiency and the required accuracy for describing both the energetic and electronic properties of these SAC systems.

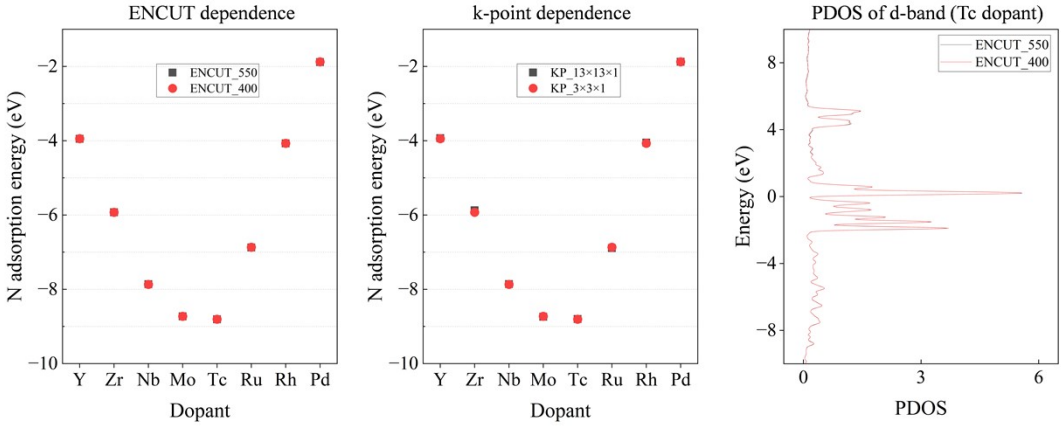

Fig. S4 Convergence tests for plane-wave cutoff energy and k-point sampling. Comparison of adsorption energies of N adatoms on N-doped graphene calculated with cutoff energies of 400 eV and 550 eV, and k-point meshes of 3×3×1 and 13×13×1. Also shown is the projected density of states (PDOS) of the d-band for the Tc dopant at different cutoff energies.

To verify that our conclusions are not sensitive to the choice of exchange–correlation

functional, we performed DFT+U calculations for N adsorption across the 4d series on N-doped graphene. The effective Hubbard parameters (U_{eff} = U−J) were adopted from the literature[1-4], with values for Y and Zr obtained by linear extrapolation:

$$U - J = 0.2131 \times n + 1.424$$

Where n = 1 for Y; n = 2 for Zr.

As shown in Fig. S5, the inclusion of U preserves the characteristic V-shaped adsorption energy trend across the series. Although a slight shift in the energetic minimum (from Tc to Mo) is observed, the overall trend remains unchanged. These results confirm that the 10-electron rule provides a robust qualitative framework, even when electron correlation effects are included.

Table S4 U−J parameters for DFT+U calculations[1].

Dopant	U / eV	J / eV	U−J / eV
Y	−	−	1.63
Zr	−	−	1.85
Nb	2.59	0.52	2.07
Mo	2.83	0.52	2.31
Tc	3.08	0.54	2.54
Ru	3.40	0.54	2.86
Rh	3.63	0.56	3.07
Pd	3.95	0.61	3.34

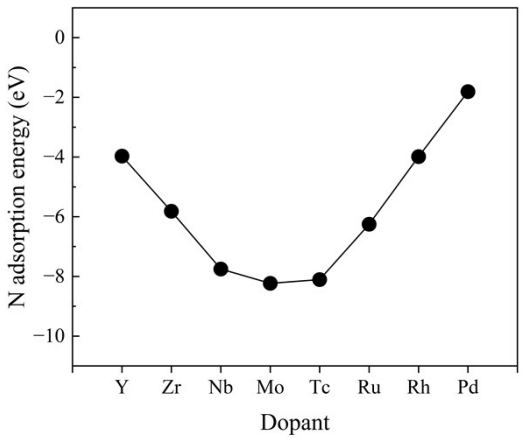

Fig. S5 N adsorption energies of 4d transition-metal dopants on N-doped graphene: DFT+U results.

References

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