Supplementary Information

Deciphering Potential-Driven Dynamics in Fe-N-C Catalysts: *Ab Initio* Insights into Fe–N Switching and Spin-State Transition

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Fe spin states	Majority spin						Minority spin				
	d_{xy}	d_{xz}	d_{yz}	d_{z^2}	$d_{x^2\!-\!y^2}$	d_{xy}	d_{xz}	d_{yz}	d_{z^2}	$d_{x^2\!-\!y^2}$	
0.0 V	0.689	0.945	0.958	0.960	0.949	0.264	0.385	0.137	0.063	0.896	
0.2 V	0.926	0.958	0.957	0.956	0.948	0.154	0.166	0.155	0.152	0.901	
0.4 V	0.929	0.969	0.964	0.969	0.948	0.188	0.181	0.151	0.068	0.773	
0.6 V	0.873	0.963	0.964	0.968	0.948	0.201	0.232	0.120	0.066	0.828	
0.8 V	0.624	0.972	0.957	0.991	0.955	0.200	0.165	0.429	0.099	0.319	
1.0 V	0.533	0.960	0.979	0.965	0.954	0.342	0.231	0.192	0.084	0.930	

Table S1. Average 3d orbital occupations for Fe ion in CP-AIMD.



Figure S1. (a) Fe–N–C models with three different FeN_4 site densities. (b) The potential of zero charge (PZC) for the three models as shown in (a). (c, d, e) Potential-dependent energies of high-spin (HS) and intermediate-spin (IS) states for the three pyridinic FeN_4 models under implicit solvation.

Note: We evaluated the potential of zero charge (PZC) as a function of Fe density (Figure S1b). The results reveal that supercell size influences the PZC, though the magnitude of the effect depends on the Fe spin state. For the intermediate-spin (IS) state, the PZC increases by 0.17 V in the $p(6\times3)$ model but remains nearly unchanged in the $p(4\times3)$ model. For the high-spin (HS) state, the PZC shifts monotonically from -0.82 V to -0.69 V as the model size increases. These variations introduce uncertainties of ~0.1 to 0.2 V in the simulated potentials (vs. SHE) due to Fe site density variation. We further examined the relative stability of Fe spin states across applied potentials for all models (Figure S1c–e). The results indicate that the IS state remains more stable than the HS state at all potentials, regardless of Fe density. Thus, while the PZC is sensitive to model size, the key conclusions—particularly the spin-state stability trends—are robust and unaffected by Fe loading variations.



Figure S2. Evolution of the electronically grand canonical free energy of system at various potentials during the CP-AIMD simulations.



Figure S3. Spin density and PDOS of bare IS (a) and HS (b) FeN₄ under implicit solvation. (c) Potential-dependent energies of HS and IS FeN₄ under implicit solvation.

Note: It is shown that under implicit solvent environment the ferrous pyridinic FeN_4 favors the IS state over the HS state. At higher potentials, the energy gap between the two states diminishes.



Figure S4. Evolution of the Fe–O distance (where O is in the adsorbed H_2O) at various potentials.



Figure S5. Evolution of the Fe magnetization (a, c) and the Fe–O distance (where O is in the adsorbed H_2O) (b, d) at potentials of 0.0 and 0.4 V during the CP-AIMD simulations. The initial state of the two CP-AIMD simulations is the HS state of bare FeN₄.

Note: Starting the CP-AIMD simulations from bare HS FeN_4 , the water molecule still binds to the Fe center shortly after the start of the simulations. The equilibrium state is also the HS H₂O*-FeN₄ with out-of-plane of displacement, which is the same as in the simulations starting from the IS FeN₄. Hence, it is demonstrated that the equilibrium states are independent of the initial state.



Figure S6. Adsorption energies of the first and second H_2O molecules on pyridinic FeN₄ center as a function of applied potential.



Figure S7. Evolution of Fe magnetization (a), Fe–O distance (where O is from the adsorbed H_2O) (dark blue curve) and height of the Fe atom above the graphene plane (red curve) (b) at U = 1 V, starting from the HS OH*-Fe³⁺N₄ state. Initial (c) and final (d) structures of the CP-AIMD simulation are also shown.

Note: It is demonstrated in **Figure S6** that at U = 1 V the CP-AIMD also converges to the IS OH*-FeN₄ with less degree of Fe out-of-plane displacement when the initial structure is set to the HS OH*-FeN₄. This calculation ensure the obtained equilibrium state at U = 1.0 V is not dependent on the initial structure.



Figure S8. Spin density and PDOS plots of the HS (a) and IS (b) states of OH*-FeN₄. (c) Potential-dependent energies of HS and IS OH*-FeN₄ under implicit solvation.

Note: The figure exhibits the relative stability of IS OH^* -FeN₄ and HS OH^* -FeN₄ as a function of applied potential. Clearly, the HS OH^* -FeN₄ is more stable than the IS counterpart. This result is in contrast with CP-AIMD simulations, which illustrates the importance of incorporating explicit solvation in the model.



Figure S9. Fe magnetization and structure evolution in the CP-AIMD simulation under implicit solvation at U = 1.0 V starting from the IS OH*-FeN₄ structure.

Note: Under implicit solvation conditions, the IS OH^* -FeN₄ transforms to the HS OH^* -FeN₄ during the CP-AIMD simulation demonstrating the HS OH^* -FeN₄ is stable under implicit solvation, which is distinct from the simulation under explicit solvation as described in the main text.



Figure S10. Energy difference between IS and HS of H_2O^* -FeN₄ and F⁻-FeN₄ at U = 1 V. (b) Structures and the orbital occupancy of different spin states.

Note: H_2O is a stronger ligand than the F⁻, so H_2O^* -FeN₄ prefers the IS state since stronger ligand induces larger d orbital splitting, whereas F⁻-FeN₄ favors HS state because of smaller orbital splitting.



Figure S11. The structural switching between H_2O^* - and OH^* -FeN₄ at U = 1 V. The O-H bond threshold set to 1.3 Å.



Figure S12. Simulated and experimental XANES of the Fe K-edge spectrum of FePc. Experimental data are reproduced from Ref. [1].



Figure S13. Probability of Fe magnetization greater than 4.2 μ B during the last 10,000 steps of CP-AIMD simulations as a function of applied potential.

Note: It is found that at U < 0.8 V the H₂O*-FeN₄ vibrates between two different states. As also described in the main text, the two states are $(d_{xy})^1(d_{xz})^1(d_{z^2})^1(d_{yz})^1(d_{x^2-y^2})^2$ and $(d_{xy})^1(d_{xz})^1(d_{z^2})^{1.5}(d_{yz})^1(d_{x^2-y^2})^1$ with m = 4 µB and 4.5 µB, respectively. **Figure S5** shows the occurring probability of these two states at various potentials. It could be seen that at the former state dominates at U < 0.8 V. At U = 0.8 V, the latter state becomes prevalent as the FeN₄ center binds a second H₂O molecule.

This work	< <u> </u>				
	0.00 V		0.8 V 1.0 V	/	
	Active site structure	Pridinic H ₂ O*-FeN ₄	Pridinic 2H₂O*-FeN₄ / H₂O*-FeN₄	Pridinic OH*-FeN ₄	
	R _{Fe-N}	2.07 Å	2.10 / 1.95 Å	1.95 Å	
	R _{Fe-O}	2.00 Å	2.02 / 1.99 Å	1.93 Å	
	Out-of-plane displacement	0.81 – 1.02 Å	1.03 / 0.40 Å	0.38 Å	
	Oxidation states	Fe(II)	Fe(II/III) U _{redox}	Fe(III)	
	spin states	HS(S = 2)		IS(S = 3/2)	
0.10 V Experiment (in situ) —					
			0.7 V 1.0 V	/	
	Active site structure	FeN ₄ ^{a,c,d}		O _x /FeN ₄ ^{a,b,c}	
	R _{Fe-N/O}	2.07ª / 2.08° Å		1.99-2.01 ^{a,c} Å	
	Out-of-plane displacement	Yes ^c		Noc	
	Oxidation states	Fe(II)	Fe(II/III) U _{redox} ^{a,b}	Fe(III)	
	spin states	HS°		1	

Figure S14. Comparison between theoretical and experimental assignment for the potential-induced structural, redox, and spin-state changes on the FeN₄ active center. ^aReference². ^bReference³. ^cReference⁴, ^dReference⁵, ^cReference⁶.



Figure S15. (a) Atomic model of the pyrrolic FeN_4 structure. (b) Optimized structures of pyrrolic H_2O^* -FeN₄ of different spin states and their corresponding PDOS. (c) Optimized structures of pyrrolic OH*-FeN₄ of different spin states and their corresponding PDOS.

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