

Supporting information

**Charge and Spin Communication between Dual Metal Single-Atom Sites on C<sub>2</sub>N Sheet: Regulating Electronic Spin Moments of Fe Atom for N<sub>2</sub> Activation and Reduction**

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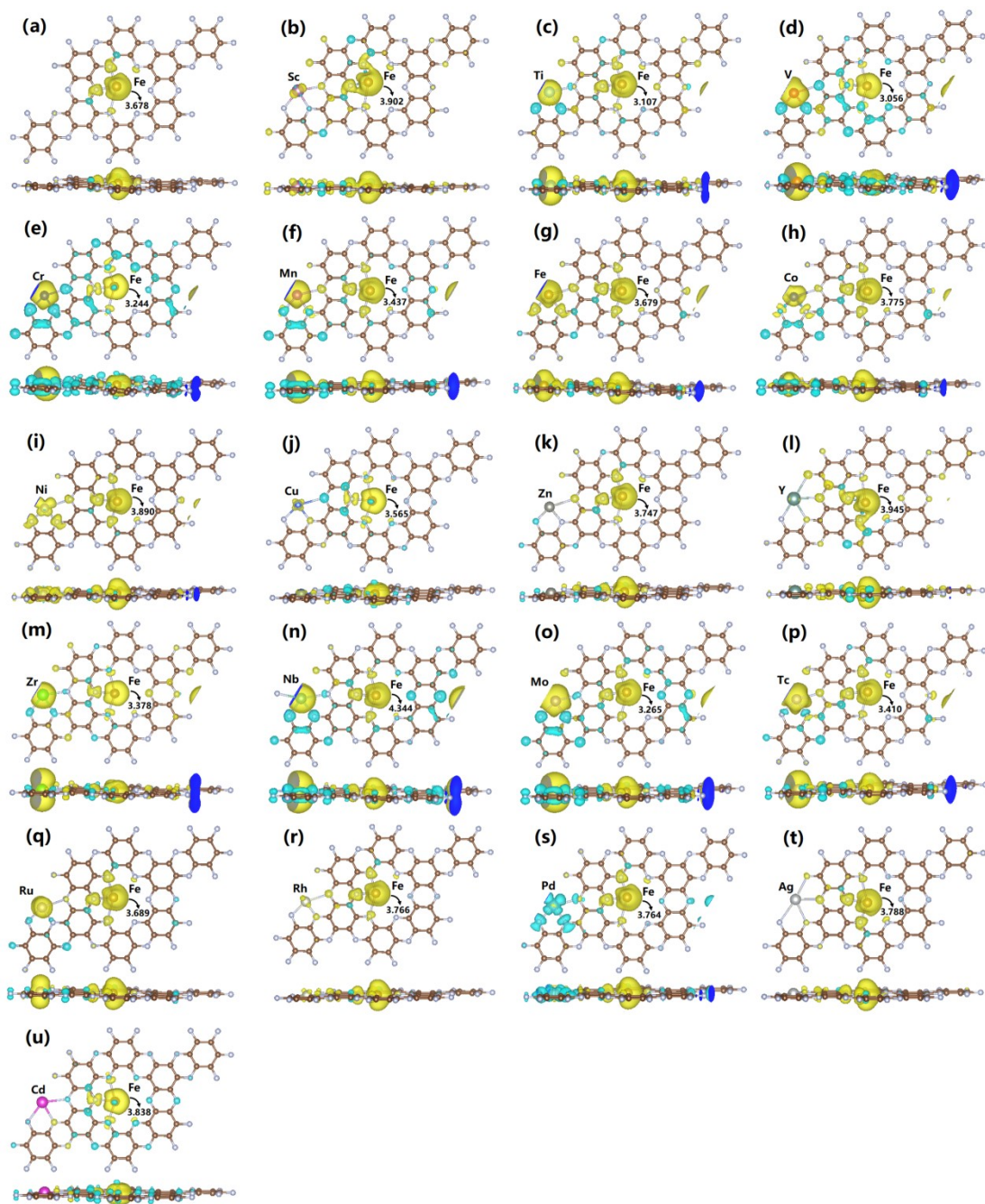
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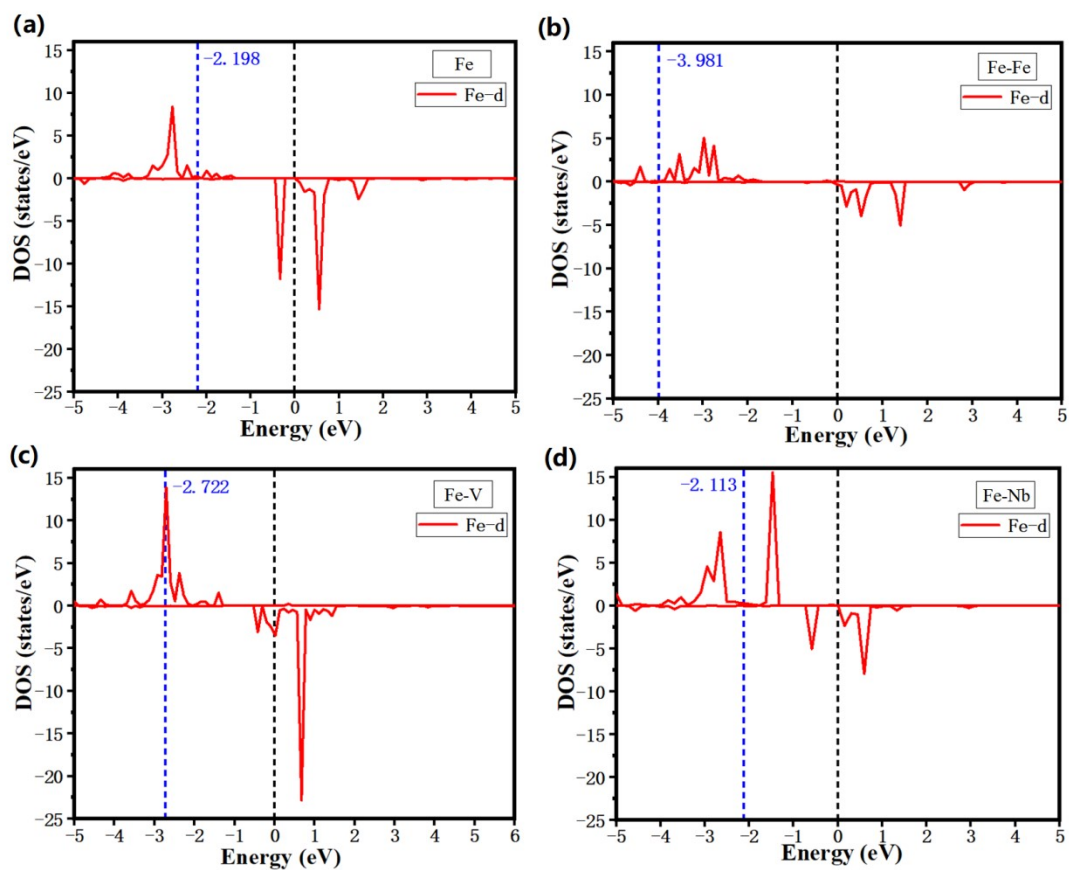
[tsb1980@xmu.edu.cn](mailto:tsb1980@xmu.edu.cn),

**Table S1.** The electronic spin moments (in  $\mu_B$ ) of reactive Fe atom in Fe-TM dual single-metal atom catalysts with different supercell size of  $C_2N$  sheet.

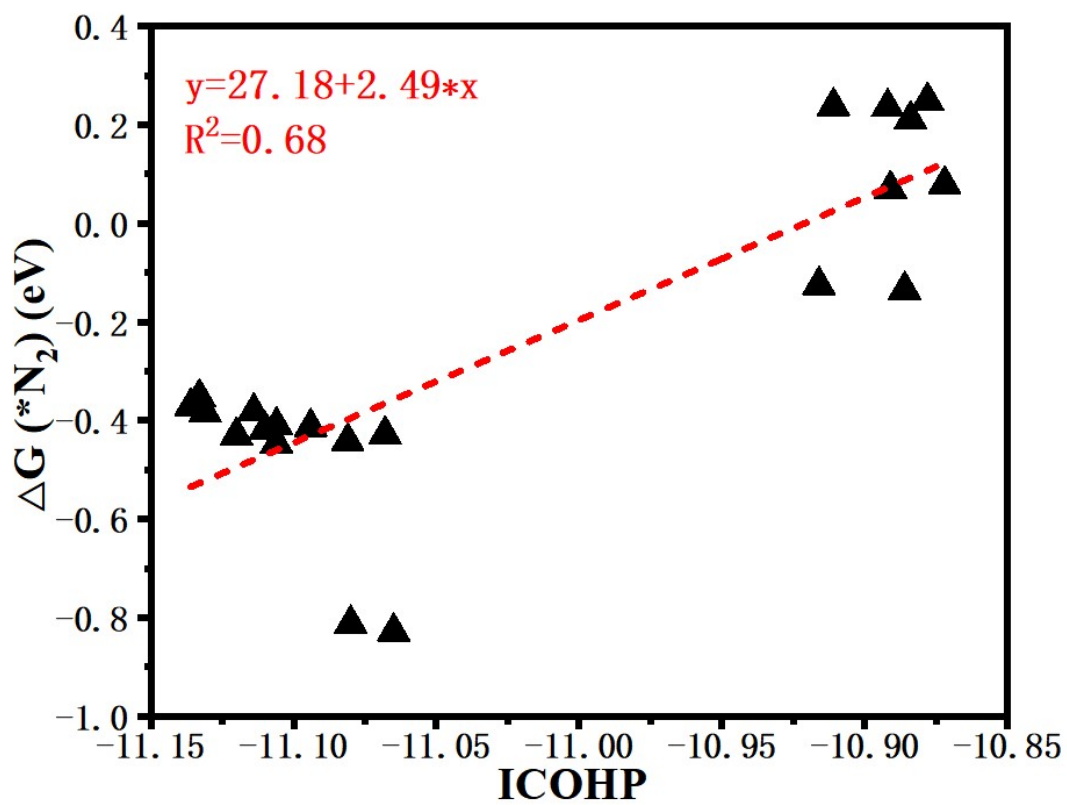
substrate	$2 \times 2 \times 1$	$3 \times 3 \times 1$
Fe-Fe	3.679	3.677
Fe-Co	3.775	3.774
Fe-Ni	3.890	3.767
Fe-Mo	3.265	3.268
Fe-Ag	3.788	3.862
Fe-V	3.056	3.222



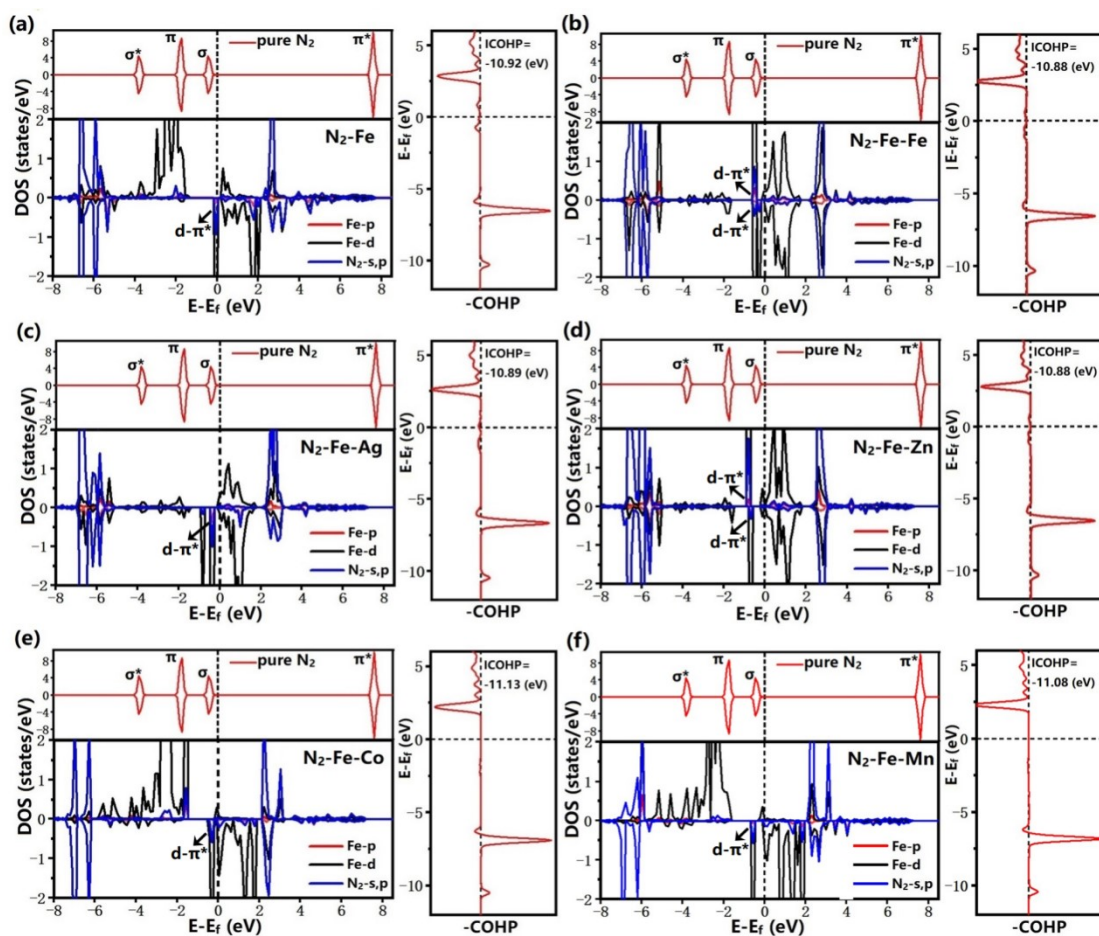
**Figure S1.** Spin density distribution of Fe and TM bimetallic single-atom site catalysts on  $C_2N$ : (a) isolated Fe, (b) TM = Sc, (c) Ti, (d) V, (e) Cr, (f) Mn, (g) Fe, (h) Co, (i) Ni, (j) Cu, (k) Zn, (l) Y, (m) Zr, (n) Nb, (o) Mo, (p) Tc, (q) Ru, (r) Rh, (s) Pd, (t) Ag, (u) Cd, with the yellow and blue areas for the majority and minority spin, respectively. The isosurface values are set to  $0.002 e/\text{\AA}^3$ . The spin moments of reaction Fe atom site are shown in  $\mu_B$ .



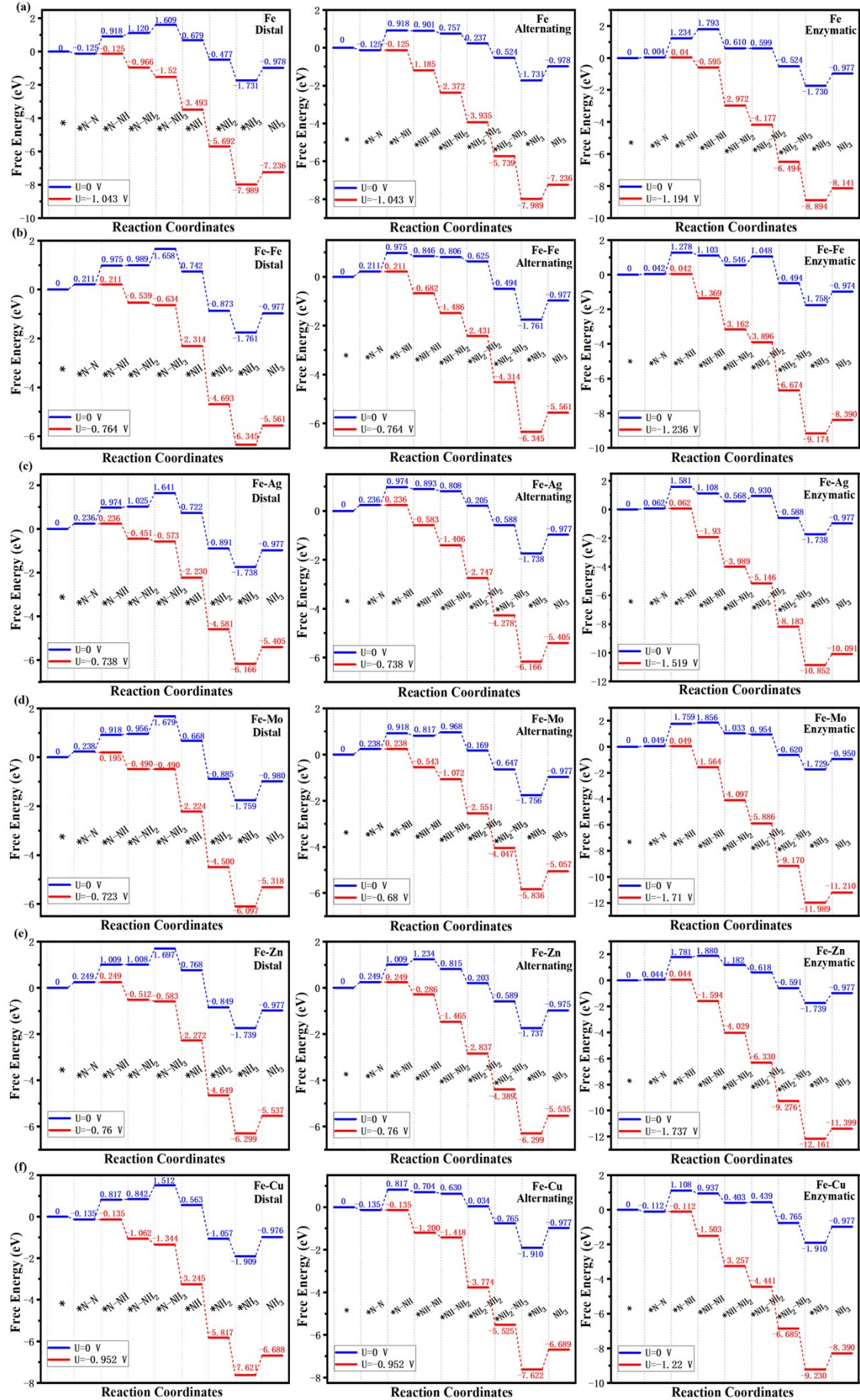
**Figure S2.** Spin polarized partial density of states (PDOS) of d orbital of Fe atom on (a) isolated Fe SAC, (b) Fe-Fe, (c) Fe-V, and (d) Fe-Nb catalysts. The vertical blue line defines the d-band center of Fe. The Fermi level is set to zero.



**Figure S3.** Change of N<sub>2</sub> adsorption free energy ( $\Delta G(*N_2)$ ) on Fe atom with the ICOHP of N≡N bond for the Fe-TM catalysts.



**Figure S4.** DOS of N<sub>2</sub> before and after adsorption and partial DOS of p and d orbitals of reaction Fe atom after N<sub>2</sub> interaction (left panel) and the COHP of the N≡N bond (right panel) on (a) isolated Fe SAC, (b) Fe-Fe, (c) Fe-Ag, (d) Fe-Zn, (e) Fe-Co, and (f) Fe-Mn catalysts. The Fermi level is set to 0.



**Figure S5.** Free-energy diagrams of eNRR through the distal (left panel), alternating (middle panel), and enzymatic pathways (right panel) catalyzed by (a) the isolated Fe SAC, (b) Fe-Fe, (c) Fe-Ag, (d) Fe-Mo, (e) Fe-Zn, and (f) Fe-Cu catalysts at zero and limiting potential.

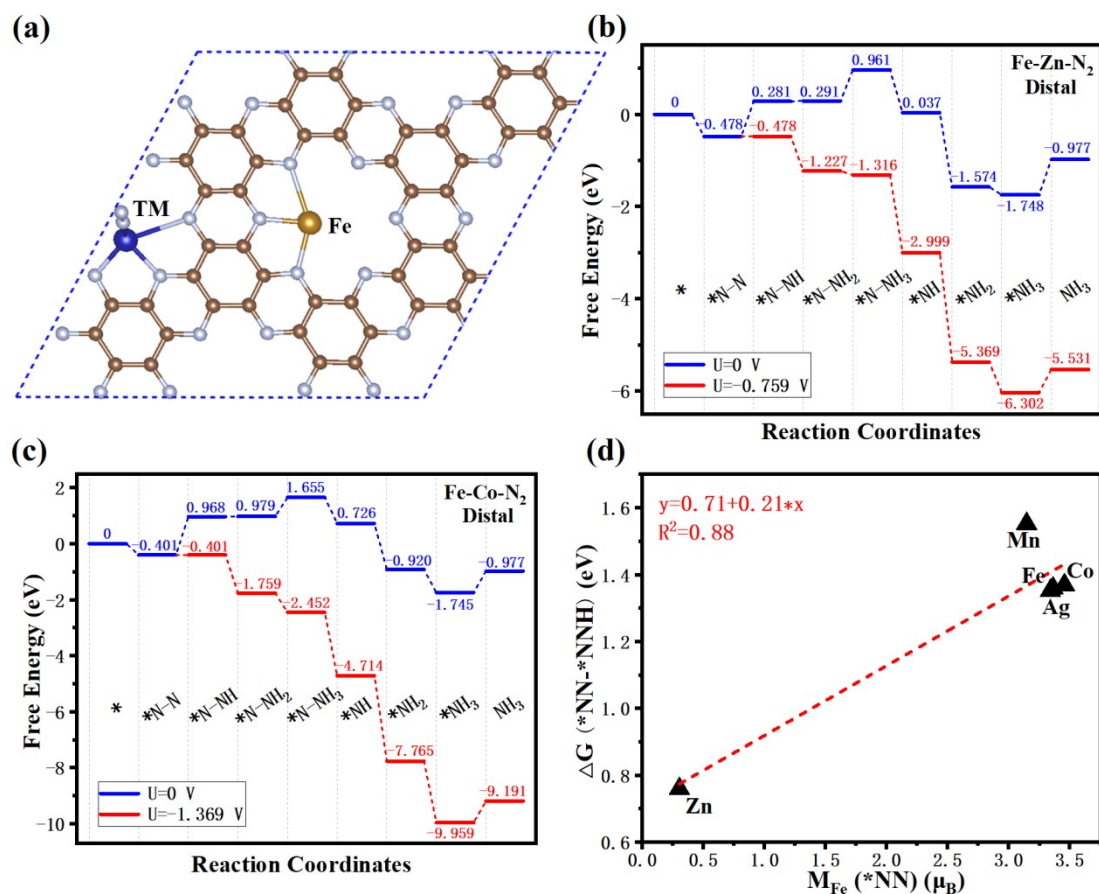
**Table S2.** Free energy corrections:  $E_{ZPE}$  and  $S$  represents the zero-point energy change and the entropy change, respectively. Note that  $T$  is set to 298.15 K, and all the energies are in  $eV$ .

Species	$E_{ZPE}$ (eV)	$TS$ (eV)	$E_{ZPE} - TS$ (eV)
Distal			
*N <sub>2</sub>	0.206	0.163	0.043
*N <sub>2</sub> H	0.452	0.205	0.247
*N <sub>2</sub> H <sub>2</sub>	0.779	0.237	0.542
*N <sub>2</sub> H <sub>3</sub>	1.027	0.361	0.666
*NH	0.329	0.099	0.230
*NH <sub>2</sub>	0.670	0.132	0.538
*NH <sub>3</sub>	1.036	0.106	0.930
Alternating			
*N <sub>2</sub>	0.206	0.163	0.043
*N <sub>2</sub> H	0.452	0.205	0.247
*NH-NH	0.816	0.210	0.606
*NH-NH <sub>2</sub>	1.115	0.231	0.884
*NH <sub>2</sub> -NH <sub>2</sub>	1.497	0.185	1.312
*NH <sub>2</sub> -NH <sub>3</sub>	1.633	0.328	1.305
*NH <sub>3</sub>	1.036	0.106	0.930
Enzymatic			
*N-*N	0.175	0.203	-0.028
*N-*NH	0.470	0.163	0.307
*NH-*NH	0.797	0.169	0.628
*NH-*NH <sub>2</sub>	1.149	0.120	1.029
*NH <sub>2</sub> -*NH <sub>2</sub>	1.481	0.121	1.360
*NH <sub>2</sub> -NH <sub>3</sub>	1.633	0.328	1.305
*NH <sub>3</sub>	1.036	0.106	0.930



**Table S3.** Free energy changes (in eV) of all elementary steps for distal mechanism catalyzed by isolated Fe SAC and Fe-TM catalysts. Numbers in red indicate the maximum free energy barrier among all elementary steps.

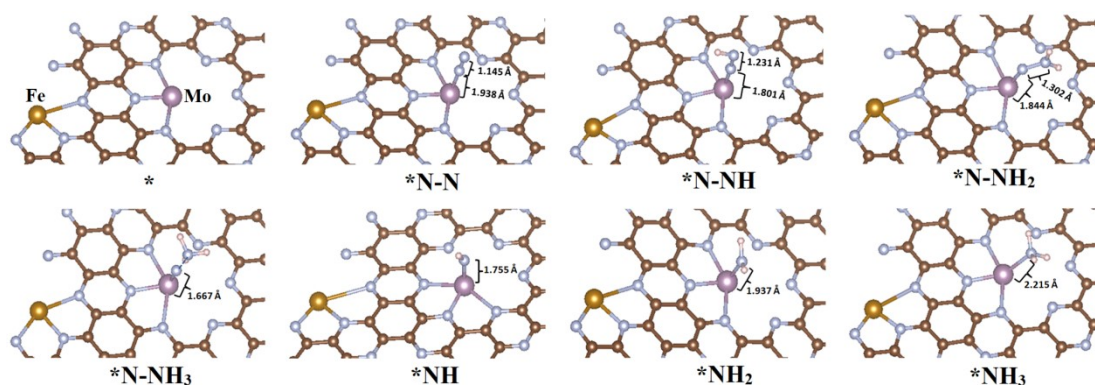
catalysts	*→	*N-N→	*N-NH→	*N-NH <sub>2</sub> →	*N-NH <sub>3</sub> →	*NH→	*NH <sub>2</sub> →	*NH <sub>3</sub> →
	*N-N	*N-NH	*N-NH <sub>2</sub>	*N-NH <sub>3</sub>	*NH	*NH <sub>2</sub>	*NH <sub>3</sub>	*
Isolated Fe	-0.125	<b>1.043</b>	0.202	0.489	-0.930	-1.156	-1.254	0.753
Fe-Sc	-0.828	<b>1.406</b>	0.004	0.738	-0.956	-1.674	-0.380	0.739
Fe-Ti	-0.447	<b>1.411</b>	0.016	0.707	-0.978	-1.690	-0.825	0.829
Fe-V	-0.419	<b>1.296</b>	0.084	0.687	-0.922	-1.490	-1.011	0.798
Fe-Cr	-0.413	<b>1.372</b>	0.049	0.684	-0.996	-1.536	-0.904	0.767
Fe-Mn	-0.442	<b>1.392</b>	0.038	0.648	-0.89	-1.615	-0.897	0.789
Fe-Fe	0.211	<b>0.764</b>	0.014	0.669	-0.916	-1.615	-0.888	0.784
Fe-Co	-0.384	<b>1.519</b>	-0.186	0.680	-0.930	-1.598	-0.878	0.733
Fe-Ni	-0.382	<b>1.359</b>	0.021	0.657	-0.924	-1.091	-1.397	0.780
Fe-Cu	-0.135	<b>0.952</b>	0.025	0.670	-0.949	-1.620	-0.852	0.933
Fe-Zn	0.249	<b>0.760</b>	-0.001	0.689	-0.929	-1.617	-0.89	0.762
Fe-Y	-0.812	<b>1.377</b>	-0.043	0.735	-0.907	-1.659	-0.925	1.257
Fe-Zr	-0.430	<b>1.345</b>	0.024	0.762	-0.983	-1.666	-0.865	0.836
Fe-Nb	-0.428	<b>1.348</b>	-0.005	0.757	-0.910	-1.216	-1.377	0.854
Fe-Mo	0.238	0.680	0.038	<b>0.723</b>	-1.011	-1.553	-0.871	0.779
Fe-Tc	-0.410	<b>1.394</b>	-0.031	0.712	-0.895	-1.499	-1.05	0.802
Fe-Ru	-0.371	<b>1.308</b>	0.056	0.667	-0.941	-1.600	-0.864	0.768
Fe-Rh	-0.353	<b>1.341</b>	0.028	0.673	-0.915	-1.632	-0.881	0.762
Fe-Pd	0.070	<b>1.112</b>	-0.163	0.652	-1.119	-1.429	-0.876	0.769
Fe-Ag	0.236	<b>0.738</b>	0.051	0.616	-0.919	-1.613	-0.847	0.761
Fe-Cd	-0.330	<b>1.539</b>	-0.646	0.660	-0.889	-1.671	-0.851	1.211



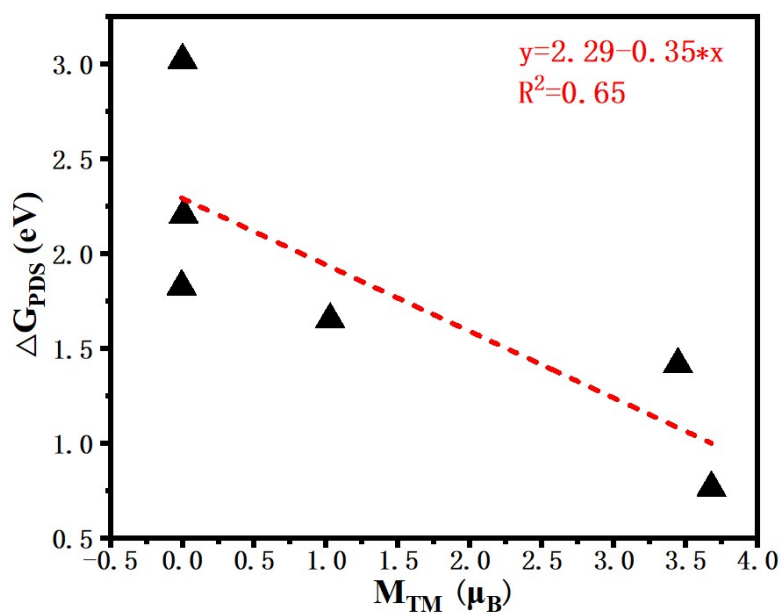
**Figure S6.** (a) Schematic structure of Fe SACs on C<sub>2</sub>N with N<sub>2</sub> adsorbed on the neighboring TM atom (namely Fe-TM-N<sub>2</sub>). Free-energy diagrams of eNRR through the distal pathways catalyzed by (b) Fe-Zn-N<sub>2</sub> and (c) Fe-Co-N<sub>2</sub> at 0 and limiting potential. (d) Relation between free energy change for \*NN to \*N-NH and spin moments of Fe active center with adsorbed N<sub>2</sub>.

**Table S4.** Free energy changes (in eV) of all elementary steps for distal mechanism catalyzed by Fe-TM catalysts with TM atom as active site. Numbers in red indicate the maximum free energy barrier among all elementary steps.

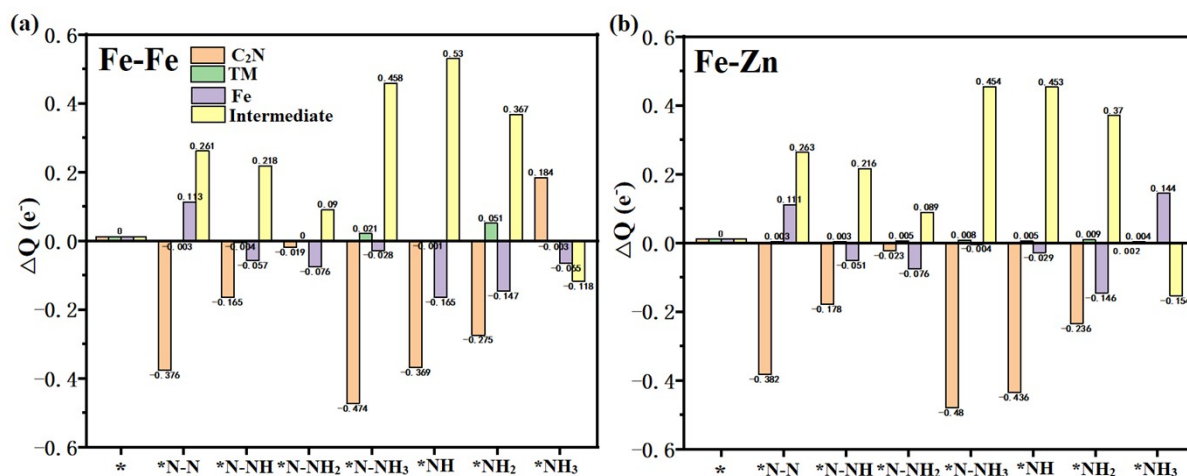
substrate	*→	*N-N→	*N-NH→	*N-NH <sub>2</sub> →	*N-NH <sub>3</sub> →	*NH→	*NH <sub>2</sub> →	*NH <sub>3</sub> →
	*N-N	*N-NH	*N-NH <sub>2</sub>	*N-NH <sub>3</sub>	*NH	*NH <sub>2</sub>	*NH <sub>3</sub>	*
Fe-Fe	0.211	<b>0.764</b>	0.014	0.669	-0.916	-1.615	-0.888	0.784
Fe-Ni	-0.404	1.345	0.245	<b>1.652</b>	-1.751	-1.607	-1.315	0.858
Fe-Cu	-0.514	1.935	-0.247	<b>2.204</b>	-1.883	-1.994	-1.41	0.882
Fe-Zn	-0.065	1.644	-0.474	<b>1.826</b>	-2.162	-1.983	-1.127	1.364
Fe-Mo	-0.457	<b>1.415</b>	-0.59	-0.986	-0.273	-0.523	0.639	-0.202
Fe-Ag	-0.585	<b>3.201</b>	-0.989	2.944	-2.736	-0.875	-2.709	0.772



**Figure S7.** Geometry structures of all intermediates adsorbed on Mo atom for N<sub>2</sub> reduction to NH<sub>3</sub> catalyzed by Fe-Mo catalyst with Mo as active site.

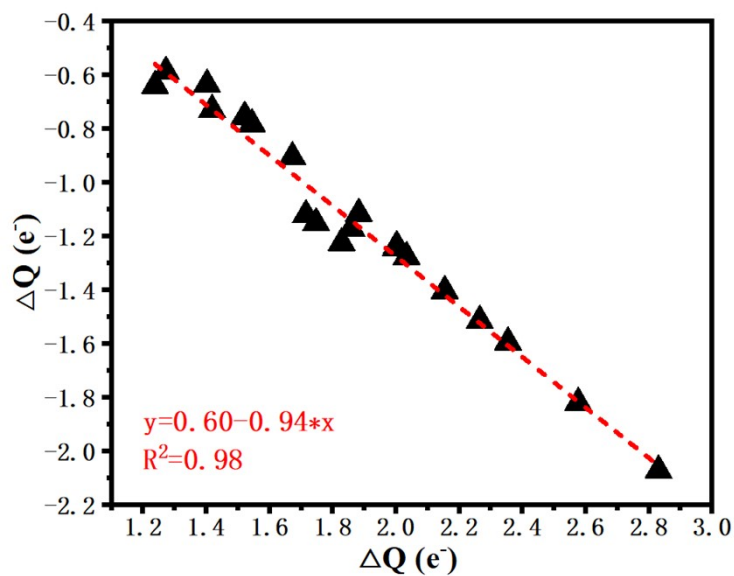


**Figure S8.** Correlation of Gibbs free energy change of PDS for eNRR on Fe-TM catalysts with electronic spin moments of reactive TM atom

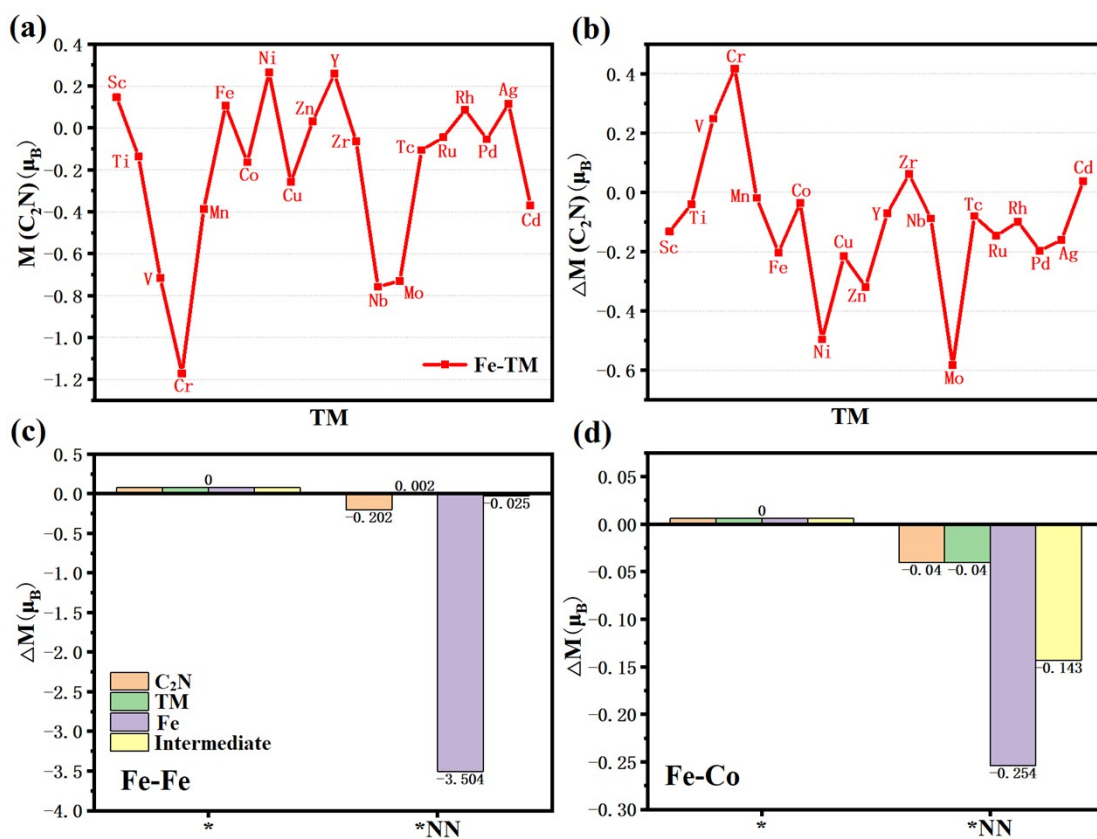


**Figure S9.** Charge transfer change of four fragments (C<sub>2</sub>N, TM, Fe, intermediate) on (a) the Fe-Fe and (b) Fe-Zn catalysts with intermediate interaction relative to that of corresponding fragment on the clean catalyst surface. It noted that the polarized charges of adsorbed intermediate are defined as its charge transfer.

As shown in Figure S11a and b, when the N<sub>2</sub> and key intermediate \*N-NH are adsorbed at Fe site, about 0.26 and 0.21 e are found to transfer from the substrate to intermediates, respectively. The neighboring C and N atoms in C<sub>2</sub>N sheet donate most of electrons, and the Fe active center also takes part in the charge transfer. In contrast, the neighboring metal atom contributes a very minor charge.



**Figure S10.** Scaling relation between polarized charges of C<sub>2</sub>N sheet and TM atom of Fe-TM catalysts with N<sub>2</sub> interaction.



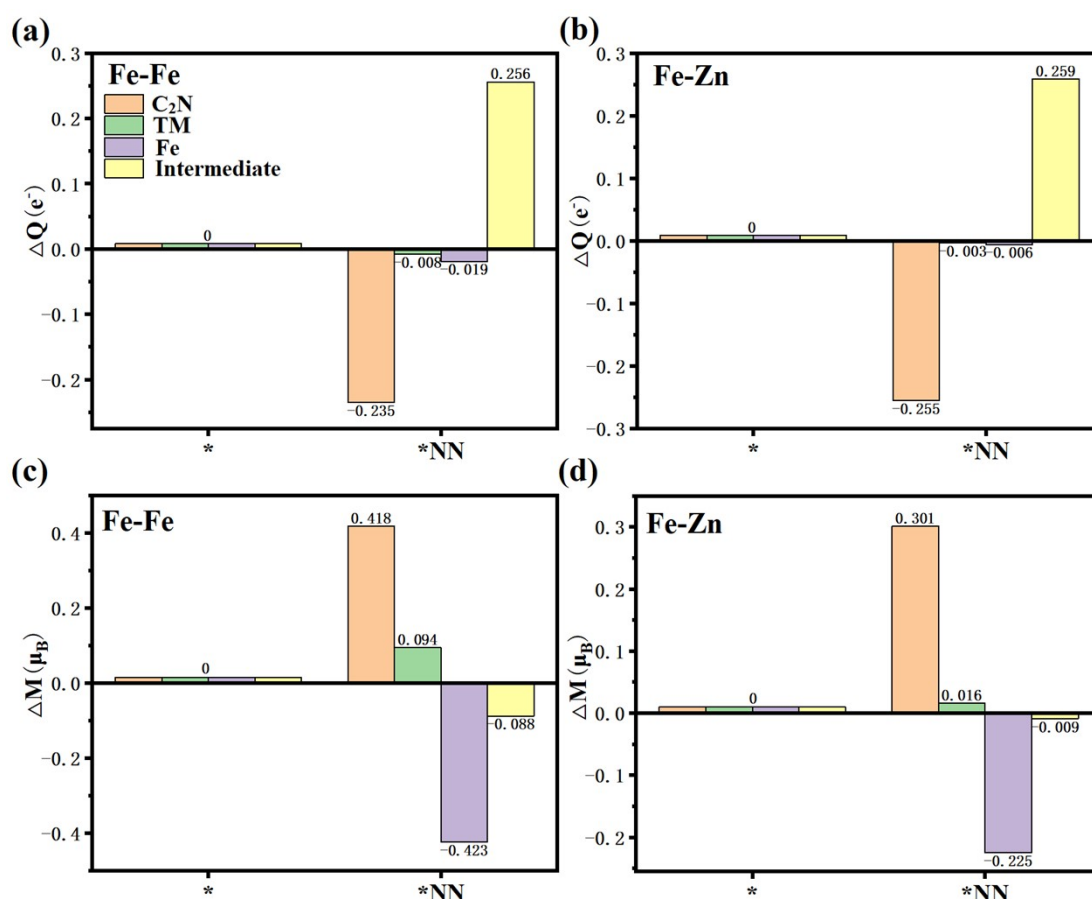
**Figure S11.** (a) Electronic spin moments of  $C_2N$  sheet ( $M(C_2N)$ ) on Fe-TM substrate. (b) The difference of  $M(C_2N)$  ( $\Delta M(C_2N)$ ) between Fe-TM catalyst before and after  $N_2$  interaction. Spin moment change of four fragments ( $C_2N$ , TM, Fe,  $*N_2$ ) on (c) the  $N_2$  adsorbed Fe-Fe and (d) Fe-Co catalysts relative to that of the clean catalyst surface.

**Table S5.** The calculated total spin moments (in  $\mu_B$ ) of Fe-TM catalysts without and with  $N_2$  adsorption.

$N_2$ adsorption	Fe-Sc	Fe-Ti	Fe-V	Fe-Cr	Fe-Mn	Fe-Fe	Fe-Co	Fe-Ni	Fe-Cu	Fe-Zn
without	4.092	5.548	6.026	6.306	8.034	7.438	5.781	5.162	3.335	3.775
with	3.431	4.996	5.967	6.389	7.530	3.709	5.310	1.760	2.376	0.089
$N_2$ adsorption	Fe-Y	Fe-Zr	Fe-Nb	Fe-Mo	Fe-Tc	Fe-Ru	Fe-Rh	Fe-Pd	Fe-Ag	Fe-Cd
without	4.241	5.062	5.127	6.457	6.360	4.540	3.869	2.711	3.904	3.223
with	3.699	4.799	4.506	2.675	5.888	3.672	3.258	3.526	0.019	2.588

**Table S6.** Comparison of total energy (in eV) of systems without and with total spin ( $\mu_B$ ) constraint.

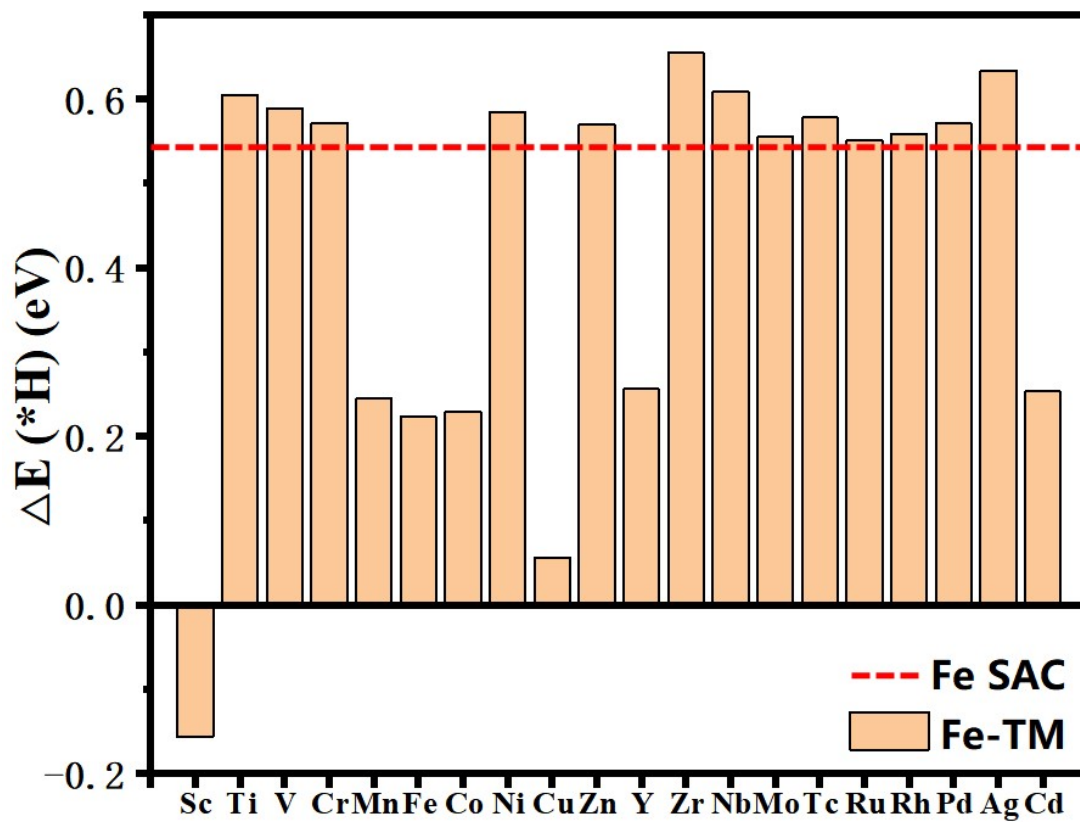
systems	spin relaxation		spin constraint	
	spin	total energy	spin	total energy
Fe-Fe	7.438	-644.484	7	-644.478
Fe-Fe with $N_2$	3.709	-661.363	7	-661.429
Fe-Zn	3.775	-638.110	4	-638.109
Fe-Zn with $N_2$	0.089	-654.953	4	-655.006



**Figure S12.** Charge transfer (a, b) and spin moments change (c, d) of four fragments (C<sub>2</sub>N, TM, Fe, \*N<sub>2</sub>) on the Fe-Fe (a, c) and Fe-Zn (b, d) catalysts with N<sub>2</sub> interaction relative to that of corresponding fragment on the clean catalyst surface when setting the total spin of system with N<sub>2</sub> as that of clean system.

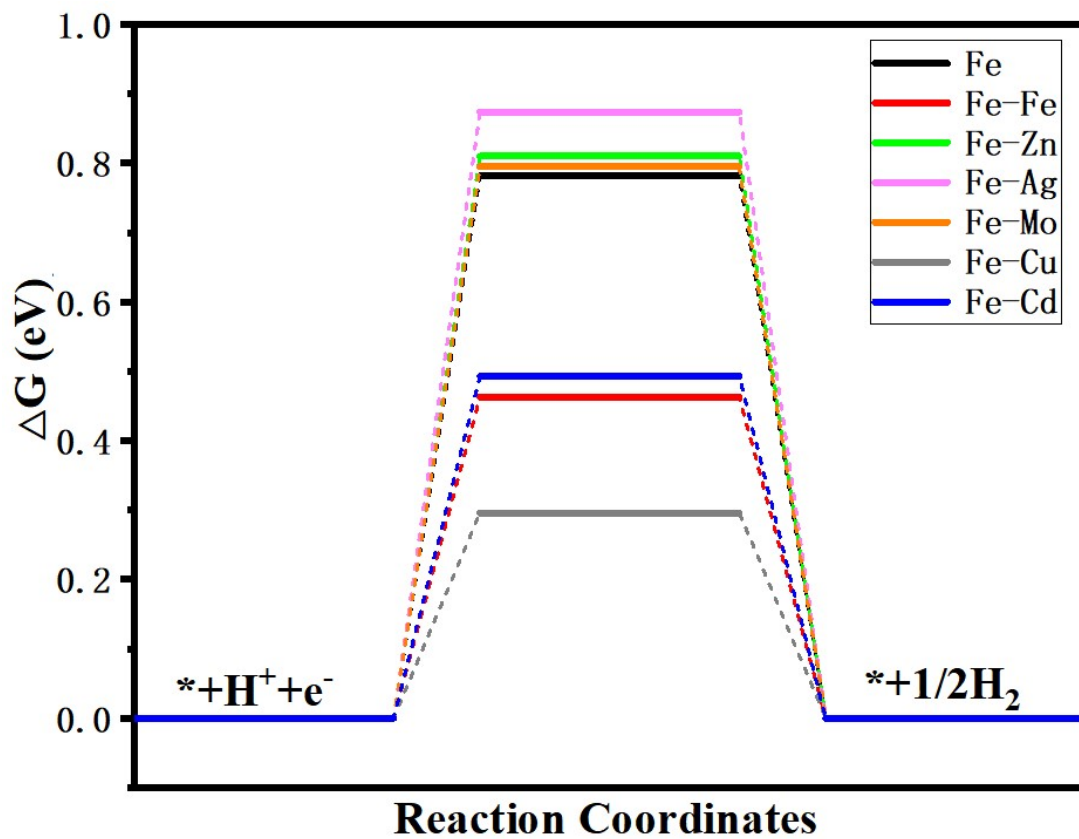
Without any spin limiting, the total spin moments of substrate are different from that of catalyst with N<sub>2</sub> adsorption for most of neighboring TM atoms due to the nonmagnetic N<sub>2</sub> interaction (see Table S5). To maintain spin-conservation, we set the total spin of Fe-TM catalysts (TM = Fe, Zn) with N<sub>2</sub> interaction as that of clean catalyst. As shown in Table S6, the energy difference between systems with and without spin constraint is negligible.

Similar to the systems without spin constraint, the C<sub>2</sub>N play a crucial role in charge transfer when maintaining the total spin (Figure S12a and b). After N<sub>2</sub> interaction, the C<sub>2</sub>N sheet accommodates most of the spin transferred from Fe active site (Figure S12c and d). In contrast, the neighboring TM atom merely hosts minimal spin. As a result, the synergetic effect between reactive Fe atom and neighboring C and N atoms in C<sub>2</sub>N sheet is constructed. The spin-conservation rule is manipulated by the synergetic charge transfer, provided by the p-block C<sub>2</sub>N sheet, and spin selection, preserved by transferring spin from metal center to C<sub>2</sub>N.

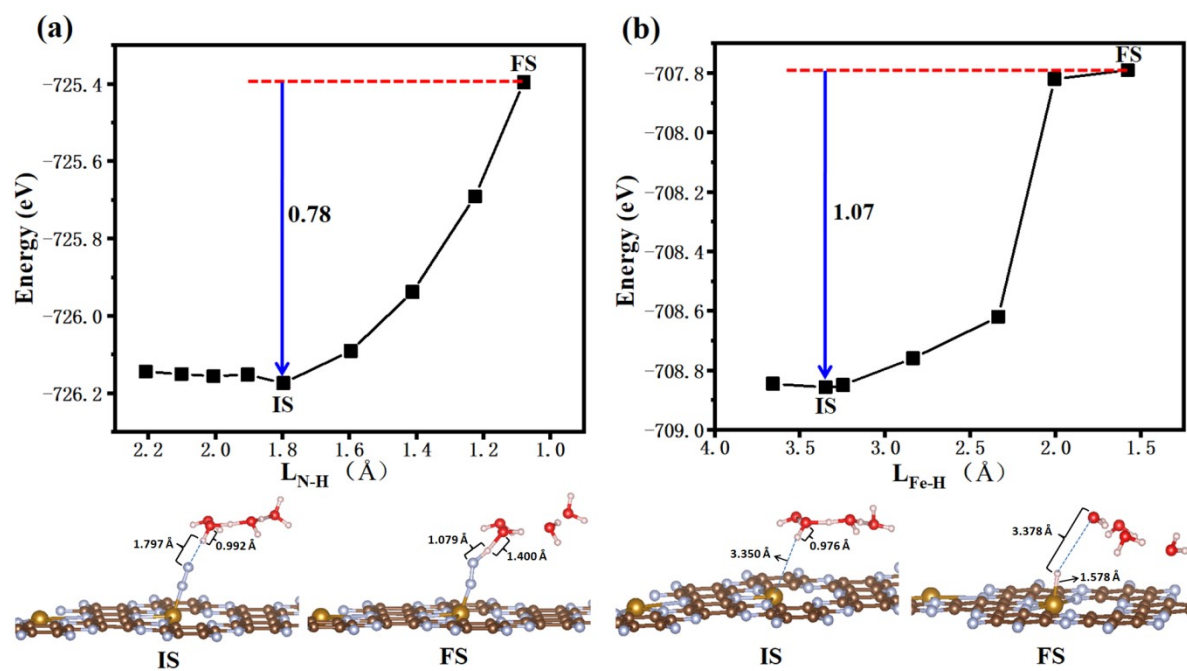


**Figure S13.** H adsorption energy ( $\Delta E(*H)$ ) on reaction Fe atom for considered Fe-TM catalysts with TM = 3d and 4d metal atoms. The horizontal red line defines the  $\Delta E(*H)$  on isolated Fe SAC for comparison.

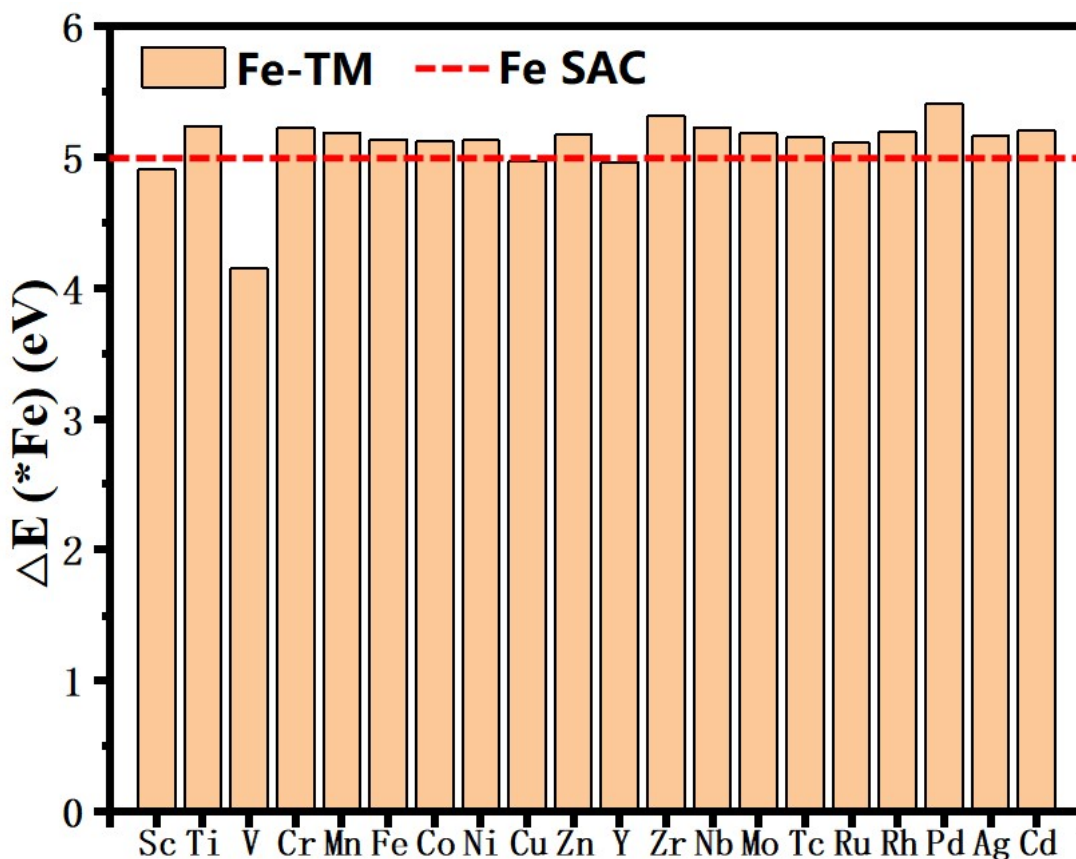




**Figure S14.** Free-energy diagrams for the HER on isolated Fe SAC and several Fe-TM catalysts.

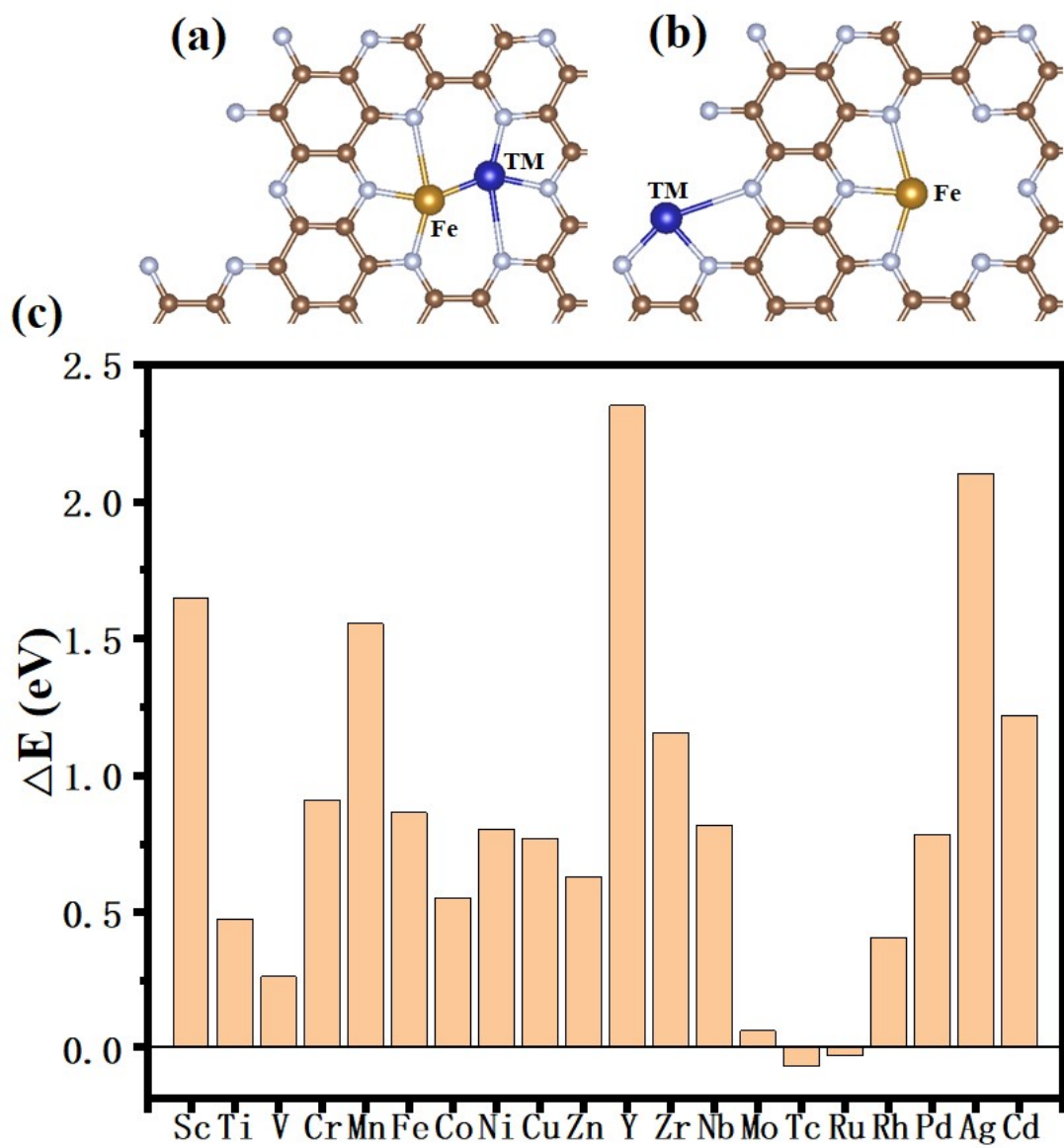


**Figure S15.** The minimal energy path for (a)  $*N-NH$  formation and (b)  $*H$  formation on Fe-Fe catalyst containing  $3H_2O$  and  $H_3O^+$ , which is realized by scanning the total energy of system with the  $N-N\cdots H$  ( $L_{N-H}$ ) and  $Fe\cdots H$  ( $L_{Fe-H}$ ) distance. Insets show the atomic structures of the initial state (IS) and final state (FS).



**Figure S16.** The binding energy of Fe atom ( $\Delta E(*Fe)$ ) anchored by cavity of  $C_2N$  as a function of neighboring TM atom. The horizontal red line defines the  $\Delta E(*Fe)$  value of isolated Fe SACs.

To evaluate the effect of adjacent TM atom on the thermodynamics stability of Fe SACs, the binding energy of Fe atom is calculated by:  $\Delta E(*Fe) = E(TM-C_2N) + E(Fe) - E(Fe-TM-C_2N)$ , where the  $E(TM-C_2N)$ ,  $E(Fe)$ , and  $E(Fe-TM-C_2N)$  are the total energies of TM atom-adsorbed  $C_2N$  (namely TM- $C_2N$ ), free Fe atom, and Fe adsorbed on TM- $C_2N$  systems. It should be noted that more positive  $\Delta E(*Fe)$  indicates the monodispersed Fe catalysts with high stability, thermodynamically.



**Figure S17.** Schematic structure of Fe and TM atoms adsorbed on (a) the single hole and (b) two neighboring holes and (c) the total energy difference ( $\Delta E$ ) between them. It is noted that the positive  $\Delta E$  suggests that the formed Fe and TM bimetallic single-atom catalyst in (b) is more stable than the Fe-TM metal dimer in (a).