Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

″Sabatier principle″ of *d* electron number for describing the nitrogen reduction reaction performance on single-atom alloy catalysts

Tianyi Dai, Zhili Wang, Xingyou Lang,* Qing Jiang*

Key Laboratory of Automobile Materials, Ministry of Education, and School of Materials Science and Engineering, Jilin University, Changchun 130022, China

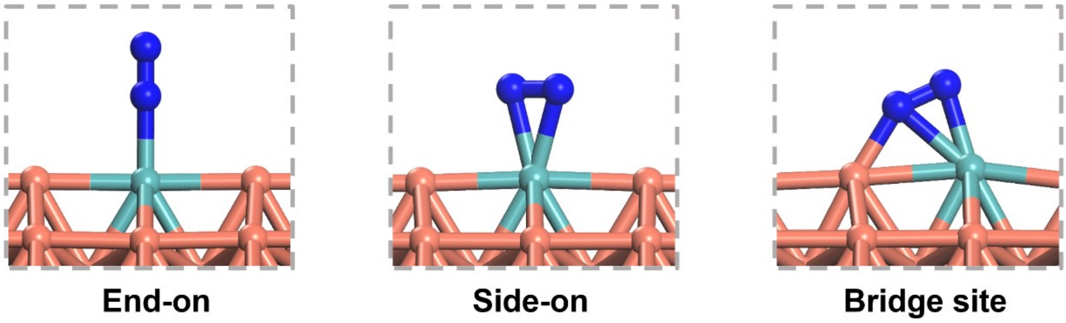

Fig. S1 The illustrations of the N_2 adsorption configurations.

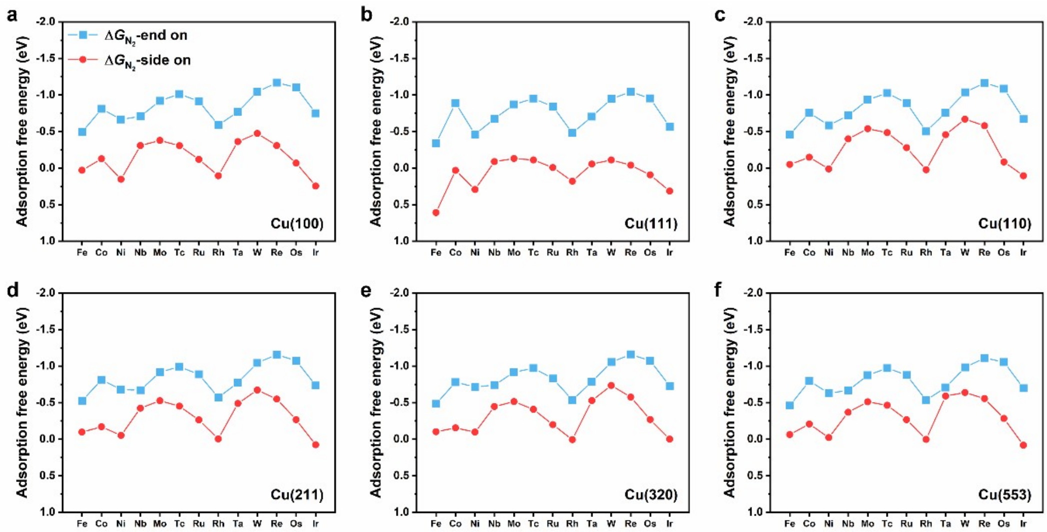

Fig. S2 Adsorption free energy values of N_2 in different adsorption configurations on the Cu-based SAAs.

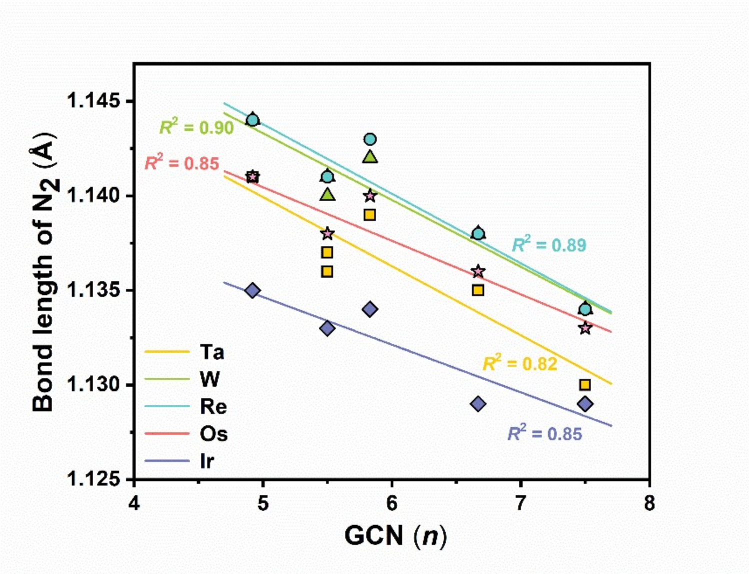

Fig. S3 The linear relation between the bond lengths of adsorbed N_2 and the generalized coordination number (GCN) of the relative catalytic sites.

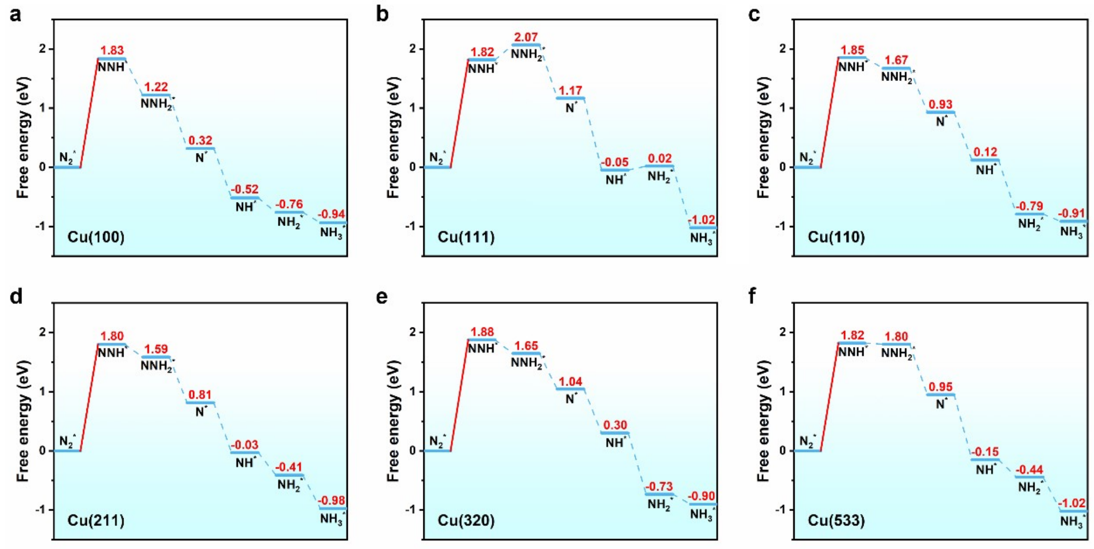

Fig. S4 Gibbs free energy diagrams for NRR on (a) Cu(100), (b) Cu(111), (c) Cu(110), (d) Cu(211), (e) Cu(320) and (f) Cu(553).

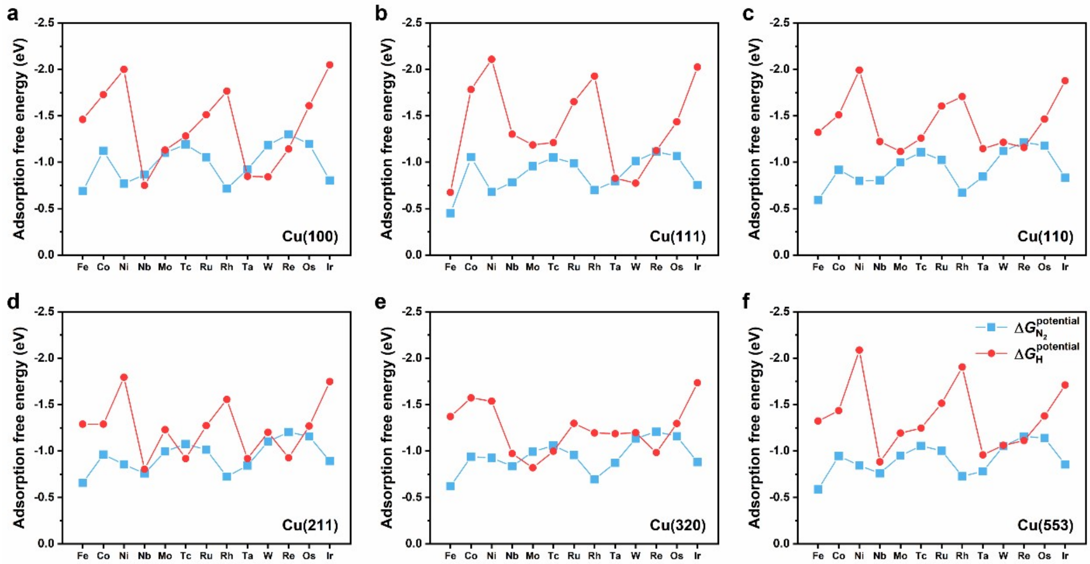

Fig. S5 Adsorption free energy values of N_2 (blue) and H^+ (red) under the limiting potential (U_L) on the Cu-based SAAs.

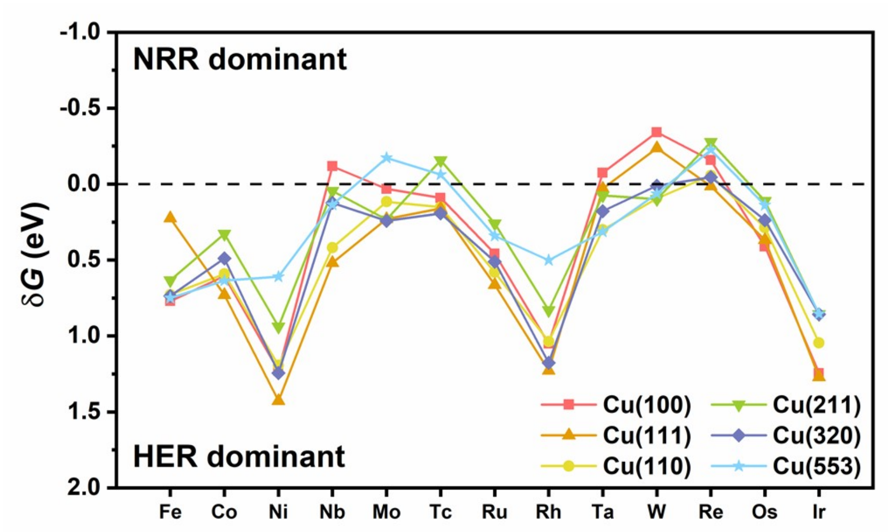

Fig. S6 Adsorption free energy difference (δG) values of N_2^* and H^* under the U_L on the Cu-based SAAs.

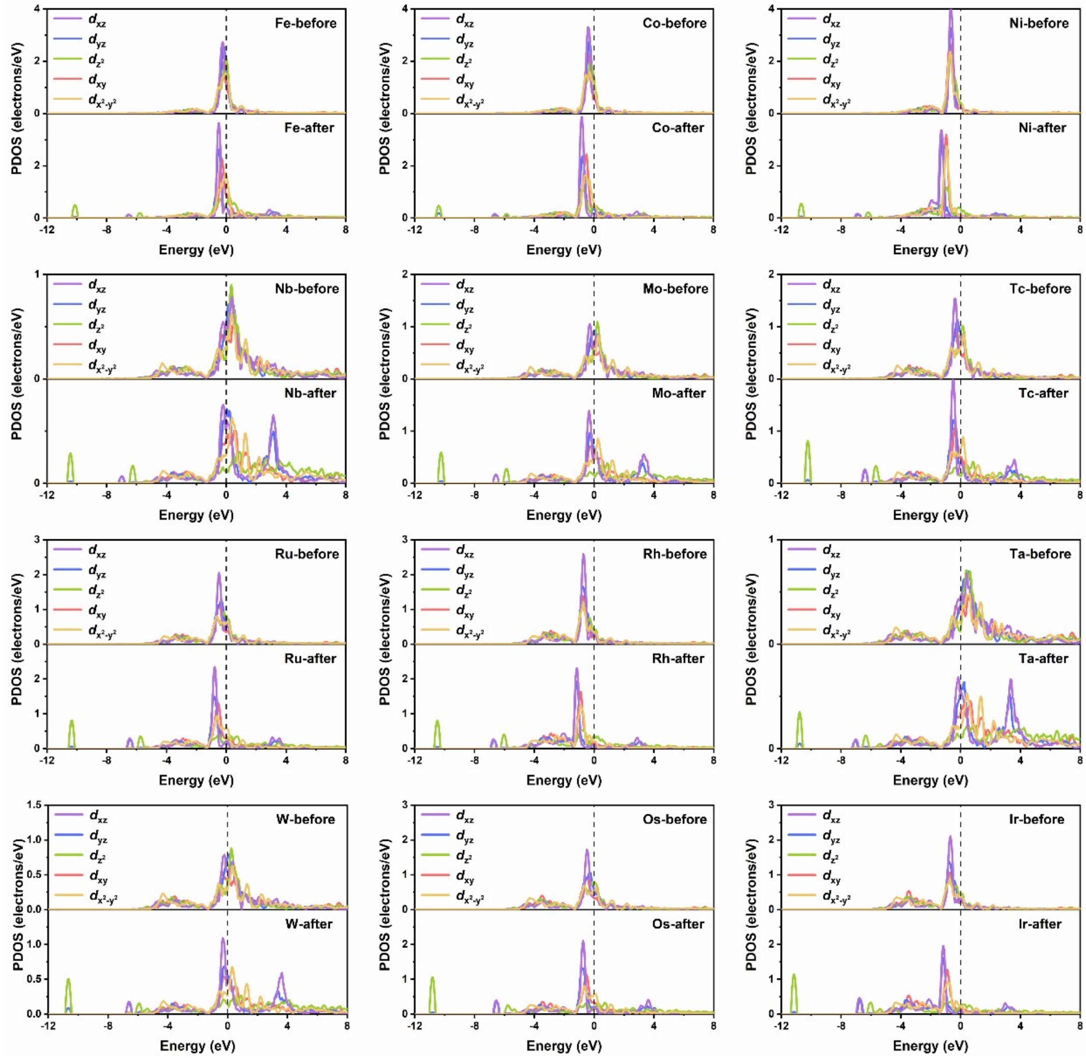

Fig. S7 The PDOS of TM-*d* orbitals in TM-Cu(553) before and after N_2 adsorption.

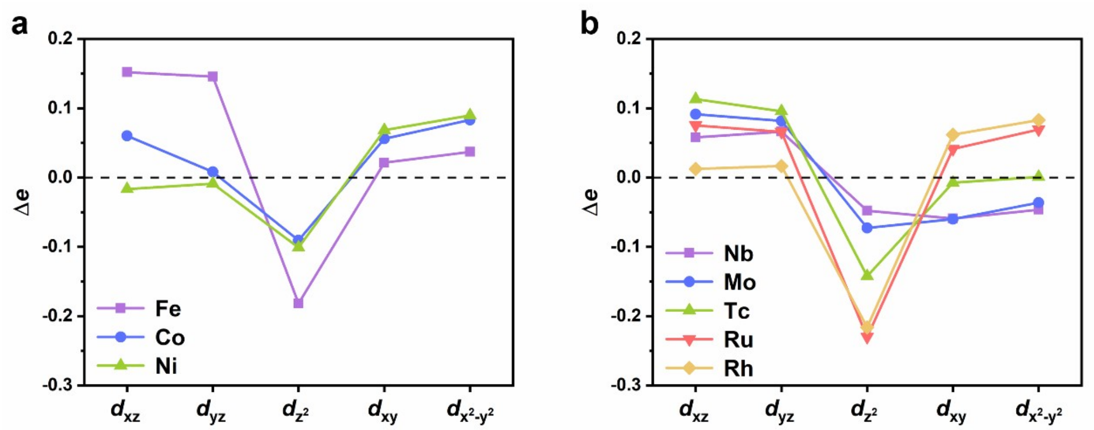

Fig. S8 The difference of the integral PDOS of *d* orbitals in the N_2 adsorption process.

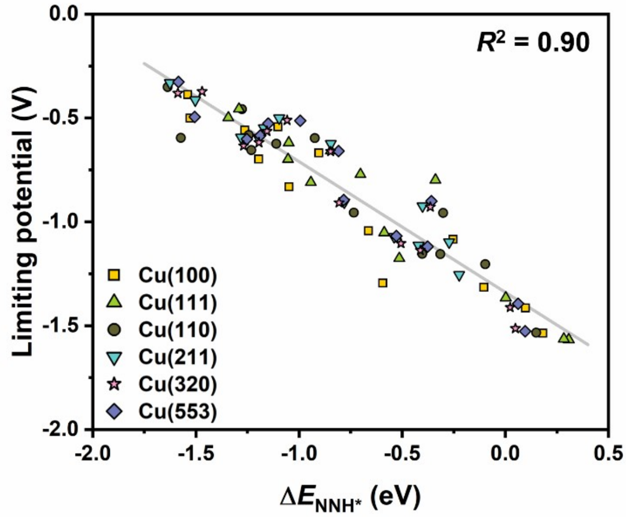

Fig. S9 The scaling relationship between the computed U_L and the adsorption energy of NNH^* species (ΔE_{NNH^*}).

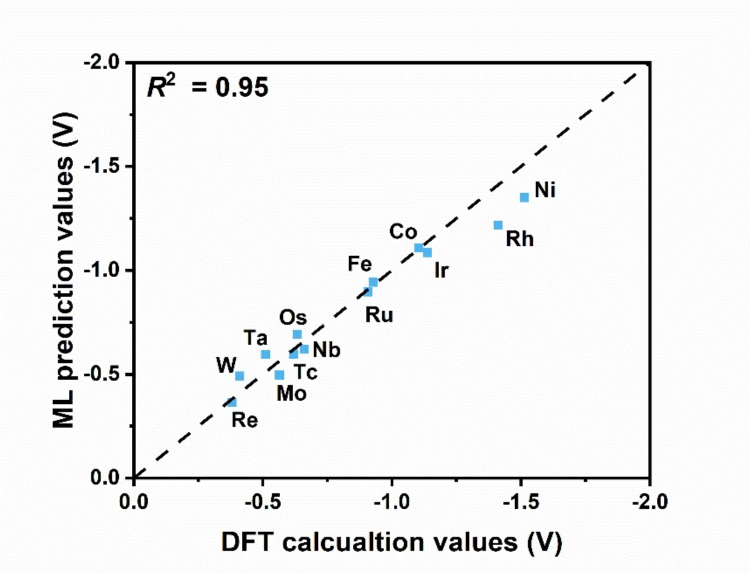

Fig. S10 Parity plot comparing DFT-calculated and ML-predicted values for U_L of the NRR on the TM-Cu(311) system.

Table S1 The reduction potential of the transition metals.

Element	**Reaction**	***E*⁰/V**
Fe	$Fe^{3+} + 3e^{-} \rightleftharpoons Fe$	–0.037
Co	$Co^{2+} + 2e^{-} \rightleftharpoons Co$	–0.280
Ni	$Ni^{2+} + 2e^{-} \rightleftharpoons Ni$	–0.257
Nb	$Nb^{3+} + 3e^{-} \rightleftharpoons Nb$	–1.099
Mo	$Mo^{3+} + 3e^{-} \rightleftharpoons Mo$	–0.200
Tc	$Ta^{2+} + 2e^{-} \rightleftharpoons Ta$	0.400
Ru	$Ru^{2+} + 2e^{-} \rightleftharpoons Ru$	0.455
Rh	$Rh^{3+} + 3e^{-} \rightleftharpoons Rh$	0.758
Ta	$Ta^{3+} + 3e^{-} \rightleftharpoons Ta$	–0.600
W	$W^{3+} + 3e^{-} \rightleftharpoons W$	0.100
Re	$Re^{3+} + 3e^{-} \rightleftharpoons Re$	0.300
Os	$OsO_4 + 8H^{+} + 8e^{-} \rightleftharpoons Os + 4H_2O$	0.838
Ir	$Ir^{3+} + 3e^{-} \rightleftharpoons Ir$	1.156

Table S2 The differences of ΔG_{N_2} values (ΔG_{N_2}(end-on) – ΔG_{N_2}(side-on)) of N_2 in end-on and side-on adsorption configurations.

Catalysts	Energy difference/eV	Catalysts	Energy difference/eV
Fe-Cu(100)	-0.52	Fe-Cu(111)	-0.95
Co-Cu(100)	-0.68	Co-Cu(111)	-0.92
Ni-Cu(100)	-0.82	Ni-Cu(111)	-0.75
Nb-Cu(100)	-0.40	Nb-Cu(111)	-0.59
Mo-Cu(100)	-0.54	Mo-Cu(111)	-0.74
Tc-Cu(100)	-0.71	Tc-Cu(111)	-0.84
Ru-Cu(100)	-0.80	Ru-Cu(111)	-0.83
Rh-Cu(100)	-0.69	Rh-Cu(111)	-0.66
Ta-Cu(100)	-0.41	Ta-Cu(111)	-0.65
W-Cu(100)	-0.57	W-Cu(111)	-0.84
Re-Cu(100)	-0.86	Re-Cu(111)	-1.00
Os-Cu(100)	-1.04	Os-Cu(111)	-1.05
Ir-Cu(100)	-1.00	Ir-Cu(111)	-0.88
Fe-Cu(110)	-0.41	Fe-Cu(211)	-0.43
Co-Cu(110)	-0.61	Co-Cu(211)	-0.64
Ni-Cu(110)	-0.59	Ni-Cu(211)	-0.63
Nb-Cu(110)	-0.32	Nb-Cu(211)	-0.25
Mo-Cu(110)	-0.40	Mo-Cu(211)	-0.39
Tc-Cu(110)	-0.54	Tc-Cu(211)	-0.54
Ru-Cu(110)	-0.61	Ru-Cu(211)	-0.62
Rh-Cu(110)	-0.53	Rh-Cu(211)	-0.57
Ta-Cu(110)	-0.30	Ta-Cu(211)	-0.28
W-Cu(110)	-0.37	W-Cu(211)	-0.37
Re-Cu(110)	-0.59	Re-Cu(211)	-0.61
Os-Cu(110)	-1.00	Os-Cu(211)	-0.81
Ir-Cu(110)	-0.78	Ir-Cu(211)	-0.81
Fe-Cu(320)	-0.40	Fe-Cu(553)	-0.38
Co-Cu(320)	-0.59	Co-Cu(553)	-0.63
Ni-Cu(320)	-0.61	Ni-Cu(553)	-0.62
Nb-Cu(320)	-0.30	Nb-Cu(553)	-0.29
Mo-Cu(320)	-0.36	Mo-Cu(553)	-0.40
Tc-Cu(320)	-0.51	Tc-Cu(553)	-0.56
Ru-Cu(320)	-0.61	Ru-Cu(553)	-0.63
Rh-Cu(320)	-0.54	Rh-Cu(553)	-0.54
Ta-Cu(320)	-0.12	Ta-Cu(553)	-0.26
W-Cu(320)	-0.34	W-Cu(553)	-0.32
Re-Cu(320)	-0.56	Re-Cu(553)	-0.59
Os-Cu(320)	-0.77	Os-Cu(553)	-0.80
Ir-Cu(320)	-0.78	Ir-Cu(553)	-0.73

Table S3 The calculated N≡N bond length and charge of N_2 on Cu-based SAAs.

Catalysts	Bond length/Å	Charge/|*e*|
Fe-Cu(100)	1.132	–0.092
Co-Cu(100)	1.134	–0.093
Ni-Cu(100)	1.128	–0.046
Nb-Cu(100)	1.133	–0.099
Mo-Cu(100)	1.134	–0.127
Tc-Cu(100)	1.134	–0.010
Ru-Cu(100)	1.132	–0.119
Rh-Cu(100)	1.127	–0.080
Ta-Cu(100)	1.135	–0.081
W-Cu(100)	1.138	–0.115
Re-Cu(100)	1.138	–0.123
Os-Cu(100)	1.136	–0.105
Ir-Cu(100)	1.129	–0.066
Fe-Cu(111)	1.133	–0.099
Co-Cu(111)	1.131	–0.074
Ni-Cu(111)	1.126	–0.024
Nb-Cu(111)	1.126	–0.056
Mo-Cu(111)	1.130	–0.093
Tc-Cu(111)	1.131	–0.074
Ru-Cu(111)	1.129	–0.098
Rh-Cu(111)	1.125	–0.060
Ta-Cu(111)	1.130	–0.042
W-Cu(111)	1.134	–0.077
Re-Cu(111)	1.134	–0.093
Os-Cu(111)	1.133	–0.085
Ir-Cu(111)	1.129	–0.048
Fe-Cu(110)	1.132	–0.079
Co-Cu(110)	1.133	–0.083
Ni-Cu(110)	1.127	–0.044
Nb-Cu(110)	1.134	–0.099
Mo-Cu(110)	1.138	–0.130
Tc-Cu(110)	1.137	–0.103
Ru-Cu(110)	1.135	–0.128
Rh-Cu(110)	1.128	–0.086
Ta-Cu(110)	1.139	–0.084
W-Cu(110)	1.142	–0.116
Re-Cu(110)	1.143	–0.130
Os-Cu(110)	1.140	–0.118
Ir-Cu(110)	1.134	–0.080
Fe-Cu(211)	1.132	–0.080
Co-Cu(211)	1.134	–0.084
Ni-Cu(211)	1.128	–0.041
Nb-Cu(211)	1.132	–0.081

Mo-Cu(211)	1.135	–0.118
Tc-Cu(211)	1.134	–0.086
Ru-Cu(211)	1.132	–0.114
Rh-Cu(211)	1.127	–0.079
Ta-Cu(211)	1.137	–0.075
W-Cu(211)	1.141	–0.105
Re-Cu(211)	1.141	–0.113
Os-Cu(211)	1.138	–0.105
Ir-Cu(211)	1.133	–0.071
Fe-Cu(320)	1.131	–0.076
Co-Cu(320)	1.132	–0.080
Ni-Cu(320)	1.128	–0.049
Nb-Cu(320)	1.134	–0.117
Mo-Cu(320)	1.137	–0.139
Tc-Cu(320)	1.137	–0.101
Ru-Cu(320)	1.135	–0.126
Rh-Cu(320)	1.128	–0.090
Ta-Cu(320)	1.141	–0.102
W-Cu(320)	1.144	–0.127
Re-Cu(320)	1.144	–0.130
Os-Cu(320)	1.141	–0.117
Ir-Cu(320)	1.135	–0.085
Fe-Cu(553)	1.132	–0.067
Co-Cu(553)	1.132	–0.074
Ni-Cu(553)	1.127	–0.031
Nb-Cu(553)	1.133	–0.079
Mo-Cu(553)	1.135	–0.105
Tc-Cu(553)	1.135	–0.080
Ru-Cu(553)	1.134	–0.111
Rh-Cu(553)	1.126	–0.070
Ta-Cu(553)	1.136	–0.059
W-Cu(553)	1.140	–0.092
Re-Cu(553)	1.141	–0.107
Os-Cu(553)	1.138	–0.098
Ir-Cu(553)	1.133	–0.064

Table S4 The calculated ΔG_{PDS} of the NRR on Cu-based SAAs.

Catalysts	**PDS**	**ΔG_{PDS}/eV**
Fe-Cu(100)	$N_2^* \rightarrow NNH^*$ (R1)	1.08
Co-Cu(100)	$N_2^* \rightarrow NNH^*$ (R1)	1.30
Ni-Cu(100)	$N_2^* \rightarrow NNH^*$ (R1)	1.54
Nb-Cu(100)	$N_2^* \rightarrow NNH^*$ (R1)	0.67
Mo-Cu(100)	$N_2^* \rightarrow NNH^*$ (R1)	0.56
Tc-Cu(100)	$N_2^* \rightarrow NNH^*$ (R1)	0.70
Ru-Cu(100)	$N_2^* \rightarrow NNH^*$ (R1)	1.04
Rh-Cu(100)	$N_2^* \rightarrow NNH^*$ (R1)	1.42
Ta-Cu(100)	$N_2^* \rightarrow NNH^*$ (R1)	0.54
W-Cu(100)	$N_2^* \rightarrow NNH^*$ (R1)	0.39
Re-Cu(100)	$N_2^* \rightarrow NNH^*$ (R1)	0.50
Os-Cu(100)	$N_2^* \rightarrow NNH^*$ (R1)	0.83
Ir-Cu(100)	$N_2^* \rightarrow NNH^*$ (R1)	1.32
Fe-Cu(111)	$N_2^* \rightarrow NNH^*$ (R1)	0.80
Co-Cu(111)	$N_2^* \rightarrow NNH^*$ (R1)	1.18
Ni-Cu(111)	$N_2^* \rightarrow NNH^*$ (R1)	1.57
Nb-Cu(111)	$N_2^* \rightarrow NNH^*$ (R1)	0.77
Mo-Cu(111)	$N_2^* \rightarrow NNH^*$ (R1)	0.62
Tc-Cu(111)	$N_2^* \rightarrow NNH^*$ (R1)	0.70
Ru-Cu(111)	$N_2^* \rightarrow NNH^*$ (R1)	1.05
Rh-Cu(111)	$N_2^* \rightarrow NNH^*$ (R1)	1.56
Ta-Cu(111)	$N_2^* \rightarrow NNH^*$ (R1)	0.66
W-Cu(111)	$N_2^* \rightarrow NNH^*$ (R1)	0.46
Re-Cu(111)	$N_2^* \rightarrow NNH^*$ (R1)	0.50
Os-Cu(111)	$N_2^* \rightarrow NNH^*$ (R1)	0.81
Ir-Cu(111)	$N_2^* \rightarrow NNH^*$ (R1)	1.37
Fe-Cu(110)	$N_2^* \rightarrow NNH^*$ (R1)	0.96
Co-Cu(110)	$N_2^* \rightarrow NNH^*$ (R1)	1.15
Ni-Cu(110)	$N_2^* \rightarrow NNH^*$ (R1)	1.53
Nb-Cu(110)	$N_2^* \rightarrow NNH^*$ (R1)	0.60
Mo-Cu(110)	$N_2^* \rightarrow NNH^*$ (R1)	0.46
Tc-Cu(110)	$N_2^* \rightarrow NNH^*$ (R1)	0.58
Ru-Cu(110)	$N_2^* \rightarrow NNH^*$ (R1)	0.96
Rh-Cu(110)	$N_2^* \rightarrow NNH^*$ (R1)	1.20
Ta-Cu(110)	$NH_2^* \rightarrow NH_3^*$ (R6)	0.62
W-Cu(110)	$NH_2^* \rightarrow NH_3^*$ (R6)	0.60
Re-Cu(110)	$NH_2^* \rightarrow NH_3^*$ (R6)	0.35
Os-Cu(110)	$N_2^* \rightarrow NNH^*$ (R1)	0.65
Ir-Cu(110)	$N_2^* \rightarrow NNH^*$ (R1)	1.16
Fe-Cu(211)	$N_2^* \rightarrow NNH^*$ (R1)	0.92
Co-Cu(211)	$N_2^* \rightarrow NNH^*$ (R1)	1.07
Ni-Cu(211)	$N_2^* \rightarrow NNH^*$ (R1)	1.26
Nb-Cu(211)	$N_2^* \rightarrow NNH^*$ (R1)	0.62

Mo-Cu(211)	$N_2^* \rightarrow NNH^*$ (R1)	0.55
Tc-Cu(211)	$N_2^* \rightarrow NNH^*$ (R1)	0.59
Ru-Cu(211)	$N_2^* \rightarrow NNH^*$ (R1)	0.91
Rh-Cu(211)	$N_2^* \rightarrow NNH^*$ (R1)	1.10
Ta-Cu(211)	$NH_2^* \rightarrow NH_3^*$ (R6)	0.50
W-Cu(211)	$NH_2^* \rightarrow NH_3^*$ (R6)	0.41
Re-Cu(211)	$N_2^* \rightarrow NNH^*$ (R1)	0.33
Os-Cu(211)	$N_2^* \rightarrow NNH^*$ (R1)	0.59
Ir-Cu(211)	$N_2^* \rightarrow NNH^*$ (R1)	1.11
Fe-Cu(320)	$N_2^* \rightarrow NNH^*$ (R1)	0.99
Co-Cu(320)	$N_2^* \rightarrow NNH^*$ (R1)	1.12
Ni-Cu(320)	$N_2^* \rightarrow NNH^*$ (R1)	1.51
Nb-Cu(320)	$N_2^* \rightarrow NNH^*$ (R1)	0.68
Mo-Cu(320)	$N_2^* \rightarrow NNH^*$ (R1)	0.54
Tc-Cu(320)	$N_2^* \rightarrow NNH^*$ (R1)	0.62
Ru-Cu(320)	$N_2^* \rightarrow NNH^*$ (R1)	0.90
Rh-Cu(320)	$N_2^* \rightarrow NNH^*$ (R1)	1.14
Ta-Cu(320)	$N_2^* \rightarrow NNH^*$ (R1)	0.61
W-Cu(320)	$NH_2^* \rightarrow NH_3^*$ (R6)	0.57
Re-Cu(320)	$N_2^* \rightarrow NNH^*$ (R1)	0.34
Os-Cu(320)	$N_2^* \rightarrow NNH^*$ (R1)	0.60
Ir-Cu(320)	$N_2^* \rightarrow NNH^*$ (R1)	1.10
Fe-Cu(553)	$N_2^* \rightarrow NNH^*$ (R1)	0.90
Co-Cu(553)	$N_2^* \rightarrow NNH^*$ (R1)	1.07
Ni-Cu(553)	$N_2^* \rightarrow NNH^*$ (R1)	1.53
Nb-Cu(553)	$N_2^* \rightarrow NNH^*$ (R1)	0.66
Mo-Cu(553)	$N_2^* \rightarrow NNH^*$ (R1)	0.53
Tc-Cu(553)	$N_2^* \rightarrow NNH^*$ (R1)	0.58
Ru-Cu(553)	$N_2^* \rightarrow NNH^*$ (R1)	0.89
Rh-Cu(553)	$N_2^* \rightarrow NNH^*$ (R1)	1.39
Ta-Cu(553)	$N_2^* \rightarrow NNH^*$ (R1)	0.51
W-Cu(553)	$NH_2^* \rightarrow NH_3^*$ (R6)	0.50
Re-Cu(553)	$N_2^* \rightarrow NNH^*$ (R1)	0.33
Os-Cu(553)	$N_2^* \rightarrow NNH^*$ (R1)	0.60
Ir-Cu(553)	$N_2^* \rightarrow NNH^*$ (R1)	1.12