Electronic Supplementary Information

Electroreduction of N_2 to NH_3 Catalyzed by Mn/Re(111) Single-Atom Alloy Catalyst with High Activity and Selectivity: A New Insight from the First-Principal Study

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Table S1. Calculated binding energies (E_b) and cohesive energies (E_c) for all SAA

catalysts. The difference between binding energies and cohesive energies ($E_b - E_c$) for

all SAA catalysts.

Metal	E_b (eV)	E_c (eV)	$E_b - E_c$ (eV)
Cr	−7.42	−5.02	−2.39
Mn	−5.80	−3.78	−2.02
Fe	−7.28	−4.88	−2.39
Co	−7.26	−5.11	−2.15
Ni	−7.45	−5.10	−2.35
Cu	−5.68	−3.50	−2.18
Mo	−8.74	−5.87	−2.87
Tc	−9.47	−6.95	−2.52
Ru	−10.45	−7.91	−2.54
Rh	−8.85	−6.04	−2.81
Pd	−6.52	−3.76	−2.76
Ag	−4.57	−2.51	−2.06
W	−11.22	−8.40	−2.82
Os	−10.73	−8.19	−2.54
Ir	−10.30	−7.32	−2.98
Pt	−8.87	−5.57	−3.31
Au	−5.85	−3.00	−2.85

Table S2. Bader charge transfer from the support to the TM atoms when different TM atoms are anchored to the defective Re(111) surface. A negative value represents the transfer of Bader charge from the TM atom to the support and a positive value represents the transfer of Bader charge from the support to the TM atom.

Metal	Charge transfer (e⁻)
Cr	–0.62
Mn	–0.29
Fe	–0.25
Co	0.04
Ni	0.10
Cu	0.03
Mo	–0.47
Tc	–0.06
Ru	0.23
Rh	0.40
Pd	0.38
Ag	0.19
W	–0.45
Os	0.41
Ir	0.65
Pt	0.70
Au	0.56

Table S3. Summary of adsorption energies of *N_2, adsorption free energies of *N_2, and the N-N bond lengths of *N_2.

Metal	End-on			Side-on		
	E_{ad} (eV)	G_{ad} (eV)	N-N bond length (Å)	E_{ad} (eV)	G_{ad} (eV)	N-N bond length (Å)
Cr	–0.59	0.04	1.130	–0.55	0.04	1.317
Mn	–0.80	–0.23	1.130	–0.56	–0.01	1.288
Fe	–0.33	0.25	1.133	0.00	0.55	1.272
Co	–0.59	–0.01	1.134	×	×	×
Ni	–0.25	0.34	1.129	×	×	×
Cu	0.00	0.53	1.114	×	×	×
Mo	–0.58	0.01	1.128	–0.34	0.24	1.310
Tc	–0.58	–0.04	1.130	–0.19	0.38	1.304
Ru	–0.56	–0.01	1.131	0.10	0.65	1.262
Rh	–0.45	0.10	1.129	–0.22	0.32	1.261
Pd	0.05	0.63	1.122	×	×	×
Ag	–0.01	0.50	1.114	×	×	×
W	–0.62	–0.05	1.130	–0.33	0.25	1.326
Os	–0.53	0.03	1.133	0.19	0.75	1.290
Ir	–0.41	0.18	1.132	0.55	1.07	1.237
Pt	0.09	0.63	1.126	×	×	×
Au	–0.01	0.52	1.114	×	×	×

Table S4. Free energy changes of six PCET processes on seven highly reactive SAA catalysts (Distal mechanism).

	$*N_2\rightarrow$ $*NNH$ (eV)	$*NNH\rightarrow$ $*NNH_2$ (eV)	$*NNH_2$ $\rightarrow*N$ (eV)	$*N\rightarrow$ $*NH$ (eV)	$*NH\rightarrow$ $*NH_2$ (eV)	$*NH_2\rightarrow$ $*NH_3$ (eV)
Cr	0.91	–0.26	–0.26	–0.79	–0.20	–0.45
Mn	0.91	0.05	–0.53	–0.35	–0.18	–0.53
Fe	0.87	0.42	–0.59	–0.14	–0.84	–0.72
Tc	0.85	–0.07	–0.65	–0.36	–0.15	–0.58
Ru	1.00	0.28	–0.73	0.01	–0.62	–0.85
W	0.90	–0.35	0.05	–1.32	–0.23	–0.25
Os	0.86	0.21	–0.88	0.02	–0.49	–0.68

Table S5. Free energy changes of six PCET processes on seven highly reactive SAA catalysts (Alternating mechanism).

	$*N_2\rightarrow$ $*NNH$ (eV)	$*NNH\rightarrow$ $*NHNH$ (eV)	$*NHNH\rightarrow$ $*NHNH_2$ (eV)	$*NHNH_2\rightarrow$ $*NH_2NH_2$ (eV)	$*NHNH2$ $\rightarrow*NH_2$ (eV)	$*NH_2\rightarrow$ $*NH_3$ (eV)
Cr	0.91	0.41	–0.42	–0.11	–1.40	–0.45
Mn	0.91	0.50	–0.09	0.03	–1.46	–0.53
Fe	0.87	0.53	–0.17	–0.34	–1.16	–0.72
Tc	0.85	0.57	–0.34	–0.17	–1.29	–0.58
Ru	1.00	0.45	–0.19	–0.29	–1.03	–0.85
W	0.90	0.38	–0.52	–0.03	–1.67	–0.25
Os	0.86	0.49	–0.24	–0.23	–1.17	–0.68

Table S6. Free energy changes of the second *NH$_3$ desorption from the catalysts.

Metal	ΔG (eV)
Cr	0.32
Mn	0.15
Fe	0.04
Co	0.06
Ni	–0.06
Cu	–0.33
Mo	0.41
Tc	0.30
Ru	0.22
Rh	0.18
Pd	–0.08
Ag	–0.30
W	0.54
Os	0.23
Ir	0.12
Pt	–0.10
Au	–0.46

Table S7. Bader charge transfer from the catalysts to the N_2 when they are adsorbed to the SAA catalysts.

Metal	Charge transfer (e^-)
Cr	0.27
Mn	0.27
Fe	0.28
Co	0.30
Ni	0.23
Cu	0.01
Mo	0.26
Tc	0.28
Ru	0.25
Rh	0.20
Pd	0.12
Ag	0.01
W	0.27
Os	0.26
Ir	0.23
Pt	0.14
Au	0.01
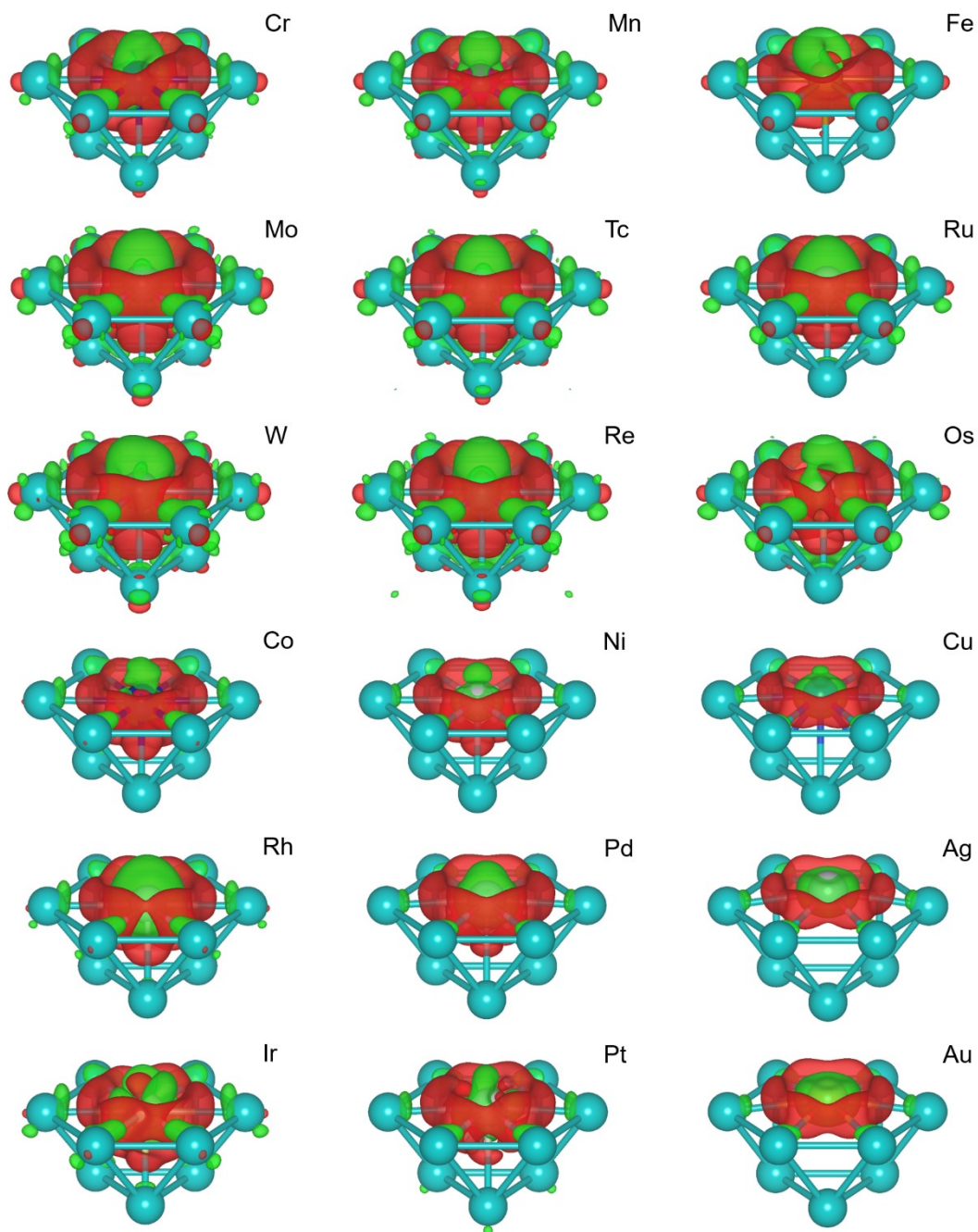
Figure S1. The charge density difference of different TM atoms anchored to the defective Re(111). Red and green isosurfaces represent charge accumulation and depletion in the space. The isosurface value was set to be 0.005 e·Å^{-3}.
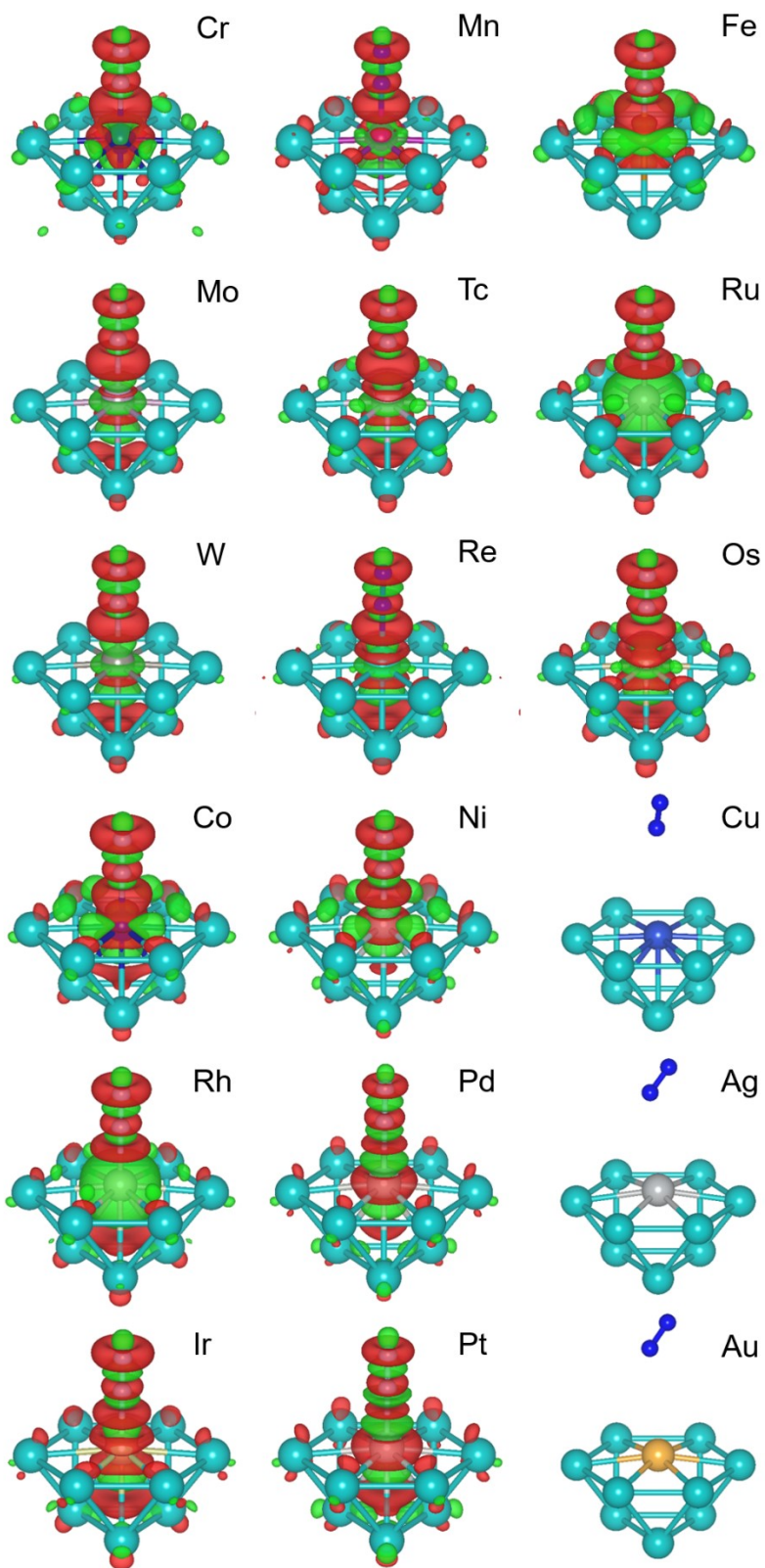
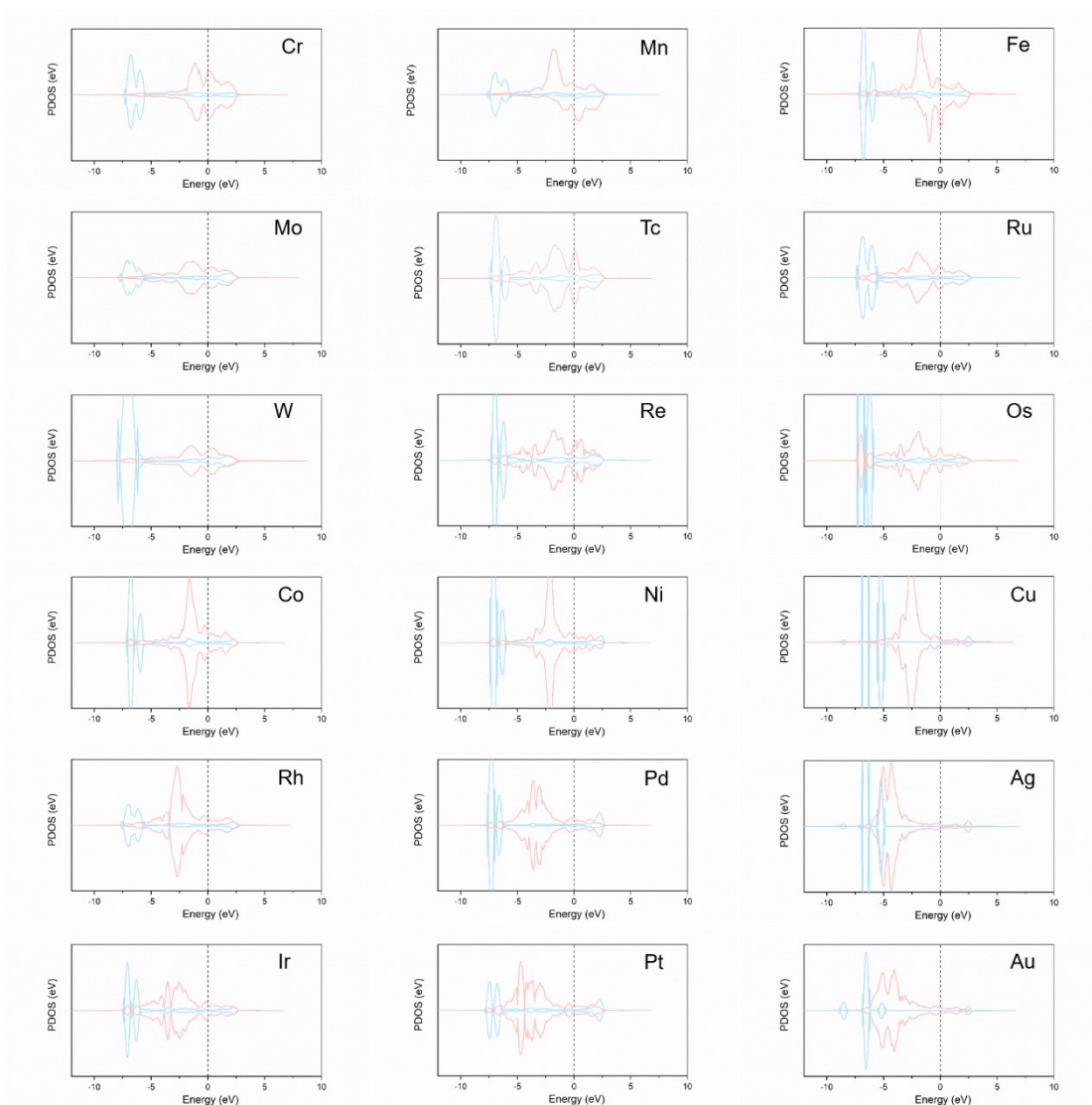**Figure S2.** The charge density difference of N_2 adsorbed to the 18 catalysts in the end-on configuration. Red and green isosurfaces represent charge accumulation and depletion in the space. The isosurface value was set to be 0.0015 $e \cdot Å^{-3}$.

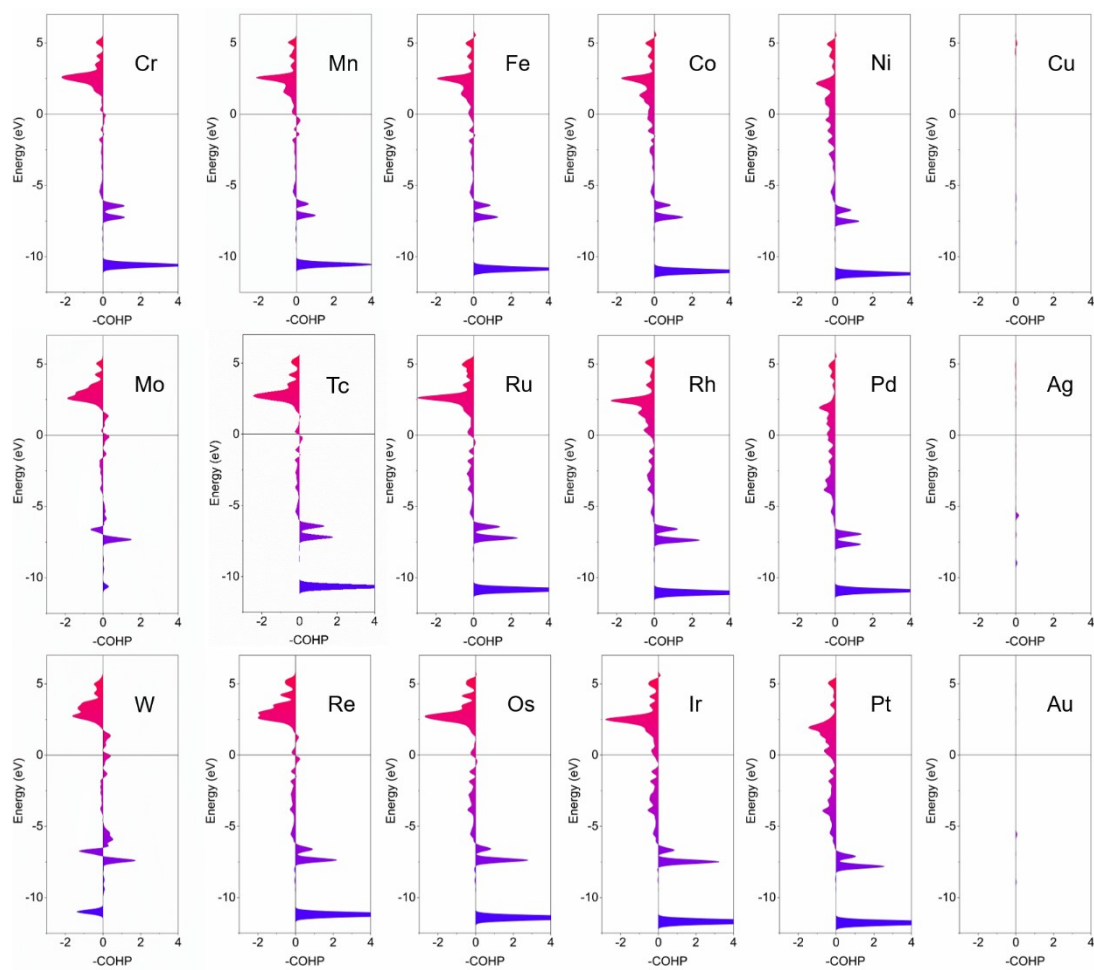**Figure S3.** The partial density of states (PDOS) of various TM atom (d orbital) and N_2 molecule.

Figure S4. The projected crystal orbital Hamilton population (pCOHP) between TM-N on the SAA catalysts. The dashed lines indicate the Fermi level (E_F).
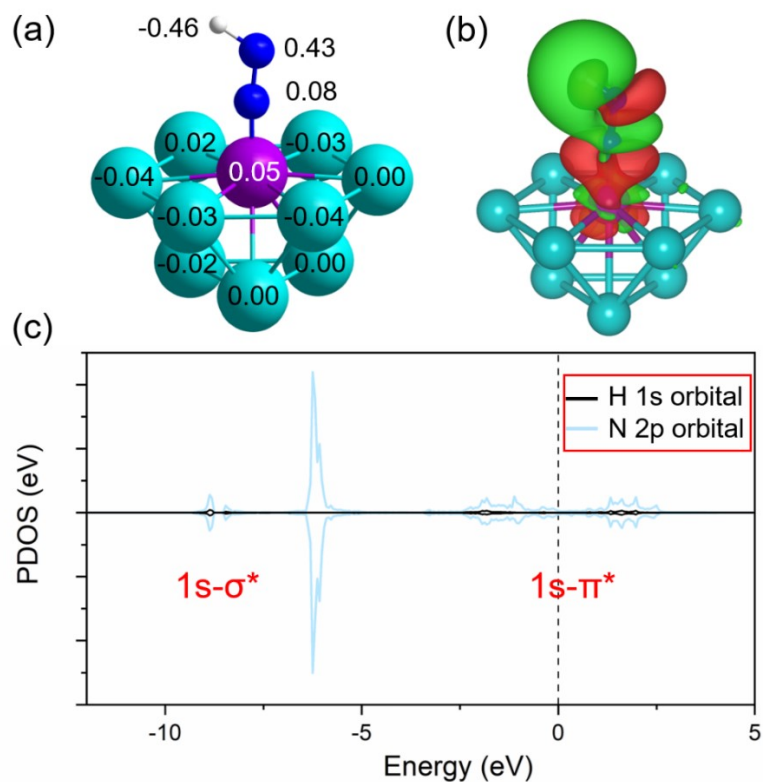
Figure S5. (a) Bader charge transfer in the *NNH intermediate. (b) The charge density difference of H adsorbed to the $*N_2$ intermediate. Red and green isosurfaces represent charge accumulation and depletion in the space. The isosurface value was set to be 0.0015 e·Å^{-3}. (c) The partial density of states (PDOS) of the H atom (1s orbital) and N atoms (2p orbital) in the *NNH intermediate.