Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electrocatalytic nitrogen reduction on the transition-metal dimer anchored N-doped graphene: performance prediction and synergetic effect

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Supporting Information

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Table S1. The calculated zero-point energy (E_{ZPE} in eV) and the product (TS in eV) of the temperature (298.15 K) and entropy for the adsorbed H, N_2, NNH, NH_2, and NH_3, displayed outside and inside the parentheses, respectively.

M1M2	*H	*N_2	*NNH	*NH_2	*NH_3
V_2	0.19 (0.01)	0.21 (0.08)	0.50 (0.09)	0.70 (0.07)	1.02 (0.16)
Cr_2	0.20 (0.01)	0.20 (0.11)	0.49 (0.12)	0.71 (0.07)	1.03 (0.14)
Mn_2	0.21 (0.01)	0.21 (0.14)	0.50 (0.07)	0.71 (0.07)	1.02 (0.17)
Fe_2	0.32 (0.00)	0.20 (0.16)	0.52 (0.11)	0.73 (0.06)	1.02 (0.17)
Co_2	0.22 (0.00)	0.22 (0.11)	0.53 (0.10)	0.75 (0.05)	1.01 (0.19)
Ni_2	0.23 (0.00)	0.19 (0.18)	0.41 (0.14)	0.75 (0.05)	1.00 (0.22)
Cu_2	0.22 (0.00)	0.19 (0.19)	0.48 (0.15)	0.71 (0.07)	1.00 (0.21)
VCr	0.19 (0.01)	0.19 (0.11)	0.48 (0.12)	0.70 (0.08)	1.02 (0.18)
VMn	0.21 (0.01)	0.19 (0.10)	0.49 (0.11)	0.70 (0.07)	1.02 (0.17)
VFe	0.25 (0.01)	0.19 (0.20)	0.51 (0.12)	0.72 (0.06)	1.02 (0.17)
VCo	0.22 (0.00)	0.21 (0.15)	0.50 (0.13)	0.72 (0.06)	1.03 (0.15)
VNi	0.21 (0.00)	0.19 (0.19)	0.46 (0.11)	0.67 (0.12)	1.02 (0.16)
VCu	0.19 (0.01)	0.19 (0.11)	0.44 (0.14)	0.65 (0.13)	1.03 (0.15)
CrMn	0.20 (0.01)	0.21 (0.11)	0.50 (0.11)	0.71 (0.07)	1.03 (0.15)
CrFe	0.24 (0.01)	0.22 (0.09)	0.50 (0.12)	0.72 (0.06)	1.01 (0.19)
CrCo	0.22 (0.00)	0.22 (0.14)	0.51 (0.12)	0.73 (0.05)	1.01 (0.18)
CrNi	0.22 (0.00)	0.20 (0.15)	0.48 (0.14)	0.71 (0.07)	1.02 (0.16)
CrCu	0.19 (0.01)	0.19 (0.19)	0.48 (0.17)	0.70 (0.08)	1.02 (0.16)
MnFe	0.24 (0.01)	0.22 (0.09)	0.48 (0.18)	0.72 (0.06)	1.02 (0.17)
MnCo	0.22 (0.01)	0.21 (0.16)	0.51 (0.11)	0.72 (0.06)	1.01 (0.18)
MnNi	0.20 (0.01)	0.18 (0.22)	0.49 (0.14)	0.69 (0.08)	1.01 (0.18)
MnCu	0.19 (0.01)	0.20 (0.16)	0.48 (0.17)	0.68 (0.08)	1.02 (0.16)
FeCo	0.25 (0.00)	0.20 (0.17)	0.52 (0.11)	0.74 (0.05)	1.01 (0.18)
FeNi	0.26 (0.00)	0.20 (0.17)	0.51 (0.13)	0.74 (0.05)	1.01 (0.17)
FeCu	0.23 (0.01)	0.21 (0.16)	0.48 (0.05)	0.64 (0.14)	1.02 (0.17)
CoNi	0.23 (0.00)	0.21 (0.15)	0.49 (0.14)	0.73 (0.05)	1.02 (0.18)
CoCu	0.19 (0.02)	0.21 (0.16)	0.47 (0.11)	0.71 (0.07)	1.02 (0.16)
NiCu	0.22 (0.00)	0.20 (0.19)	0.48 (0.16)	0.73 (0.06)	1.00 (0.19)

Table S2. The calculated zero-point energy (E_{ZPE} in eV) and the product (TS in eV) of the temperature (298.15 K) and entropy for the various species along the reaction pathways.

	E_{ZPE}	TS
*NH-NH	0.84	0.13
*NH-NH_2	1.18	0.14
*NH_2-NH_2	1.49	0.25
*NH_2-NH_3	1.70	0.24
*N-NH_2	0.84	0.13
*N-NH_3	1.05	0.30
*N	0.09	0.04
*NH	0.36	0.07
*N*NH	0.44	0.12
*NH-*NH	0.85	0.10
*NH*NH	0.73	0.13
NH-NH_2	1.16	0.14
NHNH_2	1.07	0.14
*NH_2*NH_2	1.38	0.17
*NH_2*NH_3	1.73	0.21
N-NH_2	0.86	0.09
NNH_2	0.78	0.13
NNH_3	1.12	0.18

Table S3. The calculated parameters for the free-standing M1M2@NG catalysts. The shortest distances between the anchored TM atoms and its neighboring N atoms ($d_{\mathrm{M1\text{-}N}}$ or $d_{\mathrm{M2\text{-}N}}$ in Å), the sum of the covalent radii of the TM and N atoms ($r_{\mathrm{M1\text{-}N}}$ or $r_{\mathrm{M2\text{-}N}}$ in Å), the bond length between M1 and M2 atoms and their covalent radii sum ($d_{\mathrm{M1\text{-}M2}}$ and $r_{\mathrm{M1\text{-}M2}}$, respectively, in Å), the number of the electron (Q in e) transferred from the anchored TM dimers to the N-doped graphene support, the spin magnetic moment for the M1 and M2 atoms (M in μ_{B}).

M1M2	$d_{\mathrm{M1\text{-}N}}$	$r_{\mathrm{M1\text{-}N}}$	$d_{\mathrm{M2\text{-}N}}$	$r_{\mathrm{M2\text{-}N}}$	$d_{\mathrm{M1\text{-}M2}}$	$r_{\mathrm{M1\text{-}M2}}$	Q	M
V_2	1.92	2.24	1.93	2.24	2.42	3.06	-2.13	3.04, 3.04
Cr_2	1.95	2.10	1.95	2.10	2.57	2.78	-2.00	4.17, 4.17
Mn_2	1.95	2.10	1.95	2.10	2.44	2.78	-1.94	3.41, 3.59
Fe_2	1.91	2.03	1.91	2.03	2.22	2.64	-1.67	2.34, 2.34
Co_2	1.88	1.97	1.88	1.97	2.25	2.52	-1.39	1.24, 1.24
Ni_2	1.87	1.95	1.87	1.95	2.37	2.48	-1.21	0.00, 0.00
Cu_2	1.92	2.03	1.92	2.03	2.40	2.64	-1.41	0.25, 0.25
VCr	1.95	2.24	1.94	2.10	2.63	2.92	-2.18	3.00, 3.96
VMn	1.96	2.24	1.95	2.10	2.57	2.92	-2.09	2.55, 3.55
VFe	1.98	2.24	1.94	2.03	1.96	2.85	-1.76	1.07, 0.00
VCo	1.97	2.24	1.88	1.97	2.07	2.79	-1.71	1.56, 0.00
VNi	1.93	2.24	1.86	1.95	2.22	2.77	-1.70	2.19, -0.25
VCu	1.95	2.24	1.91	2.03	2.46	2.85	-1.79	2.73, 0.00
CrMn	1.94	2.10	1.90	2.10	2.55	2.78	-2.08	3.98, 3.97
CrFe	1.90	2.10	1.94	2.03	2.20	2.71	-1.87	2.49, 0.00
CrCo	1.93	2.10	1.86	1.97	2.24	2.65	-1.71	2.92, -0.41
CrNi	1.95	2.10	1.89	1.95	2.36	2.63	-1.63	3.45, -0.31
CrCu	1.94	2.10	1.91	2.03	2.43	2.71	-1.74	3.78, 0.00
MnFe	1.95	2.10	1.90	2.03	2.31	2.71	-1.80	3.11, -0.17
MnCo	1.93	2.10	1.88	1.97	2.30	2.65	-1.64	3.60, -0.54
MnNi	1.92	2.10	1.89	1.95	2.29	2.63	-1.61	3.71, 0.03
MnCu	1.90	2.10	1.90	2.03	2.43	2.71	-1.79	3.34, 0.00
FeCo	1.90	2.03	1.90	1.97	2.18	2.58	-1.52	2.49, 1.06
FeNi	1.91	2.03	1.89	1.95	2.31	2.56	-1.50	2.59, 0.12
FeCu	1.88	2.03	1.89	2.03	2.43	2.64	-1.58	2.07, 0.00
CoNi	1.88	1.97	1.86	1.95	2.33	2.50	-1.28	1.20, 0.03
CoCu	1.85	1.97	1.88	2.03	2.43	2.58	-1.35	0.28, 0.00
NiCu	1.87	1.95	1.89	2.03	2.41	2.56	-1.37	0.11, 0.00

Table S4. The definition of the binding energy ($E_b = E_{DAC} - E_{M1} - E_{M2} - E_{NPG}$) means that the binding process is a two-step process. We assume that A atom (M1/M2) is firstly embedded into the N-doped porous graphene, and then B atom (M2/M1) is embedded into the N-doped porous graphene with the A atom to form the DACs. The binding energy for the A atom (the first step) is $E_b(A) = E_{NPG+A} - E_A - E_{NPG}$, where E_{NPG+A} and E_A are the total energies of the N-doped porous graphene with the A atom and the isolated A atom, respectively. The binding energy for the B atom (the second step) is $E_b(B) = E_{DAC} - E_B - E_{NPG+A}$. Obviously, $E_b(A) + E_b(B) = E_{DAC} - E_A - E_B - E_{NPG} = E_b$. $E_b(A)$, $E_b(B)$, and E_b are in eV.

	V_2	**Cr_2**	**Mn_2**	**Fe_2**	**Co_2**	**Ni_2**	**Cu_2**
$E_b(A)$	-7.79	-6.69	-6.25	-6.65	-6.79	-6.58	-5.02
$E_b(B)$	-5.04	-3.43	-3.67	-5.55	-5.91	-6.26	-4.41
E_b	-12.83	-10.12	-9.92	-12.20	-12.70	-12.84	-9.43
	VCr	**VMn**	**VFe**	**VCo**	**VNi**	**VCu**	**CrMn**
$E_b(A)$	-7.79	-7.79	-7.79	-7.79	-7.79	-7.79	-6.69
$E_b(B)$	-3.67	-3.43	-5.31	-5.51	-5.34	-3.50	-3.29
E_b	-11.46	-11.22	-13.10	-13.30	-13.13	-11.29	-9.98
	CrFe	**CrCo**	**CrNi**	**CrCu**	**MnFe**	**MnCo**	**MnNi**
$E_b(A)$	-6.69	-6.79	-6.69	-6.69	-6.65	-6.79	-6.58
$E_b(B)$	-4.76	-4.87	-4.97	-3.65	-4.60	-4.79	-5.31
E_b	-11.45	-11.66	-11.66	-10.34	-11.25	-11.58	-11.89
	MnCu	**FeCo**	**FeNi**	**FeCu**	**CoNi**	**CoCu**	**NiCu**
$E_b(A)$	-6.25	-6.79	-6.65	-6.65	-6.79	-6.79	-6.58
$E_b(B)$	-3.66	-5.90	-5.81	-4.11	-5.86	-4.34	-4.52
E_b	-9.91	-12.69	-12.46	-10.76	-12.65	-11.13	-11.10

Table S5. The calculated U_L (in V), PDS, ΔG(*N_2→*NNH) in eV, and ΔG(*NH_2→*NH_3) in eV for NRR on the M1M2@NG DACs.

	U_L	PDS	ΔG(*N_2→*NNH)	ΔG(*NH_2→*NH_3)
V_2	-1.01	*NH_2→*NH_3	0.04	1.01
Cr_2	-0.84	*NH_2→*NH_3	0.26	0.84
Mn_2	-0.48	*NH_2→*NH_3	0.47	0.48
Fe_2	-0.62	*N_2→*NNH	0.62	0.02
Co_2	-0.48	*N_2→*NNH	0.48	0.43
Ni_2	-1.36	*N_2→*NNH	1.36	-0.62
Cu_2	-1.86	*N_2→*NNH	1.86	-0.91
VCr	-0.24	*NH_2→*NH_3	-0.04	0.24
VMn	-0.71	*NH_2→*NH_3	0.35	0.71
VFe	-0.38	*N_2→*NNH	0.38	0.36
VCo	-0.60	*N_2→*NNH	0.60	0.07
VNi	-0.82	*N_2→*NNH	0.82	0.35
VCu	-0.74	*N_2→*NNH	0.74	0.34
CrMn	-0.44	*N_2→*NNH	0.44	0.09
CrFe	-0.49	*NH_2→*NH_3	0.48	0.49
CrCo	-0.54	*NH_2→*NH_3	0.51	0.54
CrNi	-0.83	*N_2→*NNH	0.83	0.02
CrCu	-0.87	*N_2→*NNH	0.87	-0.20
MnFe	-0.90	*N_2→*NNH	0.90	0.56
MnCo	-0.70	*N_2→*NNH	0.70	0.12
MnNi	-1.04	*N_2→*NNH	1.04	-0.52
MnCu	-0.88	*N_2→*NNH	0.88	-0.28
FeCo	-0.53	*N_2→*NNH	0.53	0.06
FeNi	-0.87	*N_2→*NNH	0.87	-0.43
FeCu	-1.11	*N_2→*NNH	1.11	-0.49
CoNi	-1.14	*N_2→*NNH	1.14	-0.23
CoCu	-1.48	*N_2→*NNH	1.48	-0.53
NiCu	-1.54	*N_2→*NNH	1.54	-0.70

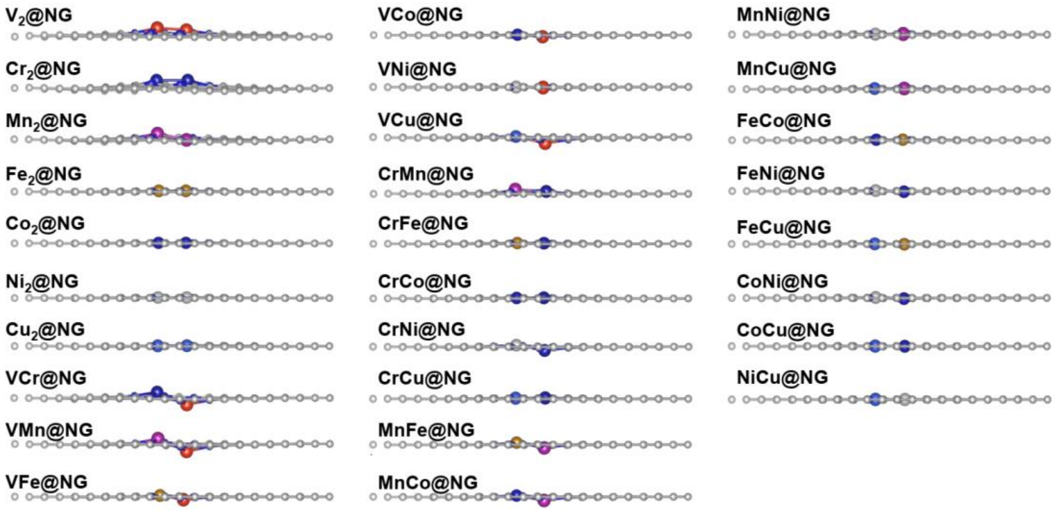


Figure S1. The side views of the studied M1M2@NG catalysts, where the larger spheres are the TM atoms, and the right and left atoms are M1 and M2, respectively.

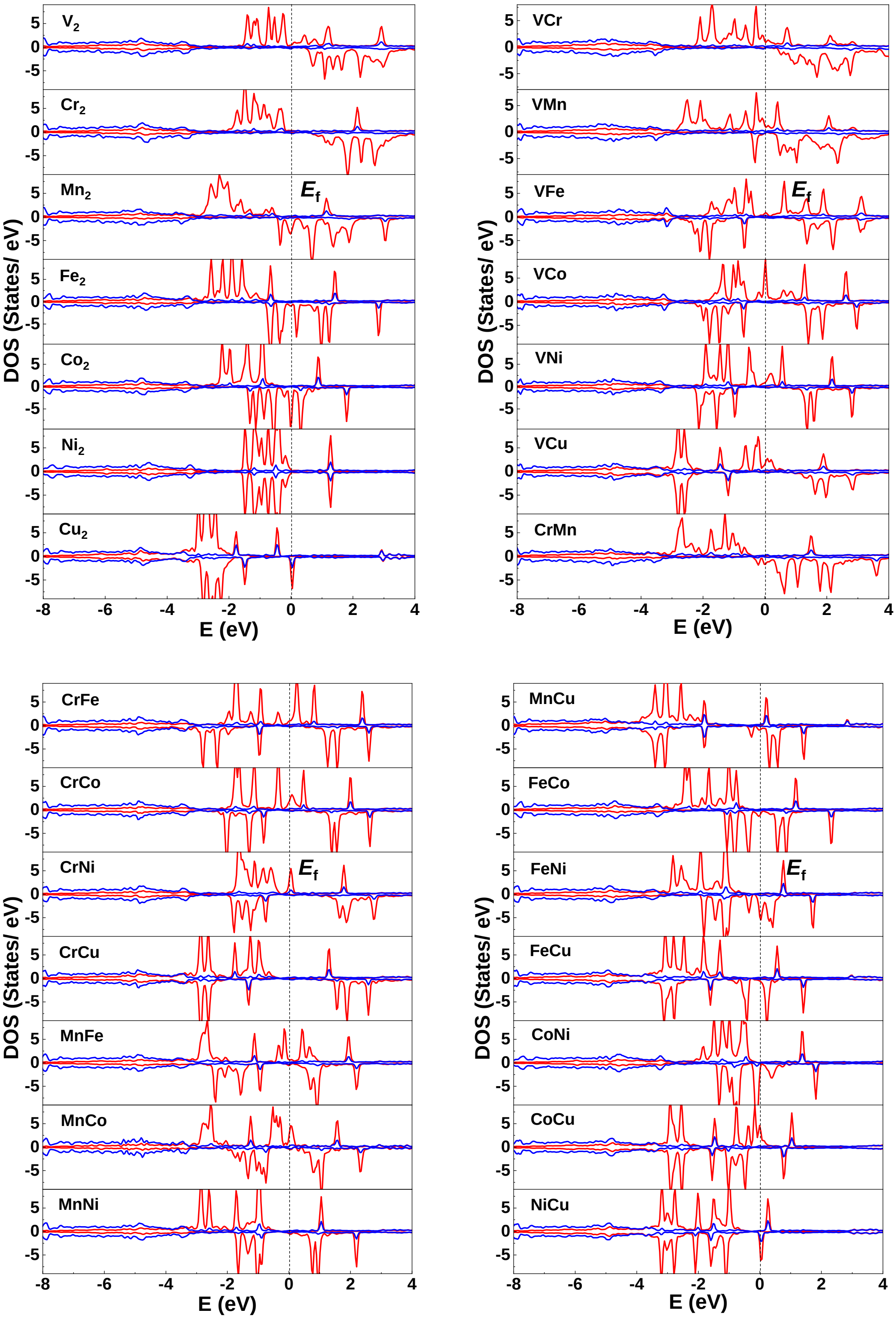


Figure S2. The LDOS projected on the anchored TM dimer (red line) and its neighboring N atoms (blue line). The dashed vertical lines indicate the Fermi level.

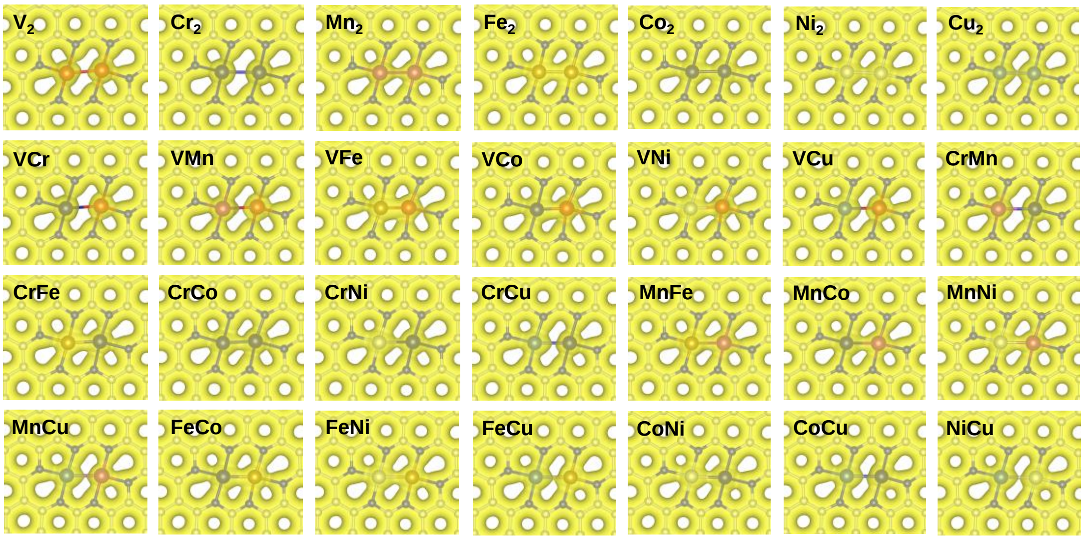


Figure S3. The total electron density distribution of M1M2@NG systems. The isosurface is taken as 0.05 e/bohr^3.

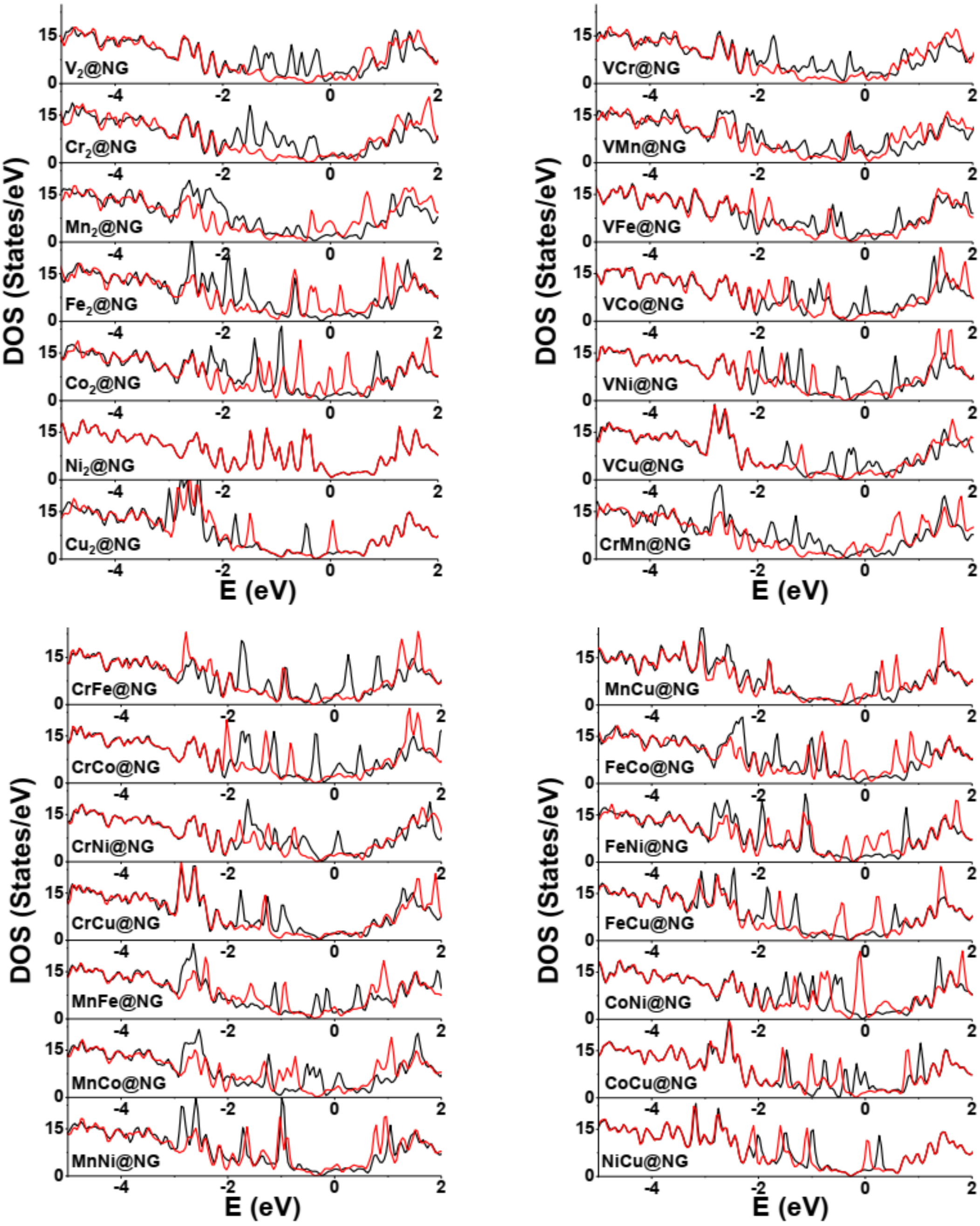


Figure S4. The total DOS of the studied M1M2@NG catalysts. The black and red lines denote the spin-up and spin-down states, respectively. The Fermi level is set to be 0 eV.

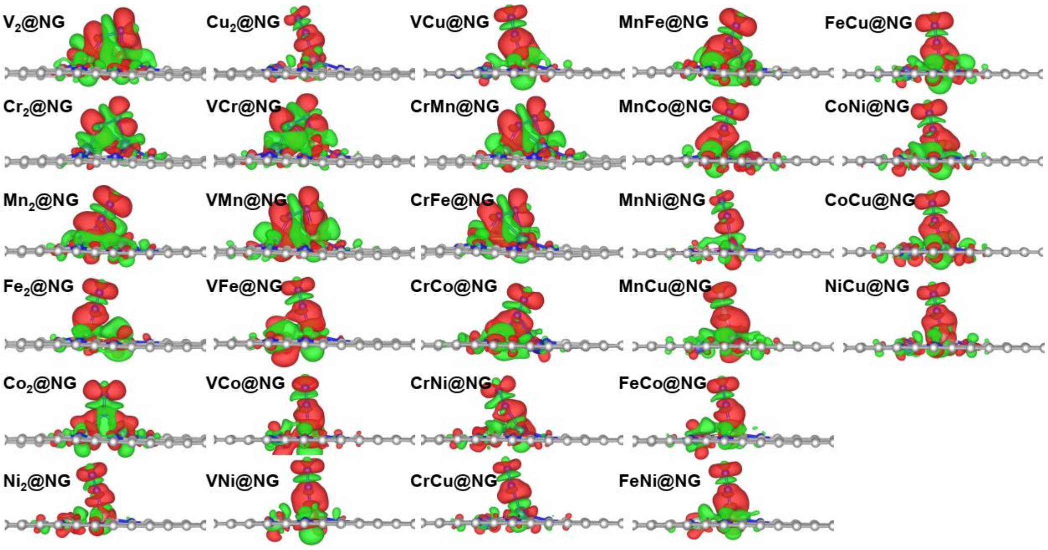


Figure S5. The side views of the most favorable configuratoins for N_2 adsorption on M1M2@NG catalysts. For the calculated charge density difference, the red and green regions represent the electron accumulation and depletion, respectively. The isosurface value is set to be 0.001 e/bohr^3.

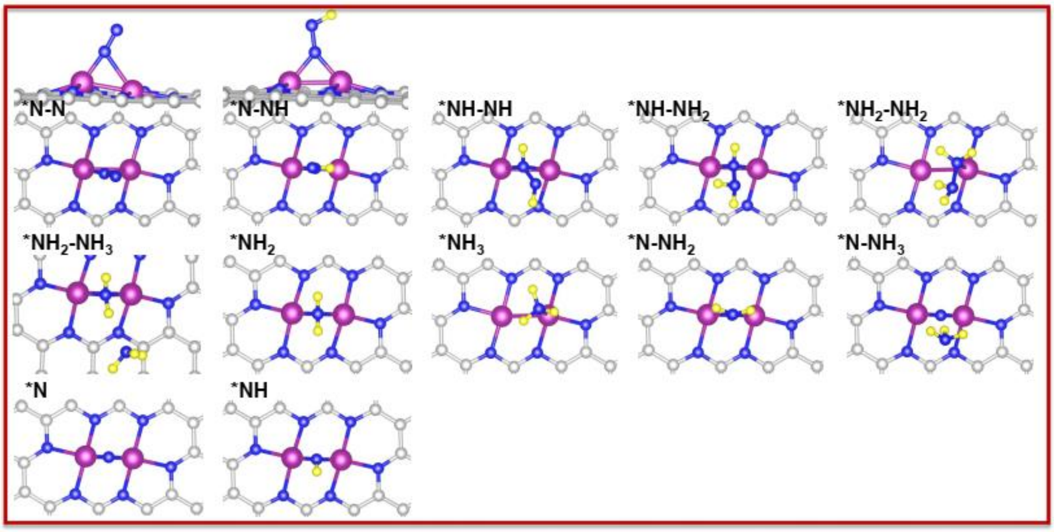


Figure S6. The intermediates for the NRR on the Mn_2@NG catalysts. The grey, blue, yellow, and large purple spheres denote the C, N, H, and Mn atoms, respectively.

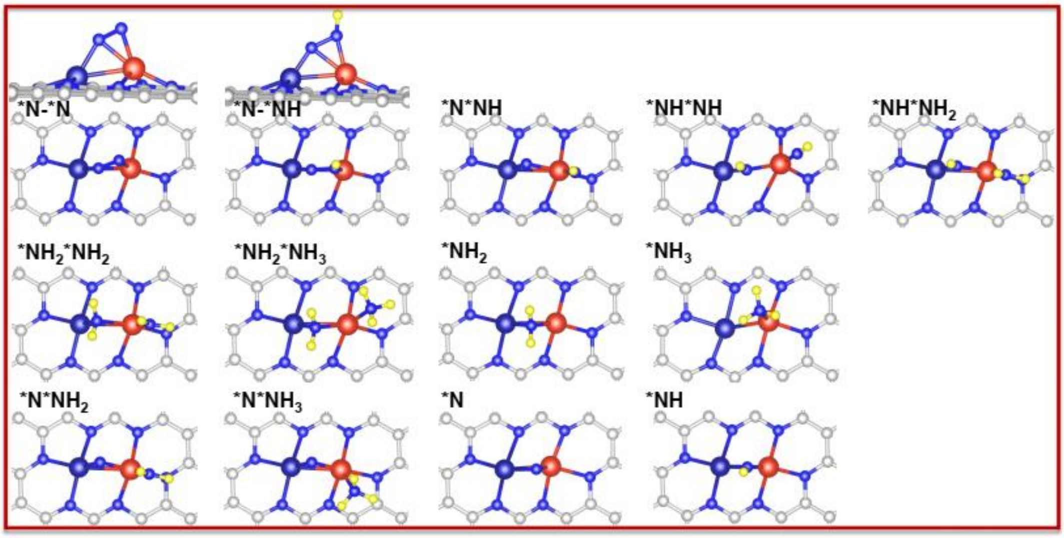


Figure S7. The intermediates for the NRR on the VCr@NG catalysts. The grey, blue, yellow, and large red and blue spheres denote the C, N, H, V, and Cr atoms, respectively.

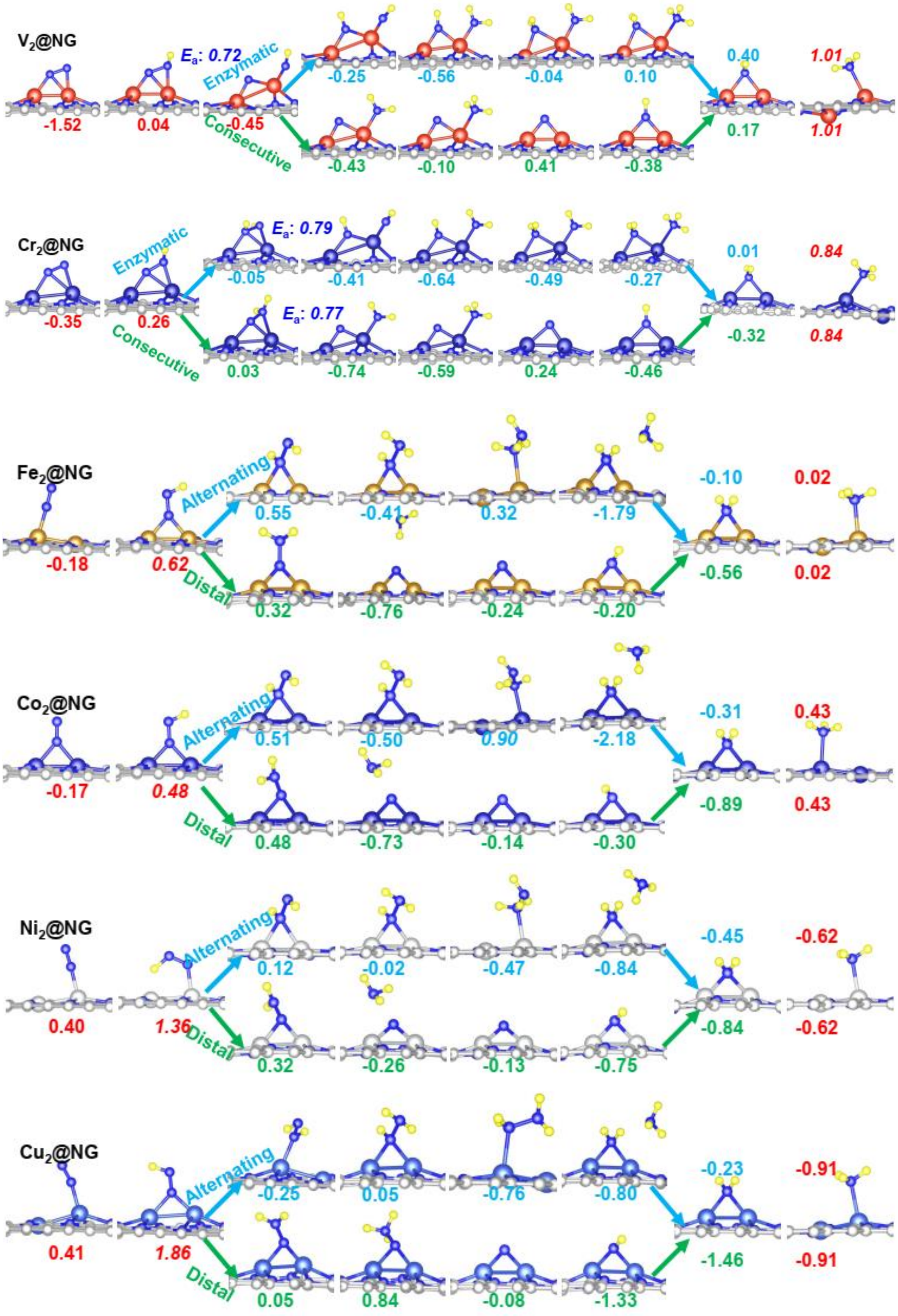
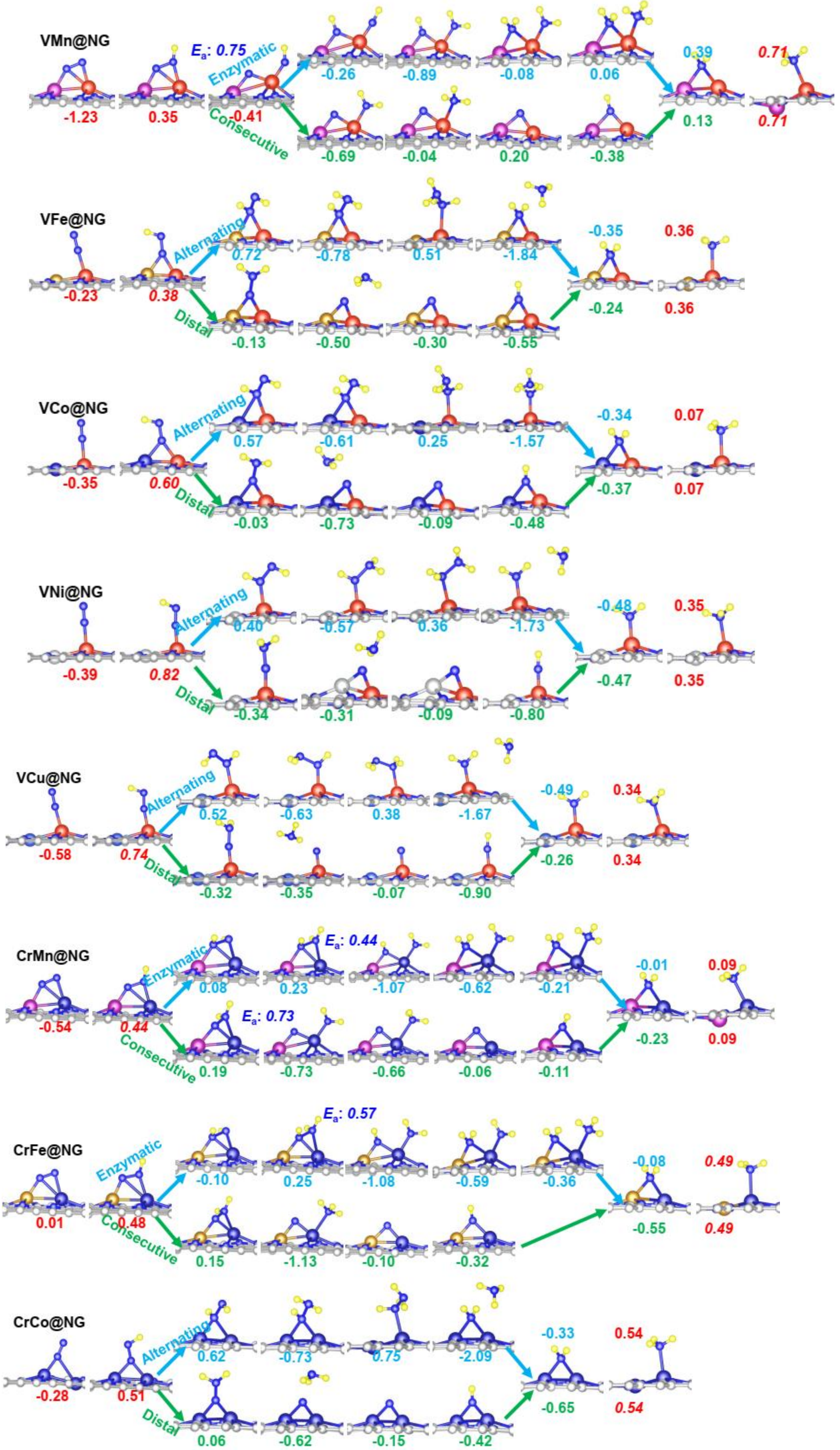
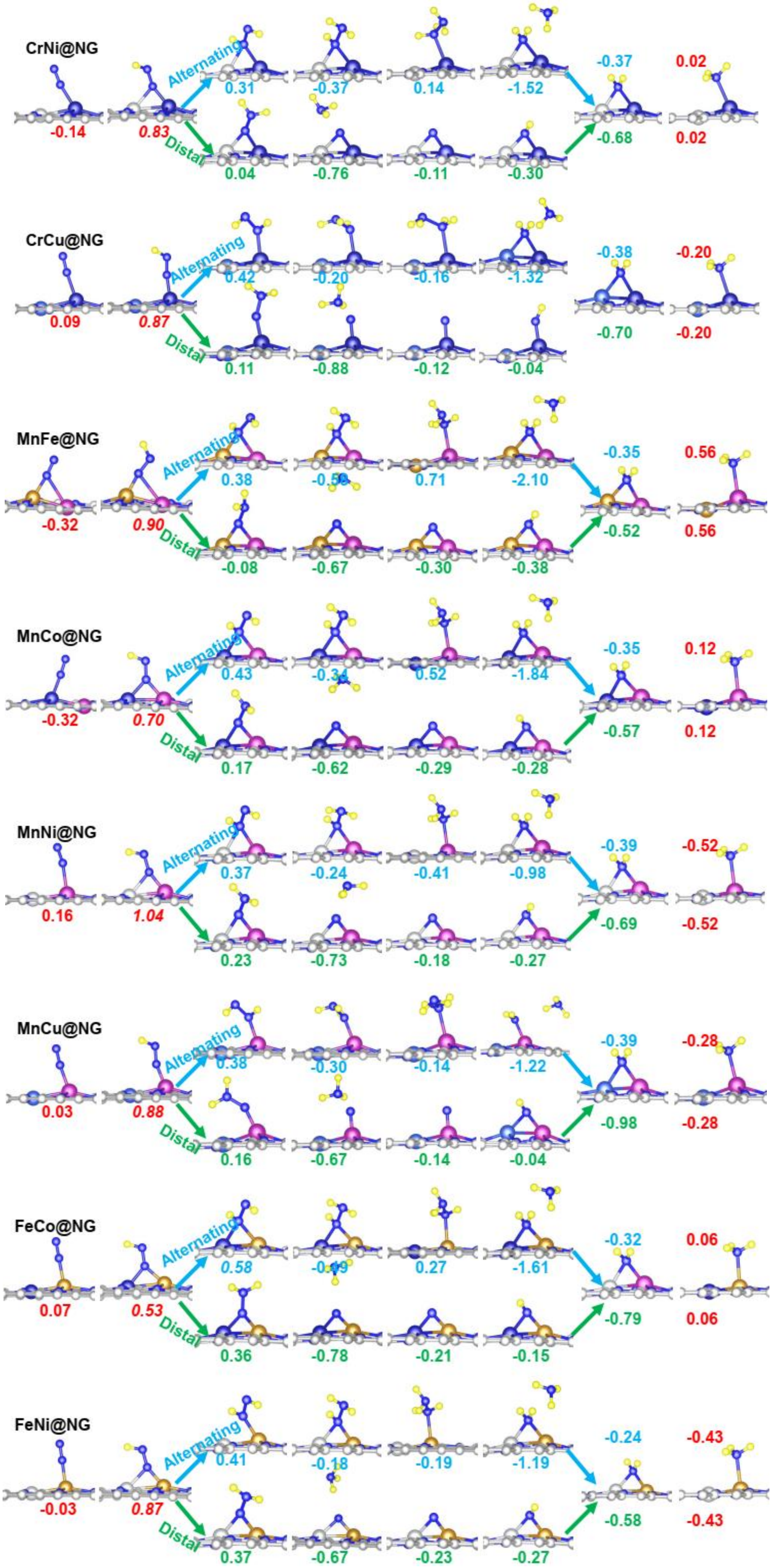


Figure S8. The intermediates and the free energy changes (in eV) for the NRR on the homonuclear M1M2@NG catalysts, except Mn_2@NG. The grey, blue, yellow spheres denote the C, N, and H atoms, respectively. The larger spheres are the TM atoms. E_a denotes the energy barrier (E_a in eV) for the dissociation of the adsorbed species.


VMn@NG
-1.23
0.35
E_a: 0.75
Enzymatic
-0.41
Consecutive
-0.26
-0.89
-0.08
0.06
0.39
0.71
-0.69
-0.04
0.20
-0.38
0.13
0.71
VFe@NG
-0.23
0.38
Alternating
Distal
0.72
-0.78
0.51
-1.84
-0.35
0.36
-0.13
-0.50
-0.30
-0.55
-0.24
0.36
VCo@NG
-0.35
0.60
Alternating
Distal
0.57
-0.61
0.25
-1.57
-0.34
0.07
-0.03
-0.73
-0.09
-0.48
-0.37
0.07
VNi@NG
-0.39
0.82
Alternating
Distal
0.40
-0.57
0.36
-1.73
-0.48
0.35
-0.34
-0.31
-0.09
-0.80
-0.47
0.35
VCu@NG
-0.58
0.74
Alternating
Distal
0.52
-0.63
0.38
-1.67
-0.49
0.34
-0.32
-0.35
-0.07
-0.90
-0.26
0.34
CrMn@NG
-0.54
0.44
Enzymatic
Consecutive
0.08
0.23
E_a: 0.44
-1.07
-0.62
-0.21
-0.01
0.09
E_a: 0.73
0.19
-0.73
-0.66
-0.06
-0.11
-0.23
0.09
CrFe@NG
0.01
0.48
Enzymatic
Consecutive
E_a: 0.57
-0.10
0.25
-1.08
-0.59
-0.36
-0.08
0.49
0.15
-1.13
-0.10
-0.32
-0.55
0.49
CrCo@NG
-0.28
0.51
Alternating
Distal
0.62
-0.73
0.75
-2.09
-0.33
0.54
0.06
-0.62
-0.15
-0.42
-0.65
0.54


CrNi@NG
-0.14
0.83
Alternating
0.31
-0.37
0.14
-1.52
-0.37
0.02
Distal
0.04
-0.76
-0.11
-0.30
-0.68
0.02
CrCu@NG
0.09
0.87
Alternating
0.42
-0.20
-0.16
-1.32
-0.38
-0.20
Distal
0.11
-0.88
-0.12
-0.04
-0.70
-0.20
MnFe@NG
-0.32
0.90
Alternating
0.38
-0.58
0.71
-2.10
-0.35
0.56
Distal
-0.08
-0.67
-0.30
-0.38
-0.52
0.56
MnCo@NG
-0.32
0.70
Alternating
0.43
-0.34
0.52
-1.84
-0.35
0.12
Distal
0.17
-0.62
-0.29
-0.28
-0.57
0.12
MnNi@NG
0.16
1.04
Alternating
0.37
-0.24
-0.41
-0.98
-0.39
-0.52
Distal
0.23
-0.73
-0.18
-0.27
-0.69
-0.52
MnCu@NG
0.03
0.88
Alternating
0.38
-0.30
-0.14
-1.22
-0.39
-0.28
Distal
0.16
-0.67
-0.14
-0.04
-0.98
-0.28
FeCo@NG
0.07
0.53
Alternating
0.58
-0.49
0.27
-1.61
-0.32
0.06
Distal
0.36
-0.78
-0.21
-0.15
-0.79
0.06
FeNi@NG
-0.03
0.87
Alternating
0.41
-0.18
-0.19
-1.19
-0.24
-0.43
Distal
0.37
-0.67
-0.23
-0.27
-0.58
-0.43

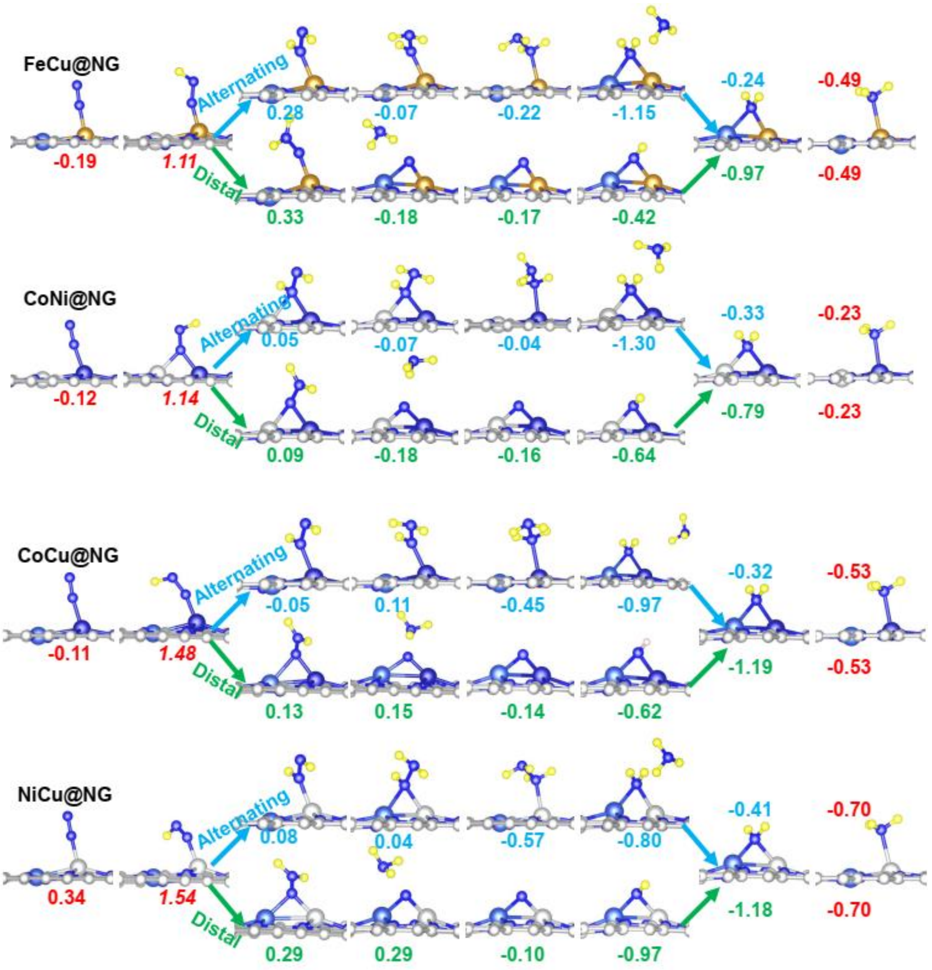


Figure S9. The intermediates and the free energy changes (in eV) for the NRR on the heteronuclear M1M2@NG catalysts, except VCr@NG. The grey, blue, yellow spheres denote the C, N, and H atoms, respectively. The larger spheres are the TM atoms. E_a denotes the energy barrier (E_a in eV) for the dissociation of the adsorbed species.

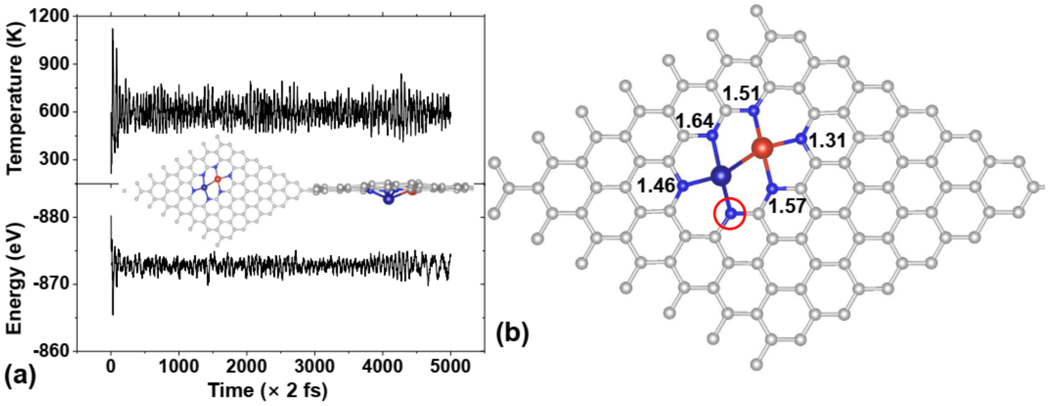


Figure S10. (a) Variation of the temperature and total energy against time for the ab initio molecular dynamics simulation of VCr@NG. The simulation was performed under 600 K for 10 ps with a time-step of 2 fs. The top and side views of the final configuration after the simulation are shown as insets. (b) The top view of the VCr@NG catalyst with the calculated free energy changes for H adsorption (in eV) on the various N sites. It is noted that the N atom enclosed by the red circle is unable to adsorb H atom.

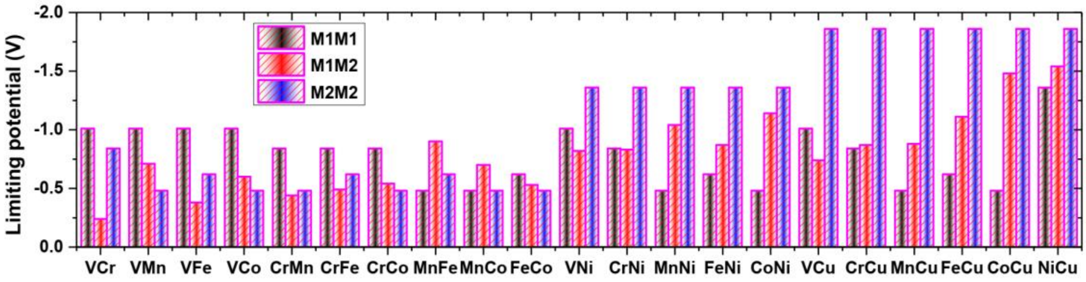


Figure S11. A comparation of the calculated limiting potentials of the heteronuclear DACs with their homonuclear counterparts. In each group, M1M1, M1M2, and M2M2 represent the M1M1@, M1M2@, and M2M2@NG systems from left to right. For example, for VCr, from left to right, the corrsponding catalysts are V_2, VCr, and Cr_2@NG systems.

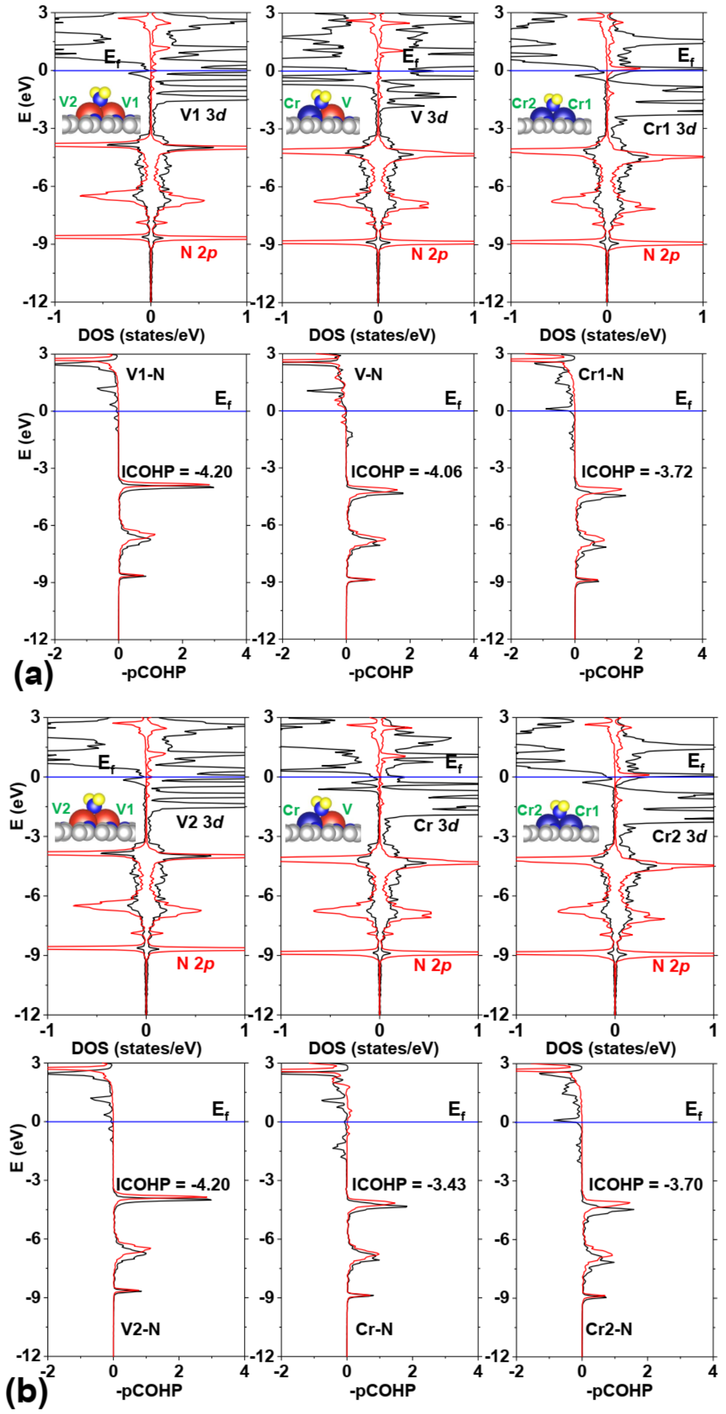


Figure S12. The LDOS projected on the N atom of the adsorbed NH$_2$ species (red line) and its bonded TM atoms (black line), and the relevant pCOHP and ICOHP. (a) and (b) are for the M1-N and M2-N interaction, respectively. For the LDOS the positive and negative values present the spin-up and spin-down states, respectively, while for the pCOHP the positive and negative values stand for the bonding and antibonding contributions, respectively. In addition, for pCOHP the black and red lines denote the contributions from the spin-up and spin-down states, respectively.