Supplementary Information (SI) for Journal of Materials Chemistry A.
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Supporting Information

Regulating Spin States of Single Transition Metal Atoms on N-Doped Graphene for Efficient Ammonia Synthesis

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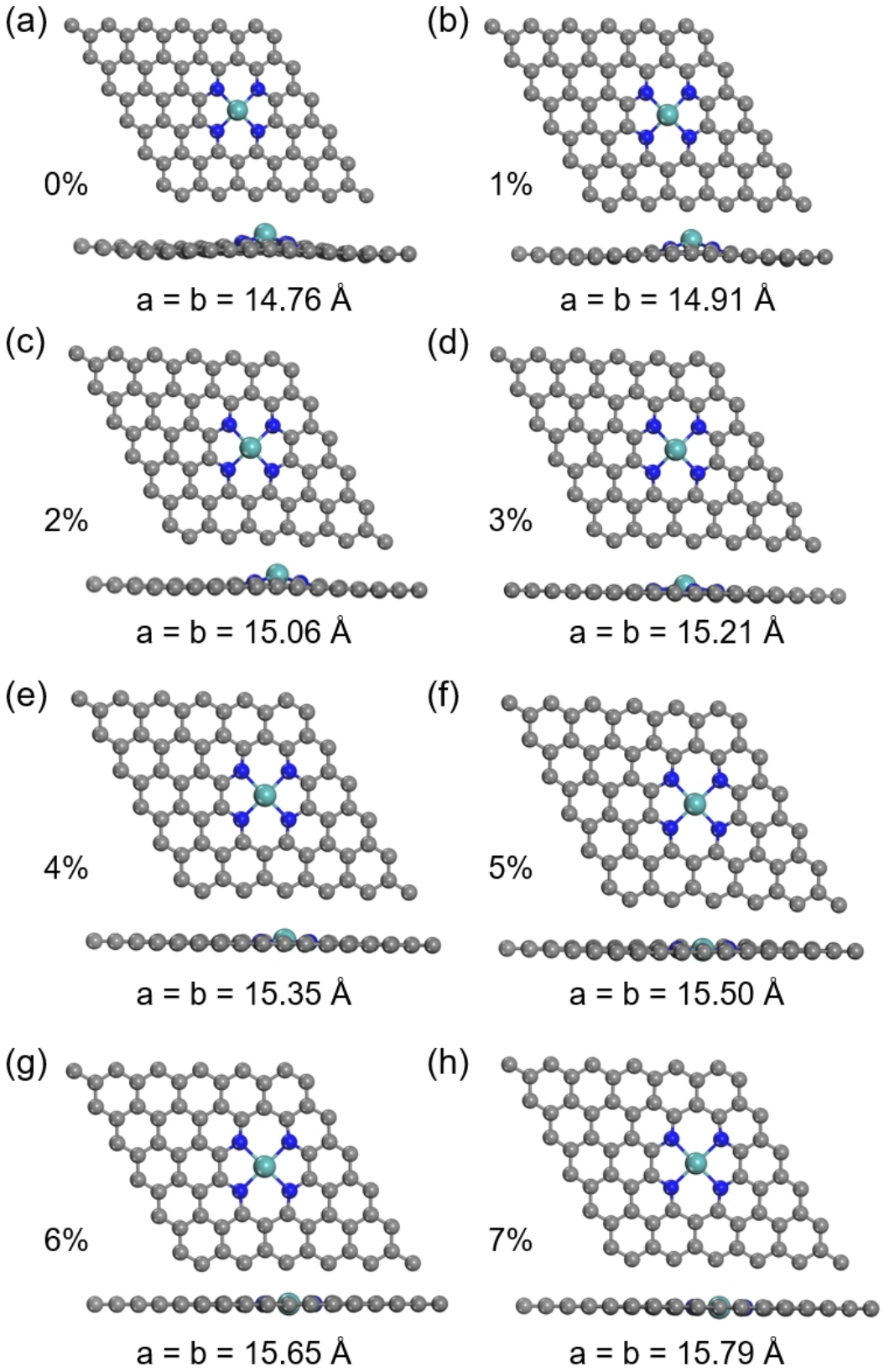

Figure S1. Optimized configurations of Mo-N/G with tensile strain ranging from 0% to 7%.

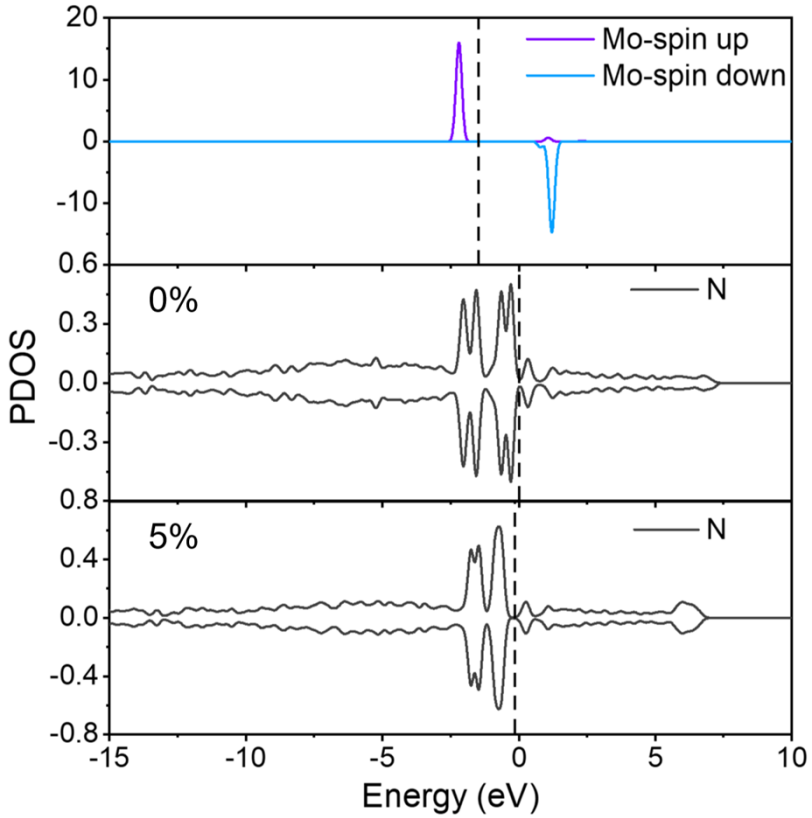

Figure S2. Spin-resolved PDOS of an isolated Mo atom and the N atom in N/G (without Mo) under 0% and 5% strain.

It can be clearly seen that for an isolated Mo atom, it has the largest spin splitting that all electrons occupied the spin-up states. However, for the N atom in N/G, it is spin degenerate under both 0% and 5% strain. The strong bonding of one Mo atom with four N atoms will weaken the spin splitting of the Mo atom. Therefore, weakening the Mo-N bonding by applying tensile strain (refer to ICOHP in Table S3) will make the spin state more like the isolated Mo atom (i.e. enlarged spin splitting).

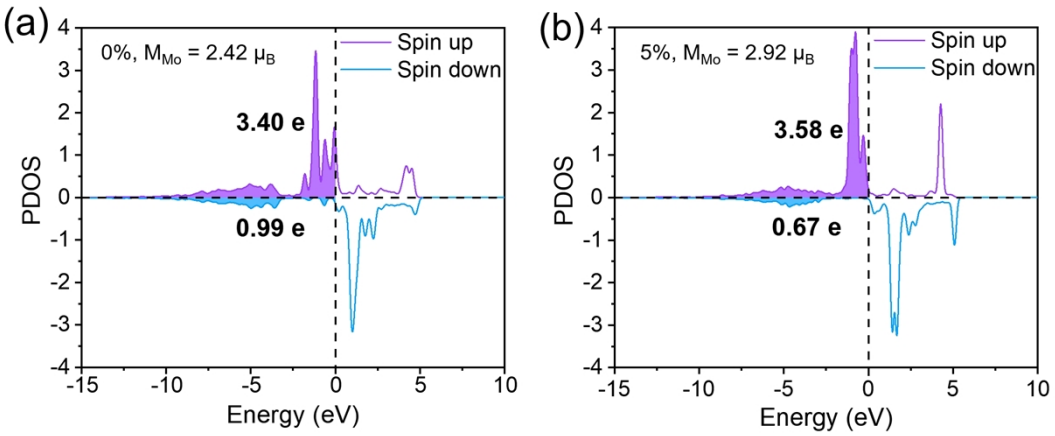

Figure S3. Spin-resolved PDOS and corresponding number of electrons of the Mo atom under 0% and 5% strain.

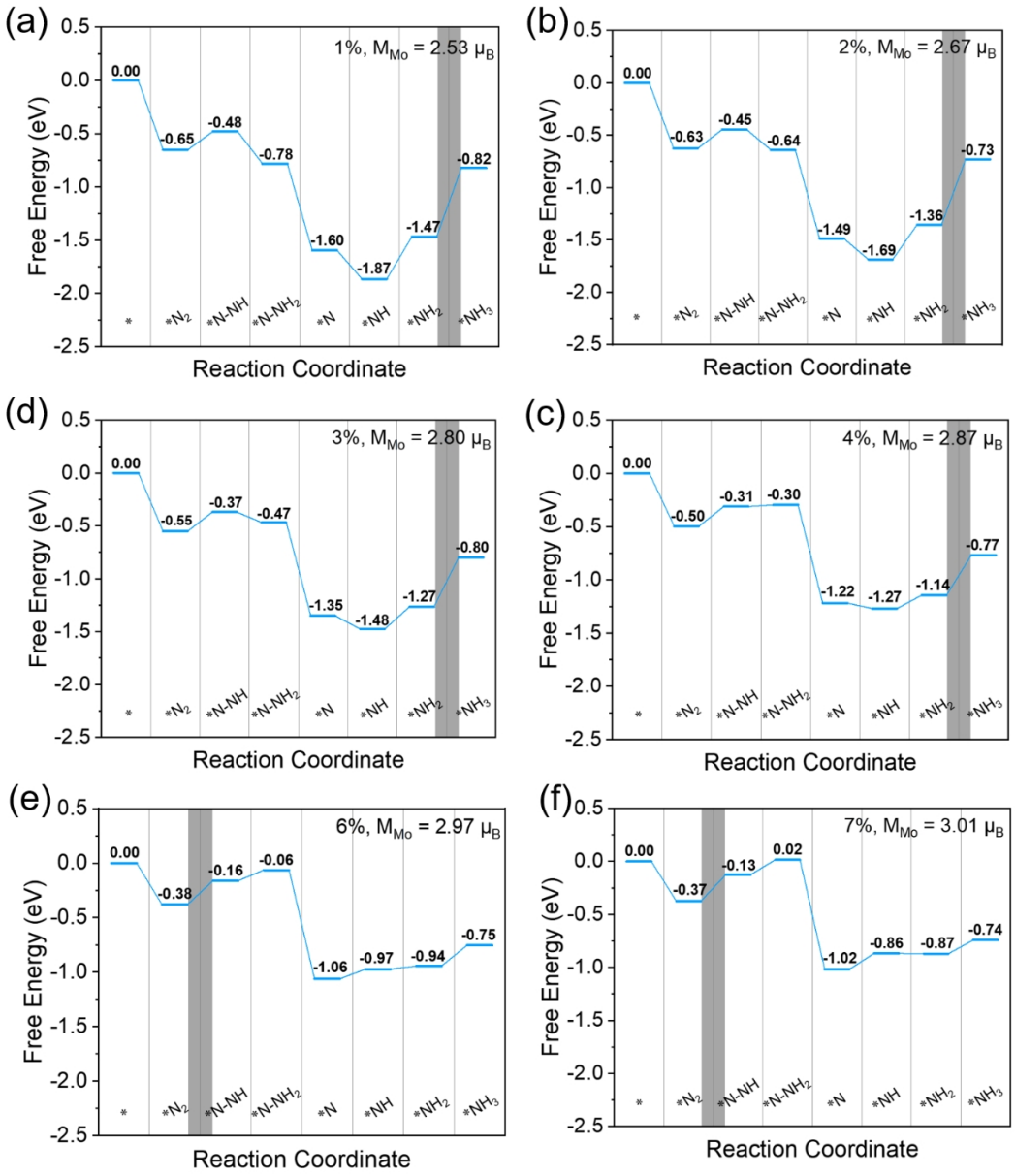

Figure S4. Free energy diagrams for NRR on Mo-N/G with tensile strain ranging from 1% to 7%, excluding 5% which can be found in Figure 2b in the main text.

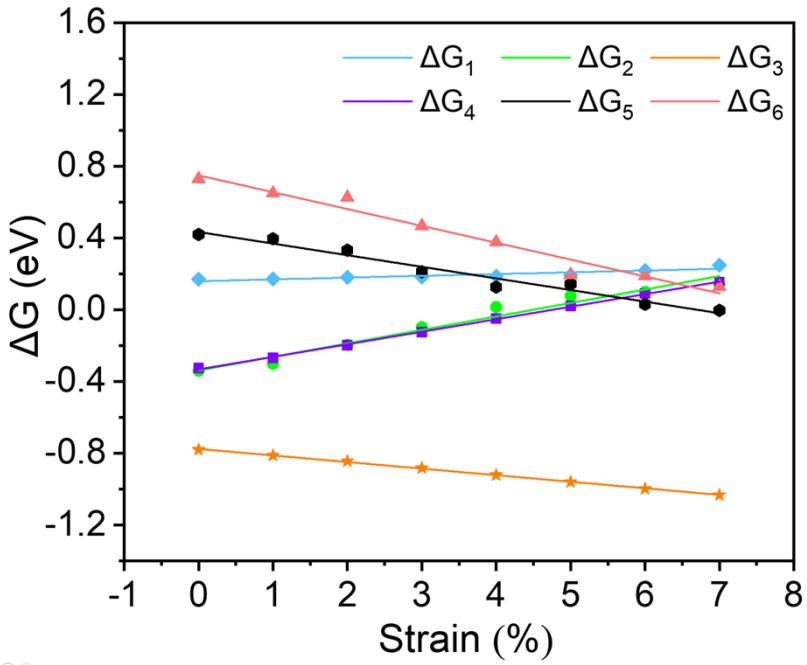

Figure S5. Changes of all hydrogenation steps during NRR on Mo-N/G with respect to the applied strain.

It can be clearly seen that all hydrogenation steps show good linear relationships with the applied strain, where ΔG_1 (blue), ΔG_2 (green), and ΔG_4 (violet) are all increasing, while ΔG_3 (orange), ΔG_5 (black) and ΔG_6 (red) are all decreasing. In addition, ΔG_6 and ΔG_1 correspond to PDS under 0%~5% and 6%~7% strain, respectively.

Considering the trends of ΔG_1 and ΔG_6, as well as the stability of the system under high strain, the strain range was limited to 0%~7% when studying the strain effect of NRR on Mo-N/G.

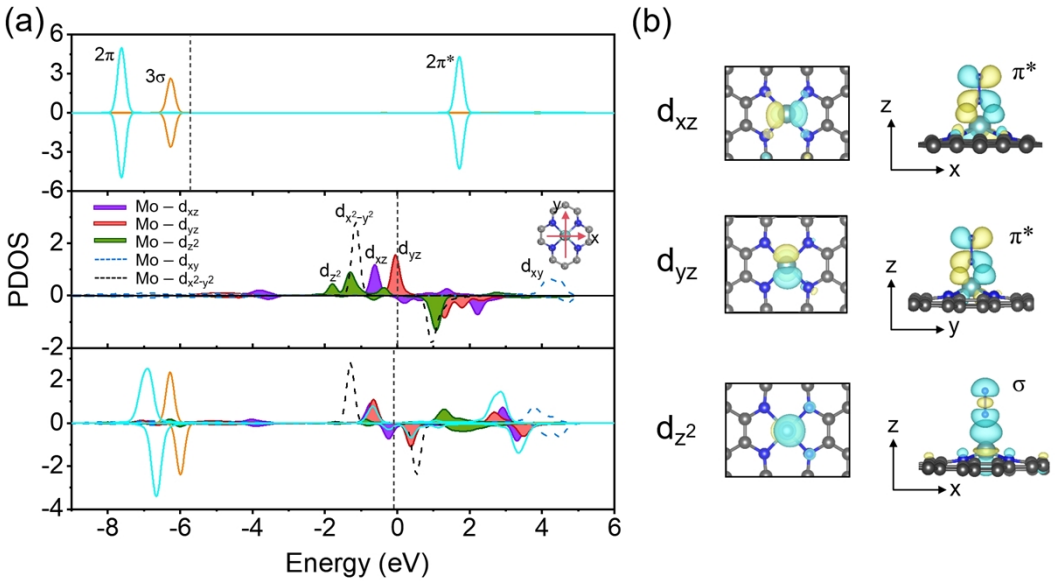

Figure S6. (a) PDOS of the N_2 molecule and the Mo atom of the catalyst before (upper and middle panels) and after (bottom panel) Mo-N bonding. The dashed black lines represent the Fermi level (E_F). (b) Schematic diagram of orbital matching between Mo-$d_{xz}/d_{yz}/d_{z^2}$ and N_2-π*/σ, where cyan and yellow regions stand for different phases.

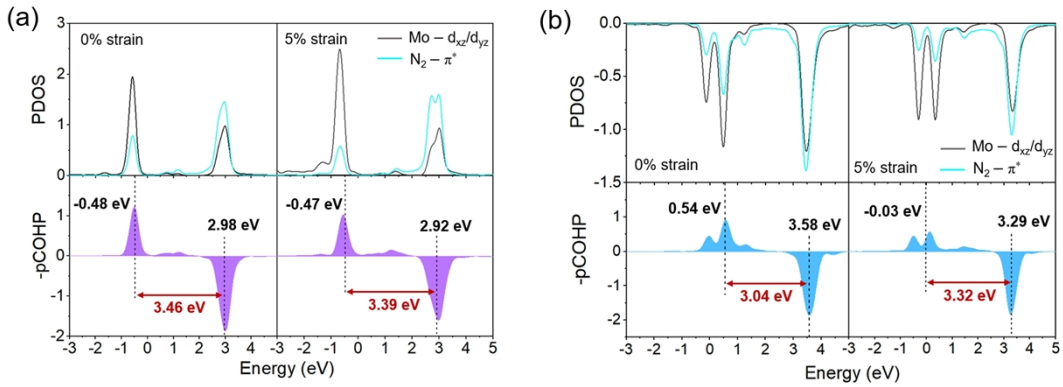

Figure S7. (a) Spin-up and (b) spin-down components of the PDOS and pCOHP of Mo-d_{xz}/d_{yz} and N_2-π* after Mo-N bonding under 0% and 5% strain.

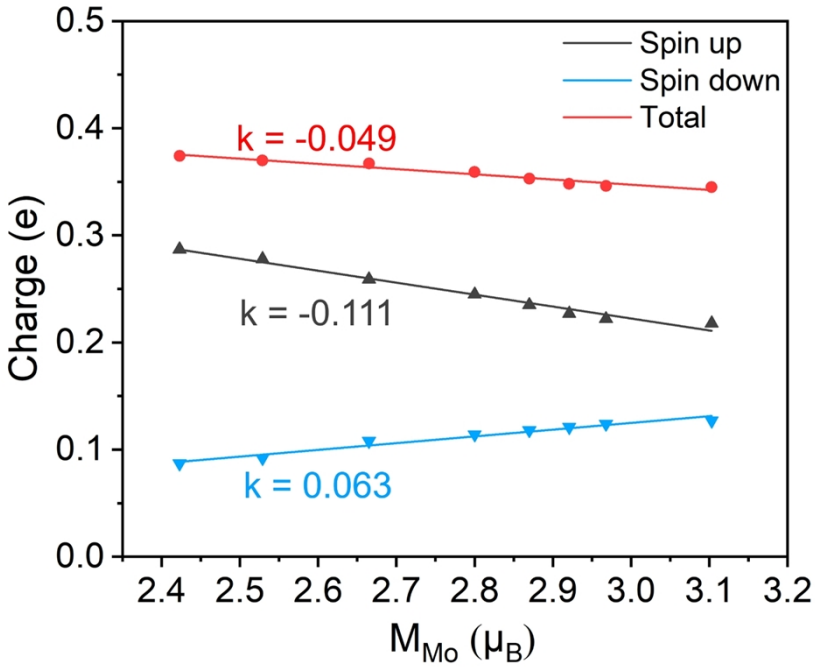

Figure S8. Variation of electron filling into the N_2-π* orbital with respect to M_{Mo}, where *k* is the corresponding slope of each linear fitting line.

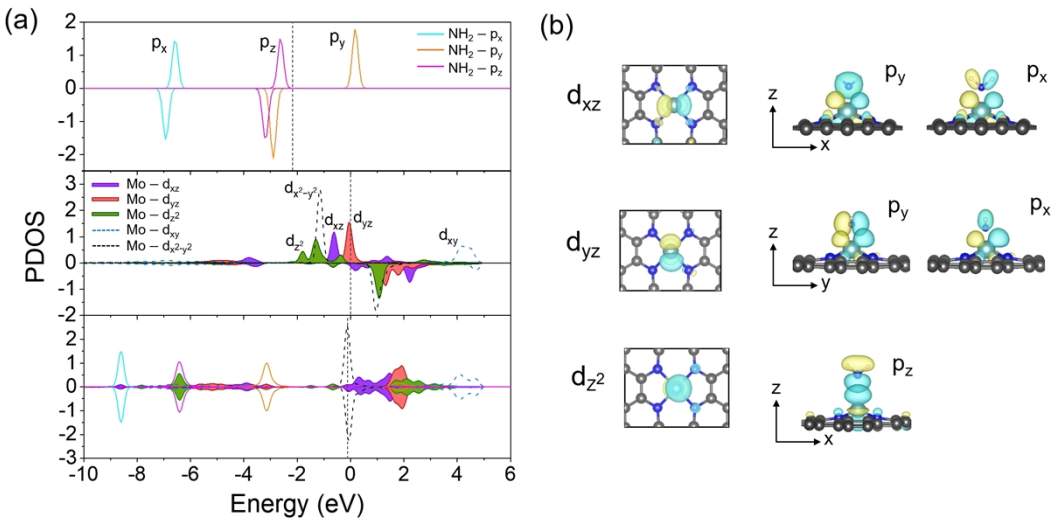

Figure S9. (a) PDOS of the NH_2 and the Mo atom of the catalyst before (upper and middle panels) and after (bottom panel) Mo-N bonding. The dashed black lines represent the Fermi level (E_F). (b) Schematic diagram of orbital matching between Mo-$d_{xz}/d_{yz}/d_{z^2}$ and NH_2-$p_x/p_y/p_z$, where cyan and yellow regions stand for different phases.

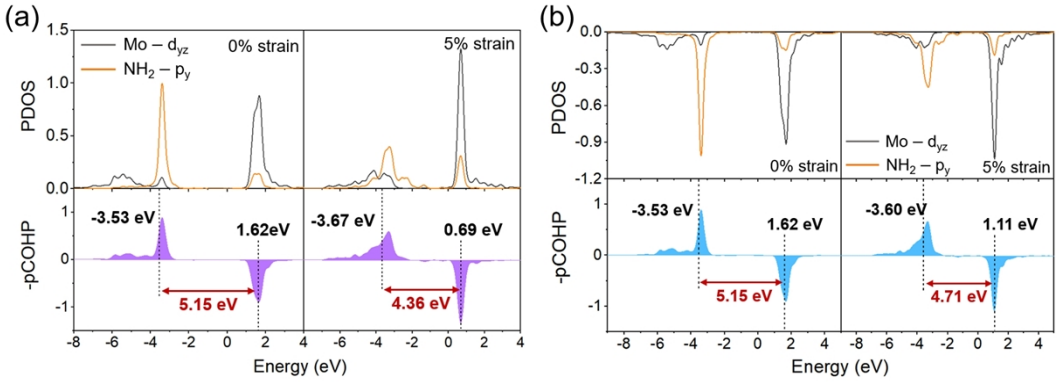

Figure S10. (a) Spin-up and (b) spin-down components of the PDOS and pCOHP of Mo-d_{yz} and NH_2-p_y after Mo-N bonding under 0% and 5% strain.

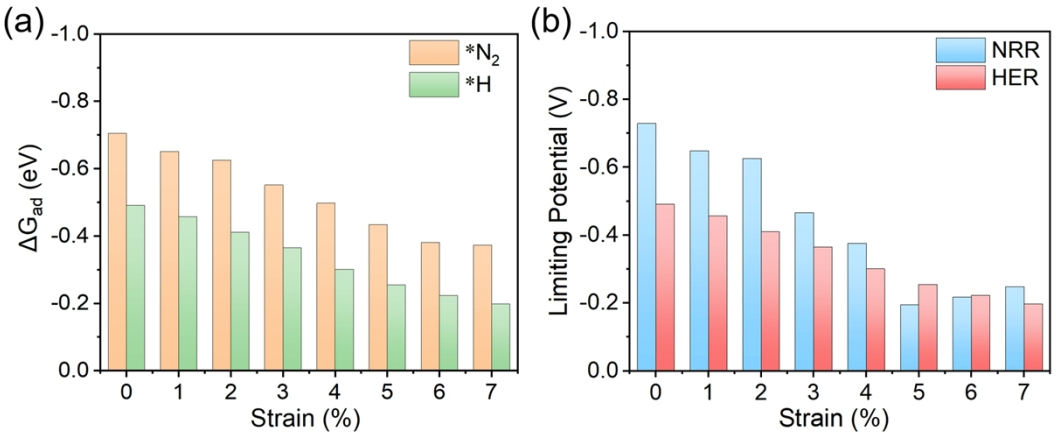

Figure S11. (a) Adsorption free energy of N_2 and H with respect to the applied strain. (b) Limiting potential of NRR and HER with respect to the applied strain.

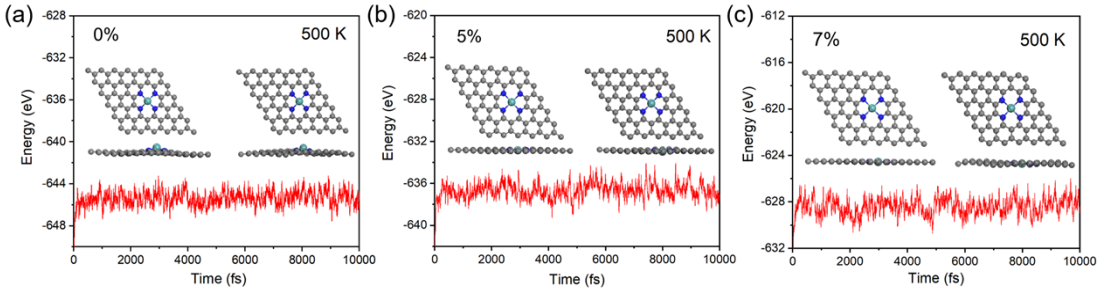

Figure S12. Evolution of total energy of Mo-N/G under strains of (a) 0% (pristine), (b) 5% (best performance) and (c) 7% (largest value in this work) in AIMD simulations at 500 K. Insets: the initial (0 ps) and final (10 ps) structures of Mo-N/G.

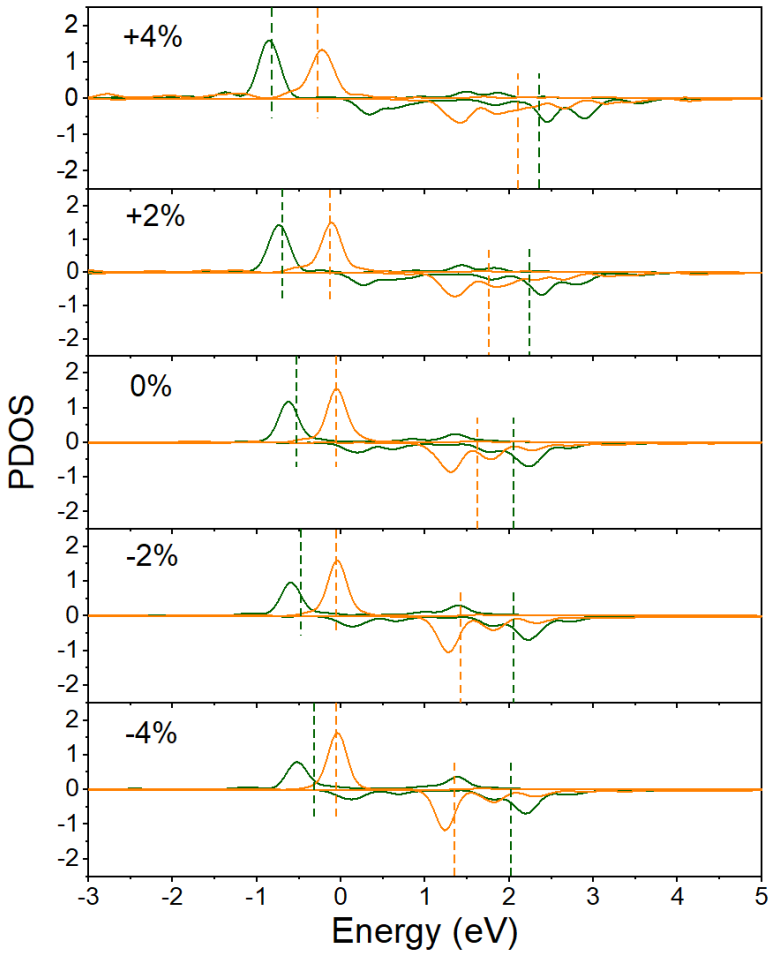

Figure S13. PDOS of Mo-d_{xz} and d_{yz} orbitals under different strains. The dashed lines are the centers of the corresponding orbitals for quantification of the spin splitting.

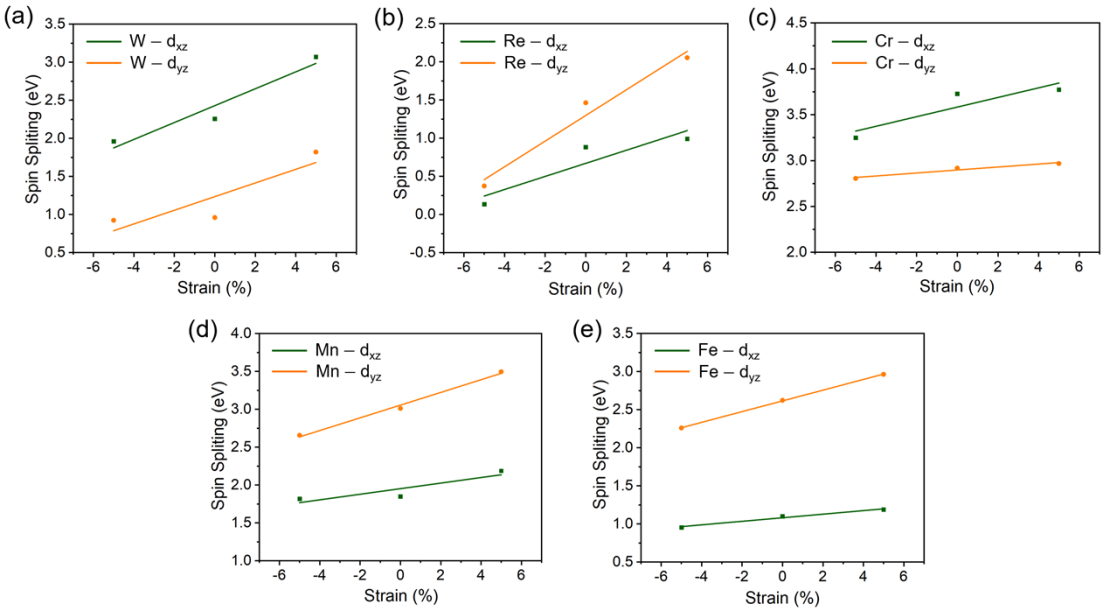

Figure S14. Spin splitting of d_{xz} and d_{yz} orbitals of (a) W, (b) Re, (c) Cr, (d) Mn, and (e) Fe with respect to the applied strain from −5% to 5%. The values of spin splitting of d_{xz} and d_{yz} orbitals were obtained from Figure S15.

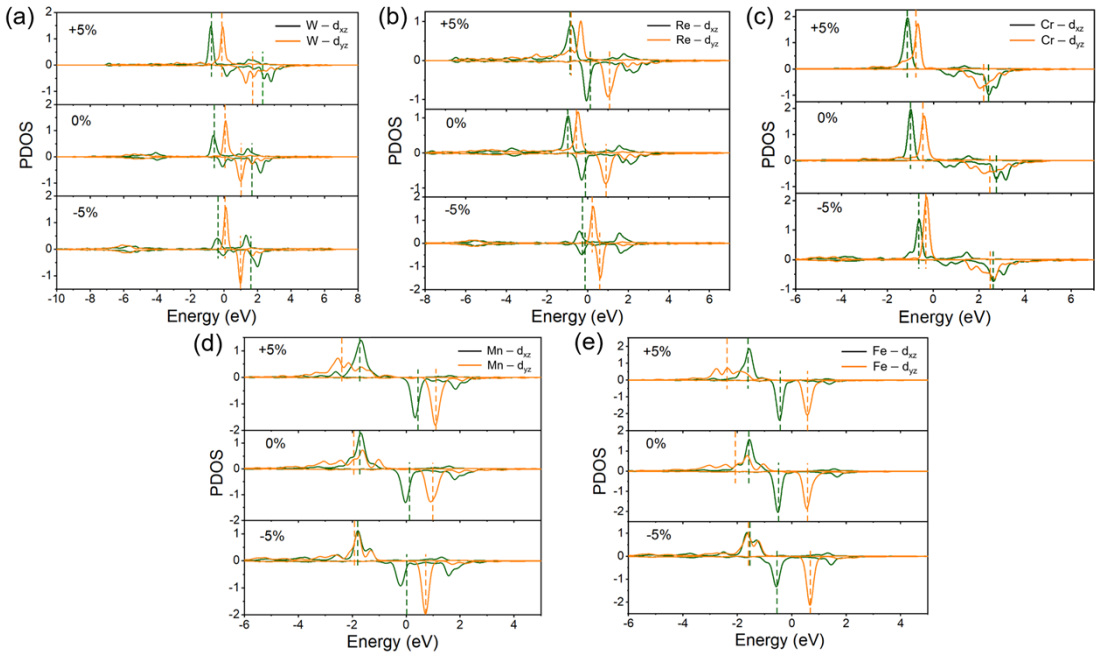

Figure S15. PDOS of d_{xz} and d_{yz} orbitals under different strains. The dashed lines are the centers of the corresponding orbitals for quantification of the spin splitting.

Table S1. Calculated E_{ZPE} and TS of gas molecules under 298 K and 1 bar.

Species	E_{ZPE} (eV)	TS (eV)
N_2(g)	0.15	0.59
H_2(g)	0.27	0.40
NH_3(g)	0.91	0.61

Table S2. Calculated E_{ZPE} and TS of intermediates on catalyst under 298 K.

Species	E_{ZPE} (eV)	TS (eV)	Species	E_{ZPE} (eV)	TS (eV)
$*N_2$	0.21	0.12	*NH	0.37	0.06
*N-NH	0.50	0.14	$*NH_2$	0.67	0.08
$*N\text{-}NH_2$	0.84	0.14	$*NH_3$	1.06	0.10
*N	0.09	0.05	*H	0.15	0.04

Table S3. Mo-N bond length and ICOHP[(#)] in Mo-N/G with tensile strain ranging from 0% to 7%.

Strain (%)	0	1	2	3	4	5	6	7
d_{Mo-N} (Å)	2.040	2.048	2.057	2.072	2.097	2.126	2.155	2.186
ICOHP	-1.63	-1.58	-1.53	-1.48	-1.41	-1.35	-1.29	-1.22

[(#)] ICOHP (integrated crystal orbital Hamilton population). The absolute value of ICOHP can quantify the bonding strength, where larger absolute values correspond to larger bonding strength.

Table S4. N_2 adsorption energy(#) and bond length on Mo-N/G under different strains (or M_{Mo}).

Strain (%)	0	1	2	3	4	5	6	7
M_{Mo} (μ_B)	2.42	2.53	2.67	2.80	2.87	2.92	2.97	3.01
E_{ad} (eV)	-1.28	-1.18	-1.16	-1.08	-1.03	-0.97	-0.91	-0.90
d_{N-N} (Å)	1.157	1.156	1.153	1.151	1.150	1.149	1.148	1.147

(#) The adsorption energy of N_2 on Mo-N/G is defined as:

$$E_{ad} = E_{N_2-Mo-N/G} - E_{Mo-N/G} - E_{N_2},$$

where $E_{N_2-Mo-N/G}$ is the energy of Mo-N/G with adsorbed N_2, $E_{Mo-N/G}$ is the energy of Mo-N/G, and E_{N_2} is the energy of free N_2.

Table S5. Binding energy(#) between Mo and N/G under different strains.

Strain (%)	0	1	2	3	4	5	6	7
E_b (eV)	-7.27	-7.33	-7.42	-7.56	-7.68	-7.76	-7.79	-7.86

(#) The binding energy is defined as:

$$E_b = E_{Mo-N/G} - E_{N/G} - E_{Mo},$$

where $E_{Mo-N/G}$ is the energy of Mo-N/G, $E_{N/G}$ is the energy of N/G without the Mo atom, and E_{Mo} is the energy of an isolated Mo atom.

Table S6. Magnetic moments of TM (TM = Re, Mo, W, Cr, Mn, Fe) in TM-N/G under −5%, 0% and 5% strain, respectively.

	−5%	0%	5%
Re	0.36	2.39	2.61
Mo	2.17	2.42	2.92
W	1.21	2.01	2.73
Cr	3.18	3.34	3.52
Mn	2.92	3.06	3.22
Fe	1.80	1.91	2.01