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Supporting information

Mo-based 2D MOF as a Highly Efficient Electrocatalyst for Reduction of N_2 to NH_3: A Density Functional Theory Study

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Calculational methods

The reaction energy (ΔE) of each reduction step which defines isolated N_2, H_2 molecules and clear Mo-HAB as zero can be expressed as to:

$$\Delta E = E\left(* N_{2-x}H_y\right) + xE(NH_3) - E(*) - E(N_2) - \frac{y}{2}E(H_2)$$

Where * represents the adsorbate, x is the number of N atom converting to NH_3 and releasing from the surface of adsorbate, and y is the number of proton and electron couples (H^+/e^-) participating into the reaction. According to standard hydrogen electrode (SHE),[1-3] $\mu(H^+/e^-) = \frac{1}{2}\,\mu(H_2)$ at 101325 Pa and $U = 0$.

The entropy term is computed by the following equation:

$$S = S_t + S_r + S_v + S_e$$

Where S_t, S_r, S_v and S_e represent entropy contributed by translation, rotation, vibration and electron, respectively. $S_e \approx 0$ at fundamental electronic level. Therefore, $S = S_t + S_r + S_v$ is eligible for calculating entropy of gas molecule. However, for solids and adsorbates, both S_t and S_r can be neglected and thus $S = S_v$

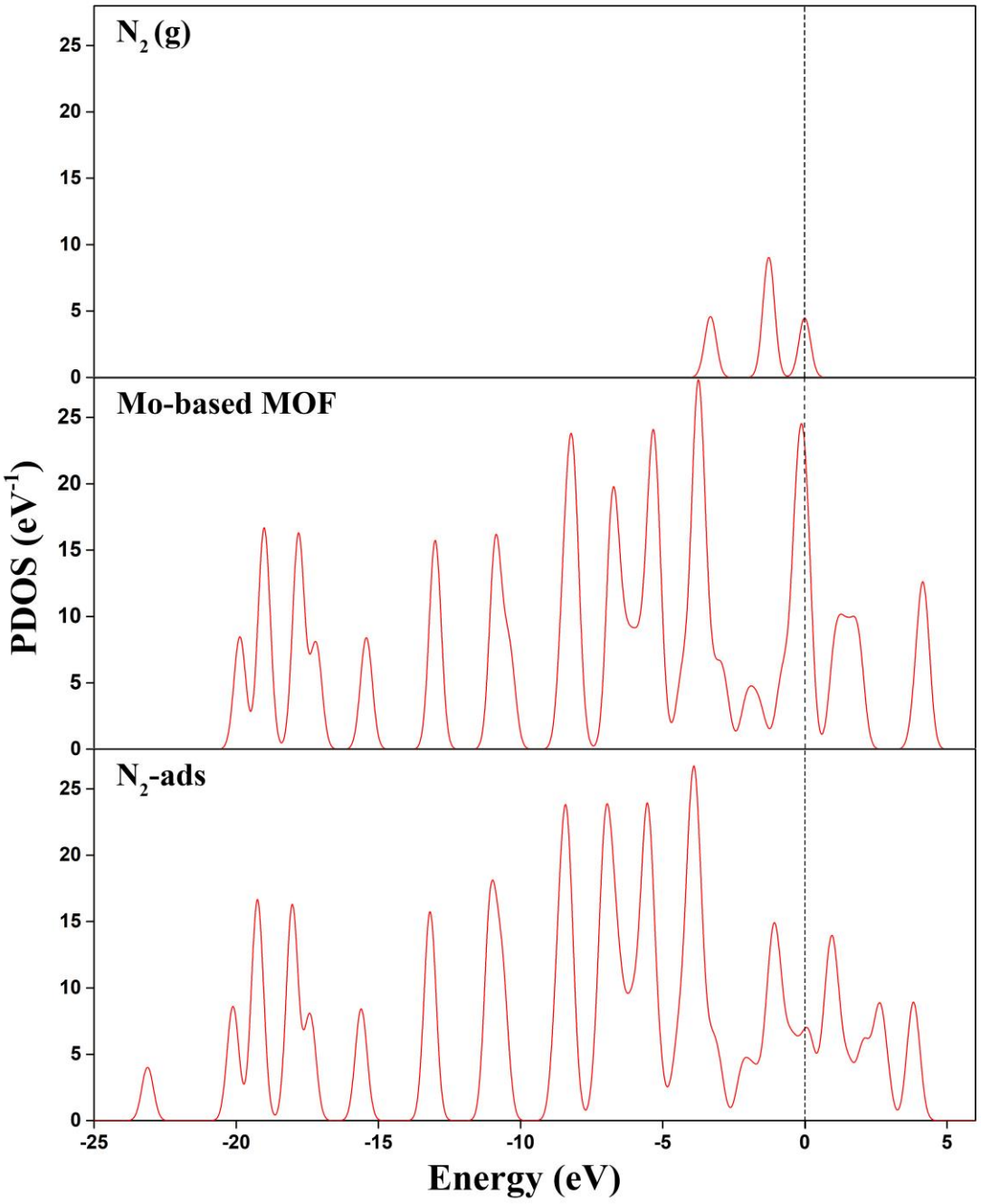
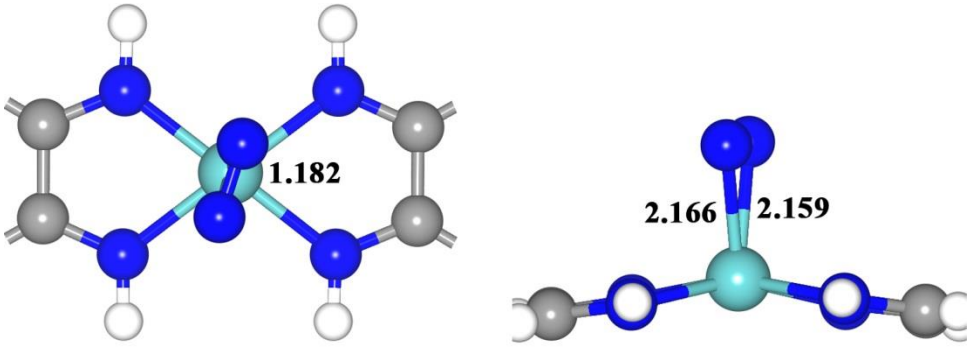


Fig. S1 The projected density of states (PDOS) of isolated N_2, clean Mo-based MOF and the N_2 adsorbed species on the surface of Mo-based MOF. The black dashed line setting at zero sites indicates the Fermi level.



(a) (b)

ΔE_{ads} = -0.21 eV

Fig. S2 Top (a) and side (b) views of configuration of N_2 lying on the surface of Mo--based MOF.

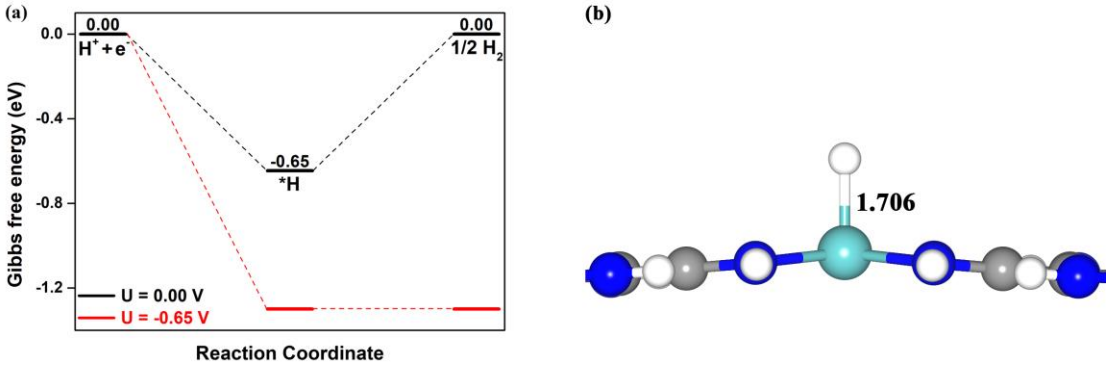


Fig. S3 Gibbs free energy diagram of hydrogen evolution reaction (HER) on the surface of Mo-based MOF (a) and the configuration of H adsorption (b). The bond length is labeled in Å. *H represents chemisorbed species.

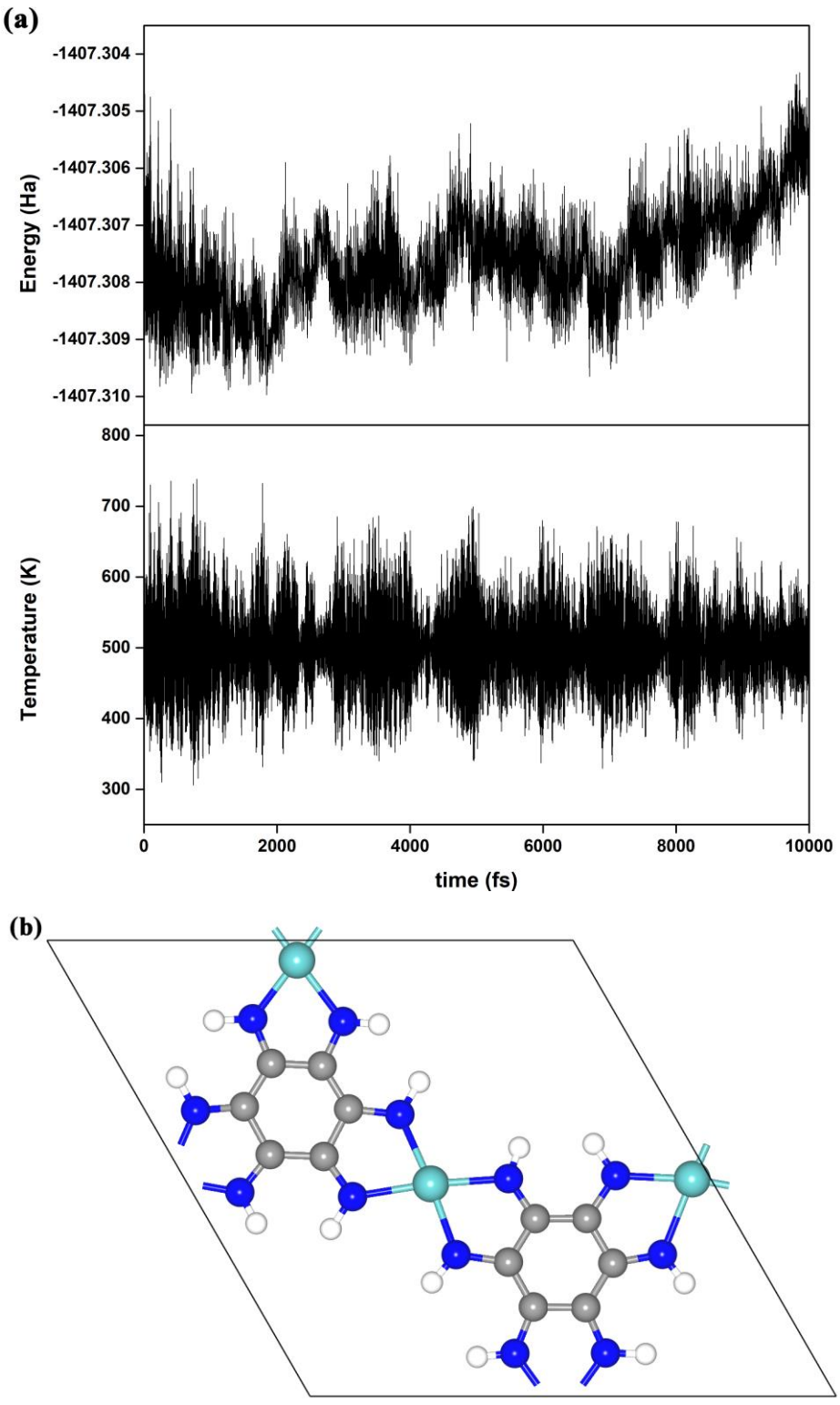


Fig. S4 (a) The molecule dynamic (MD) simulations for variation of total energy and temperature of Mo-based MOF at 500 K for 10 ps with each step of 1 fs. The Nosé-Hoover method is employed with controlling temperature. (b) Geometry snapshot of the atomic configuration after MD simulation.

Table S1. The optimized lattice length of 2D MOFs with various transition metal center.

Metal	a=b (Å)	c (Å)	Metal	a=b (Å)	c (Å)
Co	13.419	25.00	Cu	13.702	25.00
Ni	13.367		Mo	14.328	

Table S2. Thermodynamic parameters in eV, for the free gas molecules including N_2, H_2, NH_3 and H_2O at 298.15 K and 101325 Pa.[4]

Species	$-TS_t$	$-TS_r$	$-TS_v$	ZPE
N_2(g)	-0.45	-0.13	0.00	0.15
H_2(g)	-0.35	-0.04	0.00	0.27
NH_3(g)	-0.43	-0.13	0.00	0.58
H_2O(g)	-0.43	-0.12	0.00	0.56

Table S3. The adsorption energies (eV) of N_2 and H_2O gas molecules on the surface of various TM-based MOFs, respectively, corresponding to Figure 2.

Metal	N_2	H_2O	Metal	N_2	H_2O
Co	-0.114	-0.145	Cu	-0.566	-0.757
Ni	-0.062	-0.192	Mo	-0.831	-0.354

Table S4. Information of structures that N_2 adsorption that on the surface of various TM-based MOFs with the lowest energy. There are distance (Å) between the N_2 captured and the metal center, the N-N bond length (Å) of the adsorbed N_2, and charge transfer of N_2 by adsorption.

Metal	N_2-M distance (Å)	N-N bond length (Å)	Charge transfer (e)
Co	1.845	1.120	0.140
Ni	3.195	1.109	-0.007
Cu	3.507	1.108	0.004
Mo	1.963	1.144	-0.182

Table S5. Parameters about the structures that H_2O adsorption that on various

TM-based MOFs with the lowest energy. There are the distance (Å) between the H_2O molecule and the surface of HAB-CP, the H-O bond length (Å) and angle of H-O-H in the adsorbed H_2O and charge transfer of H_2O due to adsorption.

Metal	H_2O-M distance (Å)	H-O bond length (Å)	Angle (°)	Charge transfer (e)
Co	2.285	0.976	103.6	0.157
Ni	2.718	0.977	100.8	-0.009
Cu	2.706	0.987	103.7	-0.019
Mo	2.198	0.978	105.2	0.231

Table S6. Magnetic moment (μ_B) of various TM-based MOFs by Hirshfeld method.

Metal	total	metal atom
Co	1.01	1.52
Ni	0	0
Cu	1.28	0.60
Mo	2.19	2.55

Table S7. Variation of charge determined by Mulliken analysis of the three moieties of the catalyst corresponding to the distal and alternating mechanisms, respectively (exhibited in Figure 6). The step 0 means the N_2 adsorbed on the surface of Mo-HAB, and subsequent reaction step corresponding hydrogenation reaction step.

reaction		**distal**			**alternating**	
sequences	moiety1	moiety2	moiety3	moiety1	moiety2	moiety3
0	-0.18	0.16	0.02	-0.18	0.16	0.02
1	-0.20	0.21	-0.01	-0.20	0.21	-0.01
2	-0.01	0.17	-0.16	-0.05	0.13	-0.08
3	-0.50	0.30	0.20	0.11	0.18	-0.29
4	-0.27	0.22	0.05	0.39	0.09	-0.49
5	-0.08	0.26	-0.18	-0.05	0.22	-0.18
6	0.37	0.12	-0.49	0.37	0.12	-0.49

References

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4 Computational Chemistry Comparison and Benchmark Database. https://cccbdb.nist.gov/.