Supplementary Material

Boosting Electrochemical Nitrogen Reduction Performance over Binuclear Mo Atoms on N-doped Nanoporous Graphene: A Theoretical Investigation

Ruijie Guo, Min Hu, Weiqing Zhang, Jia He*

Tianjin Key Lab of Advanced Functional Porous Materials, Institute for New Energy Materials and Low-Carbon Technologies, School of Materials Science and Engineering, Tianjin University of Technology, Tianjin 300384, China.

**E-mail: hejia@tjut.edu.cn*

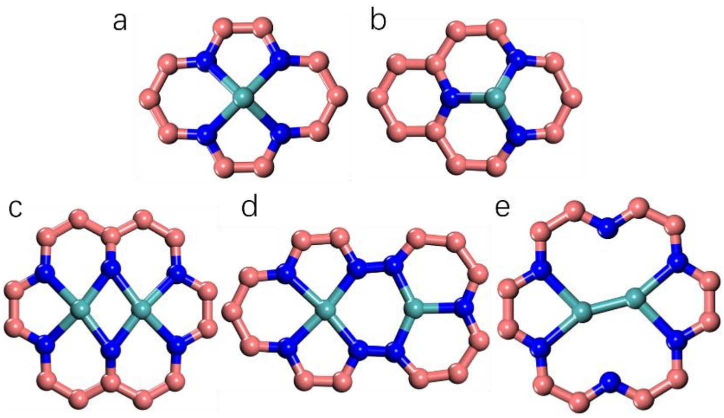


Figure S1. Different possible structures of SAC and BAC for the Mo atoms.

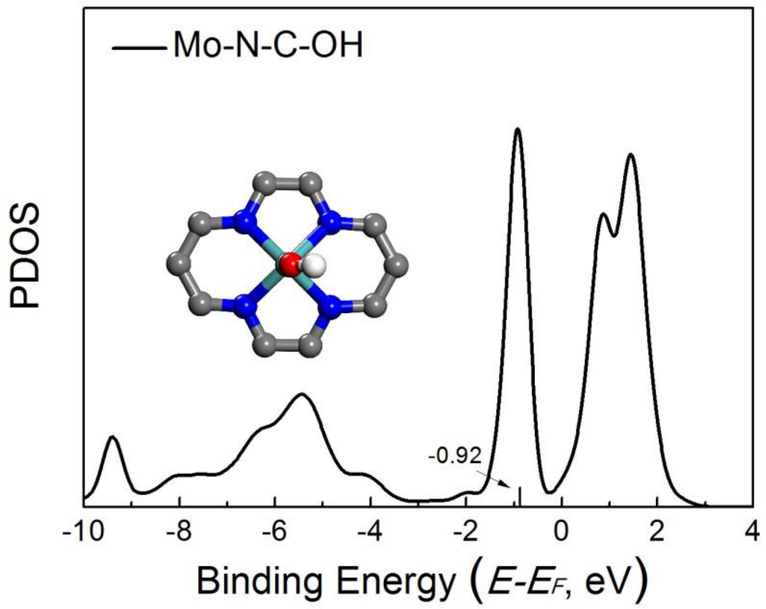


Figure S2. PDOS of Mo atoms on OH pre-adsorbed Mo-N-C catalysts.

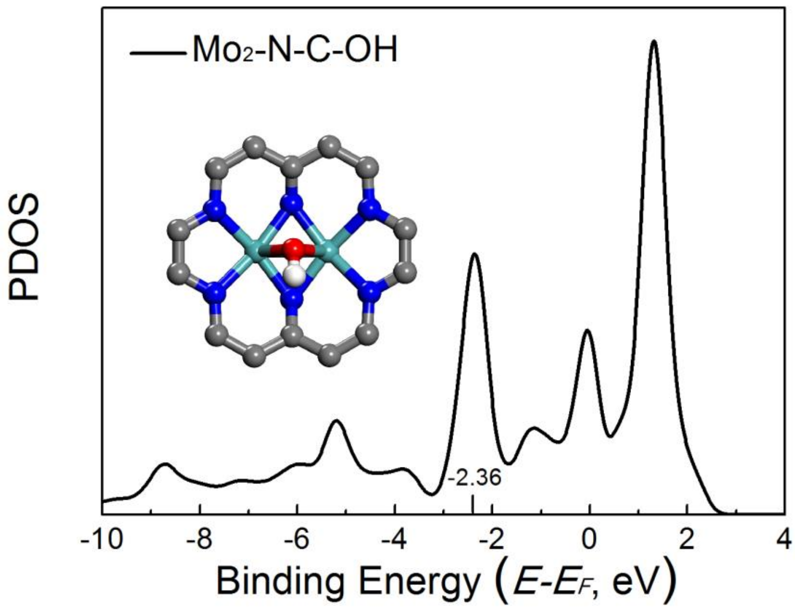


Figure S3. PDOS of Mo atoms on OH pre-adsorbed Mo_2-N-C catalysts.

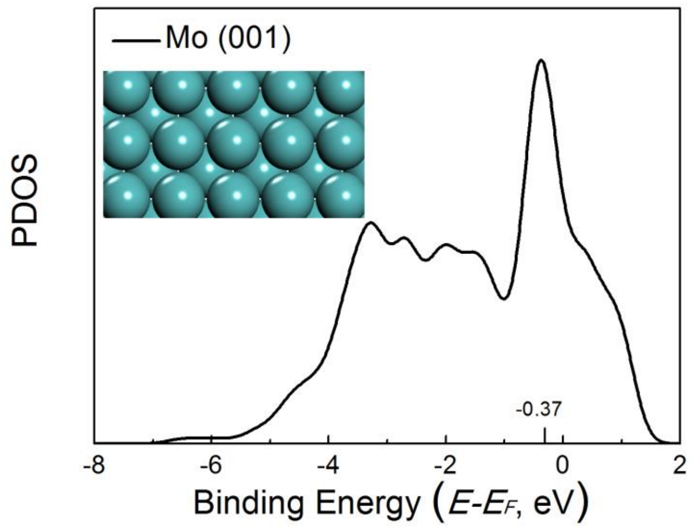


Figure S4. PDOS of Mo atoms on Mo (001) catalysts.

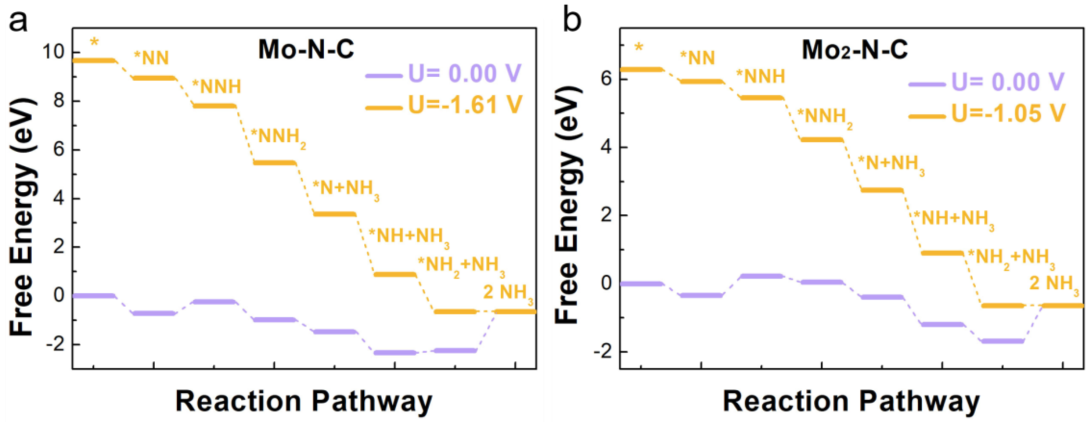


Figure S5. Free-energy diagrams for the NRR on Mo-N-C (**a**) and Mo_2-N-C (**b**) catalysts under different potentials via distal pathway.

Table S1. The adsorption energy (E_{ads}, eV) and the cohesive energy (E_{coh}, eV) of the corresponding SAC and BAC for the Mo atoms in Figure S1.

	E_{ads}	E_{ads} + E_{coh}
a	-6.37	0.45
b	2.72	9.54
c	-18.32	-4.68
d	7.53	21.17
e	4.66	18.30

Table S2. The adsorption energy (E_{ads}, eV) and the cohesive energy (E_{coh}, eV) of the different transition metals doped on N-C nanosheets.

SAC	E_{ads}	E_{ads} + E_{coh}
Cr	-6.84	-2.74
Fe	-7.76	-3.48
Ni	-7.93	-3.49
Cu	-5.22	-1.73
Zn	-3.60	-2.25
Mo	-6.37	0.45
Rh	-7.60	-1.85
BAC	E_{ads}	E_{ads} + E_{coh}

Cr	-15.55	-7.35
Fe	-16.51	-7.95
Ni	-13.10	-4.22
Cu	-11.24	-4.26
Zn	-6.79	-4.09
Mo	-18.32	-4.68
Rh	-16.61	-5.11

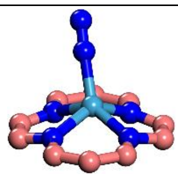
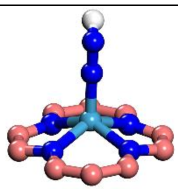
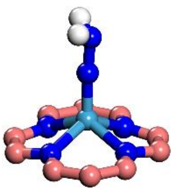
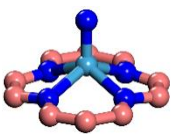
Table S3. Calculated values of $E^{o}_{M^{z+}/M\text{-}N\text{-}C}$ (V).

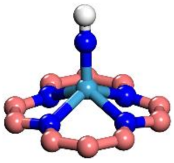
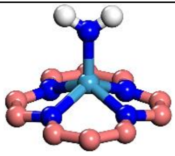
SAC			
metal	$E^{o}_{M^{z+}/M}$	z	$E^{o}_{M^{z+}/M\text{-}N\text{-}C}$
Cr	−0.74	3	0.173
Fe	−0.44	2	1.299
Ni	−0.25	2	1.494
Cu	0.337	2	1.202
Zn	−0.7618	2	0.363
Mo	no data		
Rh	0.76	3	1.376
BAC			
metal	$E^{o}_{M^{z+}/M}$	z	$E^{o}_{M^{z+}/M\text{-}N\text{-}C}$
Cr	−0.74	3	1.709
Fe	−0.44	2	3.533
Ni	−0.25	2	1.859
Cu	0.337	2	2.466
Zn	−0.7618	2	1.282
Mo	no data		
Rh	0.76	3	2.463

Table S4. Adsorption energy (eV) of N_2, NNH, and NH_2 intermediates on the different N-C monolayers.

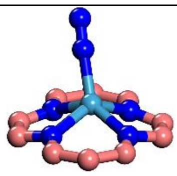
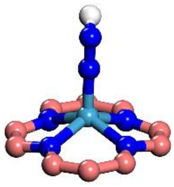
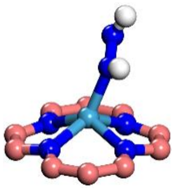
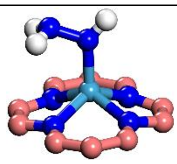
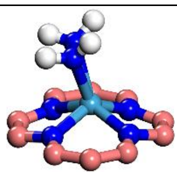
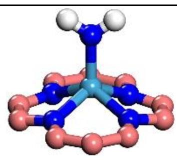
	SAC			BAC		
	N_2	NNH	NH_2	N_2	NNH	NH_2
Cr	-0.35	0.25	-1.02	0.48	0.05	-1.72
Fe	-0.73	1.02	-0.69	-0.58	-0.01	-1.16
Ni	-0.15	1.74	0.66	-0.13	1.67	0.37
Cu	-0.42	1.84	1.01	-0.49	2.24	1.04
Zn	-0.38	2.03	0.06	-0.26	1.71	-0.28
Mo	-1.29	-1.43	-2.78	-0.82	-1.07	-2.25
Rh	-0.09	0.42	-0.69	-0.15	2.01	0.45

Table S5. Atomic configurations and corresponding adsorption energy and free energy correction of each elementary steps, along the different pathways for Mo-N-C.

Distal			
Species	configurations	ΔE (eV)	$\Delta ZPE - T\Delta S + \int C_p dT$ (eV)
NN		-1.25	0.16
NNH		-1.1	0.46
NNH_2		-2.14	0.74
N		-1.44	0.11

NH		-2.58	0.34
NH_2		-2.78	0.6

Alternating

species	configurations	ΔE (eV)	$\Delta ZPE - T\Delta S + \int C_p dT$ (eV)
NN		-1.25	0.16
NNH		-1.1	0.46
NHNH		-0.68	0.74
$NHNH_2$		-2.06	1.01
NH_2NH_2		-1.53	1.43
NH_2		-2.78	0.6

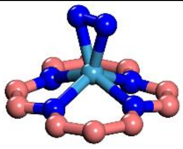
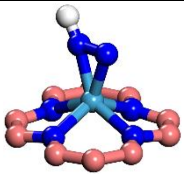
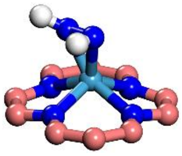
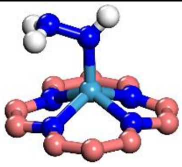
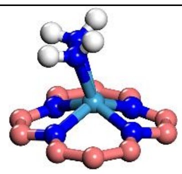
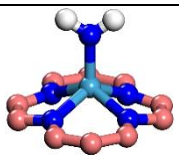
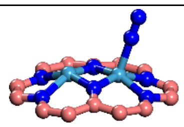
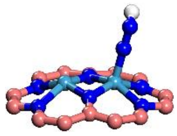
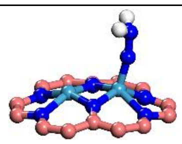
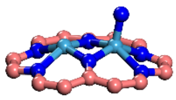
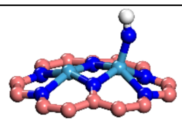
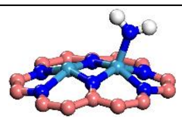
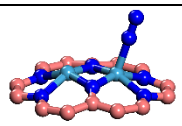
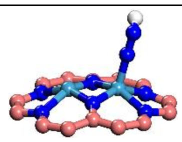
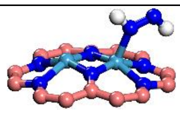
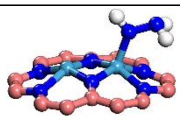
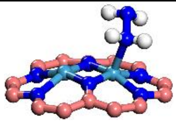
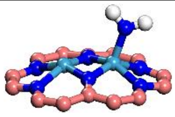
Enzymatic			
species	configurations	ΔE (eV)	ΔZPE − TΔS +∫CpdT (eV)
NN		-1.29	0.19
NNH		-1.43	0.45
NHNH		-1.5	0.74
$NHNH_2$		-2.37	1.08
NH_2NH_2		-1.7	1.42
NH_2		-2.78	0.6

Table S6. Atomic configurations and corresponding adsorption energy and free energy correction of each elementary steps, along the different pathways for Mo_2-N-C.

Distal			
species	configurations	ΔE (eV)	ΔZPE − TΔS +∫CpdT (eV)
NN		-0.82	0.11
NNH		-0.6	0.42
NNH_2		-1.11	0.72
N		-0.31	0.05
NH		-1.41	0.32
NH_2		-2.25	0.64
Alternating			
species	configurations	ΔE (eV)	ΔZPE − TΔS +∫CpdT (eV)
NN		-0.82	0.11
NNH		-0.60	0.42

NHNH		-0.54	0.73
NHNH2		-1.67	1.08
NH2NH2		-1.61	1.38
NH2		-2.25	0.64

Enzymatic

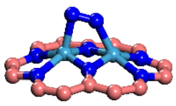
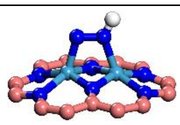
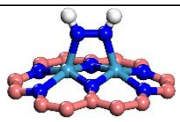
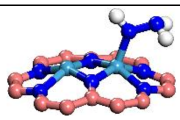
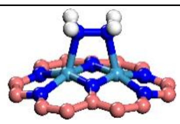
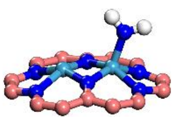
species	configurations	ΔE (eV)	ΔZPE − TΔS +∫CpdT (eV)
NN		-0.32	0.19
NNH		-1.07	0.53
NHNH		-1.92	0.85
NHNH2		-1.59	1.13
NH2NH2		-0.98	1.34
NH2		-2.25	0.64

Table S7. Different two-dimensional NRR electrocatalysts reported in the literature.

Electrocatalysts	$\Delta G_{[*NH2-NH3(g)]}$ (eV)	References
Mo-B-N	~ 0.98	*J. Am. Chem. Soc.* **2017,** *139*, 12480-12487.
BC_3	~ 2.13	*Joule* **2018,** *2*, 1–13
NPC-pyridinic N	~ -0.15	*ACS Catal.* **2018,** *8*, 1186-1191.
B_{int}-doped C_2N	3.03	*J. Mater. Chem. A* **2019,** *7*, 2392-2399.
Ru/Bα	0.26	*J. Mater. Chem. A* **2019,** *7*, 4771-4776.
Boron Antisites of BNNT	1.53	*Phys. Chem. Chem. Phys.* **2017,** *19*, 15377-15387.
Mo_2-N-C	1.05	This work