

Supporting Information

for

Discovery of cobweb-like MoC₆ and its application for nitrogen fixation

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Calculation method

The spin-polarized DFT calculations with norm-conserving pseudopotentials as implemented in the CASTEP code are performed in this work.^{1, 2} The exchange-correlation effects are described by the generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof functional (PBE).³ The minimum energies for all structures are obtained until energy, maximum force, and maximum displacement have become less than 1×10^{-5} eV/atom, 0.03 eV/Å, and 0.001 Å, respectively. The calculations are carried out using plane-wave cutoff energy of 650 eV. To accurately describe the van der Waals interactions, the DFT-D method within the Grimme scheme is used in all calculations for dispersion corrections.⁴ Concerning with the properties of charge transfers, atom charges would be calculated via the Mulliken population analysis.⁵ For transition states (TS) searching, the calculation first performed a linear synchronous transit (LST) maximum, which is followed by an energy minimization in directions conjugating to the reaction pathway.⁶ The TS approximation obtained via LST/optimization is then used to perform a quadratic synchronous transit (QST) maximization to find more accurate transitional states. The $\sqrt{3} \times \sqrt{3}$ supercell of MoC₆ is used for evaluating the stability and the catalytic activity. The corresponding k-point sampling of the Brillouin zone is set as $3 \times 3 \times 1$ grid. To match the lattices between MoC₆ and Cu(111), we apply 2×2 supercell of MoC₆ and 5×5 supercell of Cu(111) for designing the synthetic route.

The cohesive energy value E_b is defined as $E_b = (E_{\text{MoC}_6} - 2E_{\text{Mo}} - 12E_C)/14$, where E_{MoC_6} , E_{Mo} and E_C are the total energies of MoC₆ unit cell, the free Mo atom and the

free C atom, respectively. The adsorption energy values of ΔE_{M^*} are determined by $\Delta E_{M^*} = (E_{M^*} - E_{\text{sub}} - nE_M)/n$, where E_{M^*} , E_{sub} and E_M are the total energies of the adsorbed system, the isolate substrate and the adsorbates, respectively. Moreover, free energies of the NRR intermediates are calculated based on a computational hydrogen electrode (CHE) model suggested by Nørskov et al.⁷ Free energy change (ΔG) is determined by $\Delta G(U) = \Delta E + \Delta ZPE - T\Delta S - neU$ at pH = 0, where ΔE is the reaction energy, ΔZPE is the zero point energy, T is temperature, ΔS is the change in the entropy, n is the number of electrons and U is the applied potential involved in the reaction.

Figure S1. Atomic configuration of a bare 2×2 GY sheet, for which sp - and sp^2 -hybridized C atoms coexist. The grey balls represent the C atoms. The primitive cell of the GY sheet is enclosed by the dashed lines.

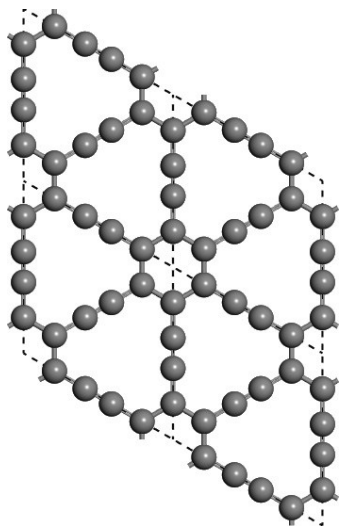


Figure S2. Both side and top views of the N_2 adsorption on the bridge and top site of MoC_6 . The blue and dark blue balls represent Mo and N atoms.

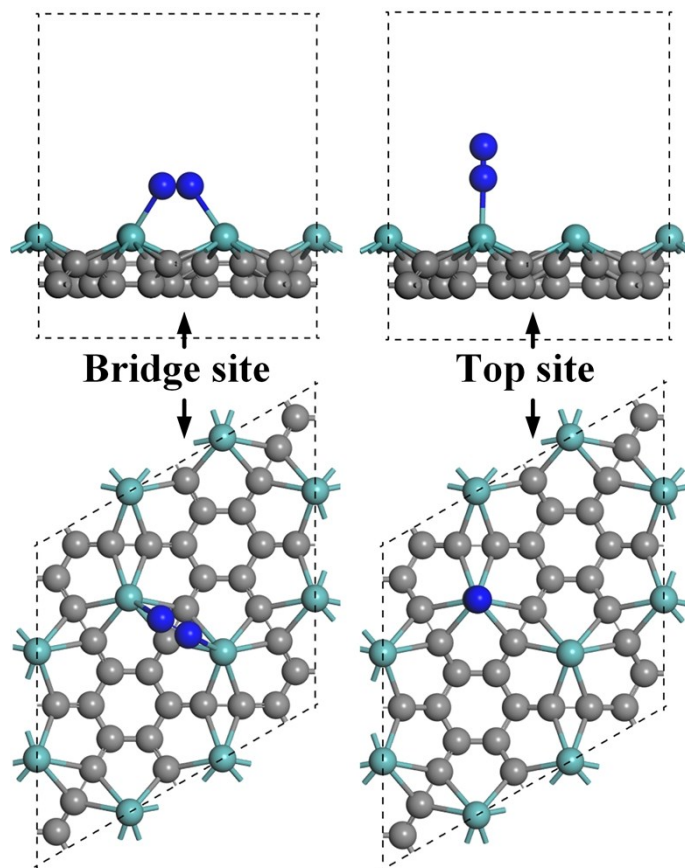


Figure S3. The reaction path of N-N bond breakage for the intermediate state of N_2^* .

TS indicates the corresponding transition state.

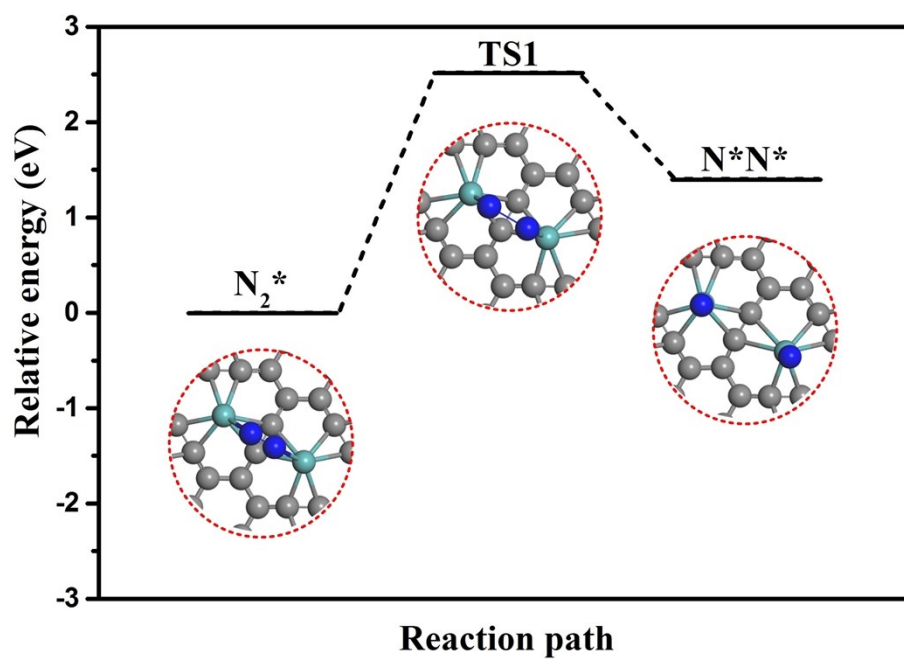


Figure S4. The reaction path of N-N bond breakage for the intermediate state of NNH^* .

The white balls represent H atoms.

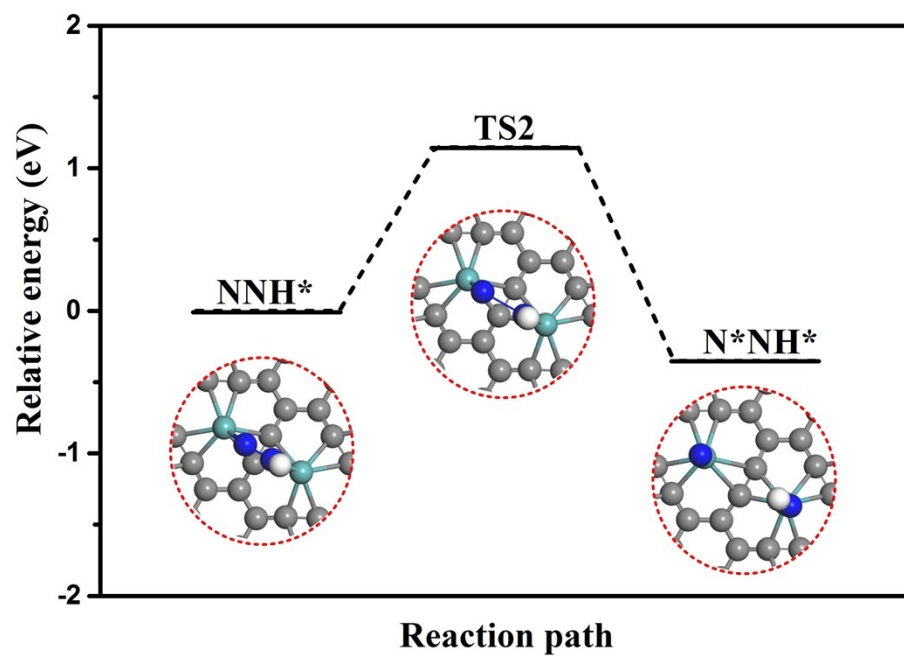


Figure S5. The reaction path of N-N bond breakage for the intermediate state of NHNH^* .

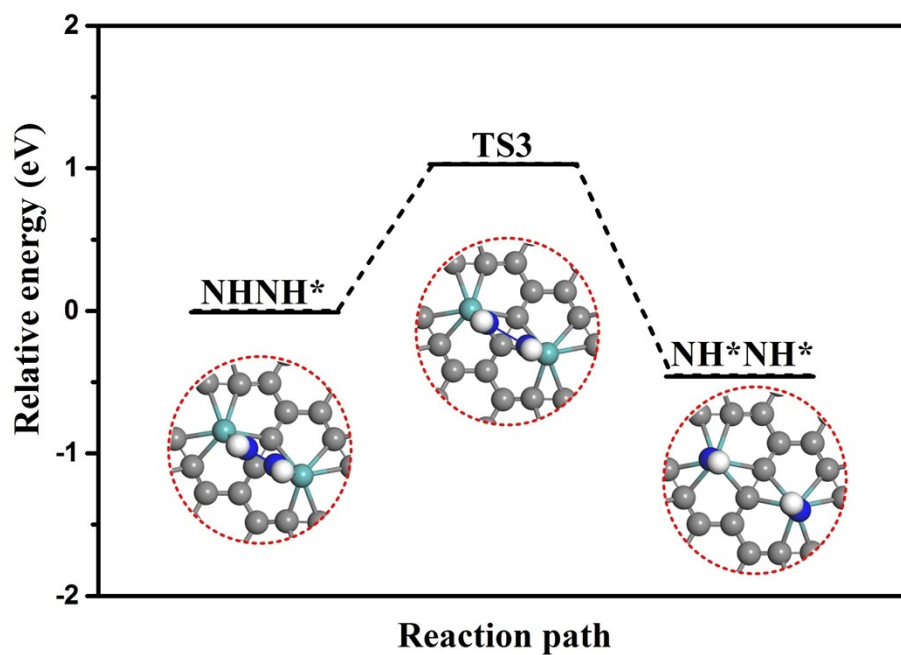


Figure S6. The reaction path of N-N bond breakage for the intermediate state of NHNH_2^* .

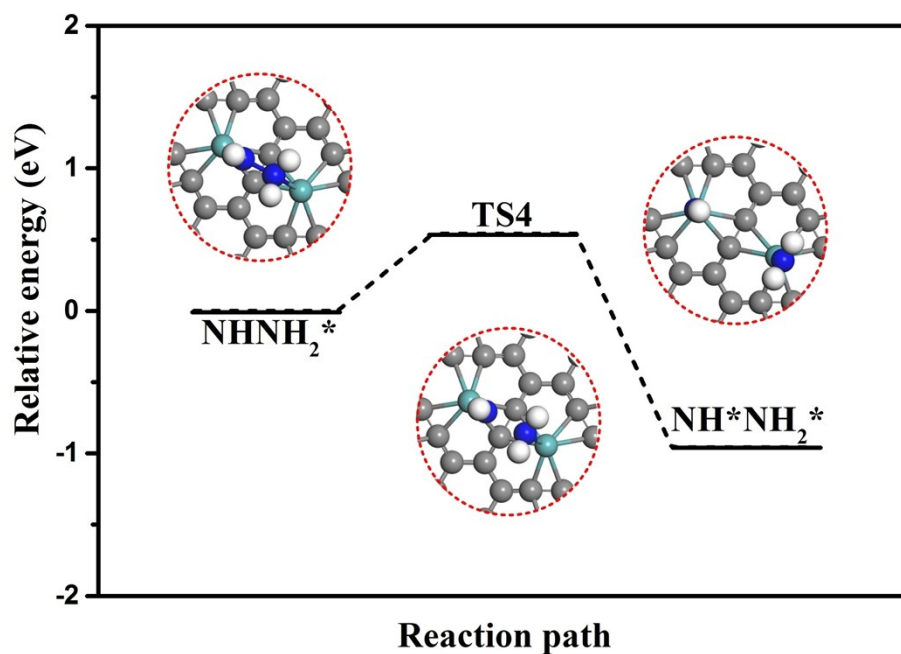


Figure S7. The reaction path of N-N bond breakage for the intermediate state of NH_2NH_2^* .

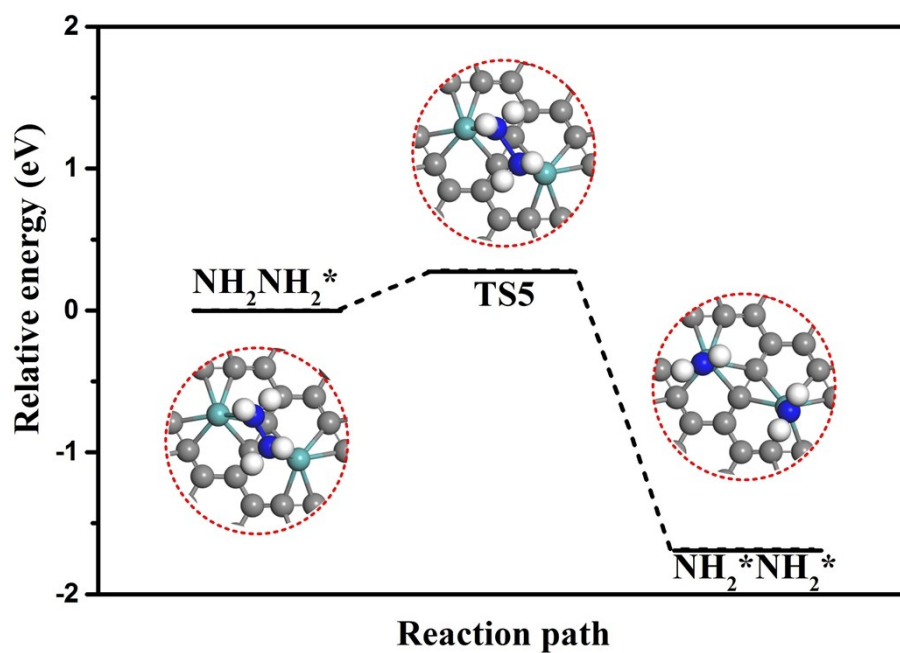


Figure S8. The distal mechanism for nitrogen reduction reaction (NRR) on MoC_6 . The free energy profiles and the structures of intermediates are shown in the reaction path.

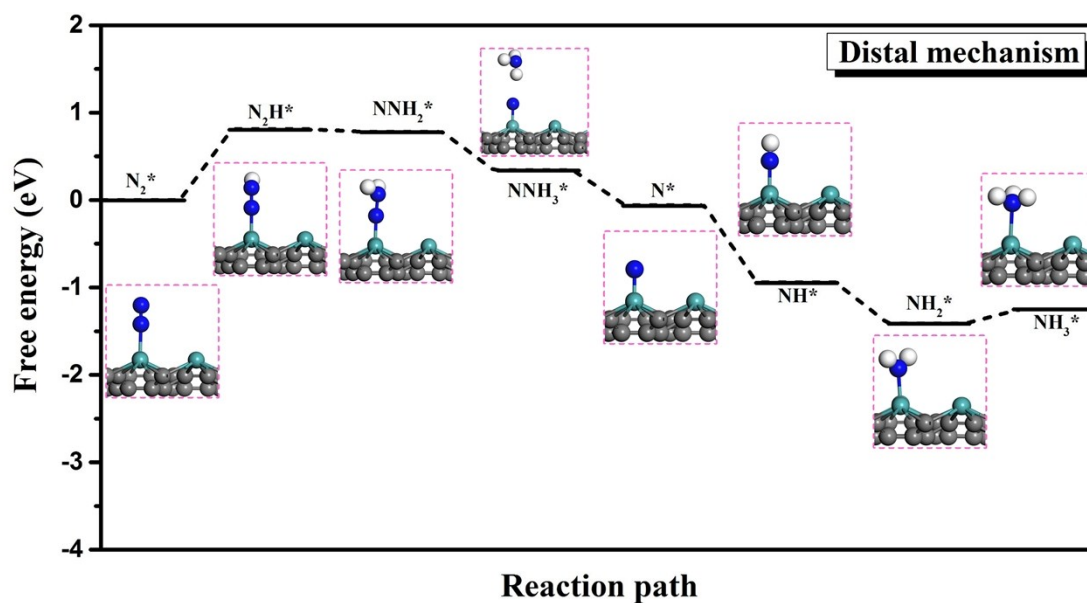
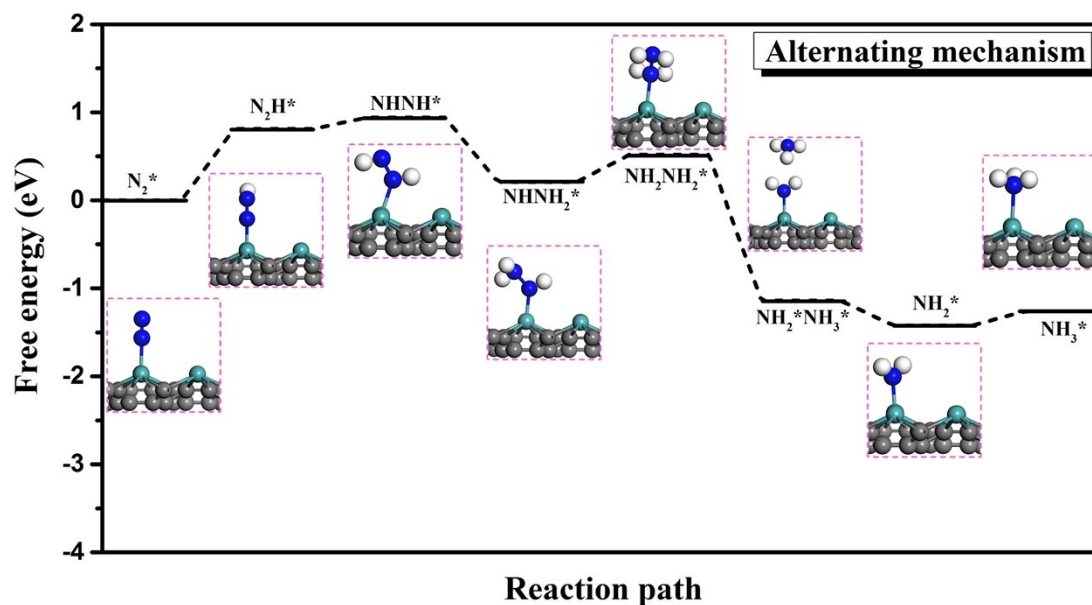


Figure S9. The alternating mechanism for nitrogen reduction reaction (NRR) on MoC₆. The free energy profiles and the structures of intermediates are shown in the reaction path.



References

1. M. D. Segall, Philip J. D. Lindan, M. J. Probert, C. J. Pickard, P. J. Hasnip, S. J. Clark and M. C. Payne, *J. Phys. Condens. Matter.*, 2002, **14**, 2717-2744.
2. D. R. Hamann, M. Schlüter and C. Chiang, *Phys. Rev. Lett.*, 1979, **43**, 1494-1497.
3. J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865-3868.
4. S. Grimme, *J. Comput. Chem.*, 2006, **27**, 1787-1799.
5. M. D. Segall, R. Shah, C. J. Pickard and M. C. Payne, *Phys. Rev. B*, 1996, **54**, 16314-16317
6. T. A. Halgren and W. N. Lipscomb, *Chem. Phys. Lett.*, 1977, **49**, 225-232.
7. E. Skulason, T. Bligaard, S. Gudmundsdottir, F. Studt, J. Rossmeisl, F. Abild-Pedersen, T. Vegge, H. Jonsson and J. K. Nørskov, *Phys. Chem. Chem. Phys.*, 2012, **14**, 1235-1245.

