Supporting Information

for

Activated Basal Plane of WS_2 by Intrinsic Defects as a Catalyst for Electrocatalytic Nitrogen Reduction Reaction

X. Yao, Z. W. Chen, Y. R. Wang, X. Y. Lang, W. Gao, Y. F. Zhu* and Q. Jiang*

Key Laboratory of Automobile Materials, Ministry of Education (Jilin University), School of Materials Science and Engineering, Jilin University, Changchun 130022, China

* Corresponding authors: Y. F. Zhu; Q. Jiang. Fax: 86-431-85095876.

E-mails: yfzhu@jlu.edu.cn; jiangq@jlu.edu.cn

Computational details of formation energies

Our calculations give that $E_{S(single)}$ = -397.990901 Ha, $E_{W(single)}$ = -137.310857 Ha, and $E_{m\text{-}WS_2}$ = -933.7120494 Ha. According to the relationship that $E_{Bond} = (E_{m\text{-}WS_2} - E_{W(single)} - 2E_{S(single)})/3$, it gives E_{Bond} = -0.1397968 Ha, and then E_{S0} = -398.1306978 Ha and E_{W0} = -137.4506538 Ha. Moreover, the E_{defect} values have been calculated to be -14678.5807089 Ha for W_S, -14280.4258873 Ha for W_{S2}, -14541.2188587 Ha for V_S, and -14143.0592056 Ha for V_{S2}. Based on the equation that $E_f = E_{defect} - N_S \times E_{S0} - N_W \times E_{W0}$, it has E_f = 0.1320375, 0.1561613, 0.0432339 and 0.0721892 Ha for W_S, W_{S2}, V_S and V_{S2}, respectively. Namely, E_f = 3.59 eV for W_S, 4.25 eV for W_{S2}, 1.18 eV for V_S, and 1.96 eV for V_{S2}.

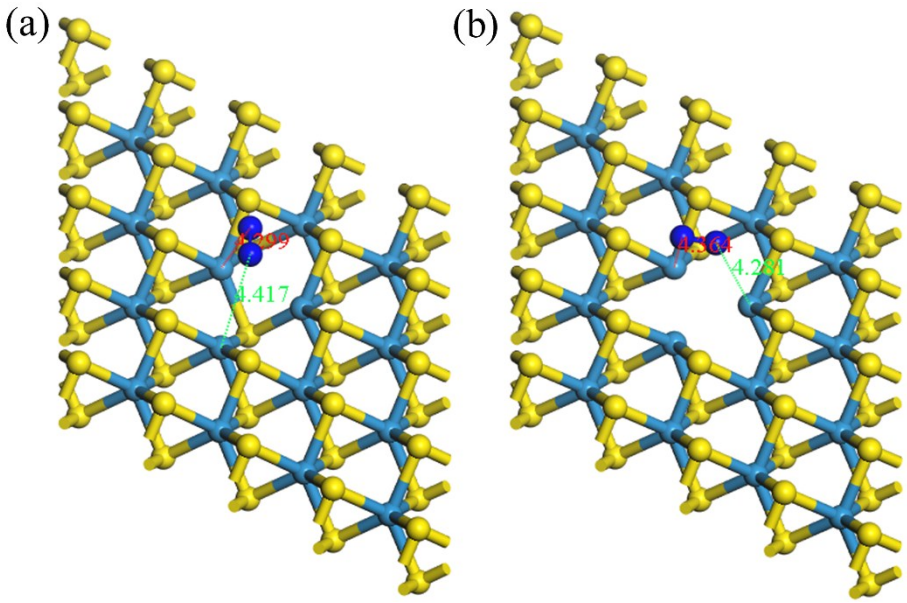

Fig. S1 The optimized structures of N_2 adsorbed on (a) V_S and (b) V_{S2}, including the nearest distances between any N atom and any exposed W atom.

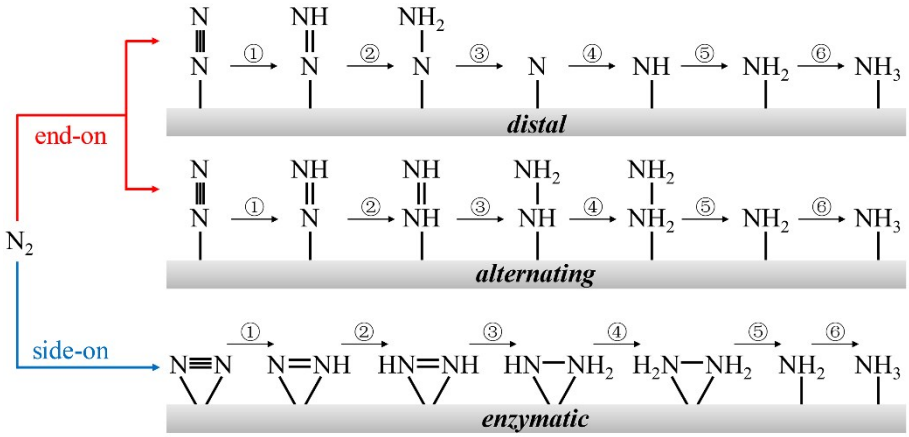

Fig. S2 Schematic illustration of the distal, alternating, and enzymatic mechanisms for the reduction of N_2 to NH_3.

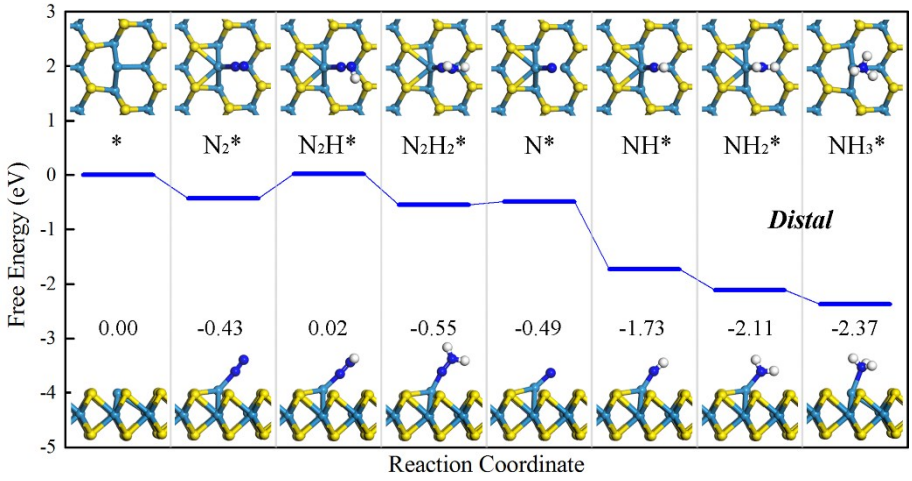

Fig. S3 Free energy profile and the corresponding geometric structures of intermediate states of NRR on W_{S2} at an applied potential of 0 V for the distal mechanism.

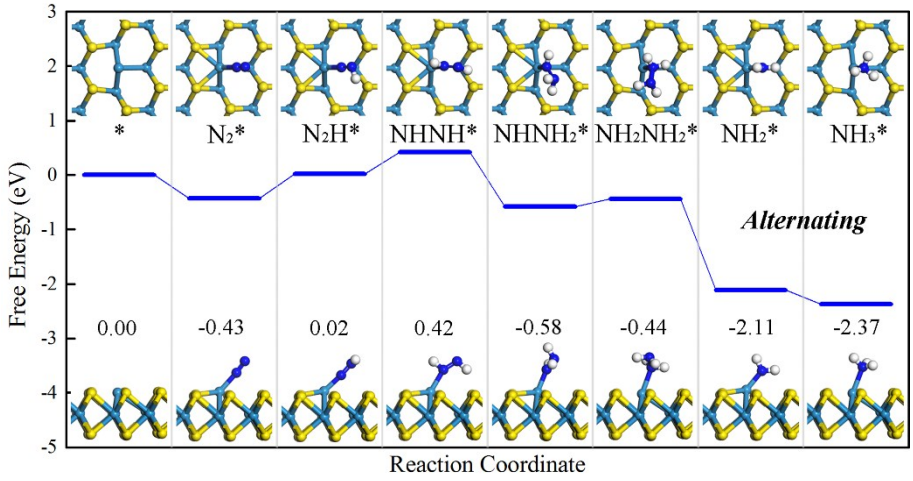

Fig. S4 Free energy profile and the corresponding geometric structures of intermediate states of NRR on W_{S2} at an applied potential of 0 V for the alternating mechanism.

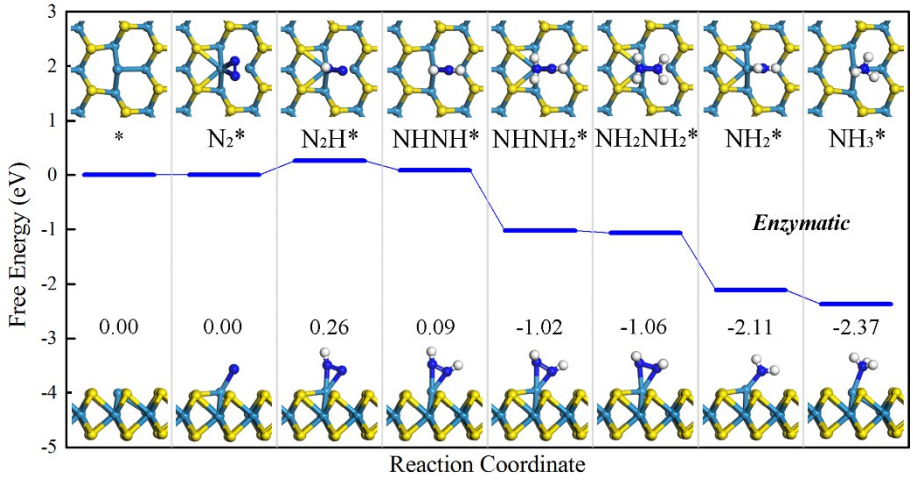

Fig. S5 Free energy profile and the corresponding geometric structures of intermediate states of NRR on W_{S2} at an applied potential of 0 V for the enzymatic mechanism. [a]

[a] The adsorption of side-on adsorbed N_2 on W_{S2} (E_{ad} = -0.39 eV) is weaker than that of H atom (E_{ad} = -0.50 eV), suggesting that the enzymatic mechanism is significantly difficult to be present for NRR on W_{S2}.

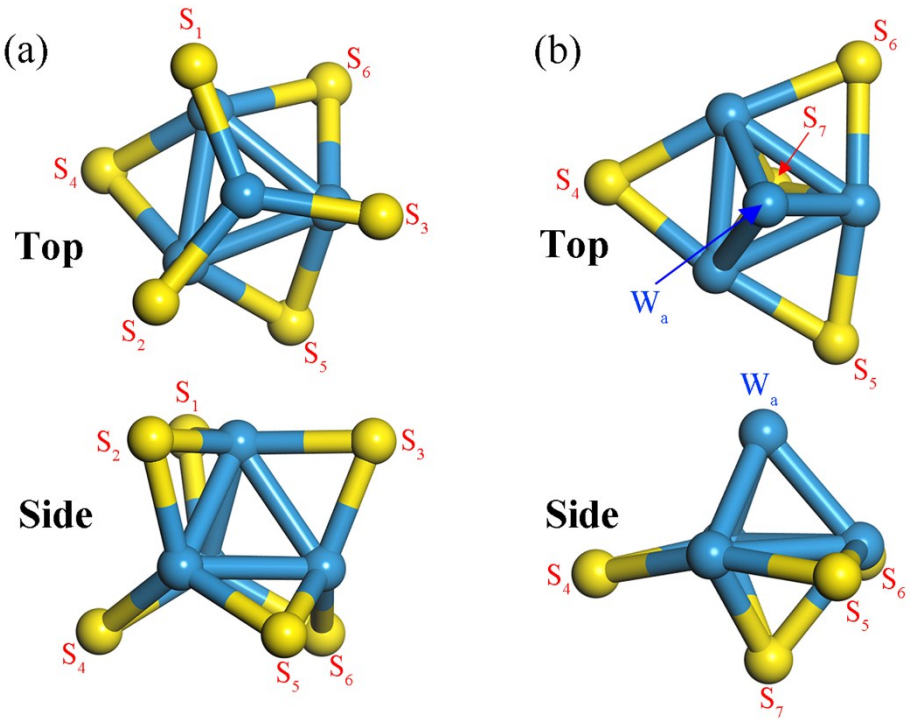

Fig. S6 The top (the upper) and side views (the lower) of (a) W_4S_6 cluster and (b) W_4S_4 cluster. [a]

[a] To model the coordination environment of active W_0 atom in W_S, a tetrahedron containing as least four W atoms is required. According to the literatures,[1, 2] W_4S_6 is the most stable one among W_4S_x clusters with x = 1-12. Considering that active W atom only form bonds with W atoms while other W atoms should be bonded to as many S atoms as possible, S_1, S_2, and S_3 atoms in W_4S_6 are removed and S_7 atom is added to fabricate W_4S_4 cluster. In addition, the active W atom (W_a) of W_4S_4 is positive with the charge of 0.28, similar to the active W_0 atom (0.29) of W_S.

References

1. P. Murugan, V. Kumar, Y. Kawazoe and N. Ota, *J. Phys. Chem. A*, 2007, **111**, 2778-2782.
2. N. Bertram, Y. D. Kim, G. Ganteför, Q. Sun, P. Jena, J. Tamuliene and G. Seifert, *Chem. Phys. Lett.*, 2004, **396**, 341-345.