Supporting Information

# Isolated Boron Sites for Electroreduction of Dinitrogen to Ammonia

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## Supplementary Figures

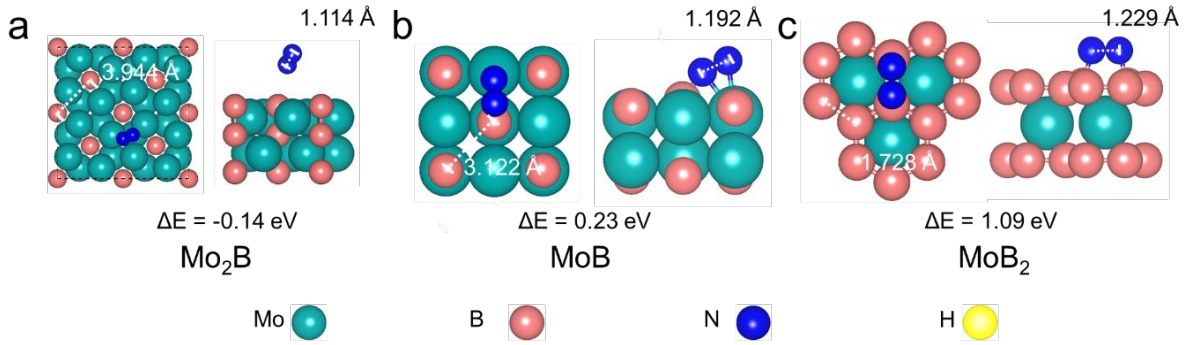


**Figure S1** Atomic configurations of $N_2$ side-on adsorption on (a) $Mo_2B$, (b) α-MoB and (c) $MoB_2$.

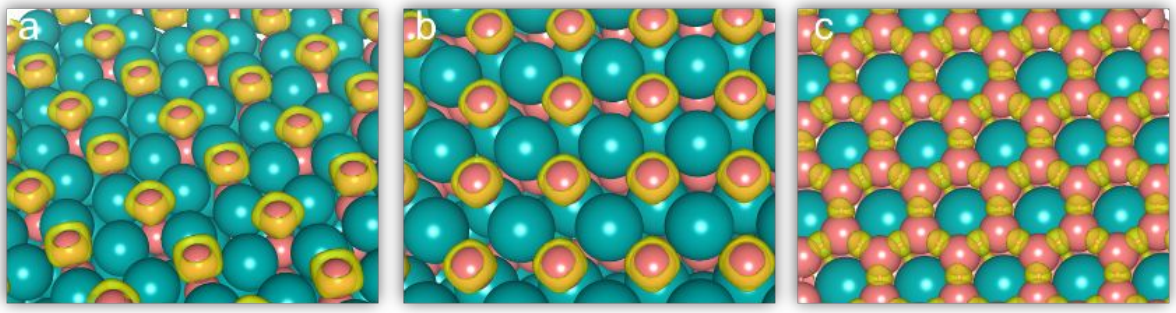


**Figure S2.** The electron localization function (ELF) of (a) $Mo_2B$, (b) α-MoB and (c) $MoB_2$. The value of isosurface is set to 0.75 a.u.

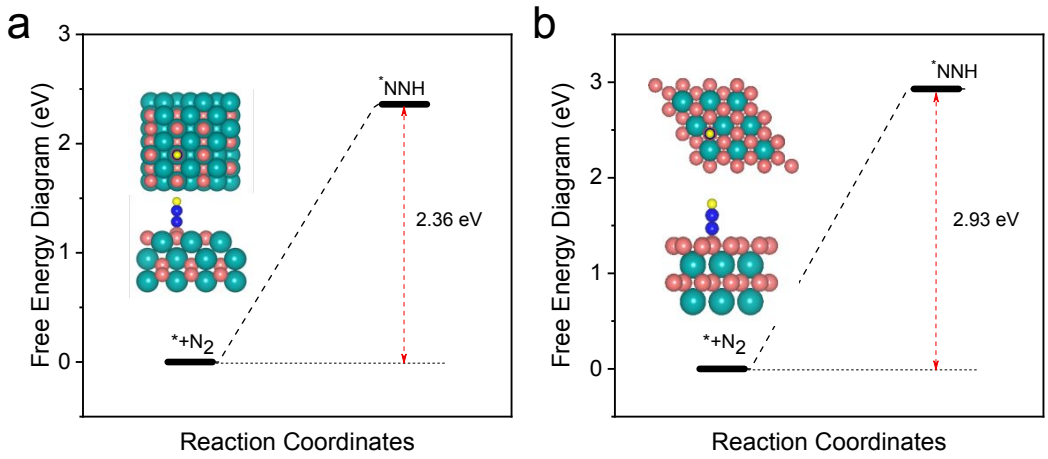


**Figure S3.** Free energy change of the first protonation step on (a) α-MoB and (b) $MoB_2$ via a distal or alternating pathway at 0V vs standard hydrogen electrode (SHE).

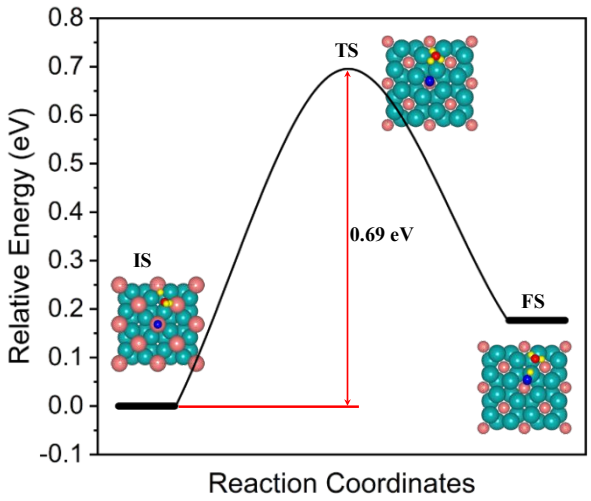


**Figure S4.** Kinetic barriers for the first protonation step on $Mo_2B$. Insets are the corresponding structures of initial (IS), transition (TS), and final states (FS). Cyan, pink, blue, red and white balls represent the Mo, B, N, O and H atoms, respectively.

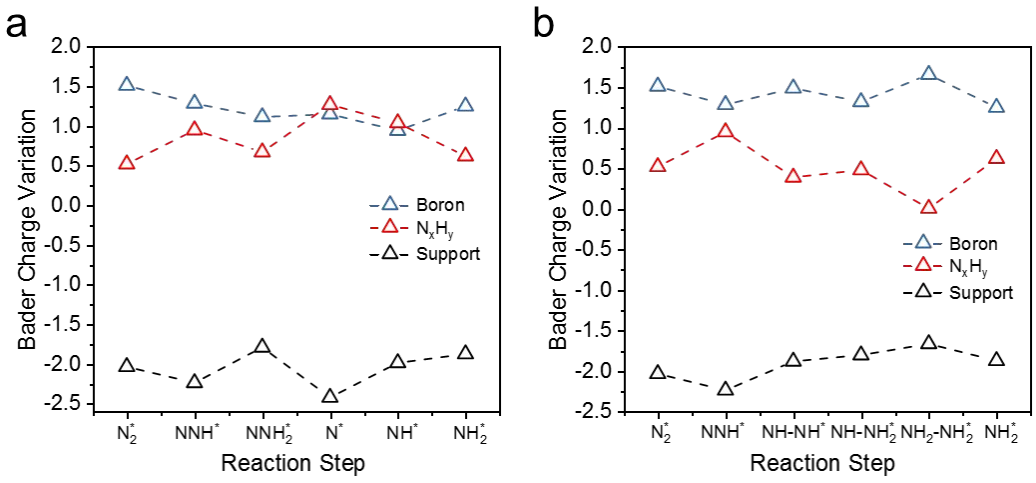


**Figure S5.** (a) Bader charge variation of three moieties along the (a) distal and (b) alternating pathway. Positive and negative value indicate electron accumulation and loss, respectively.

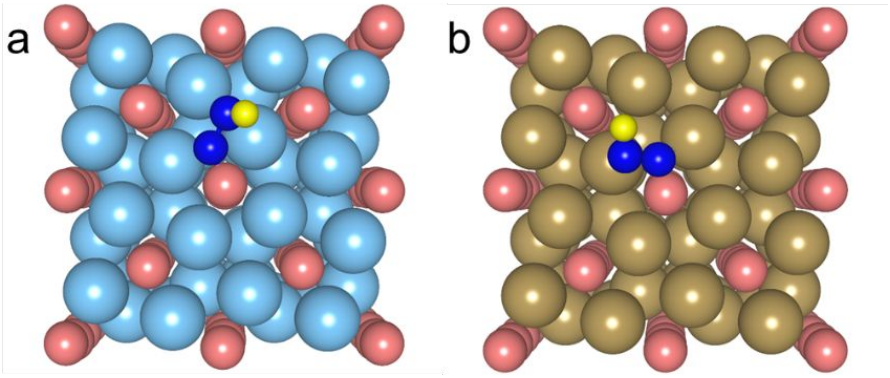


**Figure S6.** Atomic configuration of *NNH adsorption on (a) $Ti_2B$ and (b) $Ta_2B$.

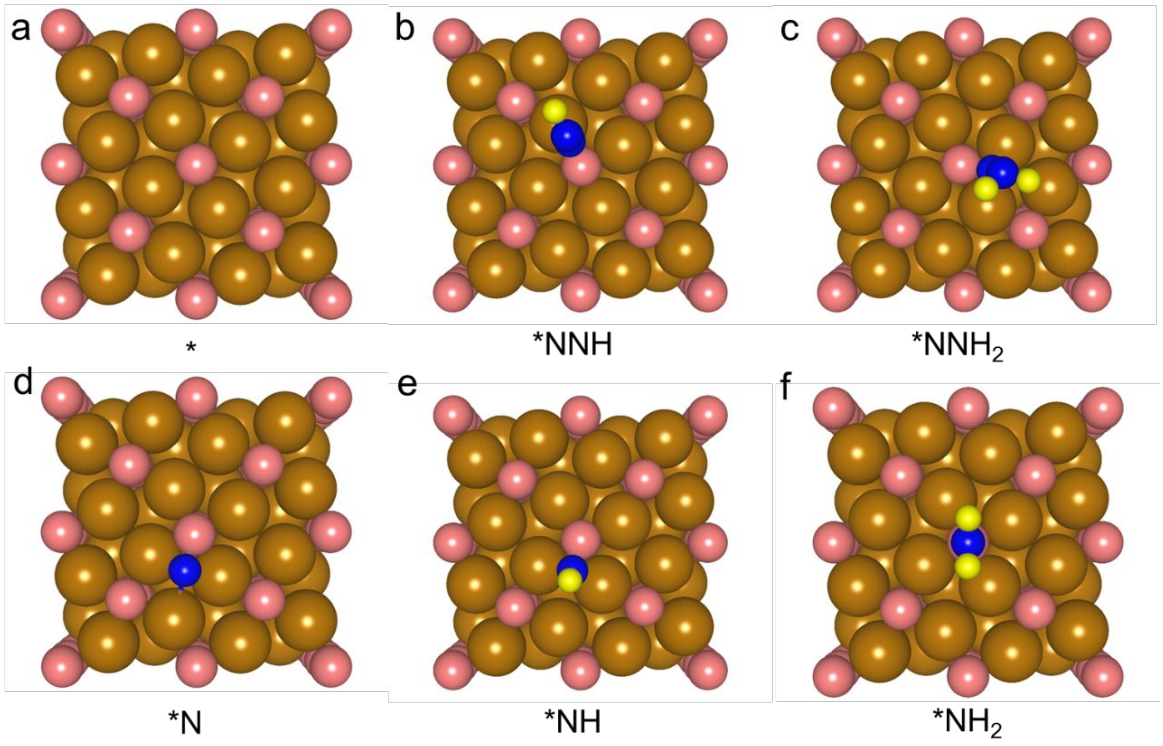


**Figure S7.** Atomic configurations of reaction intermediates via distal pathway of $Fe_2B$.

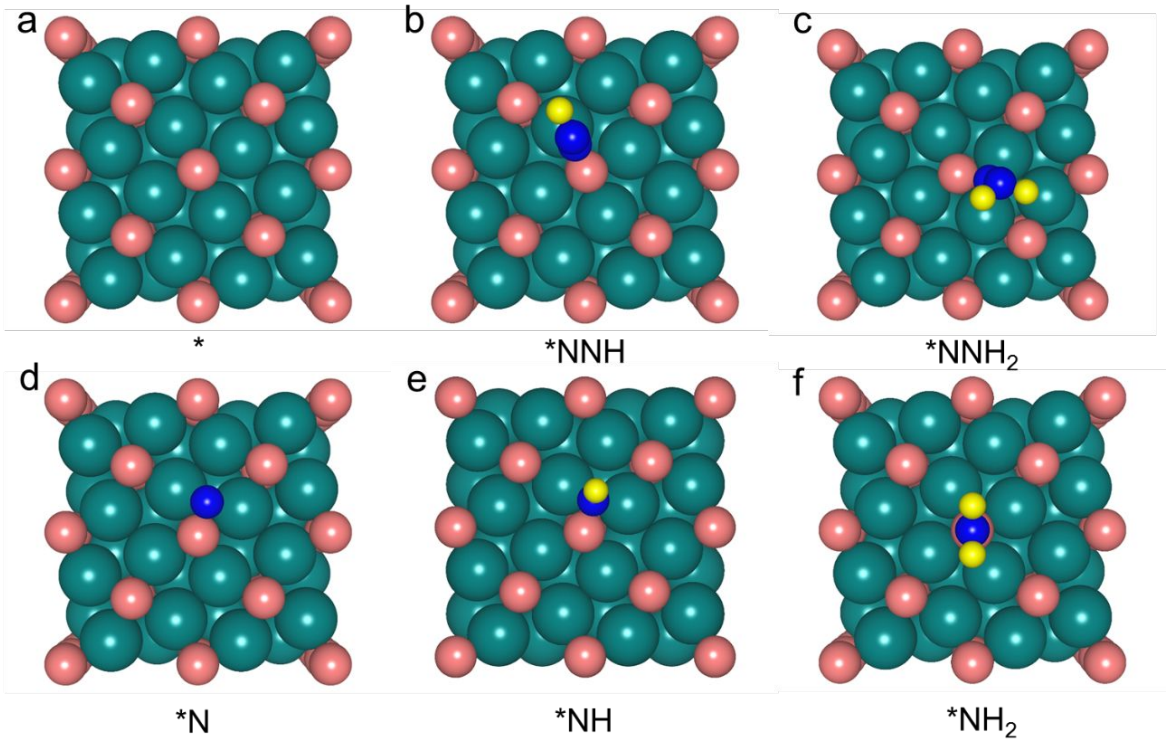

**Figure S8.** Atomic configurations of reaction intermediates via distal pathway of $Co_2B$.

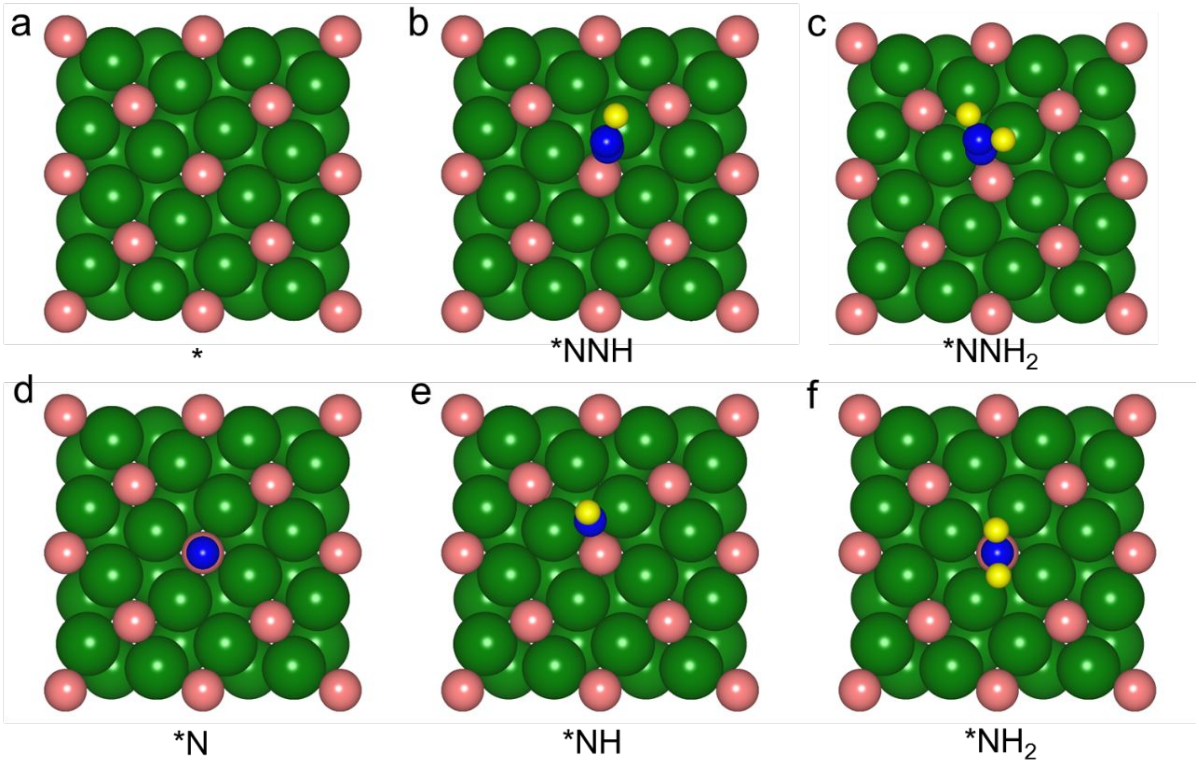


**Figure S9.** Atomic configurations of reaction intermediates via distal pathway of $Cr_2B$.

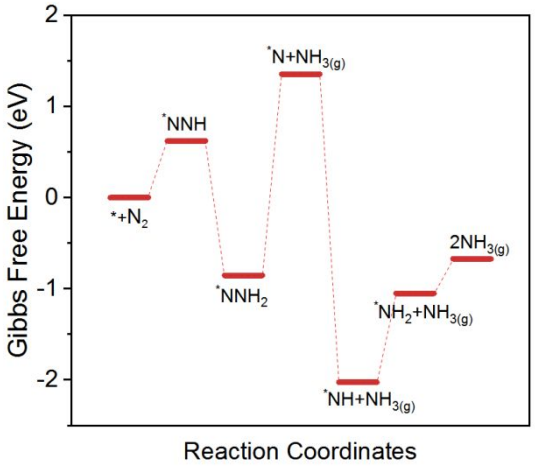


**Figure S10.** The free energy diagrams of eNRR via a distal pathway on $Cr_2B$. The third protonation step is the potential determining step with a free energy change of 2.21 eV.

**Supplementary Tables**

**Table S1.** Crystallographic information for the studied molybdenum borides.

| **Phase** | **$Mo_2B$** | **α-MoB** | **$MoB_2$** |
|---|---|---|---|
| **Crystal system** | Tetragonal | Tetragonal | Hexagonal |
| **Space group** | I4/mcm | $I4_1$/amd | P6/mmm |
| **a(Å)** | 5.56 | 3.13 | 3.03 |
| **b(Å)** | 5.56 | 3.13 | 3.03 |
| **c(Å)** | 4.78 | 17.05 | 3.35 |

**Table S2.** Crystallographic information for the studied molybdenum borides.

| **$M_2B$** | **$Ti_2B$** | **$Cr_2B$** | **$Mn_2B$** | **$Fe_2B$** | **$Co_2B$** | **$Ni_2B$** | **$Ta_2B$** | **$W_2B$** |
|---|---|---|---|---|---|---|---|---|
| **a(Å)** | 5.81 | 5.51 | 5.07 | 5.06 | 4.95 | 4.97 | 5.81 | 5.59 |
| **b(Å)** | 5.81 | 5.51 | 5.07 | 5.06 | 4.95 | 4.97 | 5.81 | 5.59 |
| **c(Å)** | 4.91 | 4.28 | 4.10 | 4.24 | 4.27 | 4.26 | 4.91 | 4.80 |

**Table S3**. Calculated surface energies, $\boldsymbol{\gamma_s}$ , for the studied metal borides.

| Materials | $Mo_2B$ | α-MoB | $MoB_2$ | $Cr_2B$ | $Mn_2B$ | $Fe_2B$ | $Co_2B$ | $Ni_2B$ | $W_2B$ |
|---|---|---|---|---|---|---|---|---|---|
| Surface Energy (eV/ Å) | 0.202 | 0.180 | 0.155 | 0.285 | 0.346 | 0.277 | 0.219 | 0.138 | 0.168 |
| Surface Energy ($J/m^2$) | 3.242 | 2.880 | 2.482 | 4.559 | 5.539 | 4.443 | 3.501 | 2.214 | 2.699 |

**Table S4.** The geometric and electronic structure of molybdenum borides.

| **Electrocatalysts** | **$p_x$ filling** | **$p_y$ filling** | **$p_z$ filling** |
|---|---|---|---|
| **$Mo_2B$** | 0.407 | 0.406 | 0.288 |
| **α-MoB** | 0.369 | 0.362 | 0.293 |
| **$MoB_2$** | 0.413 | 0.415 | 0.378 |