Supporting Information

Computational screening of MBene monolayers with high electrocatalytic activity for nitrogen reduction reaction

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1. Definition of energy

The exfoliation energy for MB ((M=Sc, Ti, V, Cr, Mo, and W) monolayer was respectively calculated with the following equations as follows

$$E_{\text{exf}}(M_2AB_2) = E(M_2AB_2) + E(Al) - E(MAB), \quad (1)$$

$$E_{\text{exf}}(M_2B_2) = E(M_2B_2) + E(Al) - E(M_2AB_2), \quad (2)$$

$$E_{\text{exf}}(MB) = 2E(MB) - E(M_2B_2), \quad (3)$$

where the $E(MAB)$, $E(M_2AB_2)$, $E(M_2B_2)$, $E(MB)$, and $E(Al)$ are the total energy of MAB, M_2AB_2, M_2B_2, MB (M=Sc, Ti, V, Cr, Mo, and W; A=Al), and exfoliated Al, respectively.

2. Additional information

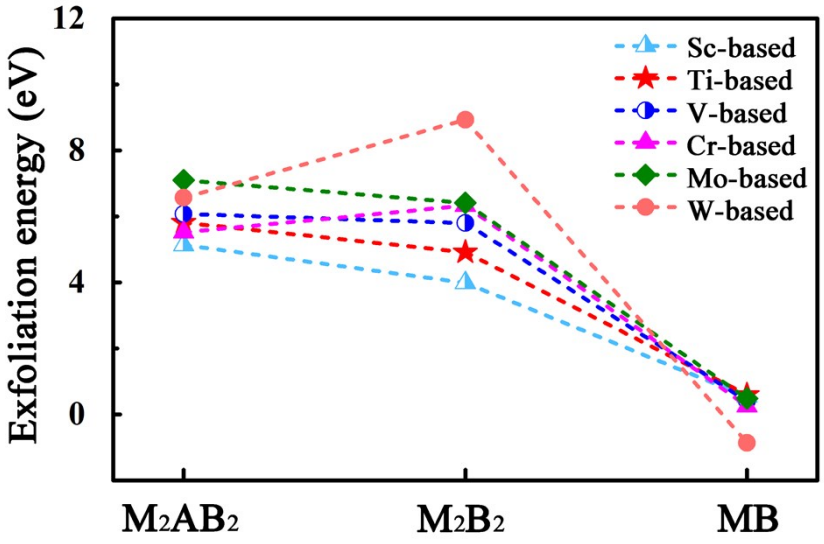

Fig. S1 The calculated exfoliation energy from MAB to M_2AB_2, and from M_2AB_2 to M_2B_2, and from M_2B_2 to MB (M=Sc, Ti, V, Cr, Mo, and W; A=Al).

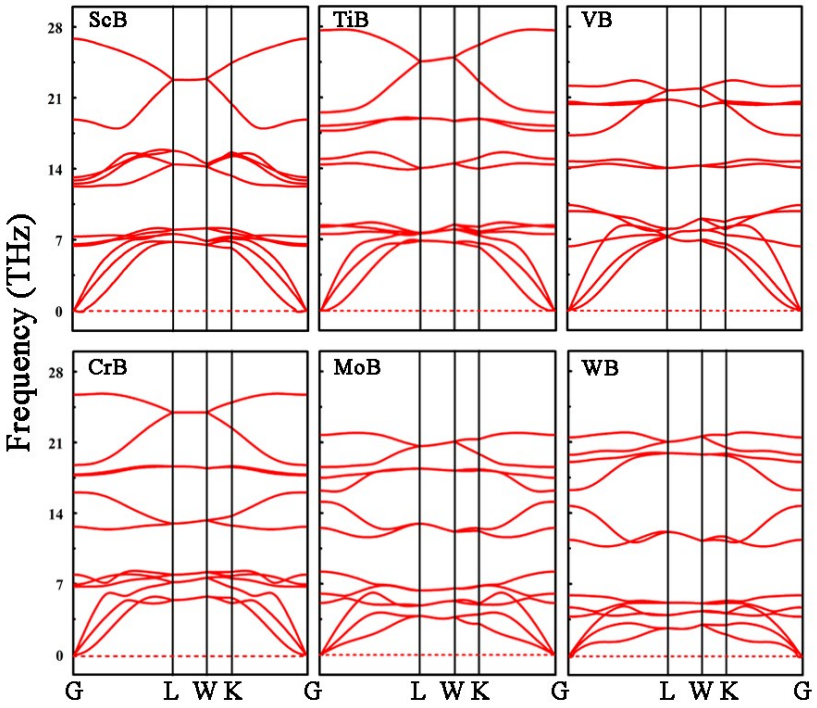

Fig. S2 The calculated phonon dispersion curves of MB (M=Sc, Ti, V, Cr, Mo, and W) monolayers.

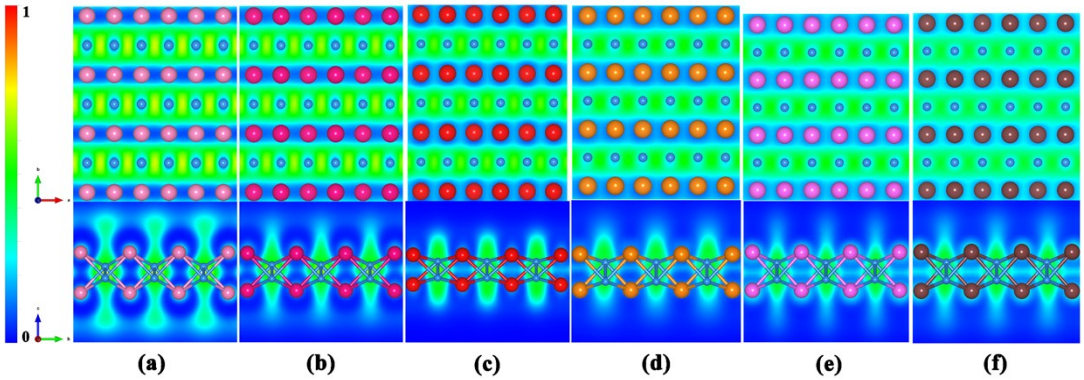

Fig. S3 The electron localization functions (ELFs) of (a) ScB, (b) TiB, (c) CrB, (d) MoB, (e) WB, (f) VB monolayers from top (001) and side (100) views. ELF=0 means that the electrons are completely delocalized or do not exist, and ELF=1 illustrates that the electrons are completely localized.

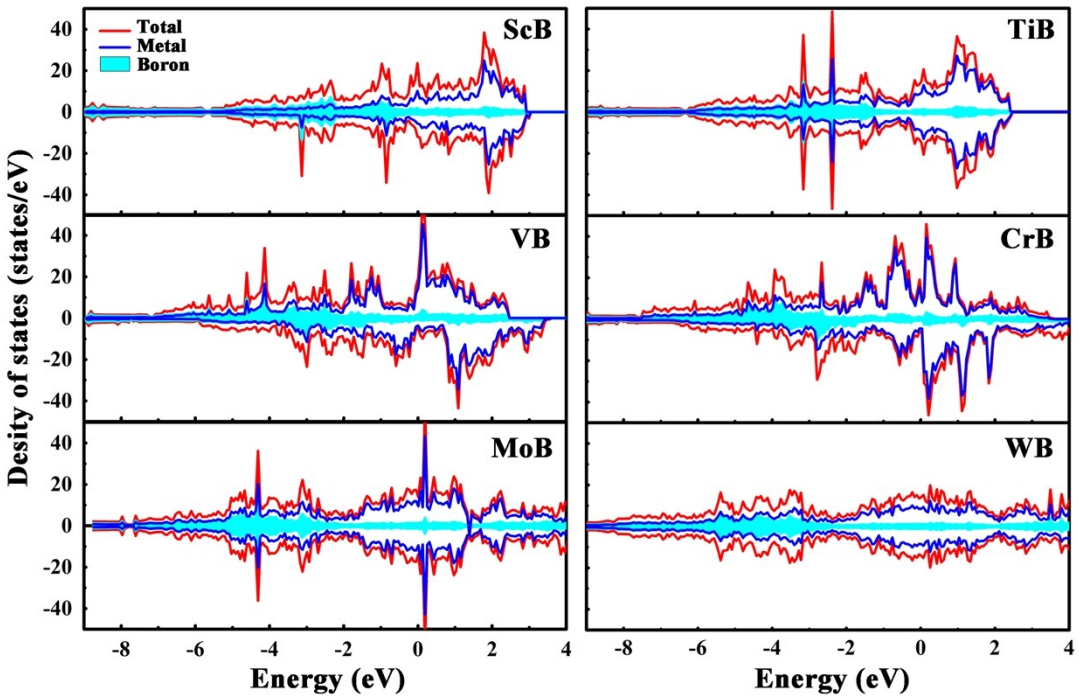

Fig. S4 The density of states of states for ScB, TiB, VB, CrB, MoB, WB monolayers, respectively.

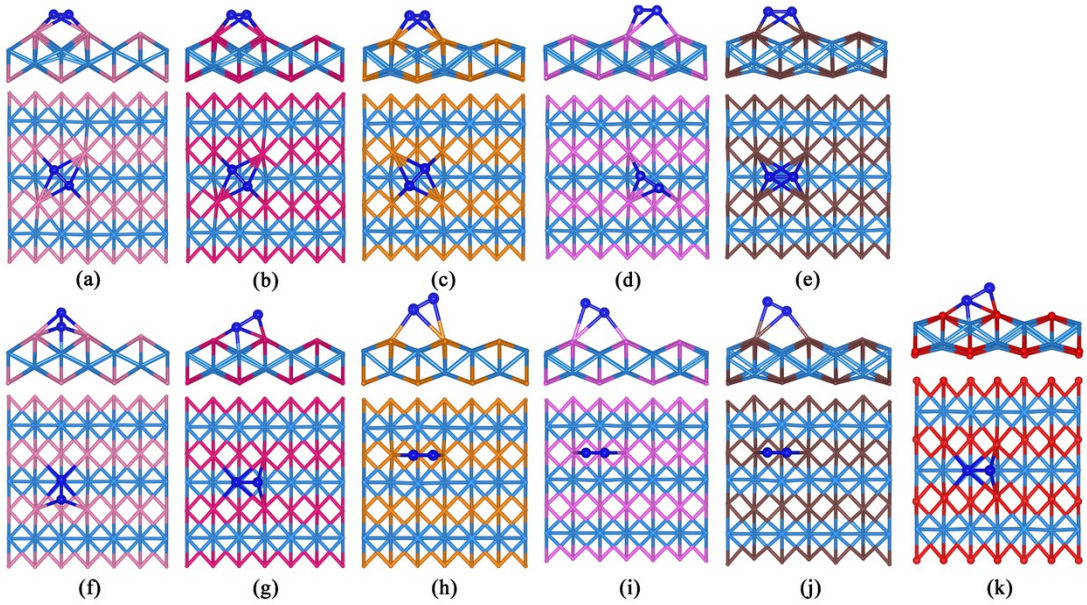

Fig. S5 The side and top views of structures for N_2 molecules with (**a-e**) side-on adsorption configurations on ScB, TiB, CrB, MoB, WB monolayer, respectively, and (**f-k**) end-on adsorption configurations on ScB, TiB, CrB, MoB, WB, VB monolayers, respectively.

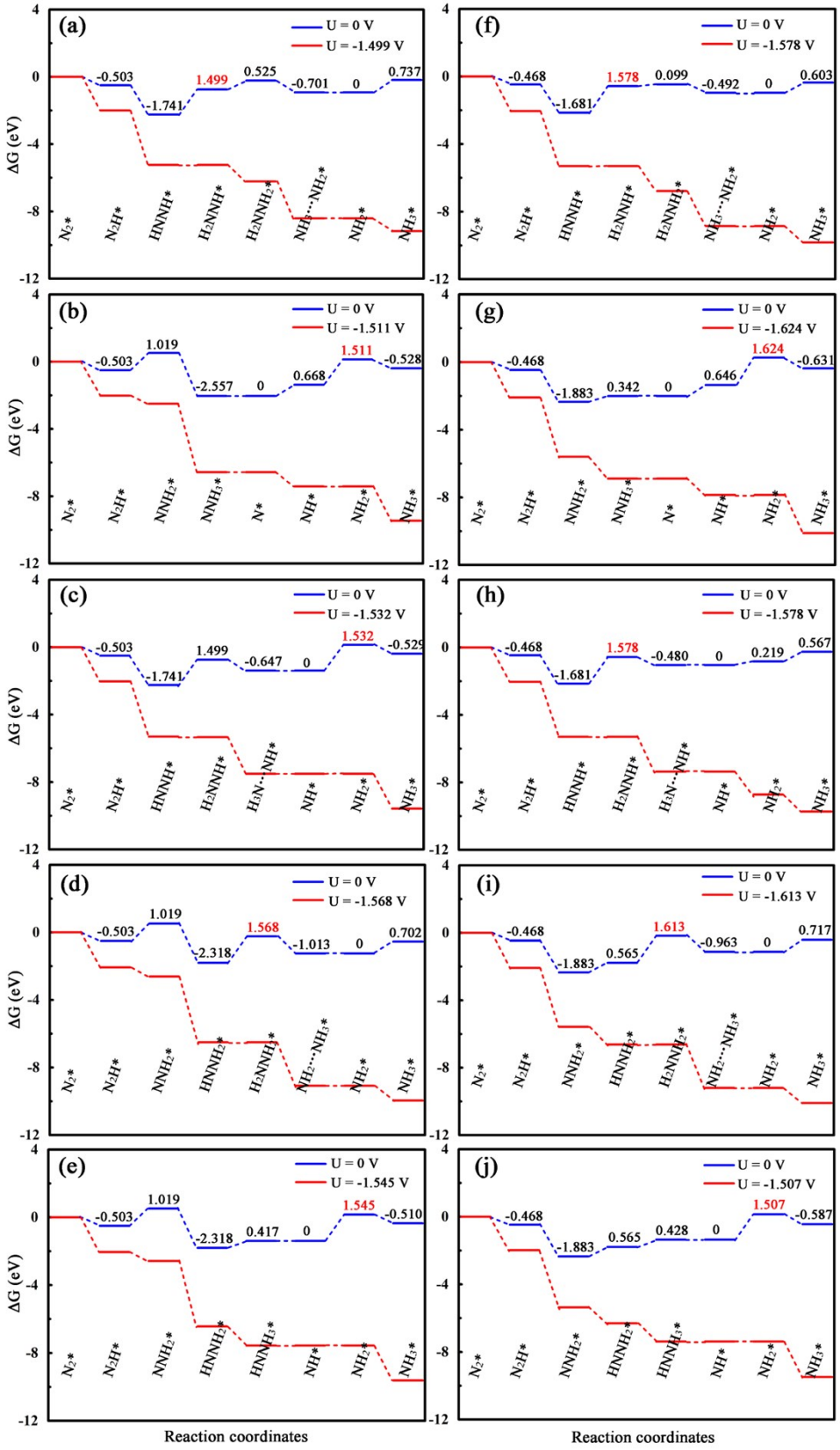

Fig. S6 Free energy diagrams of N_2 conversion into ammonia on ScB monolayer *via* five difference reaction pathways at N_2 adsorption configurations with **(a-e)** side-on and **(f-j)** end-on types, respectively.

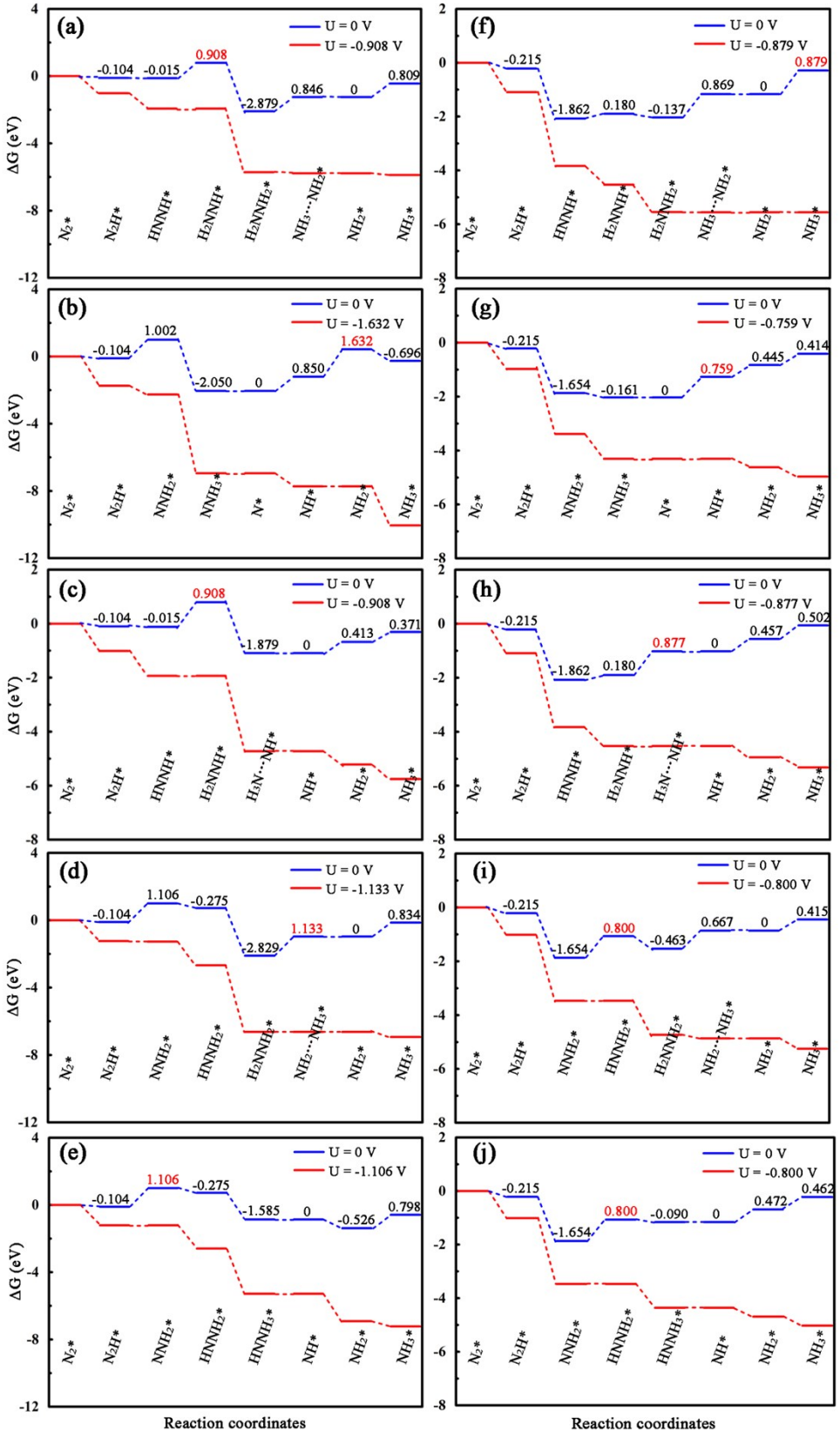

Fig. S7 Free energy diagrams of N_2 conversion into ammonia on TiB monolayer *via* five difference reaction pathways at N_2 adsorption configurations with **(a-e)** side-on and **(f-j)** end-on types, respectively.

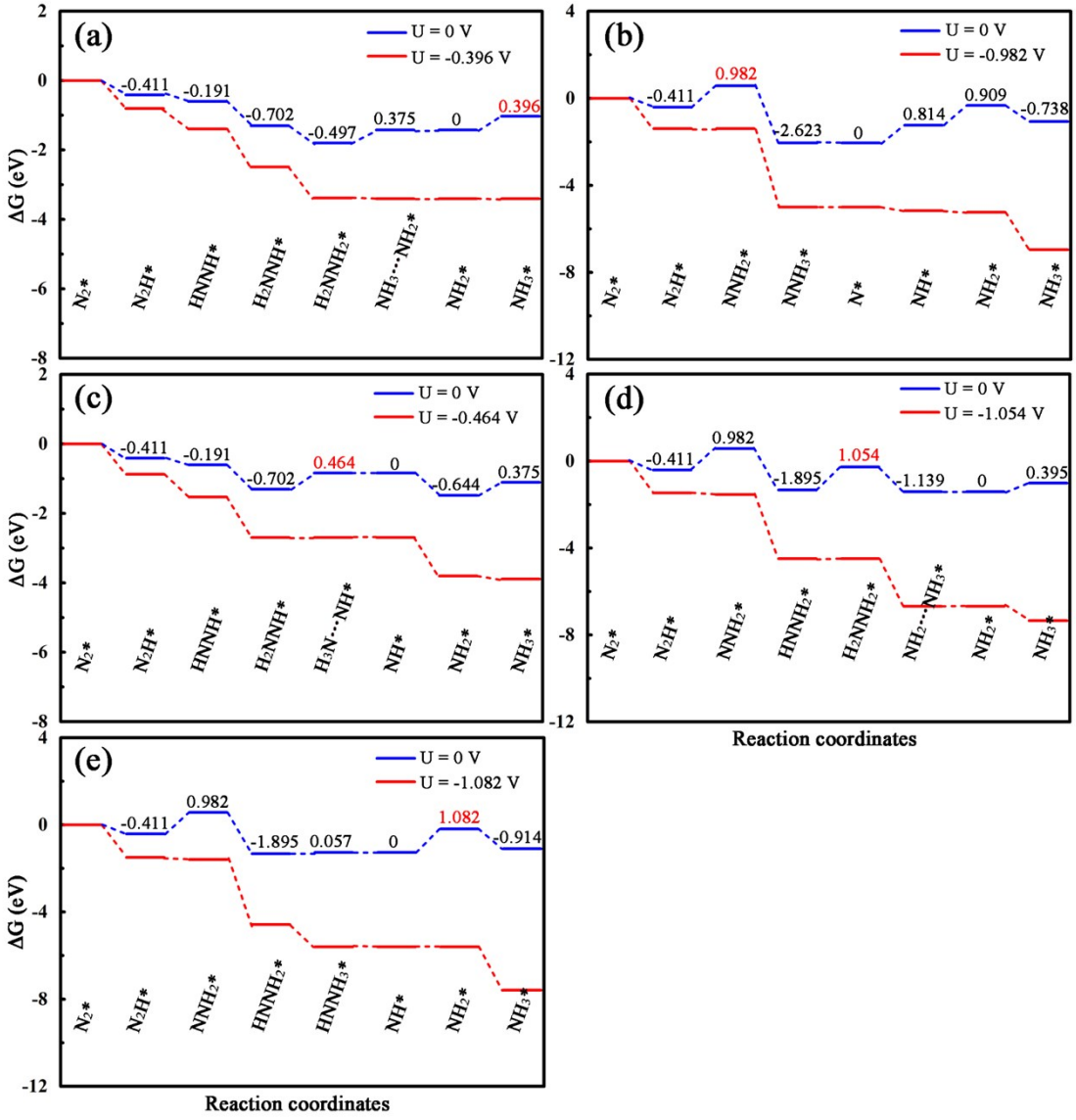

Fig. S8 Free energy diagrams of N_2 conversion into ammonia on VB monolayer *via* five difference reaction pathways at N_2 adsorption configurations with **(a-e)** end-on type, respectively.

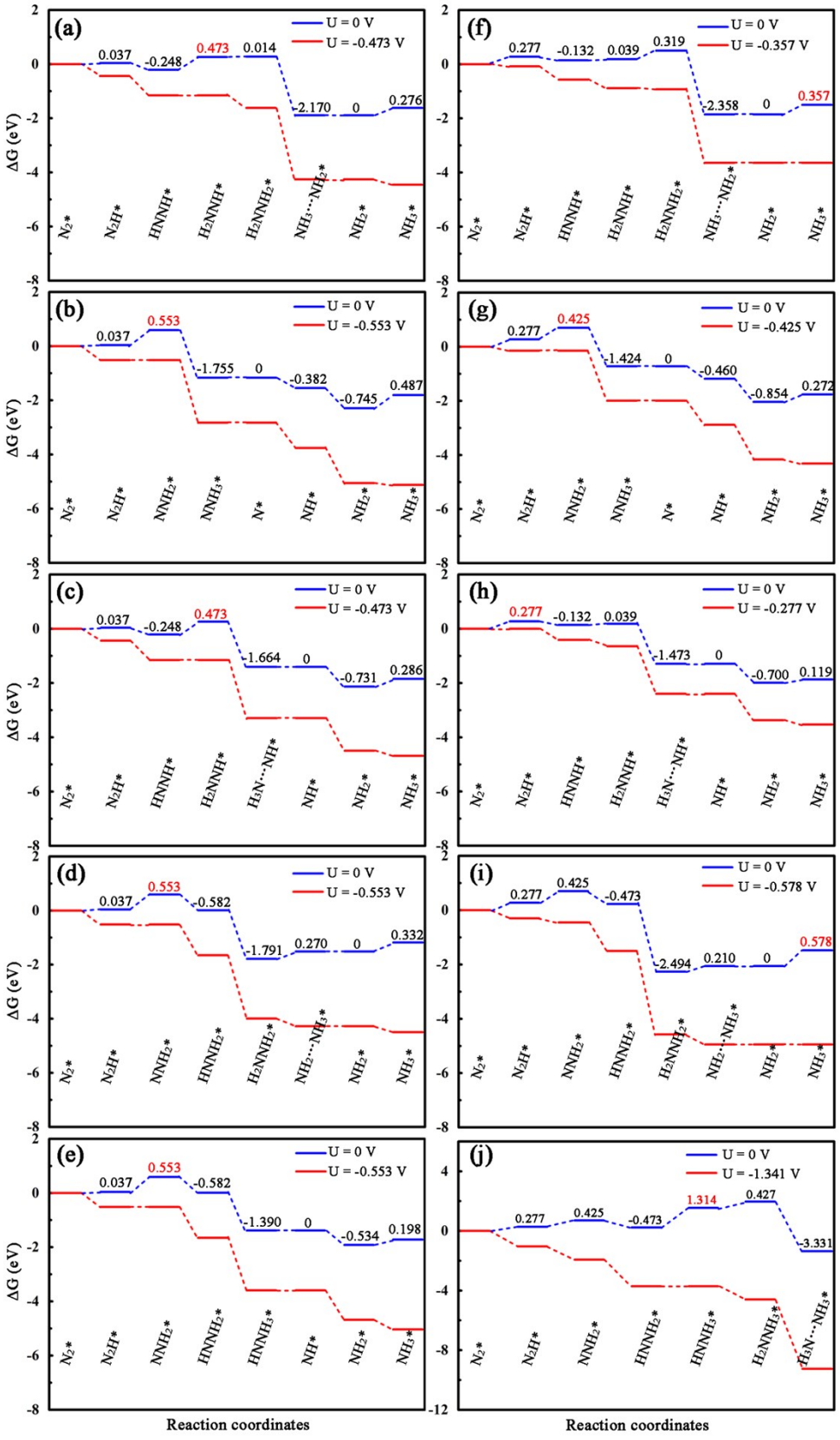

Fig. S9 Free energy diagrams of N_2 conversion into ammonia on CrB monolayer *via* five difference reaction pathways at N_2 adsorption configurations with **(a-e)** side-on and **(f-j)** end-on types, respectively.

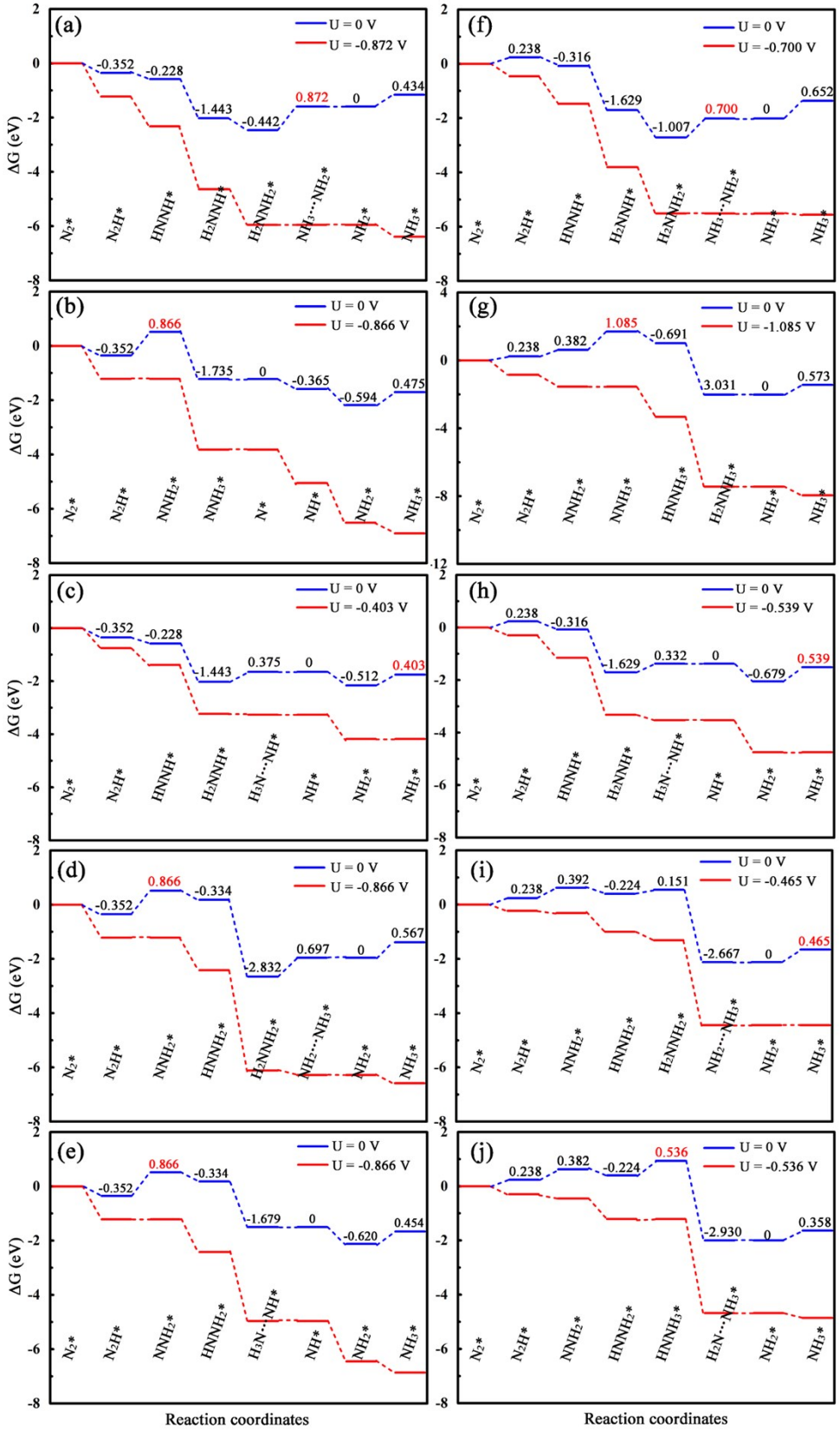

Fig. S10 Free energy diagrams of N_2 conversion into ammonia on MoB monolayer *via* five difference reaction pathways at N_2 adsorption configurations with **(a-e)** side-on and **(f-j)** end-on types, respectively.

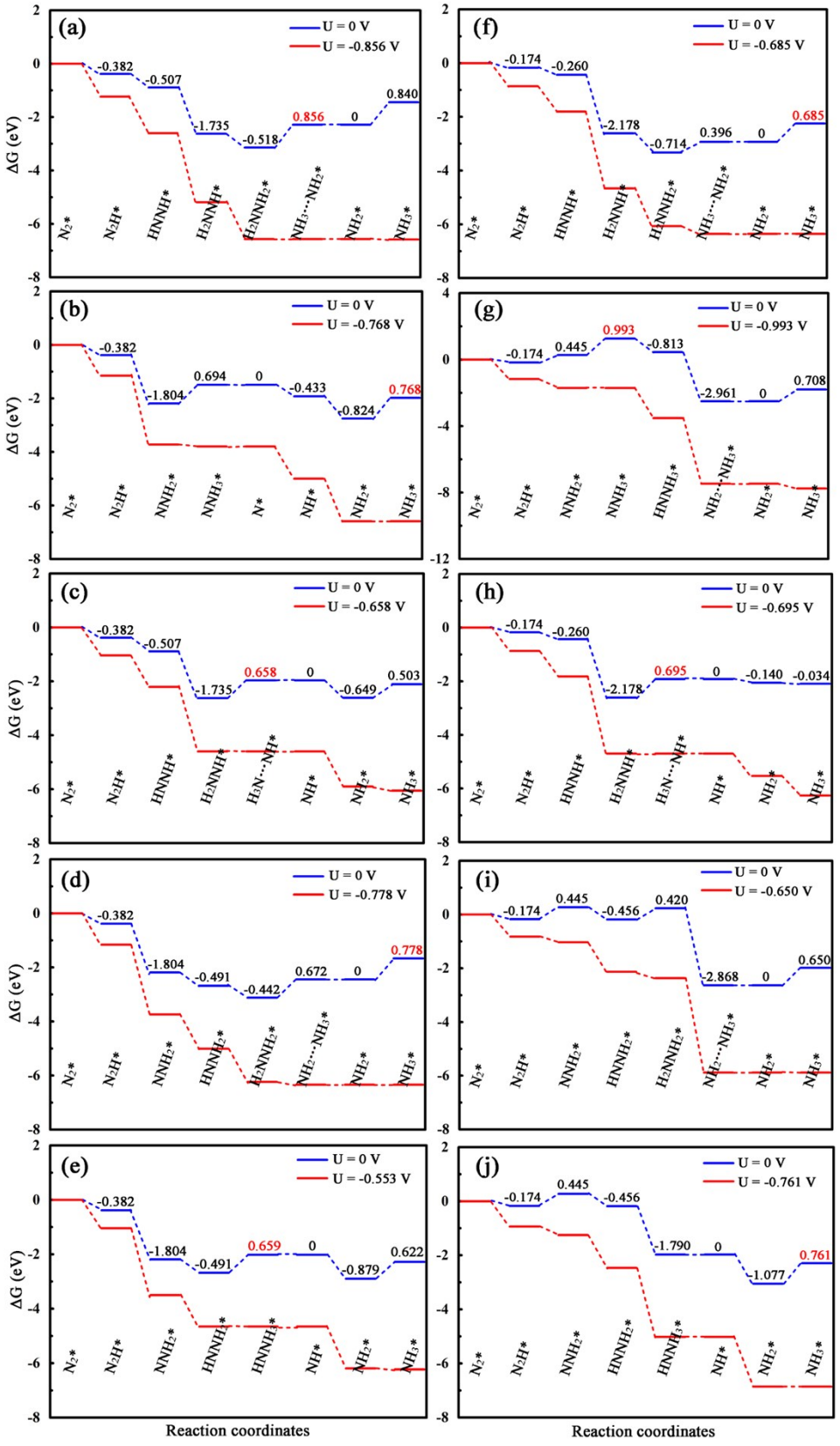

Fig. S11 Free energy diagrams of N_2 conversion into ammonia on WB monolayer *via* five difference reaction pathways at N_2 adsorption configurations with **(a-e)** side-on and **(f-j)** end-on types, respectively.

Table S1. The energy required to release the ammonia from MB (M=Sc, Ti, V, Cr, Mo, and W) monolayers with the five possible reaction pathways of side-on or end-on configurations (the Gibs free energy of single NH_3 gas is -19.224 eV).

Desorption energy (eV)	**side-on configuration**					**end-on configuration**					
	ScB	**TiB**	**CrB**	**MoB**	**WB**	**ScB**	**TiB**	**VB**	**CrB**	**MoB**	**WB**
Alternating	**0.591**	**0.569**	0.712	2.729	1.364	0.574	0.536	**3.651**	0.611	2.575	1.509
Distal	0.592	0.559	0.684	2.673	1.443	0.631	**0.621**	3.671	0.663	2.572	1.413
Mixed I	0.608	0.625	**0.658**	**2.747**	**1.594**	0.609	0.543	3.655	**0.809**	2.625	1.285
Mixed II	0.611	0.592	0.619	2.588	1.416	0.604	0.605	3.653	0.531	**2.689**	**1.561**
Mixed III	0.580	0.589	0.675	2.692	1.559	**0.659**	0.569	3.665	0.632	2.761	1.429