Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

A systematic computational investigations of water splitting and N_2 reduction reaction performances of monolayer MBenes

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1. Calculation methods of evaluating HER, OER and NRR activity

1.1 Hydrogen evolution reaction of MBenes

Under the standard conditions, the HER catalytic activity of materials can be evaluated by the change of the reaction Gibbs free energy of hydrogen adsorption (ΔG_{H^*}). ΔG_{H^*} evaluated via eq (S1):

$$\Delta G_{H^*}=\Delta E_H+\Delta E_{ZPE}-T\Delta S_H \quad (S1)$$

Where ΔE_H, ΔE_{ZPE} and ΔS_H are the difference of hydrogen adsorption energy, zero-point energy and the entropy between adsorbed hydrogen and hydrogen in gas phase, respectively.

The ΔS_H can be approximated by eq (S2)

$$\Delta S_H \cong -\frac{1}{2}S^0_{H_2} \quad (S2)$$

due to the fact that the vibrational entropy in the adsorbed state is small according to previous study,[1] and $S^0_{H_2}$ is the entropy of H_2 gas under the standard condition.[2] Thus, eq (S1) can be written as eq (S3)

$$\Delta G_{H^*}=\mu_{H^*}-\mu_{H^+}-\mu_{e^-}-\mu_*-\frac{1}{2}\mu_{H_2}-\mu_* \quad (S3)$$

$$=\left(E_{H^*}+E_{ZPE(H^*)}-TS_{*H}\right)-\frac{1}{2}\left(E_{H_2}+E_{ZPE(H_2)}-TS_{H_2}\right)-(E_*+E_{ZPE(*)}-TS_*)$$

$$=\Delta E_{(H^*)}+\Delta E_{ZPE(H^*)}-T\Delta S_{H^*}$$

Here, the values of ΔE_{ZPE} and $T\Delta S$ are referred from Ref 5. The theoretical calculation overptotentialis defined as $\eta_{HER}=-|\Delta G_{H^*}|/e\times10^3$ in unit of mV. The optimal ΔG_{H^*} is 0 eV, therefore the ideal overpotantial is 0 mV as well.[3]

1.2 Oxygen evolution reaction of MBenes

The proposed mechanism for OER consists of four intermediate steps under the standard conditions at electrode potential U, each step on the active sites releases of a proton and an electron.[4] The schematic of OER on MBenes is shown in Figure S4, it can be composed by four elementary steps, as follows:

$$H_2O(l)+*\rightarrow HO^*+(H^++e^-) \quad \Delta G_1 \quad (S4)$$

$$HO^*\rightarrow O^*+(H^++e^-) \quad \Delta G_2 \quad (S5)$$

$$O^*+H_2O(l)\rightarrow HOO^*+(H^++e^-) \quad \Delta G_3 \quad (S6)$$

$$HOO^*\rightarrow *+O_2(g)+(H^++e^-) \quad \Delta G_4 \quad (S7)$$

where O*, OH*, OOH* are the adsorbed intermediates, * represents active sites on the catalyst surface, (l) and (g) refer to liquid and gas phases, respectively. ΔG_1, ΔG_2, ΔG_3 and ΔG_4 are the reaction Gibbs free energy of (S4)-(S7). The thermochemistry of these electrochemical reactions was obtained by using DFT calculations combined with SHE model developed by Nørskov and co-work.[1] Considering the ZPE and entropy corrections, the free energies of adsorption, ΔG_{ads}, can obtained by following equation:

$$\Delta G_{ads}=\Delta E+\Delta ZPE-T\Delta S \quad (S8)$$

For each step, the ΔG is defined as the difference between free energies of the initial and final

states, and is given by the expression:

$$\Delta G=\Delta E+\Delta ZPE-\mathrm{T}\Delta \mathrm{S}+\mathrm{e}U-\Delta G_{\mathrm{pH}} \quad \text{(S9)}$$

Where ΔE is the change of the energy after adsorbed intermediate species, U is the potential at the electrode. T is the room temperature, which is equal to 298K. ΔG_{pH} is the contributions of pH, which can be defined as $\Delta G_{\mathrm{pH}}=-\mathrm{k_B T ln}\left[\mathrm{H^+}\right]=\mathrm{pH}\times \mathrm{k_B ln}10$. The pH will not change the overpotential and thus only the pH = 0 is considered in this work. The values of ΔE_{ZPE} and ΔS of intermediates adsorbates (O*, HO*, HOO*) are referred from previous literature.[5] The theoretical onset overpotential η, which is determined by the potential limiting steps (PLS), can be obtained from the following equation.[6,7]

$$\eta=\max(\Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4)/\mathrm{e}-1.23[\mathrm{V}] \quad \text{(S10)}$$

1.3 N_2 Reduction Reaction of MBenes

The calculations of the reaction Gibbs free energy (ΔG) of each elemental step was based on the computational hydrogen electrode model proposed by Nørskov and coauthors.[7,8] which can be calculated by:

$$\Delta G=\Delta E_{\mathrm{DFT}}^{\mathrm{NRR}}+\Delta ZPE-\mathrm{T}\Delta \mathrm{S}+\mathrm{e}U-\Delta G_{\mathrm{pH}} \quad \text{(S10)}$$

The ΔE_{ZPE} and ΔS are the difference of zero point energy and the difference of entropy between the adsorbed state and the free-standing state, respectively, which are referenced the latest works about NRR.[9-11] The calculated values of zero point energy and the entropy are derived from the previous work.[9] The adsorption energy (ΔE_{DFT}) of different intermediates is calculated by

$$\Delta E_{\mathrm{DFT}}=E_{\mathrm{total}}-(E_{\mathrm{catal}}+E_{\mathrm{adsorp}}) \quad \text{(S11)}$$

where E_{total} and E_{catal} are the total energies of the slab with and without intermediates. E_{adsorp} is the total energy of an isolate intermediate, such as *N_2 and *NNH. The η_{onset} is determined by the potential limiting steps (PLS), corresponding to the most positive reaction Gibbs free energy (ΔG_{max}), and can be calculated by: U_{onset} = -ΔGmax/e. Therefore, the calculated overpotential η_{NRR} can be computed via η_{NRR} = $U_{\mathrm{equilibrium}}$-U_{onset}. Thus, the overpotential under a given pH (η) will be:

$$\eta_{\mathrm{NRR}} = U_{\mathrm{equilibrium}}-U_{\mathrm{onset}}= = \Delta G\mathrm{max/e} \quad \text{(S12)}$$

1.4 formation energy of MBenes

The formation energy of MBenes is obtained via eq (S14)

$$E_{\mathrm{f}}=\mathrm{E_{MB}}-n\mathrm{E_M}-m\mathrm{E_B}/m+n \quad \text{(S13)}$$

Where the E_{f}, E_{M}, E_{B} are the total energy of MBene, the total energy of isolated metal, and the total energy of isolated B atom, respectively. n and m are the number of metal and B atoms in MBenes, respectively.

2. Figures and tables

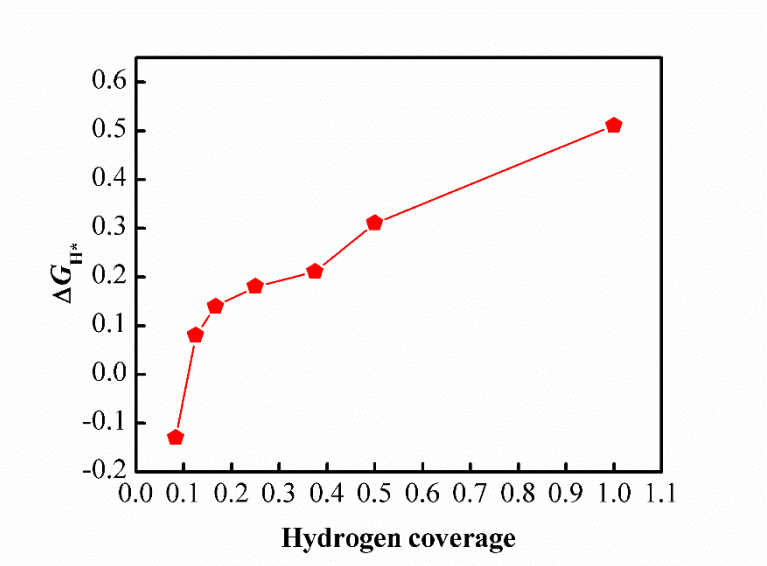

Figure S1. The reactions Gibbs free energies (ΔG_{H^*}) (eV) of hydrogen of NiB-B at different hydrogen coverage (θ_H).

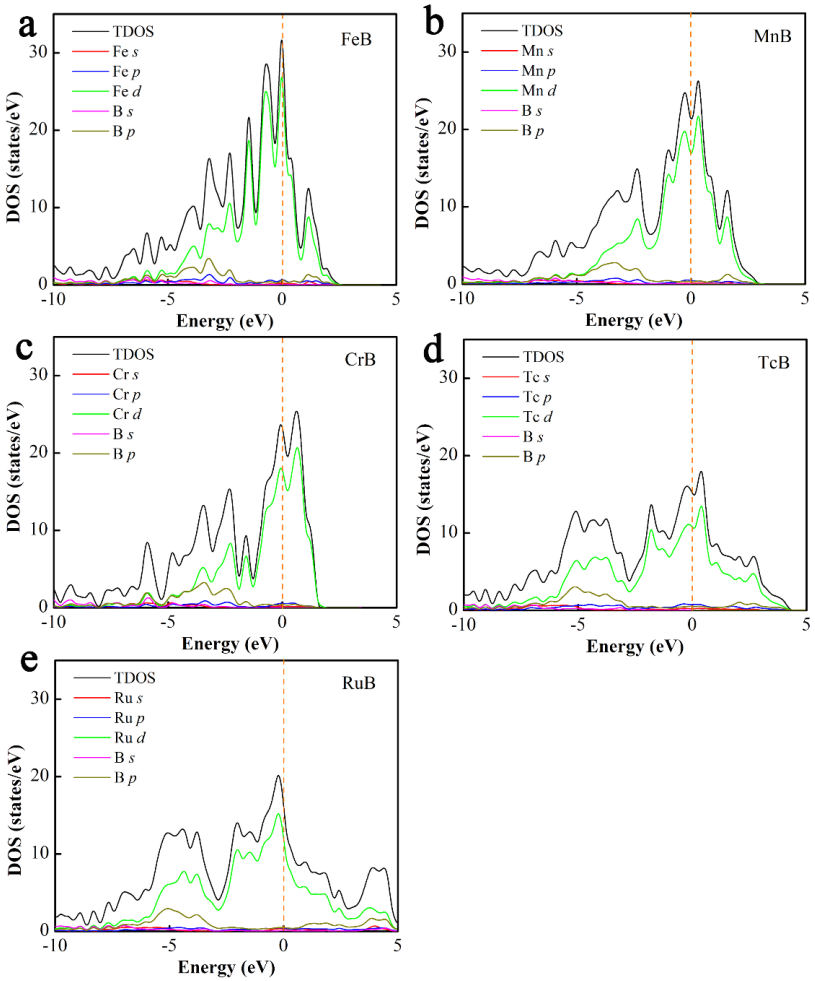

Figure S2. Density of states of MBenes. (a) FeB, (b) MnB, (c) CrB, (d) TcB, and (e) RuB.

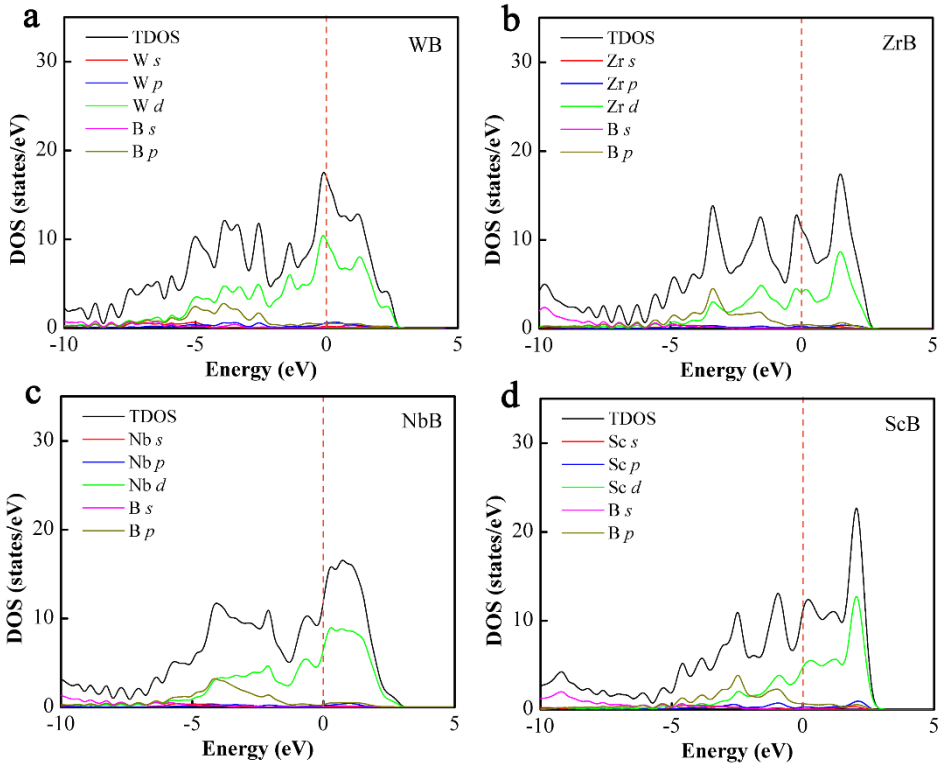

Figure S3. Density of states of MBenes. (a) WB, (b) ZrB, (c) NbB, and (d) ScB.

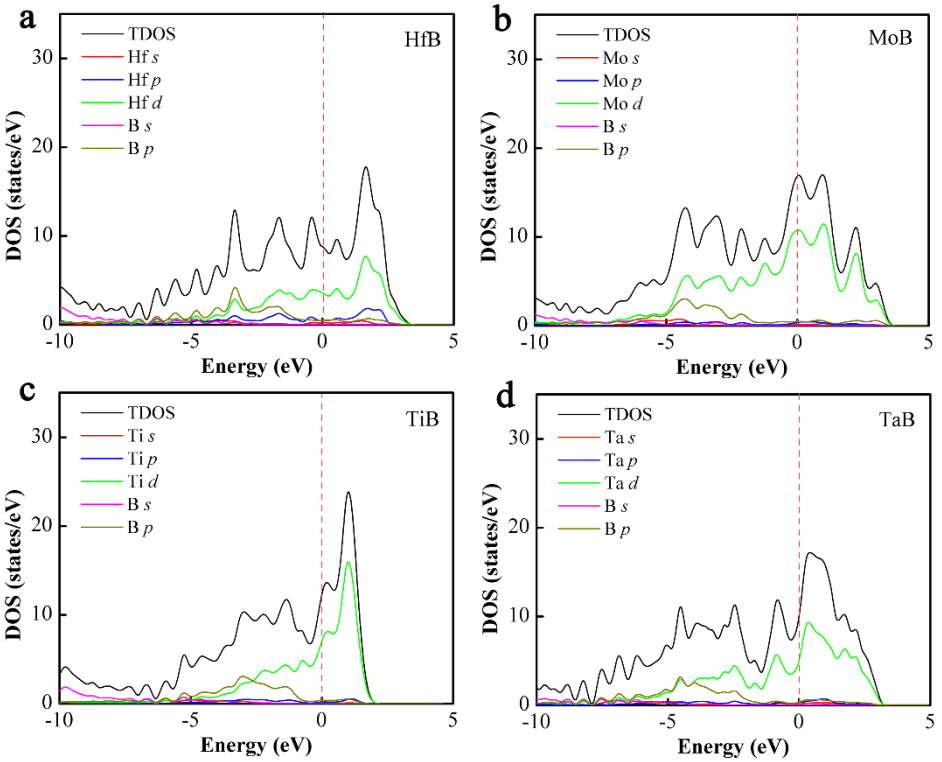

Figure S4. Density of states of MBenes. (a) HfB, (b) MoB, (c) TiB, (d) TcB, and (e) TaB.

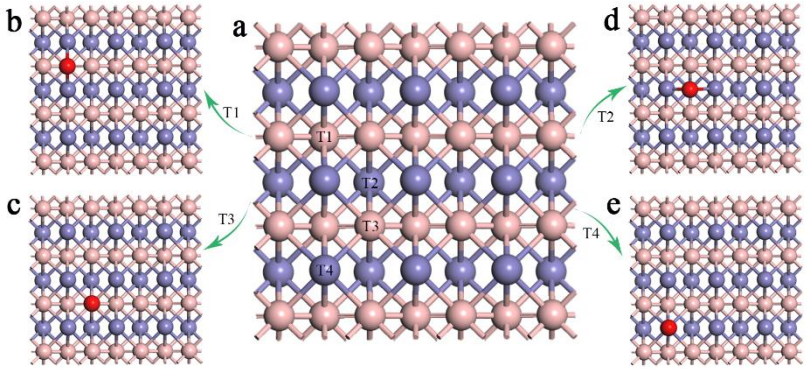

Figure S5. Schematic structure of MBenes with oxygen terminal. (a) Lattice structure of MBenes, MBenes with oxygen occupied on (b) T1 site, (c) T3 site, (d) T2 site, and (e) T4 site.

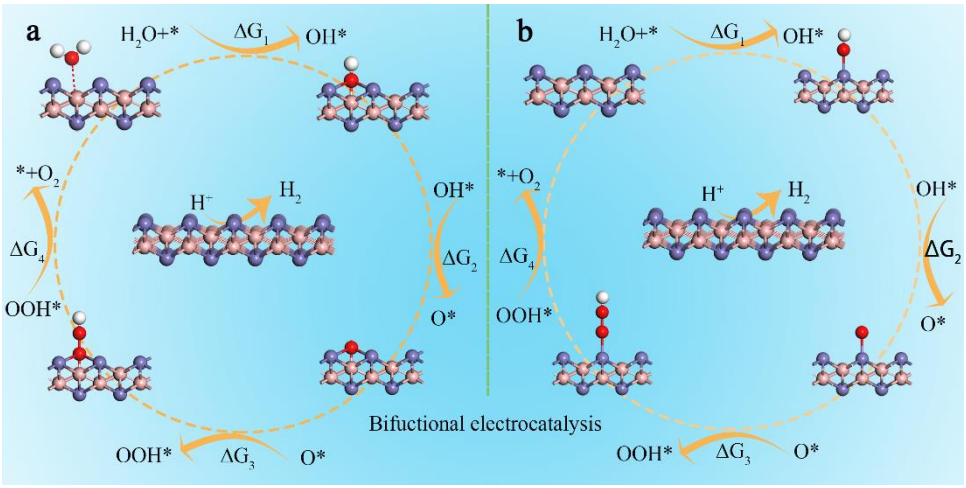

Figure S6. Schematic of MB-O* as bifunctional catalyst for overall water splitting. Elementary reaction structures of OER and HER at (a) B site and (b) metal site of MB surface. The adsorbed states for reactions include *H, *O, *OH, and *OOH species.

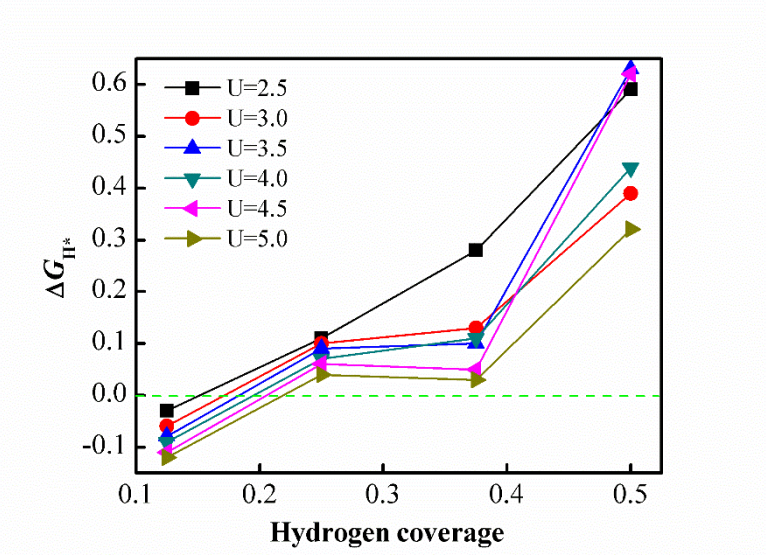

Figure S7. The reaction Gibbs free energy of hydrogen adsorption with considering Hubbard U

correction.

Table S1. The lattice parameters of bulk MAlB and M_2AlB_2, and bond lengths of M-B and M-Al bonds (M= Fe, Mn, Cr, Ni, Ru, Tc, Hf, Mo, Ta, Ti, W, Zr, Nb, and Sc).

MAlB	*a*(Å)	*b*(Å)	*c*(Å)	*b*/*a*	d_{M-B}(Å)	d_{M-A}(Å)
Fe_2AlB_2	2.917	11.010	2.833	3.774	2.151,2.139	2.593
Mn_2AlB_2	2.906	11.021	2.841	3.792	2.138,2.168	2.589
Cr_2AlB_2	2.922	11.093	2.916	3.796	2.161, 2.179	2.637
Ni_2AlB_2	2.968	10.959	2.892	3.692	2.181,2.219	2.574
Ru_2AlB_2	2.921	11.821	3.595	4.046	2.507,2.609	2.775
Tc_2AlB_2	2.973	11.615	3.415	3.906	2.412,2.490	2.761
HfAlB	3.444	15.549	3.158	4.514	2.519	2.938
MoAlB	3.217	14.057	3.109	4.369	2.372	2.713
TaAlB	3.336	14.698	3.094	4.405	2.434	2.807
TiAlB	3.277	14.683	3.061	4.481	2.378	2.779
WAlB	3.223	14.006	3.121	4.332	2.373	2.717
ZrAlB	3.479	15.832	3.171	4.550	2.558	2.984
NbAlB	3.341	14.709	3.116	4.402	2.440	2.816
ScAlB	3.567	14.672	3.196	4.113	2.542	2.975

Table S2. The exfoliation energy (E_{xf}) of MAlB (M_2AlB_2)) exfoliated into MBenes and the bonding energy (E_{b-Al}) of Al with MB in MAlB.

System	E_{xf} (eV/Å^2)	E_{b-Al} (eV)
Fe_2AlB_2	0.185	-2.89
Mn_2AlB_2	0.188	-3.21
Cr_2AlB_2	0.224	-3.17
Ni_2AlB_2	0.123	-1.81
Ru_2AlB_2	0.145	-1.89
Tc_2AlB_2	0.187	-1.49
HfAlB	0.238	-3.91
MoAlB	0.419	-8.11
TaAlB	0.368	-6.49
TiAlB	0.329	-6.23
WAlB	0.428	-8.27
ZrAlB	0.195	-4.03
NbAlB	0.354	-6.61
ScAlB	0.186	-3.09

Table S3. Average valence electrons of Metal, Al, and B atoms in MAlB systems based on the Bader charge analysis.

System	Metal (*e*)	Al (*e*)	B (*e*)
Fe_2AlB_2	-0.28	+3	-1.22
Mn_2AlB_2	-0.43	+3	-1.07
Cr_2AlB_2	-0.09	+3	-1.41

Ni_2AlB_2	-0.77	+3	-0.73
Ru_2AlB_2	-1.28	+3	-0.44
Tc_2AlB_2	-0.87	+3	-0.62
HfAlB	+0.31	+1.41	-1.72
MoAlB	-1.09	+2.17	-1.08
TaAlB	-0.23	+1.93	-1.70
TiAlB	+1.13	+2.71	-1.58
WAlB	-1.91	+3	-1.09
ZrAlB	+0.95	+0.93	-1.88
NbAlB	-0.14	+1.86	-1.72
ScAlB	-0.87	+2.75	-1.88

Table S4. The electronic character and formation energy of MBenes (M= Fe, Mn, Cr, Ni, Ru, Tc, Hf, Mo, Ta, Ti, W, Zr, Nb, and Sc).

MB	Metallic	E_f
FeB	Yes	-1.42
MnB	Yes	-1.21
CrB	Yes	-1.12
NiB	Yes	-0.81
RuB	Yes	-1.45
TcB	Yes	-1.29
HfB	Yes	-1.58
MoB	Yes	-1.06
TaB	Yes	-1.26
TiB	Yes	-1.66
WB	Yes	-0.77
ZrB	Yes	-1.70
NbB	Yes	-1.45
ScB	Yes	-1.72

Table S5. Relative energy (eV) of terminal oxygen occupied at different sites of MBO and terminal oxygen bonding energy ($E_{b\text{-}O}$) of MBO.

System	T1 (bottom B)	T2 (bottom metal)	T3 (top metal)	T4 (top B)	$E_{b\text{-}O}$ (eV)
FeB-O*	-1.14	-1.81	-1.46	-2.09	-2.57
MnBO*	-1.22	18.54	-36.25	-38.98	-3.03
CrB-O*	-3.04	-1.52	-1.99	-3.42	-3.15
NiB-O*	-1.89	-11.64	5.65	-28.86	-2.71
RuB-O*	-1.11	-22.13	92.37	-41.54	-3.24
TcB-O*	-1.45	-19.91	83.54	-38.08	-3.13
MoB-O*	-1.19	-2.18	0.55	-1.68	-3.64
NbB-O*	-2.65	1.17	-22.08	-17.68	-4.39
ScB-O*	-5.33	-1.74	-83.21	-32.61	-5.46

Table S6. The reactions Gibbs free energies (ΔG) (eV) of hydrogen on MBO surface at different hydrogen coverage (θ_H).

System	θ_H=0.125	θ_H=0.25	θ_H=0.375	θ_H=0.50
FeBO	-0.87	-1.24	-0.37	0.69
MnBO	-0.71	0.56	0.79	0.84
CrBO	0.08	-0.49	-0.07	0.35
NiBO	0.16	0.73	-0.94	0.68
RuBO	-0.37	0.53	-0.09	-0.32
TcBO	-1.37	-0.87	-1.08	0.65
MoBO	-0.47	-0.61	-0.45	-0.29
NbBO	1.25	2.15	-1.41	2.43
ScBO	0.46	0.74	0.91	1.28

Table S7. The reactions Gibbs free energies ($\Delta G_{1\text{-}4}$) of four elementary steps on B site of MBenes. The data are bold faced representing the potential limiting steps (ΔG_{max}).

System	ΔG_1	ΔG_2	ΔG_3	ΔG_4
FeB-B	0.22	0.06	3.01	1.63
MnB-B	0.91	-0.77	2.84	1.94
CrB-B	-1.12	0.52	2.59	2.93
NiB-B	-0.47	-0.40	3.59	2.20
RuB-B	-0.32	-2.08	-1.29	8.61
TcB-B	-2.19	0.61	-0.46	6.96
HfB-B	-0.61	0.28	3.36	1.89
MoB-B	-1.08	0.65	-0.63	5.98
TaB-B	-2.75	0.04	-2.83	10.46
TiB-B	-0.09	-1.92	3.96	2.97
WB-B	-1.43	-2.12	0.48	7.99
ZrB-B	-3.09	2.19	-1.90	7.72
NbB-B	-0.87	-0.58	-0.89	7.26
ScB-B	-1.45	-1.16	-0.32	7.85

Table S8. The reactions Gibbs free energies ($\Delta G_{1\text{-}4}$) of four elementary steps on metal site of MBenes.

System	ΔG_1	ΔG_2	ΔG_3	ΔG_4
FeB-Fe	0.47	0.48	3.52	0.45
MnB-Mn	0.14	0.35	3.10	1.33
CrB-Cr	-0.71	0.61	3.32	1.70
NiB-Ni	0.21	1.53	1.60	1.58
RuB-Ru	0.17	1.55	3.22	-0.02
TcB-Tc	-0.08	0.48	2.86	1.66
HfB-Hf	-0.72	-1.14	4.80	1.98
MoB-Mo	-0.74	-0.21	3.24	2.63
TaB-Ta	-2.76	-0.02	-2.05	9.75
TiB-Ti	-1.06	0.31	3.84	1.83

WB-W	-1.04	-0.29	3.60	2.65
ZrB-Zr	-8.64	6.91	3.59	10.24
NbB-Nb	-0.93	-0.29	1.19	4.95
ScB-Sc	-1.14	-0.49	3.95	2.60

Table S9. The NRR overpotential (V) of end-on (via alternating and distal mechanism) and side-on (via enzymatic and consecutive mechanism) configurations on B site of MBenes.

System	Alternating	Distal	Enzymatic	Consecutive
FeB-B	1.10	1.10	0.42	0.77
MnB-B	0.41	0.41	0.55	0.71
CrB-B	0.76	0.49	0.39	0.20
NiB-B	1.07	0.68	1.30	1.70
RuB-B	0.67	0.57	0.71	0.60
TcB-B	0.81	0.77	1.25	1.35
HfB-B	1.31	1.54	1.72	1.54
MoB-B	1.22	1.22	0.27	0.80
TaB-B	1.49	1.60	1.74	0.28
TiB-B	1.25	1.00	1.36	1.50
WB-B	1.68	1.28	0.65	0.51
ZrB-B	0.67	0.80	1.56	0.80
NbB-B	1.19	0.82	0.70	0.36
ScB-B	0.99	0.66	0.55	0.66

Table S10. The NRR overpotential (V) of end-on (via alternating and distal mechanism) and side-on (via enzymatic and consecutive mechanism) configurations on metal site of MBenes.

System	Alternating	Distal	Enzymatic	Consecutive
FeB-Fe	0.11	0.37	1.15	1.32
MnB-Mn	0.31	0.85	0.86	0.86
CrB-Cr	0.56	0.60	0.28	0.60
NiB-Ni	1.65	1.65	1.50	1.50
RuB-Ru	1.18	1.18	0.54	0.33
TcB-Tc	1.37	1.54	1.38	1.79
HfB-Hf	0.85	0.51	1.72	1.39
MoB-Mo	0.76	0.76	0.50	0.50
TaB-Ta	1.50	1.50	0.88	0.96
TiB-Ti	0.96	0.96	0.75	0.75
WB-W	0.55	0.55	0.63	1.49
ZrB-Zr	1.61	0.82	1.44	1.03
NbB-Nb	0.93	0.33	0.61	1.11
ScB-Sc	1.06	1.06	1.63	0.83

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