Supplementary Information

First-principles study of the Pt@($Hf_{2-x}Zr_x$)B_2O_2 bifunctional ORR/OER catalysts

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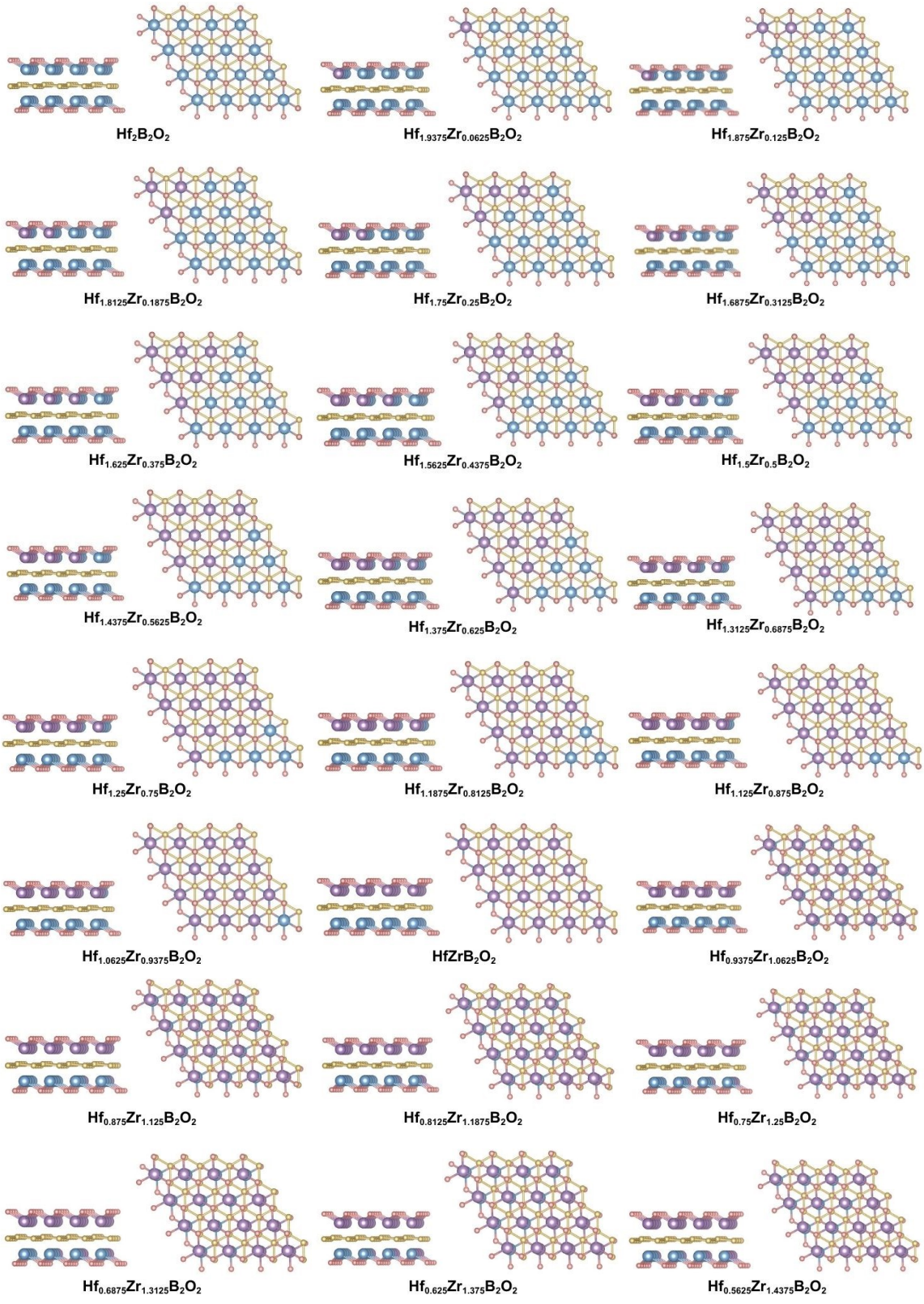
$Hf_2B_2O_2$
$Hf_{1.9375}Zr_{0.0625}B_2O_2$
$Hf_{1.875}Zr_{0.125}B_2O_2$
$Hf_{1.8125}Zr_{0.1875}B_2O_2$
$Hf_{1.75}Zr_{0.25}B_2O_2$
$Hf_{1.6875}Zr_{0.3125}B_2O_2$
$Hf_{1.625}Zr_{0.375}B_2O_2$
$Hf_{1.5625}Zr_{0.4375}B_2O_2$
$Hf_{1.5}Zr_{0.5}B_2O_2$
$Hf_{1.4375}Zr_{0.5625}B_2O_2$
$Hf_{1.375}Zr_{0.625}B_2O_2$
$Hf_{1.3125}Zr_{0.6875}B_2O_2$
$Hf_{1.25}Zr_{0.75}B_2O_2$
$Hf_{1.1875}Zr_{0.8125}B_2O_2$
$Hf_{1.125}Zr_{0.875}B_2O_2$
$Hf_{1.0625}Zr_{0.9375}B_2O_2$
$HfZrB_2O_2$
$Hf_{0.9375}Zr_{1.0625}B_2O_2$
$Hf_{0.875}Zr_{1.125}B_2O_2$
$Hf_{0.8125}Zr_{1.1875}B_2O_2$
$Hf_{0.75}Zr_{1.25}B_2O_2$
$Hf_{0.6875}Zr_{1.3125}B_2O_2$
$Hf_{0.625}Zr_{1.375}B_2O_2$
$Hf_{0.5625}Zr_{1.4375}B_2O_2$

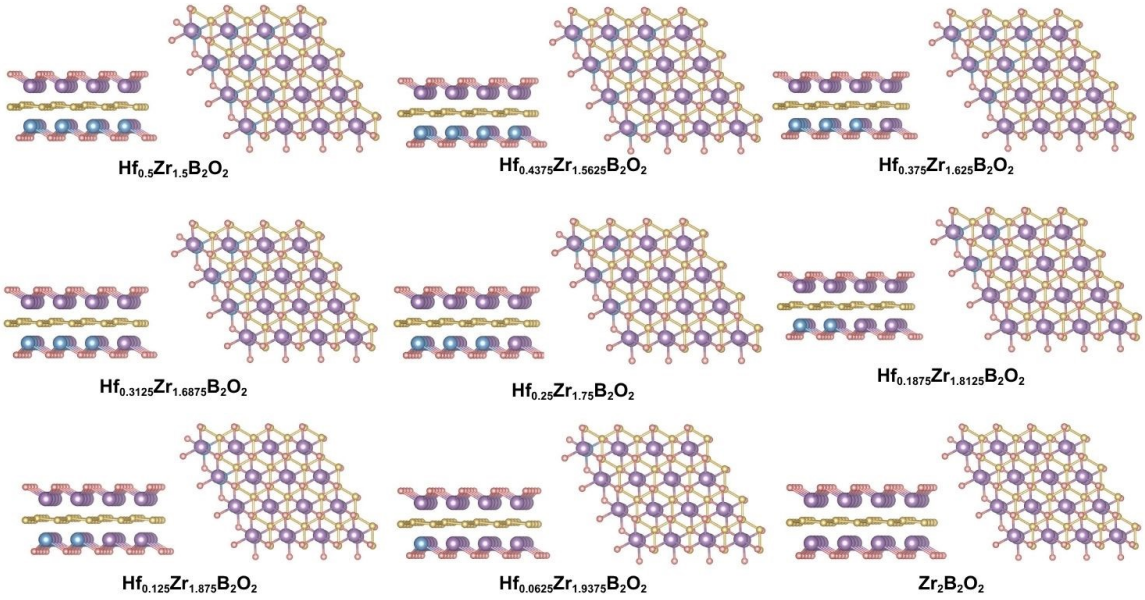

Fig. S1 The side views (left) and top views (right) of the optimized structure of hexagonal $Hf_{2-x}Zr_xCO_2$ (x=n/16, n=0-32, n is an integer).

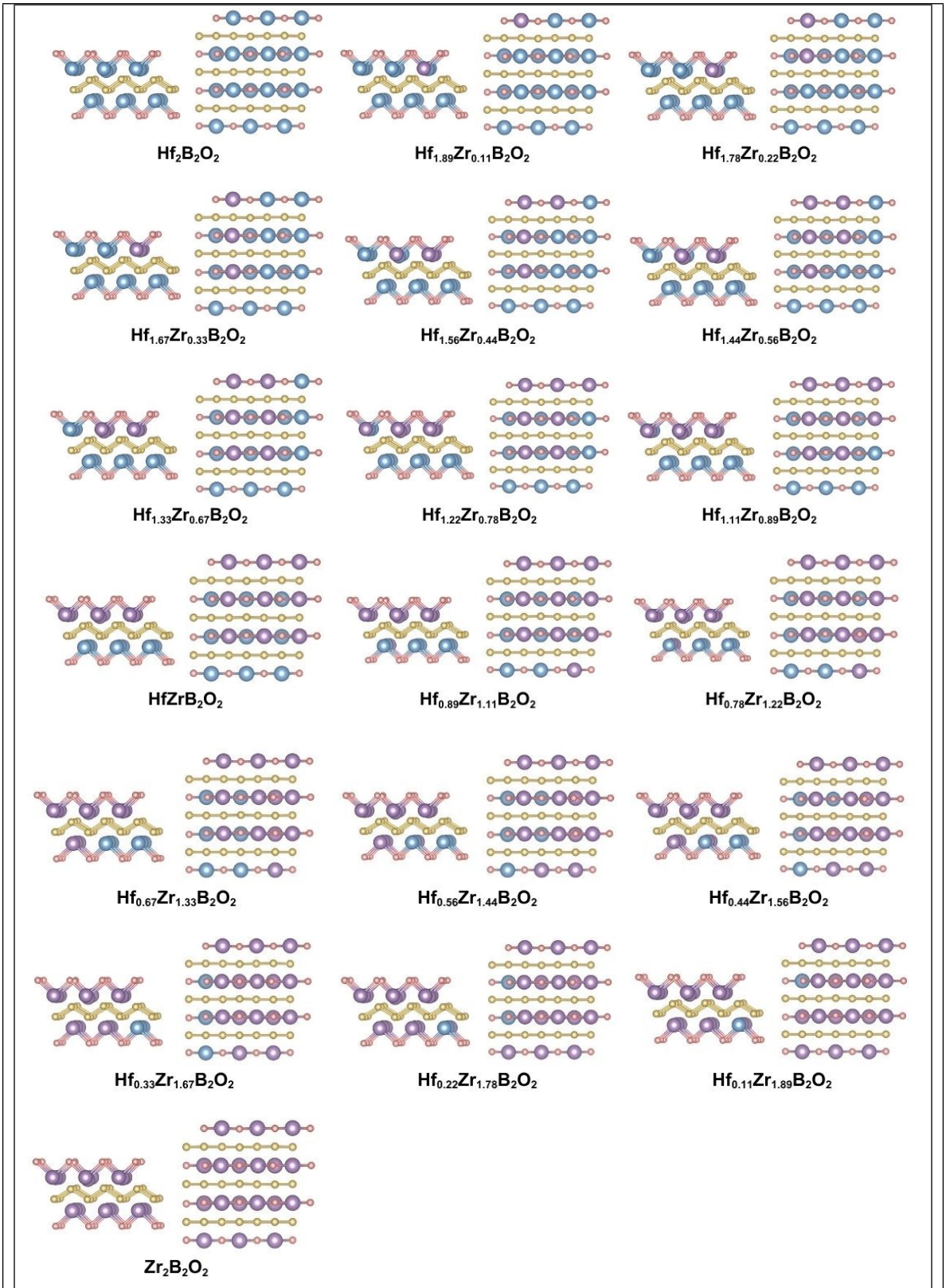

Fig. S2 The side views (left) and top views (right) of the optimized structure of orthorhombic $Hf_{2-x}Zr_xCO_2$ (x=n/9, n=0-18, n is an integer).

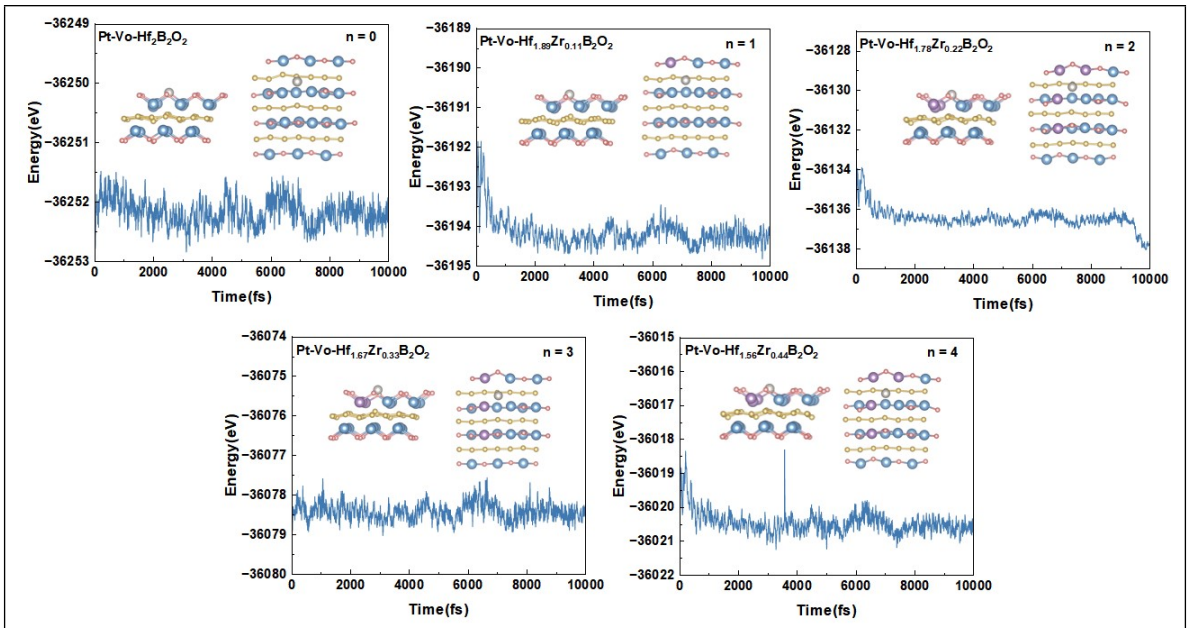

Fig. S3 Energy fluctuations of the orthorhombic Pt-V_O-$Hf_{2-x}Zr_xB_2O_2$ in 300 K AIMD simulations (10 ps).

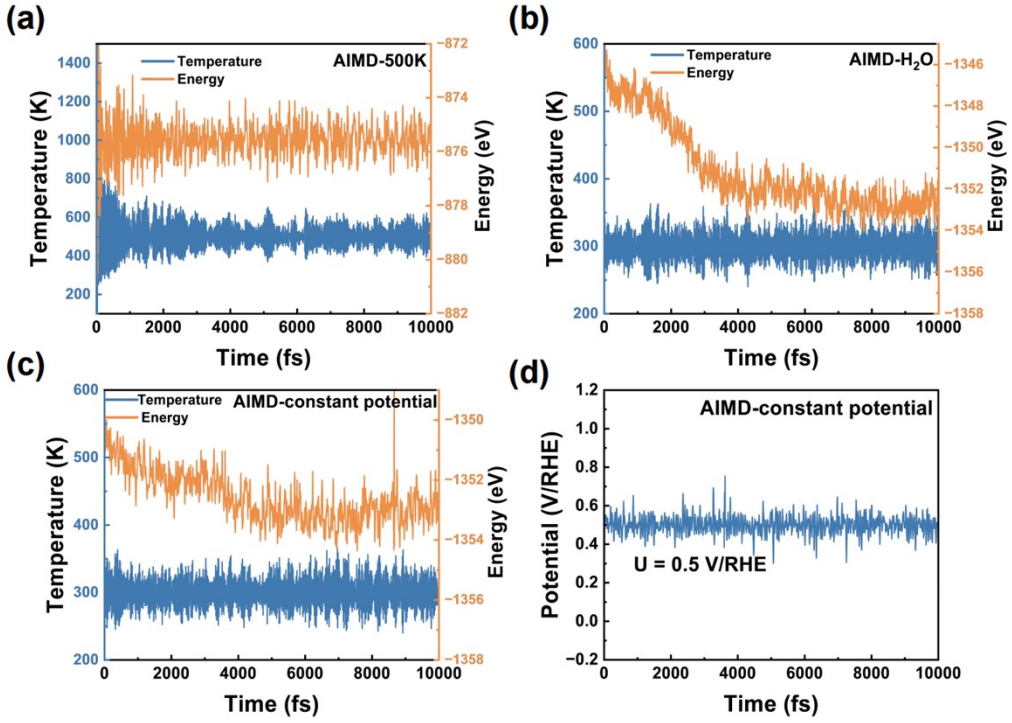

Fig. S4 AIMD simulation results (10 ps) of Pt@$Hf_{1.375}Zr_{0.625}B_2O_2$ under various conditions: (a) at 500 K, (b) in explicit aqueous solution, and (c) under constant potential. (d) The applied potential during the constant-potential AIMD simulations.

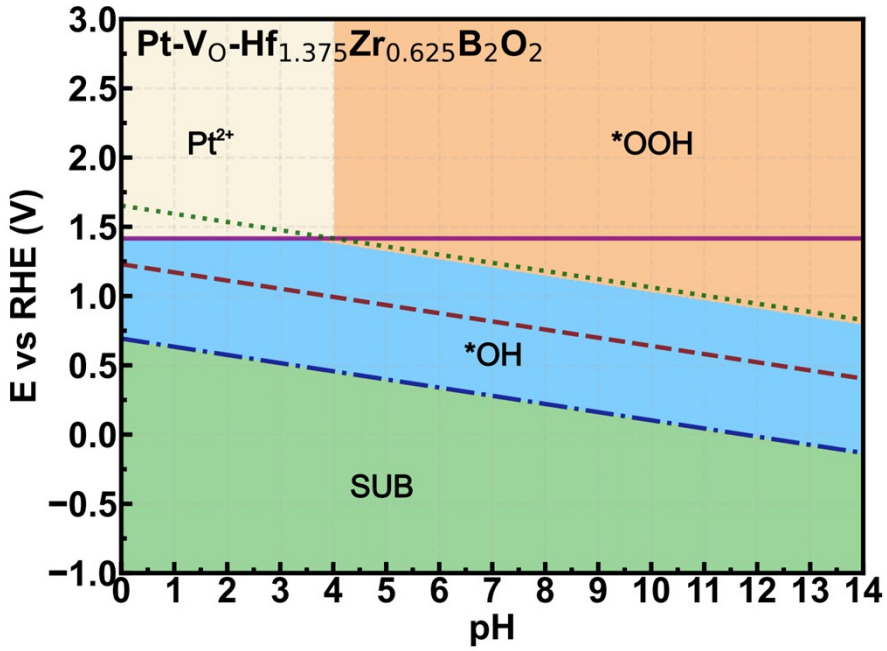

Fig. S5 Pourbaix diagram for Pt@$Hf_{1.375}Zr_{0.625}B_2O_2$, the blue, green and red dashed line represent the working potentials of ORR, OER, and standard equilibrium potential (1.23 V) at varying pH values. SUB denotes the clean substrate surface, *O and *OH denotes *O and *OH adsorbed surface.

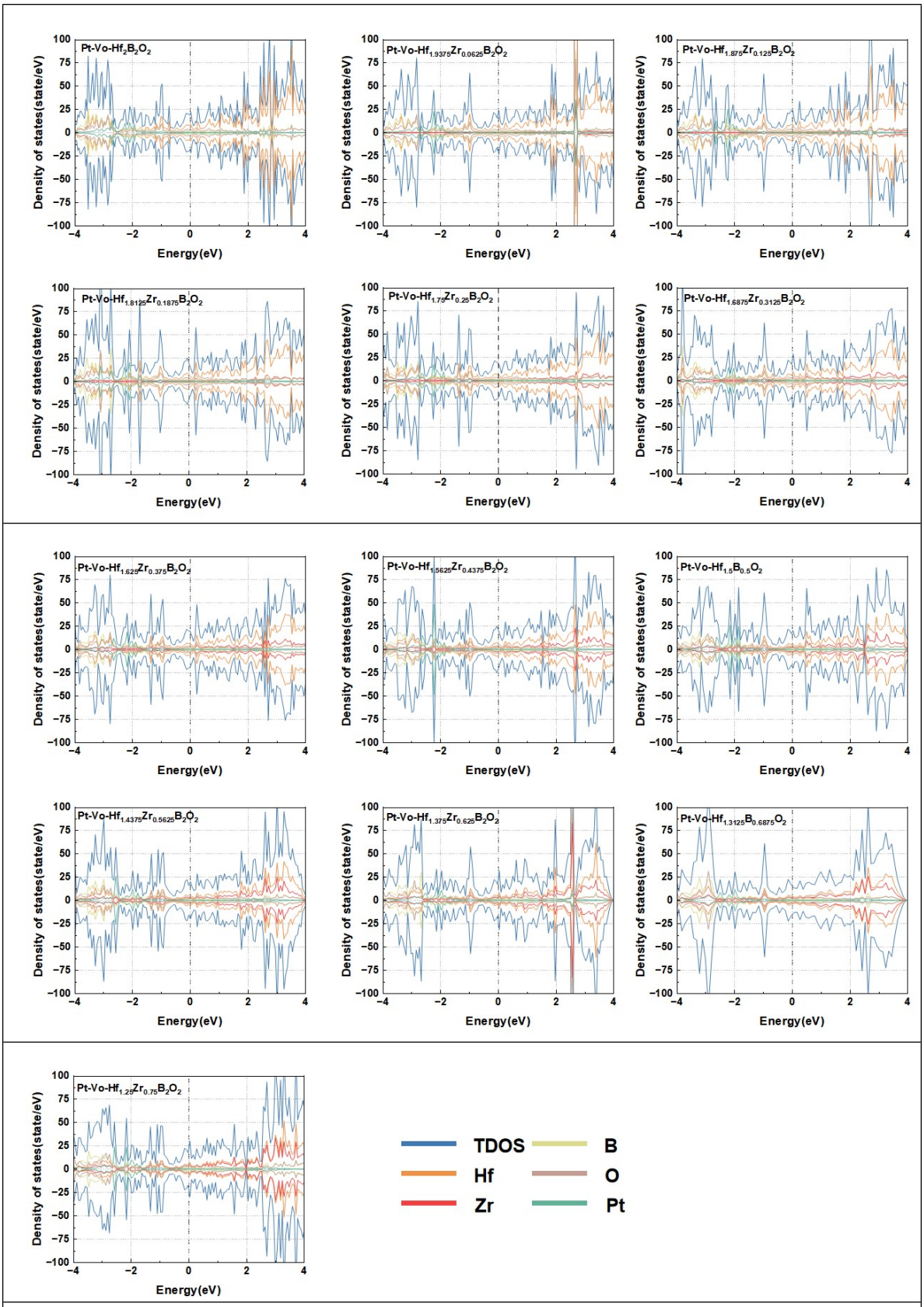

Fig. S6 The density of states (DOS) of hexagonal Pt-V_O-$Hf_{2-x}Zr_xB_2O_2$.

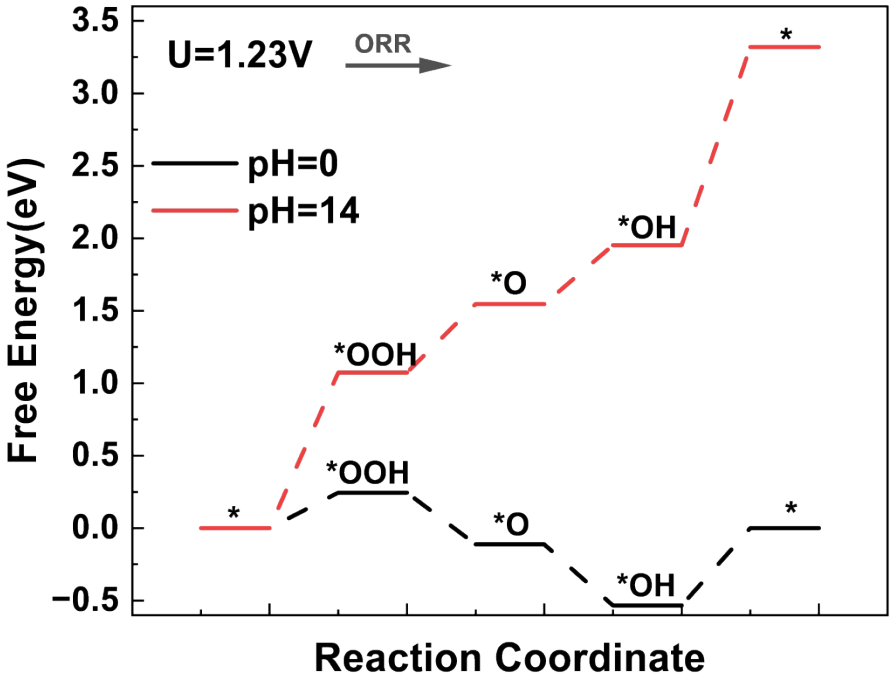

Fig. S7 ORR/OER Gibbs free energy diagram for Pt@$Hf_{1.375}Zr_{0.625}B_2O_2$ under conditions of pH = 0 and pH = 14, U is 1.23 V in both cases.

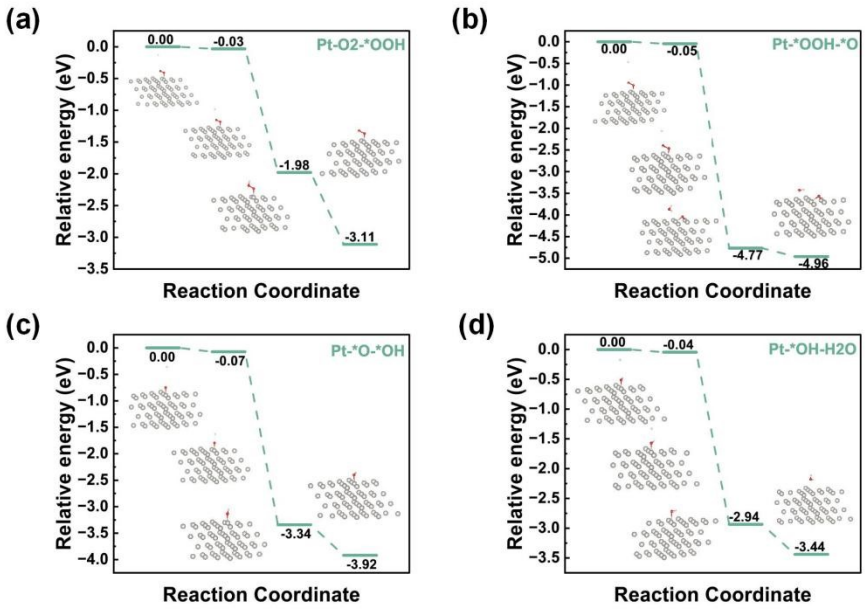

Fig. S8 The four-step NEB process of ORR on the Pt (111) catalyst: (a) O_2 → *OOH, (b) *OOH → *O, (c) *O → *OH, (d) *OH → H_2O.

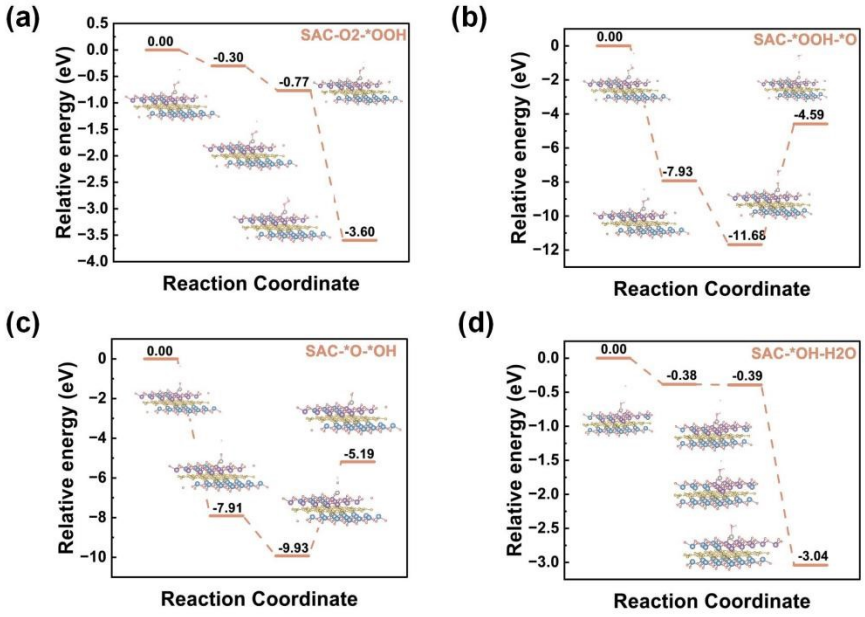

Fig. S9 The four-step NEB process of $Pt@Hf_{1.375}Zr_{0.625}B_2O_2$ on the Pt (111) catalyst: (a) O_2 → *OOH, (b) *OOH → *O, (c) *O → *OH, (d) *OH → H_2O.

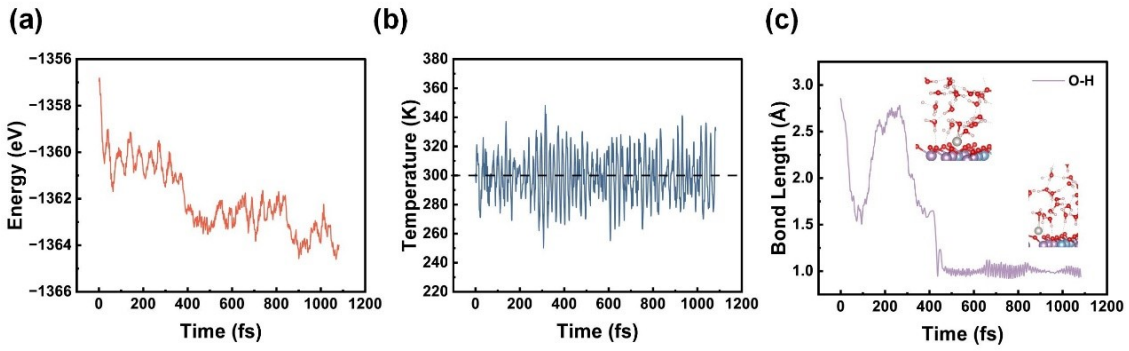

Fig. S10 (a) and (b) AIMD simulations on Pt@$Hf_{1.375}Zr_{0.625}B_2O_2$ for *OH → *H_2O hydrogenation process at 300 K, (c) the dynamic evolution of the O-H bond length between *OH and H_2O.

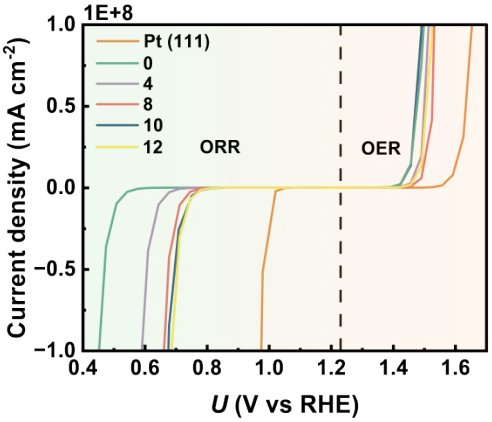

Fig. S11 Theoretical polarization curves for Pt-V_O-$Hf_{2-x}Zr_xB_2O_2$ (x = n/16, n = 0, 4, 8, 10, 12) and Pt (111).

Table S1 The cohesive energies (E_{coh}) comparison for preferential Zr substitution sites in hexagonal and orthorhombic structures (*position*1, 2 can be seen in Figure 1 (a,b), *hex* represents the hexagonal structure and *orth* represents the orthorhombic structure).

position	*hex* (eV)	*orth* (eV)
1	7.44112	7.06911
2	7.44102	7.06917

Table S2 The lattice constant of a_1 and a_2 of the 4×4×1 cell for hexagonal and orthorhombic $Hf_{2-x}Zr_xB_2O_2$, respectively, and the vertical distance between the Pt atom and the nearest Hf/Zr layer on the surface of hexagonal Pt-V_O-$Hf_{2-x}Zr_xB_2O_2$ SACs (hexagonal: *hex-x*=*n*/16, *n*=0-32; orthorhombic: *orth-x*=*n*/9, *n*=0-18; where *n* is an integer).

n	*hex-x*	*orth-x*	a_1 (Å)	a_2 (Å)	distance (Å)
0	0	0	12.648	9.566	1.83
1	0.0625	0.11	12.673	9.570	1.83
2	0.125	0.22	12.677	9.573	1.82
3	0.1875	0.33	12.682	9.578	1.82
4	0.25	0.44	12.686	9.586	1.81
5	0.3125	0.55	12.690	9.583	1.82
6	0.375	0.67	12.695	9.595	1.82
7	0.4375	0.78	12.700	9.590	1.82
8	0.5	0.89	12.704	9.591	1.83
9	0.5625	1	12.709	9.597	1.84
10	0.625	1.11	12.714	9.598	1.84
11	0.6875	1.22	12.717	9.602	1.84
12	0.75	1.33	12.720	9.614	1.84
13	0.8125	1.44	12.723	9.618	1.84
14	0.875	1.56	12.728	9.616	1.85
15	0.9375	1.67	12.735	9.620	1.85
16	1	1.78	12.741	9.622	1.85
17	1.0625	1.89	12.745	9.626	1.84
18	1.125	2	12.748	9.630	1.84
19	1.1875	/	12.752	/	1.84
20	1.25	/	12.756	/	1.84
21	1.3125	/	12.760	/	1.84
22	1.375	/	12.764	/	1.84

23	1.4375	/	12.769	/	1.84
24	1.5	/	12.772	/	1.84
25	1.5625	/	12.776	/	1.84
26	1.625	/	12.778	/	1.83
27	1.6875	/	12.782	/	1.83
28	1.75	/	12.783	/	1.84
29	1.8125	/	12.788	/	1.84
30	1.875	/	12.791	/	1.84
31	1.9375	/	12.798	/	1.84
32	2	/	12.802	/	1.84

Table S3 The binding energies (*hex-*E_b, *orth-*E_b) and the formation energies (*hex-*$E_{f\text{-}Pt}$, *orth-*$E_{f\text{-}Pt}$) of the single Pt atom embedded in the oxygen vacancies of hexagonal and orthorhombic $Hf_{2-x}Zr_xB_2O_2$.

n	*hex-x*	*orth-x*	*hex-*E_b (eV)	*orth-*E_b (eV)	*hex-*$E_{f\text{-}Pt}$ (eV)	*orth-*$E_{f\text{-}Pt}$ (eV)
0	0	0	-6.482	-5.927	6.058	-0.386
1	0.0625	0.11	-6.571	-5.912	6.056	-0.370
2	0.125	0.22	-6.560	-5.780	6.057	-0.238
3	0.1875	0.33	-6.554	-5.788	6.057	-0.246
4	0.25	0.44	-6.537	-5.803	6.053	-0.261
5	0.3125	0.55	-6.468	-5.673	5.955	-0.132
6	0.375	0.67	-6.457	-5.686	5.953	-0.145
7	0.4375	0.78	-6.441	-5.693	5.945	-0.152
8	0.5	0.89	-6.359	-5.631	5.836	-0.089
9	0.5625	1	-6.278	-5.640	5.724	-0.098
10	0.625	1.11	-6.263	-5.658	5.719	-0.117
11	0.6875	1.22	-6.257	-5.663	5.717	-0.121
12	0.75	1.33	-6.245	1.398	5.710	6.939
13	0.8125	1.44	-6.235	-5.661	5.707	-0.119
14	0.875	1.56	-6.220	-5.656	5.690	-0.114
15	0.9375	1.67	-6.203	-5.650	5.675	-0.108
16	1	1.78	-6.180	-4.086	5.661	1.455
17	1.0625	1.89	-6.176	-4.109	5.660	1.432
18	1.125	2	-6.173	-4.091	5.660	1.450
19	1.1875	/	-6.174	/	5.660	/
20	1.25	/	-6.185	/	5.660	/
21	1.3125	/	-6.194	/	5.682	/
22	1.375	/	-6.203	/	5.680	/
23	1.4375	/	-6.204	/	5.678	/

24	1.5	/	-6.196	/	5.655	/
25	1.5625	/	-6.188	/	5.631	/
26	1.625	/	-6.193	/	5.635	/
27	1.6875	/	-6.206	/	5.654	/
28	1.75	/	-6.199	/	5.625	/
29	1.8125	/	-6.202	/	5.643	/
30	1.875	/	-6.207	/	5.641	/
31	1.9375	/	-6.209	/	5.639	/
32	2	/	-6.230	/	5.646	/

Table S4 The dissolution potentials of hexagonal (*hex*-U_{diss} (V)) and orthorhombic (*orth*-U_{diss} (V)) Pt-V_O-$Hf_{2-x}Zr_xB_2O_2$ SACs.

n	*hex-x*	*orth-x*	*hex-*U_{diss} (V)	*orth-*U_{diss} (V)
0	0	0	1.650	1.373
1	0.0625	0.11	1.695	1.365
2	0.125	0.22	1.689	1.299
3	0.1875	0.33	1.686	1.303
4	0.25	0.44	1.678	1.311
5	0.3125	0.55	1.643	1.246
6	0.375	0.67	1.638	1.252
7	0.4375	0.78	1.630	1.256
8	0.5	0.89	1.589	1.225
9	0.5625	1	1.549	1.229
10	0.625	1.11	1.541	1.238
11	0.6875	1.22	1.538	1.241
12	0.75	1.33	1.532	-2.290
13	0.8125	1.44	1.527	1.240
14	0.875	1.56	1.520	1.237
15	0.9375	1.67	1.511	1.234
16	1	1.78	1.500	0.452
17	1.0625	1.89	1.497	0.464
18	1.125	2	1.496	0.455
19	1.1875	/	1.497	/
20	1.25	/	1.502	/
21	1.3125	/	1.506	/
22	1.375	/	1.511	/
23	1.4375	/	1.511	/

24	1.5	/	1.507	/
25	1.5625	/	1.503	/
26	1.625	/	1.506	/
27	1.6875	/	1.512	/
28	1.75	/	1.509	/
29	1.8125	/	1.510	/
30	1.875	/	1.513	/
31	1.9375	/	1.514	/
32	2	/	1.524	/

Table S5 The overpotentials of Pt-V_O-$Hf_{2-x}Zr_xB_2O_2$ SACs toward ORR, OER.

n	pH = 0		
	η^{ORR} (V)	η^{OER} (V)	η^{Bi} (V)
0	0.777	0.412	1.189
1	0.672	0.494	1.166
2	0.653	0.498	1.150
3	0.651	0.514	1.165
4	0.646	0.511	1.157
5	0.610	0.480	1.090
6	0.598	0.471	1.069
7	0.609	0.502	1.111
8	0.578	0.469	1.047
9	0.555	0.443	0.998
10	0.537	0.423	0.960
11	0.521	0.446	0.967
12	0.529	0.477	1.005

Table S6 Comparison of ORR/OER energetics calculated using PBE+D3 and SCAN for $Pt@Hf_{1.375}Zr_{0.625}B_2O_2$.

Reaction	*Elementary step*	ΔG (PBE+D3) (eV)	ΔG (SCAN) (eV)
ORR	$* \rightarrow *OOH$	-0.99	-1.21
	$*OOH \rightarrow *O$	-1.59	-1.59
	$*O \rightarrow *OH$	-1.65	-1.69
	$*OH \rightarrow *$	-0.69	-0.43
OER	$* \rightarrow *OH$	0.69	0.43
	$*OH \rightarrow *O$	1.65	1.69
	$*O \rightarrow *OOH$	1.59	1.59
	$*OOH \rightarrow *$	0.99	1.21

Table S7 The charge transfer of Pt, O and H of Pt-V_O-$Hf_{2-x}Zr_xB_2O_2$ before and after intermediate adsorption.

Catalysts	*Charge transfer* (e)											
	sup	**OOH*				**O*				**OH*		
	Pt	*O_1*	*O_2*	*H*	*OOH*	*Pt*	*O*	*Pt*	*O*	*H*	*OH*	*Pt*
0	-0.13	0.47	0.34	-0.33	0.48	-0.04	0.71	-0.09	0.70	-0.20	0.50	-0.17
1	-0.33	0.45	0.42	-0.35	0.52	-0.29	0.79	-0.48	0.72	-0.22	0.50	0.01
2	-0.27	0.49	0.07	-0.06	0.50	-0.18	0.81	-0.30	0.85	-0.30	0.55	-0.01
3	-0.24	0.47	0.23	-0.22	0.48	-0.16	0.66	-0.17	0.69	-0.19	0.50	-0.14
4	-0.22	0.42	0.37	-0.31	0.48	-0.08	0.63	-0.14	0.66	-0.18	0.48	-0.11
5	-0.38	0.45	0.25	-0.27	0.43	0.06	0.65	0.01	0.60	-0.11	0.49	0.05
6	-0.33	0.41	0.42	-0.35	0.48	0.01	0.67	-0.02	0.62	-0.14	0.48	0.02
7	-0.32	0.47	0.23	-0.20	0.50	-0.11	0.67	-0.03	0.62	-0.13	0.49	-0.002
8	-0.25	0.51	0.33	-0.31	0.53	-0.08	0.81	-0.22	0.67	-0.23	0.44	0.01
9	-0.35	0.50	0.41	-0.43	0.48	-0.11	0.72	-0.17	0.68	-0.24	0.44	-0.02
10	-0.34	0.55	-0.33	0.35	0.57	-0.30	0.78	-0.21	0.78	-0.29	0.49	-0.07
11	-0.27	0.56	-0.30	0.34	0.60	-0.32	0.79	-0.19	0.70	-0.24	0.46	0.06
12	-0.08	0.46	0.27	-0.25	0.48	-0.12	0.74	-0.14	0.71	-0.26	0.45	0.14

More calculation details

The dissolution potential (U_{diss}) can be obtained by the following formula:

$$U_{diss} = U_{diss-bulk} - E_{cluster}/n_e$$

where $U_{diss-bulk}$ is the standard electrode potential, as found in the handbook of chemistry and physics. (Acree, W. E. NIST Chemistry Webbook, NIST Standard Reference Database No. 69; National Institute of Standards and Technology: Gaithersburg, MD, 2018; http://webbook.nist.gov/ chemistry (accessed May 10, 2021)). $n_e$is the number of transferred electrons in the dissolution reaction.

The adsorption energy(E_{ads}) of intermediates can be calculated by the following formulas:

$$E_{ads}(O) = E_{*O} - E_{*} - (E_{H_2O} - E_{H_2})$$

$$E_{ads}(OH) = E_{*OH} - E_{*} - (E_{H_2O} - \frac{1}{2}E_{H_2})$$

$$E_{ads}(OOH) = E_{*OOH} - E_{*} - (2E_{H_2O} - \frac{3}{2}E_{H_2})$$

$$E_{ads}(H) = E_{*H} - E_{*} - \frac{1}{2}E_{H_2}$$

$$E_{ads}(O_2) = E_{*O_2} - E_{*} - E_{O_2}$$

The E_{*O}, E_{*OH}, E_{*OOH}, E_{*H}, E_{*O_2}, and E_{*} are the total energies of catalysts with O, OH, OOH, H, O_2 and without adsorbents. The E_{H_2O}, E_{H_2}, and E_{O_2} are total energies of free H_2O, H_2 and O_2 molecules in liquid and gas phases. Furthermore, we use 1/2 H_2 to represent the free energy of (H^+ + e^-).

The input files for VASP calculation:

INCAR

Global Parameters

LREAL = Auto
ENCUT = 600
PREC = Accurate
ADDGRID = .TRUE.
ISMEAR = 0
SIGMA = 0.05
NELM = 120
NELMIN = 4
EDIFF = 1E-05
EDIFFG = -2E-02
IVDW = 11
ISYM = 0

Structural optimization

ALGO = Fast
LWAVE = .FALSE.
LCHARG = .FALSE.
NSW = 100
IBRION = 2

The input files for CP2K calculation: cp2k.inp

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  PRINT_LEVEL LOW
  RUN_TYPE MD
&END GLOBAL

&FORCE_EVAL
  METHOD Quickstep
  &SUBSYS
    &CELL
      A      12.71624900       0.00000000       0.00000000
      B      -6.35885466      11.01225738       0.00000000
      C      -0.00895307      -0.00165284      20.62451899
      PERIODIC XYZ #Direction(s) of applied PBC (geometry aspect)
    &END CELL
    &COORD
      Hf             -0.00024805       0.00294227       8.49474438
      Hf              3.17543590       0.00366986       8.48490649
      Hf             -3.18193491      11.00642156      12.08386443
      Hf             -1.58902836       2.75477416       8.48325653
      Hf              1.58769285       2.76121266       8.52908421
      Hf              6.35522941       0.00225912       8.49959115
      Hf              6.35160049       0.00111286      12.08456566
      Hf              9.53199241       0.00170894       8.49416690
      Hf              9.53654550      -0.00087027      12.09607414
      Hf              4.76251886       2.75513819       8.47541921
      Hf              4.76762204       2.75220485      12.09908532
      Hf              7.94296961       2.75258142       8.49950865
      Hf              7.94214429       2.75607132      12.08452441
      Hf             -3.18069409       5.50796946       8.49816805
      Hf              0.00390784       5.50242820       8.52425807
      Hf             -4.77183835       8.25942481       8.51310021
      Hf             -1.59339258       8.25753190       8.49814743
      Hf              3.16975583       5.50159087       8.52916671
      Hf              6.35154559       5.50544871       8.48492711
      Hf              6.36055665       5.50900358      12.08376130
      Hf              1.58673169       8.25579316       8.48325653
      Hf              4.76434564       8.25602350       8.49476501
      Zr             -6.35718131      11.00521038      12.08180198
      Zr             -1.58982964       2.75210435      12.11636867
      Zr              1.58729069       2.71653500      12.11335749
      Zr             -3.18691332       5.51392572      12.08792746
      Zr             -0.03500416       5.52484695      12.12453598
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Zr	-4.77154680	8.25911622	12.08902056
Zr	-1.60186885	8.25977701	12.08825745
Zr	3.20817187	5.52426418	12.11354311
Zr	1.58863861	8.25774849	12.11651304
Zr	4.77401050	8.25931504	12.08149261
B	1.59176687	0.91582832	10.38168163
B	-0.00593658	1.83469561	10.18766678
B	4.76900530	0.91733720	10.37922731
B	3.18115527	1.83520322	10.17457021
B	-0.00594761	3.66661150	10.40195553
B	-1.59528851	4.58534812	10.18958486
B	3.18429417	3.66634756	10.39752126
B	1.58815991	4.58781003	10.24995282
B	7.94345666	0.91880161	10.38188787
B	6.35539439	1.83541295	10.16836223
B	11.11855835	0.91374703	10.38139288
B	9.53177748	1.83511518	10.17391022
B	6.35722862	3.66840832	10.37924793
B	4.76848859	4.58466656	10.17452896
B	9.52713458	3.66737305	10.38077415
B	7.94314609	4.58692437	10.17087842
B	-1.59398136	6.42506233	10.38333159
B	-3.18128693	7.34107785	10.18434623
B	1.58890652	6.42899222	10.40189365
B	-0.00161691	7.34596687	10.18960548
B	-3.18162785	9.18267494	10.38083602
B	-4.77189388	10.09736942	10.17644704
B	-0.00369755	9.18498751	10.38093914
B	-1.59228874	10.09669811	10.17091967
B	4.76979653	6.42091085	10.38161975
B	3.17514458	7.34504199	10.18772865
B	7.94003420	6.42049247	10.38054728
B	6.35280698	7.34051687	10.17622017
B	3.17669336	9.18402939	10.38151663
B	1.58521442	10.09710532	10.17395147
B	6.35367353	9.17803928	10.37464867
B	4.76475944	10.09507896	10.17529206
O	-1.63849694	4.57263540	13.13231185
O	-0.03368107	1.80907655	13.13008440
O	3.25282559	1.79013848	13.09256840
O	-0.00534804	3.67217426	7.49670329
O	1.58478935	0.92798666	7.48591666
O	3.17364742	3.67251623	7.48940221
O	4.76492651	0.91916581	7.48637040

```
      O              4.84331212     4.54504186    13.09265090
      O              7.90644789     4.55357669    13.08858787
      O              6.36161062     1.83198658    13.07355260
      O              9.47866761     1.81486098    13.09271277
      O              6.35380466     3.67139322     7.48634978
      O              7.94709408     0.91669950     7.48086365
      O              9.53960473     3.67079822     7.49057780
      O             11.12323229     0.92071798     7.49330024
      O             -4.72991187    10.11353198    13.10488124
      O             -1.58168156    10.14546884    13.08856725
      O             -3.18623911     7.34403566    13.12602137
      O             -0.01226914     7.38971399    13.13235310
      O             -3.18426124     9.17474579     7.49926073
      O             -1.58175709     6.41781688     7.48995907
      O             -0.00034381     9.17259909     7.49053655
      O              1.58437563     6.42575618     7.49672391
      O              1.57624397    10.15339733    13.09269215
      O              4.72220360    10.11967698    13.10296316
      O              3.18360549     7.38200560    13.13008440
      O              6.35974700     7.29584773    13.10473687
      O              3.17302008     9.17643113     7.49336211
      O              4.75587032     6.42083456     7.48604041
      O              6.35549554     9.17683839     7.49583706
      O              7.94567162     6.42686821     7.49934322
      Pt             1.59888751     4.58168659    13.96779049
    &END COORD
#   &VELOCITY #You can set initial atomic velocities in this section
#   &END VELOCITY
    &KIND Hf
      ELEMENT Hf
      BASIS_SET DZVP-MOLOPT-SR-GTH-q12
      POTENTIAL GTH-PBE
    &END KIND
    &KIND Zr
      ELEMENT Zr
      BASIS_SET DZVP-MOLOPT-SR-GTH-q12
      POTENTIAL GTH-PBE
    &END KIND
    &KIND B
      ELEMENT B
      BASIS_SET DZVP-MOLOPT-SR-GTH-q3
      POTENTIAL GTH-PBE
    &END KIND
    &KIND O
```

```
      ELEMENT O
      BASIS_SET DZVP-MOLOPT-SR-GTH-q6
      POTENTIAL GTH-PBE
    &END KIND
    &KIND Pt
      ELEMENT Pt
      BASIS_SET DZVP-MOLOPT-SR-GTH-q18
      POTENTIAL GTH-PBE
    &END KIND
  &END SUBSYS

  &DFT
    BASIS_SET_FILE_NAME    BASIS_MOLOPT
    POTENTIAL_FILE_NAME    POTENTIAL
#   WFN_RESTART_FILE_NAME cp2k10-RESTART.wfn
    CHARGE       0 #Net charge
    MULTIPLICITY       1 #Spin multiplicity
    &QS
      EPS_DEFAULT 1.0E-10 #Set all EPS_xxx to values such that the energy will be correct up to this value
      EXTRAPOLATION ASPC #Extrapolation for wavefunction during e.g. MD. ASPC is default, PS can also be used
      EXTRAPOLATION_ORDER 3 #Order for PS or ASPC extrapolation. 3 is default
    &END QS
    &POISSON
      PERIODIC XYZ #Direction(s) of PBC for calculating electrostatics
      PSOLVER PERIODIC #The way to solve Poisson equation
    &END POISSON
    &XC
      &XC_FUNCTIONAL PBE
      &END XC_FUNCTIONAL
      &VDW_POTENTIAL
        POTENTIAL_TYPE PAIR_POTENTIAL
        &PAIR_POTENTIAL
          PARAMETER_FILE_NAME dftd3.dat
          TYPE DFTD3
          REFERENCE_FUNCTIONAL PBE
          #CALCULATE_C9_TERM T #Calculate C9-related three-body term, more accurate for large system
        &END PAIR_POTENTIAL
      &END VDW_POTENTIAL
    &END XC
    &MGRID
      CUTOFF    500
```

```
      REL_CUTOFF    55
    &END MGRID
    &SCF
      MAX_SCF 128 #Maximum number of steps of inner SCF
      EPS_SCF 1.0E-05 #Convergence threshold of density matrix of inner SCF
#       SCF_GUESS RESTART #Use wavefunction from WFN_RESTART_FILE_NAME file as initial guess
#       IGNORE_CONVERGENCE_FAILURE #Continue calculation even if SCF not converged, works for version >= 2024.1
      &OT
        PRECONDITIONER FULL_ALL #Usually best but expensive for large system. Cheaper: FULL_SINGLE_INVERSE and FULL_KINETIC
        MINIMIZER DIIS #CG is worth to consider in difficult cases
        LINESEARCH 2PNT #1D line search algorithm for CG. 2PNT is default. 3PNT is more expensive but may be better. GOLD is best but very expensive
        ALGORITHM STRICT #Algorithm of OT. Can be STRICT (default) or IRAC
      &END OT
      &OUTER_SCF
        MAX_SCF 20 #Maximum number of steps of outer SCF
        EPS_SCF 1.0E-05 #Convergence threshold of outer SCF
      &END OUTER_SCF
      &PRINT
        &RESTART OFF #Do not generate wfn file to suppress meaningless I/O cost
        &END RESTART
      &END PRINT
    &END SCF
  &END DFT
&END FORCE_EVAL

&MOTION
  &MD
    ENSEMBLE NVT
    STEPS 5000 #Number of steps to run
    TIMESTEP 2.0 #Step size in fs. Decrease it properly for high temperature simulation
    TEMPERATURE 500 #Initial and maintained temperature (K)
#     COMVEL_TOL 0 #Uncomment this can remove translation motion of center-of-mass every step
    &THERMOSTAT
      TYPE CSVR
      &CSVR
        TIMECON 200 #Time constant in fs. Smaller/larger results in stronger/weaker temperature coupling
      &END CSVR
    &END THERMOSTAT
```

```
    &PRINT
      &PROGRAM_RUN_INFO
        &EACH
          MD          1 #Output frequency of MD information, 0 means never
        &END EACH
      &END PROGRAM_RUN_INFO
    &END PRINT
  &END MD
  &PRINT
    &TRAJECTORY
      &EACH
        MD      1 #Output frequency of coordinates, 0 means never
      &END EACH
      FORMAT xyz
    &END TRAJECTORY
    &VELOCITIES
      &EACH
        MD          0 #Output frequency of velocities, 0 means never
      &END EACH
    &END VELOCITIES
    &FORCES
      &EACH
        MD          0 #Output frequency of forces, 0 means never
      &END EACH
    &END FORCES
    &RESTART
      BACKUP_COPIES 0 #Maximum number of backing up restart file, 0 means never
      &EACH
        MD    1 #Frequency of updating last restart file, 0 means never
      &END EACH
    &END RESTART
    &RESTART_HISTORY OFF
    &END RESTART_HISTORY
  &END PRINT
&END MOTION
```

The optimized atomic coordinates of Pt-V_O-$Hf_{1.375}Zr_{0.625}B_2O_2$ (4×4×1 supercell):

CONTCAR

Hf22 Zr10 B32 Pt1 O31

1.00000000000000

11.0122965673159356 -6.3586384391362651 -0.0027536341925885

-0.0002072600427606 12.7163221602735383 0.0009384463758615

-0.0042997458502392 0.0015241554405765 20.6245199825259853

Hf Zr B O Pt

22 10 32 31 1

Selective dynamics

Direct

0.0004354015824362	0.0003285495601304	0.4118759496709004	T	T	F
0.2502021221613120	0.0003945433177464	0.4113994655763520	T	T	F
0.2500225919009651	0.9995576309210676	0.5858983621382308	T	T	T
0.0004522249134595	0.2502167980335344	0.4113187377450629	T	T	F
0.2505619340498200	0.2508023937119361	0.4135411707827998	T	T	F
0.5001962628937235	0.0002672436309581	0.4121105188834662	T	T	F
0.4999938365621972	0.0001886979302128	0.5859320102725221	T	T	T
0.7499904305446563	0.0002167023564539	0.4118483022046107	T	T	F
0.7503664993705783	0.0000090670021535	0.5864899707634379	T	T	T
0.4999508573330971	0.2502503605667741	0.4109391134730842	T	T	F
0.5003555726537527	0.2500102715759454	0.5866358564316201	T	T	T
0.7499450078435359	0.2500179241370546	0.4121071939256282	T	T	F
0.7501737250627798	0.2503607178014704	0.5859298549821261	T	T	T
0.0003051295546470	0.5002292073074699	0.4120422975070639	T	T	F
0.2504899005232843	0.4997259183636018	0.4133070697908465	T	T	F
0.0001203890636958	0.7500825684579908	0.4127662060365225	T	T	F
0.2499854113729398	0.7499106883190834	0.4120412443863586	T	T	F
0.4994126148524174	0.4996498268839034	0.4135454931637952	T	T	F
0.7498006324596815	0.4999998435479256	0.4113995002625757	T	T	F
0.7508069852204073	0.5003491436654173	0.5858933752487232	T	T	T
0.4999888884218180	0.7497529975249364	0.4113187568322942	T	T	F
0.7498857852724470	0.7497736167250864	0.4118771493512909	T	T	F
0.0002684344296426	0.9994484059694386	0.5857975803728124	T	T	T
0.0004050922303307	0.2500010922183620	0.5874737281753610	T	T	T
0.2486371997989494	0.2467713704174770	0.5873277702210373	T	T	T
0.0002220783758347	0.5007962051810182	0.5860947337994986	T	T	T
0.2485842528593096	0.5017875787264927	0.5878698199131236	T	T	T
0.0002641306010531	0.7500808728087023	0.5861475211743183	T	T	T
0.2495563213715002	0.7501406821501746	0.5861108705769382	T	T	T
0.5035989390434281	0.5017354329943302	0.5873373178100820	T	T	T
0.5003650708869287	0.7499572456500871	0.5874806390886320	T	T	T
0.7509306829474340	0.7500989943954437	0.5857828207085234	T	T	T
0.1671551261869908	0.0832400348029481	0.5033657252699939	T	T	T

0.0832295128899005	0.1666790010048516	0.4939588413917377	T	T	T
0.4170803731197594	0.0833773878096622	0.5032472355634496	T	T	T
0.3338837469628899	0.1667245264301584	0.4933238321880324	T	T	T
0.1664230941107405	0.3330334809209532	0.5043491340347472	T	T	T
0.0831487206042496	0.4164596876562427	0.4940519584800214	T	T	T
0.4172900086633788	0.3330090099203318	0.5041340927828557	T	T	T
0.3336083467977957	0.4166839621514455	0.4969789134437477	T	T	T
0.6667838149501009	0.0835097329536723	0.5033756579858419	T	T	T
0.5835136157537235	0.1667437887523988	0.4930226731386966	T	T	T
0.9162430946255284	0.0830510723388969	0.5033522167346121	T	T	T
0.8332901326220110	0.1667168858887180	0.4932917224493707	T	T	T
0.6669007634903252	0.3331961362194207	0.5032479020502194	T	T	T
0.5835618485076708	0.4163976912268552	0.4933221179508607	T	T	T
0.9161337193470587	0.3331016455689522	0.5033216668509866	T	T	T
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0.1667988966981042	0.5835222386654948	0.5034460546662416	T	T	T
0.0835624403431297	0.6667016956808141	0.4937976943776476	T	T	T
0.4172791264907971	0.5838792968716149	0.5043455581371958	T	T	T
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0.1671682032009656	0.8339352765952199	0.5033254174046107	T	T	T
0.0836381194112903	0.9169946307242043	0.4934148559299132	T	T	T
0.4171842887088673	0.8341448549073291	0.5033299900162476	T	T	T
0.3336497219590910	0.9169345063061911	0.4931465801758677	T	T	T
0.6670551702170258	0.5831447262190679	0.5033631650562285	T	T	T
0.5836091691223189	0.6670621790745415	0.4939619988268475	T	T	T
0.9163422477077390	0.5831070894677737	0.5033113273966805	T	T	T
0.8332926687970996	0.6666508122491521	0.4934040971334568	T	T	T
0.6672446966652856	0.8340576577940695	0.5033584026506475	T	T	T
0.5835457369204207	0.9169714685159249	0.4932943958474425	T	T	T
0.9168089651277569	0.8335144475502929	0.5030246839461512	T	T	T
0.8334915137836560	0.9167872202569995	0.4933587032985614	T	T	T
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0.0799956723047046	0.1643737579871143	0.6366249226341267	T	T	T
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0.1670487630966591	0.0843226150139529	0.3629615322753565	T	T	F
0.4166226041806951	0.3335480333764309	0.3631313277313666	T	T	F
0.4167328660261091	0.0835224674729389	0.3629838452783432	T	T	F
0.5877569859107510	0.4128211256785193	0.6348099205717830	T	T	T
0.8290277156332664	0.4135964589232657	0.6346131293581792	T	T	T
0.5839567910296779	0.1664539340630853	0.6338839344101999	T	T	T
0.8283041399163338	0.1648989087531234	0.6348130863940469	T	T	T
0.6666576113939584	0.3334459616680405	0.3629827124323270	T	T	F
0.6668652615786286	0.0832981783476896	0.3627169628876175	T	T	F

0.9171606385749698	0.3333919323328587	0.3631883240794167	T	T	F
0.9168182998794592	0.0836626813498356	0.3633200611020584	T	T	F
0.0877836133063497	0.9184843790459993	0.6354028995603898	T	T	T
0.3368084952155144	0.9213835530288534	0.6346120835839741	T	T	T
0.0834183236164705	0.6669916233243711	0.6364276323019666	T	T	T
0.3350917370201643	0.6711399570890464	0.6367348891783280	T	T	T
0.1664918697491302	0.8331942044074765	0.3636092557200143	T	T	F
0.1673224806134144	0.5828428632000566	0.3631580695747090	T	T	F
0.4167756692777331	0.8329994157458103	0.3631860553540278	T	T	F
0.4166657783980270	0.5835636364052164	0.3634864240805484	T	T	F
0.5855072442496834	0.9221041154659915	0.6348124185962334	T	T	T
0.8313728754057621	0.9190423124655780	0.6353096701598702	T	T	T
0.5860635350888046	0.6704399939590218	0.6366252222362050	T	T	T
0.8319205399846581	0.6626162643791957	0.6353960938957997	T	T	T
0.6665015980052900	0.8333465435082701	0.3633233774714952	T	T	F
0.6658471589652706	0.5831174359337012	0.3629682627645252	T	T	F
0.9167892582812627	0.8333838872504415	0.3634429127008829	T	T	F
0.9169659669706505	0.5836650823168483	0.3636126231158556	T	T	F
0.3343135591569393	0.4161549559791240	0.6772418060978680	T	T	T