Supporting Information for

Cooperativity in Bimetallic SACs: An Efficient Strategy for Designing Bifunctional Catalysts for Overall Water Splitting

Afshan Mohajeri* and Nasimeh Lari Dashti

Department of Chemistry, College of Sciences, Shiraz University, Shiraz 7194684795, Iran

E-mail: amohajeri@shirazu.ac.ir , Phone: +98 71 36137161

Content:

Calculation details for OER and HER

REFERENCES

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The Gibbs reaction free energy for the adsorption of the intermediate are expressed as

$\Delta G_{*OH} = (G+ZPE)_{*OH} - (G+ZPE)_{*} - (G+ZPE)_{H2O} + 1/2\ (G+ZPE)_{H2}$

$\Delta G_{*O} = (G+ZPE)_{*O} - (G+ZPE)_{*} - (G+ZPE)_{H2O} + (G+ZPE)_{H2}$

$\Delta G_{*OOH} = (G+ZPE)_{*OOH} - (G+ZPE)_{*} - 2(G+ZPE)_{H2O} + 3/2\ (G+ZPE)_{H2}$

The value of ΔG_i for reactions 2-5 in the manuscript text can be calculated by

$\Delta G_1 = E_{*OH} - E_{*} - E_{H2O} + 1/2\ E_{H_2} + \Delta ZPE - T\Delta S - e\varphi$

$\Delta G_2 = E_{*O} - E_{*OH} + 1/2\ E_{H_2} + \Delta ZPE - T\Delta S - e\varphi$

$\Delta G_3 = E_{*OOH} - E_{*O} - E_{H2O} + 1/2\ E_{H_2} + \Delta ZPE - T\Delta S - e\varphi$

$\Delta G_4 = E_{*} - E_{*OOH} + 2E_{H2O} + 3/2\ E_{H_2} + 4.92 + \Delta ZPE - T\Delta S - e\varphi$

Table S1. Cohesive Energy (eV) and Electronegativity of Transition Metals from 3d Atoms.*

Metal	$E_{Cohesive}$ (eV)	Electronegativity
Sc	3.90	1.30
Ti	4.85	1.54
V	5.31	1.63
Cr	4.10	1.66
Mn	2.92	1.55
Fe	4.28	1.83
Co	4.39	1.88
Ni	4.44	1.91
Cu	3.49	1.90
Zn	1.35	1.60

*Cohesive energies are taken from Reference (1)

Table S2. Adsorption Energies, Structural Parameters, and Spin Multiplicity for Different Orientation of Adsorbate (X=O, OH, OOH, and H) on TM/B_{36} Systems.

TM/B_{36}-X	TM-X (Å)	TM-B (Å)	E_{ads} (eV)	Spin Multiplicity
Ti/B_{36}-OH	1.774	2.236	-4.87	2
Ti/B_{36}-OH	1.779	2.240	-3.44	4
Ti/B_{36}-O	1.608	2.315	-8.28	1
Ti/B_{36}-O	1.604	2.336	-8.45	3
Ti/B_{36}-O	1.603	2.352	-7.24	5
Ti/B_{36}-OOH	1.787	2.245	-3.15	2
Ti/B_{36}-OOH	1.791	2.241	-1.73	4
Ti/B_{36}-H	1.739	2.219	-2.21	2
Ti/B_{36}-H	1.767	2.231	-0.87	4
Ti/B_{36}-BH	1.309	2.22	-2.39	2
V/B_{36}-OH	1.708	2.126	-4.89	1
V/B_{36}-OH	2.698	2.145	-4.16	3
V/B_{36}-OH	1.750	2.144	-2.51	5
V/B_{36}-O	1.563	2.171	-9.16	2
V/B_{36}-O	1.578	2.166	-7.48	4
V/B_{36}-O	1.579	2.176	-6.33	6
V/B_{36}-OOH	1.749	2.128	-3.27	1

V/B_{36}-OOH	1.755	2.160	-2.40	3
V/B_{36}-OOH	1.774	2.124	-0.96	5
V/B_{36}-H	1.650	2.118	-2.25	1
V/B_{36}-H	1.713	2.138	-1.51	3
V/B_{36}-H	1.703	2.128	-0.05	5
V/B_{36}-BH	1.479	2.080	-1.54	1
Cr/B_{36}-OH	1.796	2.088	-4.14	4
Cr/B_{36}-OH	1.790	2.113	-3.31	6
Cr/B_{36}-O	1.530	2.094	-10.04	1
Cr/B_{36}-O	1.543	2.096	-8.46	3
Cr/B_{36}-O	1.555	2.098	-7.21	5
Cr/B_{36}-O	1.561	2.137	-6.09	7
Cr/B_{36}-OOH	1.732	2.093	-2.33	2
Cr/B_{36}-OOH	1.765	2.096	-2.75	4
Cr/B_{36}-OOH	1.780	2.111	-1.57	6
Cr/B_{36}-H	1.604	2.070	-2.25	2
Cr/B_{36}-H	1.605	2.120	-2.36	4
Cr/B_{36}-H	1.690	2.339	-2.33	6
Cr/B_{36}-BH	1.688	1.962	-1.99	2
Cr/B_{36}-BH	1.866	2.084	-3.51	4
Cr/B_{36}-BH	1.807	2.073	-2.29	6
Mn/ B_{36}-OH	1.728	2.088	-2.98	3
Mn/ B_{36}-OH	1.785	2.101	-2.57	5
Mn/ B_{36}-OH	1.793	2.139	-1.76	7
Mn B_{36}-O	1.544	2.046	-7.16	2
Mn/ B_{36}-O	1.567	2.043	-5.97	4
Mn/ B_{36}-O	1.573	2.043	-4.62	6
Mn/ B_{36}-O	1.598	2.115	-3.98	8
Mn/ B_{36}-OOH	1.650	2.060	-1.50	1
Mn/ B_{36}-OOH	1.712	2.077	-1.48	3
Mn/ B_{36}-OOH	1.783	2.076	-0.93	5
Mn/ B_{36}-OOH	1.799	2.131	-0.27	7
Mn/ B_{36}-H	1.565	2.047	0.12	1
Mn/ B_{36}-H	1.559	2.057	-1.36	3
Mn/ B_{36}-H	1.614	2.057	-0.90	5
Mn/ B_{36}-H	1.623	2.106	-0.08	7
Mn/ B_{36}-BH	1.562	1.921	-0.77	1
Mn/ B_{36}-BH	1.551	1.934	-1.48	3
Mn/ B_{36}-BH	1.330	1.965	-1.09	5
Fe/ B_{36}-OH	1.722	2.059	-2.62	2
Fe/ B_{36}-OH	1.773	2.088	-3.68	4
Fe/ B_{36}-O	1.575	2.076	-6.25	1
Fe/ B_{36}-O	1.572	2.082	-6.64	3
Fe/ B_{36}-O	1.616	2.036	-5.74	5
Fe/ B_{36}-O	1.617	2.098	-4.84	7
Fe/ B_{36}-OOH	1.694	2.063	-1.50	2

Fe/ B_{36}-OOH	1.771	2.090	-2.12	4
Fe/ B_{36}-H	1.493	2.456	-1.02	2
Fe/ B_{36}-H	1.594	2.061	-2.02	4
Fe/ B_{36}-H	1.596	2.083	-1.08	6
Fe/ B_{36}-BH	1.495	1.945	-1.61	2
Fe/ B_{36}-BH	1.358	1.956	-1.72	4
Co/ B_{36}-OH	1.764	2.071	-2.24	1
Co/ B_{36}-OH	1.772	2.073	-3.41	3
Co/ B_{36}-OH	1.735	2.156	-2.44	5
Co/ B_{36}-O	1.617	2.088	-5.91	2
Co/ B_{36}-O	1.624	2.073	-6.64	4
Co/ B_{36}-O	1.622	2.071	-5.76	6
Co/ B_{36}-OOH	1.744	2.019	-1.03	1
Co/ B_{36}-OOH	1.778	2.033	-1.92	3
Co/ B_{36}-OOH	1.755	2.109	-0.97	5
Co/ B_{36}-H	1.441	1.978	-1.37	1
Co/ B_{36}-H	1.541	2.038	-1.71	3
Co/ B_{36}-H	1.575	2.074	-0.70	5
Co/ B_{36}-BH	1.452	1.881	-1.71	1
Co/ B_{36}-BH	1.314	1.943	-2.04	3
Ni/B_{36}-OH	1.794	2.119	-2.60	2
Ni/B_{36}-OH	1.753	2.170	-1.72	4
Ni/B_{36}-O	1.668	2.134	-4.37	1
Ni/B_{36}-O	1.684	2.116	-5.76	3
Ni/B_{36}-O	1.661	2.122	-4.75	5
Ni/B_{36}-OOH	1.810	2.087	-1.35	2
Ni/B_{36}-OOH	1.752	2.148	-0.32	4
Ni/B_{36}-H	1.484	1.995	-1.30	2
Ni/B_{36}-H	1.542	2.103	0.09	4
Ni/B_{36}-BH	1.281	1.931	-1.59	2
Cu/B_{36}-OH	1.816	2.167	-3.17	1
Cu/B_{36}-OH	1.794	2.198	-1.86	3
Cu/B_{36}-O	1.762	2.135	-4.88	2
Cu/B_{36}-O	1.723	2.217	-5.00	4
Cu/B_{36}-OOH	1.844	2.129	-1.81	1
Cu/B_{36}-OOH	1.875	2.140	-0.97	3
Cu/B_{36}-H	1.532	2.132	-2.15	1
Cu/B_{36}-H	1.598	2.131	-0.75	3
Cu/B_{36}-BH	1.231	2.088	-2.58	1

Table S3. Gibbs Free Energy for the Adsorption of OER Intermediates on Pristine and Doped B_{36}.

System	ΔG_{*OH}(eV)	ΔG_{*O}(eV)	ΔG_{*OOH}(eV)
Pristine B_{36}	0.55	0.37	4.95
Ti/B_{36}	-2.12	-0.28	1.18
V/B_{36}	-1.89	-1.59	1.32
Cr/B_{36}	-1.36	1.54	2.10
Mn/B_{36}	-1.39	-0.85	1.76
Fe/B_{36}	0.06	2.49	3.09
Co/B_{36}	0.44	1.78	4.13
Ni/B_{36}	0.33	1.88	3.16
Cu/B_{36}	2.28	4.83	4.57

Table S4. Previous Reports of Overpotentials for OER and Gibbs Free energy for HER on Some Catalysts.

Catalyst	η^{OER} (V)	ΔG_{*H} (eV)	Ref
Transition metal doped boron -β_{12}	Ti/β_{12} =2.12 V/β_{12}=2.16 Mn/β_{12} =1.92 Fe/β_{12}=1.31 Co/β_{12}=0.85 Ni/β_{12}=0.40 Ti/β_{12}=2.12 Ti/β_{12}=2.12 Ti/β_{12}=2.12 Ti/β_{12}=2.12	Ni/β_{12}=0.06 and 0.20	(2)
Pd-Co@CN	Pd-Co@CN = 1.00	Site1=0.08 Site2=0.02 Site6= 1.06	(3)
Transition metal doped-BH(borophene hydride)	Cr-BH= 1.77 Mn-BH= 1.09 Fe-BH= 0.55 Co-BH= 0.37 Ni-BH= 0.74		(4)

	Cu-BH= 0.70 Ru-BH=1.02 Rh-BH= 0.24 Ag-BH= 0.98		
Transition metal doped on MoP		Cu/MoP=0.17 Cr/MoP=0.14 Mn/MoP=0.00 W/MoP=-0.03 Fe/MoP=-0.06 Ni/MoP=-0.07 N/MoP=-0.08 Co/MoP=-0.09 S/MoP= -0.17	(5)
Transition metal doped on Single layer TiO_2 nanosheet		Nb/LNS=1.25 V/LNS=0.75 Cr/LNS=0.03 Mn/LNS=-0.03 Fe/LNS=1.00 Ni/LNS=-1.15 Co/LNS=-1.50 Cu/LNS=-1.70 Zn/LNS=-2.7	(6)
$Pt@Fe_2O_3$	Pure Fe_2O_3=0.71 $Pt@Fe_2O_3$-site1=1.77 $Pt@Fe_2O_3$-site2=1.72		(7)
Transition metal doped on TiO_2 surfaces	Pure $Ti(OH)_3$-O-$Ti(OH)_3$ = 3.53 TiO_2 anatase(001)=1.31 Co-TiO_2 anatase(100)=0.32 Co@TiO_2NC(nanocrystaline)=0.43 Ti@$Ti(OH)_3$-O-$Ti(OH)_3$ = 3.50 V@$Ti(OH)_3$-O-$Ti(OH)_3$ = 3.48 Cr@$Ti(OH)_3$-O-$Ti(OH)_3$ = 0.56 Mn@$Ti(OH)_3$-O-$Ti(OH)_3$ = 1.17 Fe@$Ti(OH)_3$-O-$Ti(OH)_3$ = 0.78 Co@$Ti(OH)_3$-O-$Ti(OH)_3$ = 1.15		(8)

	$Ni@Ti(OH)_3$-O-$Ti(OH)_3$ = 1.30 $V@Ti(OH)_2$-O_2-$Ti(OH)_2$ = 3.53 $Cr@Ti(OH)_2$-O_2-$Ti(OH)_2$ = 3.40 $Mn@Ti(OH)_2$-O_2-$Ti(OH)_2$ = 0.53 $Fe@Ti(OH)_2$-O_2-$Ti(OH)_2$ = 0.55 $Ni@Ti(OH)_2$-O_2-$Ti(OH)_2$ = 0.48 $Co@Ti@Ti(OH)_2$-O_2-$Ti(OH)_2$ =0.4		
C_3N_4 quantume dots and g-C_3N_4 Nanosheets		CNQDs=-0.85 CNQDs@G=1.17 CNNSs=-0.53 CNNSs@G=-0.10	(9)
Metal free boron sheet		**α- sheet** site1= 0.03 site2=-0.61 **β- sheet** site1=0.11 site2=0.95 site3=0.02 **β_{12}-Ag(111)** site1=0.08 site2=-0.22 site3=0.1 **β_{12}-Cu(111)** site1=-0.28 site2=-0.82 site3=-0.31	(10)
	Fe@CdS NT= 1.03 Co@CdS NT=0.64 Ni@CdS NT=1.06 Cu@CdS NT=1.39 Ru@CdS NT=2.12 Rh@CdS NT=1.03 Pd@CdS NT=0.53 Ag@CdS NT=1.09	Fe@CdS NT= -0.88 Co@CdS NT=-0.42 Ni@CdS NT=-0.28 Cu@CdS NT=0.36 Ru@CdS NT=0.19 Rh@CdS NT=0.36 Pd@CdS NT=-0.50 Ag@CdS NT=0.52	(11)

Transition Metal doped on CdS Nanotubes	Os@CdS NT=2.24 Ir@CdS NT=1.66 Pt@CdS NT=0.66 Au@CdS NT=0.76 Bulk CdS=1.65 CdS NT=1.55	Os@CdS NT=-0.34 Ir@CdS NT=-0.56 Pt@CdS NT=-0.36 Au@CdS NT=0.52 Bulk CdS=1.20 CdS NT=1.60	
Transition metal doped on Graphdiyne	Sc@GDY= 1.68 Ti@GDY =1.92 V@GDY= 2.22 Cr@GDY= 1.80 Mn@GDY= 1.81 Fe@GDY= 1.66 Co@GDY= 0.84 Ni@GDY= 0.29 Cu@GDY= 0.92 Pt@GDY =0.46	Sc@GDY= 0.39 Ti@GDY =−0.10 V@GDY= 0.08 Cr@GDY= 0.38 Mn@GDY= 0.62 Fe@GDY= 0.22 Co@GDY= 0.22 Ni@GDY= 1.02 Cu@GDY= 0.24 Pt@GDY =0.73	(12)

Table S5. Gibbs Free Energy for the Adsorption of HER Intermediates on Pristine and Doped B_{36}.

System	ΔG_{*H} (TM- reaction site)	ΔG_{*H} (Boron-reaction site)
Pristine B_{36}	-	2.00
Ti/B_{36}	0.12	0.28
V/B_{36}	0.41	1.07
Cr/B_{36}	-0.17	0.20
Mn/B_{36}	0.60	0.53
Fe/B_{36}	1.37	1.05
Co/B_{36}	1.24	0.85
Ni/B_{36}	1.17	1.01
Cu/B_{36}	0.69	0.26

Table S6. Adsorption Energies, Structural Parameters, and Spin Multiplicity for Different Orientation of Adsorbate (X=O, OH, OOH, and H) on FeTM2/B_{38} Systems.

	TM2-X (Å)	TM2-B (Å)	E_{ads} (eV)	Spin Multiplicity
FeCr/B_{38}-OH(Fe)	1.732	2.053	-1.48	2
FeCr/B_{38}-OH(Fe)	1.768	2.109	-3.69	4
FeCr/B_{38}-OH(Fe)	1.758	2.112	-3.47	6
FeCr/B_{38}-OH(Fe)	1.775	2.154	-3.68	8
FeCr/B_{38}-O(Fe)	1.556	2.062	-5.18	1
FeCr/B_{38}-O(Fe)	1.561	2.072	-6.47	3
FeCr/B_{38}-O(Fe)	1.570	2.076	-6.83	5
FeCr/B_{38}-O(Fe)	1.577	2.106	-6.82	7
FeCr/B_{38}-O(Fe)	1.596	2.099	-6.35	9
FeCr/B_{38}-OOH(Fe)	1.702	2.06	-0.81	2
FeCr/B_{38}-OOH(Fe)	1.724	2.052	-1.62	4
FeCr/B_{38}-OOH(Fe)	1.760	2.112	-2.09	6
FeCr/B_{38}-OOH(Fe)	1.765	2.118	-2.06	8
FeCr/B_{38}-OH(Cr)	1.715	2.048	-2.35	2
FeCr/B_{38}-OH(Cr)	1.729	2.111	-4.04	4
FeCr/B_{38}-OH(Cr)	1.717	2.071	-4.17	6
FeCr/B_{38}-OH(Cr)	1.712	2.075	-3.05	8
FeCr/B_{38}-O(Cr)	1.536	2.011	-5.32	1
FeCr/B_{38}-O(Cr)	1.543	2.11	-6.52	3
FeCr/B_{38}-O(Cr)	1.546	2.083	-6.78	5
FeCr/B_{38}-O(Cr)	1.556	2.09	-8.46	7
FeCr/B_{38}-O(Cr)	1.572	2.159	-8.71	9
FeCr/B_{38}-OOH(Cr)	1.720	2.055	-0.62	2
FeCr/B_{38}-OOH(Cr)	1.719	2.062	-1.76	4
FeCr/B_{38}-OOH(Cr)	1.715	2.068	-2.62	6
FeCr/B_{38}-OOH(Cr)	1.726	2.052	-1.39	8
FeCr/B_{38}-H(Fe)	1.509	2.022	-1.10	2
FeCr/B_{38}-H(Fe)	1.584	2.048	-1.39	4
FeCr/B_{38}-H(Fe)	1.605	2.099	-2.04	6
FeCr/B_{38}-H(Fe)	1.612	2.138	-1.98	8
FeCr/B_{38}-H(Cr)	1.625	2.002	-0.29	2

FeCr/B_{38}-H(Cr)	1.630	2.013	-1.12	4
FeCr/B_{38}-H(Cr)	1.638	2.009	-1.86	6
FeCr/B_{38}-H(Cr)	1.630	2.011	-1.01	8
FeCr/B_{38}-B1H	1.597	1.903	-1.16	2
FeCr/B_{38}-B1H	1.633	1.922	-1.39	4
FeCr/B_{38}-B1H	1.816	1.278	-1.48	6
FeCr/B_{38}-B1H	1.964	2.007	-2.05	8
FeCr/B_{38}-B2H	1.511	2.002	-2.12	2
FeCr/B_{38}-B2H	1.501	2.043	-2.15	4
FeCr/B_{38}-B2H	1.506	2.001	-2.08	6
FeCr/B_{38}-B2H	1.423	2.063	-2.18	8
FeCr/B_{38}-B3H	1.629	1.971	-2.07	2
FeCr/B_{38}-B3H	1.637	1.965	-2.07	4
FeCr/B_{38}-B3H	1.657	1.972	-2.62	6
FeCr/B_{38}-B3H	1.700	1.977	-2.08	8
FeCo/B_{38}-OH(Fe)	1.730	2.065	-1.58	1
FeCoB_{38}-OH(Fe)	1.747	2.069	-3.60	3
FeCo/B_{38}-OH(Fe)	1.740	2.074	-3.43	5
FeCo/B_{38}-OH(Fe)	1.779	2.102	-3.81	7
FeCo/B_{38}-O(Fe)	1.593	2.119	-5.71	2
FeCo/B_{38}-O(Fe)	1.576	2.095	-6.71	4
FeCo/B_{38}-O(Fe)	1.632	2.081	-6.60	6
FeCo/B_{38}-O(Fe)	1.614	2.086	-6.22	8
FeCo/B_{38}-OOH(Fe)	1.821	2.056	-0.27	1
FeCo/B_{38}-OOH(Fe)	1.727	2.068	-1.88	3
FeCo/B_{38}-OOH(Fe)	1.801	2.112	-2.21	5
FeCo/B_{38}-OOH(Fe)	1.842	2.144	-2.56	7
FeCo/B_{38}-OH(Co)	1.779	1.956	-1.91	1
FeCo/B_{38}-OH(Co)	1.775	1.986	-2.64	3
FeCo/B_{38}-OH(Co)	1.776	2.006	-3.01	5
FeCo/B_{38}-OH(Co)	1.747	2.061	-3.73	7
FeCo/B_{38}-O(Co)	1.958	1.974	-7.59	2
FeCo/B_{38}-O(Co)	1.849	2.040	-7.18	4
FeCo/B_{38}-O(Co)	1.618	2.044	-6.39	6
FeCo/B_{38}-O(Co)	1.599	2.060	-6.08	8
FeCo/B_{38}-OOH(Co)	1.778	1.948	-0.44	1

FeCo/B_{38}-OOH(Co)	1.770	2.002	-1.04	3
FeCo/B_{38}-OOH(Co)	1.803	2.037	-1.91	5
FeCo/B_{38}-OOH(Co)	1.848	2.054	-2.38	7
FeCo/B_{38}-H(Fe)	1.522	2.035	-0.51	1
FeCo/B_{38}-H(Fe)	1.516	2.040	-1.72	3
FeCo/B_{38}-H(Fe)	1.530	2.058	-1.84	5
FeCo/B_{38}-H(Fe)	1.593	2.087	-2.14	7
FeCo/B_{38}-H(Co)	1.508	1.968	-0.39	1
FeCo/B_{38}-H(Co)	1.538	1.964	-1.23	3
FeCo/B_{38}-H(Co)	1.498	1.992	-1.97	5
FeCo/B_{38}-H(Co)	1.528	2.003	-2.06	7
FeCo/B_{38}-B1H	1.547	1.925	-0.40	1
FeCo/B_{38}-B1H	1.609	1.947	-1.83	3
FeCo/B_{38}-B1H	1.601	1.984	-1.83	5
FeCo/B_{38}-B1H	1.728	1.996	-1.12	7
FeCo/B_{38}-B2H	1.795	1.941	-0.41	1
FeCo/B_{38}-B2H	1.575	1.965	-1.74	3
FeCo/B_{38}-B2H	1.718	1.952	-1.45	5
FeCo/B_{38}-B2H	1.760	1.967	-1.62	7
FeCo/B_{38}-B3H	1.520	1.923	-1.47	1
FeCo/B_{38}-B3H	1.892	1.975	-1.04	3
FeCo/B_{38}-B3H	1.669	1.981	-2.03	5
FeCo/B_{38}-B3H	1.610	1.986	-1.61	7
FeNi/B_{38}-OH(Fe)	1.732	2.072	-2.28	2
FeNi/B_{38}-OH(Fe)	1.750	2.117	-3.44	4
FeNi/B_{38}-OH(Fe)	1.748	2.119	-3.26	6
FeNi/B_{38}-OH(Fe)	1.751	2.132	-3.44	8
FeNi/B_{38}-O(Fe)	1.596	2.065	-5.26	1
FeNi/B_{38}-O(Fe)	1.643	2.160	-7.70	3
FeNi/B_{38}-O(Fe)	1.630	2.095	-7.44	5
FeNi/B_{38}-O(Fe)	1.656	2.080	-6.06	7
FeNi/B_{38}-O(Fe)	1.708	2.147	-5.96	9
FeNi/B_{38}-OOH(Fe)	1.726	2.077	-1.14	2
FeNi/B_{38}-OOH(Fe)	1.803	2.112	-1.95	4
FeNi/B_{38}-OOH(Fe)	1.798	2.113	-1.88	6
FeNi/B_{38}-OOH(Fe)	1.813	2.113	-1.80	8

FeNi/B_{38}-OH(Ni)	1.778	2.016	-2.78	4
FeNi/B_{38}-OH(Ni)	1.772	2.037	-2.82	6
FeNi/B_{38}-OH(Ni)	1.817	2.066	-3.07	8
FeNi/B_{38}-O(Ni)	1.657	2.002	-6.00	5
FeNi/B_{38}-O(Ni)	1.656	2.021	-5.30	7
FeNi/B_{38}-O(Ni)	1.677	2.077	-6.23	9
FeNi/B_{38}-OOH(Ni)	1.790	1.994	-1.87	4
FeNi/B_{38}-OOH(Ni)	1.808	2.014	-2.06	6
FeNi/B_{38}-OOH(Ni)	1.780	2.073	-1.90	8
FeNi/B_{38}-H(Fe)	1.502	2.044	-1.67	4
FeNi/B_{38}-H(Fe)	1.595	2.101	-2.82	6
FeNi/B_{38}-H(Fe)	1.603	2.121	-1.75	8
FeNi/B_{38}-H(Ni)	1.525	2.009	-2.56	6
FeNi/B_{38}-H(Ni)	1.513	2.011	-1.74	8
FeNi/B_{38}-B1H	1.673	2.003	-1.92	6
FeNi/B_{38}-B1H	2.030	2.007	-1.86	8
FeNi/B_{38}-B2H	1.749	2.001	-1.99	6
FeNi/B_{38}-B2H	2.067	2.063	-1.82	8
FeNi/B_{38}-B3H	1.647	1.972	-2.21	6
FeNi/B_{38}-B3H	1.700	1.977	-1.91	8
FeCu/B_{38}-OH(Fe)	1.755	2.158	-4.19	5
FeCu/B_{38}-OH(Fe)	1.747	2.180	-3.97	7
FeCu/B_{38}-O(Fe)	1.616	2.152	-6.76	4
FeCu/B_{38}-O(Fe)	1.627	2.156	-6.96	6
FeCu/B_{38}-O(Fe)	1.611	2.176	-6.13	8
FeCu/B_{38}-OOH(Fe)	1.782	2.103	-2.53	5
FeCu/B_{38}-OOH(Fe)	1.787	2.220	-2.65	7
FeCu/B_{38}-OH(Cu)	1.801	2.116	-2.26	5
FeCu/B_{38}-OH(Cu)	1.795	2.107	-3.00	7
FeCu/B_{38}-O(Cu)	1.765	2.075	-6.28	6
FeCu/B_{38}-O(Cu)	1.770	2.114	-4.80	8
FeCu/B_{38}-OOH(Cu)	1.844	2.076	-1.72	5
FeCu/B_{38}-OOH(Cu)	1.852	2.077	-1.51	7
FeCu/B_{38}-H(Fe)	1.598	2.148	-2.24	7
FeCu/B_{38}-H(Cu)	1.518	2.071	-2.83	5
FeCu/B_{38}-H(Cu)	1.534	2.083	-1.40	7
FeCu/B_{38}-B1H	2.075	2.002	-2.42	5

FeCu/B_{38}-B1H	2.043	2.045	-1.86	7
FeCu/B_{38}-B2H	1.260	2.064	-2.84	5
FeCu/B_{38}-B2H	1.268	2.056	-1.65	7
FeCu/B_{38}-B3H	1.999	1.967	-2.44	5
FeCu/B_{38}-B3H	2.086	1.996	-2.07	7

Table S7. Gibbs Free Energy for the Adsorption of OER Intermediates on Bimetal Doped B_{38}.

System	Fe- reaction site			
	ΔG_{*OH}(eV)	ΔG_{*O}(eV)	ΔG_{*OOH}(eV)	η^{OER}(V)
$FeCr/B_{38}$	-0.03	-0.62	**1.86**	1.82
$FeCo/B_{38}$	-0.35	1.09	**2.87**	0.81
$FeNi/B_{38}$	-0.13	1.70	**3.46**	0.59
$FeCu/B_{38}$	-1.51	0.99	**3.46**	1.28
System	TM2 -reaction site			
	ΔG_{*OH}(eV)	ΔG_{*O}(eV)	ΔG_{*OOH}(eV)	η^{OER}(V)
$FeCr/B_{38}$	-2.58	-2.20	**1.05**	2.63
$FeCo/B_{38}$	0.10	0.55	**3.47**	1.69
$FeNi/B_{38}$	0.56	1.68	**2.79**	0.89
$FeCu/B_{38}$	-0.01	2.91	**3.51**	1.68

Table S8. Gibbs Free Energy for the Adsorption of HER Intermediates Bimetal Doped B_{38}

System	ΔG_{*H} (Fe)	ΔG_{*H} (TM2)	ΔG_{*H} (B1)	ΔG_{*H} (B2)	ΔG_{*H} (B3)
Pristine B_{38}			1.17	0.45	0.34
$FeCr/B_{38}$	-0.74	-0.20	0.38	-1.00	-0.99
$FeCo/B_{38}$	0.79	0.59	0.85	0.57	0.99
$FeNi/B_{38}$	0.77	0.26	0.77	0.89	0.55
$FeCu/B_{38}$	0.27	0.83	0.16	0.90	0.20

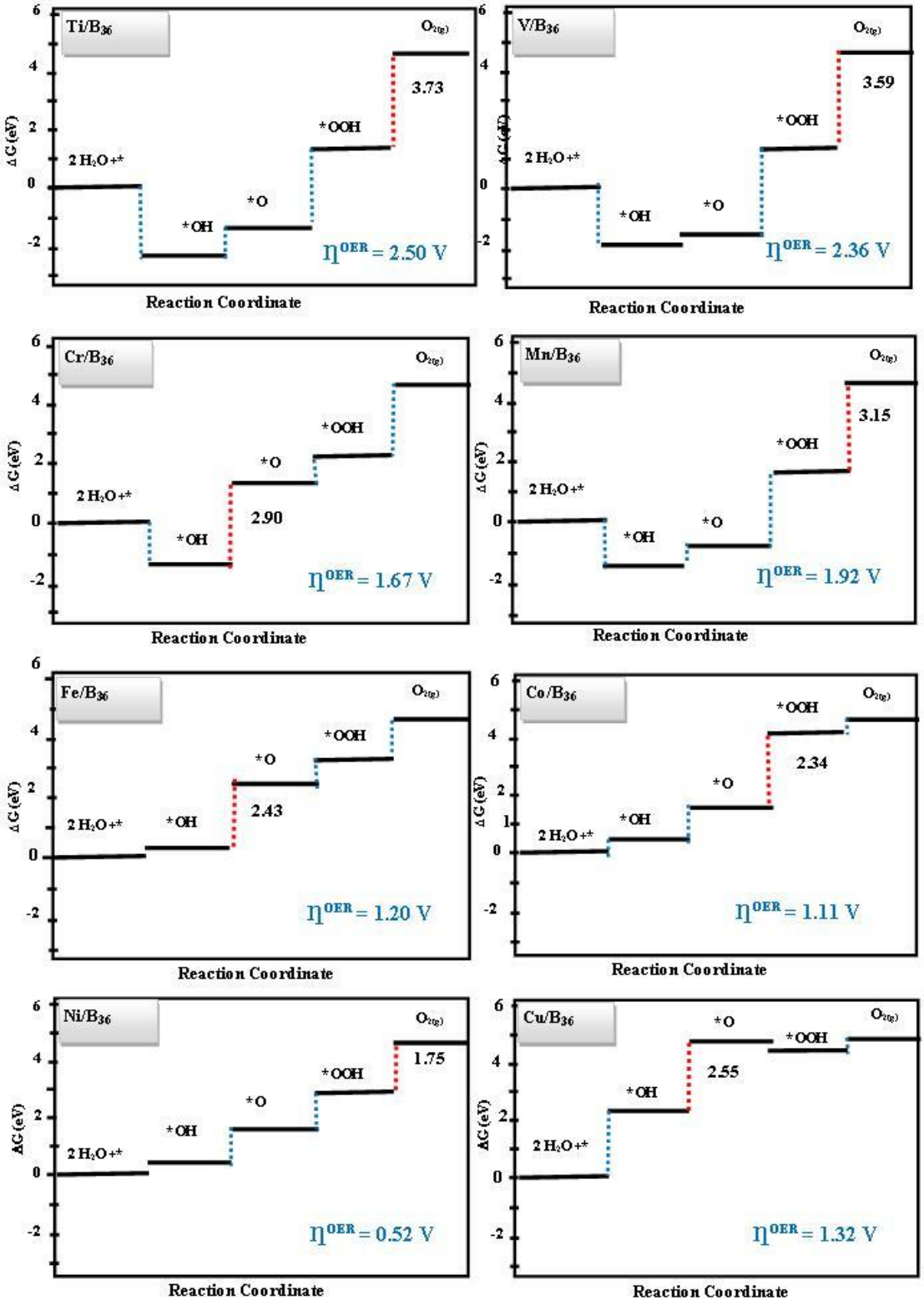

Figure S1. Reaction free energy profile for OER at zero potential (ϕ= 0) for TM/B_{36} systems.

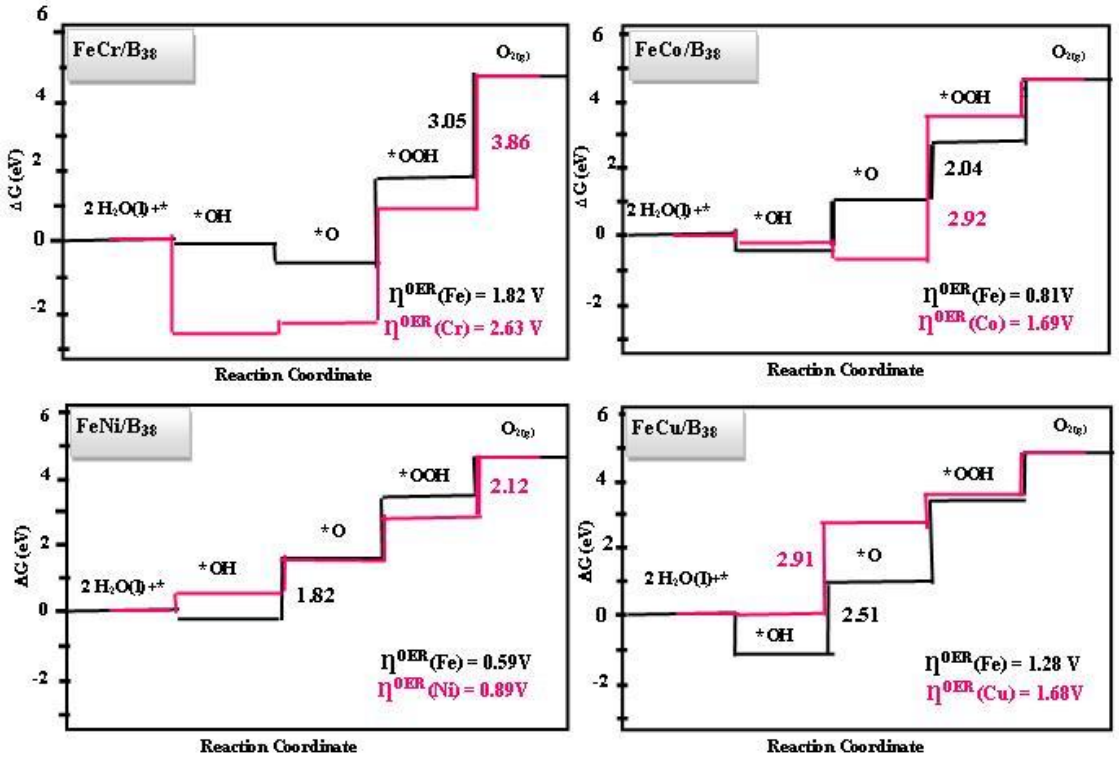

Figure S2. Reaction free energy profile for OER at zero potential (ϕ= 0) for FeTM2/B_{38} systems.

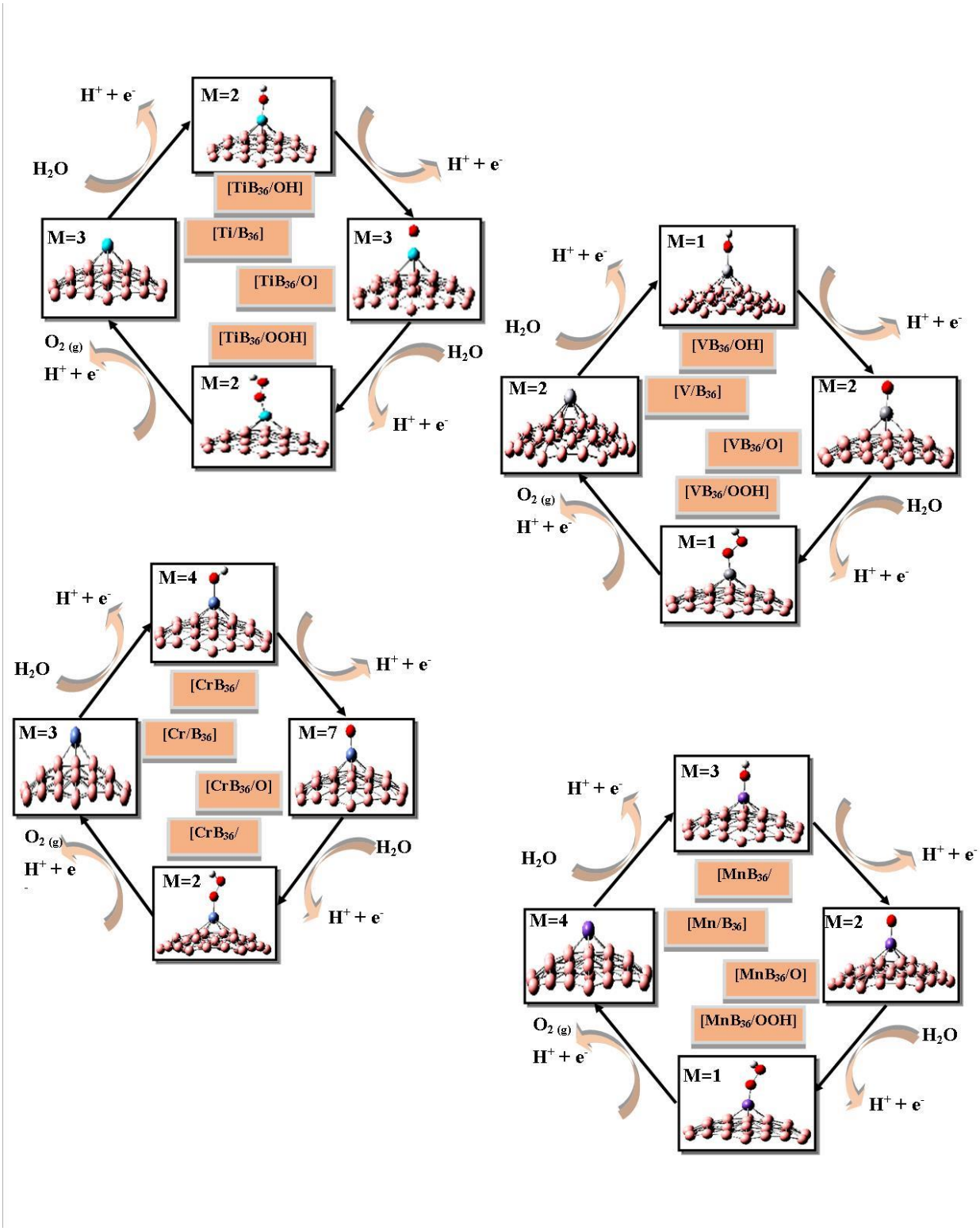

Figure S3. The structures of intermediates together with their spin multiplicity (M) for each step of OER for TM/B_{36} systems.

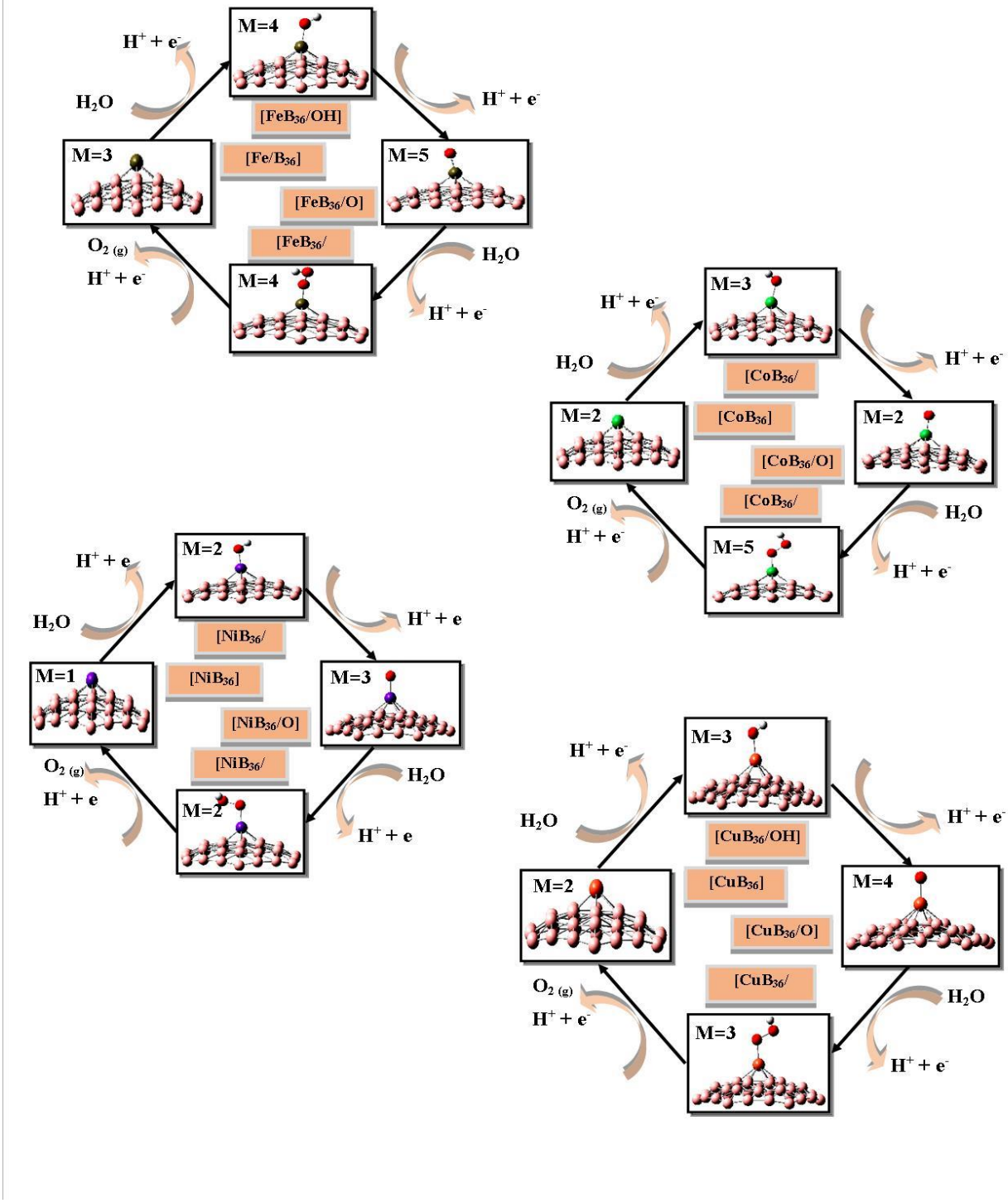

Figure S3. The structures of intermediates together with their spin multiplicity (M) for each step of OER for TM/B_{36} systems.

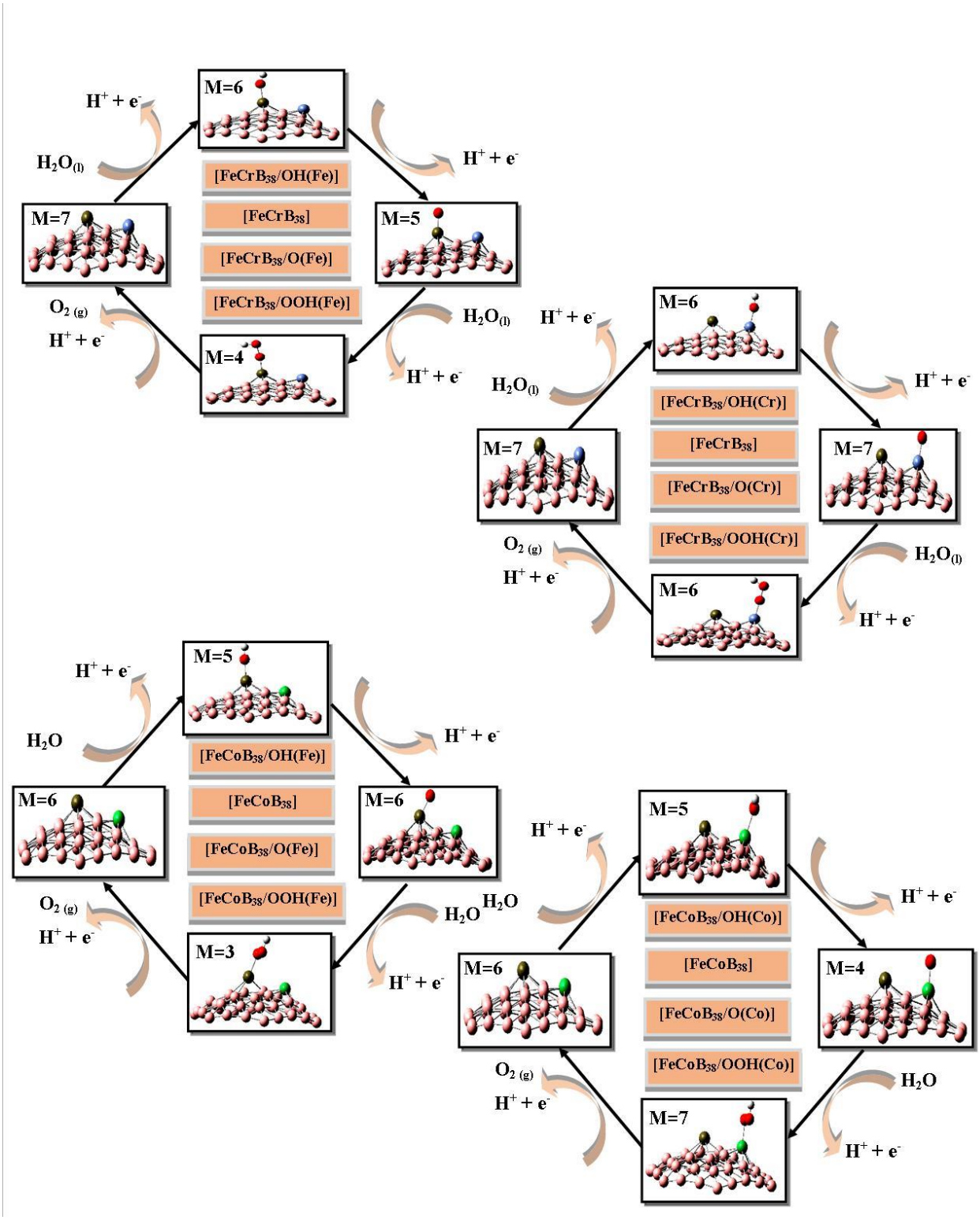

Figure S4. The structures of intermediates together with their spin multiplicity (M) for each step of OER for FeTM2/B_{38} systems.

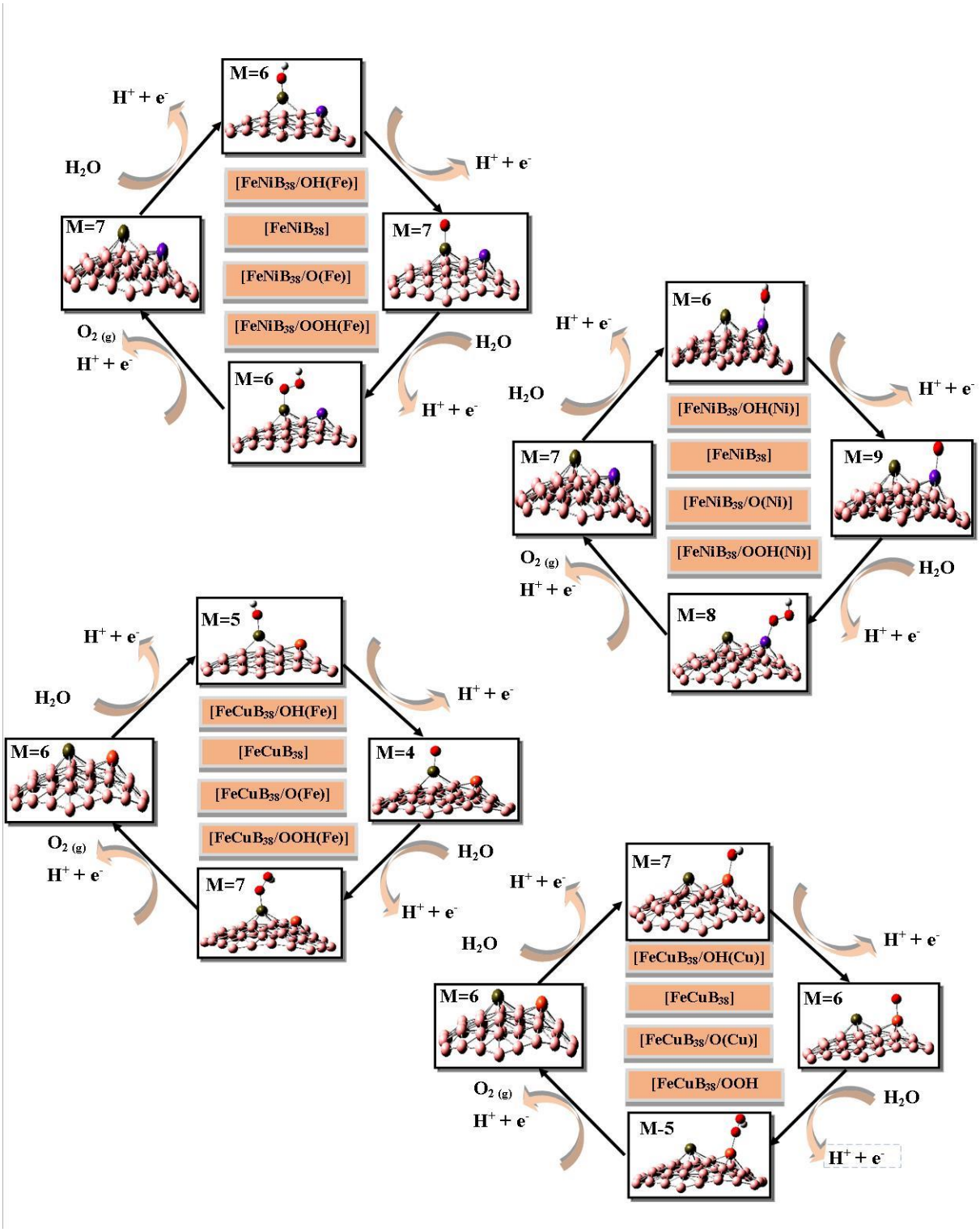

Figure S4. The structures of intermediates together with their spin multiplicity (M) for each step of OER for FeTM2/B_{38} systems.

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