Supporting information

Electrochemical CO_2 Reduction Reaction on Metal Oxide Surfaces as a function of CO Coverage

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Table S1. Relative energy of CO molecules on different TMOs for 50% and 75% CO coverage with respect to lowest energy configuration for different CO configurations. The lowest energy configurations are indicated with green colored boxes in the table. The candidates desorbing the CO from their surfaces are shown with term "des." in the table. NbO_2 with pink color data is explained in the main text.

Catalysts	Energy/eV					
	50% CO coverage				75% CO coverage	
	br-br	CUS-CUS	br-nCUS	br-fCUS	br-CUS-CUS	br-br-CUS
HfO_2	0.79	2.15	0.00	0.33	0.48	0.00
MoO_2	0.07	1.08	0.00	0.43	0.40	0.00
OsO_2	0.88	0.10	0.00	0.06	0.21	0.00
NbO_2	-0.54	1.75	0.00	0.20	0.48	0.00
TiO_2	0.00	1.93	0.61	0.62	0.78	0.00
IrO_2	0.49	0.00	0.10	0.20	0.00	0.18
RuO_2	0.12	0.39	0.00	0.18	0.22	0.00
CrO_2	0.00	0.57	0.25	0.30	0.57	0.00
PtO_2	0.00	1.84	0.61	0.60	0.95	0.00
RhO_2	0.19	0.10	0.00	0.05	0.14	0.00
MnO_2	0.00	des	des	des	des	des
PdO_2	0.00	1.47	0.70	0.76	0.85	0.00

Table S2. Zero-point energy, entropy, and specific heat capacity corrections.

Adsorbate	ZPE	TS	CPdt
CO_2(g)	0.31	0.65	0.10
CO(g)	0.14	0.67	0.09
H_2(g)	0.27	0.42	0.09
H_2O(l)	0.58	0.65	0.10
CH_3OH(aq)	1.35	0.79	0.11
HCOOH(g)	0.90	1.02	0.11
OH*	0.40	0.04	0.03
O*	0.08	0.03	0.02
CO*	0.22	0.08	0.05
OCHO*	0.63	0.20	0.10
COOH*	0.63	0.17	0.09
HCOOH*	0.92	0.22	0.09
H_2COOH*	1.25	0.25	0.11
CH_3OH*	1.51	0.18	0.08
CHO*	0.48	0.18	0.07
COH*	0.52	0.15	0.06
CH_2O*	0.82	0.12	0.07
CH_3O*	1.15	0.14	0.08
H*	0.20	0.00	0.00
CO_2*	0.33	0.17	0.09
OCO*	0.29	0.17	0.09
CO_2*-linear	0.33	0.23	0.11

Table S3. Electronic and binding free energy for all the intermediates with a) 0% CO coverage and b) 25%, 50% and 75% CO coverages on all TMOs studied in this work.

a) 0% CO coverage

TMOs	CO_2(g)→COOH		CO_2(g)→OCHO		OCHO→HCOOH(aq)		OCHO→HCOOH		H_2(g)→H	
	ΔE	ΔG	ΔE	ΔG	ΔE	ΔG	ΔE	ΔG	ΔE	ΔG
HfO_2	-3.20	-2.73	-4.73	-4.28	4.81	4.21	1.23	1.47	-1.44	-1.26
MoO_2	-1.49	-1.02	-2.57	-2.12	2.65	2.05	1.47	1.71	-0.69	-0.51
OsO_2	-1.59	-1.12	-2.23	-1.78	2.31	1.71	0.89	1.13	-1.11	-0.93
NbO_2	-1.69	-1.22	-2.22	-1.77	2.30	1.70	1.03	1.27	-1.31	-1.13
TiO_2	-0.73	-0.26	-1.96	-1.51	2.04	1.44	0.21	0.45	-0.51	-0.33
IrO_2	-1.46	-0.99	-1.78	-1.33	1.86	1.26	0.78	1.02	-0.90	-0.72
RuO_2	-0.46	0.01	-1.30	-0.85	1.38	0.78	0.46	0.70	-0.60	-0.42
CrO_2	0.53	1.00	-0.73	-0.28	0.81	0.21	0.30	0.54	0.17	0.35
PtO_2	-0.95	-0.48	-0.76	-0.31	0.84	0.24	0.00	0.24	-0.53	-0.35
RhO_2	-0.06	0.41	-0.71	-0.26	0.79	0.19	-0.06	0.18	-0.17	0.01
MnO_2	0.65	1.12	-0.10	0.35	0.18	-0.42	-0.48	-0.24	0.60	0.78
PdO_2	0.16	0.63	0.15	0.60	-0.07	-0.67	-0.54	-0.30	0.11	0.29

b) 25%, 50% and 75% CO coverages

HfO_2								
Intermediates	**25%**		**50%**		**75%-br**		**75%-CUS**	
	ΔE	**ΔG**	**ΔE**	**ΔG**	**ΔE**	**ΔG**	**ΔE**	**ΔG**
$CO_2(g) + * + (H^+ + e^-) \rightarrow OCHO$	-2.93	-2.48	-2.73	-2.28	-1.97	-1.54	-1.64	-1.21
$OCHO + (H^+ + e^-) \rightarrow HCOOH(aq) + *$	3.01	2.41	2.82	2.22	2.05	1.47	1.72	1.14
$OCHO + (H^+ + e^-) \rightarrow HCOOH$	1.26	1.50	-0.73	-0.49	0.41	0.67	0.54	0.80
$HCOOH + (H^+ + e^-) \rightarrow H_2COOH$	-1.18	-0.88	0.78	1.08	-0.72	-0.42	-0.67	-0.37
$H_2COOH + (H^+ + e^-) \rightarrow CH_3OH(aq) + O$	-0.21	-0.60	-0.21	-0.60	---	---	---	---
$H_2COOH + (H^+ + e^-) \rightarrow H_2CO + H_2O(l)$	0.61	0.28	0.73	0.40	-0.06	-0.38	1.10	0.77
$H_2COOH + (H^+ + e^-) \rightarrow H_3CO + OH$	-1.79	-1.43	-1.59	-1.24	---	---	---	---
$O + (H^+ + e^-) \rightarrow OH$	0.04	0.34	0.07	0.37	---	---	---	---
$H_2CO + (H^+ + e^-) \rightarrow H_3CO$	-0.69	-0.39	-0.87	-0.57	-0.42	-0.12	-1.70	-1.40
$H_3CO + OH + (H^+ + e^-) \rightarrow H_3CO + H_2O(l)$	1.70	1.32	1.45	1.07	---	---	---	---
$H_3CO + OH + (H^+ + e^-) \rightarrow CH_3OH(aq) + OH$	1.62	1.18	1.45	1.01	---	---	---	---
$OH + (H^+ + e^-) \rightarrow H_2O(l) + *$	2.32	1.94	2.13	1.75	---	---	---	---
$H_3CO + (H^+ + e^-) \rightarrow H_3COH(aq) + *$	2.24	1.80	2.13	1.69	2.07	1.57	1.68	1.18
$O + OH + (H^+ + e^-) \rightarrow O + H_2O(l)$	0.95	0.57	1.74	1.36	---	---	---	---
$H_2 + * \rightarrow H + (H^+ + e^-)$	-0.94	-0.76	-0.72	-0.54	-0.77	-0.59	0.15	0.33
MoO_2								

Intermediates	25%		50%		75%-br		75%-CUS	
	ΔE	ΔG	ΔE	ΔG	ΔE	ΔG	ΔE	ΔG
$CO_2(g) + * + (H^+ + e^-) \rightarrow OCHO$	-2.41	-1.96	-1.93	-1.48	-1.52	-1.09	-0.67	-0.67
$OCHO + (H^+ + e^-) \rightarrow HCOOH(aq) + *$	2.50	1.90	2.01	1.41	1.60	1.02	0.75	0.75
$OCHO + (H^+ + e^-) \rightarrow HCOOH$	1.25	1.49	0.05	0.29	-0.46	-0.20	---	---
$HCOOH + (H^+ + e^-) \rightarrow H_2COOH$	-1.32	-1.02	-0.53	-0.23	0.23	0.53	---	---
$H_2COOH + (H^+ + e^-) \rightarrow CH_3OH(aq) + O$	0.07	-0.31	0.54	0.15	-0.36	-0.74	---	---
$H_2COOH + (H^+ + e^-) \rightarrow H_2CO + H_2O(l)$	0.68	0.35	1.17	0.84	0.00	-0.33	---	---
$H_2COOH + (H^+ + e^-) \rightarrow H_3CO + OH$	-1.05	-0.70	-0.58	-0.22	---	---	---	---
$O + (H^+ + e^-) \rightarrow OH$	-0.17	0.13	-0.06	0.24	-0.23	0.07	---	---
$H_2CO + (H^+ + e^-) \rightarrow H_3CO$	-0.83	-0.53	-1.09	-0.79	-0.64	-0.34	---	---
$H_3CO + OH + (H^+ + e^-) \rightarrow H_3CO + H_2O(l)$	0.90	0.52	0.66	0.28	---	---	---	---
$H_3CO + OH + (H^+ + e^-) \rightarrow CH_3OH(aq) + OH$	0.95	0.51	1.05	0.61	---	---	---	---
$OH + (H^+ + e^-) \rightarrow H_2O(l) + *$	1.90	1.52	1.24	0.86	---	---	---	---
$H_3CO + (H^+ + e^-) \rightarrow H_3COH(aq) + *$	1.95	1.51	1.64	1.20	1.69	1.19	---	---
$O + OH + (H^+ + e^-) \rightarrow O + H_2O(l)$	0.29	0.47	0.80	0.42	---	---	---	---
$H_2 + * \rightarrow H + (H^+ + e^-)$	-0.59	-0.41	0.35	0.53	0.25	0.43	0.32	0.50
OsO_2								
Intermediates	**25%**		**50%**		**75%-br**		**75%-CUS**	
	ΔE	**ΔG**	**ΔE**	**ΔG**	**ΔE**	**ΔG**	**ΔE**	**ΔG**
$CO_2(g) + * + (H^+ + e^-) \rightarrow OCHO$	-2.39	-1.94	-2.14	-1.69	-1.47	-1.04	-0.42	0.01
$OCHO + (H^+ + e^-) \rightarrow HCOOH(aq) + *$	2.46	1.86	2.22	1.62	1.56	0.98	0.51	-0.07
$OCHO + (H^+ + e^-) \rightarrow HCOOH$	0.96	1.20	0.59	0.83	-0.15	0.11	---	---
$HCOOH + (H^+ + e^-) \rightarrow H_2COOH$	-1.18	-0.88	-1.00	-0.70	-0.17	0.12	---	---
$H_2COOH + (H^+ + e^-) \rightarrow CH_3OH(aq) + O$	0.93	0.54	1.04	0.65	0.46	0.07	---	---
$H_2COOH + (H^+ + e^-) \rightarrow H_2CO + H_2O(l)$	0.44	0.11	0.71	0.38	0.54	0.21	---	---
$H_2COOH + (H^+ + e^-) \rightarrow H_3CO + OH$	-0.96	-0.61	-0.76	-0.40	---	---	---	---
$O + (H^+ + e^-) \rightarrow OH$	-0.84	-0.54	-0.93	-0.63	-1.10	-0.80	---	---
$H_2CO + (H^+ + e^-) \rightarrow H_3CO$	-0.45	-0.15	-0.80	-0.50	-1.30	-1.00	---	---
$H_3CO + OH + (H^+ + e^-) \rightarrow H_3CO + H_2O(l)$	0.95	0.57	0.67	0.29	---	---	---	---
$H_3CO + OH + (H^+ + e^-) \rightarrow CH_3OH(aq) + OH$	1.05	0.61	0.86	0.42	---	---	---	---
$OH + (H^+ + e^-) \rightarrow H_2O(l) + *$	1.83	1.45	1.75	1.37	---	---	---	---
$H_3CO + (H^+ + e^-) \rightarrow H_3COH(aq) + *$	1.93	1.49	1.95	1.51	1.86	1.36	---	---
$O + OH + (H^+ + e^-) \rightarrow O + H_2O(l)$	0.91	0.53	0.78	0.40	---	---	---	---
$H_2 + * \rightarrow H + (H^+ + e^-)$	-1.15	-0.97	-1.14	-0.96	-1.05	-0.87	-0.26	-0.08
NbO_2								

Intermediates	25%		50%		75%-br		75%-CUS	
	ΔE	ΔG	ΔE	ΔG	ΔE	ΔG	ΔE	ΔG
$CO_2(g) + * + (H^+ + e^-) \rightarrow OCHO$	-1.65	-1.20	-1.69	-1.24	-1.48	-1.05	-0.82	-0.39
$OCHO + (H^+ + e^-) \rightarrow HCOOH(aq) + *$	1.73	1.13	1.77	1.17	1.56	0.98	0.90	0.32
$OCHO + (H^+ + e^-) \rightarrow HCOOH$	0.18	0.42	1.03	1.27	0.67	0.93	---	---
$HCOOH + (H^+ + e^-) \rightarrow H_2COOH$	-0.39	-0.09	-1.14	-0.84	-1.01	-0.72	---	---
$H_2COOH + (H^+ + e^-) \rightarrow CH_3OH(aq) + O$	-0.52	-0.91	-0.57	-0.96	-0.47	-0.86	---	---
$H_2COOH + (H^+ + e^-) \rightarrow H_2CO + H_2O(l)$	0.43	0.10	0.58	0.25	0.28	-0.05	---	---
$H_2COOH + (H^+ + e^-) \rightarrow H_3CO + OH$	-1.56	-1.21	-1.57	-1.22	---	---	---	---
$O + (H^+ + e^-) \rightarrow OH$	0.00	0.30	0.02	0.32	-0.21	0.09	---	---
$H_2CO + (H^+ + e^-) \rightarrow H_3CO$	-1.01	-0.71	-1.20	-0.90	-0.98	-0.68	---	---
$H_3CO + OH + (H^+ + e^-) \rightarrow H_3CO + H_2O(l)$	0.98	0.60	0.95	0.57	---	---	---	---
$H_3CO + OH + (H^+ + e^-) \rightarrow CH_3OH(aq) + OH$	1.05	0.61	1.03	0.59	---	---	---	---
$OH + (H^+ + e^-) \rightarrow H_2O(l) + *$	1.68	1.30	1.65	1.27	---	---	---	---
$H_3CO + (H^+ + e^-) \rightarrow H_3COH(aq) + *$	1.74	1.30	1.72	1.28	1.84	1.34	---	---
$O + OH + (H^+ + e^-) \rightarrow O + H_2O(l)$	1.12	0.74	1.10	0.72	---	---	---	---
$H_2 + * \rightarrow H + (H^+ + e^-)$	-1.02	-0.84	-1.02	-0.84	-0.99	-0.81	0.56	0.74
TiO_2								
Intermediates	**25%**		**50%**		**75%-br**		**75%-CUS**	
	ΔE	**ΔG**	**ΔE**	**ΔG**	**ΔE**	**ΔG**	**ΔE**	**ΔG**
$CO_2(g) + * + (H^+ + e^-) \rightarrow OCHO$	-1.51	-1.06	-1.31	-0.86	---	---	-0.33	0.10
$OCHO + (H^+ + e^-) \rightarrow HCOOH(aq) + *$	1.59	0.99	1.39	0.79	---	---	0.41	-0.17
$OCHO + (H^+ + e^-) \rightarrow HCOOH$	0.70	0.94	0.83	1.07	---	---	---	---
$HCOOH + (H^+ + e^-) \rightarrow H_2COOH$	-0.70	-0.40	-0.62	-0.32	---	---	---	---
$H_2COOH + (H^+ + e^-) \rightarrow CH_3OH(aq) + O$	-0.33	-0.72	0.23	-0.16	---	---	---	---
$H_2COOH + (H^+ + e^-) \rightarrow H_2CO + H_2O(l)$	0.78	0.45	0.99	0.66	---	---	---	---
$H_2COOH + (H^+ + e^-) \rightarrow H_3CO + OH$	-1.13	-0.78	-0.40	-0.05	---	---	---	---
$O + (H^+ + e^-) \rightarrow OH$	-0.17	0.13	-0.34	-0.04	---	---	---	---
$H_2CO + (H^+ + e^-) \rightarrow H_3CO$	-1.35	-1.05	-1.35	-1.05	---	---	---	---
$H_3CO + OH + (H^+ + e^-) \rightarrow H_3CO + H_2O(l)$	0.56	0.18	0.04	-0.34	---	---	---	---
$H_3CO + OH + (H^+ + e^-) \rightarrow CH_3OH(aq) + OH$	0.63	0.19	0.29	-0.15	---	---	---	---
$OH + (H^+ + e^-) \rightarrow H_2O(l) + *$	1.32	0.94	0.52	0.14	---	---	---	---
$H_3CO + (H^+ + e^-) \rightarrow H_3COH(aq) + *$	1.39	0.95	0.77	0.33	---	---	---	---
$O + OH + (H^+ + e^-) \rightarrow O + H_2O(l)$	0.76	0.38	-0.45	-0.83	---	---	---	---
$H_2 + * \rightarrow H + (H^+ + e^-)$	0.01	0.19	0.82	1.00	-0.01	0.17	0.75	0.93
IrO_2								

Intermediates	25%		50%		75%-br		75%-CUS	
	ΔE	ΔG	ΔE	ΔG	ΔE	ΔG	ΔE	ΔG
$CO_2(g) + * + (H^+ + e^-) \rightarrow OCHO$	-1.77	-1.32	-1.66	-1.21	-1.23	-0.80	-0.60	-0.17
$OCHO + (H^+ + e^-) \rightarrow HCOOH(aq) + *$	1.85	1.25	1.75	1.15	1.31	0.73	0.68	0.10
$OCHO + (H^+ + e^-) \rightarrow HCOOH$	0.91	1.15	0.02	0.34	-0.55	-0.29	---	---
$HCOOH + (H^+ + e^-) \rightarrow H_2COOH$	-0.89	-0.59	-0.44	-0.22	0.14	0.44	---	---
$H_2COOH + (H^+ + e^-) \rightarrow CH_3OH(aq) + O$	1.12	0.73	1.11	0.73	0.44	0.05	---	---
$H_2COOH + (H^+ + e^-) \rightarrow H_2CO + H_2O(l)$	0.25	-0.08	0.43	0.10	0.60	0.27	---	---
$H_2COOH + (H^+ + e^-) \rightarrow H_3CO + OH$	-0.60	-0.25	-0.62	-0.27	---	---	---	---
$O + (H^+ + e^-) \rightarrow OH$	-1.44	-1.14	-1.08	-0.78	-0.94	-0.64	---	---
$H_2CO + (H^+ + e^-) \rightarrow H_3CO$	-0.37	-0.07	-0.57	-0.27	-1.25	-0.95	---	---
$H_3CO + OH + (H^+ + e^-) \rightarrow H_3CO + H_2O(l)$	0.48	0.10	0.48	0.10	---	---	---	---
$H_3CO + OH + (H^+ + e^-) \rightarrow CH_3OH(aq) + OH$	0.27	-0.17	0.65	0.21	---	---	---	---
$OH + (H^+ + e^-) \rightarrow H_2O(l) + *$	1.38	1.00	1.36	0.98	---	---	---	---
$H_3CO + (H^+ + e^-) \rightarrow H_3COH(aq) + *$	1.18	0.74	1.53	1.09	1.59	1.09	---	---
$O + OH + (H^+ + e^-) \rightarrow O + H_2O(l)$	0.05	-0.33	0.40	0.02	---	---	---	---
$H_2 + * \rightarrow H + (H^+ + e^-)$	-0.88	-0.70	-0.88	-0.70	-0.93	-0.75	-0.69	-0.51
RuO_2								
Intermediates	**25%**		**50%**		**75%-br**		**75%-CUS**	
	ΔE	**ΔG**	**ΔE**	**ΔG**	**ΔE**	**ΔG**	**ΔE**	**ΔG**
$CO_2(g) + * + (H^+ + e^-) \rightarrow OCHO$	-1.50	-1.05	-1.19	-0.74	-0.71	-0.28	0.19	0.62
$OCHO + (H^+ + e^-) \rightarrow HCOOH(aq) + *$	1.58	0.98	1.27	0.67	0.80	0.22	-0.11	-0.69
$OCHO + (H^+ + e^-) \rightarrow HCOOH$	0.56	0.80	0.23	0.47	---	---	---	---
$HCOOH + (H^+ + e^-) \rightarrow H_2COOH$	-0.64	-0.34	-0.39	-0.09	---	---	---	---
$H_2COOH + (H^+ + e^-) \rightarrow CH_3OH(aq) + O$	1.27	0.88	1.28	0.90	---	---	---	---
$H_2COOH + (H^+ + e^-) \rightarrow H_2CO + H_2O(l)$	0.69	0.37	0.81	0.48	---	---	---	---
$H_2COOH + (H^+ + e^-) \rightarrow H_3CO + OH$	-0.17	0.19	0.01	0.36	---	---	---	---
$O + (H^+ + e^-) \rightarrow OH$	-1.32	-1.02	-1.40	-1.10	---	---	---	---
$H_2CO + (H^+ + e^-) \rightarrow H_3CO$	-0.82	-0.52	-1.04	-0.74	---	---	---	---
$H_3CO + OH + (H^+ + e^-) \rightarrow H_3CO + H_2O(l)$	0.04	-0.34	-0.24	-0.62	---	---	---	---
$H_3CO + OH + (H^+ + e^-) \rightarrow CH_3OH(aq) + OH$	0.12	-0.32	-0.12	-0.56	---	---	---	---
$OH + (H^+ + e^-) \rightarrow H_2O(l) + *$	0.94	0.56	0.77	0.39	---	---	---	---
$H_3CO + (H^+ + e^-) \rightarrow H_3COH(aq) + *$	1.01	0.57	0.88	0.44	---	---	---	---
$O + OH + (H^+ + e^-) \rightarrow O + H_2O(l)$	0.03	-0.35	-0.10	-0.48	---	---	---	---
$H_2 + * \rightarrow H + (H^+ + e^-)$	-0.43	-0.25	-0.35	-0.17	-0.36	-0.18	0.43	0.61
CrO_2								

Intermediates	25%		50%		75%-br		75%-CUS	
	ΔE	ΔG	ΔE	ΔG	ΔE	ΔG	ΔE	ΔG
$CO_2(g) + * + (H^+ + e^-) \rightarrow OCHO$	-0.78	-0.33	-0.60	-0.15	---	---	0.49	0.92
$OCHO + (H^+ + e^-) \rightarrow HCOOH(aq) + *$	0.87	0.27	0.69	0.09	---	---	-0.41	-0.99
$OCHO + (H^+ + e^-) \rightarrow HCOOH$	0.01	0.25	0.00	0.24	---	---	---	---
$HCOOH + (H^+ + e^-) \rightarrow H_2COOH$	0.03	0.33	0.42	0.71	---	---	---	---
$H_2COOH + (H^+ + e^-) \rightarrow CH_3OH(aq) + O$	0.46	0.07	0.80	0.41	---	---	---	---
$H_2COOH + (H^+ + e^-) \rightarrow H_2CO + H_2O(l)$	0.83	0.50	0.12	-0.21	---	---	---	---
$H_2COOH + (H^+ + e^-) \rightarrow H_3CO + OH$	-0.09	0.26	0.20	0.55	---	---	---	---
$O + (H^+ + e^-) \rightarrow OH$	-1.02	-0.72	-1.00	-0.70	---	---	---	---
$H_2CO + (H^+ + e^-) \rightarrow H_3CO$	-1.32	-1.02	-0.54	-0.24	---	---	---	---
$H_3CO + OH + (H^+ + e^-) \rightarrow H_3CO + H_2O(l)$	-0.41	-0.79	-0.63	-1.01	---	---	---	---
$H_3CO + OH + (H^+ + e^-) \rightarrow CH_3OH(aq) + OH$	-0.47	-0.91	-0.40	-0.84	---	---	---	---
$OH + (H^+ + e^-) \rightarrow H_2O(l) + *$	0.60	0.22	-0.31	-0.69	---	---	---	---
$H_3CO + (H^+ + e^-) \rightarrow H_3COH(aq) + *$	0.55	0.11	-0.08	-0.52	---	---	---	---
$O + OH + (H^+ + e^-) \rightarrow O + H_2O(l)$	-0.18	-0.56	-0.57	-0.95	---	---	---	---
$H_2 + * \rightarrow H + (H^+ + e^-)$	0.11	0.29	1.06	1.24	---	---	1.15	1.33
PtO_2								
Intermediates	**25%**		**50%**		**75%-br**		**75%-CUS**	
	ΔE	**ΔG**	**ΔE**	**ΔG**	**ΔE**	**ΔG**	**ΔE**	**ΔG**
$CO_2(g) + * + (H^+ + e^-) \rightarrow OCHO$	-0.31	0.14	-0.55	-0.10	-0.12	0.31	0.26	0.69
$OCHO + (H^+ + e^-) \rightarrow HCOOH(aq) + *$	0.39	-0.21	0.63	0.03	0.20	-0.38	-0.18	-0.76
$OCHO + (H^+ + e^-) \rightarrow HCOOH$	-0.28	-0.04	-0.27	-0.03	---	---	---	---
$HCOOH + (H^+ + e^-) \rightarrow H_2COOH$	-0.20	0.10	0.36	0.66	---	---	---	---
$H_2COOH + (H^+ + e^-) \rightarrow CH_3OH(aq) + O$	1.05	0.66	2.36	1.97	---	---	---	---
$H_2COOH + (H^+ + e^-) \rightarrow H_2CO + H_2O(l)$	-0.14	-0.47	0.14	-0.19	---	---	---	---
$H_2COOH + (H^+ + e^-) \rightarrow H_3CO + OH$	-0.42	-0.07	0.50	0.85	---	---	---	---
$O + (H^+ + e^-) \rightarrow OH$	-1.51	-1.21	-2.23	-1.93	---	---	---	---
$H_2CO + (H^+ + e^-) \rightarrow H_3CO$	-0.50	-0.20	-0.15	0.15	---	---	---	---
$H_3CO + OH + (H^+ + e^-) \rightarrow H_3CO + H_2O(l)$	-0.22	-0.60	-0.52	-0.90	---	---	---	---
$H_3CO + OH + (H^+ + e^-) \rightarrow CH_3OH(aq) + OH$	-0.03	-0.47	-0.37	-0.81	---	---	---	---
$OH + (H^+ + e^-) \rightarrow H_2O(l) + *$	0.55	0.17	-0.36	-0.74	---	---	---	---
$H_3CO + (H^+ + e^-) \rightarrow H_3COH(aq) + *$	0.73	0.29	-0.22	-0.66	---	---	---	---
$O + OH + (H^+ + e^-) \rightarrow O + H_2O(l)$	-0.36	-0.74	-0.37	-0.75	---	---	---	---
$H_2 + * \rightarrow H + (H^+ + e^-)$	-0.34	-0.16	-0.50	-0.32	-0.39	-0.21	-0.56	-0.38
RhO_2								

Intermediates	25%		50%		75%-br		75%-CUS	
	ΔE	ΔG	ΔE	ΔG	ΔE	ΔG	ΔE	ΔG
$CO_2(g) + * + (H^+ + e^-) \rightarrow OCHO$	-0.68	-0.23	-0.76	-0.31	-0.61	-0.18	0.38	0.81
$OCHO + (H^+ + e^-) \rightarrow HCOOH(aq) + *$	0.76	0.16	0.84	0.24	0.69	0.11	-0.29	-0.87
$OCHO + (H^+ + e^-) \rightarrow HCOOH$	0.20	0.44	0.20	0.44	---	---	---	---
$HCOOH + (H^+ + e^-) \rightarrow H_2COOH$	-0.32	-0.02	-0.30	0.00	---	---	---	---
$H_2COOH + (H^+ + e^-) \rightarrow CH_3OH(aq) + O$	1.27	0.88	1.34	0.95	---	---	---	---
$H_2COOH + (H^+ + e^-) \rightarrow H_2CO + H_2O(l)$	0.45	0.12	0.77	0.44	---	---	---	---
$H_2COOH + (H^+ + e^-) \rightarrow H_3CO + OH$	0.20	0.55	0.15	0.50	---	---	---	---
$O + (H^+ + e^-) \rightarrow OH$	-1.48	-1.18	-1.57	-1.27	---	---	---	---
$H_2CO + (H^+ + e^-) \rightarrow H_3CO$	-0.80	-0.50	-1.09	-0.79	---	---	---	---
$H_3CO + OH + (H^+ + e^-) \rightarrow H_3CO + H_2O(l)$	-0.55	-0.93	-0.47	-0.85	---	---	---	---
$H_3CO + OH + (H^+ + e^-) \rightarrow CH_3OH(aq) + OH$	-0.42	-0.86	-0.39	-0.83	---	---	---	---
$OH + (H^+ + e^-) \rightarrow H_2O(l) + *$	0.32	-0.06	0.40	0.02	---	---	---	---
$H_3CO + (H^+ + e^-) \rightarrow H_3COH(aq) + *$	0.46	0.02	0.49	0.05	---	---	---	---
$O + OH + (H^+ + e^-) \rightarrow O + H_2O(l)$	-0.78	-1.16	-0.45	-0.83	---	---	---	---
$H_2 + * \rightarrow H + (H^+ + e^-)$	-0.22	-0.04	-0.21	-0.03	-0.19	-0.01	0.26	0.44
MnO_2								
Intermediates	**25%**		**50%**		**75%-br**		**75%-CUS**	
	ΔE	**ΔG**	**ΔE**	**ΔG**	**ΔE**	**ΔG**	**ΔE**	**ΔG**
$CO_2(g) + * + (H^+ + e^-) \rightarrow OCHO$	0.10	0.55	0.54	0.99	---	---	---	---
$OCHO + (H^+ + e^-) \rightarrow HCOOH(aq) + *$	-0.02	-0.62	-0.46	-1.06	---	---	---	---
$OCHO + (H^+ + e^-) \rightarrow HCOOH$	-0.33	-0.09	-0.84	-0.60	---	---	---	---
$HCOOH + (H^+ + e^-) \rightarrow H_2COOH$	0.37	0.67	0.74	1.04	---	---	---	---
$H_2COOH + (H^+ + e^-) \rightarrow CH_3OH(aq) + O$	0.38	-0.01	1.42	1.03	---	---	---	---
$H_2COOH + (H^+ + e^-) \rightarrow H_2CO + H_2O(l)$	0.07	-0.26	-0.31	-0.64	---	---	---	---
$H_2COOH + (H^+ + e^-) \rightarrow H_3CO + OH$	0.01	0.37	0.12	0.48	---	---	---	---
$O + (H^+ + e^-) \rightarrow OH$	-1.27	-0.97	-1.89	-1.59	---	---	---	---
$H_2CO + (H^+ + e^-) \rightarrow H_3CO$	-0.88	-0.58	-0.32	-0.02	---	---	---	---
$H_3CO + OH + (H^+ + e^-) \rightarrow H_3CO + H_2O(l)$	-0.82	-1.20	-0.76	-1.14	---	---	---	---
$H_3CO + OH + (H^+ + e^-) \rightarrow CH_3OH(aq) + OH$	-0.90	-1.34	-0.59	-1.03	---	---	---	---
$OH + (H^+ + e^-) \rightarrow H_2O(l) + *$	0.05	-0.33	-0.66	-1.04	---	---	---	---
$H_3CO + (H^+ + e^-) \rightarrow H_3COH(aq) + *$	-0.03	-0.47	-0.50	-0.94	---	---	---	---
$O + OH + (H^+ + e^-) \rightarrow O + H_2O(l)$	-1.11	-1.49	-0.56	-0.94	---	---	---	---
$H_2 + * \rightarrow H + (H^+ + e^-)$	0.45	0.63	0.93	1.11	---	---	---	---
PdO_2								

Intermediates	25%		50%		75%-br		75%-CUS	
	ΔE	**ΔG**	**ΔE**	**ΔG**	**ΔE**	**ΔG**	**ΔE**	**ΔG**
$CO_2(g) + * + (H^+ + e^-) \rightarrow OCHO$	0.26	0.71	0.33	0.78	-0.09	0.34	0.68	1.11
$OCHO + (H^+ + e^-) \rightarrow HCOOH(aq) + *$	-0.17	-0.77	-0.25	-0.85	0.17	-0.41	-0.60	-1.18
$OCHO + (H^+ + e^-) \rightarrow HCOOH$	-0.46	-0.22	-0.76	-0.52	---	---	---	---
$HCOOH + (H^+ + e^-) \rightarrow H_2COOH$	0.23	0.53	0.97	1.27	---	---	---	---
$H_2COOH + (H^+ + e^-) \rightarrow CH_3OH(aq) + O$	1.23	0.85	2.37	1.98	---	---	---	---
$H_2COOH + (H^+ + e^-) \rightarrow H_2CO + H_2O(l)$	0.10	-0.23	-0.50	-0.83	---	---	---	---
$H_2COOH + (H^+ + e^-) \rightarrow H_3CO + OH$	0.35	0.70	0.50	0.85	---	---	---	---
$O + (H^+ + e^-) \rightarrow OH$	-1.92	-1.62	-2.44	-2.14	---	---	---	---
$H_2CO + (H^+ + e^-) \rightarrow H_3CO$	-0.80	-0.50	0.22	0.52	---	---	---	---
$H_3CO + OH + (H^+ + e^-) \rightarrow H_3CO + H_2O(l)$	-1.05	-1.43	-0.79	-1.17	---	---	---	---
$H_3CO + OH + (H^+ + e^-) \rightarrow CH_3OH(aq) + OH$	-1.04	-1.48	-0.57	-1.01	---	---	---	---
$OH + (H^+ + e^-) \rightarrow H_2O(l) + *$	-0.02	-0.40	-1.16	-1.54	---	---	---	---
$H_3CO + (H^+ + e^-) \rightarrow H_3COH(aq) + *$	-0.01	-0.45	-0.95	-1.39	---	---	---	---
$O + OH + (H^+ + e^-) \rightarrow O + H_2O(l)$	-1.16	-1.54	-0.82	-1.20	---	---	---	---
$H_2 + * \rightarrow H + (H^+ + e^-)$	0.11	0.29	0.47	0.65	-0.12	0.06	0.15	0.33

Table S4. Electronic and binding free energy of CO_2 binding through O bidentate (O_b) and/or linear (O_l) and/or through carbon (C) at 0%, 25%, 50% and 75% CO coverages on all TMOs studied in this work.

TMOs	coverage	O_b		O_l		C	
		ΔE	ΔG	ΔE	ΔG	ΔE	ΔG
HfO_2	0%	----	----	----	----	-3.78	-3.60
	25%	-0.80	-0.65	-0.32	0.12	----	----
	50%	----	----	-0.25	0.20	-0.87	-0.69
	75%-br	----	----	-0.23	0.22	-1.38	-1.20
	75%-CUS	---	---	-0.50	-0.06	0.18	0.36
MoO_2	0%	-0.75	-0.60	-0.23	0.21	-0.52	-0.34
	25%	-0.14	0.00	-0.48	-0.04	----	----
	50%	0.05	0.20	-0.56	-0.11	0.27	0.46
	75%-br	---	---	-0.65	-0.20	0.25	0.43
	75%-CUS	---	---	-0.62	-0.17	---	---
OsO_2	0%	-0.33	-0.18	0.04	0.48	-1.48	-1.29
	25%	----	----	-0.40	0.04	----	----
	50%	-0.14	0.00	-0.41	0.03	-0.65	-0.47
	75%-br	---	---	-0.53	-0.08	-0.14	0.04
	75%-CUS	---	---	-0.51	-0.06	----	----
NbO_2	0%	-0.47	-0.32	-0.21	0.23	-2.42	-2.24
	25%	0.19	0.33	-0.03	0.41	-0.26	-0.08
	50%	-0.09	0.36	-0.89	-0.44	----	----
	75%-br	---	---	0.00	0.44	-0.15	0.04
	75%-CUS	----	---	-0.59	-0.14	---	---
TiO_2	0%	-0.24	-0.09	-0.17	0.27	-1.72	-1.54
	25%	0.34	0.49	0.02	0.46	-0.35	-0.17
	50%	----	----	-0.27	0.17	----	----
	75%-br	----	----	----	----	----	----
	75%-CUS	---	---	-0.27	0.18	---	---
IrO_2	0%	0.04	0.19	-0.05	0.40	-0.88	-0.70
	25%	0.10	0.24	-0.21	0.24	-0.82	-0.64
	50%	----	----	----	----	-1.09	-0.91
	75%-br	---	---	0.04	0.49	-0.47	-0.29
	75%-CUS	---	---	-0.67	-0.22	---	---
RuO_2	0%	---	---	-0.02	0.43	-0.37	-0.19
	25%	----	----	-0.26	0.18	---	---
	50%	---	---	-0.36	0.09	---	---
	75%-br	---	---	-0.42	0.03	---	---
	75%-CUS	---	---	-0.38	0.06	----	---
CrO_2	0%	----	----	----	----	0.60	0.78
	25%	----	----	----	----	----	----
	50%	----	----	----	----	----	----

	75%-br	----	----	----	----	----	----
	75%-CUS	----	----	----	----	----	----
PtO_2	0%	----	----	----	----	-0.37	-0.19
	25%	----	----	----	----	0.60	0.78
	50%	----	----	----	----	----	----
	75%-br	----	----	----	----	0.17	0.36
	75%-CUS	----	----	----	----	----	----

*RhO_2, MnO_2 and PdO_2 do not bind CO_2 on their surfaces at any coverages.

Table S5. Selectivity of different TMOs toward CO_2RR or HER products and their free energy binding strength order for 0%, 25%, 50% and 75% CO coverage with br-br-CUS configuration (vacant CUS) and br-CUS-CUS configuration (vacant br) at U=0. CO_2 can either adsorb through its oxygen atom both bidentate (O_b) and linear (O_l) and through its carbon atom (C). In the case of MnO_2, 75% CO coverage formation is not possible (shown with dashed line).

Catalysts		CO coverage				
		0%	25%	50%	75%	
					vacant CUS	vacant br
HfO_2	Binding strength	H < C	O_l < O_b < H	O_l < H < C	C < H < O_l	O_l < H < C
	Selectivity at U=0	CO_2RR	HER	CO_2RR	CO_2RR	CO_2RR
	Possible product at U=0	CO	H_2	CO	CO /HCOOH/CH_3OH	CO
MoO_2	Binding strength	O_l < C < H < O_b	O_b < O_l < H	H < C < O_b < O_l	H < O_l	H = C < O_l
	Selectivity at U=0	CO_2RR	HER	CO_2RR	CO_2RR	CO_2RR
	Possible product at U=0	HCOOH/CH_3OH	H_2	CO /HCOOH/CH_3OH	CO /HCOOH/CH_3OH	CO /HCOOH/CH_3OH
OsO_2	Binding strength	O_l < O_b < H < C	O_l < H	O_l < O_b < C < H	O_l < H	C < O_l < H
	Selectivity at U=0	CO_2RR	HER	HER	HER	HER
	Possible product at U=0	CO	H_2	H_2	H_2	H_2
NbO_2	Binding strength	O_l < O_b < H < C	O_l < O_b < C < H	O_b < O_l < H	H< O_l	O_l < C < H
	Selectivity at U=0	CO_2RR	HER	HER	CO_2RR	HER
	Possible product at U=0	CO	H_2	H_2	CO /HCOOH/CH_3OH	H_2
TiO_2	Binding strength	O_l < O_b < H< C	O_b < O_l < H < C	H < O_l	H < O_l	H
	Selectivity at U=0	CO_2RR	CO_2RR	CO_2RR	CO_2RR	HER
	Possible product at U=0	CO	CO	CO /HCOOH/CH_3OH	CO /HCOOH/CH_3OH	H_2
IrO_2	Binding strength	O_l < O_b < H = C	O_b < O_l < C < H	H < C	O_l < H	O_l < C < H
	Selectivity at U=0	HER/CO_2RR	HER	CO_2RR	HER	HER
	Possible product at U=0	H_2/CO	H_2	CO	H_2	H_2
RuO_2	Binding strength	O_l < C < H	O_l < H	O_l < H	O_l < H	O_l < H
	Selectivity at U=0	HER	HER	HER	HER	HER
	Possible product at U=0	H_2	H_2	H_2	H_2	H_2
CrO_2	Binding strength	C < H	H	H	H	H
	Selectivity at U=0	HER	HER	HER	HER	HER
	Possible product at U=0	H_2	H_2	H_2	H_2	H_2
PtO_2	Binding strength	C < H	C < H	H	H	C < H
	Selectivity at U=0	HER	HER	HER	HER	HER
	Possible product at U=0	H_2	H_2	H_2	H_2	H_2
RhO_2	Binding strength	H	H	H	H	H
	Selectivity at U=0	HER	HER	HER	HER	HER
	Possible product at U=0	H_2	H_2	H_2	H_2	H_2
MnO_2	Binding strength	H	H	H	---	---
	Selectivity at U=0	HER	HER	HER	---	---

	Possible product at U=0	H_2	H_2	H_2	---	---
PdO_2	Binding strength	H	H	H	H	H
	Selectivity at U=0	HER	HER	HER	HER	HER
	Possible product at U=0	H_2	H_2	H_2	H_2	H_2

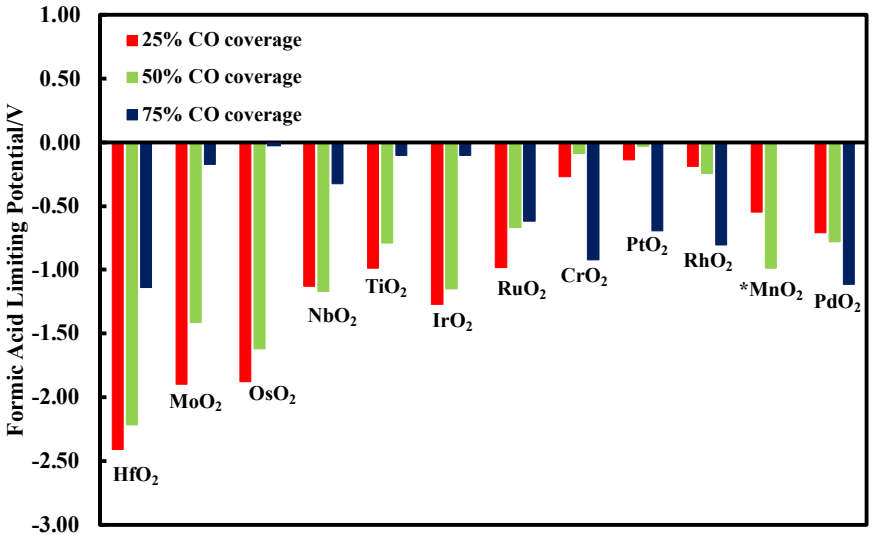


Figure S1. Limiting potentials towards formic acid formation at varying CO coverages (75% CO coverage with br-br-CUS configuration). MnO_2 is not able to hold the third CO (75% coverage) on its surface and therefore, there is one data column missing for it in the diagram.

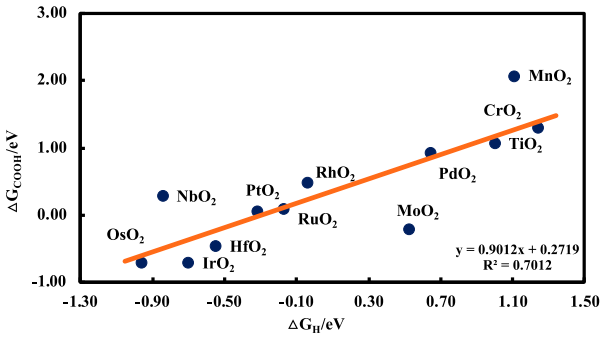


Figure S2. Scaling relation for TMOs for H vs. COOH for 50% CO coverage.

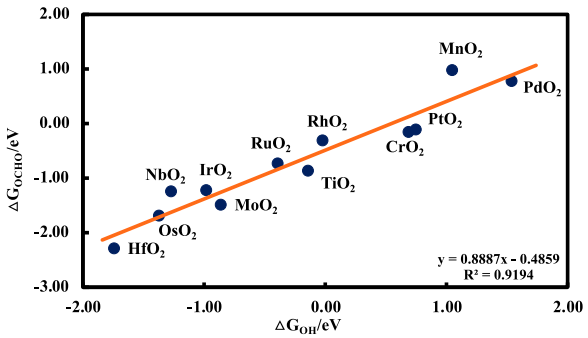
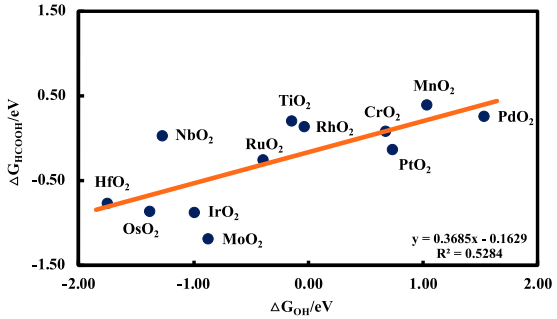


Figure S3. Scaling relation for TMOs for OH vs. OCHO for 50% CO coverage.



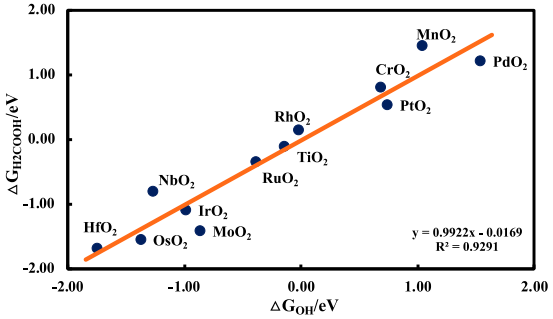


Figure S4. Scaling relation for TMOs for OH vs. HCOOH for 50% CO coverage.

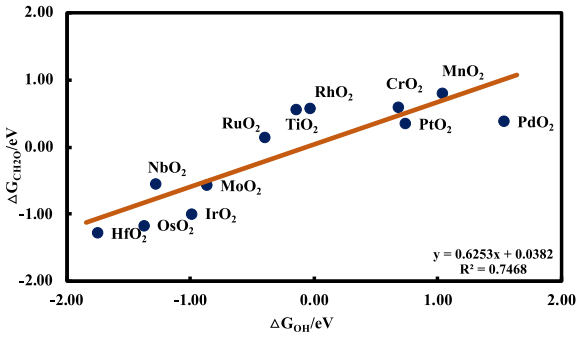


Figure S5. Scaling relation for TMOs for OH vs. H_2COOH for 50% CO coverage.

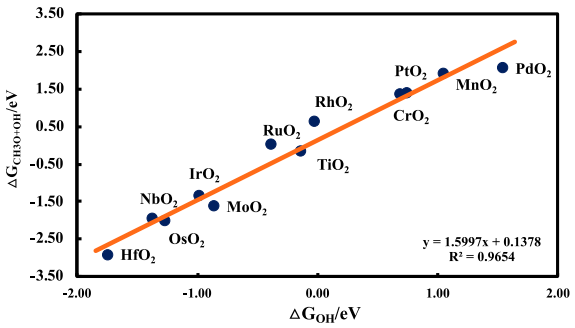


Figure S6. Scaling relation for TMOs for OH vs. CH_2O for 50% CO coverage.

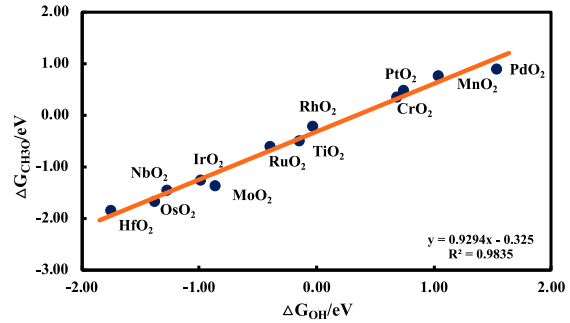


Figure S7. Scaling relation for TMOs for OH vs. CH_3O+OH for 50% CO coverage.

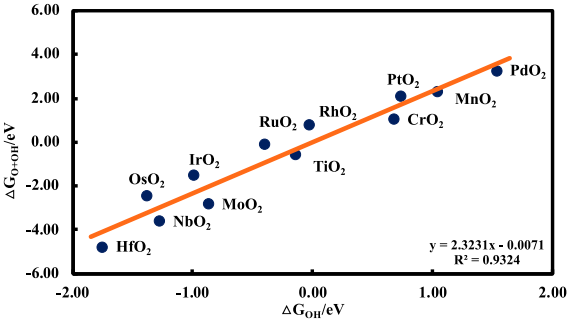


Figure S8. Scaling relation for TMOs for OH vs. CH_3O for 50% CO coverage.

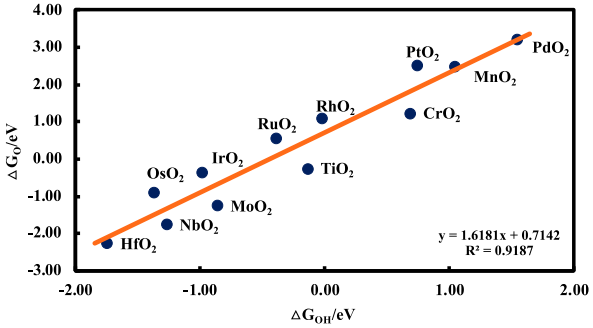


Figure S9. Scaling relation for TMOs for OH vs. O+OH for 50% CO coverage.

Figure S10. Scaling relation for TMOs for OH vs. O for 50% CO coverage.

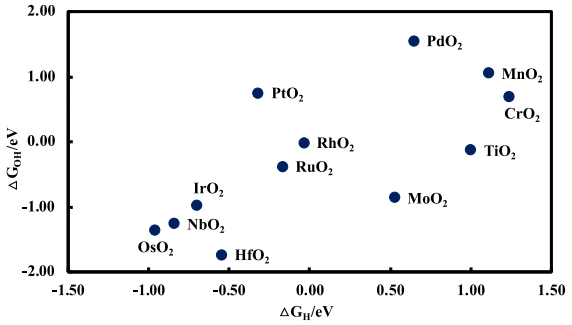


Figure S11. Scaling relation for TMOs for H vs. OH for 50% CO coverage.

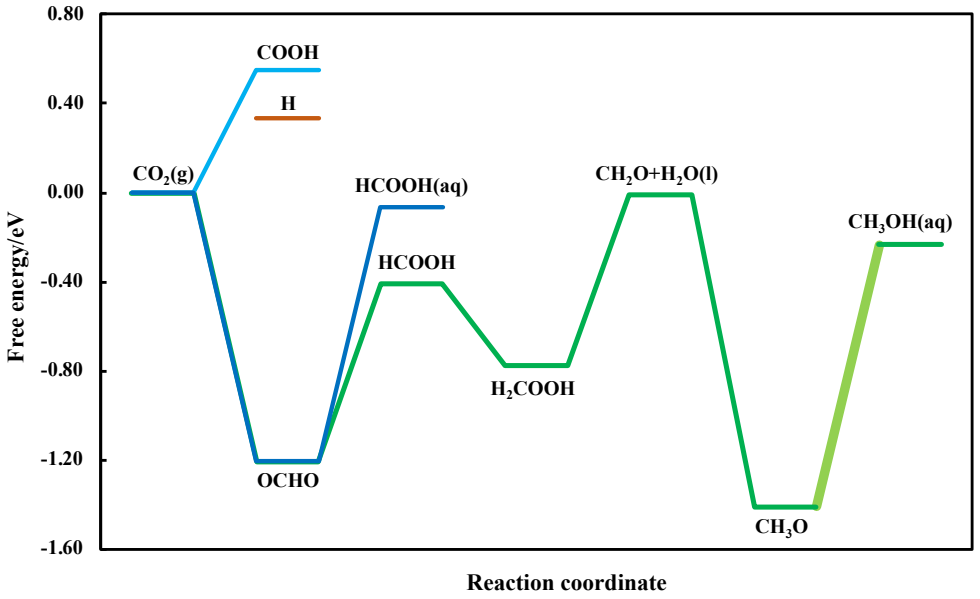


Figure S12. Free energy diagram for HfO_2 for 75% CO coverage with br-br-CUS CO configuration. Different reaction pathways for formic acid and methanol products are presented. Potential limiting step is presented for methanol with light green line.

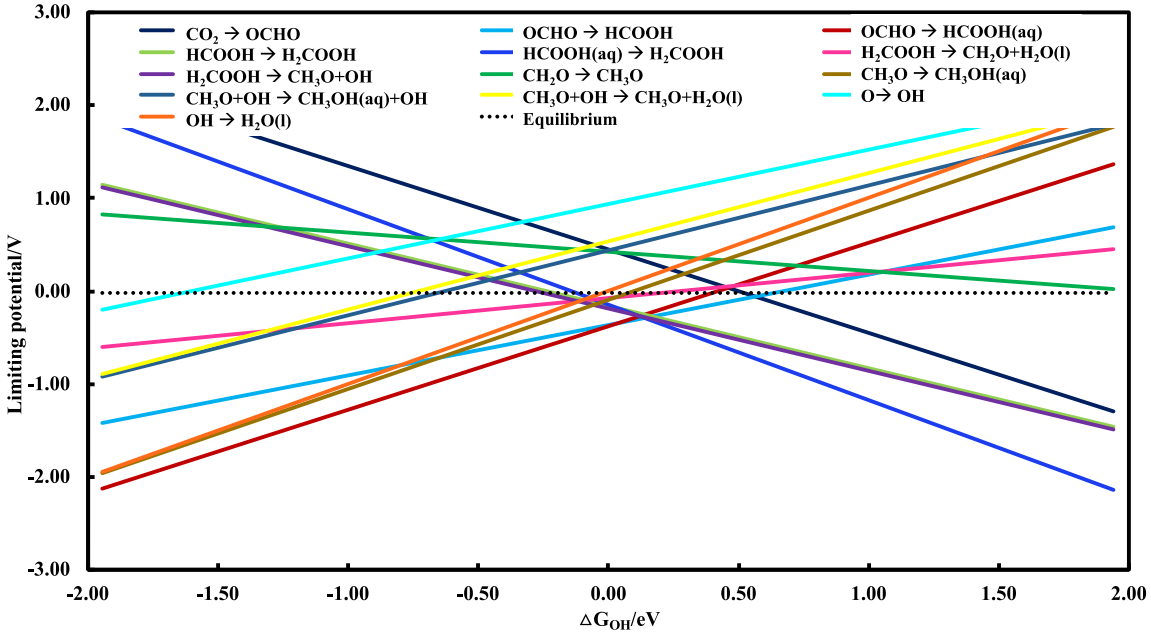


Figure S13. Theoretical volcano for formation of methanol including 50% CO coverage on the TMO surfaces. Each line indicates a reaction step.

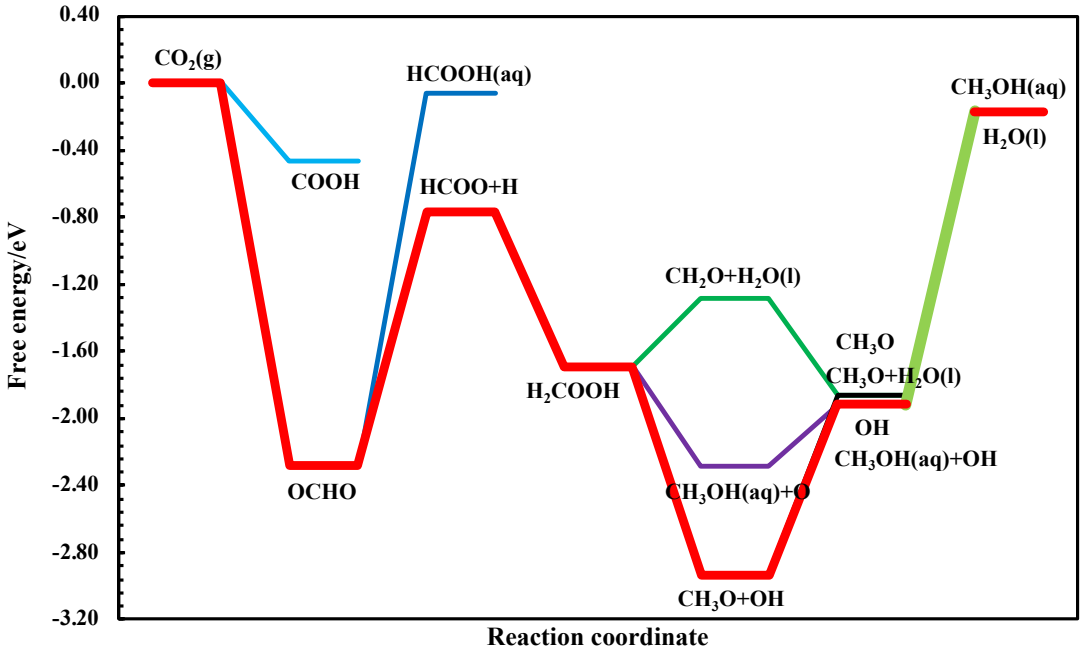


Figure S14. Free energy diagram for HfO_2 for 50% CO coverage. Different reaction pathways for formic acid and methanol products are presented. Potential limiting step is presented for methanol with light green line.

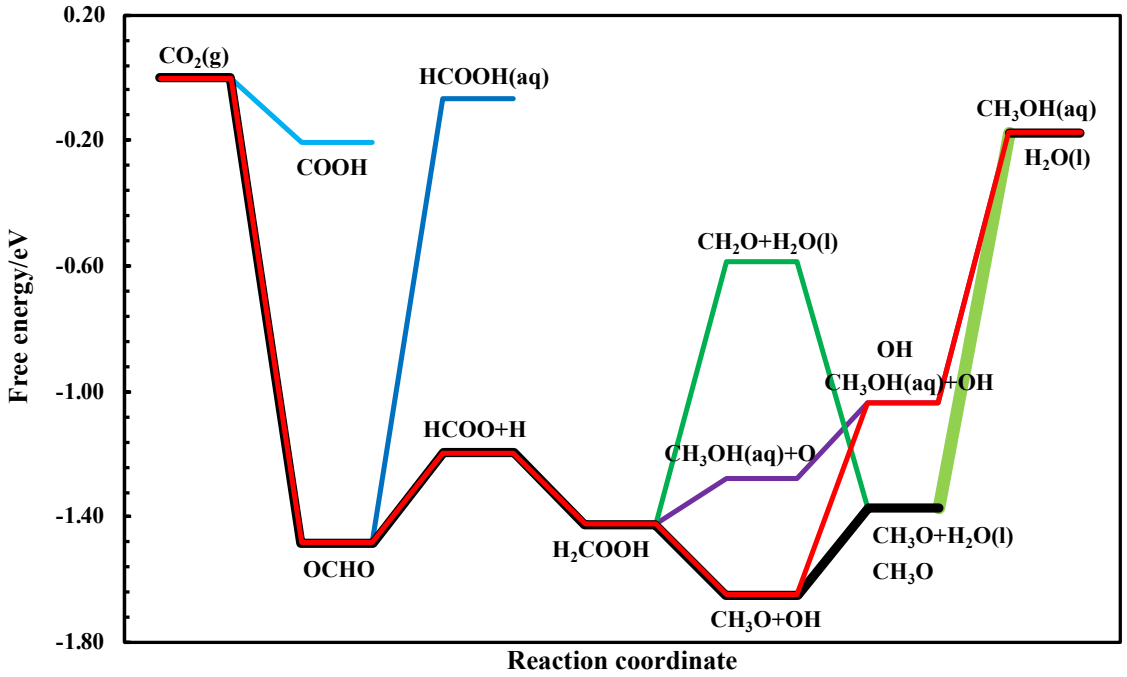


Figure S15. Free energy diagram for MoO_2 for 50% CO coverage. Different reaction pathways for formic acid and methanol products are presented. Potential limiting step is presented for methanol with light green line.

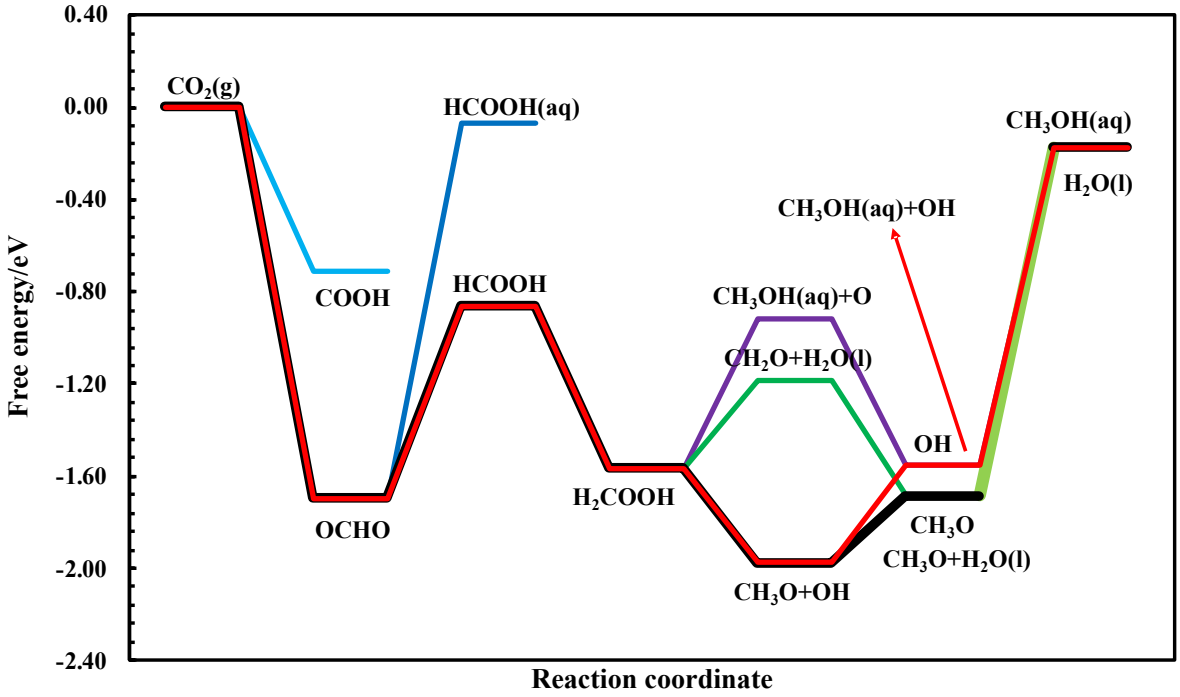


Figure S16. Free energy diagram for OsO_2 for 50% CO coverage. Different reaction pathways for formic acid and methanol products are presented. Potential limiting step is presented for methanol with light green line.

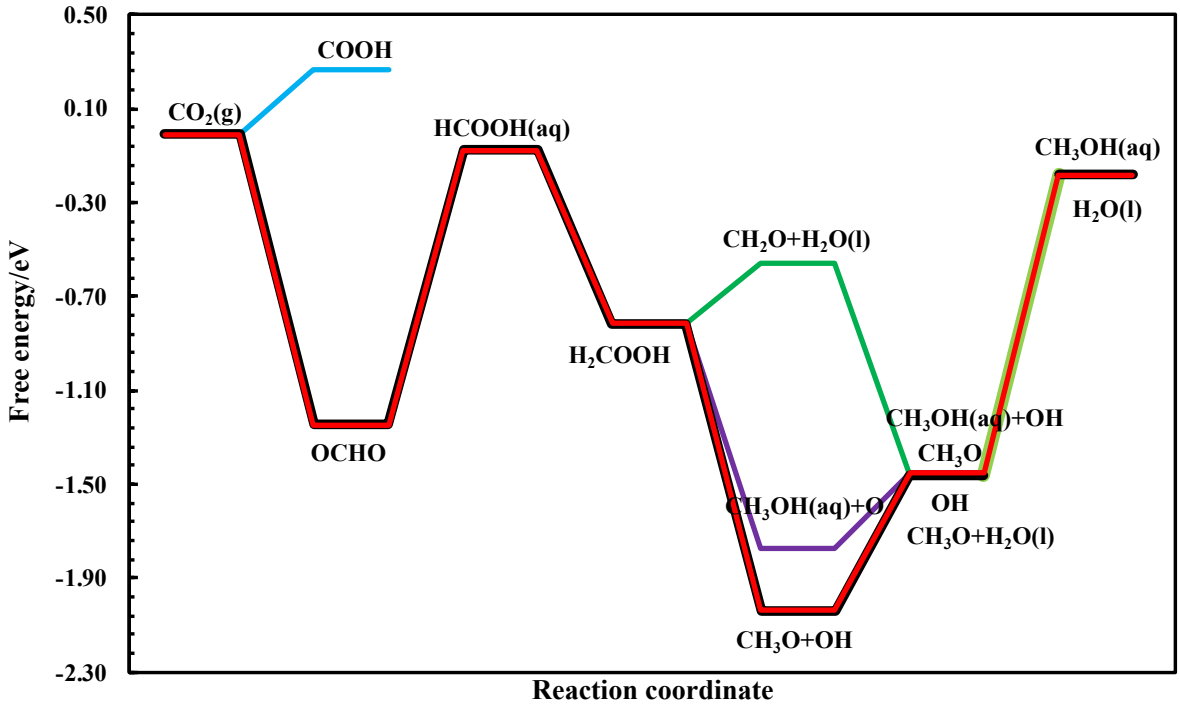


Figure S17. Free energy diagram for NbO_2 for 50% CO coverage. Different reaction pathways for formic acid and methanol products are presented. Potential limiting step is presented for methanol with light green line.

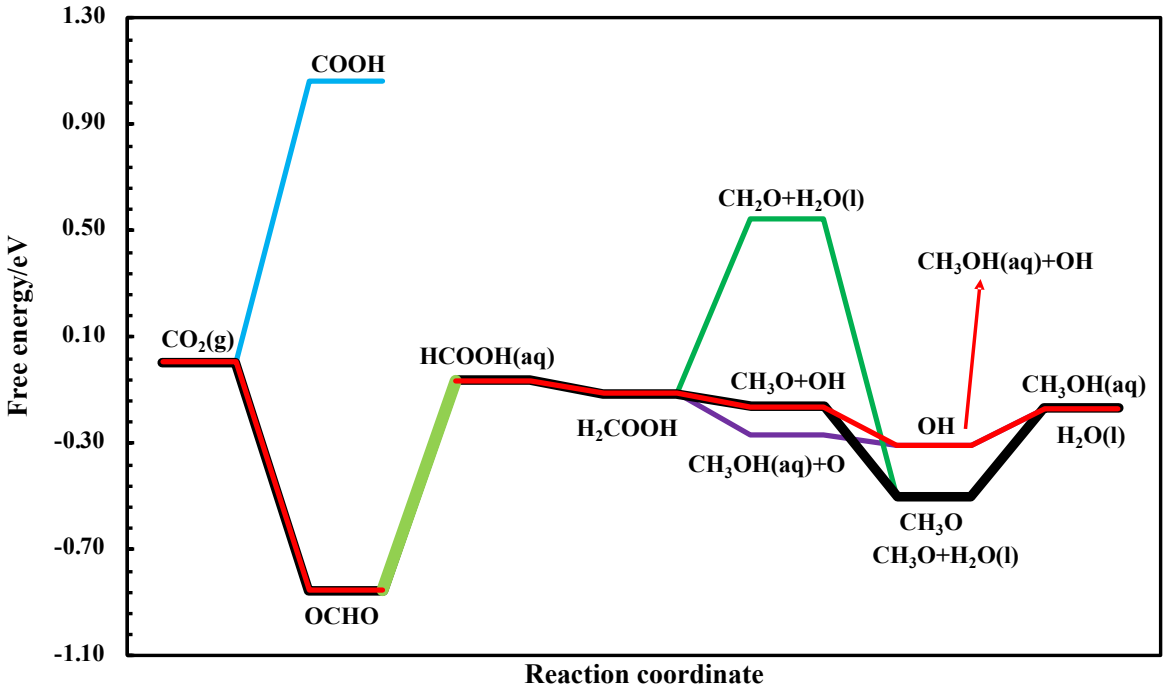


Figure S18. Free energy diagram for TiO_2 for 50% CO coverage. Different reaction pathways for formic acid and methanol products are presented. Potential limiting step is presented for methanol with light green line.

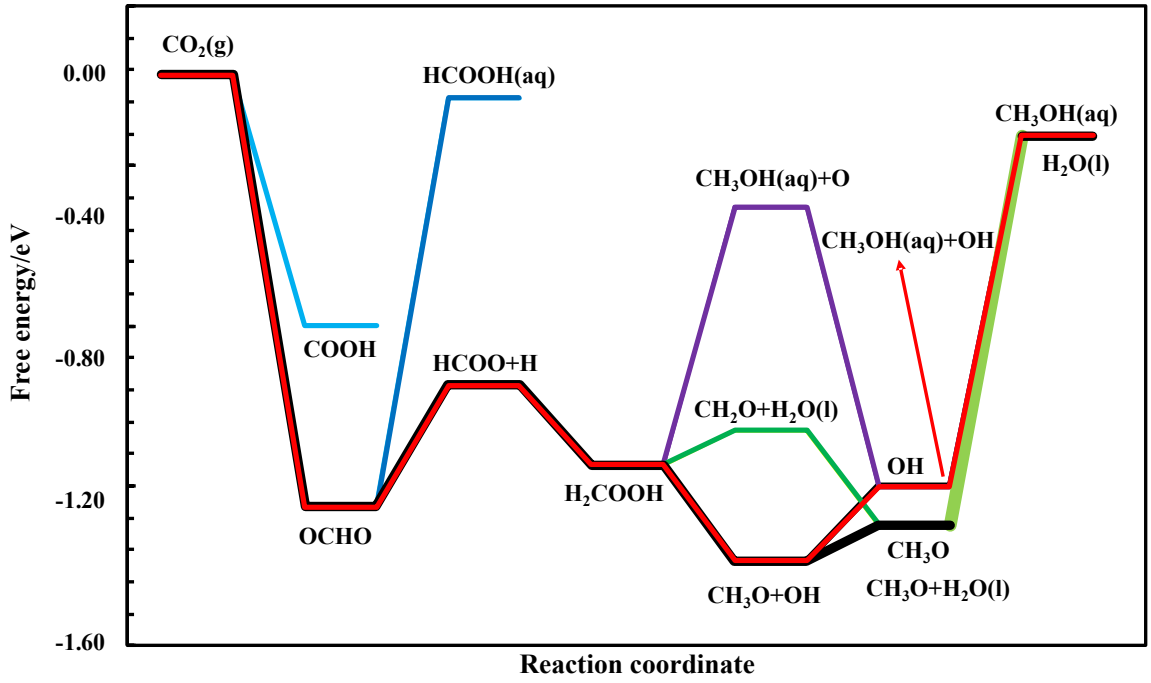


Figure S19. Free energy diagram for IrO_2 for 50% CO coverage. Different reaction pathways for formic acid and methanol products are presented. Potential limiting step is presented for methanol with light green line.

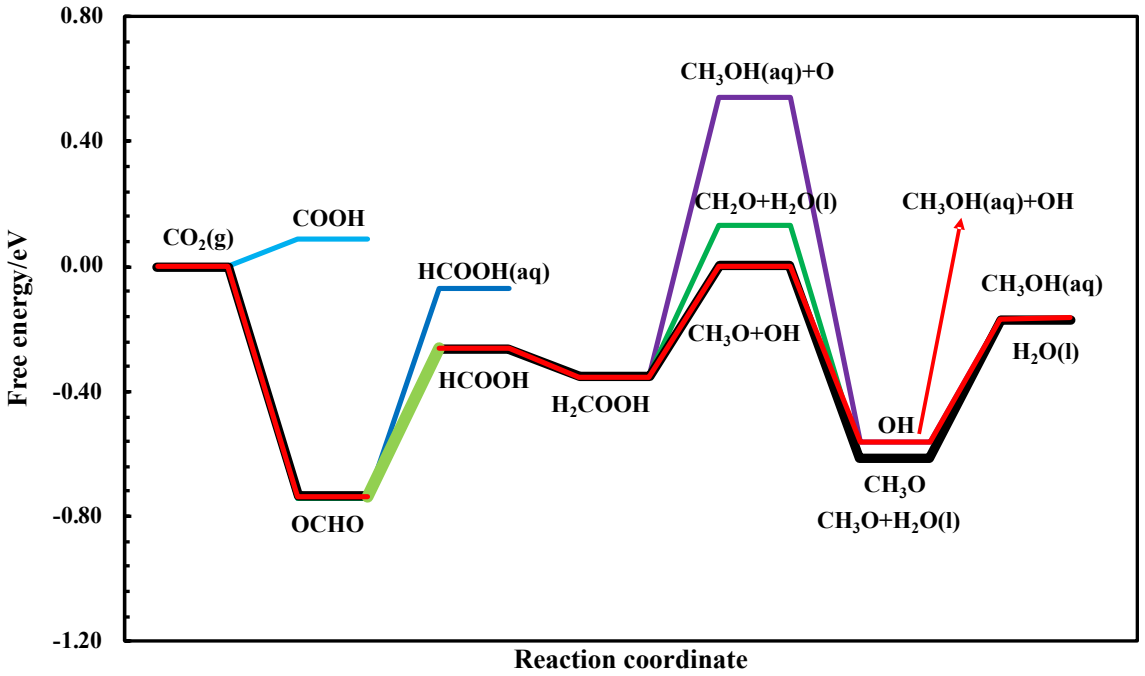


Figure S20. Free energy diagram for RuO_2 for 50% CO coverage. Different reaction pathways for formic acid and methanol products are presented. Potential limiting step is presented for methanol with light green line.

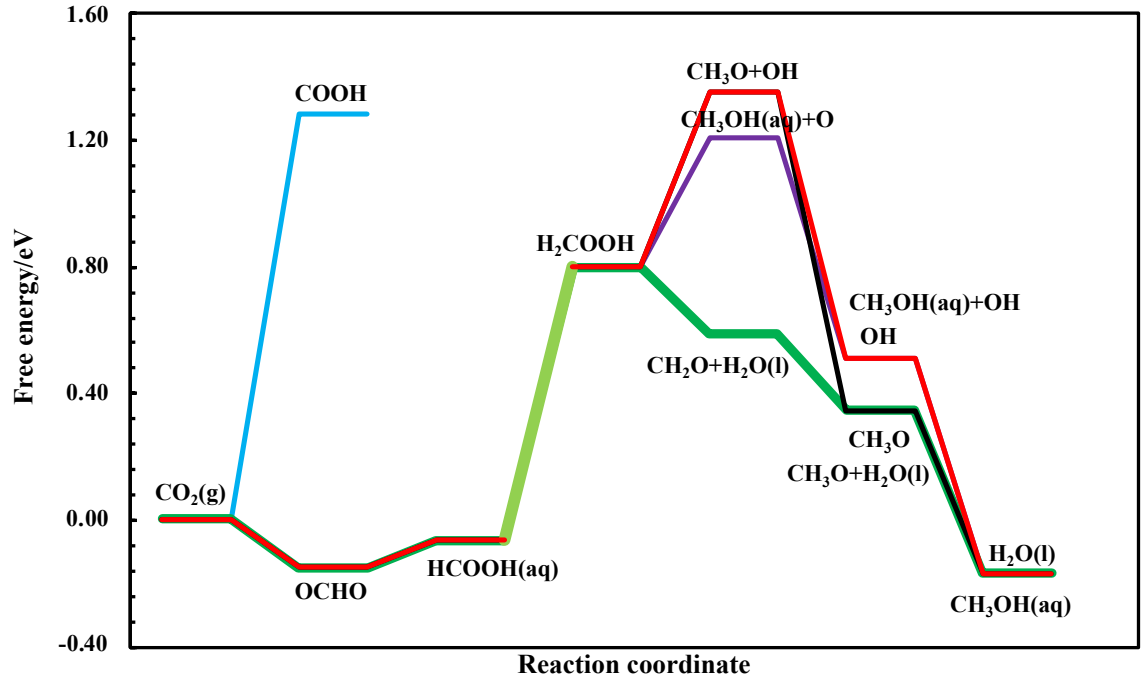


Figure S21. Free energy diagram for CrO_2 for 50% CO coverage. Different reaction pathways for formic acid and methanol products are presented. Potential limiting step is presented for methanol with light green line.

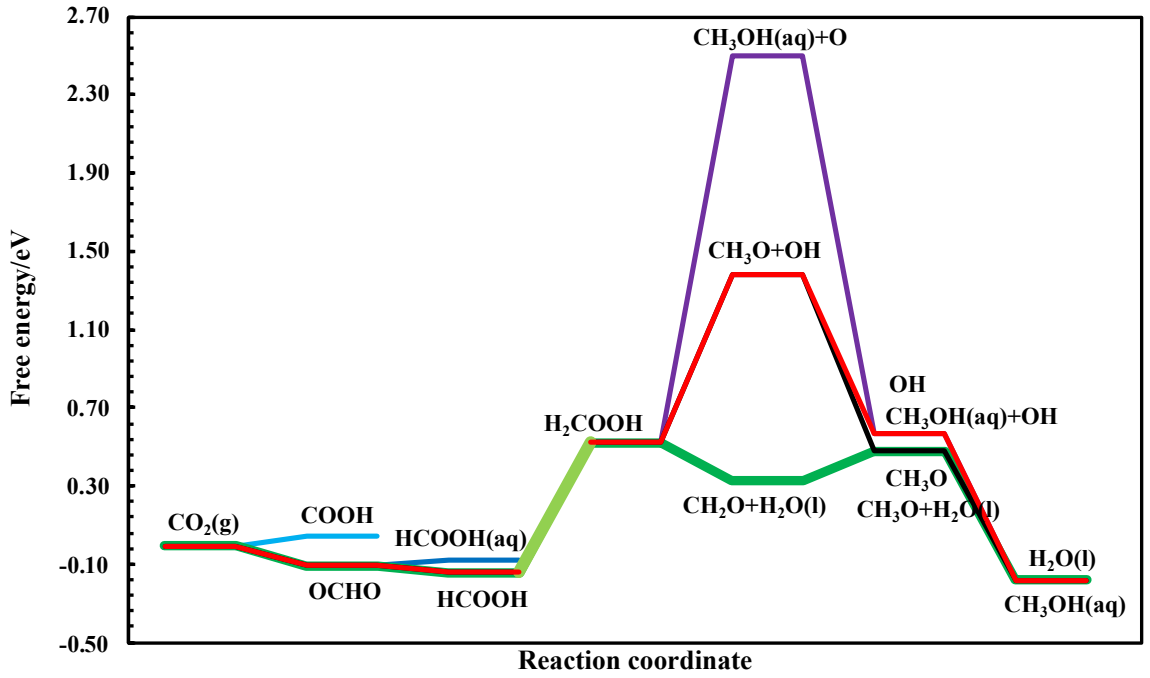


Figure S22. Free energy diagram for PtO_2 for 50% CO coverage. Different reaction pathways for formic acid and methanol products are presented. Potential limiting step is presented for methanol with light green line.

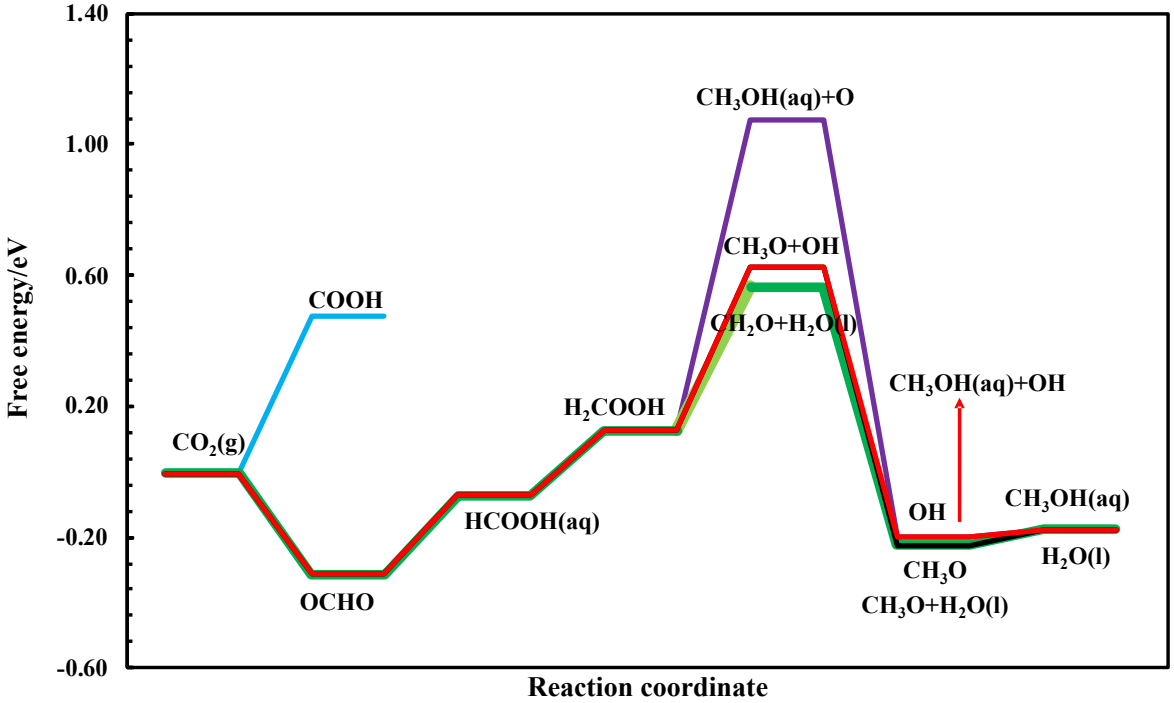


Figure S23. Free energy diagram for RhO_2 for 50% CO coverage. Different reaction pathways for formic acid and methanol products are presented. Potential limiting step is presented for methanol with light green line.

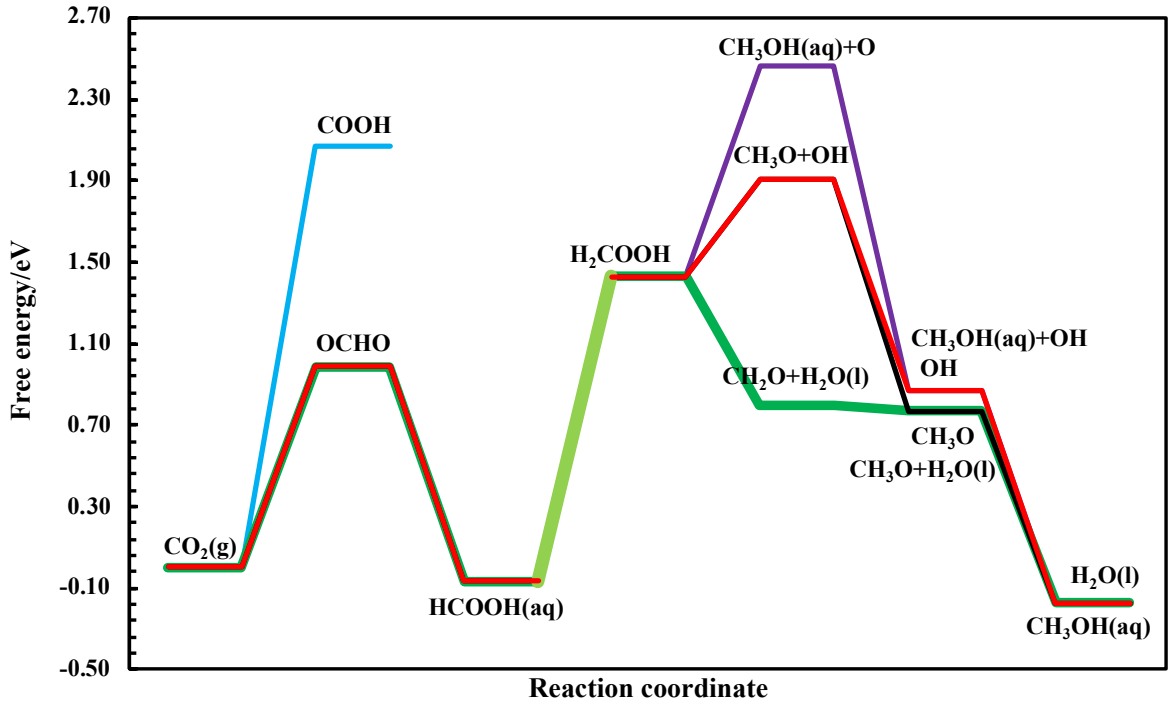


Figure S24. Free energy diagram for MnO_2 for 50% CO coverage. Different reaction pathways for formic acid and methanol products are presented. Potential limiting step is presented for methanol with light green line.

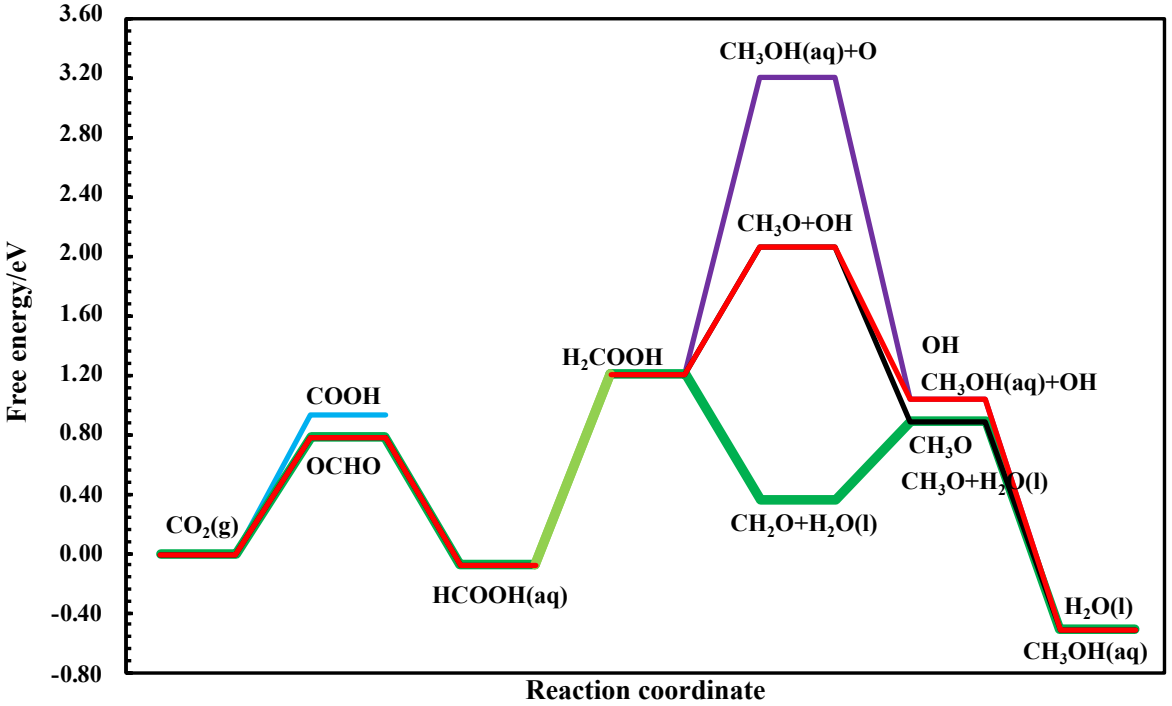


Figure S25. Free energy diagram for PdO_2 for 50% CO coverage. Different reaction pathways for formic acid and methanol products are presented. Potential limiting step is presented for methanol with light green line.

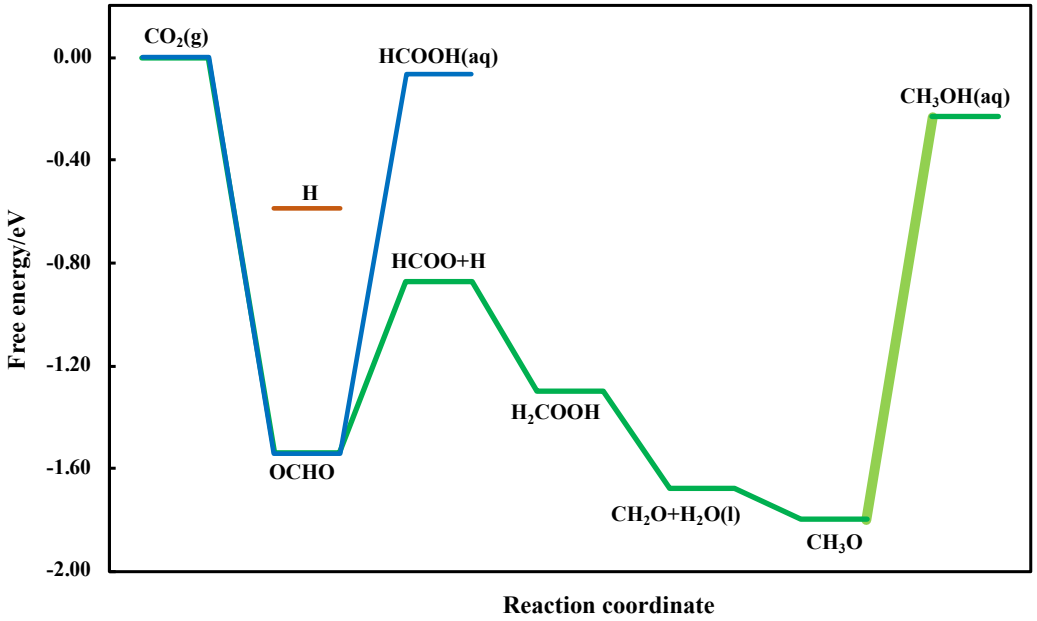


Figure S26. Free energy diagram for HfO_2 for 75% CO coverage with br-CUS-CUS CO configuration. Different reaction pathways for formic acid and methanol products are presented. Potential limiting step is presented for methanol with light green line. COOH intermediate formation is absent and the reason to this is that its formation causes the third CO desorption from the surface.

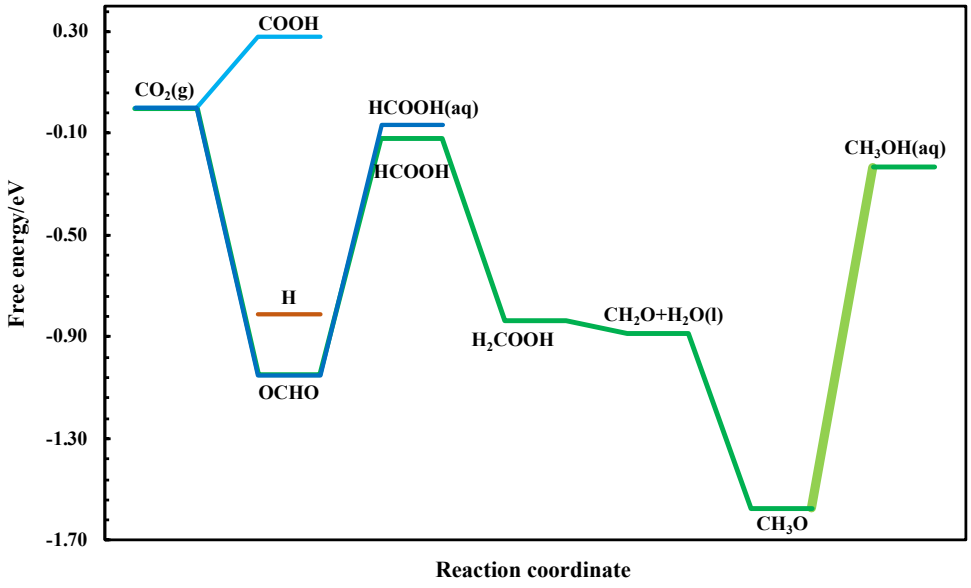


Figure S27. Free energy diagram for NbO_2 for 75% CO coverage with br-CUS-CUS CO configuration. Different reaction pathways for formic acid and methanol products are presented. Potential limiting step is presented for methanol with light green line.

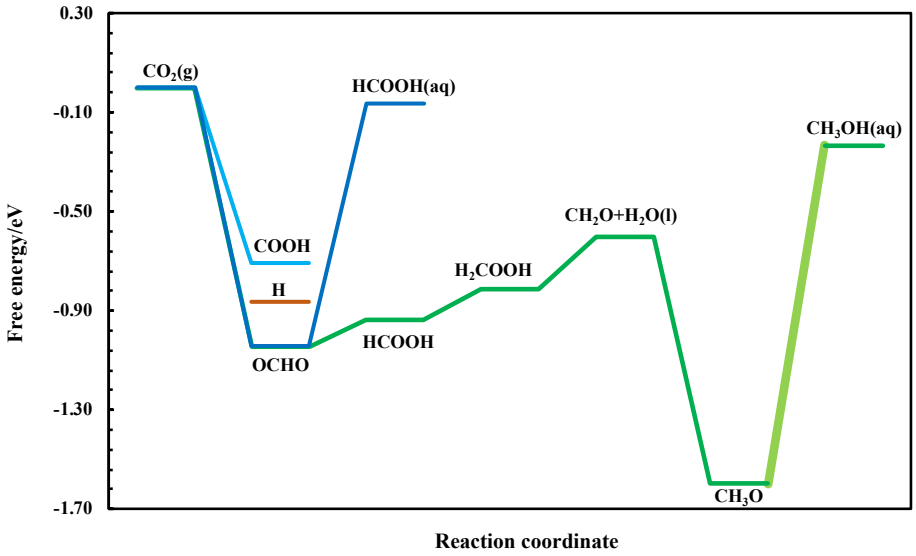


Figure S28. Free energy diagram for OsO_2 for 75% CO coverage with br-CUS-CUS CO configuration. Different reaction pathways for formic acid and methanol products are presented. Potential limiting step is presented for methanol with light green line.

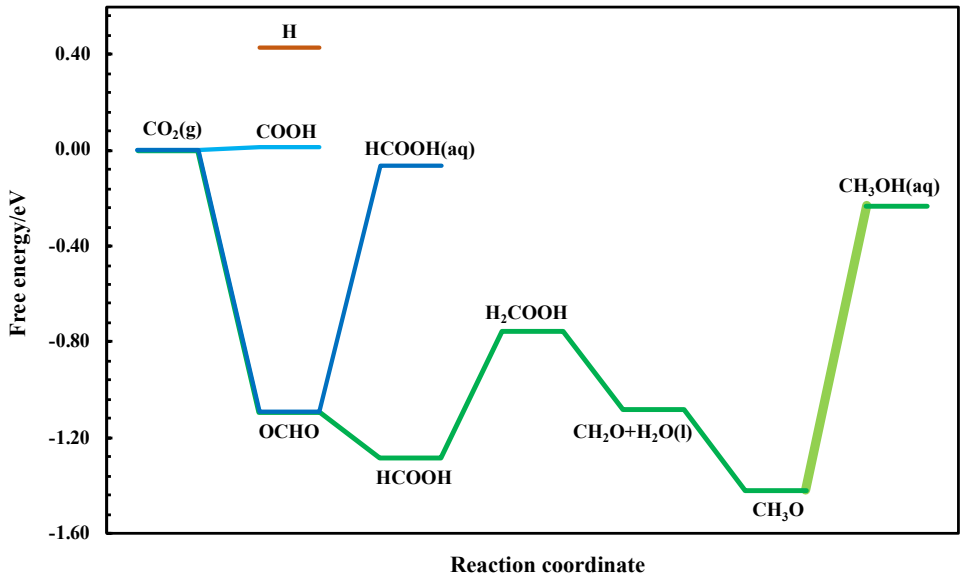


Figure S29. Free energy diagram for MoO_2 for 75% CO coverage with br-CUS-CUS CO configuration. Different reaction pathways for formic acid and methanol products are presented. Potential limiting step is presented for methanol with light green line.

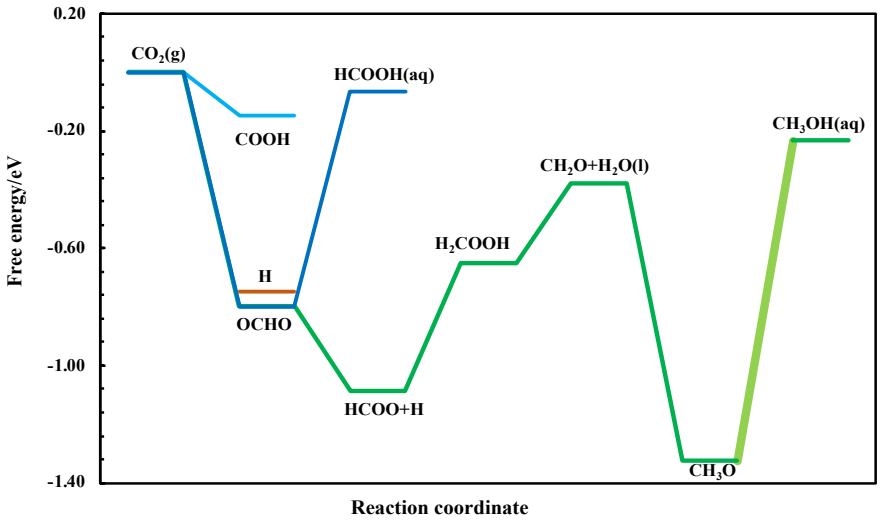


Figure S30. Free energy diagram for IrO_2 for 75% CO coverage with br-CUS-CUS CO configuration. Different reaction pathways for formic acid and methanol products are presented. Potential limiting step is presented for methanol with light green line.

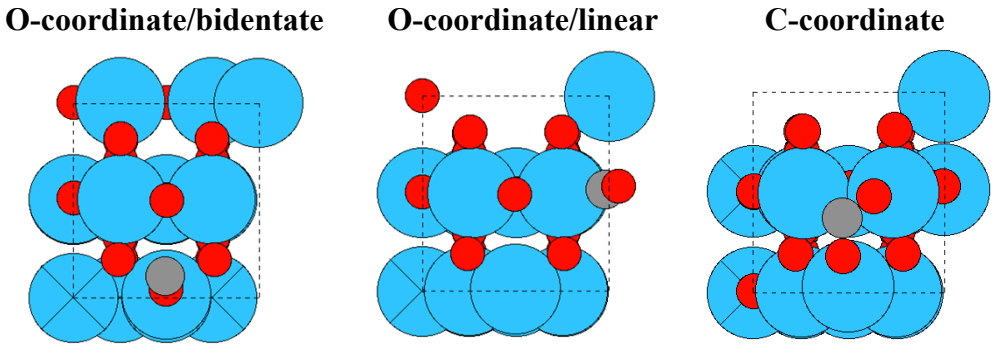


Figure S31. CO_2 adsorption on HfO_2 through a) O-coordinate and bidentate which is dissociated, b) O-coordinate and linear which is dissociated and c) C-coordinate which becomes flat on the surface.

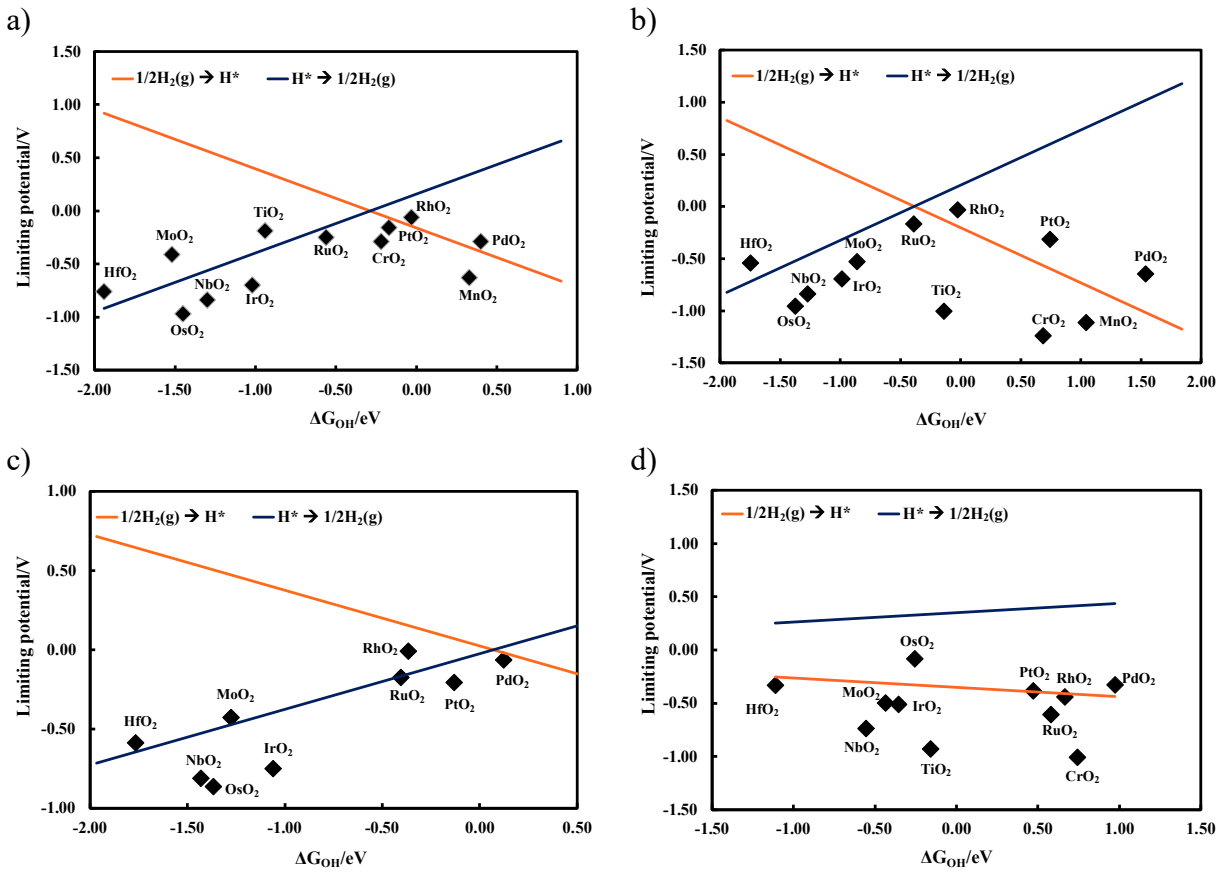


Figure S32. Theoretical volcanoes for HER for a) 25% CO coverage, b) 50% CO coverage and c) 75% CO coverage with br-CUS-CUS configuration and d) 75% CO coverage with br-br-CUS configuration. For each of the TMOs the explicit limiting potential values are included (diamond). Each line is for one electron-proton transfer step, indicated by different colors.

Spin polarization calculations and the relevant tags and values used in the current study in INCAR file for TMOs:

In order to perform spin polarized calculations, in the INCAR file the ISPIN tag should be 2 (ISPIN = 2) and a magnetic moment tag should be introduced as well (MAGMOM). The Magnetic moments are taken from the Materials Project INCAR files which is as follows.

HfO_2:

MAGMOM = 16*2 32*0.6
*16:Hf, 32:O

MoO_2:

MAGMOM = 16*0.6 32*0.6
*16:Mo, 32:O

OsO_2:

MAGMOM = 16*0 32*0.6
*16:Os, 32:O

NbO_2:

MAGMOM = 5 -5 5 -5 5 -5 5 -5 5 -5 5 -5 5 -5 5 -5 32*0.6
*5, -5:Nb, 32:O

TiO_2:

MAGMOM = 16*0.6 32*0.6
*16:Ti, 32:O

IrO_2:

MAGMOM = 16*5 32*0.6
*16:Ir, 32:O

RuO_2:

MAGMOM = 16*5 32*0.6
*16:Ru, 32:O

CrO_2:

MAGMOM = 16*0.6 32*0.6
*16:Cr, 32:O

PtO_2:

MAGMOM = 16*0.6 32*0.6
*16:Pt, 32:O

RhO_2:

MAGMOM = 16*0.6 32*0.6
*16:Rh, 32:O

MnO_2:

MAGMOM = 3 -3 3 -3 3 -3 3 -3 3 -3 3 -3 3 -3 3 -3 32*0.6
*3, -3:Mn, 32:O

PdO_2:

MAGMOM = 16*0.6 32*0.6
*16:Pd, 32:O