Supplementary Information (SI) for Journal of Materials Chemistry A.

Exploring reaction mechanisms for CO_2 reduction on Carbides

Supplementary Information (SI)

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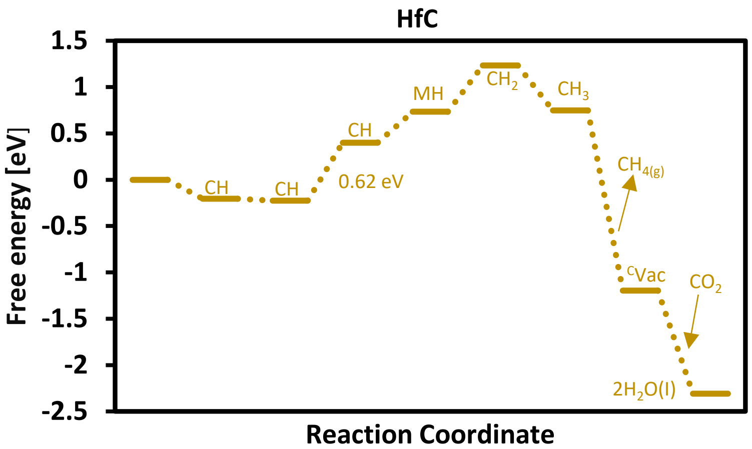
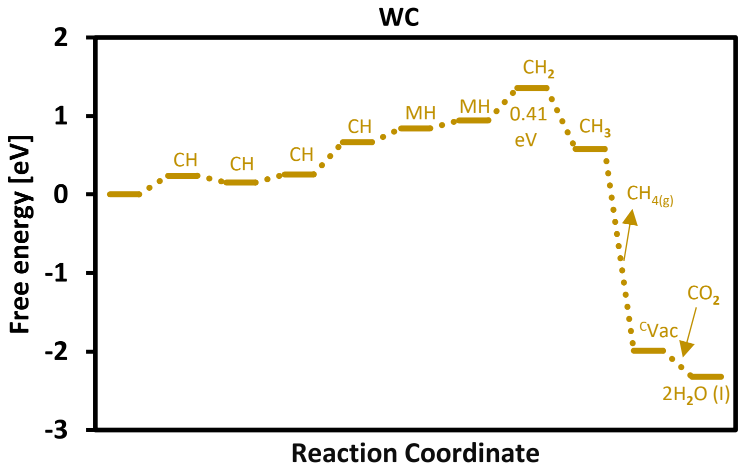
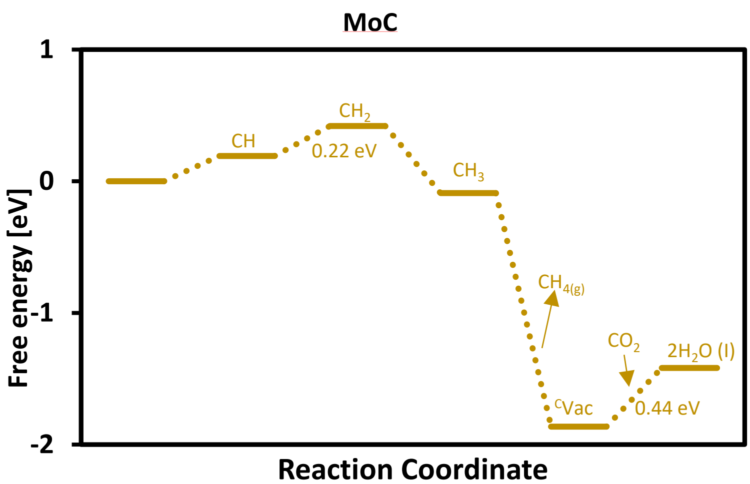
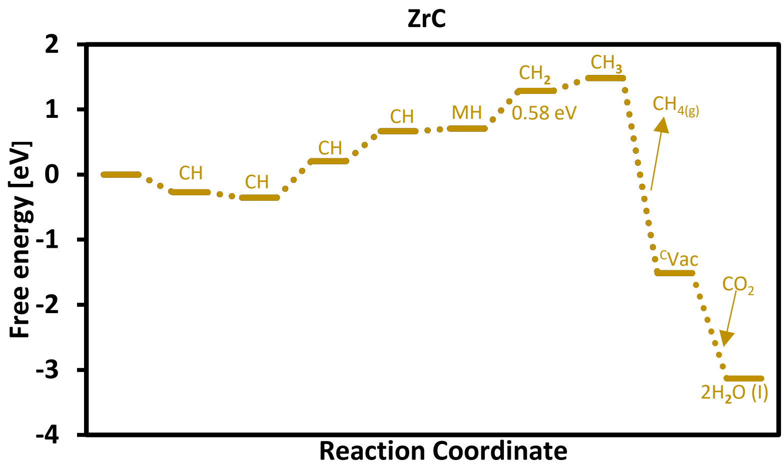
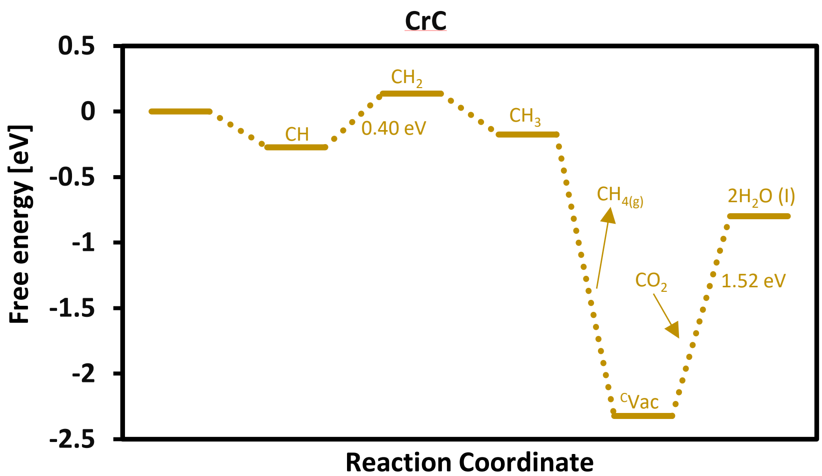
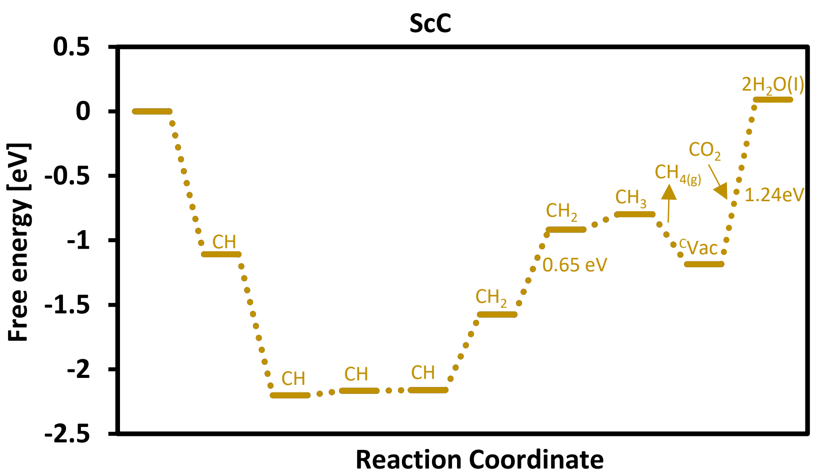


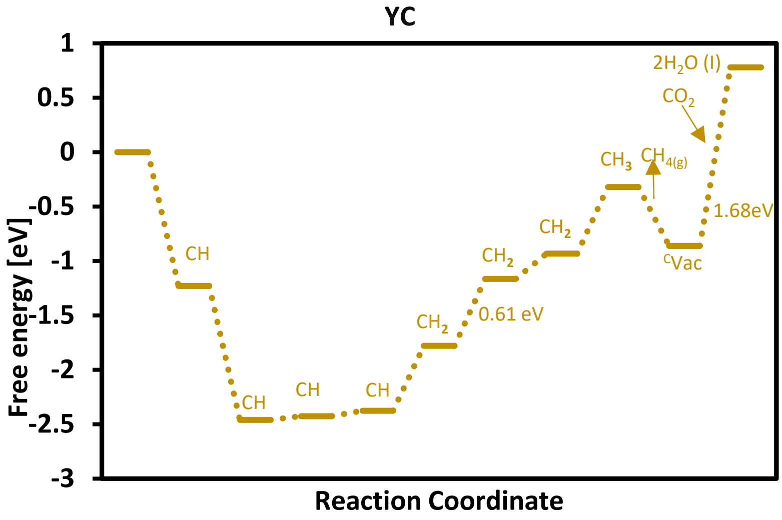


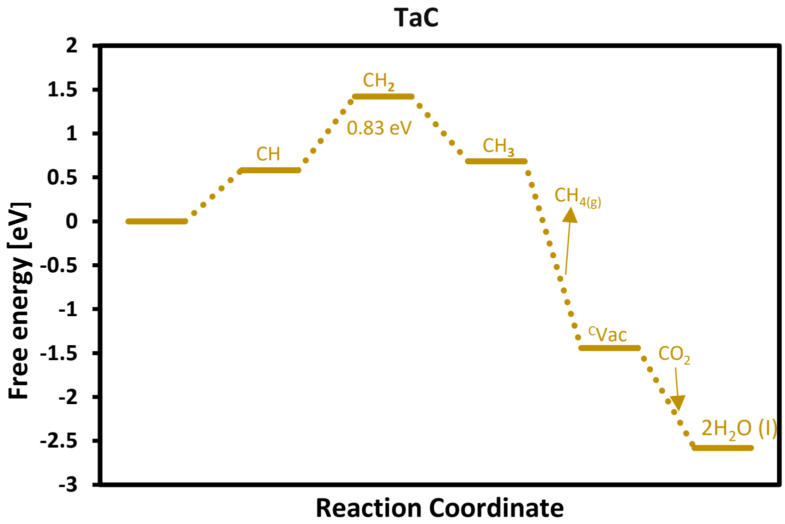


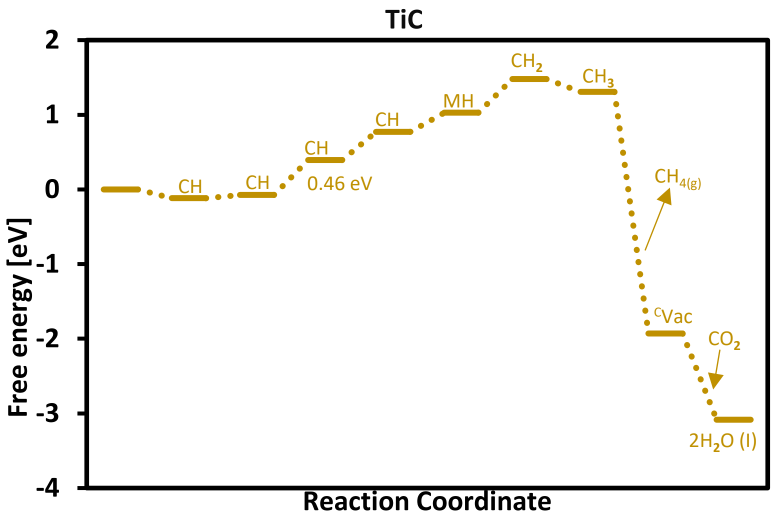

ZrC
Free energy [eV]
2
1
0
-1
-2
-3
-4
CH
CH
CH
CH
MH
CH$_2$
0.58 eV
CH$_3$
CH$_{4(g)}$
^{C}Vac
CO$_2$
2H$_2$O (l)
Reaction Coordinate


CrC
Free energy [eV]
0.5
0
-0.5
-1
-1.5
-2
-2.5
CH
CH$_2$
0.40 eV
CH$_3$
CH$_{4(g)}$
CO$_2$
^{C}Vac
2H$_2$O (l)
1.52 eV
Reaction Coordinate


ScC
Free energy [eV]
0.5
0
-0.5
-1
-1.5
-2
-2.5
CH
CH
CH
CH
CH$_2$
CH$_2$
0.65 eV
CH$_3$
CH$_{4(g)}$
CO$_2$
^{C}Vac
1.24eV
2H$_2$O(l)
Reaction Coordinate


YC
Free energy [eV]
1
0.5
0
-0.5
-1
-1.5
-2
-2.5
-3
Reaction Coordinate
CH
CH
CH
CH
CH$_2$
0.61 eV
CH$_2$
CH$_2$
CH$_3$
CH$_{4(g)}$
^{c}Vac
CO$_2$
2H$_2$O (l)
1.68eV


TaC
Free energy [eV]
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
-2.5
-3
Reaction Coordinate
CH
CH$_2$
0.83 eV
CH$_3$
CH$_{4(g)}$
^{c}Vac
CO$_2$
2H$_2$O (l)


TiC
Free energy [eV]
2
1
0
-1
-2
-3
-4
Reaction Coordinate
CH
CH
CH
0.46 eV
CH
MH
CH$_2$
CH$_3$
CH$_{4(g)}$
^{c}Vac
CO$_2$
2H$_2$O (l)

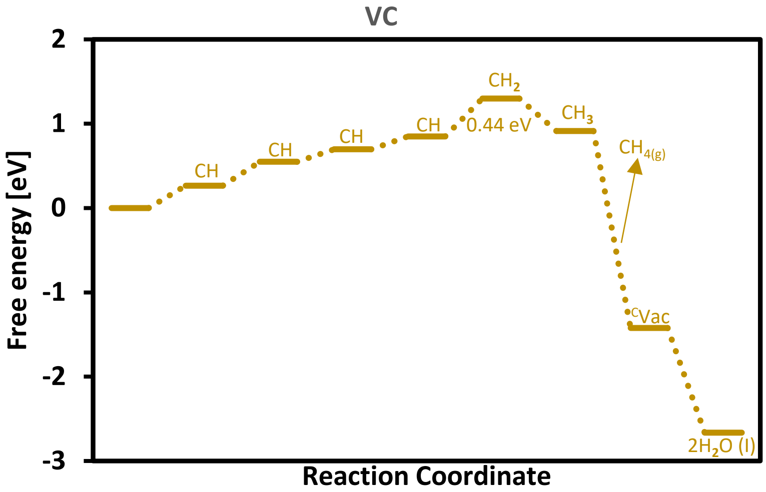
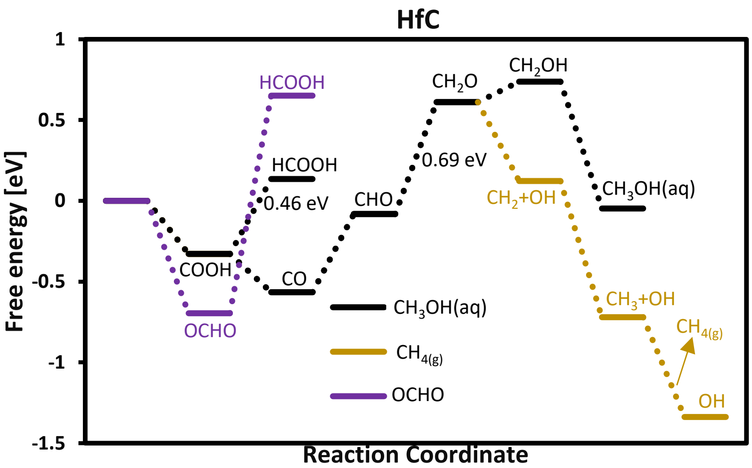
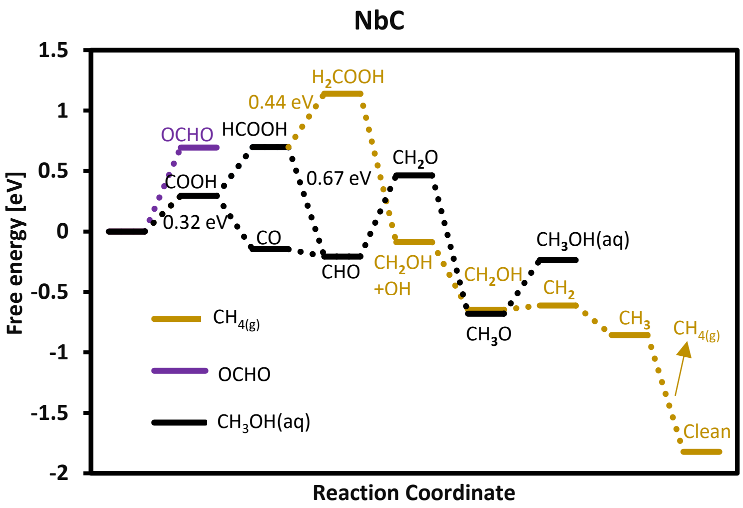
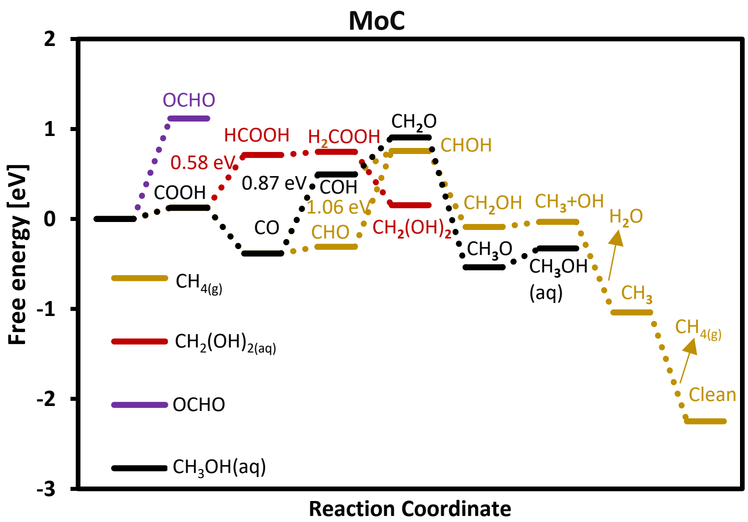
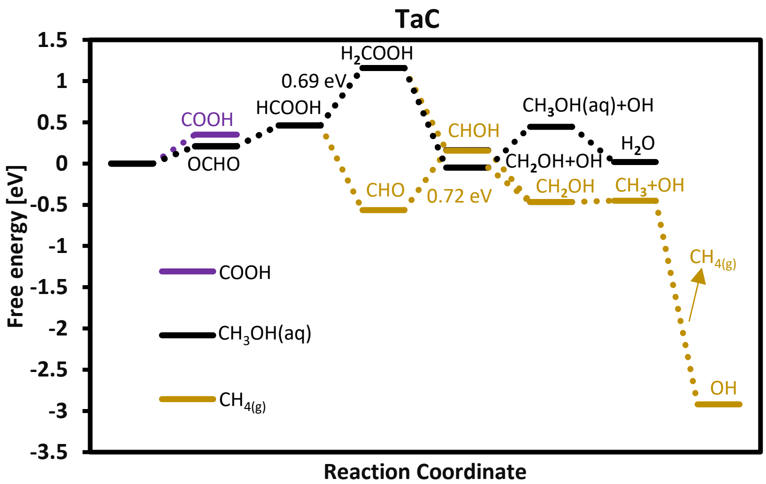


Fig S1: Methane formation free energy diagrams via the MvK mechanism




NbC
1.5
1
0.5
0
-0.5
-1
-1.5
-2
Free energy [eV]
Reaction Coordinate
H2COOH
0.44 eV
OCHO
HCOOH
COOH
0.32 eV
CO
0.67 eV
CHO
CH2O
CH2OH
+OH
CH2OH
CH3O
CH3OH(aq)
CH2
CH3
CH4(g)
Clean
CH4(g)
OCHO
CH3OH(aq)


MoC
2
1
0
-1
-2
-3
Free energy [eV]
Reaction Coordinate
OCHO
HCOOH
H2COOH
CH2O
CHOH
0.58 eV
0.87 eV
COH
COOH
1.06 eV
CO
CHO
CH2(OH)2
CH2OH
CH3+OH
H2O
CH3O
CH3OH
(aq)
CH3
CH4(g)
Clean
CH4(g)
CH2(OH)2(aq)
OCHO
CH3OH(aq)


TaC
1.5
1
0.5
0
-0.5
-1
-1.5
-2
-2.5
-3
-3.5
Free energy [eV]
Reaction Coordinate
H2COOH
0.69 eV
HCOOH
COOH
OCHO
CH3OH(aq)+OH
CHOH
H2O
CH2OH+OH
CHO
0.72 eV
CH2OH
CH3+OH
CH4(g)
OH
COOH
CH3OH(aq)
CH4(g)

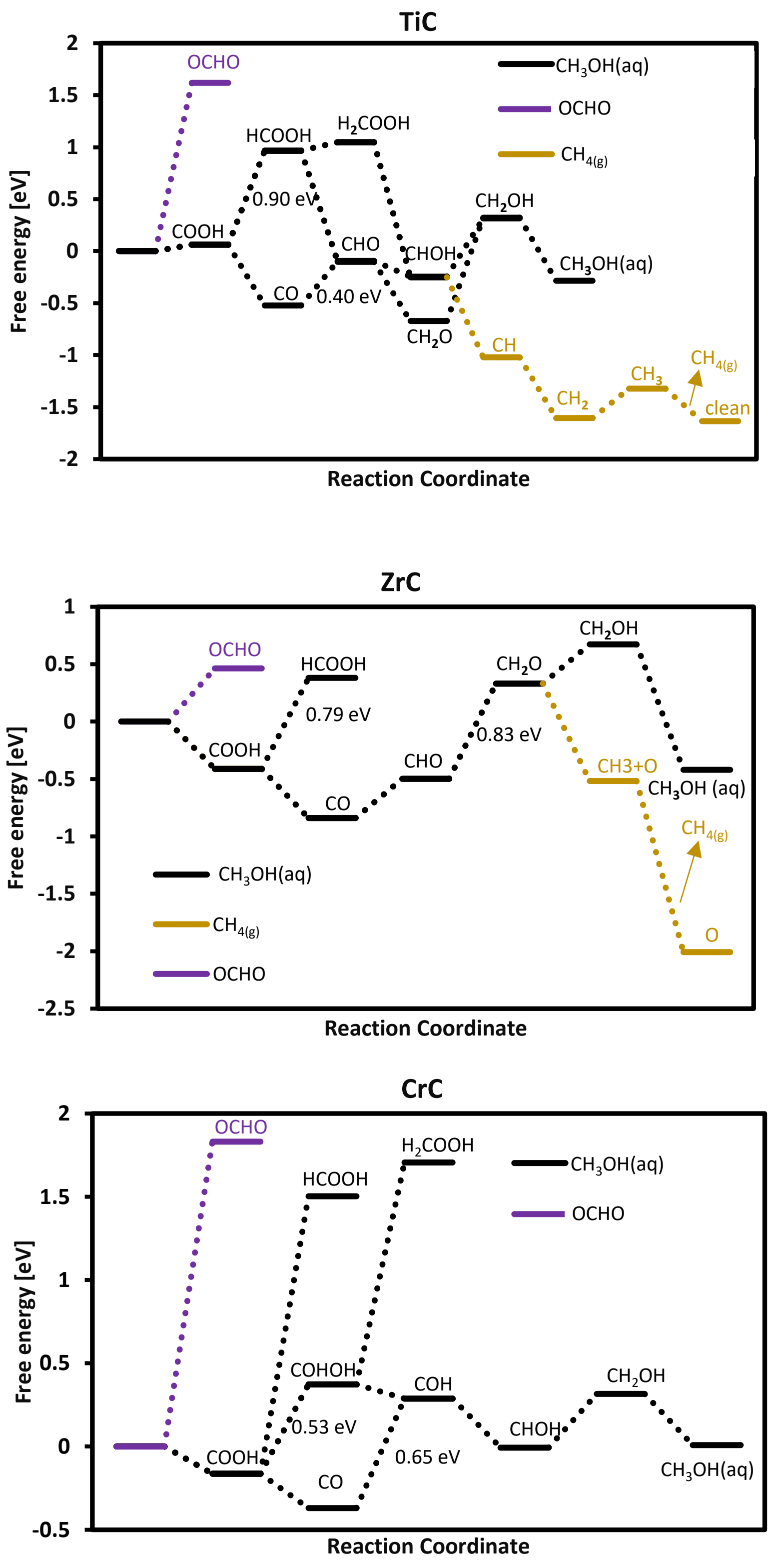


Fig S2: Formic acid, Methanol, methanediol and Methane formation free energy diagrams via the conventional mechanism.

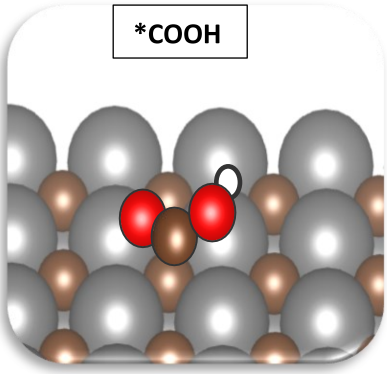


Fig S3: Schematic diagram of adsorption of COOH and OCHO on the carbon site. Red color indicates the Oxygen atoms, white hydrogen atoms, brown carbon atoms and gray indicates the metal atoms.

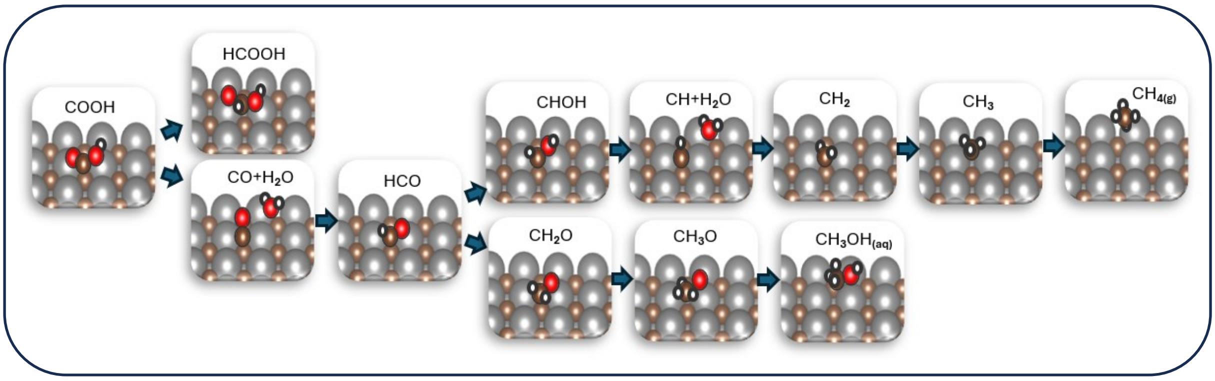


Fig S4: Configuration of formation of formic acid, methanol, and methane on WC catalyst. Silver, brown, red, and white colors indicate the metal, carbon, oxygen, and hydrogen atoms.

Table S1: Calculated each intermediate's Gibbs free energy ΔG (eV). The sign of (-) denotes that these intermediates are not formed on these catalysts.

	(ΔG)	(ΔG)	(ΔG)	(ΔG)	(ΔG)	(ΔG)	(ΔG)	(ΔG)	(ΔG)	(ΔG)	(ΔG)	(ΔG)	(ΔG)	(ΔG)	(ΔG)	(ΔG)	(ΔG)	(ΔG)	(ΔG)	(ΔG)
Catalyst	COOH	OCHO	CO	HOCOH	HCOOH	H_2COOH	$CH_2(OH)_2$	COH	CHO	CHOH	CH_2O	CH_2OH	CH_2OH+ OH	CH_2OH+ H_2O	CH_3+OH	CH_3+ H_2O	CH_3O	CH_3OH	CH	MH
CrC	-0.16	1.83	-0.21	0.54	1.67	1.17	-	0.28	0.28	0.24	0.37	0.07	-	0.07	-	-	-0.61	-0.06	-0.27	0.66
HfC	-0.32	-0.69	-0.24	1.51	0.46	-0.28	-	0.91	0.16	0.89	0.46	0.28	-	-	-0.39	-0.95		-0.33	-0.20	1.60
MoC	0.12	1.11	-0.51	0.88	0.59	0.16	-0.01	1.00	0.20	-0.25	-0.10	0.16	-	-	-0.19	-0.84	-0.44	0.11	0.05	0.75
ScC	-1.08		-1.55	0.86	1.21	0.48	-	1.83	0.92		-	-		-	-	-	-	-	-1.08	-
YC	-2.20	-	-1.43	1.08	unstable	0.47	-	1.33	1.33	-0.17	0.96	0.75		-	-	-	-	-	-1.19	-
NbC	0.30	0.69	-0.44	1.06	0.40	0.74	-	1.06	0.24	0.43	0.23	0.18	-0.83	0.18	-	-	-0.91	0.67	0.39	0.67
ZrC	-0.41	0.46	-0.43	1.53	0.79	-0.28	-0.30	0.59	-0.07	0.67	0.40	0.27		-	-	-	-0.30	-0.69	-0.27	-
TaC	0.21	0.35	-0.60	1.71	0.25	0.91	-	2.59	0.77	0.97	0.51	0.57	-0.96	0.49	-0.94	-	unstable	-0.51	0.58	0.37
TiC	0.06	1.62	-0.58	0.90	0.90	0.14	-	1.09	0.47	0.75	0.32	-0.01	-	-	-	-	cal..	-0.27	-0.11	-
WC	0.22	0.58	-0.08	0.97	0.31	0.83	-	0.68	-0.21	0.61	0.29	-0.04	-	-	-	-	-0.63	-0.43	-0.08	0.38
VC	0.60	-0.16	-0.83	1.08	-0.06	-0.11	-	1.15	0.43	0.14	0.25	0.04	-	-	-	-	-0.56	0.18	0.26	0.90