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

Supporting Information:

DFT insights into Electrocatalytic CO_2 Reduction to Methanol on $\alpha-Fe_2O_3$(0001) Surface

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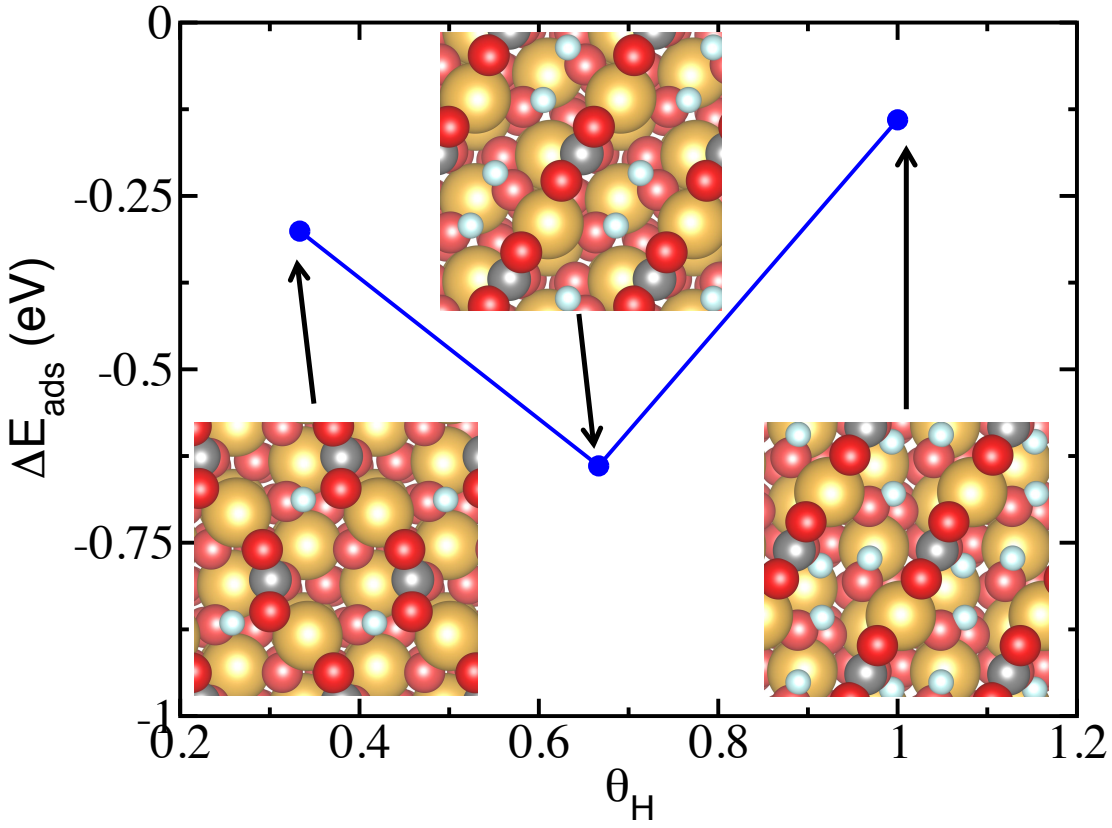


Figure S1: Adsorption energy of CO_2 for various surface H coverages. Top view of the geometries are also given. Fe, O, C and H atoms are respectively represented by orange, red, grey and cyan colour balls. For clear visualisation the surface atoms are represented with reduced brightness.

Table S1: Distinct reaction steps and their reaction energies (ΔE) at U = 0 V.

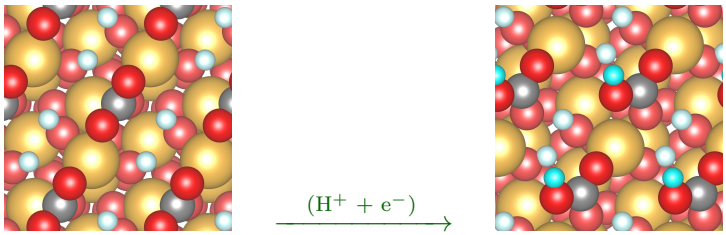
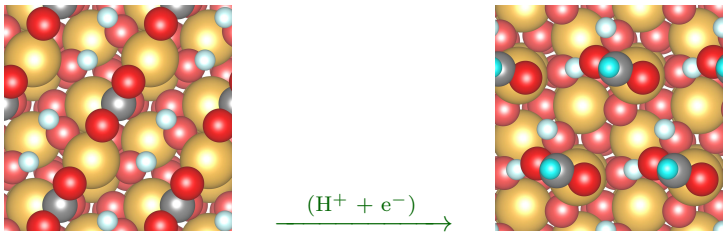
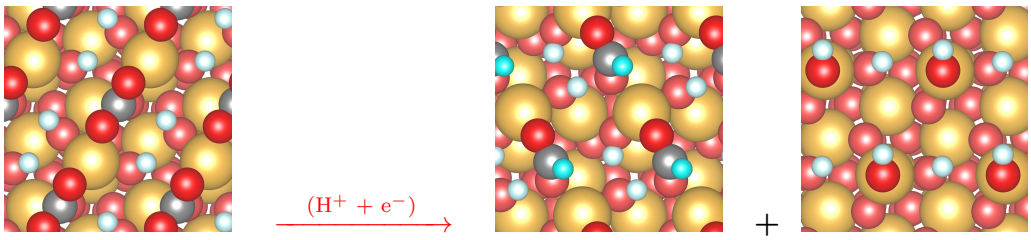
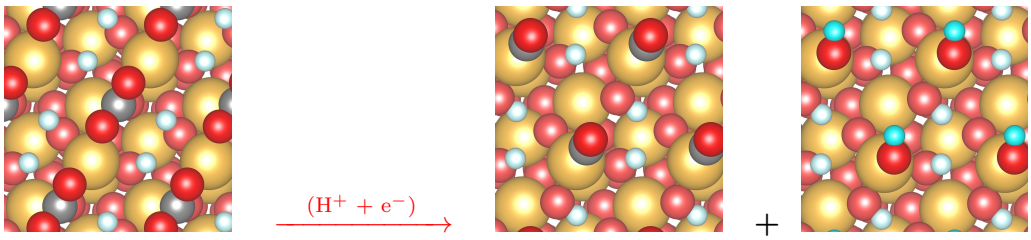
Index	**Reaction step**	ΔE **(eV)**
1	 *CO_2 → *COOH	-0.76
2	 *CO_2 → *HCOO	0.18
3	 *CO_2 → *CHO + *O	-0.18
4	 *CO_2 → *CO + *OH	1.20

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Table S1 – *Continued from previous page*

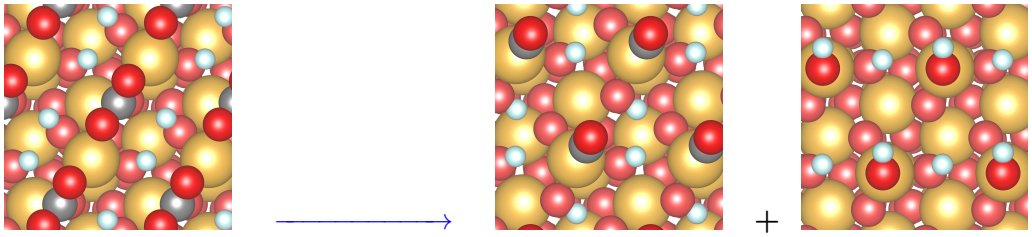
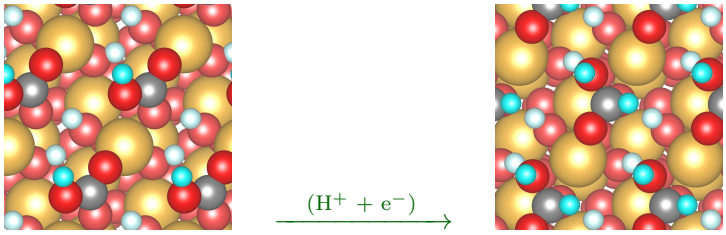
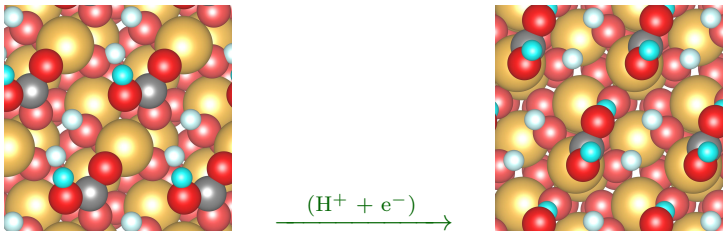
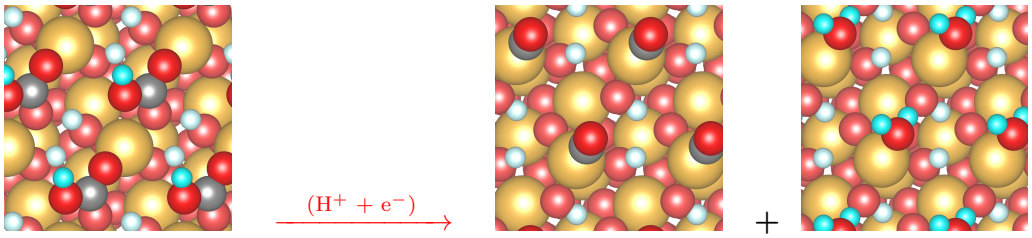
Index	Reaction step	ΔE (eV)
5	 $*CO_2$ $\longrightarrow$ $*CO$ + $*O$	1.73
6	 $*COOH$ $\xrightarrow{(H^+ + e^-)}$ $*HCOOH$	0.95
7	 $*COOH$ $\xrightarrow{(H^+ + e^-)}$ $*COHOH$	1.22
8	 $*COOH$ $\xrightarrow{(H^+ + e^-)}$ $*CO$ + $*H_2O$	1.05

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Table S1 – *Continued from previous page*

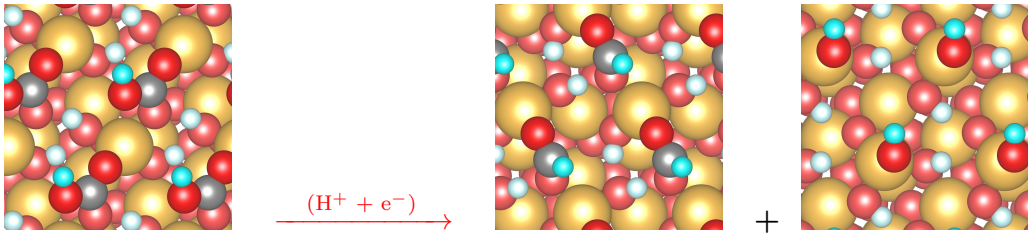
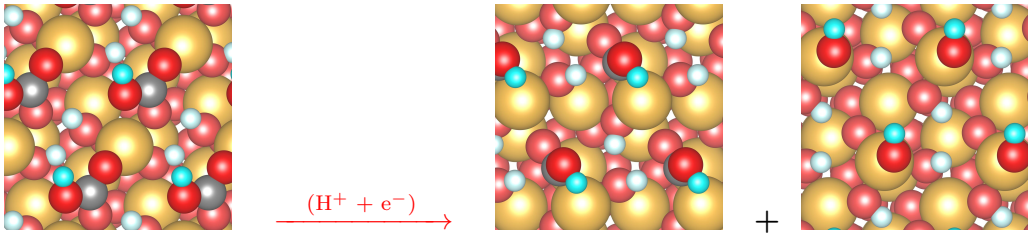
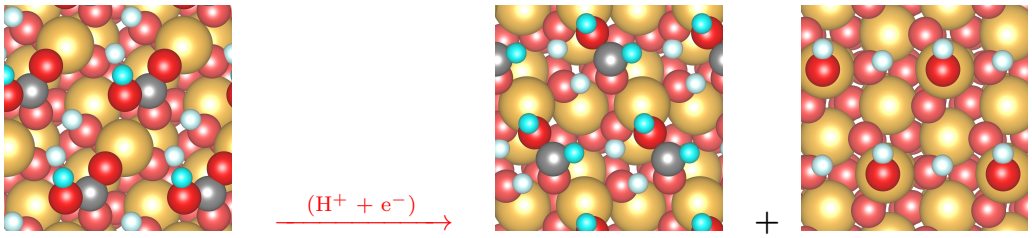
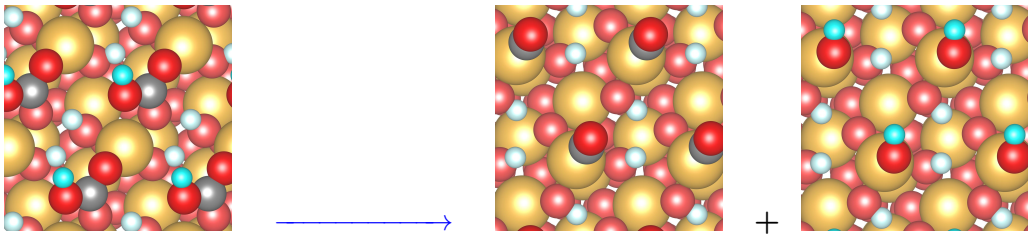
Index	Reaction step	ΔE (eV)
9	 *COOH → *CHO + *OH	0.04
10	 *COOH → *COH + *OH	1.52
11	 *COOH → *HCOH + *O	2.36
12	 *COOH → *CO + *OH	1.96

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Table S1 – *Continued from previous page*

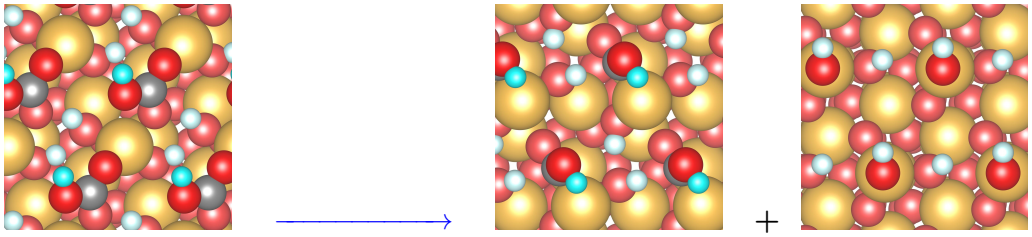
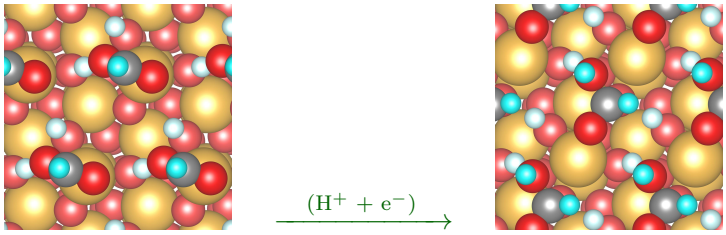
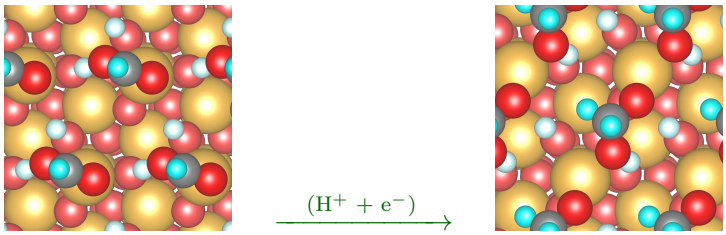
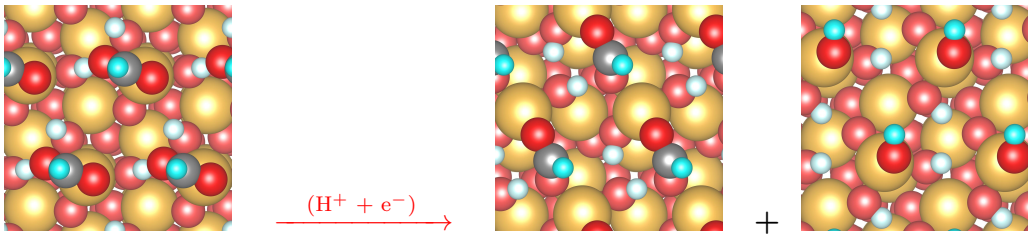
Index	Reaction step	ΔE (eV)
13	 *COOH → *COH + *O	2.06
14	 *HCOO → *HCOOH	0.01
15	 *HCOO → *OCH_2O	1.01
16	 *HCOO → *CHO + *OH	-0.90

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Table S1 – *Continued from previous page*

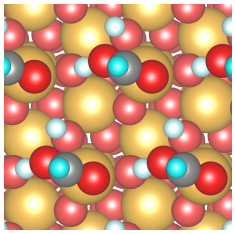
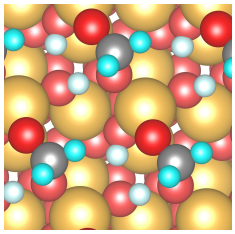
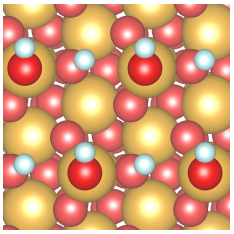
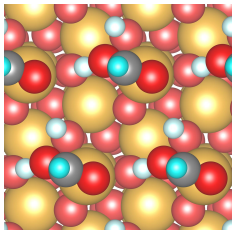
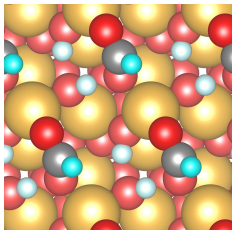
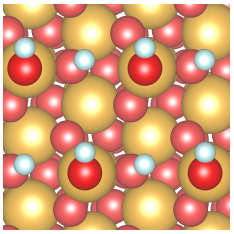
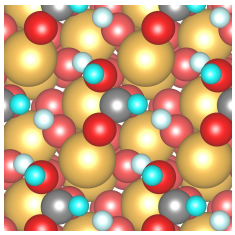
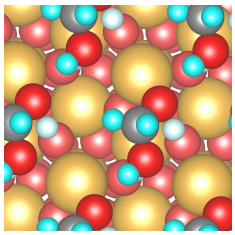
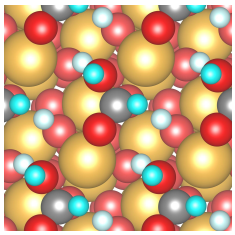
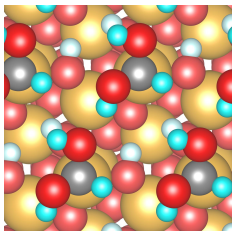
Index	Reaction step	ΔE (eV)
17	 $\xrightarrow{(H^+ + e^-)}$  +  *HCOO → *CH_2O + *O	0.45
18	 $\longrightarrow$  +  *HCOO → *CHO + *O	-0.36
19	 $\xrightarrow{(H^+ + e^-)}$  *HCOOH → *OCH_2OH	-0.13
20	 $\xrightarrow{(H^+ + e^-)}$  *HCOOH → *HCOHOH	1.05

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Table S1 – *Continued from previous page*

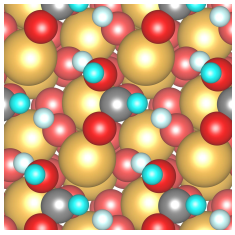
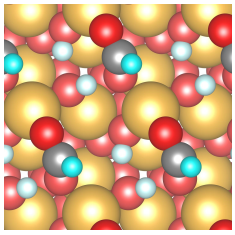
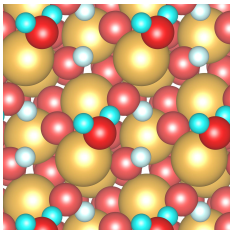
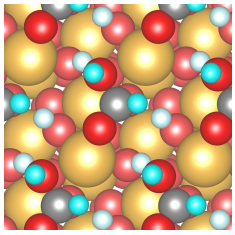
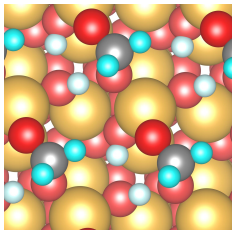
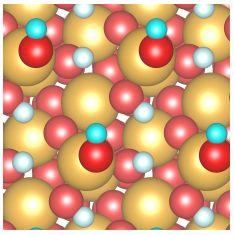
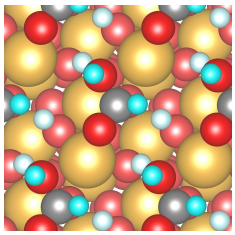
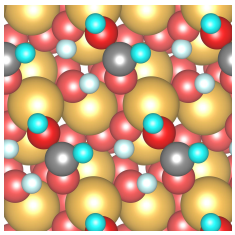
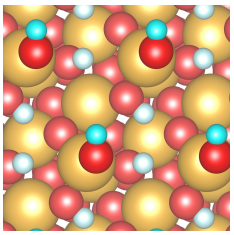
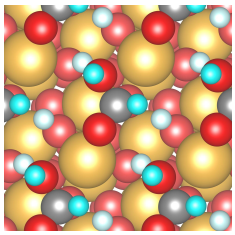
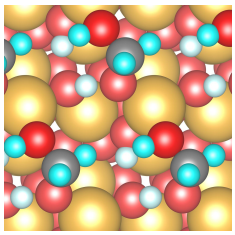
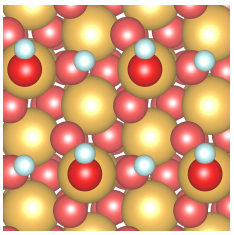
Index	Reaction step	ΔE (eV)
21	 *HCOOH $\xrightarrow{(H^+ + e^-)}$  *CHO +  *H_2O	-1.82
22	 *HCOOH $\xrightarrow{(H^+ + e^-)}$  *CH_2O +  *OH	-0.09
23	 *HCOOH $\xrightarrow{(H^+ + e^-)}$  *HCOH +  *OH	0.87
24	 *HCOOH $\xrightarrow{(H^+ + e^-)}$  *CH_2OH +  *O	-0.16

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Table S1 – *Continued from previous page*

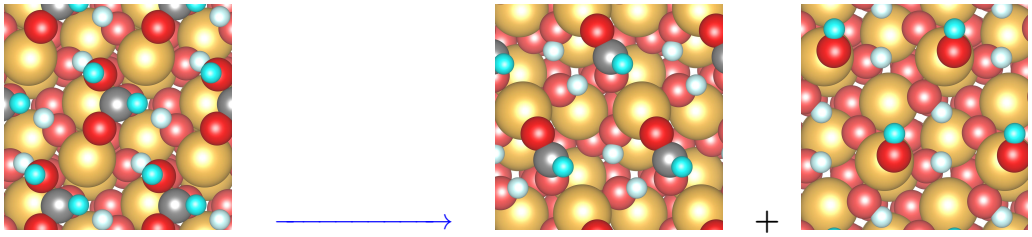
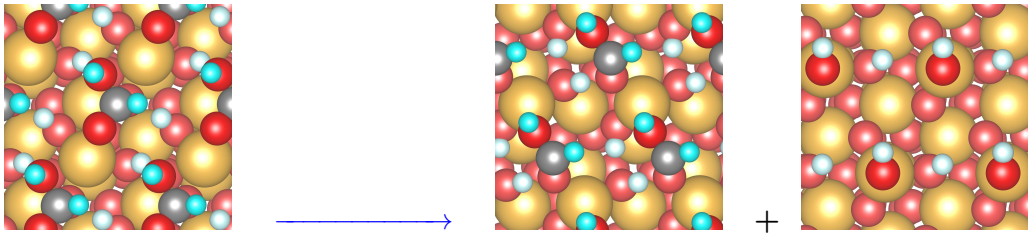
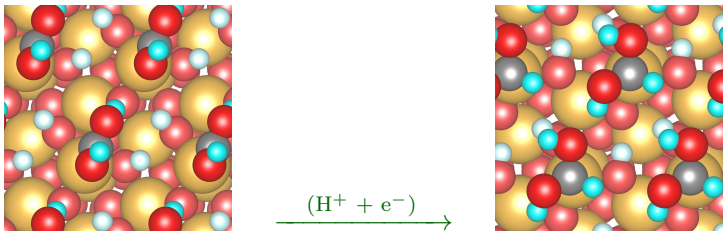
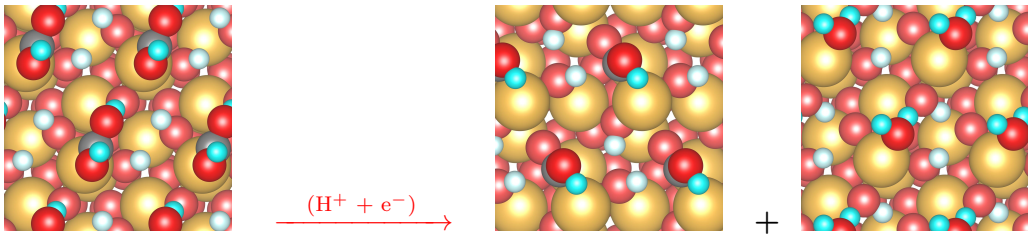
Index	Reaction step	ΔE (eV)
25	 *HCOOH → *CHO + *OH	-0.91
26	 *HCOOH → *HCOH + *O	1.41
27	 *COHOH $\xrightarrow{(H^+ + e^-)}$ *HCOHOH	0.78
28	 *COHOH $\xrightarrow{(H^+ + e^-)}$ *COH + *H_2O	-0.61

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Table S1 – *Continued from previous page*

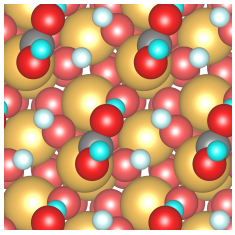
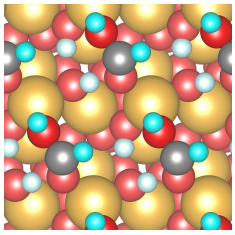
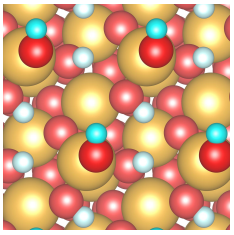
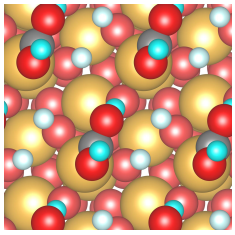
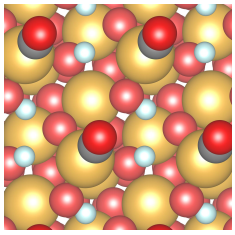
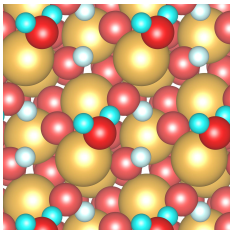
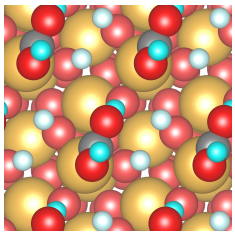
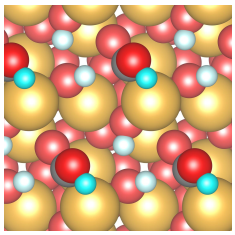
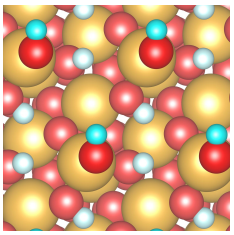
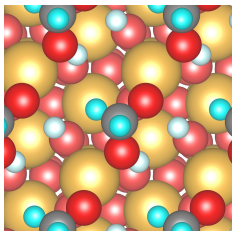
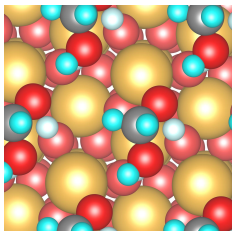
Index	Reaction step	ΔE (eV)
29	 *COHOH $\xrightarrow{(H^+ + e^-)}$  *HCOH +  *OH	0.60
30	 *COHOH $\longrightarrow$  *CO +  *H_2O	-0.17
31	 *COHOH $\longrightarrow$  *COH +  *OH	0.30
32	 *OCH_2O $\xrightarrow{(H^+ + e^-)}$  *OCH_2OH	-1.14

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Table S1 – *Continued from previous page*

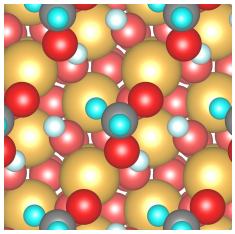
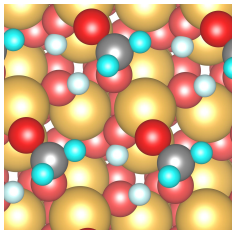
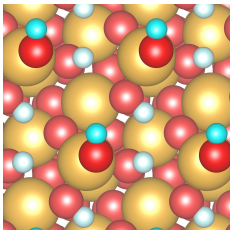
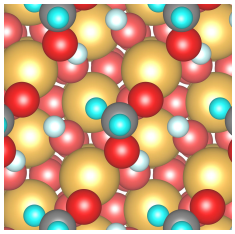
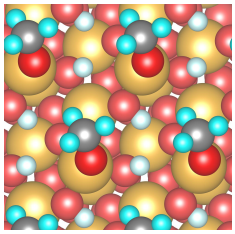
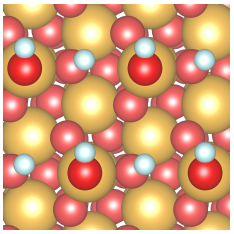
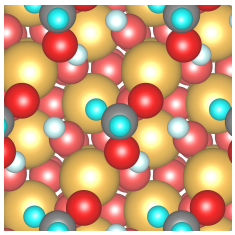
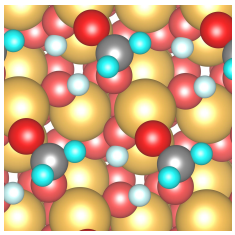
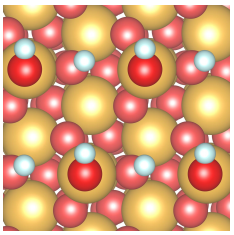
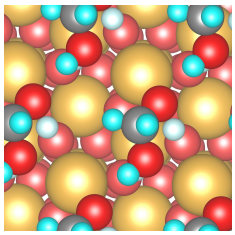
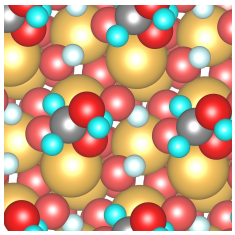
Index	Reaction step	ΔE (eV)
33	 $\xrightarrow{(H^+ + e^-)}$  +  $*OCH_2O$ $*CH_2O$ $*OH$	-1.10
34	 $\xrightarrow{(H^+ + e^-)}$  +  $*OCH_2O$ $*CH_3O$ $*O$	-0.72
35	 $\longrightarrow$  +  $*OCH_2O$ $*CH_2O$ $*O$	-0.56
36	 $\xrightarrow{(H^+ + e^-)}$  $*OCH_2OH$ $*HOCH_2OH$	-0.59

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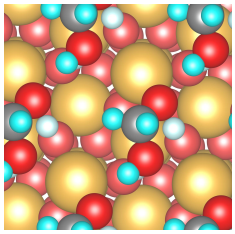
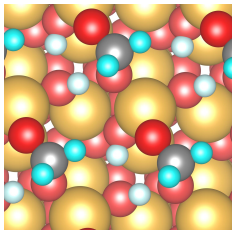
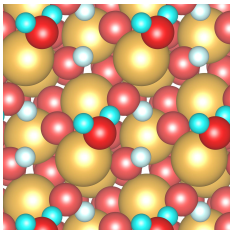
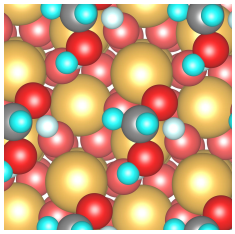
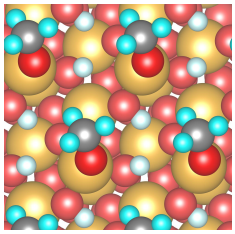
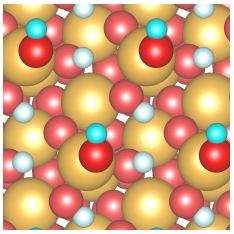
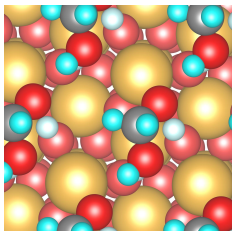
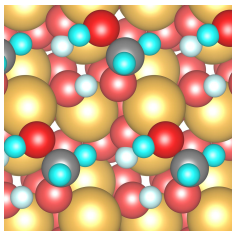
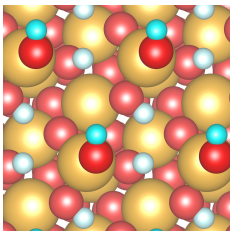
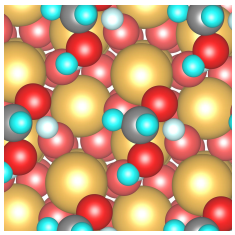
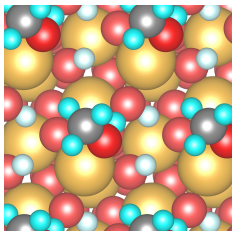
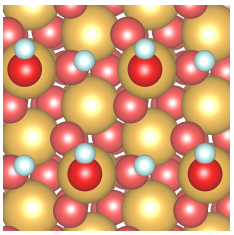
Table S1 – *Continued from previous page*

Index	Reaction step						ΔE (eV)
37		$\xrightarrow{(H^+ + e^-)}$		+			-0.87
	*OCH_2OH		*CH_2O		*H_2O		
38		$\xrightarrow{(H^+ + e^-)}$		+			-0.12
	*OCH_2OH		*CH_3O		*OH		
39		$\xrightarrow{(H^+ + e^-)}$		+			-0.56
	*OCH_2OH		*CH_2OH		*OH		
40		$\xrightarrow{(H^+ + e^-)}$		+			-0.46
	*OCH_2OH		*CH_3OH		*O		

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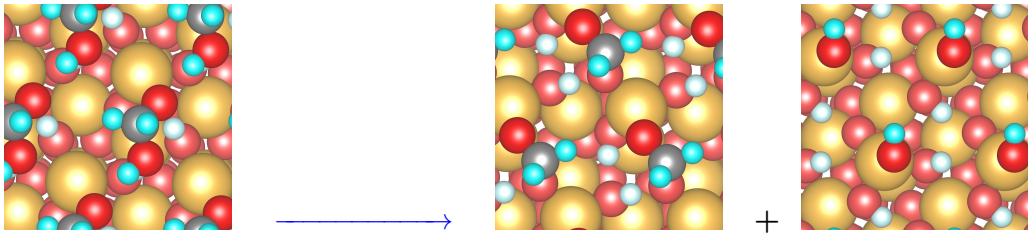
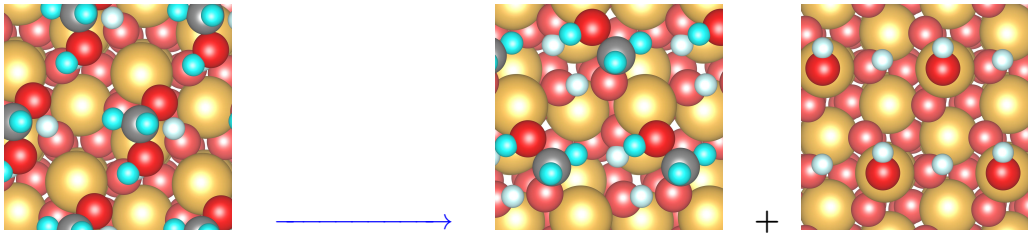
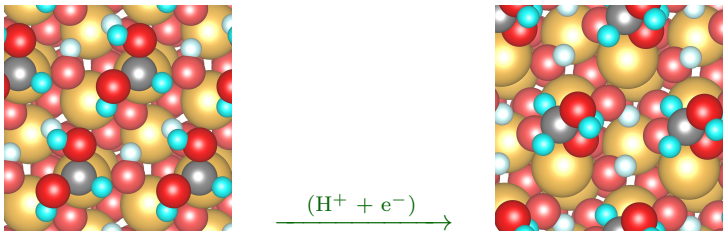
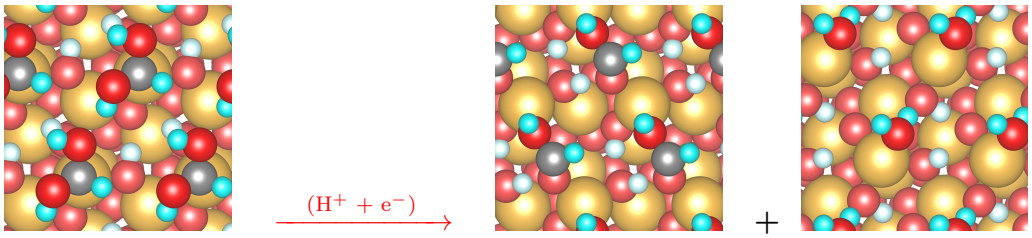
Index	Reaction step	ΔE (eV)
41	 *OCH_2OH → *CH_2O + *OH	0.04
42	 *OCH_2OH → *CH_2OH + *O	-0.03
43	 *HCOHOH $\xrightarrow{(H^+ + e^-)}$ *$HOCH_2OH$	-1.78
44	 *HCOHOH $\xrightarrow{(H^+ + e^-)}$ *HCOH + *H_2O	-1.09

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Table S1 – *Continued from previous page*

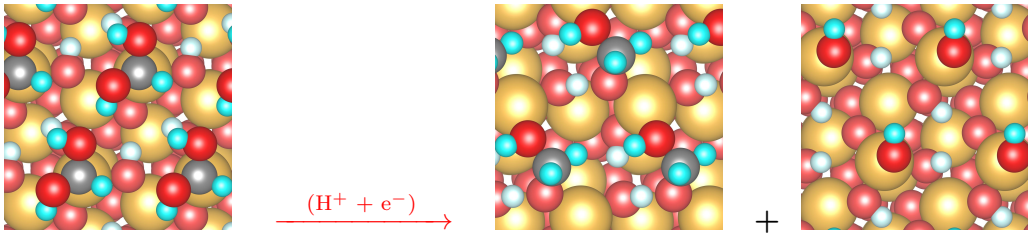
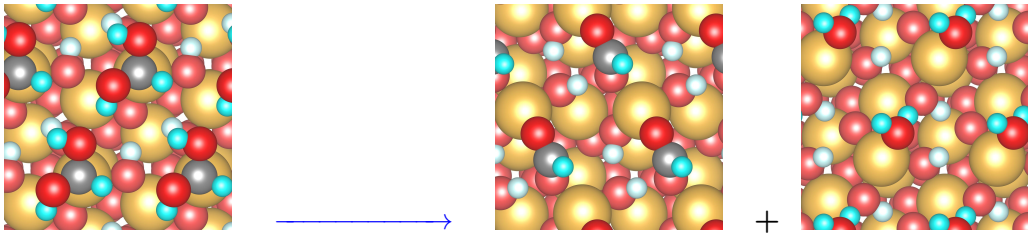
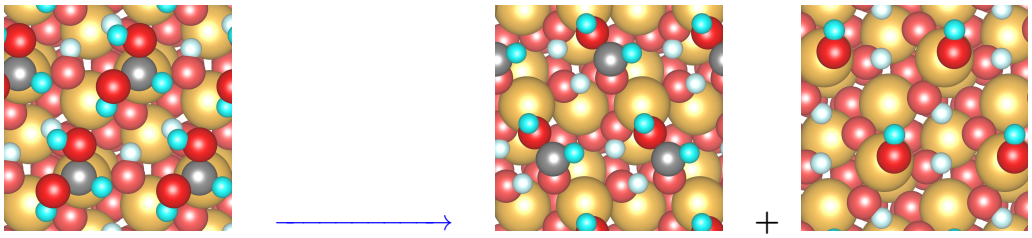
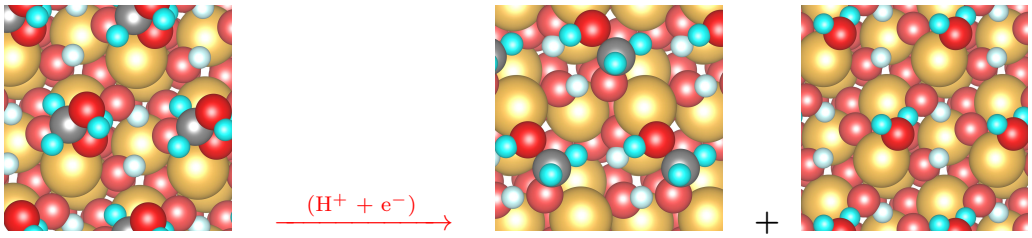
Index	Reaction step	ΔE (eV)
45	 *HCOHOH → *CH_2OH + *OH	-1.09
46	 *HCOHOH → *CHO + *H_2O	-2.86
47	 *HCOHOH → *HCOH + *OH	-0.18
48	 *$HOCH_2OH$ → *CH_2OH + *H_2O	-0.88

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Table S1 – *Continued from previous page*

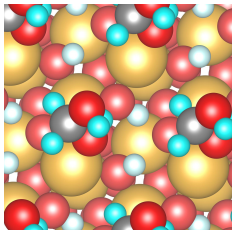
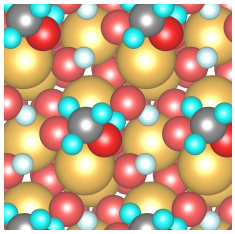
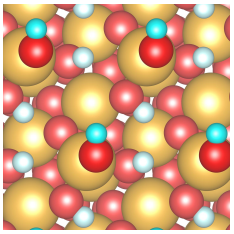
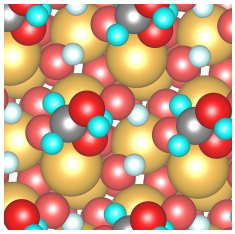
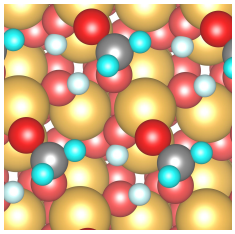
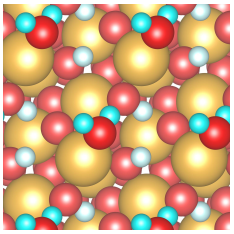
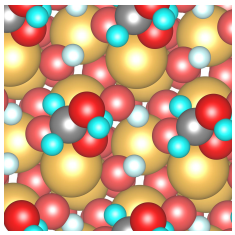
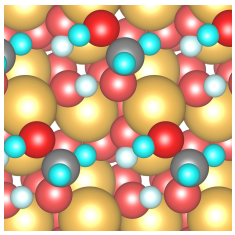
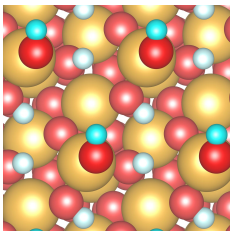
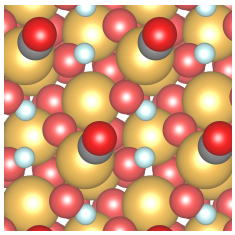
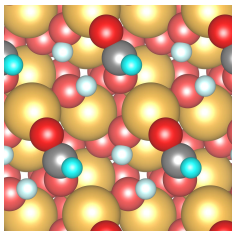
Index	Reaction step	ΔE (eV)
49	 $\xrightarrow{(H^+ + e^-)}$  +  *$HOCH_2OH$ *CH_3OH *OH	-0.40
50	 $\longrightarrow$  +  *$HOCH_2OH$ *CH_2O *H_2O	-0.28
51	 $\longrightarrow$  +  *$HOCH_2OH$ *CH_2OH *OH	0.03
52	 $\xrightarrow{(H^+ + e^-)}$  *CO *CHO	-1.91

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Table S1 – *Continued from previous page*

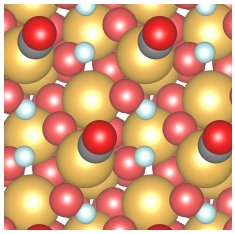
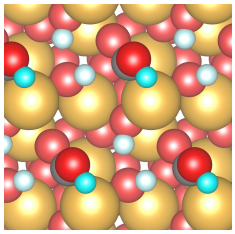
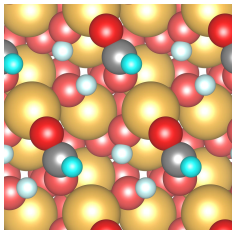
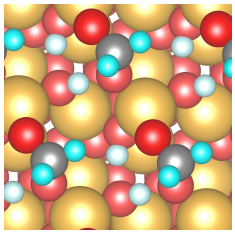
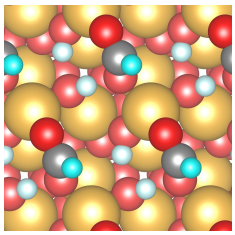
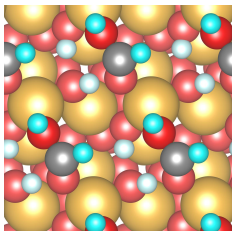
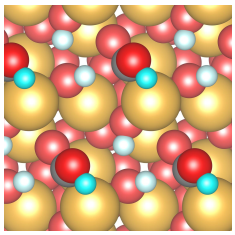
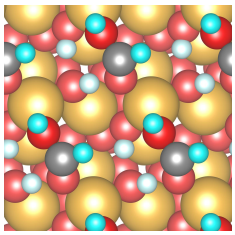
Index	Reaction step	ΔE (eV)
53	 $\xrightarrow{(H^+ + e^-)}$  *CO → *COH	-0.44
54	 $\xrightarrow{(H^+ + e^-)}$  *CHO → *CH_2O	0.81
55	 $\xrightarrow{(H^+ + e^-)}$  *CHO → *HCOH	1.78
56	 $\xrightarrow{(H^+ + e^-)}$  *COH → *HCOH	0.30

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Table S1 – *Continued from previous page*

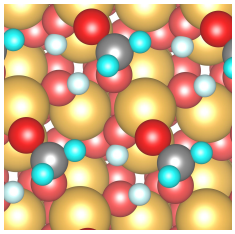
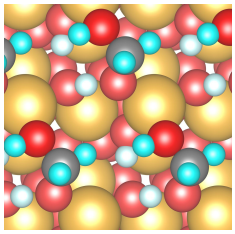
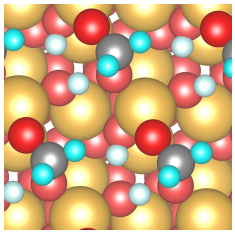
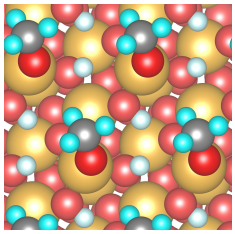
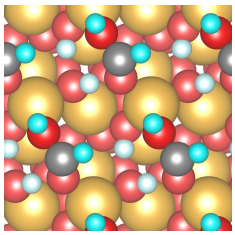
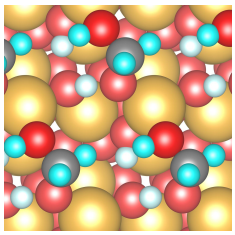
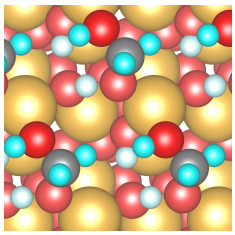
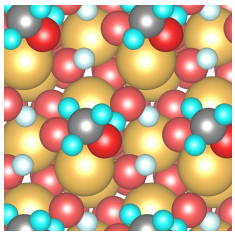
Index	Reaction step	ΔE (eV)
57	 $\xrightarrow{(H^+ + e^-)}$  *CH_2O → *CH_2OH	-0.60
58	 $\xrightarrow{(H^+ + e^-)}$  *CH_2O → *CH_3O	-0.17
59	 $\xrightarrow{(H^+ + e^-)}$  *HCOH → *CH_2OH	-1.57
60	 $\xrightarrow{(H^+ + e^-)}$  *CH_2OH → *CH_3OH	-0.43

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Table S1 – *Continued from previous page*

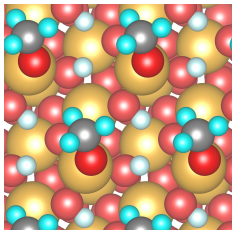
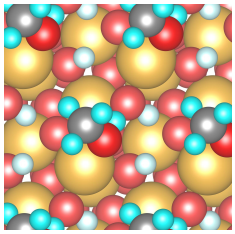
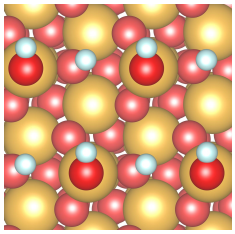
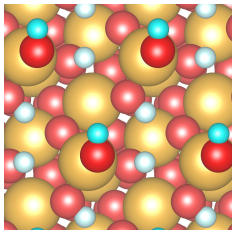
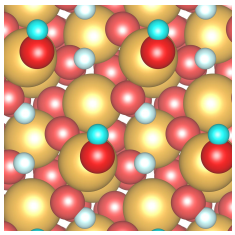
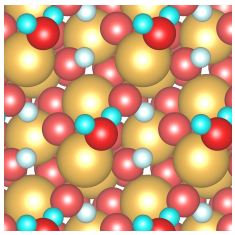
Index	Reaction step	ΔE (eV)
61	 $\xrightarrow{(H^+ + e^-)}$  *CH_3O *CH_3OH	-0.87
62	 $\xrightarrow{(H^+ + e^-)}$  *O *OH	-0.54
63	 $\xrightarrow{(H^+ + e^-)}$  *OH *H_2O	-0.91

Table S2: All the possible reaction paths for the formation of CH_2O through electrocatalytic reduction of CO_2 on hematite surface and minimum potential (U_{min}) required to make all the reaction steps downhill process. The potential determining step is given bold font.

Index	Reaction path	Path name	U_{min} (V)
1	$*CO_2 \xrightarrow{+(H^+ + e^-)} \mathbf{*COOH} \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOOH} \xrightarrow{+(H^+ + e^-)} *OCH_2OH \xrightarrow{+(H^+ + e^-)} *HOCH_2OH \xrightarrow[-*H_2O]{} *CH_2O$	$O_1C_2O_1A^1$	-0.95
2	$*CO_2 \xrightarrow{+(H^+ + e^-)} \mathbf{*COOH} \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOOH} \xrightarrow{+(H^+ + e^-)} *OCH_2OH \xrightarrow[-*H_2O]{+(H^+ + e^-)} *CH_2O$	$O_1C_2O_1A^3$	-0.95
3	$*CO_2 \xrightarrow{+(H^+ + e^-)} *COOH \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOOH} \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOHOH} \xrightarrow{+(H^+ + e^-)} *HOCH_2OH \xrightarrow[-*H_2O]{} *CH_2O$	$O_1C_1O_1C_1A^1$	-1.05
4	$*CO_2 \xrightarrow{+(H^+ + e^-)} *COOH \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOOH} \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOHOH} \xrightarrow[-*H_2O]{} *CHO \xrightarrow{+(H^+ + e^-)} *CH_2O$	$O_1C_1O_1A^1_{C_1}$	-1.05
5	$*CO_2 \xrightarrow{+(H^+ + e^-)} \mathbf{*COOH} \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOOH} \xrightarrow[-*H_2O]{+(H^+ + e^-)} *CHO \xrightarrow{+(H^+ + e^-)} *CH_2O$	$O_1C_1O_1A^3_{C_1}$	-0.95
6	$*CO_2 \xrightarrow{+(H^+ + e^-)} \mathbf{*COOH} \xrightarrow{+(H^+ + e^-)} \mathbf{*COHOH} \xrightarrow{+(H^+ + e^-)} *HCOHOH \xrightarrow{+(H^+ + e^-)} *HOCH_2OH \xrightarrow[-*H_2O]{} *CH_2O$	$O_2C_2A^1$	-1.22
7	$*CO_2 \xrightarrow{+(H^+ + e^-)} \mathbf{*COOH} \xrightarrow{+(H^+ + e^-)} \mathbf{*COHOH} \xrightarrow{+(H^+ + e^-)} *HCOHOH \xrightarrow[-*H_2O]{} *CHO \xrightarrow{+(H^+ + e^-)} *CH_2O$	$O_2C_1A^1_{C_1}$	-1.22
8	$*CO_2 \xrightarrow{+(H^+ + e^-)} \mathbf{*COOH} \xrightarrow{+(H^+ + e^-)} \mathbf{*COHOH} \xrightarrow[-*H_2O]{} *CO \xrightarrow{+(H^+ + e^-)} *CHO \xrightarrow{+(H^+ + e^-)} *CH_2O$	$O_2A^1_{C_2}$	-1.22
9	$*CO_2 \xrightarrow{+(H^+ + e^-)} \mathbf{*COOH} \xrightarrow[-*H_2O]{+(H^+ + e^-)} \mathbf{*CO} \xrightarrow{+(H^+ + e^-)} *CHO \xrightarrow{+(H^+ + e^-)} *CH_2O$	$O_2A^3_{C_2}$	-1.05
10	$\mathbf{*CO_2} \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOO} \xrightarrow{+(H^+ + e^-)} *HCOOH \xrightarrow{+(H^+ + e^-)} *OCH_2OH \xrightarrow{+(H^+ + e^-)} *HOCH_2OH \xrightarrow[-*H_2O]{} *CH_2O$	$C_1O_1C_1O_1A^1$	-0.18
11	$\mathbf{*CO_2} \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOO} \xrightarrow{+(H^+ + e^-)} *HCOOH \xrightarrow{+(H^+ + e^-)} *OCH_2OH \xrightarrow[-*H_2O]{+(H^+ + e^-)} *CH_2O$	$C_1O_1C_1O_1A^3$	-0.18
12	$*CO_2 \xrightarrow{+(H^+ + e^-)} *HCOO \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOOH} \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOHOH} \xrightarrow{+(H^+ + e^-)} *HOCH_2OH \xrightarrow[-*H_2O]{} *CH_2O$	$C_1O_2C_1A^1$	-1.05
13	$*CO_2 \xrightarrow{+(H^+ + e^-)} *HCOO \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOOH} \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOHOH} \xrightarrow[-*H_2O]{} *CHO \xrightarrow{+(H^+ + e^-)} *CH_2O$	$C_1O_2A^1_{C_1}$	-1.05
14	$*CO_2 \xrightarrow{+(H^+ + e^-)} *HCOO \xrightarrow{+(H^+ + e^-)} *HCOOH \xrightarrow[-*H_2O]{+(H^+ + e^-)} \mathbf{*CHO} \xrightarrow{+(H^+ + e^-)} \mathbf{*CH_2O}$	$C_1O_2A^3_{C_1}$	-0.81
15	$*CO_2 \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOO} \xrightarrow{+(H^+ + e^-)} \mathbf{*OCH_2O} \xrightarrow{+(H^+ + e^-)} *OCH_2OH \xrightarrow{+(H^+ + e^-)} *HOCH_2OH \xrightarrow[-*H_2O]{} *CH_2O$	$C_2O_2A^1$	-1.01

Continued on next page

Table S2 – *Continued from previous page*

Index	Reaction path	Path name	U_{min} (V)
16	$*CO_2 \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOO} \xrightarrow{+(H^+ + e^-)} \mathbf{*OCH_2CO} \xrightarrow{+(H^+ + e^-)} *OCH_2OH \xrightarrow[-*H_2O]{+(H^+ + e^-)} *CH_2O$	$C_2O_2A^3$	-1.01
17	$*CO_2 \xrightarrow{+(H^+ + e^-)} \mathbf{*COOH} \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOOH} \xrightarrow{+(H^+ + e^-)} *OCH_2OH \xrightarrow[-*OH]{} *CH_2O$	$O_1C_2B^1$	-0.95
18	$*CO_2 \xrightarrow{+(H^+ + e^-)} \mathbf{*COOH} \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOOH} \xrightarrow[-*OH]{+(H^+ + e^-)} *CH_2O$	$O_1C_2B^3$	-0.95
19	$*CO_2 \xrightarrow{+(H^+ + e^-)} \mathbf{*COOH} \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOOH} \xrightarrow[-*OH]{} *CHO \xrightarrow{+(H^+ + e^-)} *CH_2O$	$O_1C_1B^1_{C_1}$	-0.95
20	$*CO_2 \xrightarrow{+(H^+ + e^-)} *COOH \xrightarrow[-*OH]{+(H^+ + e^-)} \mathbf{*CHO} \xrightarrow{+(H^+ + e^-)} \mathbf{*CH_2O}$	$O_1C_1B^3_{C_1}$	-0.81
21	$*CO_2 \xrightarrow{+(H^+ + e^-)} \mathbf{*COOH} \xrightarrow[-*OH]{} \mathbf{*CO} \xrightarrow{+(H^+ + e^-)} *CHO \xrightarrow{+(H^+ + e^-)} *CH_2O$	$O_1B^1_{C_2}$	-1.96
22	$\mathbf{*CO_2} \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOO} \xrightarrow{+(H^+ + e^-)} *HCOOH \xrightarrow{+(H^+ + e^-)} *OCH_2OH \xrightarrow[-*OH]{} *CH_2O$	$C_1O_1C_1B^1$	-0.18
23	$\mathbf{*CO_2} \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOO} \xrightarrow{+(H^+ + e^-)} *HCOOH \xrightarrow[-*OH]{+(H^+ + e^-)} *CH_2O$	$C_1O_1C_1B^3$	-0.18
24	$*CO_2 \xrightarrow{+(H^+ + e^-)} *HCOO \xrightarrow{+(H^+ + e^-)} *HCOOH \xrightarrow[-*OH]{} \mathbf{*CHO} \xrightarrow{+(H^+ + e^-)} \mathbf{*CH_2O}$	$C_1O_1B^1_{C_1}$	-0.81
25	$*CO_2 \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOO} \xrightarrow{+(H^+ + e^-)} \mathbf{*OCH_2O} \xrightarrow{+(H^+ + e^-)} *OCH_2OH \xrightarrow[-*OH]{} *CH_2O$	$C_2O_1B^1$	-1.01
26	$*CO_2 \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOO} \xrightarrow{+(H^+ + e^-)} \mathbf{*OCH_2O} \xrightarrow[-*OH]{+(H^+ + e^-)} *CH_2O$	$C_2O_1B^3$	-1.01
27	$*CO_2 \xrightarrow{+(H^+ + e^-)} *HCOO \xrightarrow[-*OH]{+(H^+ + e^-)} \mathbf{*CHO} \xrightarrow{+(H^+ + e^-)} \mathbf{*CH_2O}$	$C_1O_1B^3_{C_1}$	-0.81
28	$\mathbf{*CO_2} \xrightarrow[-*OH]{+(H^+ + e^-)} \mathbf{*CO} \xrightarrow{+(H^+ + e^-)} *CHO \xrightarrow{+(H^+ + e^-)} *CH_2O$	$O_1B^3_{C_2}$	-1.20
29	$*CO_2 \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOO} \xrightarrow{+(H^+ + e^-)} \mathbf{*OCH_2O} \xrightarrow[-*O]{} *CH_2O$	C_2C^1	-1.01
30	$*CO_2 \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOO} \xrightarrow[-*O]{+(H^+ + e^-)} \mathbf{*CH_2O}$	C_2C^3	-0.45
31	$*CO_2 \xrightarrow{+(H^+ + e^-)} *HCOO \xrightarrow[-*O]{} \mathbf{*CHO} \xrightarrow{+(H^+ + e^-)} \mathbf{*CH_2O}$	$C_1C^1_{C_1}$	-0.81
32	$*CO_2 \xrightarrow[-*O]{+(H^+ + e^-)} \mathbf{*CHO} \xrightarrow{+(H^+ + e^-)} \mathbf{*CH_2O}$	$C_1C^3_{C_1}$	-0.81
33	$\mathbf{*CO_2} \xrightarrow[-*O]{} \mathbf{*CO} \xrightarrow{+(H^+ + e^-)} *CHO \xrightarrow{+(H^+ + e^-)} *CH_2O$	$C^1_{C_2}$	-1.73

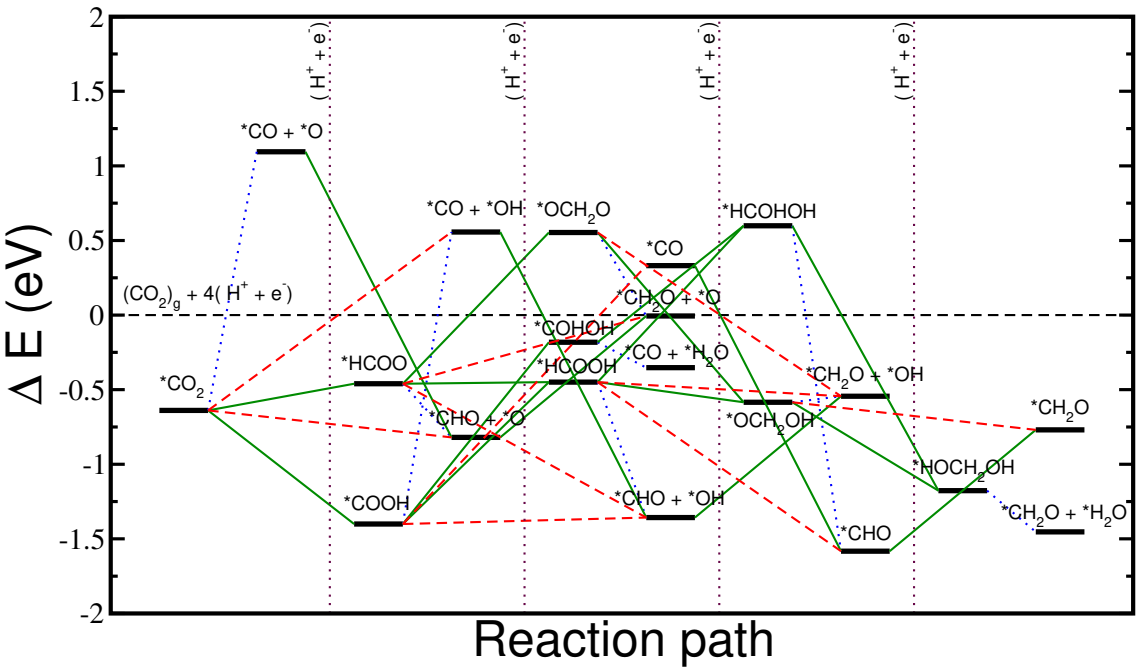


Figure S2: The free energy diagram of electrocatalytic reduction of CO_2 to CH_2O on hematite surface at 0 V (RHE). The reaction step types (1), (2) and (3) presented in Section-2 of main article are respectively represented by blue dotted lines, green solid lines and red dashed lines. The vertical lines represents the proton-electron transfer step.

Table S3: All the possible reaction paths for the formation of CH_3OH through electrocatalytic reduction of CO_2 on hematite surface and minimum potential (U_{min}) required to make all the reaction steps downhill process. The potential determining step is given bold font.

Index	Reaction path	Path name	U_{min} (V)
1	$*CO_2 \xrightarrow{+(H^+ + e^-)} \mathbf{*COOH} \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOOH} \xrightarrow{+(H^+ + e^-)} *OCH_2OH \xrightarrow{+(H^+ + e^-)} *HOCH_2OH \xrightarrow[-*H_2O]{+(H^+ + e^-)} *CH_2OH \xrightarrow{+(H^+ + e^-)} *CH_3OH$	$O_1C_2O_2A^3_{C_1}$	-0.95
2	$*CO_2 \xrightarrow{+(H^+ + e^-)} \mathbf{*COOH} \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOOH} \xrightarrow{+(H^+ + e^-)} *OCH_2OH \xrightarrow{+(H^+ + e^-)} *HOCH_2OH \xrightarrow[-*H_2O]{} *CH_2O \xrightarrow{+(H^+ + e^-)} *CH_2OH \xrightarrow{+(H^+ + e^-)} *CH_3OH$	$O_1C_2O_1A^1_{O_1C_1}$	-0.95
3	$*CO_2 \xrightarrow{+(H^+ + e^-)} \mathbf{*COOH} \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOOH} \xrightarrow{+(H^+ + e^-)} *OCH_2OH \xrightarrow{+(H^+ + e^-)} *HOCH_2OH \xrightarrow[-*H_2O]{} *CH_2O \xrightarrow{+(H^+ + e^-)} *CH_3O \xrightarrow{+(H^+ + e^-)} *CH_3OH$	$O_1C_2O_1A^1_{C_1O_1}$	-0.95
4	$*CO_2 \xrightarrow{+(H^+ + e^-)} \mathbf{*COOH} \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOOH} \xrightarrow{+(H^+ + e^-)} *OCH_2OH \xrightarrow[-*H_2O]{+(H^+ + e^-)} *CH_2O \xrightarrow{+(H^+ + e^-)} *CH_2OH \xrightarrow{+(H^+ + e^-)} *CH_3OH$	$O_1C_2O_1A^3_{O_1C_1}$	-0.95
5	$*CO_2 \xrightarrow{+(H^+ + e^-)} \mathbf{*COOH} \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOOH} \xrightarrow{+(H^+ + e^-)} *OCH_2OH \xrightarrow[-*H_2O]{+(H^+ + e^-)} *CH_2O \xrightarrow{+(H^+ + e^-)} *CH_3O \xrightarrow{+(H^+ + e^-)} *CH_3OH$	$O_1C_2O_1A^3_{C_1O_1}$	-0.95

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Table S3 – *Continued from previous page*

Index	Reaction path	Path name	U_{min} (V)
6	$*CO_2 \xrightarrow{+(H^+ + e^-)} *COOH \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOOH} \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOHOH} \xrightarrow{+(H^+ + e^-)} *HOCH_2OH \xrightarrow[-*H_2O]{+(H^+ + e^-)} *CH_2OH \xrightarrow{+(H^+ + e^-)} *CH_3OH$	$O_1C_1O_1C_1O_1A^3_{C_1}$	-1.05
7	$*CO_2 \xrightarrow{+(H^+ + e^-)} *COOH \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOOH} \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOHOH} \xrightarrow{+(H^+ + e^-)} *HOCH_2OH \xrightarrow[-*H_2O]{} *CH_2O \xrightarrow{+(H^+ + e^-)} *CH_2OH \xrightarrow{+(H^+ + e^-)} *CH_3OH$	$O_1C_1O_1C_1A^1_{O_1C_1}$	-1.05
8	$*CO_2 \xrightarrow{+(H^+ + e^-)} *COOH \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOOH} \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOHOH} \xrightarrow{+(H^+ + e^-)} *HOCH_2OH \xrightarrow[-*H_2O]{} *CH_2O \xrightarrow{+(H^+ + e^-)} *CH_3O \xrightarrow{+(H^+ + e^-)} *CH_3OH$	$O_1C_1O_1C_1A^1_{C_1O_1}$	-1.05
9	$*CO_2 \xrightarrow{+(H^+ + e^-)} *COOH \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOOH} \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOHOH} \xrightarrow[-*H_2O]{+(H^+ + e^-)} *HCOH \xrightarrow{+(H^+ + e^-)} *CH_2OH \xrightarrow{+(H^+ + e^-)} *CH_3OH$	$O_1C_1O_2A^3_{C_2}$	-1.05
10	$*CO_2 \xrightarrow{+(H^+ + e^-)} *COOH \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOOH} \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOHOH} \xrightarrow[-*H_2O]{} *CHO \xrightarrow{+(H^+ + e^-)} *CH_2O \xrightarrow{+(H^+ + e^-)} *CH_2OH \xrightarrow{+(H^+ + e^-)} *CH_3OH$	$O_1C_1O_1A^1_{C_1O_1C_1}$	-1.05
11	$*CO_2 \xrightarrow{+(H^+ + e^-)} *COOH \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOOH} \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOHOH} \xrightarrow[-*H_2O]{} *CHO \xrightarrow{+(H^+ + e^-)} *CH_2O \xrightarrow{+(H^+ + e^-)} *CH_3O \xrightarrow{+(H^+ + e^-)} *CH_3OH$	$O_1C_1O_1A^1_{C_2O_1}$	-1.05
12	$*CO_2 \xrightarrow{+(H^+ + e^-)} *COOH \xrightarrow{+(H^+ + e^-)} *HCOOH \xrightarrow{+(H^+ + e^-)} *HCOHOH \xrightarrow[-*H_2O]{} * \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOH} \xrightarrow{+(H^+ + e^-)} *CH_2OH \xrightarrow{+(H^+ + e^-)} *CH_3OH$	$O_1C_1O_1A^1_{O_1C_2}$	-1.78
13	$*CO_2 \xrightarrow{+(H^+ + e^-)} \mathbf{*COOH} \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOOH} \xrightarrow[-*H_2O]{+(H^+ + e^-)} *CHO \xrightarrow{+(H^+ + e^-)} *CH_2O \xrightarrow{+(H^+ + e^-)} *CH_2OH \xrightarrow{+(H^+ + e^-)} *CH_3OH$	$O_1C_1O_1A^3_{C_1O_1C_1}$	-0.95
14	$*CO_2 \xrightarrow{+(H^+ + e^-)} \mathbf{*COOH} \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOOH} \xrightarrow[-*H_2O]{+(H^+ + e^-)} *CHO \xrightarrow{+(H^+ + e^-)} *CH_2O \xrightarrow{+(H^+ + e^-)} *CH_3O \xrightarrow{+(H^+ + e^-)} *CH_3OH$	$O_1C_1O_1A^3_{C_2O_1}$	-0.95
15	$*CO_2 \xrightarrow{+(H^+ + e^-)} *COOH \xrightarrow{+(H^+ + e^-)} *HCOOH \xrightarrow[-*H_2O]{+(H^+ + e^-)} \mathbf{*CHO} \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOH} \xrightarrow{+(H^+ + e^-)} *CH_2OH \xrightarrow{+(H^+ + e^-)} *CH_3OH$	$O_1C_1O_1A^3_{O_1C_2}$	-1.78
16	$*CO_2 \xrightarrow{+(H^+ + e^-)} \mathbf{*COOH} \xrightarrow{+(H^+ + e^-)} \mathbf{*COHOH} \xrightarrow{+(H^+ + e^-)} *HCOHOH \xrightarrow{+(H^+ + e^-)} *HOCH_2OH \xrightarrow[-*H_2O]{+(H^+ + e^-)} *CH_2OH \xrightarrow{+(H^+ + e^-)} *CH_3OH$	$O_2C_2A^3_{O_1C_1}$	-1.22
17	$*CO_2 \xrightarrow{+(H^+ + e^-)} \mathbf{*COOH} \xrightarrow{+(H^+ + e^-)} \mathbf{*COHOH} \xrightarrow{+(H^+ + e^-)} *HCOHOH \xrightarrow{+(H^+ + e^-)} *HOCH_2OH \xrightarrow[-*H_2O]{} *CH_2O \xrightarrow{+(H^+ + e^-)} *CH_2OH \xrightarrow{+(H^+ + e^-)} *CH_3OH$	$O_2C_2A^1_{O_1C_1}$	-1.22
18	$*CO_2 \xrightarrow{+(H^+ + e^-)} \mathbf{*COOH} \xrightarrow{+(H^+ + e^-)} \mathbf{*COHOH} \xrightarrow{+(H^+ + e^-)} *HCOHOH \xrightarrow{+(H^+ + e^-)} *HOCH_2OH \xrightarrow[-*H_2O]{} *CH_2O \xrightarrow{+(H^+ + e^-)} *CH_3O \xrightarrow{+(H^+ + e^-)} *CH_3OH$	$O_2C_2A^1_{C_1O_1}$	-1.22

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Table S3 – *Continued from previous page*

Index	Reaction path	Path name	U_{min} (V)
19	$*CO_2 \xrightarrow{+(H^+ + e^-)} \mathbf{*COOH} \xrightarrow{+(H^+ + e^-)} \mathbf{*COHOH} \xrightarrow{+(H^+ + e^-)} *HCOHOH \xrightarrow[-*H_2O]{+(H^+ + e^-)} *HCOH \xrightarrow{+(H^+ + e^-)} *CH_2OH \xrightarrow{+(H^+ + e^-)} *CH_3OH$	$O_2C_1O_1A^3_{C_2}$	-1.22
20	$*CO_2 \xrightarrow{+(H^+ + e^-)} \mathbf{*COOH} \xrightarrow{+(H^+ + e^-)} \mathbf{*COHOH} \xrightarrow{+(H^+ + e^-)} *HCOHOH \xrightarrow[-*H_2O]{} *CHO \xrightarrow{+(H^+ + e^-)} *CH_2O \xrightarrow{+(H^+ + e^-)} *CH_2OH \xrightarrow{+(H^+ + e^-)} *CH_3OH$	$O_2C_1A^1_{C_1O_1C_1}$	-1.22
21	$*CO_2 \xrightarrow{+(H^+ + e^-)} \mathbf{*COOH} \xrightarrow{+(H^+ + e^-)} \mathbf{*COHOH} \xrightarrow{+(H^+ + e^-)} *HCOHOH \xrightarrow[-*H_2O]{} *CHO \xrightarrow{+(H^+ + e^-)} *CH_2O \xrightarrow{+(H^+ + e^-)} *CH_3O \xrightarrow{+(H^+ + e^-)} *CH_3OH$	$O_2C_1A^1_{C_2O_1}$	-1.22
22	$*CO_2 \xrightarrow{+(H^+ + e^-)} *COOH \xrightarrow{+(H^+ + e^-)} *COHOH \xrightarrow{+(H^+ + e^-)} *HCOHOH \xrightarrow[-*H_2O]{} \mathbf{*CHO} \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOH} \xrightarrow{+(H^+ + e^-)} *CH_2OH \xrightarrow{+(H^+ + e^-)} *CH_3OH$	$O_2C_1A^1_{O_1C_2}$	-1.78
23	$*CO_2 \xrightarrow{+(H^+ + e^-)} \mathbf{*COOH} \xrightarrow{+(H^+ + e^-)} \mathbf{*COHOH} \xrightarrow[-*H_2O]{+(H^+ + e^-)} *COH \xrightarrow{+(H^+ + e^-)} *HCOH \xrightarrow{+(H^+ + e^-)} *CH_2OH \xrightarrow{+(H^+ + e^-)} *CH_3OH$	$O_3A^3_{C_3}$	-1.22
24	$*CO_2 \xrightarrow{+(H^+ + e^-)} \mathbf{*COOH} \xrightarrow{+(H^+ + e^-)} \mathbf{*COHOH} \xrightarrow[-*H_2O]{} *CO \xrightarrow{+(H^+ + e^-)} *CHO \xrightarrow{+(H^+ + e^-)} *CH_2O \xrightarrow{+(H^+ + e^-)} *CH_2OH \xrightarrow{+(H^+ + e^-)} *CH_3OH$	$O_2A^1_{C_2O_1C_1}$	-1.22
25	$*CO_2 \xrightarrow{+(H^+ + e^-)} \mathbf{*COOH} \xrightarrow{+(H^+ + e^-)} \mathbf{*COHOH} \xrightarrow[-*H_2O]{} *CO \xrightarrow{+(H^+ + e^-)} *CHO \xrightarrow{+(H^+ + e^-)} *CH_2O \xrightarrow{+(H^+ + e^-)} *CH_3O \xrightarrow{+(H^+ + e^-)} *CH_3OH$	$O_2A^1_{C_3O_1}$	-1.22
26	$*CO_2 \xrightarrow{+(H^+ + e^-)} *COOH \xrightarrow{+(H^+ + e^-)} *COHOH \xrightarrow[-*H_2O]{} *CO \xrightarrow{+(H^+ + e^-)} \mathbf{*CHO} \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOH} \xrightarrow{+(H^+ + e^-)} *CH_2OH \xrightarrow{+(H^+ + e^-)} *CH_3OH$	$O_2A^1_{C_1O_1C_2}$	-1.78
27	$*CO_2 \xrightarrow{+(H^+ + e^-)} \mathbf{*COOH} \xrightarrow{+(H^+ + e^-)} \mathbf{*COHOH} \xrightarrow[-*H_2O]{} *CO \xrightarrow{+(H^+ + e^-)} *COH \xrightarrow{+(H^+ + e^-)} *HCOH \xrightarrow{+(H^+ + e^-)} *CH_2OH \xrightarrow{+(H^+ + e^-)} *CH_3OH$	$O_2A^1_{O_1C_3}$	-1.22
28	$*CO_2 \xrightarrow{+(H^+ + e^-)} \mathbf{*COOH} \xrightarrow[-*H_2O]{+(H^+ + e^-)} \mathbf{*CO} \xrightarrow{+(H^+ + e^-)} *CHO \xrightarrow{+(H^+ + e^-)} *CH_2O \xrightarrow{+(H^+ + e^-)} *CH_2OH \xrightarrow{+(H^+ + e^-)} *CH_3OH$	$O_2A^3_{C_2O_1C_1}$	-1.05
29	$*CO_2 \xrightarrow{+(H^+ + e^-)} \mathbf{*COOH} \xrightarrow[-*H_2O]{+(H^+ + e^-)} \mathbf{*CO} \xrightarrow{+(H^+ + e^-)} *CHO \xrightarrow{+(H^+ + e^-)} *CH_2O \xrightarrow{+(H^+ + e^-)} *CH_3O \xrightarrow{+(H^+ + e^-)} *CH_3OH$	$O_2A^3_{C_3O_1}$	-1.05
30	$*CO_2 \xrightarrow{+(H^+ + e^-)} *COOH \xrightarrow[-*H_2O]{+(H^+ + e^-)} *CO \xrightarrow{+(H^+ + e^-)} \mathbf{*CHO} \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOH} \xrightarrow{+(H^+ + e^-)} *CH_2OH \xrightarrow{+(H^+ + e^-)} *CH_3OH$	$O_2A^3_{C_1O_1C_2}$	-1.78
31	$*CO_2 \xrightarrow{+(H^+ + e^-)} \mathbf{*COOH} \xrightarrow[-*H_2O]{+(H^+ + e^-)} \mathbf{*CO} \xrightarrow{+(H^+ + e^-)} *COH \xrightarrow{+(H^+ + e^-)} *HCOH \xrightarrow{+(H^+ + e^-)} *CH_2OH \xrightarrow{+(H^+ + e^-)} *CH_3OH$	$O_2A^3_{O_1C_3}$	-1.05

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Table S3 – *Continued from previous page*

Index	Reaction path	Path name	U_{min} (V)
32	$\mathbf{*CO_2} \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOO} \xrightarrow{+(H^+ + e^-)} *HCOOH \xrightarrow{+(H^+ + e^-)} *OCH_2OH \xrightarrow{+(H^+ + e^-)} *HOCH_2OH \xrightarrow[-*H_2O]{+(H^+ + e^-)} *CH_2OH \xrightarrow{+(H^+ + e^-)} *CH_3OH$	$C_1O_1C_1O_2A^3_{C_1}$	-0.18
33	$\mathbf{*CO_2} \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOO} \xrightarrow{+(H^+ + e^-)} *HCOOH \xrightarrow{+(H^+ + e^-)} *OCH_2OH \xrightarrow{+(H^+ + e^-)} *HOCH_2OH \xrightarrow[-*H_2O]{} *CH_2O \xrightarrow{+(H^+ + e^-)} *CH_2OH \xrightarrow{+(H^+ + e^-)} *CH_3OH$	$C_1O_1C_1O_1A^1_{O_1C_1}$	-0.18
34	$\mathbf{*CO_2} \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOO} \xrightarrow{+(H^+ + e^-)} *HCOOH \xrightarrow{+(H^+ + e^-)} *OCH_2OH \xrightarrow{+(H^+ + e^-)} *HOCH_2OH \xrightarrow[-*H_2O]{} *CH_2O \xrightarrow{+(H^+ + e^-)} *CH_3O \xrightarrow{+(H^+ + e^-)} *CH_3OH$	$C_1O_1C_1O_1A^1_{C_1O_1}$	-0.18
35	$\mathbf{*CO_2} \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOO} \xrightarrow{+(H^+ + e^-)} *HCOOH \xrightarrow{+(H^+ + e^-)} *OCH_2OH \xrightarrow[-*H_2O]{+(H^+ + e^-)} *CH_2O \xrightarrow{+(H^+ + e^-)} *CH_2OH \xrightarrow{+(H^+ + e^-)} *CH_3OH$	$C_1O_1C_1O_1A^3_{O_1C_1}$	-0.18
36	$\mathbf{*CO_2} \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOO} \xrightarrow{+(H^+ + e^-)} *HCOOH \xrightarrow{+(H^+ + e^-)} *OCH_2OH \xrightarrow[-*H_2O]{+(H^+ + e^-)} *CH_2O \xrightarrow{+(H^+ + e^-)} *CH_3O \xrightarrow{+(H^+ + e^-)} *CH_3OH$	$C_1O_1C_1O_1A^3_{C_1O_1}$	-0.18
37	$*CO_2 \xrightarrow{+(H^+ + e^-)} *HCOO \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOOH} \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOHOH} \xrightarrow{+(H^+ + e^-)} *HOCH_2OH \xrightarrow[-*H_2O]{+(H^+ + e^-)} *CH_2OH \xrightarrow{+(H^+ + e^-)} *CH_3OH$	$C_1O_2C_1O_1A^3_{C_1}$	-1.05
38	$*CO_2 \xrightarrow{+(H^+ + e^-)} *HCOO \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOOH} \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOHOH} \xrightarrow{+(H^+ + e^-)} *HOCH_2OH \xrightarrow[-*H_2O]{} *CH_2O \xrightarrow{+(H^+ + e^-)} *CH_2OH \xrightarrow{+(H^+ + e^-)} *CH_3OH$	$C_1O_2C_1A^1_{O_1C_1}$	-1.05
39	$*CO_2 \xrightarrow{+(H^+ + e^-)} *HCOO \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOOH} \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOHOH} \xrightarrow{+(H^+ + e^-)} *HOCH_2OH \xrightarrow[-*H_2O]{} *CH_2O \xrightarrow{+(H^+ + e^-)} *CH_3O \xrightarrow{+(H^+ + e^-)} *CH_3OH$	$C_1O_2C_1A^1_{C_1O_1}$	-1.05
40	$*CO_2 \xrightarrow{+(H^+ + e^-)} *HCOO \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOOH} \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOHOH} \xrightarrow[-*H_2O]{+(H^+ + e^-)} *HCOH \xrightarrow{+(H^+ + e^-)} *CH_2OH \xrightarrow{+(H^+ + e^-)} *CH_3OH$	$C_1O_3A^3_{C_2}$	-1.05
41	$*CO_2 \xrightarrow{+(H^+ + e^-)} *HCOO \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOOH} \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOHOH} \xrightarrow[-*H_2O]{} *CHO \xrightarrow{+(H^+ + e^-)} *CH_2O \xrightarrow{+(H^+ + e^-)} *CH_2OH \xrightarrow{+(H^+ + e^-)} *CH_3OH$	$C_1O_2A^1_{C_1O_1C_1}$	-1.05
42	$*CO_2 \xrightarrow{+(H^+ + e^-)} *HCOO \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOOH} \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOHOH} \xrightarrow[-*H_2O]{} *CHO \xrightarrow{+(H^+ + e^-)} *CH_2O \xrightarrow{+(H^+ + e^-)} *CH_3O \xrightarrow{+(H^+ + e^-)} *CH_3OH$	$C_1O_2A^1_{C_2O_1}$	-1.05
43	$*CO_2 \xrightarrow{+(H^+ + e^-)} *HCOO \xrightarrow{+(H^+ + e^-)} *HCOOH \xrightarrow{+(H^+ + e^-)} *HCOHOH \xrightarrow[-*H_2O]{} \mathbf{*CHO} \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOH} \xrightarrow{+(H^+ + e^-)} *CH_2OH \xrightarrow{+(H^+ + e^-)} *CH_3OH$	$C_1O_2A^1_{O_1C_2}$	-1.78
44	$*CO_2 \xrightarrow{+(H^+ + e^-)} *HCOO \xrightarrow{+(H^+ + e^-)} *HCOOH \xrightarrow[-*H_2O]{+(H^+ + e^-)} \mathbf{*CHO} \xrightarrow{+(H^+ + e^-)} \mathbf{*CH_2O} \xrightarrow{+(H^+ + e^-)} *CH_2OH \xrightarrow{+(H^+ + e^-)} *CH_3OH$	$C_1O_2A^3_{C_1O_1C_1}$	-0.81

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Index	Reaction path	Path name	U_{min} (V)
45	$*CO_2 \xrightarrow{+(H^+ + e^-)} *HCOO \xrightarrow{+(H^+ + e^-)} *HCOOH \xrightarrow[-*H_2O]{+(H^+ + e^-)} \mathbf{*CHO} \xrightarrow{+(H^+ + e^-)} \mathbf{*CH_2O} \xrightarrow{+(H^+ + e^-)} *CH_3O \xrightarrow{+(H^+ + e^-)} *CH_3OH$	$C_1O_2A^3_{C_2O_1}$	-0.81
46	$*CO_2 \xrightarrow{+(H^+ + e^-)} *HCOO \xrightarrow{+(H^+ + e^-)} *HCOOH \xrightarrow[-*H_2O]{+(H^+ + e^-)} \mathbf{*CHO} \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOH} \xrightarrow{+(H^+ + e^-)} *CH_2OH \xrightarrow{+(H^+ + e^-)} *CH_3OH$	$C_1O_2A^3_{O_1C_2}$	-1.78
47	$*CO_2 \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOO} \xrightarrow{+(H^+ + e^-)} \mathbf{*OCH_2O} \xrightarrow{+(H^+ + e^-)} *OCH_2OH \xrightarrow{+(H^+ + e^-)} *HOCH_2OH \xrightarrow[-*H_2O]{+(H^+ + e^-)} *CH_2OH \xrightarrow{+(H^+ + e^-)} *CH_3OH$	$C_2O_3A^3_{C_1}$	-1.01
48	$*CO_2 \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOO} \xrightarrow{+(H^+ + e^-)} \mathbf{*OCH_2O} \xrightarrow{+(H^+ + e^-)} *OCH_2OH \xrightarrow{+(H^+ + e^-)} *HOCH_2OH \xrightarrow[-*H_2O]{} *CH_2O \xrightarrow{+(H^+ + e^-)} *CH_2OH \xrightarrow{+(H^+ + e^-)} *CH_3OH$	$C_2O_2A^1_{O_1C_1}$	-1.01
49	$*CO_2 \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOO} \xrightarrow{+(H^+ + e^-)} \mathbf{*OCH_2O} \xrightarrow{+(H^+ + e^-)} *OCH_2OH \xrightarrow{+(H^+ + e^-)} *HOCH_2OH \xrightarrow[-*H_2O]{} *CH_2O \xrightarrow{+(H^+ + e^-)} *CH_3O \xrightarrow{+(H^+ + e^-)} *CH_3OH$	$C_2O_2A^1_{C_1O_1}$	-1.01
50	$*CO_2 \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOO} \xrightarrow{+(H^+ + e^-)} \mathbf{*OCH_2O} \xrightarrow{+(H^+ + e^-)} *OCH_2OH \xrightarrow[-*H_2O]{+(H^+ + e^-)} *CH_2O \xrightarrow{+(H^+ + e^-)} *CH_2OH \xrightarrow{+(H^+ + e^-)} *CH_3OH$	$C_2O_2A^3_{O_1C_1}$	-1.01
51	$*CO_2 \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOO} \xrightarrow{+(H^+ + e^-)} \mathbf{*OCH_2O} \xrightarrow{+(H^+ + e^-)} *OCH_2OH \xrightarrow[-*H_2O]{+(H^+ + e^-)} *CH_2O \xrightarrow{+(H^+ + e^-)} *CH_3O \xrightarrow{+(H^+ + e^-)} *CH_3OH$	$C_2O_2A^3_{C_1O_1}$	-1.01
52	$*CO_2 \xrightarrow{+(H^+ + e^-)} \mathbf{*COOH} \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOOH} \xrightarrow{+(H^+ + e^-)} *OCH_2OH \xrightarrow{+(H^+ + e^-)} *HOCH_2OH \xrightarrow[-*OH]{+(H^+ + e^-)} *CH_3OH$	$O_1C_2O_1C_1B^3$	-0.95
53	$*CO_2 \xrightarrow{+(H^+ + e^-)} \mathbf{*COOH} \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOOH} \xrightarrow{+(H^+ + e^-)} *OCH_2OH \xrightarrow{+(H^+ + e^-)} *HOCH_2OH \xrightarrow[-*OH]{} *CH_2OH \xrightarrow{+(H^+ + e^-)} *CH_3OH$	$O_1C_2O_1B^1_{C_1}$	-0.95
54	$*CO_2 \xrightarrow{+(H^+ + e^-)} \mathbf{*COOH} \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOOH} \xrightarrow{+(H^+ + e^-)} *OCH_2OH \xrightarrow[-*OH]{+(H^+ + e^-)} *CH_2OH \xrightarrow{+(H^+ + e^-)} *CH_3OH$	$O_1C_2O_1B^3_{C_1}$	-0.95
55	$*CO_2 \xrightarrow{+(H^+ + e^-)} \mathbf{*COOH} \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOOH} \xrightarrow{+(H^+ + e^-)} *OCH_2OH \xrightarrow[-*OH]{+(H^+ + e^-)} *CH_3O \xrightarrow{+(H^+ + e^-)} *CH_3OH$	$O_1C_3B^3_{O_1}$	-0.95
56	$*CO_2 \xrightarrow{+(H^+ + e^-)} \mathbf{*COOH} \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOOH} \xrightarrow{+(H^+ + e^-)} *OCH_2OH \xrightarrow[-*OH]{} *CH_2O \xrightarrow{+(H^+ + e^-)} *CH_2OH \xrightarrow{+(H^+ + e^-)} *CH_3OH$	$O_1C_2B^1_{O_1C_1}$	-0.95
57	$*CO_2 \xrightarrow{+(H^+ + e^-)} \mathbf{*COOH} \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOOH} \xrightarrow{+(H^+ + e^-)} *OCH_2OH \xrightarrow[-*OH]{} *CH_2O \xrightarrow{+(H^+ + e^-)} *CH_3O \xrightarrow{+(H^+ + e^-)} *CH_3OH$	$O_1C_2B^1_{C_1O_1}$	-0.95
58	$*CO_2 \xrightarrow{+(H^+ + e^-)} *COOH \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOOH} \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOHOH} \xrightarrow{+(H^+ + e^-)} *HOCH_2OH \xrightarrow[-*OH]{+(H^+ + e^-)} *CH_3OH$	$O_1C_1O_1C_2B^3$	-1.05
59	$*CO_2 \xrightarrow{+(H^+ + e^-)} *COOH \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOOH} \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOHOH} \xrightarrow{+(H^+ + e^-)} *HOCH_2OH \xrightarrow[-*OH]{} *CH_2OH \xrightarrow{+(H^+ + e^-)} *CH_3OH$	$O_1C_1O_1C_1B^1_{C_1}$	-1.05
60	$*CO_2 \xrightarrow{+(H^+ + e^-)} *COOH \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOOH} \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOHOH}$		

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Table S3 – *Continued from previous page*

Index	Reaction path	Path name	U_{min} (V)
	$\xrightarrow[-\,*OH]{+\,(H^+ + e^-)}$ $*CH_2OH$ $\xrightarrow{+\,(H^+ + e^-)}$ $*CH_3OH$	$O_1C_1O_1C_1B^3_{C_1}$	-1.05
61	$*CO_2$ $\xrightarrow{+\,(H^+ + e^-)}$ $*COOH$ $\xrightarrow{+\,(H^+ + e^-)}$ ***HCOOH** $\xrightarrow{+\,(H^+ + e^-)}$ ***HCOHOH**		
	$\xrightarrow[-\,*OH]{}$ $*HCOH$ $\xrightarrow{+\,(H^+ + e^-)}$ $*CH_2OH$ $\xrightarrow{+\,(H^+ + e^-)}$ $*CH_3OH$	$O_1C_1O_1B^1_{C_2}$	-1.05
62	$*CO_2$ $\xrightarrow{+\,(H^+ + e^-)}$ ***COOH** $\xrightarrow{+\,(H^+ + e^-)}$ ***HCOOH** $\xrightarrow[-\,*OH]{+\,(H^+ + e^-)}$ $*CH_2O$		
	$\xrightarrow{+\,(H^+ + e^-)}$ $*CH_2OH$ $\xrightarrow{+\,(H^+ + e^-)}$ $*CH_3OH$	$O_1C_2B^3_{O_1C_1}$	-0.95
63	$*CO_2$ $\xrightarrow{+\,(H^+ + e^-)}$ ***COOH** $\xrightarrow{+\,(H^+ + e^-)}$ ***HCOOH** $\xrightarrow[-\,*OH]{+\,(H^+ + e^-)}$ $*CH_2O$		
	$\xrightarrow{+\,(H^+ + e^-)}$ $*CH_3O$ $\xrightarrow{+\,(H^+ + e^-)}$ $*CH_3OH$	$O_1C_2B^3_{C_1O_1}$	-0.95
64	$*CO_2$ $\xrightarrow{+\,(H^+ + e^-)}$ ***COOH** $\xrightarrow{+\,(H^+ + e^-)}$ ***HCOOH** $\xrightarrow[-\,*OH]{+\,(H^+ + e^-)}$ $*HCOH$		
	$\xrightarrow{+\,(H^+ + e^-)}$ $*CH_2OH$ $\xrightarrow{+\,(H^+ + e^-)}$ $*CH_3OH$	$O_1C_1O_1B^3_{C_2}$	-0.95
65	$*CO_2$ $\xrightarrow{+\,(H^+ + e^-)}$ ***COOH** $\xrightarrow{+\,(H^+ + e^-)}$ ***HCOOH** $\xrightarrow[-\,*OH]{}$ $*CHO$		
	$\xrightarrow{+\,(H^+ + e^-)}$ $*CH_2O$ $\xrightarrow{+\,(H^+ + e^-)}$ $*CH_2OH$ $\xrightarrow{+\,(H^+ + e^-)}$ $*CH_3OH$	$O_1C_1B^1_{C_1O_1C_1}$	-0.95
66	$*CO_2$ $\xrightarrow{+\,(H^+ + e^-)}$ ***COOH** $\xrightarrow{+\,(H^+ + e^-)}$ ***HCOOH** $\xrightarrow[-\,*OH]{}$ $*CHO$		
	$\xrightarrow{+\,(H^+ + e^-)}$ $*CH_2O$ $\xrightarrow{+\,(H^+ + e^-)}$ $*CH_3O$ $\xrightarrow{+\,(H^+ + e^-)}$ $*CH_3OH$	$O_1C_1B^1_{C_2O_1}$	-0.95
67	$*CO_2$ $\xrightarrow{+\,(H^+ + e^-)}$ $*COOH$ $\xrightarrow{+\,(H^+ + e^-)}$ $*HCOOH$ $\xrightarrow[-\,*OH]{}$ ***CHO**		
	$\xrightarrow{+\,(H^+ + e^-)}$ ***HCOH** $\xrightarrow{+\,(H^+ + e^-)}$ $*CH_2OH$ $\xrightarrow{+\,(H^+ + e^-)}$ $*CH_3OH$	$O_1C_1B^1_{O_1C_2}$	-1.78
68	$*CO_2$ $\xrightarrow{+\,(H^+ + e^-)}$ ***COOH** $\xrightarrow{+\,(H^+ + e^-)}$ ***COHOH** $\xrightarrow{+\,(H^+ + e^-)}$ $*HCOHOH$		
	$\xrightarrow{+\,(H^+ + e^-)}$ $*HOCH_2OH$ $\xrightarrow[-\,*OH]{+\,(H^+ + e^-)}$ $*CH_3OH$	$O_2C_3B^3$	-1.22
69	$*CO_2$ $\xrightarrow{+\,(H^+ + e^-)}$ ***COOH** $\xrightarrow{+\,(H^+ + e^-)}$ ***COHOH** $\xrightarrow{+\,(H^+ + e^-)}$ $*HCOHOH$		
	$\xrightarrow{+\,(H^+ + e^-)}$ $*HOCH_2OH$ $\xrightarrow[-\,*OH]{}$ $*CH_2OH$ $\xrightarrow{+\,(H^+ + e^-)}$ $*CH_3OH$	$O_2C_2B^1_{C_1}$	-1.22
70	$*CO_2$ $\xrightarrow{+\,(H^+ + e^-)}$ ***COOH** $\xrightarrow{+\,(H^+ + e^-)}$ ***COHOH** $\xrightarrow{+\,(H^+ + e^-)}$ $*HCOHOH$		
	$\xrightarrow[-\,*OH]{+\,(H^+ + e^-)}$ $*CH_2OH$ $\xrightarrow{+\,(H^+ + e^-)}$ $*CH_3OH$	$O_2C_2B^3_{C_1}$	-1.22
71	$*CO_2$ $\xrightarrow{+\,(H^+ + e^-)}$ ***COOH** $\xrightarrow{+\,(H^+ + e^-)}$ ***COHOH** $\xrightarrow{+\,(H^+ + e^-)}$ $*HCOHOH$		
	$\xrightarrow[-\,*OH]{}$ $*HCOH$ $\xrightarrow{+\,(H^+ + e^-)}$ $*CH_2OH$ $\xrightarrow{+\,(H^+ + e^-)}$ $*CH_3OH$	$O_2C_1B^1_{C_2}$	-1.22
72	$*CO_2$ $\xrightarrow{+\,(H^+ + e^-)}$ ***COOH** $\xrightarrow{+\,(H^+ + e^-)}$ ***COHOH** $\xrightarrow[-\,*OH]{+\,(H^+ + e^-)}$ $*HCOH$		
	$\xrightarrow{+\,(H^+ + e^-)}$ $*CH_2OH$ $\xrightarrow{+\,(H^+ + e^-)}$ $*CH_3OH$	$O_2C_1B^3_{C_2}$	-1.22
73	$*CO_2$ $\xrightarrow{+\,(H^+ + e^-)}$ ***COOH** $\xrightarrow{+\,(H^+ + e^-)}$ ***COHOH** $\xrightarrow[-\,*OH]{}$ $*COH$		
	$\xrightarrow{+\,(H^+ + e^-)}$ $*HCOH$ $\xrightarrow{+\,(H^+ + e^-)}$ $*CH_2OH$ $\xrightarrow{+\,(H^+ + e^-)}$ $*CH_3OH$	$O_2B^1_{C_3}$	-1.22
74	$*CO_2$ $\xrightarrow{+\,(H^+ + e^-)}$ $*COOH$ $\xrightarrow[-\,*OH]{+\,(H^+ + e^-)}$ ***CHO** $\xrightarrow{+\,(H^+ + e^-)}$ ***CH_2O**		
	$\xrightarrow{+\,(H^+ + e^-)}$ $*CH_2OH$ $\xrightarrow{+\,(H^+ + e^-)}$ $*CH_3OH$	$O_1C_1B^3_{C_1O_1C_1}$	-0.81
75	$*CO_2$ $\xrightarrow{+\,(H^+ + e^-)}$ $*COOH$ $\xrightarrow[-\,*OH]{+\,(H^+ + e^-)}$ ***CHO** $\xrightarrow{+\,(H^+ + e^-)}$ ***CH_2O**		
	$\xrightarrow{+\,(H^+ + e^-)}$ $*CH_3O$ $\xrightarrow{+\,(H^+ + e^-)}$ $*CH_3OH$	$O_1C_1B^3_{C_2O_1}$	-0.81
76	$*CO_2$ $\xrightarrow{+\,(H^+ + e^-)}$ $*COOH$ $\xrightarrow[-\,*OH]{+\,(H^+ + e^-)}$ ***CHO** $\xrightarrow{+\,(H^+ + e^-)}$ ***HCOH**		
	$\xrightarrow{+\,(H^+ + e^-)}$ $*CH_2OH$ $\xrightarrow{+\,(H^+ + e^-)}$ $*CH_3OH$	$O_1C_1B^3_{O_1C_2}$	-1.78

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Index	Reaction path	Path name	U_{min} (V)
77	$*CO_2 \xrightarrow{+(H^+ + e^-)} \mathbf{*COOH} \xrightarrow[-*OH]{+(H^+ + e^-)} \mathbf{*COH} \xrightarrow{+(H^+ + e^-)} *HCOH \xrightarrow{+(H^+ + e^-)} *CH_2OH \xrightarrow{+(H^+ + e^-)} *CH_3OH$	$O_2B^3_{C_3}$	-1.52
78	$*CO_2 \xrightarrow{+(H^+ + e^-)} \mathbf{*COOH} \xrightarrow[-*OH]{} \mathbf{*CO} \xrightarrow{+(H^+ + e^-)} *CHO \xrightarrow{+(H^+ + e^-)} *CH_2O \xrightarrow{+(H^+ + e^-)} *CH_2OH \xrightarrow{+(H^+ + e^-)} *CH_3OH$	$O_1B^1_{C_2O_1C_1}$	-1.96
79	$*CO_2 \xrightarrow{+(H^+ + e^-)} \mathbf{*COOH} \xrightarrow[-*OH]{} \mathbf{*CO} \xrightarrow{+(H^+ + e^-)} *CHO \xrightarrow{+(H^+ + e^-)} *CH_2O \xrightarrow{+(H^+ + e^-)} *CH_3O \xrightarrow{+(H^+ + e^-)} *CH_3OH$	$O_1B^1_{C_3O_1}$	-1.96
80	$*CO_2 \xrightarrow{+(H^+ + e^-)} \mathbf{*COOH} \xrightarrow[-*OH]{} \mathbf{*CO} \xrightarrow{+(H^+ + e^-)} *CHO \xrightarrow{+(H^+ + e^-)} *HCOH \xrightarrow{+(H^+ + e^-)} *CH_2OH \xrightarrow{+(H^+ + e^-)} *CH_3OH$	$O_1B^1_{C_1O_1C_2}$	-1.96
81	$*CO_2 \xrightarrow{+(H^+ + e^-)} \mathbf{*COOH} \xrightarrow[-*OH]{} \mathbf{*CO} \xrightarrow{+(H^+ + e^-)} *COH \xrightarrow{+(H^+ + e^-)} *HCOH \xrightarrow{+(H^+ + e^-)} *CH_2OH \xrightarrow{+(H^+ + e^-)} *CH_3OH$	$O_1B^1_{O_1C_3}$	-1.96
82	$\mathbf{*CO_2} \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOO} \xrightarrow{+(H^+ + e^-)} *HCOOH \xrightarrow{+(H^+ + e^-)} *OCH_2OH \xrightarrow{+(H^+ + e^-)} *HOCH_2OH \xrightarrow[-*OH]{+(H^+ + e^-)} *CH_3OH$	$C_1O_1C_1O_1C_1B^3$	-0.18
83	$\mathbf{*CO_2} \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOO} \xrightarrow{+(H^+ + e^-)} *HCOOH \xrightarrow{+(H^+ + e^-)} *OCH_2OH \xrightarrow{+(H^+ + e^-)} *HOCH_2OH \xrightarrow[-*OH]{} *CH_2OH \xrightarrow{+(H^+ + e^-)} *CH_3OH$	$C_1O_1C_1O_1B^1_{C_1}$	-0.18
84	$\mathbf{*CO_2} \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOO} \xrightarrow{+(H^+ + e^-)} *HCOOH \xrightarrow{+(H^+ + e^-)} *OCH_2OH \xrightarrow[-*OH]{+(H^+ + e^-)} *CH_2OH \xrightarrow{+(H^+ + e^-)} *CH_3OH$	$C_1O_1C_1O_1B^3_{C_1}$	-0.18
85	$\mathbf{*CO_2} \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOO} \xrightarrow{+(H^+ + e^-)} *HCOOH \xrightarrow{+(H^+ + e^-)} *OCH_2OH \xrightarrow[-*OH]{+(H^+ + e^-)} *CH_3O \xrightarrow{+(H^+ + e^-)} *CH_3OH$	$C_1O_1C_2B^3_{O_1}$	-0.18
86	$\mathbf{*CO_2} \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOO} \xrightarrow{+(H^+ + e^-)} *HCOOH \xrightarrow{+(H^+ + e^-)} *OCH_2OH \xrightarrow[-*OH]{} *CH_2O \xrightarrow{+(H^+ + e^-)} *CH_2OH \xrightarrow{+(H^+ + e^-)} *CH_3OH$	$C_1O_1C_1B^1_{O_1C_1}$	-0.18
87	$\mathbf{*CO_2} \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOO} \xrightarrow{+(H^+ + e^-)} *HCOOH \xrightarrow{+(H^+ + e^-)} *OCH_2OH \xrightarrow[-*OH]{} *CH_2O \xrightarrow{+(H^+ + e^-)} *CH_3O \xrightarrow{+(H^+ + e^-)} *CH_3OH$	$C_1O_1C_1B^1_{C_1O_1}$	-0.18
88	$*CO_2 \xrightarrow{+(H^+ + e^-)} *HCOO \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOOH} \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOHOH} \xrightarrow{+(H^+ + e^-)} *HOCH_2OH \xrightarrow[-*OH]{+(H^+ + e^-)} *CH_3OH$	$C_1O_2C_2B^3$	-1.05
89	$*CO_2 \xrightarrow{+(H^+ + e^-)} *HCOO \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOOH} \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOHOH} \xrightarrow{+(H^+ + e^-)} *HOCH_2OH \xrightarrow[-*OH]{} *CH_2OH \xrightarrow{+(H^+ + e^-)} *CH_3OH$	$C_1O_2C_1B^1_{C_1}$	-1.05
90	$*CO_2 \xrightarrow{+(H^+ + e^-)} *HCOO \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOOH} \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOHOH} \xrightarrow[-*OH]{+(H^+ + e^-)} *CH_2OH \xrightarrow{+(H^+ + e^-)} *CH_3OH$	$C_1O_2C_1B^3_{C_1}$	-1.05
91	$*CO_2 \xrightarrow{+(H^+ + e^-)} *HCOO \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOOH} \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOHOH} \xrightarrow[-*OH]{} *HCOH \xrightarrow{+(H^+ + e^-)} *CH_2OH \xrightarrow{+(H^+ + e^-)} *CH_3OH$	$C_1O_2B^1_{C_2}$	-1.05
92	$*CO_2 \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOO} \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOOH} \xrightarrow[-*OH]{+(H^+ + e^-)} *CH_2O \xrightarrow{+(H^+ + e^-)} *CH_2OH \xrightarrow{+(H^+ + e^-)} *CH_3OH$	$C_1O_1C_1B^3_{O_1C_1}$	-0.18
93	$*CO_2 \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOO} \xrightarrow{+(H^+ + e^-)} \mathbf{*HCOOH} \xrightarrow[-*OH]{+(H^+ + e^-)} *CH_2O$		

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Index	Reaction path	Path name	U_{min} (V)
	$\xrightarrow{+(H^+ + e^-)}$ *CH_3O $\xrightarrow{+(H^+ + e^-)}$ *CH_3OH	$C_1O_1C_1B^3_{C_1O_1}$	-0.18
94	*CO_2 $\xrightarrow{+(H^+ + e^-)}$ *HCOO $\xrightarrow{+(H^+ + e^-)}$ **HCOOH** $\xrightarrow[-\,*OH]{+(H^+ + e^-)}$ ***HCOH**		
	$\xrightarrow{+(H^+ + e^-)}$ *CH_2OH $\xrightarrow{+(H^+ + e^-)}$ *CH_3OH	$C_1O_2B^3_{C_2}$	-0.87
95	*CO_2 $\xrightarrow{+(H^+ + e^-)}$ *HCOO $\xrightarrow{+(H^+ + e^-)}$ *HCOOH $\xrightarrow[-\,*OH]{}$ ***CHO**		
	$\xrightarrow{+(H^+ + e^-)}$ **$*CH_2O$** $\xrightarrow{+(H^+ + e^-)}$ *CH_2OH $\xrightarrow{+(H^+ + e^-)}$ *CH_3OH	$C_1O_1B^1_{C_1O_1C_1}$	-0.81
96	*CO_2 $\xrightarrow{+(H^+ + e^-)}$ *HCOO $\xrightarrow{+(H^+ + e^-)}$ *HCOOH $\xrightarrow[-\,*OH]{}$ ***CHO**		
	$\xrightarrow{+(H^+ + e^-)}$ **$*CH_2O$** $\xrightarrow{+(H^+ + e^-)}$ *CH_3O $\xrightarrow{+(H^+ + e^-)}$ *CH_3OH	$C_1O_1B^1_{C_2O_1}$	-0.81
97	*CO_2 $\xrightarrow{+(H^+ + e^-)}$ *HCOO $\xrightarrow{+(H^+ + e^-)}$ *HCOOH $\xrightarrow[-\,*OH]{}$ ***CHO**		
	$\xrightarrow{+(H^+ + e^-)}$ ***HCOH** $\xrightarrow{+(H^+ + e^-)}$ *CH_2OH $\xrightarrow{+(H^+ + e^-)}$ *CH_3OH	$C_1O_1B^1_{O_1C_2}$	-1.78
98	*CO_2 $\xrightarrow{+(H^+ + e^-)}$ **HCOO** $\xrightarrow{+(H^+ + e^-)}$ **$*OCH_2O$** $\xrightarrow{+(H^+ + e^-)}$ *OCH_2OH		
	$\xrightarrow{+(H^+ + e^-)}$ *$HOCH_2OH$ $\xrightarrow[-\,*OH]{+(H^+ + e^-)}$ *CH_3OH	$C_2O_2C_1B^3$	-1.01
99	*CO_2 $\xrightarrow{+(H^+ + e^-)}$ **HCOO** $\xrightarrow{+(H^+ + e^-)}$ **$*OCH_2O$** $\xrightarrow{+(H^+ + e^-)}$ *OCH_2OH		
	$\xrightarrow{+(H^+ + e^-)}$ *$HOCH_2OH$ $\xrightarrow[-\,*OH]{}$ *CH_2OH $\xrightarrow{+(H^+ + e^-)}$ *CH_3OH	$C_2O_2B^1_{C_1}$	-1.01
100	*CO_2 $\xrightarrow{+(H^+ + e^-)}$ **HCOO** $\xrightarrow{+(H^+ + e^-)}$ **$*OCH_2O$** $\xrightarrow{+(H^+ + e^-)}$ *OCH_2OH		
	$\xrightarrow[-\,*OH]{+(H^+ + e^-)}$ *CH_2OH $\xrightarrow{+(H^+ + e^-)}$ *CH_3OH	$C_2O_2B^3_{C_1}$	-1.01
101	*CO_2 $\xrightarrow{+(H^+ + e^-)}$ **HCOO** $\xrightarrow{+(H^+ + e^-)}$ **$*OCH_2O$** $\xrightarrow{+(H^+ + e^-)}$ *OCH_2OH		
	$\xrightarrow[-\,*OH]{+(H^+ + e^-)}$ *CH_3O $\xrightarrow{+(H^+ + e^-)}$ *CH_3OH	$C_2O_1C_1B^3_{O_1}$	-1.01
102	*CO_2 $\xrightarrow{+(H^+ + e^-)}$ **HCOO** $\xrightarrow{+(H^+ + e^-)}$ **$*OCH_2O$** $\xrightarrow{+(H^+ + e^-)}$ *OCH_2OH		
	$\xrightarrow[-\,*OH]{}$ *CH_2O $\xrightarrow{+(H^+ + e^-)}$ *CH_2OH $\xrightarrow{+(H^+ + e^-)}$ *CH_3OH	$C_2O_1B^1_{O_1C_1}$	-1.01
103	*CO_2 $\xrightarrow{+(H^+ + e^-)}$ **HCOO** $\xrightarrow{+(H^+ + e^-)}$ **$*OCH_2O$** $\xrightarrow{+(H^+ + e^-)}$ *OCH_2OH		
	$\xrightarrow[-\,*OH]{}$ *CH_2O $\xrightarrow{+(H^+ + e^-)}$ *CH_3O $\xrightarrow{+(H^+ + e^-)}$ *CH_3OH	$C_2O_1B^1_{C_1O_1}$	-1.01
104	*CO_2 $\xrightarrow{+(H^+ + e^-)}$ **HCOO** $\xrightarrow{+(H^+ + e^-)}$ **$*OCH_2O$** $\xrightarrow[-\,*OH]{+(H^+ + e^-)}$ *CH_2O		
	$\xrightarrow{+(H^+ + e^-)}$ *CH_2OH $\xrightarrow{+(H^+ + e^-)}$ *CH_3OH	$C_2O_1B^3_{O_1C_1}$	-1.01
105	*CO_2 $\xrightarrow{+(H^+ + e^-)}$ **HCOO** $\xrightarrow{+(H^+ + e^-)}$ **$*OCH_2O$** $\xrightarrow[-\,*OH]{+(H^+ + e^-)}$ *CH_2O		
	$\xrightarrow{+(H^+ + e^-)}$ *CH_3O $\xrightarrow{+(H^+ + e^-)}$ *CH_3OH	$C_2O_1B^3_{C_1O_1}$	-1.01
106	*CO_2 $\xrightarrow{+(H^+ + e^-)}$ *HCOO $\xrightarrow[-\,*OH]{+(H^+ + e^-)}$ ***CHO** $\xrightarrow{+(H^+ + e^-)}$ **$*CH_2O$**		
	$\xrightarrow{+(H^+ + e^-)}$ *CH_2OH $\xrightarrow{+(H^+ + e^-)}$ *CH_3OH	$C_1O_1B^3_{C_1O_1C_1}$	-0.81
107	*CO_2 $\xrightarrow{+(H^+ + e^-)}$ *HCOO $\xrightarrow[-\,*OH]{+(H^+ + e^-)}$ ***CHO** $\xrightarrow{+(H^+ + e^-)}$ **$*CH_2O$**		
	$\xrightarrow{+(H^+ + e^-)}$ *CH_3O $\xrightarrow{+(H^+ + e^-)}$ *CH_3OH	$C_1O_1B^3_{C_2O_1}$	-0.81
108	*CO_2 $\xrightarrow{+(H^+ + e^-)}$ *HCOO $\xrightarrow[-\,*OH]{+(H^+ + e^-)}$ ***CHO** $\xrightarrow{+(H^+ + e^-)}$ ***HCOH**		
	$\xrightarrow{+(H^+ + e^-)}$ *CH_2OH $\xrightarrow{+(H^+ + e^-)}$ *CH_3OH	$C_1O_1B^3_{O_1C_2}$	-1.78
109	**$*CO_2$** $\xrightarrow[-\,*OH]{+(H^+ + e^-)}$ ***CO** $\xrightarrow{+(H^+ + e^-)}$ *CHO $\xrightarrow{+(H^+ + e^-)}$ *CH_2O		
	$\xrightarrow{+(H^+ + e^-)}$ *CH_2OH $\xrightarrow{+(H^+ + e^-)}$ *CH_3OH	$O_1B^3_{C_2O_1C_1}$	-1.20

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Index	Reaction path	Path name	U_{min} (V)
110	$\mathbf{*CO_2} \xrightarrow[-\,*OH]{+\,(H^+ + e^-)} \mathbf{*CO} \xrightarrow{+\,(H^+ + e^-)} *CHO \xrightarrow{+\,(H^+ + e^-)} *CH_2O \xrightarrow{+\,(H^+ + e^-)} *CH_3O \xrightarrow{+\,(H^+ + e^-)} *CH_3OH$	$o_1 B^3_{C_3O_1}$	-1.20
111	$*CO_2 \xrightarrow[-\,*OH]{+\,(H^+ + e^-)} *CO \xrightarrow{+\,(H^+ + e^-)} \mathbf{*CHO} \xrightarrow{+\,(H^+ + e^-)} \mathbf{*HCOH} \xrightarrow{+\,(H^+ + e^-)} *CH_2OH \xrightarrow{+\,(H^+ + e^-)} *CH_3OH$	$o_1 B^3_{C_1O_1C_2}$	-1.78
112	$\mathbf{*CO_2} \xrightarrow[-\,*OH]{+\,(H^+ + e^-)} \mathbf{*CO} \xrightarrow{+\,(H^+ + e^-)} *COH \xrightarrow{+\,(H^+ + e^-)} *HCOH \xrightarrow{+\,(H^+ + e^-)} *CH_2OH \xrightarrow{+\,(H^+ + e^-)} *CH_3OH$	$o_1 B^3_{O_1C_3}$	-1.20
113	$*CO_2 \xrightarrow{+\,(H^+ + e^-)} \mathbf{*COOH} \xrightarrow{+\,(H^+ + e^-)} \mathbf{*HCOOH} \xrightarrow{+\,(H^+ + e^-)} *OCH_2OH \xrightarrow[-\,*O]{+\,(H^+ + e^-)} *CH_3OH$	$o_1 C_3 C^3$	-0.95
114	$*CO_2 \xrightarrow{+\,(H^+ + e^-)} \mathbf{*COOH} \xrightarrow{+\,(H^+ + e^-)} \mathbf{*HCOOH} \xrightarrow{+\,(H^+ + e^-)} *OCH_2OH \xrightarrow[-\,*O]{} *CH_2OH \xrightarrow{+\,(H^+ + e^-)} *CH_3OH$	$o_1 C_2 C^1_{C_1}$	-0.95
115	$*CO_2 \xrightarrow{+\,(H^+ + e^-)} \mathbf{*COOH} \xrightarrow{+\,(H^+ + e^-)} \mathbf{*HCOOH} \xrightarrow[-\,*O]{+\,(H^+ + e^-)} *CH_2OH \xrightarrow{+\,(H^+ + e^-)} *CH_3OH$	$o_1 C_2 C^3_{C_1}$	-0.95
116	$*CO_2 \xrightarrow{+\,(H^+ + e^-)} *COOH \xrightarrow{+\,(H^+ + e^-)} \mathbf{*HCOOH} \xrightarrow[-\,*O]{} \mathbf{*HCOH} \xrightarrow{+\,(H^+ + e^-)} *CH_2OH \xrightarrow{+\,(H^+ + e^-)} *CH_3OH$	$o_1 C_1 C^1_{C_2}$	-1.41
117	$*CO_2 \xrightarrow{+\,(H^+ + e^-)} *COOH \xrightarrow[-\,*O]{+\,(H^+ + e^-)} \mathbf{*HCOH} \xrightarrow{+\,(H^+ + e^-)} *CH_2OH \xrightarrow{+\,(H^+ + e^-)} *CH_3OH$	$o_1 C_1 C^3_{C_2}$	-2.36
118	$*CO_2 \xrightarrow{+\,(H^+ + e^-)} \mathbf{*COOH} \xrightarrow[-\,*O]{} \mathbf{*COH} \xrightarrow{+\,(H^+ + e^-)} *HCOH \xrightarrow{+\,(H^+ + e^-)} *CH_2OH \xrightarrow{+\,(H^+ + e^-)} *CH_3OH$	$o_1 C^1_{C_3}$	-2.06
119	$\mathbf{*CO_2} \xrightarrow{+\,(H^+ + e^-)} \mathbf{*HCOO} \xrightarrow{+\,(H^+ + e^-)} *HCOOH \xrightarrow{+\,(H^+ + e^-)} *OCH_2OH \xrightarrow[-\,*O]{+\,(H^+ + e^-)} *CH_3OH$	$C_1 O_1 C_2 C^3$	-0.18
120	$\mathbf{*CO_2} \xrightarrow{+\,(H^+ + e^-)} \mathbf{*HCOO} \xrightarrow{+\,(H^+ + e^-)} *HCOOH \xrightarrow{+\,(H^+ + e^-)} *OCH_2OH \xrightarrow[-\,*O]{} *CH_2OH \xrightarrow{+\,(H^+ + e^-)} *CH_3OH$	$C_1 O_1 C_1 C^1_{C_1}$	-0.18
121	$\mathbf{*CO_2} \xrightarrow{+\,(H^+ + e^-)} \mathbf{*HCOO} \xrightarrow{+\,(H^+ + e^-)} *HCOOH \xrightarrow[-\,*O]{+\,(H^+ + e^-)} *CH_2OH \xrightarrow{+\,(H^+ + e^-)} *CH_3OH$	$C_1 O_1 C_1 C^3_{C_1}$	-0.18
122	$*CO_2 \xrightarrow{+\,(H^+ + e^-)} *HCOO \xrightarrow{+\,(H^+ + e^-)} \mathbf{*HCOOH} \xrightarrow[-\,*O]{} \mathbf{*HCOH} \xrightarrow{+\,(H^+ + e^-)} *CH_2OH \xrightarrow{+\,(H^+ + e^-)} *CH_3OH$	$C_1 O_1 C^1_{C_2}$	-1.41
123	$*CO_2 \xrightarrow{+\,(H^+ + e^-)} \mathbf{*HCOO} \xrightarrow{+\,(H^+ + e^-)} \mathbf{*OCH_2O} \xrightarrow{+\,(H^+ + e^-)} *OCH_2OH \xrightarrow[-\,*O]{+\,(H^+ + e^-)} *CH_3OH$	$C_2 O_1 C_1 C^3$	-1.01
124	$*CO_2 \xrightarrow{+\,(H^+ + e^-)} \mathbf{*HCOO} \xrightarrow{+\,(H^+ + e^-)} \mathbf{*OCH_2O} \xrightarrow{+\,(H^+ + e^-)} *OCH_2OH \xrightarrow[-\,*O]{} *CH_2OH \xrightarrow{+\,(H^+ + e^-)} *CH_3OH$	$C_2 O_1 C^1_{C_1}$	-1.01
125	$*CO_2 \xrightarrow{+\,(H^+ + e^-)} \mathbf{*HCOO} \xrightarrow{+\,(H^+ + e^-)} \mathbf{*OCH_2O} \xrightarrow[-\,*O]{+\,(H^+ + e^-)} *CH_3O \xrightarrow{+\,(H^+ + e^-)} *CH_3OH$	$C_3 C^3_{O_1}$	-1.01
126	$*CO_2 \xrightarrow{+\,(H^+ + e^-)} \mathbf{*HCOO} \xrightarrow{+\,(H^+ + e^-)} \mathbf{*OCH_2O} \xrightarrow[-\,*O]{} *CH_2O$		

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Index	Reaction path	Path name	U_{min} (V)
	$\xrightarrow{+(H^+ + e^-)}$ *CH_2OH $\xrightarrow{+(H^+ + e^-)}$ *CH_3OH	$_{C_2}C^1_{O_1C_1}$	-1.01
127	*CO_2 $\xrightarrow{+(H^+ + e^-)}$ **$HCOO$** $\xrightarrow{+(H^+ + e^-)}$ **OCH_2O** $\xrightarrow[-*O]{}$ *CH_2O		
	$\xrightarrow{+(H^+ + e^-)}$ *CH_3O $\xrightarrow{+(H^+ + e^-)}$ *CH_3OH	$_{C_2}C^1_{C_1O_1}$	-1.01
128	*CO_2 $\xrightarrow{+(H^+ + e^-)}$ **$HCOO$** $\xrightarrow[-*O]{+(H^+ + e^-)}$ **CH_2O** $\xrightarrow{+(H^+ + e^-)}$ *CH_2OH		
	$\xrightarrow{+(H^+ + e^-)}$ *CH_3OH	$_{C_2}C^3_{O_1C_1}$	-0.45
129	*CO_2 $\xrightarrow{+(H^+ + e^-)}$ **$HCOO$** $\xrightarrow[-*O]{+(H^+ + e^-)}$ **CH_2O** $\xrightarrow{+(H^+ + e^-)}$ *CH_3O		
	$\xrightarrow{+(H^+ + e^-)}$ *CH_3OH	$_{C_2}C^3_{C_1O_1}$	-0.45
130	*CO_2 $\xrightarrow{+(H^+ + e^-)}$ *$HCOO$ $\xrightarrow[-*O]{}$ **CHO** $\xrightarrow{+(H^+ + e^-)}$ **CH_2O**		
	$\xrightarrow{+(H^+ + e^-)}$ *CH_2OH $\xrightarrow{+(H^+ + e^-)}$ *CH_3OH	$_{C_1}C^1_{C_1O_1C_1}$	-0.81
131	*CO_2 $\xrightarrow{+(H^+ + e^-)}$ *$HCOO$ $\xrightarrow[-*O]{}$ **CHO** $\xrightarrow{+(H^+ + e^-)}$ **CH_2O**		
	$\xrightarrow{+(H^+ + e^-)}$ *CH_3O $\xrightarrow{+(H^+ + e^-)}$ *CH_3OH	$_{C_1}C^1_{C_2O_1}$	-0.81
132	*CO_2 $\xrightarrow{+(H^+ + e^-)}$ *$HCOO$ $\xrightarrow[-*O]{}$ **CHO** $\xrightarrow{+(H^+ + e^-)}$ **$HCOH$**		
	$\xrightarrow{+(H^+ + e^-)}$ *CH_2OH $\xrightarrow{+(H^+ + e^-)}$ *CH_3OH	$_{C_1}C^1_{O_1C_2}$	-1.78
133	*CO_2 $\xrightarrow[-*O]{+(H^+ + e^-)}$ **CHO** $\xrightarrow{+(H^+ + e^-)}$ **CH_2O** $\xrightarrow{+(H^+ + e^-)}$ *CH_2OH		
	$\xrightarrow{+(H^+ + e^-)}$ *CH_3OH	$_{C_1}C^3_{C_1O_1C_1}$	-0.81
134	*CO_2 $\xrightarrow[-*O]{+(H^+ + e^-)}$ **CHO** $\xrightarrow{+(H^+ + e^-)}$ **CH_2O** $\xrightarrow{+(H^+ + e^-)}$ *CH_3O		
	$\xrightarrow{+(H^+ + e^-)}$ *CH_3OH	$_{C_1}C^3_{C_2O_1}$	-0.81
135	*CO_2 $\xrightarrow[-*O]{+(H^+ + e^-)}$ **CHO** $\xrightarrow{+(H^+ + e^-)}$ **$HCOH$** $\xrightarrow{+(H^+ + e^-)}$ *CH_2OH		
	$\xrightarrow{+(H^+ + e^-)}$ *CH_3OH	$_{C_1}C^3_{O_1C_2}$	-1.78
136	**CO_2** $\xrightarrow[-*O]{}$ **CO** $\xrightarrow{+(H^+ + e^-)}$ *CHO $\xrightarrow{+(H^+ + e^-)}$ *CH_2O		
	$\xrightarrow{+(H^+ + e^-)}$ *CH_2OH $\xrightarrow{+(H^+ + e^-)}$ *CH_3OH	$C^1_{C_2O_1C_1}$	-1.73
137	**CO_2** $\xrightarrow[-*O]{}$ **CO** $\xrightarrow{+(H^+ + e^-)}$ *CHO $\xrightarrow{+(H^+ + e^-)}$ *CH_2O		
	$\xrightarrow{+(H^+ + e^-)}$ *CH_3O $\xrightarrow{+(H^+ + e^-)}$ *CH_3OH	$C^1_{C_3O_1}$	-1.73
138	*CO_2 $\xrightarrow[-*O]{}$ *CO $\xrightarrow{+(H^+ + e^-)}$ **CHO** $\xrightarrow{+(H^+ + e^-)}$ **$HCOH$**		
	$\xrightarrow{+(H^+ + e^-)}$ *CH_2OH $\xrightarrow{+(H^+ + e^-)}$ *CH_3OH	$C^1_{C_1O_1C_2}$	-1.78
139	**CO_2** $\xrightarrow[-*O]{}$ **CO** $\xrightarrow{+(H^+ + e^-)}$ *COH $\xrightarrow{+(H^+ + e^-)}$ *$HCOH$		
	$\xrightarrow{+(H^+ + e^-)}$ *CH_2OH $\xrightarrow{+(H^+ + e^-)}$ *CH_3OH	$C^1_{O_1C_3}$	-1.73

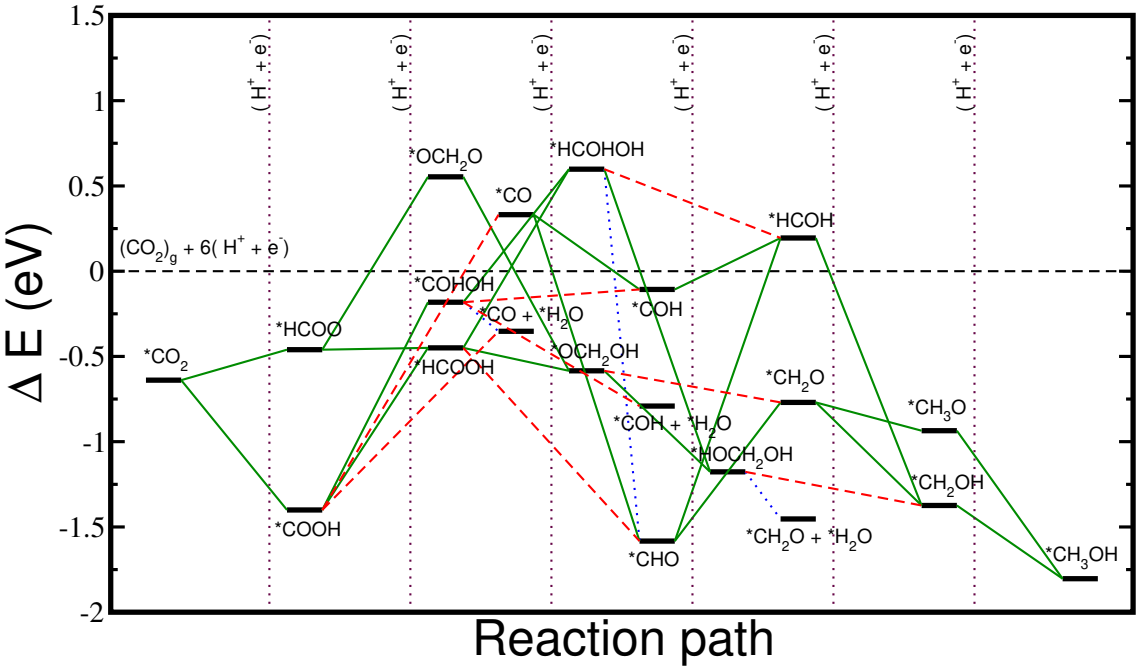

Figure S3: Mechanism type A: The free energy diagram of electrocatalytic reduction of CO_2 to CH_3OH on hematite surface at 0 V (RHE). The vertical lines represents the proton-electron transfer step. The colour code is same as Figure-S2.

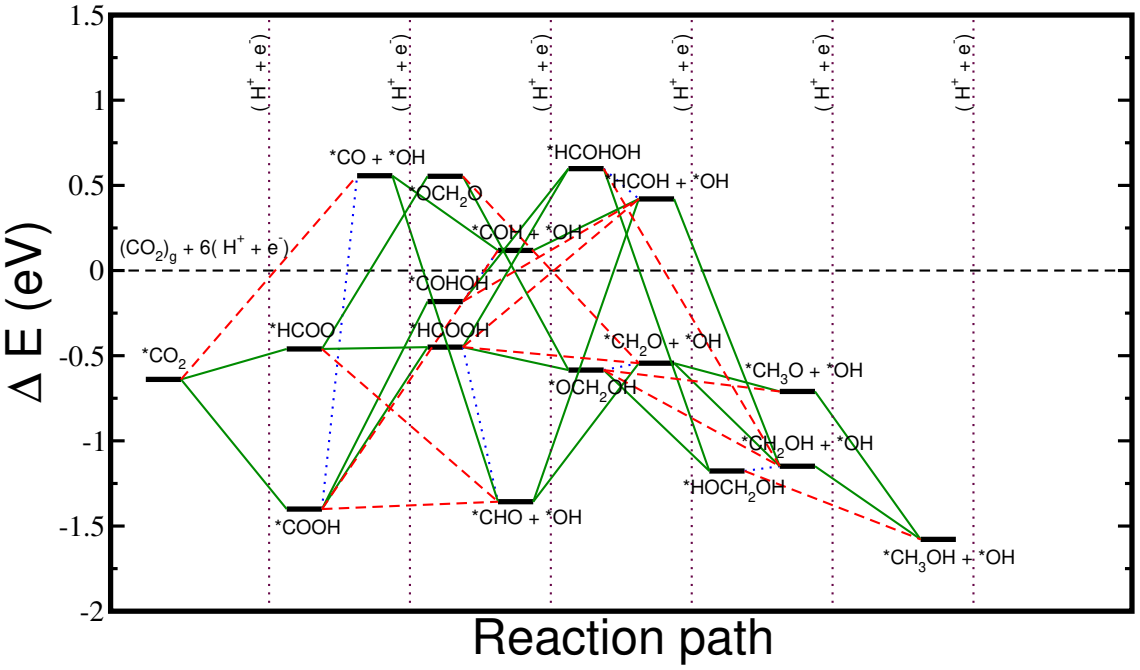

Figure S4: Mechanism type B: The free energy diagram of electrocatalytic reduction of CO_2 to CH_3OH on hematite surface at 0 V (RHE). The vertical lines represents the proton-electron transfer step. The colour code is same as Figure-S2.

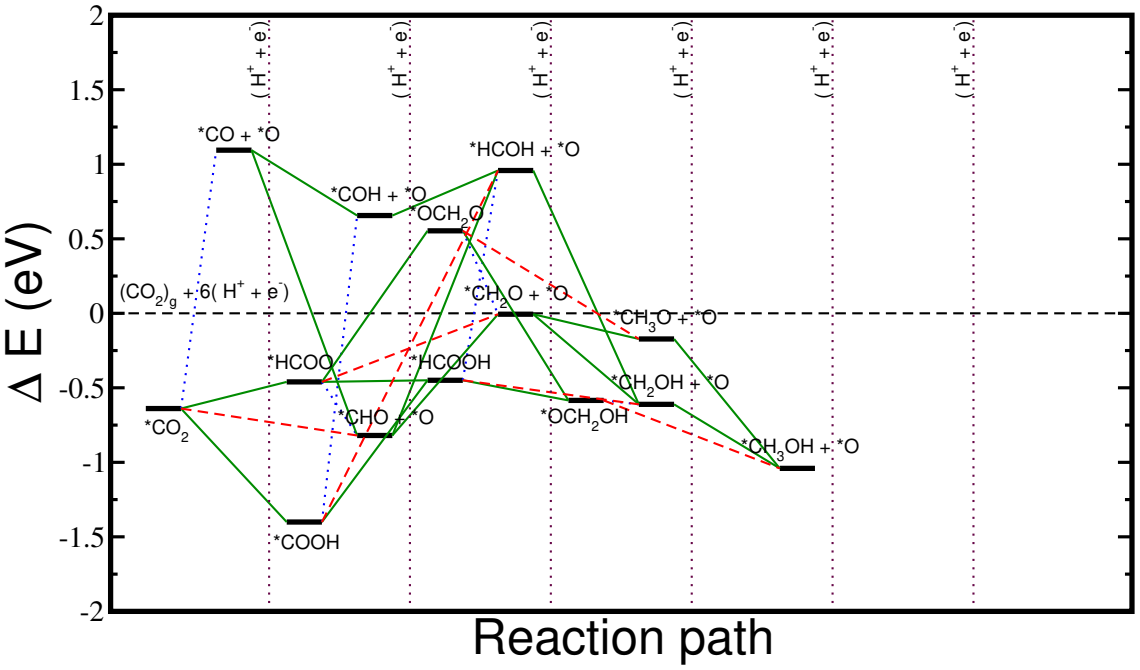

Figure S5: Mechanism type C: The free energy diagram of electrocatalytic reduction of CO_2 to CH_3OH on hematite surface at 0 V (RHE). The vertical lines represents the proton-electron transfer step. The colour code is same as Figure-S2.