

## Supplementary Information

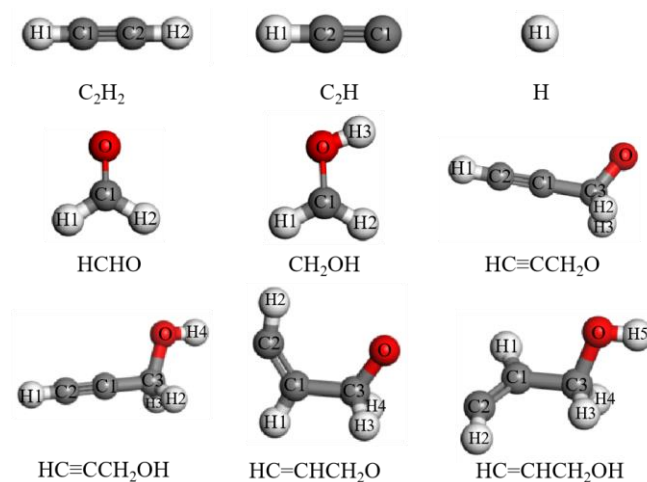


Figure S3. Optimized geometric configuration of the species

Table S1 Bader charge analysis of adsorbate before and after adsorption

$C_2H_2$			$C_2H$			H		
e	Before adsorption	After adsorption	e	Before adsorption	After adsorption	e	Before adsorption	After adsorption
H1	0.20	0.09	H1	0.28	0.30	H	0	-0.28
H2	0.14	0.09	C1	0.44	-0.01			
C1	-0.09	-0.30	C2	-0.72	-0.74			
C2	-0.25	-0.29						

Table S2 Bader charge analysis of adsorbate before and after adsorption

$C_2H_2$			$C_2H$			H		
e	Before adsorption	After adsorption	e	Before adsorption	After adsorption	e	Before adsorption	After adsorption
H1	0.20	0.09	H1	0.28	0.30	H	0	-0.28
H2	0.14	0.09	C1	0.44	-0.01			
C1	-0.09	-0.30	C2	-0.72	-0.74			
C2	-0.25	-0.29						

Table S3 Bader charge analysis of adsorbate before and after adsorption

HC≡CCH <sub>2</sub> O			HC≡CCH <sub>2</sub> OH			HC=CHCH <sub>2</sub> O			HC=CHCH <sub>2</sub> OH		
e	Before	After	e	Before	After	e	Before	After	e	Before	After
	adsorption	adsorption		adsorption	adsorption		adsorption	adsorption		adsorption	adsorption
H1	0.18	0.23	H1	0.24	0.09	H1	0.14	0.06	H1	0.10	0.05
H2	0.16	0.12	H2	0.04	0.12	H2	0.20	0.07	H2	0.15	0.06
H3	0.13	0.16	H3	0.13	0.08	H3	0.12	0.07	H3	0.06	0.09
C1	-0.38	-0.58	H4	0.66	0.65	H4	0.12	0.04	H4	0.05	0.06
C2	0.10	0.07	C1	-0.49	-0.23	C1	0.10	-0.28	H5	0.58	0.92
C3	0.51	0.42	C2	0.10	-0.33	C2	-0.28	-0.23	C1	0.04	-0.16
O	-0.69	-1.01	C3	0.46	0.32	C3	0.44	0.41	C2	-0.29	-0.27
			O	-1.14	-1.25	O	-0.86	-1.03	C3	0.40	0.33
									O	-1.08	-1.31

Table S4 Structural parameters of IS, TS and FS of acetylenyl by acetylene dehydrogenation

Geometric parameters (Å)	IS	TS	FS
d(C1-C2)	1.37	1.30	1.28
d(C1-H1)	1.10	1.40	3.22
d(C1-Cu1)	1.94	1.93	1.94
d(H1-Cu1)	2.68	1.58	1.61

Table S5 Structural parameters of IS, TS, and FS of acetylenyl addition with HCHO

Geometric parameters (Å)	IS	TS	FS
d(C1-C2)	1.28	1.29	1.28
d(C3-O1)	1.32	1.35	1.44
d(C1-C3)	2.93	1.98	1.47
d(C1-Cu1)	1.87	1.89	2.62
d(C3-Cu1)	1.93	2.17	1.88

Table S6 Structural parameters of IS, TS, and FS of HC≡CCH<sub>2</sub>O\* hydrogenation

Geometric parameters (Å)	IS	TS	FS
d(C1-C2)	1.28	1.38	1.39
d(C1-C3)	1.47	1.52	1.51
d(O1-H4)	4.19	1.54	0.98
d(O1-Cu)	1.88	2.01	2.10
d(H4-Cu)	1.51	1.55	3.45

Table S7 Structural parameters of IS, TS, and FS of acetylene and HCHO addition

Geometric parameters (Å)	IS	TS	FS
d(C1-C2)	1.37	1.36	1.39
d(C1-H1)	1.11	1.10	1.10
d(C3-O1)	1.34	1.38	1.45
d(C1-C3)	2.67	1.95	1.52
d(C1-Cu1)	1.92	1.96	2.66
d(C3-Cu1)	1.90	2.04	2.77

Table S8 Structural parameters of IS, TS, and FS of hydrogen transfer reaction

Geometric parameters (Å)	IS	TS	FS
d(C1-H1)	1.10	1.79	2.40
d(O1-H1)	2.60	1.98	0.99
d(H1-Cu1)	3.47	1.51	2.47

Table S9 Structural parameters of IS, TS, and FS of formaldehyde hydrogenation

Geometric parameters (Å)	IS	TS	FS
d(C1-O1)	1.32	1.41	1.45
d(O1-H3)	4.10	1.40	0.97

Table S10 Structural parameters of IS, TS, and FS of acetylenyl and CH<sub>2</sub>OH\* addition

Geometric parameters (Å)	IS	TS	FS
d(C1-C2)	1.28	1.30	1.39
d(C1-C3)	3.58	2.53	1.46
d(C1-Cu1)	1.95	1.80	1.93
d(C3-Cu1)	2.14	2.97	2.96
d(O1-Cu4)	2.66	2.02	2.18

Table S11 Structural parameters of IS, TS, and FS of acetylene and CH<sub>2</sub>OH\* addition

Geometric parameters (Å)	IS	TS	FS
d(C1-C2)	1.35	1.36	1.39
d(C1-H1)	1.16	1.10	1.10
d(C3-O1)	1.50	1.46	1.49
d(C1-C3)	3.14	2.20	1.50
d(C1-Cu1)	2.03	1.96	2.90
d(C3-Cu1)	2.17	2.00	3.07
d(O-Cu4)	2.68	2.04	2.10

Table S12 Structural parameters of IS, TS, and FS of HCCHCH<sub>2</sub>OH\* dehydrogenation

Geometric parameters (Å)	IS	TS	FS
d(C1-C2)	1.39	1.38	1.38
d(C1-H1)	1.10	1.93	4.60
d(C1-C3)	1.50	1.51	1.50
d(C1-Cu1)	2.90	1.87	1.93
d(H1-Cu1)	2.33	1.49	4.61

Table S13 Bader charge analysis of co-adsorption configuration of coupling reaction

e	C <sub>2</sub> H+HCHO	C <sub>2</sub> H <sub>2</sub> +HCHO	C <sub>2</sub> H+CH <sub>2</sub> OH	C <sub>2</sub> H <sub>2</sub> +CH <sub>2</sub> OH
H1	0.25	0.07	0.23	0.10
H2		0.07		0.07
C1	-0.17	-0.26	-0.21	-0.26
C2	-0.51	-0.40	-0.48	-0.38
H3	0.20	0.07	0.09	0.13
H4	0.20	0.10	0.08	0.13
H5			0.68	0.66
C3	0.39	0.49	0.03	-0.01
O1	-1.02	-1.05	-1.18	-1.14
Cu1	0.72	0.59	0.47	0.49
Cu2	0.48	0.47	0.49	0.50
Cu3	0.49	0.38	0.48	0.39
Cu4	0.52	0.54	0.36	0.38

Table S14 Bader charge analysis of adsorbate before and after adsorption

		HOCH <sub>2</sub> C≡C		HOCH <sub>2</sub> C≡CCH <sub>2</sub> O		HOCH <sub>2</sub> C≡CCH <sub>2</sub> OH		
e	Before	After	e	Before	After	e	Before	After
	adsorption	adsorption		adsorption	adsorption		adsorption	adsorption
C1	0.39	-0.06	H1	0.16	0.03	H1	0.03	0.09
C2	-0.61	-0.56	H2	0.13	0.03	H2	0.09	0.09
			C1	0.29	-0.35	H3	0.69	0.81
			C2	-0.64	-0.12	C1	0.13	-0.26
			C3	0.52	0.43	C2	-0.43	-0.23
			O1	-1.08	-0.99	C3	0.47	0.31
						O1	-1.17	-1.28

Table S15 Bader charge analysis of HOCH<sub>2</sub>C=CHCH<sub>2</sub>O\* and HOCH<sub>2</sub>C=CHCH<sub>2</sub>OH\* before and after adsorption

HOCH <sub>2</sub> C=CHCH <sub>2</sub> O			HOCH <sub>2</sub> C=CHCH <sub>2</sub> OH		
e	Before adsorption	After adsorption	e	Before adsorption	After adsorption
H1	0.10	0.06	H1	0.12	0.09
H2	0.07	0.05	H2	0.04	0.10
H3	0.07	0.08	H3	0.07	0.12
C1	-0.02	-0.28	H4	0.62	0.77
C2	-0.12	-0.17	C1	0.02	-0.25
C3	0.45	0.41	C2	-0.31	-0.16
O1	-0.70	-1.02	C3	0.44	0.29
			O1	-1.12	-1.17

Table S16 Structural parameters of IS, TS, and FS of propargyl alcohol dehydrogenation

Geometric parameters (Å)	IS	TS	FS
d(C1-C2)	1.38	1.30	1.29
d(C1-H1)	1.11	1.85	3.30
d(H1-Cu1)	2.63	1.55	1.61

Table S17 Structural parameters of IS, TS, and FS of HOCH<sub>2</sub>CC\* and HCHO addition

Geometric parameters (Å)	IS	TS	FS
d(C1-C2)	1.28	1.30	1.35
d(C1-C3)	2.89	1.94	1.49
d(C3-O1)	1.32	1.34	1.46
d(C1-Cu1)	1.87	1.90	2.06

Table S18 Structural parameters of IS, TS, and FS of HOCH<sub>2</sub>C≡CCH<sub>2</sub>O\* hydrogenation

Geometric parameters (Å)	IS	TS	FS
d(C1-C2)	1.35	1.39	1.39
d(C1-C3)	1.49	1.51	1.49
d(C3-O1)	1.47	1.44	1.46
d(O1-H3)	4.28	1.43	0.98
d(O1-Cu4)	1.86	2.02	2.08
d(H-Cu5)	1.56	1.64	3.57

Table S19 Structural parameters of IS, TS, and FS of propargyl alcohol addition with HCHO

Geometric parameters (Å)	IS	TS	FS
d(C1-C2)	1.37	1.36	1.39
d(C1-C3)	2.67	2.24	1.51
d(C3-O1)	1.34	1.33	1.44
d(C1-Cu1)	1.91	2.00	2.62
d(C3-Cu1)	1.90	2.77	2.78
d(O1-Cu4)	1.90	1.90	1.87

Table S20 Structural parameters of IS, TS, and FS of hydrogen transfer reaction

Geometric parameters (Å)	IS	TS	FS
d(C1-C2)	1.39	1.38	1.38
d(C1-H1)	1.10	1.45	2.76
d(O1-H1)	2.54	1.54	0.98
d(C1-Cu1)	2.62	1.94	1.92
d(H1-Cu1)	2.14	1.56	2.98

Table S21 Structural parameters of IS, TS, and FS of HOCH<sub>2</sub>C≡C\* and CH<sub>2</sub>OH\* addition

Geometric parameters (Å)	IS	TS	FS
d(C1-C2)	1.29	1.30	1.38
d(C1-C3)	3.58	2.55	1.50
d(C1-Cu1)	1.96	1.81	1.92
d(C3-Cu1)	2.14	3.01	2.95

Table S22 Structural parameters of IS, TS, and FS of propargyl alcohol addition with CH<sub>2</sub>OH\*

Geometric parameters (Å)	IS	TS	FS
d(C1-C3)	3.28	2.20	1.50
d(C3-O1)	1.47	1.46	1.49
d(C1-Cu1)	2.01	1.97	2.77
d(C3-Cu1)	2.20	2.00	3.00

Table S23 Structural parameters of IS, TS, and FS of HOCH<sub>2</sub>C=CHCH<sub>2</sub>OH\* dehydrogenation

Geometric parameters (Å)	IS	TS	FS
d(C1-C2)	1.39	1.38	1.38
d(C1-H1)	1.10	1.86	4.61
d(C1-C3)	1.50	1.50	1.50
d(H1-Cu1)	2.29	1.51	4.54
d(H1-Cu5)	2.82	2.13	1.56
d(C1-Cu1)	2.77	1.88	1.92
d(O1-Cu4)	2.10	2.02	2.13