Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supplementary Information

Ethylene Glycol Reforming on Pt(111): First-Principles Microkinetic Modeling in Vapor and Aqueous Phases

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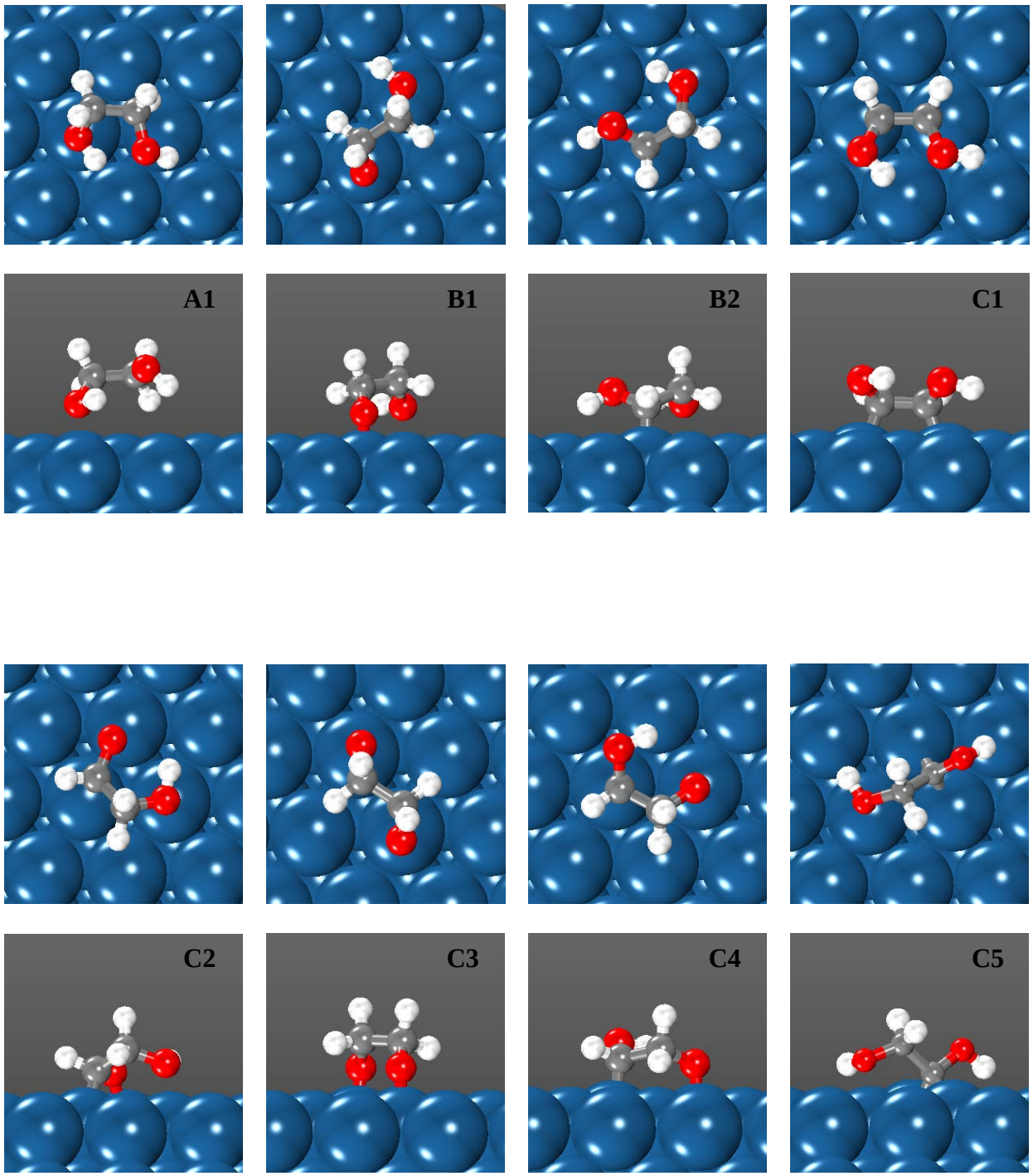
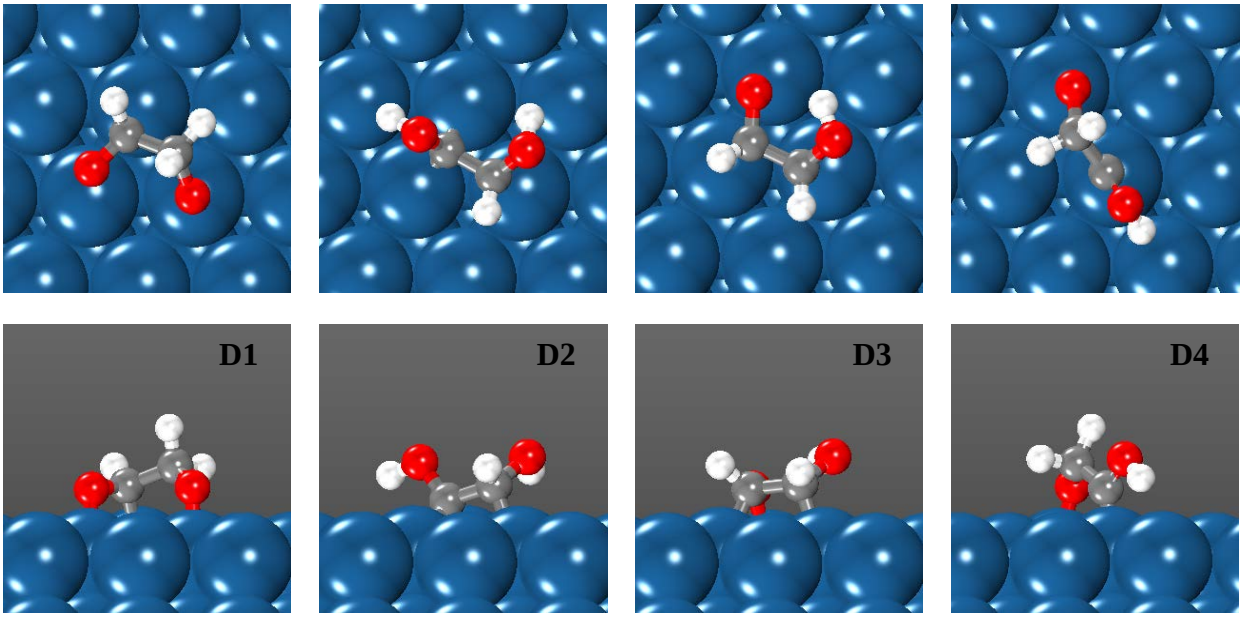
Table S1. Binding modes and number of occupied surface sites for all surface intermediates.

Fig. S1 ID	Surface Intermediate	Binding Mode	Number of Sites
A1	CH_2OHCH_2OH	O	2
B1	CH_2OCH_2OH	O	2
B2	$CHOHCH_2OH$	C	2
C1	CHOHCHOH	C, C	2
C2	$CHOCH_2OH$	C, O	3
C3	CH_2OCH_2O	O, O	2
C4	$CHOHCH_2O$	C, O	2
C5	$COHCH_2OH$	C_{bridge}	3
D1	$CHOCH_2O$	C, O, O	3
D2	COHCHOH	C, C_{bridge}	2
D3	CHOCHOH	C, C, O	3
D4	$COHCH_2O$	C, O	2
D5	$COCH_2OH$	C	2
E1	COCHOH	C, C	2
E2	$COCH_2O$	C, O	2
E3	CHOCHO	C, C, O, O	4
E4	COHCOH	C_{bridge}, C_{bridge}	2
E5	COHCHO	C_{bridge}, O	2
F1	COCHO	C, C, O	3
F2	COCOH	C, C_{bridge}	2
G1	COCO	C, C	2
H1	CH_3OH	O	1
I1	CH_3O	O	1
I2	CH_2OH	C	1
J1	CH_2O	C, O	2
J2	CHOH	C_{bridge}	1
K1	CHO	C	1
K2	COH	C_{fcc}	1
L1	CO	C_{fcc}	1
M1	H	H_{fcc}	1

Figure S1. Top and side views of most stable structures for all surface intermediates. Identification codes (side views) are listed in Table S1.

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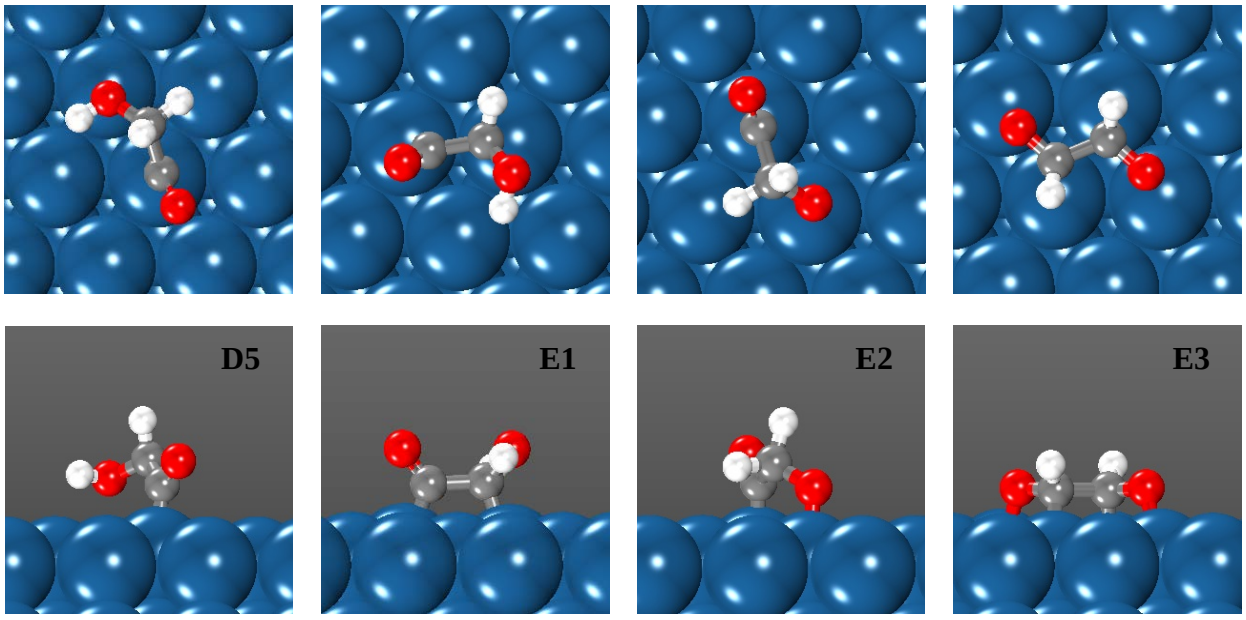
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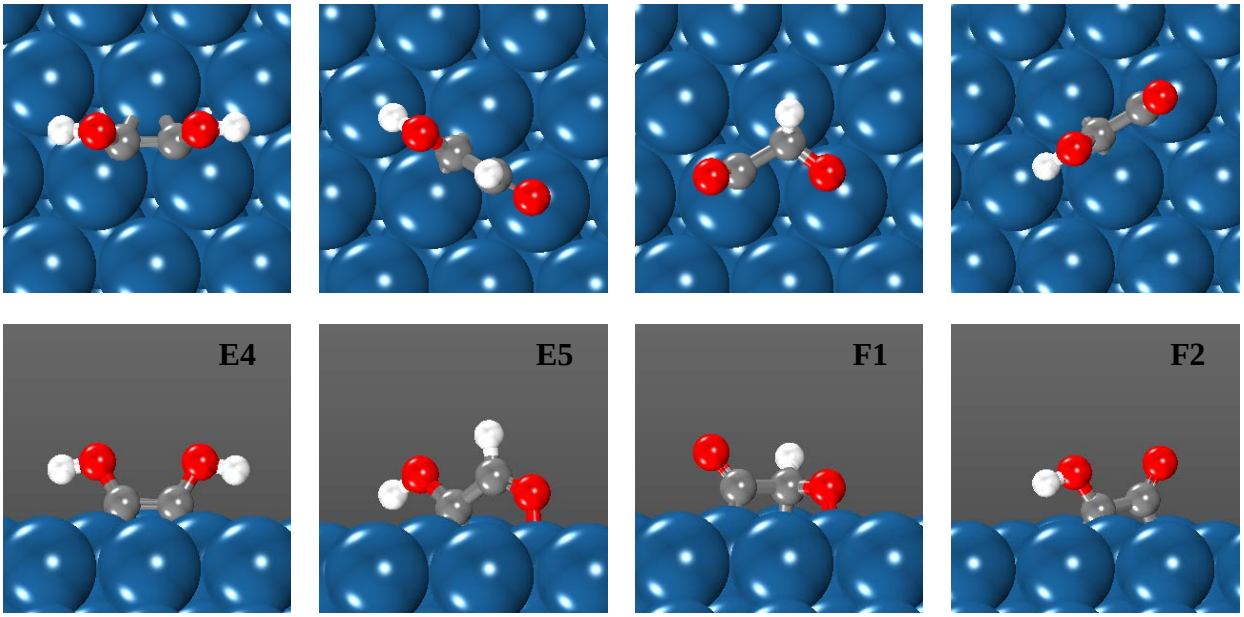
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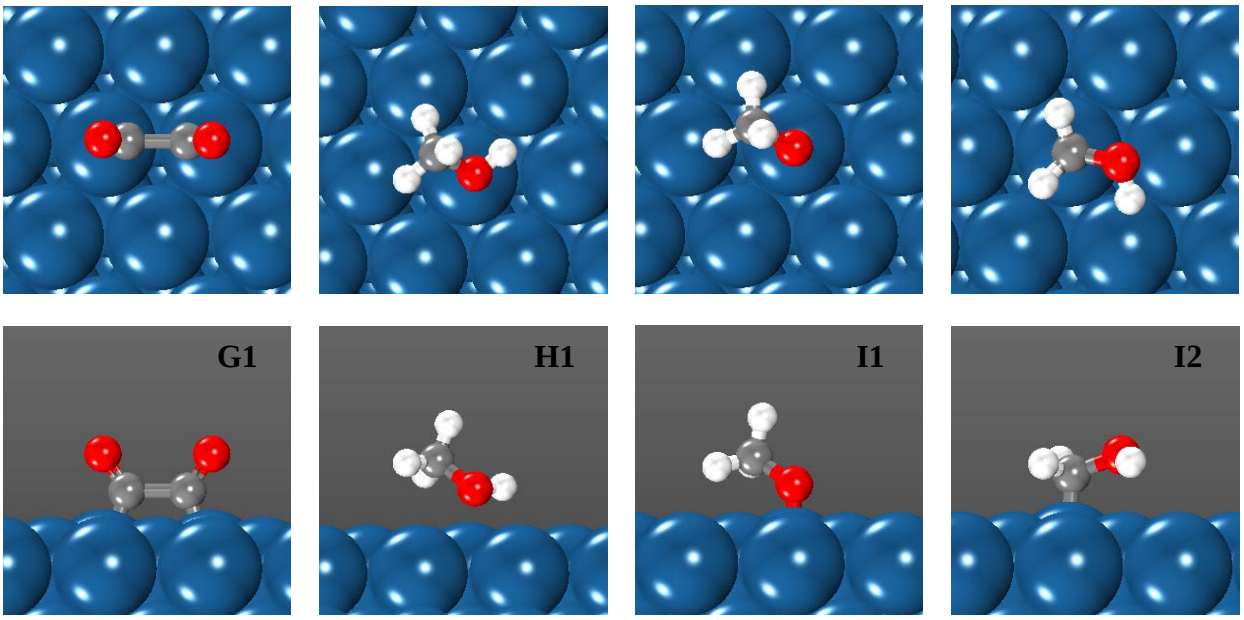
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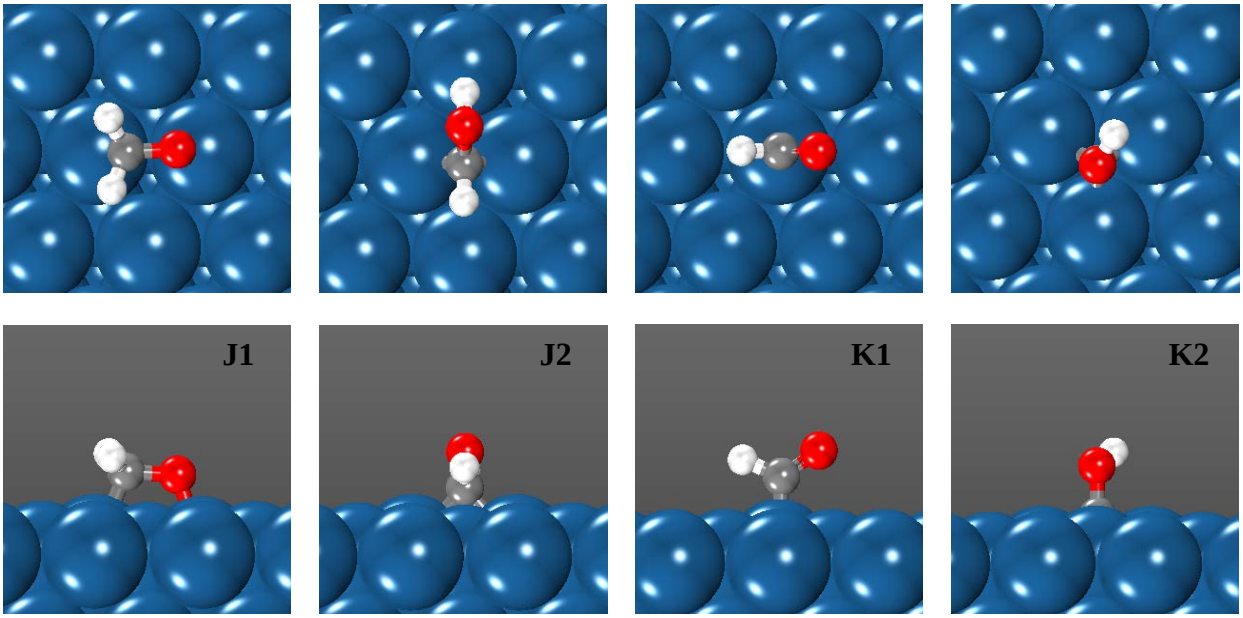
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K1
K2

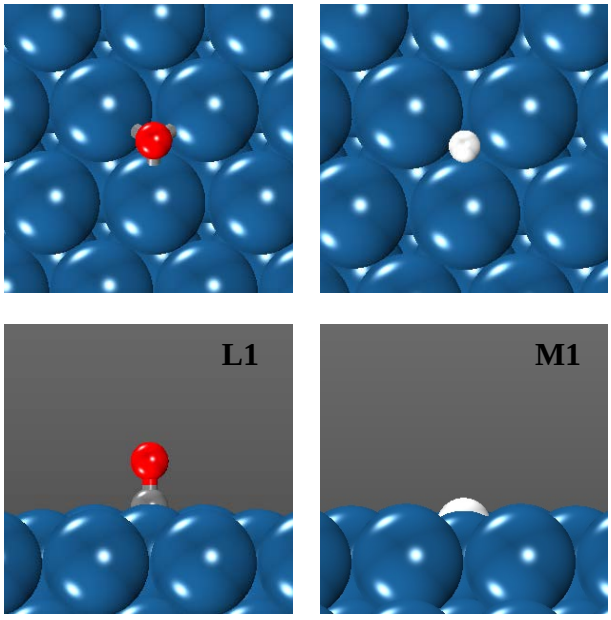

L1
M1

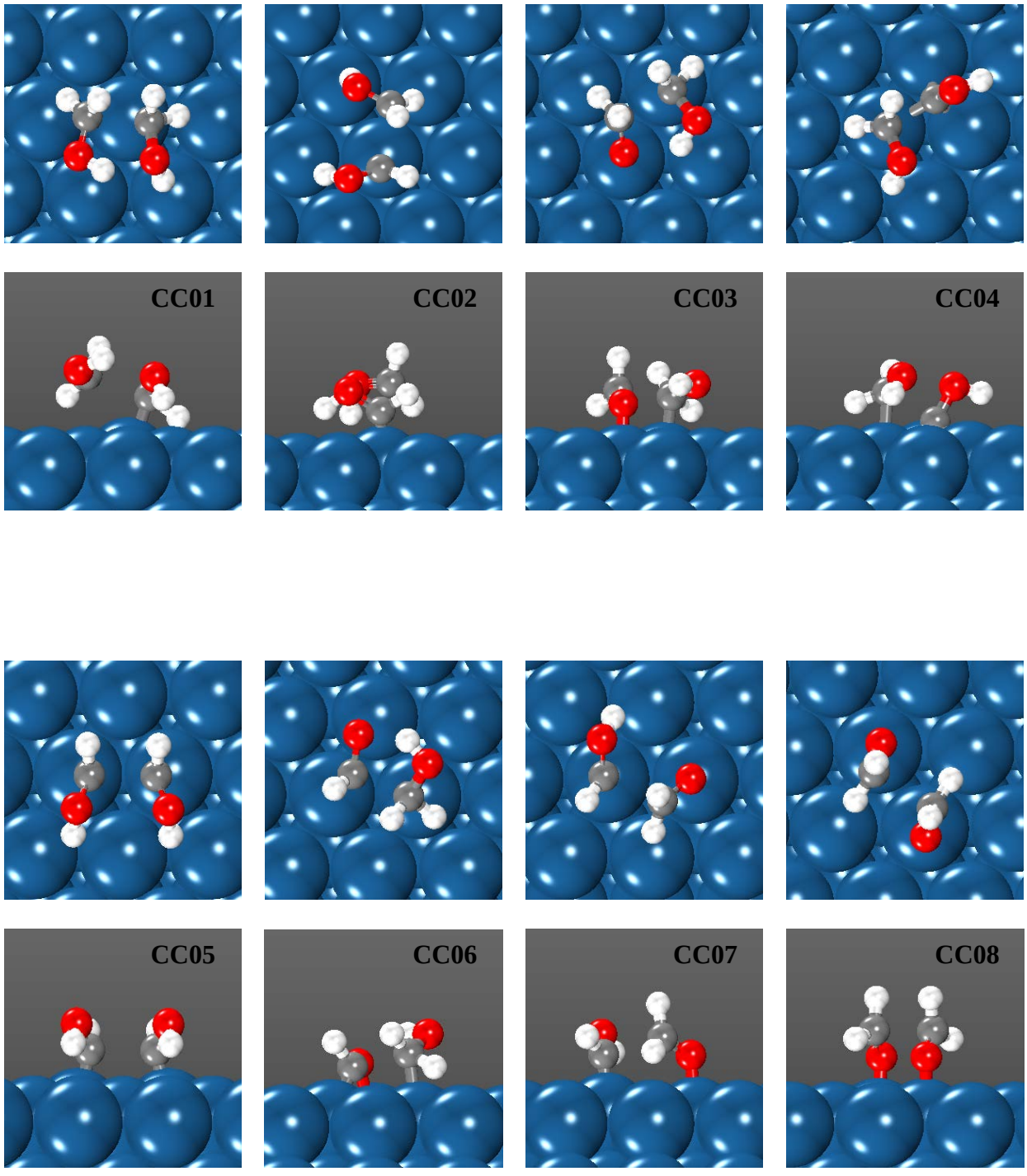
Table S2. Imaginary frequencies and transition state bond lengths for all surface reactions included in the microkinetic model.

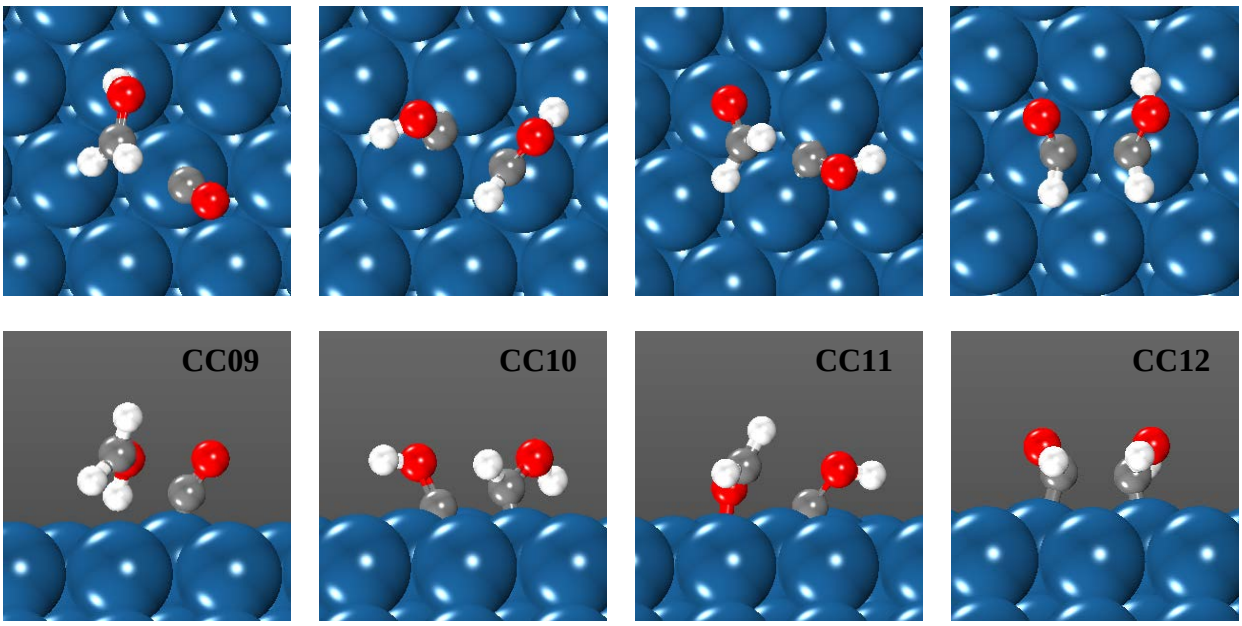
Fig. S2 ID	Reaction	$\nu\left(\mathrm{cm}^{-1}\right)$	TS Bond length (Å)
CC01	$CH_2OHCH_2OH** \rightarrow 2CH_2OH*$	493*i*	2.18
CC02	$CHOHCH_2OH** \rightarrow CHOH*+CH_2OH*$	281*i*	2.43
CC03	$CH_2OCH_2OH**+* \rightarrow CH_2O**+CH_2OH*$	686*i*	2.03
CC04	$COHCH_2OH*** \rightarrow COH*+CH_2OH*+*$	455*i*	2.09
CC05	$CHOHCHOH** \rightarrow 2CHOH*$	655*i*	2.11
CC06	$CHOCH_2OH*** \rightarrow CHO*+CH_2OH*+*$	680*i*	1.99
CC07	$CHOHCH_2O**+* \rightarrow CHOH*+CH_2O**$	474*i*	2.14
CC08	$CH_2OCH_2O**+2* \rightarrow 2CH_2O**$	344*i*	2.17
CC09	$COCH_2OH** \rightarrow CO*+CH_2OH*$	370*i*	2.38
CC10	$COHCHOH** \rightarrow COH*+CHOH*$	624*i*	2.11
CC11	$COHCH_2O**+* \rightarrow COH*+CH_2O**$	505*i*	2.20
CC12	$CHOCHOH*** \rightarrow CHO*+CHOH*+*$	747*i*	1.94
CC13	$CHOCH_2O*** \rightarrow CHO*+CH_2O**$	552*i*	2.02
CC14	$COCHOH** \rightarrow CO*+CHOH*$	567*i*	2.03
CC15	$COCH_2O**+* \rightarrow CO*+CH_2O**$	429*i*	2.09
CC16	$COHCOH** \rightarrow 2COH*$	268*i*	1.84
CC17	$COHCHO** \rightarrow COH*+CHO*$	568*i*	2.01
CC18	$CHOCHO**** \rightarrow 2CHO*+2*$	691*i*	1.77
CC19	$COCOH** \rightarrow CO*+COH*$	618*i*	1.96
CC20	$COCHO*** \rightarrow CO*+CHO*+*$	511*i*	1.84
CC21	$COCO** \rightarrow 2CO*$	423*i*	1.89
CH01	$CH_2OHCH_2OH**+* \rightarrow CHOHCH_2OH**+H*$	880*i*	1.48
CH02	$CHOHCH_2OH**+2* \rightarrow COHCH_2OH***+H*$	762*i*	1.44
CH03	$CHOHCH_2OH**+* \rightarrow CHOHCHOH**+H*$	570*i*	1.66
CH04	$CH_2OCH_2OH**+2* \rightarrow CHOCH_2OH***+H*$	546*i*	1.57
CH05	$CH_2OCH_2OH**+* \rightarrow CHOHCH_2O**+H*$	727*i*	1.66
CH06	$COHCH_2OH*** \rightarrow COHCHOH**+H*$	769*i*	1.54
CH07	$CHOHCHOH**+* \rightarrow COHCHOH**+H*$	775*i*	1.51
CH08	$CHOCH_2OH*** \rightarrow COCH_2OH**+H*$	475*i*	1.33
CH09	$CHOCH_2OH***+* \rightarrow CHOCHOH***+H*$	873*i*	1.52

Fig. S2 ID	Reaction	$\nu\left(\mathrm{cm}^{-1}\right)$	TS Bond length (Å)
CH10	$CHOHCH_2O{**}+{*} \rightarrow COHCH_2O{**}+H{*}$	970*i*	1.45
CH11	$CHOHCH_2O{**}+2{*} \rightarrow CHOCHOH{***}+H{*}$	611*i*	1.57
CH12	$CH_2OCH_2O{**}+2{*} \rightarrow CHOCH_2O{***}+H{*}$	594*i*	1.60
CH13	$COHCHOH{**}+{*} \rightarrow COHCOH{**}+H{*}$	1024*i*	1.43
CH14	$COCH_2OH{**}+{*} \rightarrow COCHOH{**}+H{*}$	697*i*	1.53
CH15	$CHOCHOH{***} \rightarrow COCHOH{**}+H{*}$	600*i*	1.45
CH16	$CHOCHOH{***} \rightarrow COHCHO{**}+H{*}$	739*i*	1.57
CH17	$COHCH_2O{**}+{*} \rightarrow COHCHO{**}+H{*}$	709*i*	1.53
CH18	$CHOCH_2O{***} \rightarrow COCH_2O{**}+H{*}$	200*i*	1.35
CH19	$CHOCH_2O{***}+2{*} \rightarrow CHOCHO{****}+H{*}$	582*i*	1.56
CH20	$COCHOH{**}+{*} \rightarrow COCOH{**}+H{*}$	826*i*	1.54
CH21	$COHCHO{**}+{*} \rightarrow COCOH{**}+H{*}$	262*i*	1.36
CH22	$COCH_2O{**}+2{*} \rightarrow COCHO{***}+H{*}$	677*i*	1.59
CH23	$CHOCHO{****} \rightarrow COCHO{***}+H{*}$	437*i*	1.39
CH24	$COCHO{***} \rightarrow COCO{**}+H{*}$	465*i*	1.39
CH25	$CH_3OH{*}+{*} \rightarrow CH_2OH{*}+H{*}$	798*i*	1.63
CH26	$CH_3O{*}+2{*} \rightarrow CH_2O{**}+H{*}$	604*i*	1.59
CH27	$CH_2OH{*}+{*} \rightarrow CHOH{*}+H{*}$	743*i*	1.66
CH28	$CH_2O{**} \rightarrow CHO{*}+H{*}$	156*i*	1.44
CH29	$CHOH{*}+{*} \rightarrow COH{*}+H{*}$	241*i*	1.51
CH30	$CHO{*}+{*} \rightarrow CO{*}+H{*}$	243*i*	1.60
OH01	$CH_2OHCH_2OH{**}+{*} \rightarrow CH_2OCH_2OH{**}+H{*}$	381*i*	1.36
OH02	$CH_2OCH_2OH{**}+{*} \rightarrow CH_2OCH_2O{**}+H{*}$	372*i*	1.69
OH03	$CHOHCH_2OH{**}+2{*} \rightarrow CHOCH_2OH{***}+H{*}$	290*i*	1.58
OH04	$CHOHCH_2OH{**}+{*} \rightarrow CHOHCH_2O{**}+H{*}$	990*i*	1.62
OH05	$CHOCH_2OH{***}+{*} \rightarrow CHOCH_2O{***}+H{*}$	677*i*	1.34
OH06	$CHOHCH_2O{**}+2{*} \rightarrow CHOCH_2O{***}+H{*}$	448*i*	1.57
OH07	$COHCH_2OH{***} \rightarrow COCH_2OH{**}+H{*}$	757*i*	1.35
OH08	$COHCH_2OH{***} \rightarrow COHCH_2O{**}+H{*}$	356*i*	1.70
OH09	$CHOHCHOH{**}+2{*} \rightarrow CHOCHOH{***}+H{*}$	420*i*	1.45
OH10	$COCH_2OH{**}+{*} \rightarrow COCH_2O{**}+H{*}$	396*i*	1.36
OH11	$COHCH_2O{**}+{*} \rightarrow COCH_2O{**}+H{*}$	1028*i*	1.44
OH12	$CHOCHOH{***}+2{*} \rightarrow CHOCHO{****}+H{*}$	391*i*	1.46

Fig. S2 ID	Reaction	$\nu\left(\mathrm{cm}^{-1}\right)$	TS Bond length (Å)
OH13	$\mathrm{COHCHOH}^{**}+{}^{*}\rightarrow\mathrm{COCHOH}^{**}+\mathrm{H}^{*}$	$1049i$	1.53
OH14	$\mathrm{COHCHOH}^{**}+{}^{*}\rightarrow\mathrm{COHCHO}^{**}+\mathrm{H}^{*}$	$210i$	1.57
OH15	$\mathrm{COCHOH}^{**}+2^{*}\rightarrow\mathrm{COCHO}^{***}+\mathrm{H}^{*}$	$829i$	1.46
OH16	$\mathrm{COHCHO}^{**}+2^{*}\rightarrow\mathrm{COCHO}^{***}+\mathrm{H}^{*}$	$1141i$	1.27
OH17	$\mathrm{COHCOH}^{**}+{}^{*}\rightarrow\mathrm{COCOH}^{**}+\mathrm{H}^{*}$	$921i$	1.34
OH18	$\mathrm{COCOH}^{**}+{}^{*}\rightarrow\mathrm{COCO}^{**}+\mathrm{H}^{*}$	$878i$	1.26
OH19	$\mathrm{CH_3OH}^{*}+{}^{*}\rightarrow\mathrm{CH_3O}^{*}+\mathrm{H}^{*}$	$293i$	1.71
OH20	$\mathrm{CH_2OH}^{*}+2^{*}\rightarrow\mathrm{CH_2O}^{**}+\mathrm{H}^{*}$	$555i$	1.57
OH21	$\mathrm{CHOH}^{*}+{}^{*}\rightarrow\mathrm{CHO}^{*}+\mathrm{H}^{*}$	$500i$	1.57
OH22	$\mathrm{COH}^{*}+{}^{*}\rightarrow\mathrm{CO}^{*}+\mathrm{H}^{*}$	$1517i$	1.31

Figure S2. Top and side views of transition state structures for all surface reactions. Identification codes (side views) are listed in Table S2.

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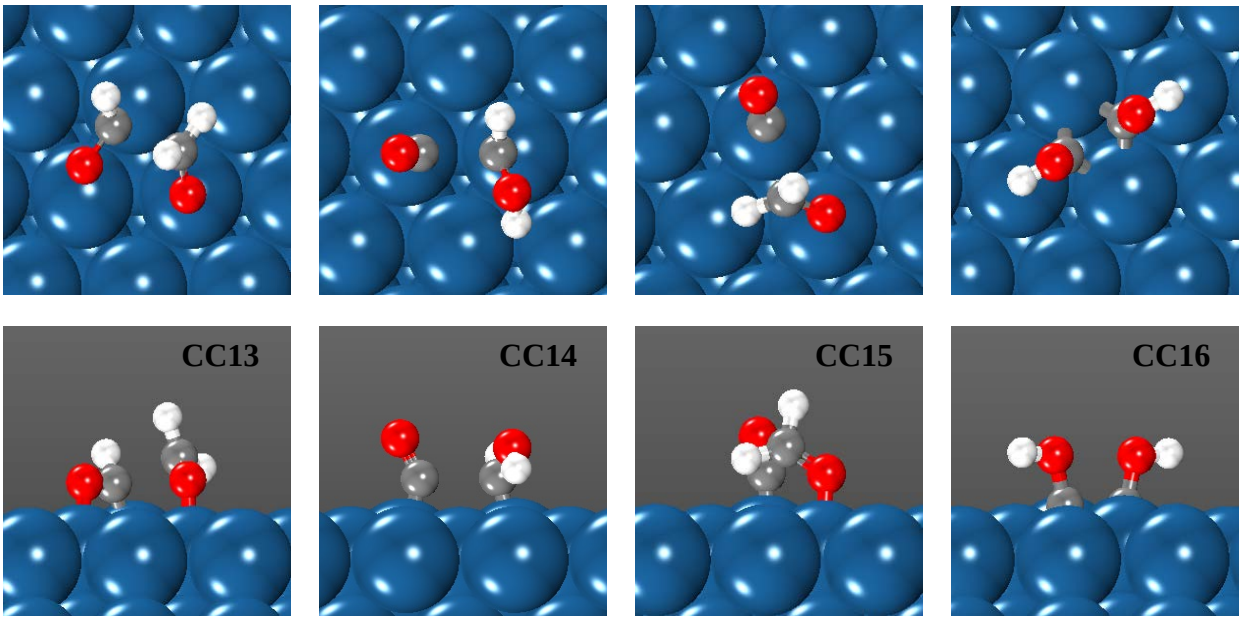
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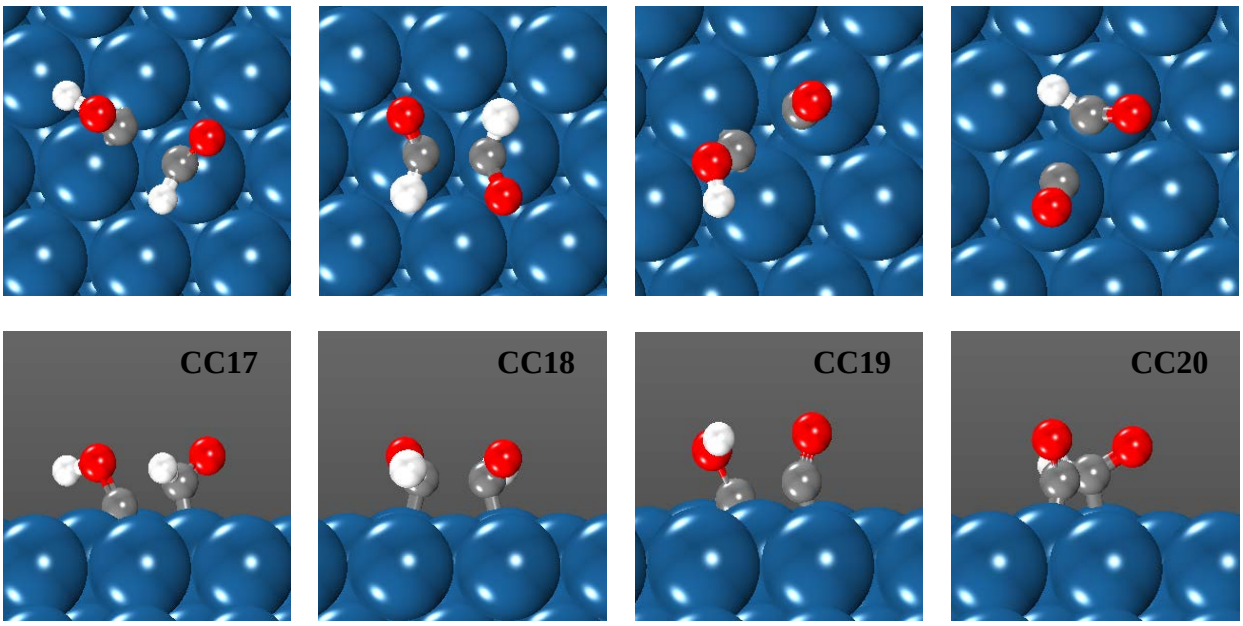
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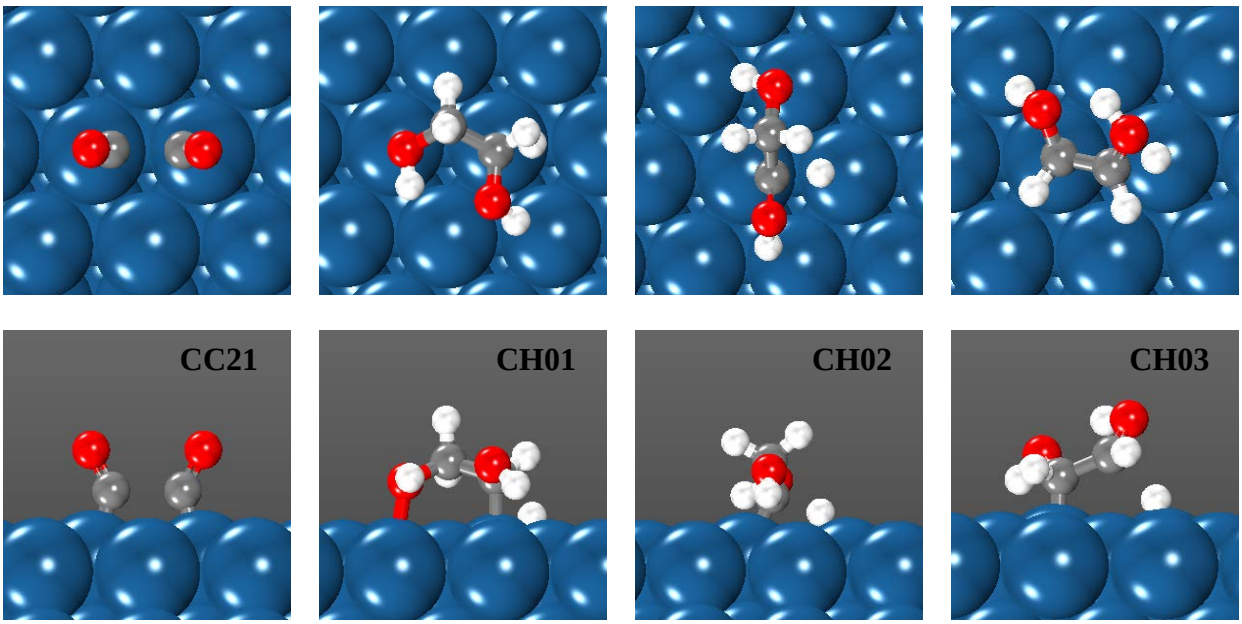
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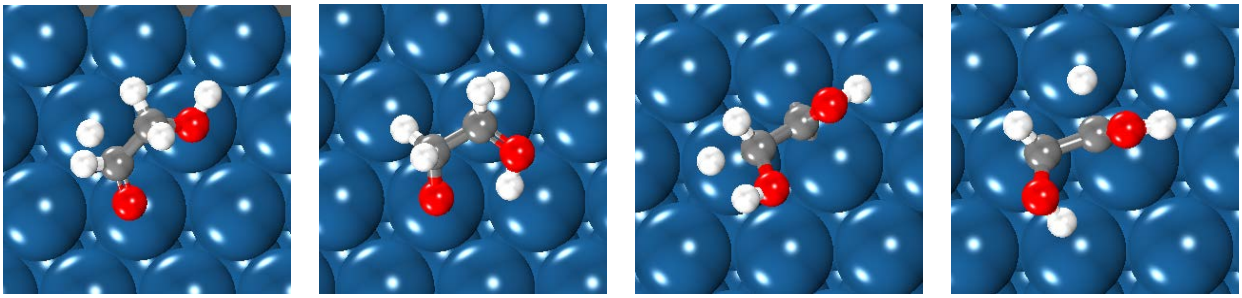

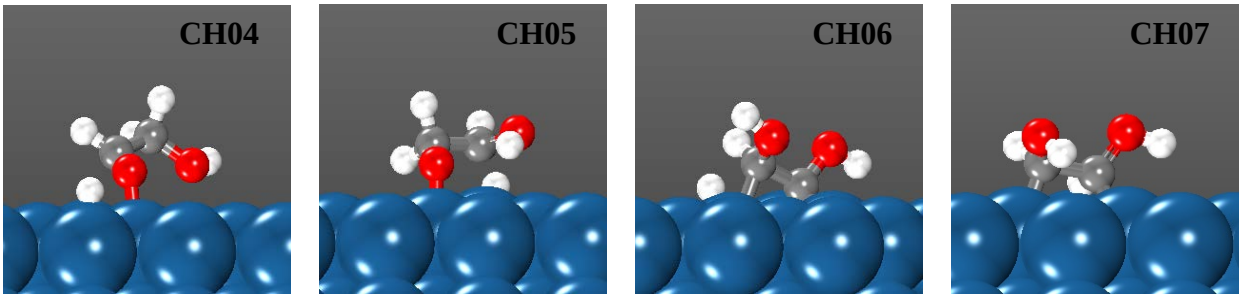
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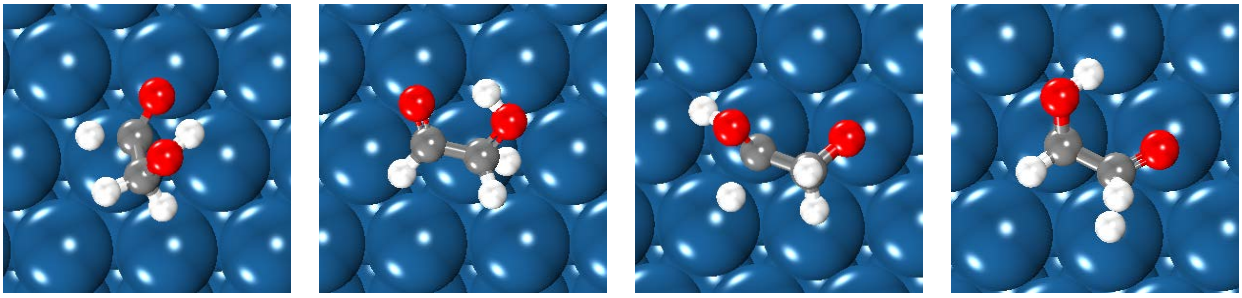

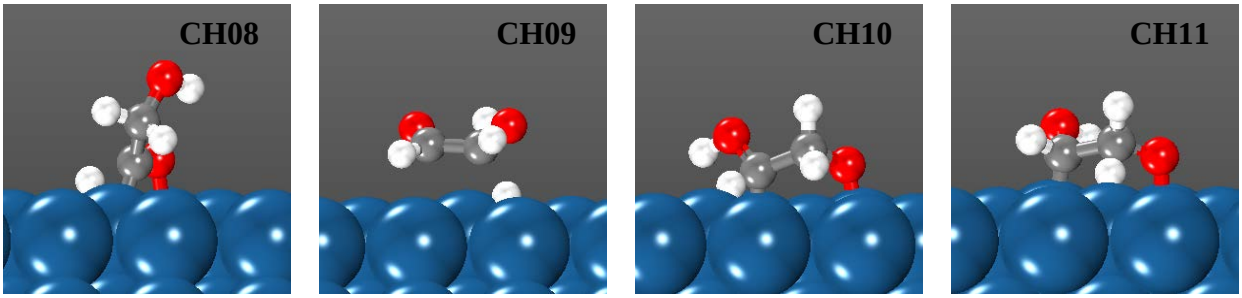
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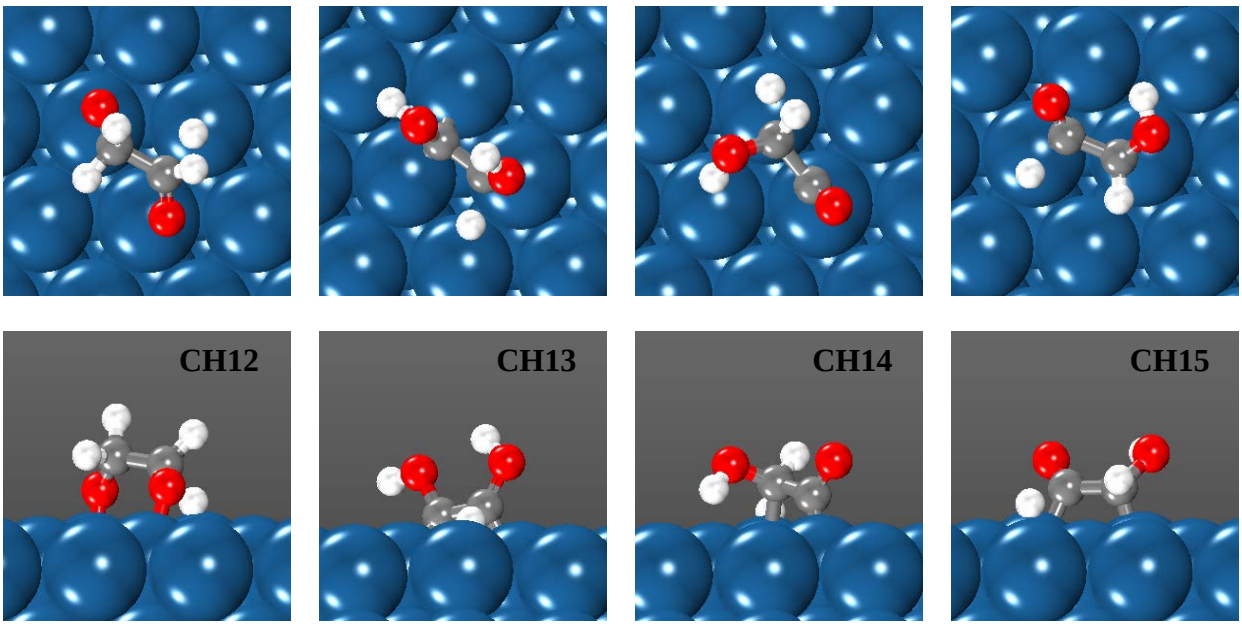
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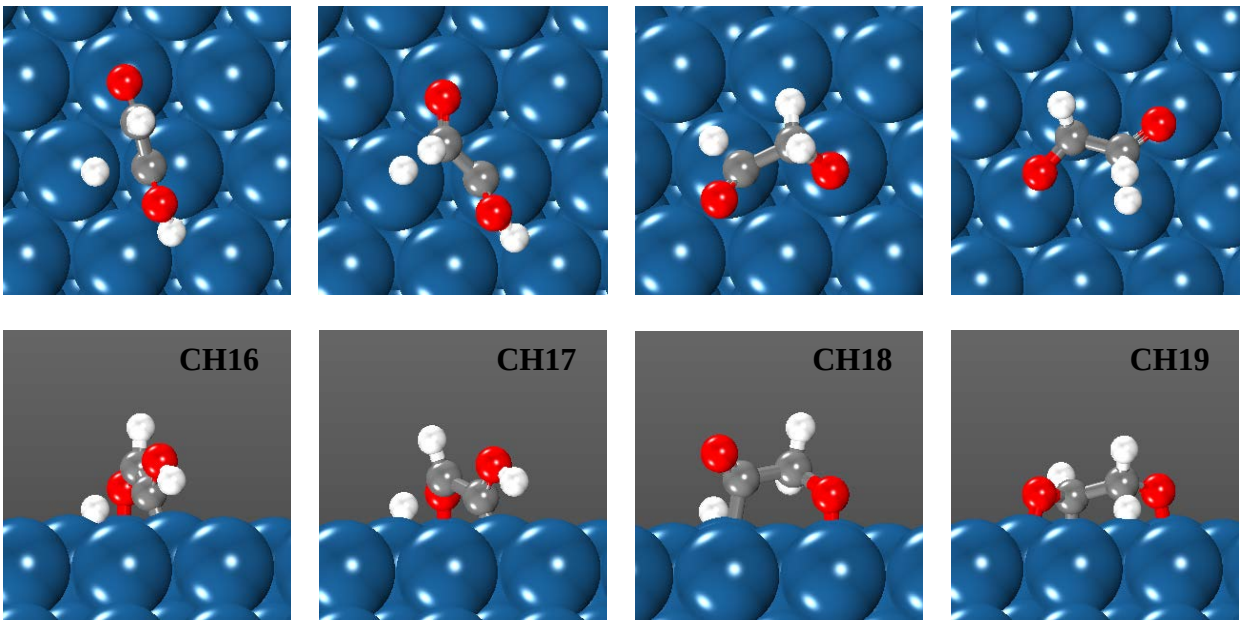
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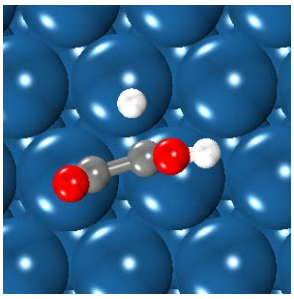

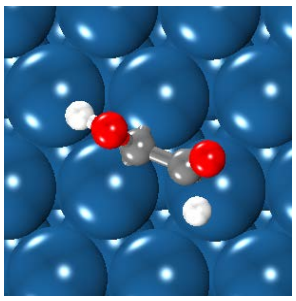

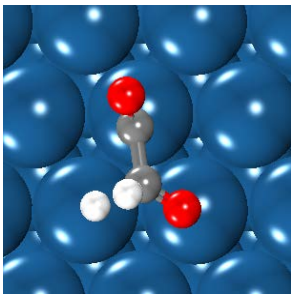

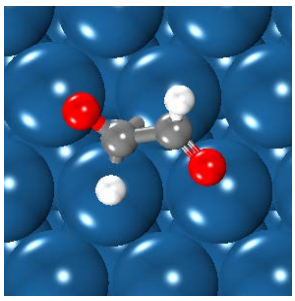

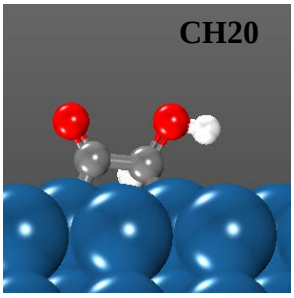
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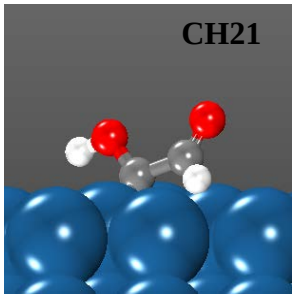
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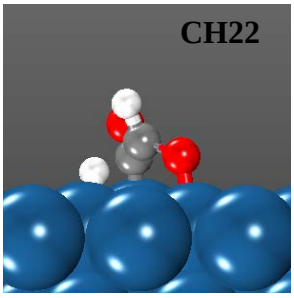
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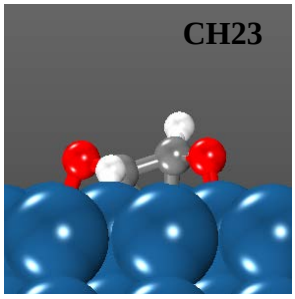
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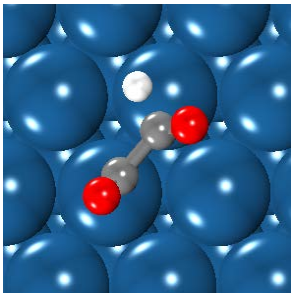

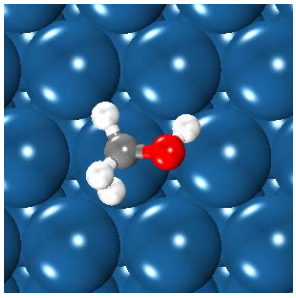

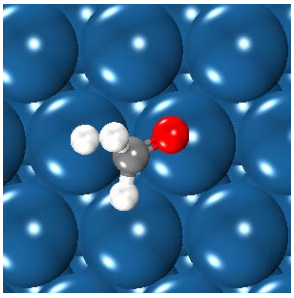

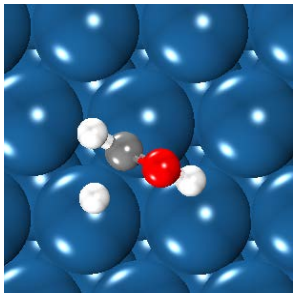

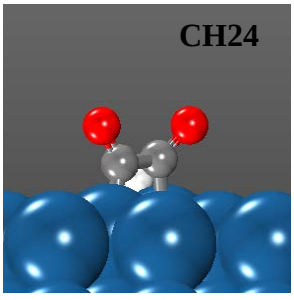
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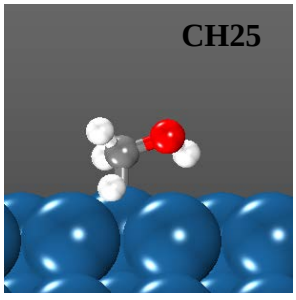
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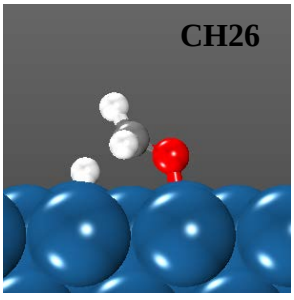
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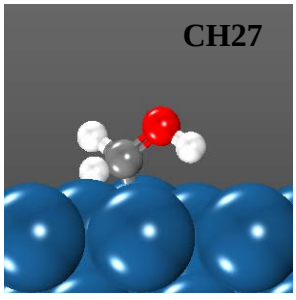
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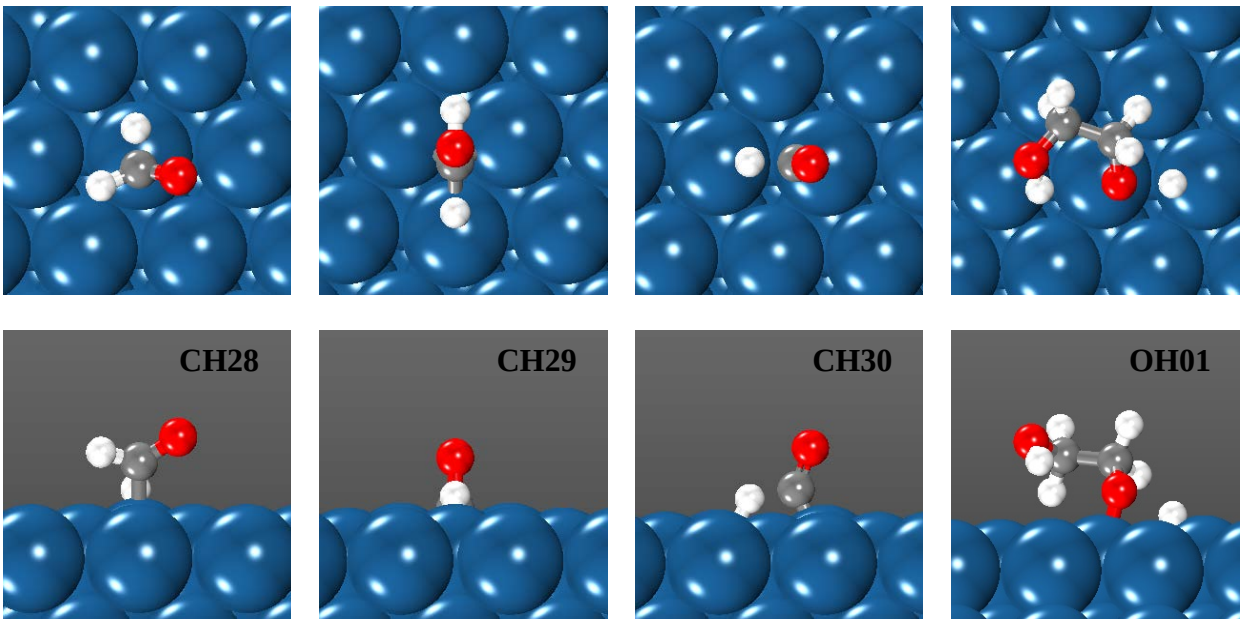
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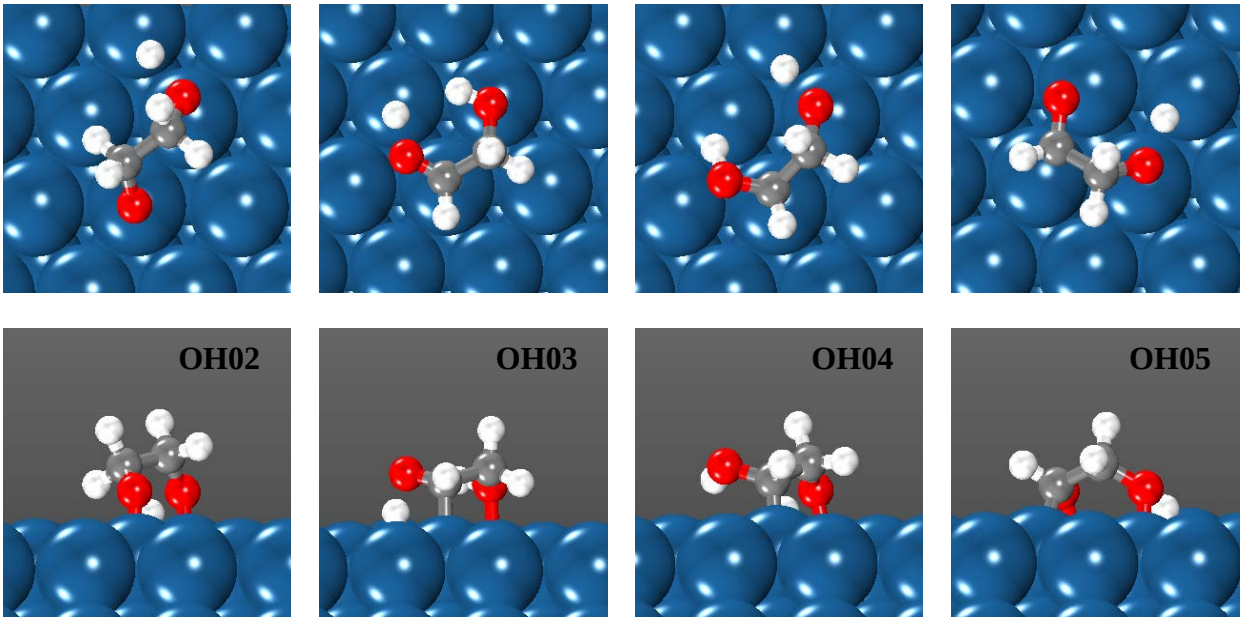
CH29
CH30
OH01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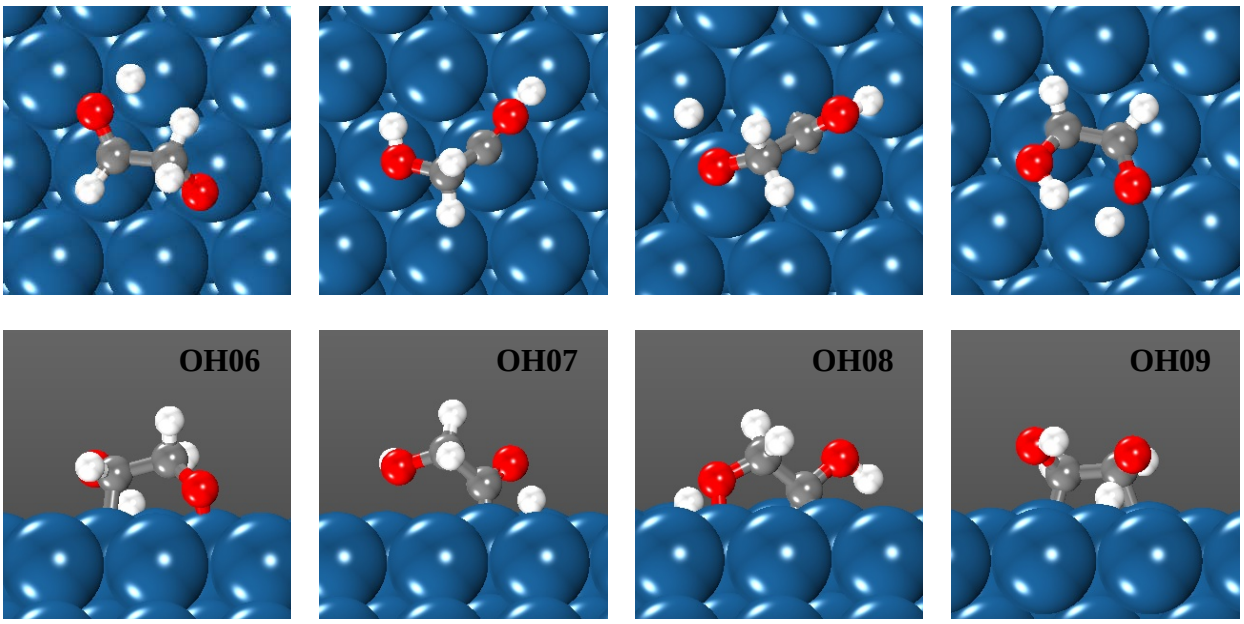
OH03
OH04
OH05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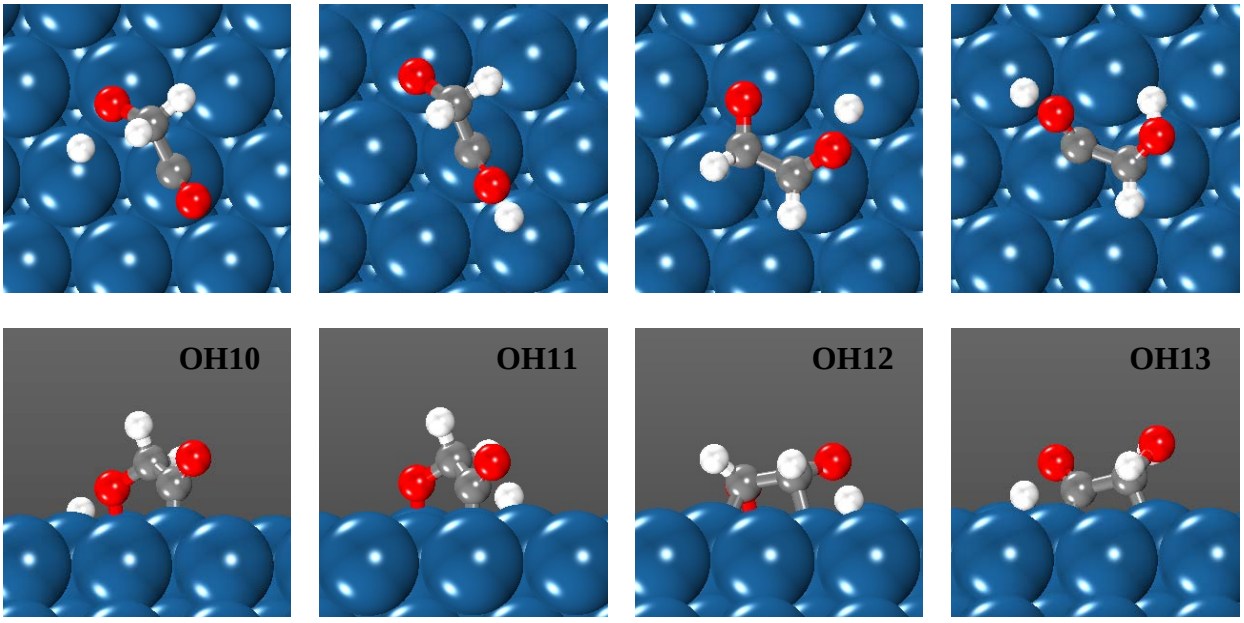
OH07
OH08
OH09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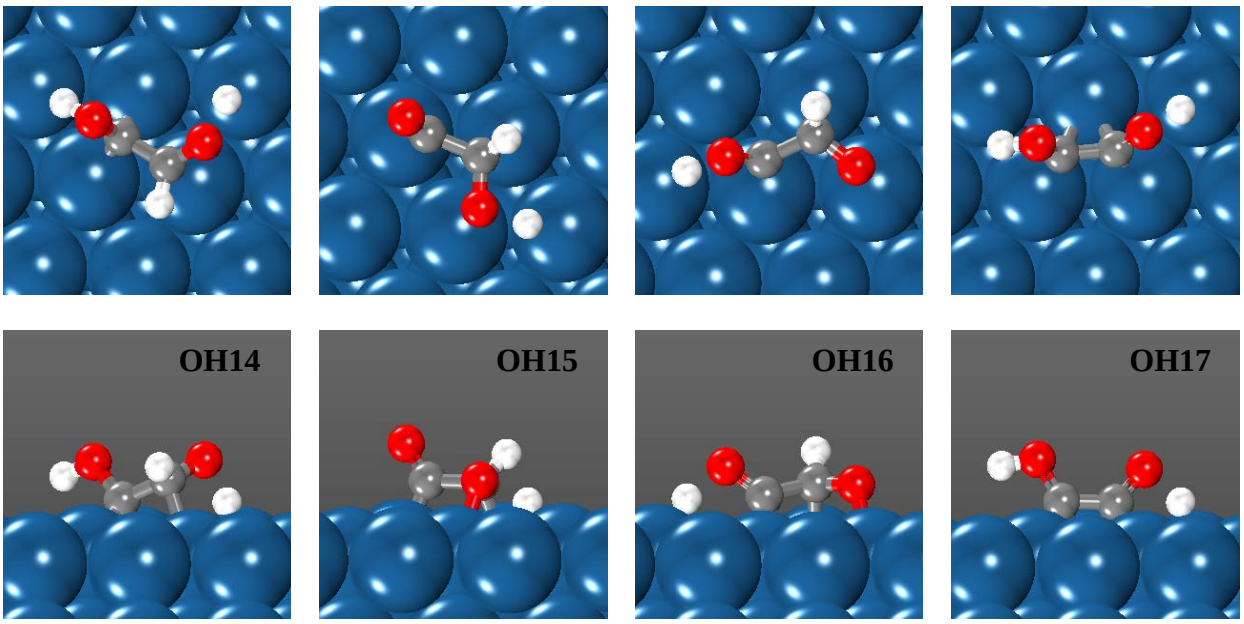
OH11
OH12
OH13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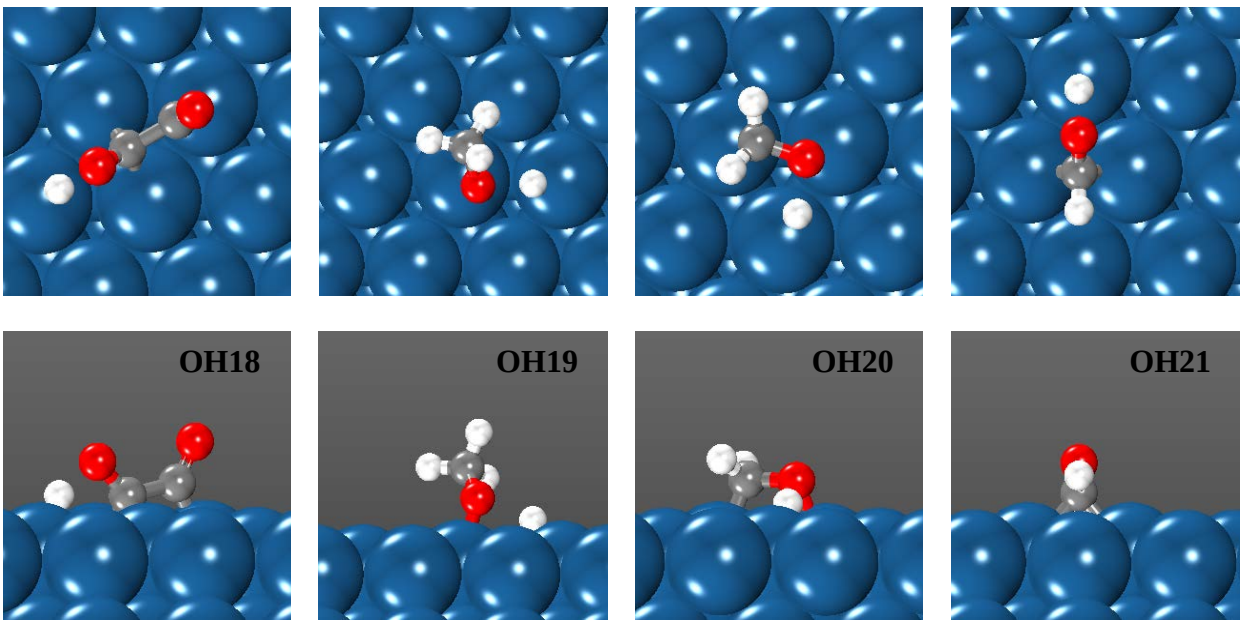
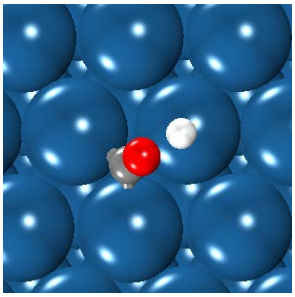
OH15
OH16
OH17


OH18
OH19
OH20
OH21



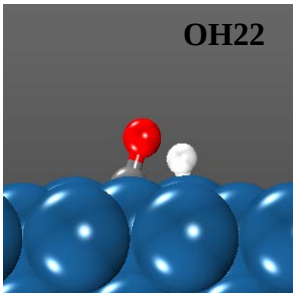

OH22

Table S3. Number of unique structures used for fitting CO–CO and H–H lateral interactions.

$\theta(\text{CO or H})$	N
1/36	1
1/9	1
2/9	2
3/9	5
4/9	5
5/9	5
6/9	5
7/9	2
8/9	1
9/9	1

Table S4. Number of unique structures used for fitting EG–CO and EG–H lateral interactions (EG = Ethylene Glycol).

$\theta(\text{CO or H})$	θ_{EG}	N
1/16	1/16	8

Table S5. Number of unique structures used for fitting CO–H lateral interactions.

θ_{CO}	θ_{H}	N
1/9	1/9	2
1/9	2/9	7
1/9	3/9	13
1/9	4/9	18
1/9	5/9	13
1/9	6/9	7
1/9	7/9	2
1/9	8/9	1
2/9	1/9	7
2/9	2/9	18
2/9	3/9	32
2/9	4/9	32
2/9	5/9	18
2/9	6/9	7
2/9	7/9	2
3/9	1/9	13
3/9	2/9	32
3/9	4/9	32
3/9	5/9	13
3/9	6/9	5
4/9	1/9	18
4/9	2/9	32
4/9	3/9	32

DFT energies for all structures at a given coverage are Boltzmann-averaged at 500 K.

Table S6. Cavity radii of transition metal atoms used for aqueous solvation calculations in different continuum/implicit solvation models.

Species	PBF[1] (Jaguar) (Å)	SM8[2] (MN-GSM) (Å)	COSMO[3] (Turbomole) (Å)	PCM[4] (Gaussian) (Å)
Ru	1.48	2.00	2.22	2.44
Rh	1.46	2.00	2.22	2.29
Pd	1.45	1.63	2.22	2.30
Pt	1.38	1.74	2.22	2.33

Figure S7. Change in solvation energy versus cavity radius of Pt from different solvation models at 423K for an adsorbed hydroxyl species over Pt(111).

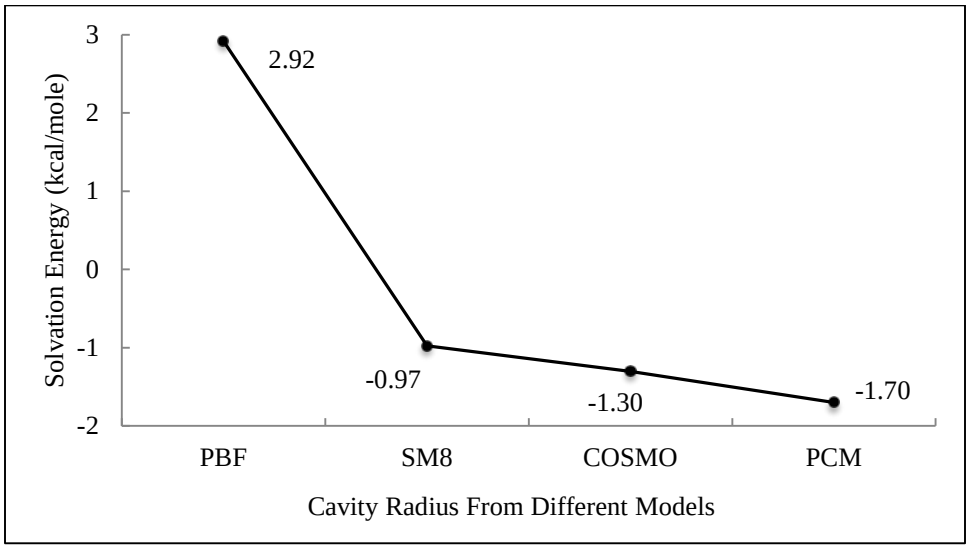


Table S8. Liquid Water Effect on the Adsorption Free Energy of Various Intermediates in Reforming of Ethylene Glycol over Pt(111) Model Surface at 500 K.

Adsorbed Species	$\Delta(\Delta G)^a$ (eV) in Water
CH_2OHCH_2OH	-0.05
CH_2OCH_2OH	-0.18
$CHOHCH_2OH$	-0.08
CHOHCHOH	-0.10
$CHOCH_2OH$	-0.10
CH_2OCH_2O	-0.07
$CHOHCH_2O$	-0.07
$COHCH_2OH$	-0.05
$CHOCH_2O$	-0.11
COHCHOH	-0.06
CHOCHOH	-0.05
$COHCH_2O$	-0.09
$COCH_2OH$	-0.12
COCHOH	-0.06
$COCH_2O$	-0.05
CHOCHO	-0.07
COHCOH	-0.09
COHCHO	-0.03
COCHO	-0.06
COCOH	-0.07
COCO	-0.05
CH_3OH	-0.06
CH_3O	-0.04
CH_2OH	-0.03
CH_2O	-0.04
CHOH	0.01
CHO	-0.02
COH	-0.09
CO	-0.03
H	0.04

[a]Δ(ΔG) represents the difference in adsorption free energy of intermediate X in the absence (X(g) + *(g) → X*(g)) and presence of solvent (X(g) + *(l) → X*(l)), where Δ(ΔG) = (ΔG) (l) - (ΔG) (g) = (G^{x*}(l) – G^{*}(l)) – (G^{x*}(g) – G^{*}(g)).

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2. Marenich, A.V., et al., *Self-consistent reaction field model for aqueous and nonaqueous solutions based on accurate polarized partial charges.* Journal of Chemical Theory and Computation, 2007. **3**(6): p. 2011-2033.
3. Schafer, A., et al., *COSMO Implementation in TURBOMOLE: Extension of an efficient quantum chemical code towards liquid systems.* Physical Chemistry Chemical Physics, 2000. **2**(10): p. 2187-2193.
4. Frisch, M.J., et al., *Gaussian 09*. 2009, Gaussian, Inc.: Wallingford, CT, USA.