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Mechanisms of H- and OH-assisted CO activation as well as C-C coupling on the flat Co(0001) surface – Revisited

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Micro-kinetics

(a) To distinguish the selectivity of CH_3O hydrogenation and dissociation, we computed the rate constant (k) on the basis of the transition state theory.[1,2] The rate constant of each reaction is calculated according to equation (1), where k_B is the Boltzmann constant, T denotes the reaction temperature, h is the Planck constant, E_a stands for the activation barrier of each reaction, and $q_{IS,vib}$ and $q_{TS,vib}$ are the harmonic vibrational partition functions for the initial state and the transition state, respectively; i.e., q_{vib} is calculated on the basis of equation (2), where ν_i is the vibrational frequency of each vibrational mode of the adsorbed intermediate derived from our DFT calculations. The computed energy barriers and reaction energy as well as rate constants are listed in the Supporting Information.

$$k = \frac{k_B T}{h} \frac{q_{TS,vib}}{q_{IS,vib}} e^{\frac{-E_a}{k_B T}} \tag{1}$$

$$q_{vib} = \prod_i \frac{1}{1 - \exp(-\frac{h\nu_i}{k_B T})} \tag{2}$$

(b) The rate equation of the related competitive reactions

In order to investigate the competition between hydrogenation and dissociation, we consider the following rate equations of the elementary steps involved on the potential energy surface.

$CO + S = C + O$ Eq. 1

$CO + H = CHO + S$ Eq. 2

$CO + H = COH + S$ Eq. 3

$CHO + S = CH + O$ Eq. 4

$CHO + H = CH_2O + S$ Eq. 5

$CHO + H = CHOH + S$ Eq. 6

$CH_2O + S = CH_2 + O$ Eq. 7

$CH_2O + H = CH_3O + S$ Eq. 8

$CH_2O + H = CH_2OH + S$ Eq. 9

$CH_3O + S = CH_3 + O$ Eq. 10

$CH_3O + H = CH_3OH + S$ Eq. 11

The rate equation of each reaction can be expressed as equations in the following:

$$r_1 = k_1[S][CO] \tag{3}$$

$$r_2 = k_2[H][CO] \tag{4}$$

$$r_3 = k_3[H][CO] \tag{5}$$

$$r_4 = k_4[S][CHO] \tag{6}$$

$$r_5 = k_5[H][CHO] \tag{7}$$

$$r_6 = k_6[H][CHO] \tag{8}$$

$$r_7 = k_7[S][CH_2O] \tag{9}$$

$$r_8 = k_8[H][CH_2O] \tag{10}$$

$$r_9 = k_9[H][CH_2O] \tag{11}$$

$$r_{10} = k_{10}[S][CH_3O] \tag{12}$$

$$r_{11} = k_{11}[H][CH_3O] \tag{13}$$

Under hydrogen rich conditions, the surface active sites can be occupied by hydrogen atoms; and these surface hydrogen atoms can be used for the hydrogenation reactions; on the other hand, there will be no free sites available to accept the O atom from the dissociation reactions. The availability of surface hydrogen atoms will accelerate all hydrogenation steps and at the same time suppress the dissociation steps.

(c) The rate equation of CH_3OH and CH_4 formation

In the process of the formation of CH_4 and CH_3OH on the Co(0001) surface, $CO \rightarrow CHO \rightarrow CH_2O \rightarrow CH_3O$ is an optimal pathway. At first, H_2 molecule adsorbs dissociative on the surface (Eq. 12); and CO molecule adsorbs on the surface (Eq. 13); and the subsequent hydrogenation of CO to form CH_3O (Eq. 2, 5 and 8), which is further hydrogenated to CH_3OH (Eq. 11); finally the surface CH_3OH desorbs (Eq. 14) from the surface.

$H_{2(g)} + 2S = 2H$ Eq. 12
$CO_{(g)} + S = CO_s$ Eq. 13
$CO + H = CHO + S$ Eq. 2
$CHO + H = CH_2O + S$ Eq. 5
$CH_2O + H = CH_3O + S$ Eq. 8
$CH_3O + S = CH_3 + O$ Eq. 10
$CH_3O + H = CH_3OH + S$ Eq. 11
$CH_3OH = CH_3OH_{(g)} + S$ Eq. 14
$CH_3 + H = CH_4 + S$ Eq. 15
$CH_4 = CH_{4(g)} + S$ Eq. 16
$O + H = OH + S$ Eq. 17
$OH + H = H_2O + S$ Eq. 18
$H_2O = H_2O_{(g)} + S$ Eq. 19

For the CH_4 formation, starting from CH_3O, CH_3 is formed via the dissociation reaction (Eq. 10), then through hydrogenation reaction to obtain CH_4 (Eq. 15), followed by desorption of CH_4 from the surface (Eq. 16). Finally the surface O is hydrogenated by H into OH (Eq. 17) and H_2O (Eq. 18), followed by H_2O desorption (Eq. 19) and the regeneration of the free surface sites.

On the basis of the potential energy surface and the computed energy barriers of these reactions, we found that CH_3O hydrogenation to CH_3OH and dissociation to CH_3 + O are competitive reactions, and these two reaction have highest barrier (1.55 and 1.56 eV, respectively), and should be the rate-determining steps for the formation of CH_3OH and CH_4, respectively. Therefore, the rate of the formation of CH_3OH and CH_4 can be defined by reactions 11 and 10. Thus, the rate equation of the formation of CH_3OH and CH_4 can be expressed as equation (14) and (15):

$$r[CH_3OH] = k_{11}(z/L)[H][CH_3O] \tag{14}$$

$$r[CH_4] = k_{10}[S][CH_3O] \tag{15}$$

Where k_{11} is the rate constant of CH_3O hydrogenation (Eq. 11), (*z*/L)[H] represents the probability of finding adjacent [CH_3O] surface species to [H] species, L represents the total surface number of active sites S for H_2 adsorption, and [CH_3O] and [H] denote surface concentrations of CH_3O and dissociated hydrogen on the surface, respectively. Since all the other steps are assumed to be in quasi-equilibrium, we can obtain the concentrations of the surface species as follows:

[H]: $[H] = K_1^{\frac{1}{2}}[S][H_{2g}]^{\frac{1}{2}}$ (16)

[CO]: $[CO] = K_2[CO_g][S]$ (17)

[CHO]: k_2[CO][H] – k_5[CHO][H] = 0, thus $[CHO] = \frac{k_2}{k_5}[CO]$ (18)

[CH$_2$O]: k_5[CHO][H] – k_8[CH$_2$O][H] = 0, thus $[CH_2O] = \frac{k_5}{k_8}[CO]$ (19)

[CH$_3$O]: k_8[CH$_2$O][H] – k_{11}[CH$_3$O][H] – k_{10}[CH$_3$O][S] = 0, thus $[CH_3O] = \frac{k_2[CO][H]}{k_{11}[H] + k_{10}[S]}$ (20)

Considering site balance for S, [L] = [S] + [H] + [CO] + [CHO] + [CH$_2$O] + [CH$_3$O] + [CH$_3$OH]

Where K_1 is the equilibrium constant of H$_2$ adsorption and desorption, K_2 is the equilibrium constant of CO adsorption and desorption, [S] denotes surface concentrations of free site, k_n is the rate constant of the corresponding reaction.

Substitute the equations (16) - (20) to (14) and (15) we can get the rate equation of CH$_3$OH and CH$_4$ formation:

$$r[CH_3OH] = k_{11}(z / L)[H]\frac{k_2 K_2 [CO_g][S] K_1^{\frac{1}{2}}[S][H_{2g}]^{\frac{1}{2}}}{k_{11} K_1^{\frac{1}{2}}[S][H_{2g}]^{\frac{1}{2}} + k_{10}[S]} \tag{21}$$

$$r[CH_4] = k_{10}[S]\frac{k_2[CO][H]}{k_{11}[H] + k_{10}[S]} \tag{22}$$

Table S1. Most stable adsorption site, adsorption energy (E_{ads}, eV), and relative bond distances ($d_{\mathrm{Co\text{-}X}}$, Å) of the surface species; the adsorption energies in the parentheses are without ZPE corrections (* own results in present work)

Species	E_{ads} (eV)	$d_{\mathrm{Co\text{-}C}}$ (Å)	$d_{\mathrm{Co\text{-}O}}$ (Å)
CH	-5.65* (-5.79)	1.873; 1.876; 1.877	
	-6.07[3a]; -5.85[3b]; -5.99[4]; -6.54[5]; 5.94[6a]; 6.68[6b]	1.878[4]; 1.86[6a]; 1.88[6b]	
CH_2	-3.29* (-3.37)	1.962; 1.965; 2.025	
	-3.74[3a]; -4.11[3b]; -3.85[4]; -3.86[5];	1.986[4]	
CH_3	-1.41* (-1.49)	2.183; 2.209; 2.222	
	-1.09[3a]; -2.09[3b]; -1.89[4]; -2.00[5];	2.174[4]	
CH_4	0.02* (-0.04)		
CHO	-1.53* (-1.61)	1.880; 2.125	2.083; 0.186
COH	-3.54* (-3.64)	1.861; 1.911; 1.917	
CHOH	-2.32* (-2.32)	1.978; 1.986; 2.065	
CH_2O	-0.19* (-0.23)	2.010	2.049; 2.073; 2.199
CH3O	-2.18* (-2.32)		2.028; 2.033; 2.034
CH_3OH	0.00* (-0.02)		2.300

Table S2. The adsorption energy (E_{ads}, eV) and the relative bond distances ($d_{\text{Co-X}}$, Å) of the surface species, as well as the reaction energy (E_{r}, eV) and the barrier energy (E_{a}, eV) in the diffusion reaction of the surface species; the adsorption energies in the parentheses are without ZPE corrections

Species	E_{ads}	E_{a}	E_{r}	$d_{\text{Co-C}}$	$d_{\text{Co-O}}$
CH-hcp	-5.65 (-5.83)			1.873; 1.876; 1.877	
TS	-5.37 (-5.54)	0.28	0.19	1.817; 1.820	
CH-fcc	-5.46 (-5.64)			1.877; 1.888; 1.890	
CH_2-hcp	-3.29 (-3.40)			1.962; 1.965; 2.025	
TS	-3.03 (-3.09)	0.26	0.02	1.934; 1.944	
CH_2-fc	-3.27 (-3.37)			1.971; 1.977; 2.034	
CH_3-hcp	-1.42 (-1.50)			2.183; 2.209; 2.222	
TS	-1.22 (-1.31)	0.19	0.01	2.131; 2.204	
CH_3-fcc	-1.41 (-1.50)			2.179; 2.196; 2.201	
CHO-1	-1.53 (-1.61)			1.912; 2.048	2.098; 2.193
TS	-1.41 (-1.46)	0.12	0.00	2.006; 2.049	2.010
CHO-2	-1.53 (-1.61)			1.912; 2.048	2.098; 2.193
COH-1	-3.54 (-3.64)			1.803; 1.907; 2.024	
TS	-3.38 (-3.45)	0.16	0.14	1.827; 1.836	
COH-2	-3.40 (-3.46)			1.857; 1.911; 1.960	
CH_2O-1	-0.19 (-0.23)			2.010	2.049; 2.073; 2.199
TS	0.13 (0.14)	0.32	0.00		
CH_2O-2	-0.19 (-0.23)			2.010	2.049; 2.073; 2.199
CH_3O-1	-2.18 (-2.32)				2.028; 2.033; 2.034
TS	-1.93 (-2.11)	0.25	0.08		1.965; 1.969
CH_3O-2	-2.10 (-2.24)				2.028; 2.035; 2.040

Table S3. Computed adsorption energies (E_{ads}, eV), and the relevant bond distances (d, Å) of the IS, TS and FS for the reactions via H-assisted pathway; the adsorption energies in the parentheses are without ZPE corrections

	E_{ads}	d_{Co-C}	d_{Co-O}	d_{Co-H}	d_{C-O}	d_{C-H}	d_{O-H}
CO+H-t1	-1.40 (-1.60)	1.754		1.738; 1.751; 1.753	1.173		
TS1	1.31 (1.15)	1.794; 1.841; 1.946	1.936; 1.942	1.673; 1.689; 1.789			
C+O+H	0.02 (-0.21)	1.758; 1.787; 1.827	1.834; 1.890; 1.900	1.733; 1.734; 1.750			
CO+H-t2	-1.34 (-1.56)	1.759		1.709; 1.770; 1.772	1.173		
TS2	0.61 (0.53)	1.772; 2.023; 2.042			1.271		
COH	-0.35 (-0.66)	1.861; 1.911; 1.917			1.351		0.978
TS3	0.07 (-0.16)	1.861			1.236	1.147	
CHO	-0.14 (-0.44)	1.880; 2.125	2.083; 0.186		1.321	1.109	
CHO+H-t1	-0.27 (-0.75)	1.881; 2.080	2.095; 2.207	1.676; 1.756; 1.829	1.319	1.109	
TS4	0.69 (0.27)	1.829; 1.875	1.959; 1.983; 2.018	1.612; 1.732		1.098	
CH+O+H	-0.57 (-1.01)	1.847; 1.860; 1.897	1.855; 1.870; 1.925	1.732; 1.743; 1.745		1.103	
CHO+H-t2	-0.11 (-0.58)	1.867; 2.184	2.414; 2.154	1.658; 1.763; ;1.845	1.315	1.110	
TS5	0.80 (0.45)	1.948; 2.039; 2.290		1.852; 1.863	1.309	1.138	
CHOH	0.12 (-0.45)	1.978; 1.986; 2.065		1.759	1.383	1.177	0.982
TS6	0.12 (-0.34)	1.887; 2.192	2.118; 2.173	1.559	1.324	1.105	
CH_2O	-0.04 (-0.65)	2.010	2.049; 2.073; 2.199		1.382	1.096; 1.100	
CH_2O+H-t1	-0.16 (-0.92)	2.031	2.035; 2.038	1.748; 1.763; 1.767	1.390	1.101; 1.103	
TS7	0.66 (-0.03)	1.932; 2.197	1.956; 1.964; 2.089	1.660; 1.746; 1.825		1.101; 1.111	
CH_2+O+H	-0.49 (-1.17)	1.931; 1.980; 2.020	1.856; 1.893; 1.900	1.692; 1.753; 1.784		1.102; 1.156	
CH_2O+H-t2	-0.12 (-0.89)	2.016	2.105; 2.106; 2.125	1.698; 1.747; 1.826		1.097; 1.099	
TS8	0.82 (0.17)	2.102	2.073	1.765; 1.809	1.379	1.104; 1.118	
CH_2OH	0.17 (-0.70)	2.104; 2.200	2.254		1.472	1.104; 1.121	0.979
CH_2O+H-t3	-0.14 (-0.93)	2.033	2.043; 2.043	1.683; 1.761; 1.762	1.385	1.102; 1.103	
TS9	0.24 (-0.51)	2.102	2.064; 2.067; 2.215	1.570	1.382	1.098; 1.100	
CH_3O	-0.71 (-1.64)		2.028; 2.033; 2.034		1.449	1.100; 1.100; 1.100	
CH_3O+H-t1	-0.83 (-1.93)		2.033; 2.034; 2.038	1.751; 1.763; 1.765	1.450	1.100; 1.100; 1.100	
TS10	0.61 (-0.37)		1.910; 1.919; 1.949	1.703; 1.773; 1.779		1.088; 1.090; 1.096	
CH_3+O+H	-0.86 (-1.85)	2.153; 2.206	1.848; 1.878; 1.964	1.710; 1.741; 1.798		1.106; 1.106; 1.117	
CH_3O+H-t2	-0.85 (-1.95)		2.026; 2.026; 2.048	1.745; 1.747 ;1.755	1.447	1.100; 1.100 ;1.100	
TS11	0.59 (-0.40)		2.054	1.700	1.449	1.101; 1.103; 1.105	
CH_3OH	-0.35 (-1.57)		2.300		1.453	1.098 ;1.102; 1.102	
TS12	0.11 (-0.82)	1.754; 2.265	1.849; 1.911; 2.018	1.665	1.175	1.099; 1.099; 1.103	
CH_4+O	-1.42 (-2.52)	1.755	1.848; 1.878; 1.964		1.175	1.096; 1.098; 1.098; 1.110	

Table S4. Computed adsorption energies (E_{ads}, eV), and the relevant bond distances (d, Å) of the IS, TS and FS for the reactions via OH-assisted pathway; the adsorption energies in the parentheses are without ZPE corrections

	E_{ads}	$d_{\mathrm{Co\text{-}C}}$	$d_{\mathrm{Co\text{-}O}}$	$d_{\mathrm{Co\text{-}H}}$	$d_{\mathrm{C\text{-}O}}$	$d_{\mathrm{O\text{-}H}}$
CO+H+OH	-1.42 (-1.52)	1.760	1.997; 2.049; 2.050	1.690; 1.776; 1.777	1.175	0.973
TS13	-0.69 (-0.59)	1.847; 1.955; 1.966	1.943; 1.951; 2.016	1.736; 1.754; 1.758	1.296	
COH+O+H	-0.75 (-0.76)	1.840; 1.906; 1.935	1.876; 1.905; 1.928	1.732; 1.755; 1.756	1.341	0.986
TS14	-0.14 (0.04)	1.854	1.928; 1.964; 1.998	1.716; 1.756; 1.766	1.196	
CHO+O+H	-0.41 (-0.37)	1.959; 2.146; 2.026	1.855; 1.892; 1.923	1.742; 1.748; 1.758	1.285	
TS15	-0.18 (-0.24)	1.914	2.042		1.190	0.983
COOH	-0.54 (-0.69)	1.928	2.071		1.272; 1.350	0.983
TS16	-0.24 (-0.23)	1.868; 1.917; 1.999	1.853; 1.893; 1.915	1.527	1.364	0.981
HCOH+O	-0.37 (-0.39)	1.943; 1.991; 2.117	1.860; 1.885; 1.907	1.785	1.378	0.982
TS17	0.50 (0.39)	1.940	2.126		1.262; 1.295	
CO_2+H	-0.47 (-0.60)	2.122; 2.265	2.203; 2.231	1.737; 1.764; 1.775	1.241; 1.244	
HCOH+OH+H	-0.45 (-0.68)	1.978; 1.986; 2.065		1.383	0.982	
TS18	0.31 (0.13)	1.858; 1.974; 2.071	2.140; 2.277		0.984	
CH+OH+OH+H	-1.05 (-1.25)	1.836; 1.872; 1.915	1.981; 2.059; 2.060		0.973	
TS19	0.42 (0.33)	2.066; 2.198; 2.228	1.918; 1.930; 2.233	1.409	0.981	
CH_2OH+O	-0.38 (-0.56)	2.245; 2.273; 2.311	1.842; 1.972; 1.999	1.452	0.980	
TS20	-0.44 (-0.60)	1.987; 2.024; 2.127	1.986	1.333	0.975	
HCO+H_2O	-0.69 (-0.86)	1.873; 2.144	2.125; 2.208; 2.343	1.327	0.976; 0.983	
TS21	0.12 (-0.11)	1.939; 2.121; 2.179		1.390	0.983	
CH_2OH(+OH)	-0.43 (-0.67)	2.165; 2.179	2.203	1.478	0.979	

Table S5. Energy barrier E_a (eV) and reaction energy E_r (eV) as well as the rate constant k (483K) of CO hydrogenation in the H-assisted pathway on the Co(0001) surface

	E_a	E_r	A	k
CO+H→TS1→C+O+H	2.71	1.42	5.52×10^{12}	2.83×10^{-16}
CO+H→TS2→COH	1.95	1.05	2.70×10^{13}	1.20×10^{-7}
CO+H→TS3→CHO	1.41	1.26	5.84×10^{12}	1.11×10^{-2}
CHO+H→TS4→CH+O+H	0.96	-0.30	4.91×10^{12}	4.67×10^{2}
CHO+H→TS5→CHOH	1.07	0.39	1.31×10^{13}	8.86×10^{2}
CHO+H→TS6→CH_2O	0.39	0.23	9.35×10^{12}	7.90×10^{8}
CH_2O+H→TS7→CH_2+O+H	0.82	-0.33	7.80×10^{12}	2.15×10^{4}
CH_2O+H→TS8→CH_2OH	0.98	0.33	1.48×10^{13}	8.73×10^{2}
CH_2O+H→TS9→CH_3O	0.40	-0.55	1.51×10^{13}	1.00×10^{9}
CH_3O+H→TS10→CH_3+O+H	1.44	-0.03	1.04×10^{13}	9.65×10^{-3}
CH_3O+H→TS11→CH_3OH	1.42	0.48	1.93×10^{13}	2.90×10^{-2}
CH_3+O+H→TS12→CH_4+O	0.97	-0.56	1.54×10^{13}	1.16×10^{3}
CH+H+CO→TS→CH_2+CO	0.66	0.26	2.04×10^{13}	2.63×10^{6}
CH+H+CO→TS→CHCO+H	0.95	0.32	1.21×10^{13}	1.47×10^{3}
CH_2+H+CO→TS→CH_3+CO	0.70	-0.33	1.84×10^{13}	9.04×10^{5}
CH_2+H+CO→TS→CH_2CO+H	0.99	0.45	9.28×10^{12}	4.29×10^{2}
CH_3+H+CO→TS→CH_4+CO	0.96	-0.42	1.79×10^{13}	1.70×10^{3}
CH_3+H+CO→TS→CH_3CO+H	1.53	0.50	3.64×10^{12}	3.90×10^{-4}

Table S6: Barriers E_a (eV) and reaction energies E_r (eV) as well as the rate constant *k* (483K) of CO activation via OH-assisted pathway

	E_a	E_r	A	*k*
CO+H+OH→TS13→COH+O+H	0.83	0.77	3.90×10^{12}	8.85×10^{3}
CO+H+OH→TS14→CHO+O+H	1.38	1.11	8.74×10^{12}	3.43×10^{-2}
CO+OH→TS15→COOH	1.24	0.88	7.86×10^{12}	8.93×10^{-1}
COH+O+H→TS16→HCOH+O	0.51	0.37	7.81×10^{12}	3.70×10^{7}
COOH→TS17→CO_2+H	1.04	0.07	1.11×10^{13}	1.54×10^{2}
HCOH→TS18→CH+OH	0.76	-0.66	6.96×10^{12}	8.10×10^{4}
HCOH+OH+H→TS19→CH_2OH+O+H	0.87	0.07	1.44×10^{12}	1.19×10^{4}
HCOH+OH+H →TS20→HCO+H_2O+H	0.01	-0.24	4.21×10^{12}	3.31×10^{12}
HCOH+OH +H→TS21→CH_2OH+OH	0.57	0.02	1.26×10^{12}	1.41×10^{7}

Figure S1. Top (a) and side (b) reviews as well as possible adsorption sites of the hcp Co(0001) surface: top site (**t**), three-fold face-centered cubic site (**fcc**), three-fold hexagonal close packed site (**hcp**) and bridge site (**b**)

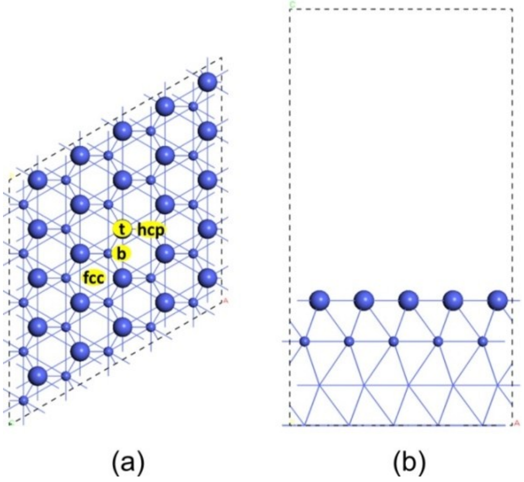
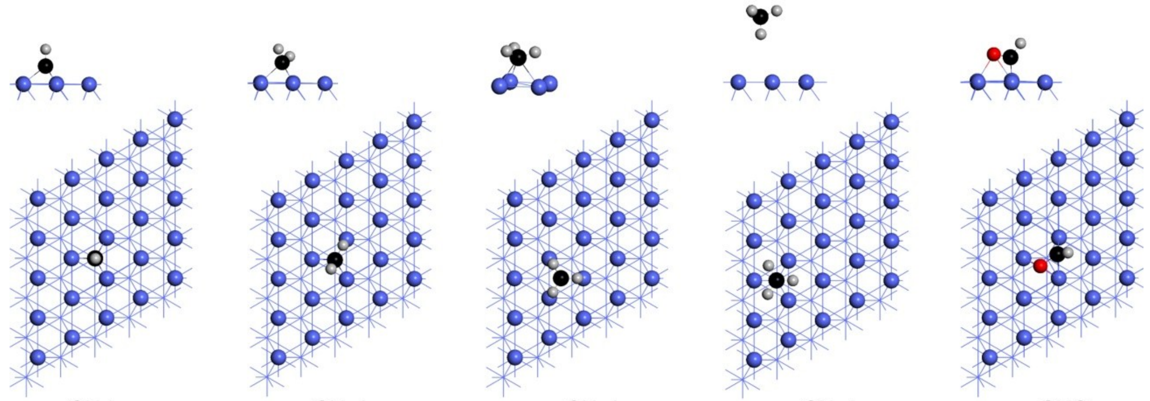
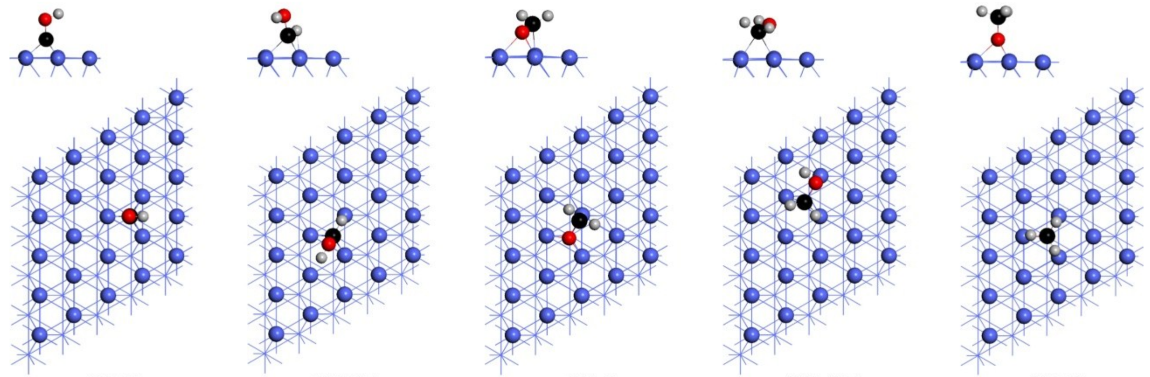


Figure S2. Top and side views of the relative surface species on the Co(0001) surface



CH-hcp CH_2-hcp CH_3-hcp CH_4-hcp CHO



COH CHOH CH_2O CH_2OH CH_3O

Figure S3. The geometries of the initial state and the final state as well as the transition state of the surface species in the diffusion reaction

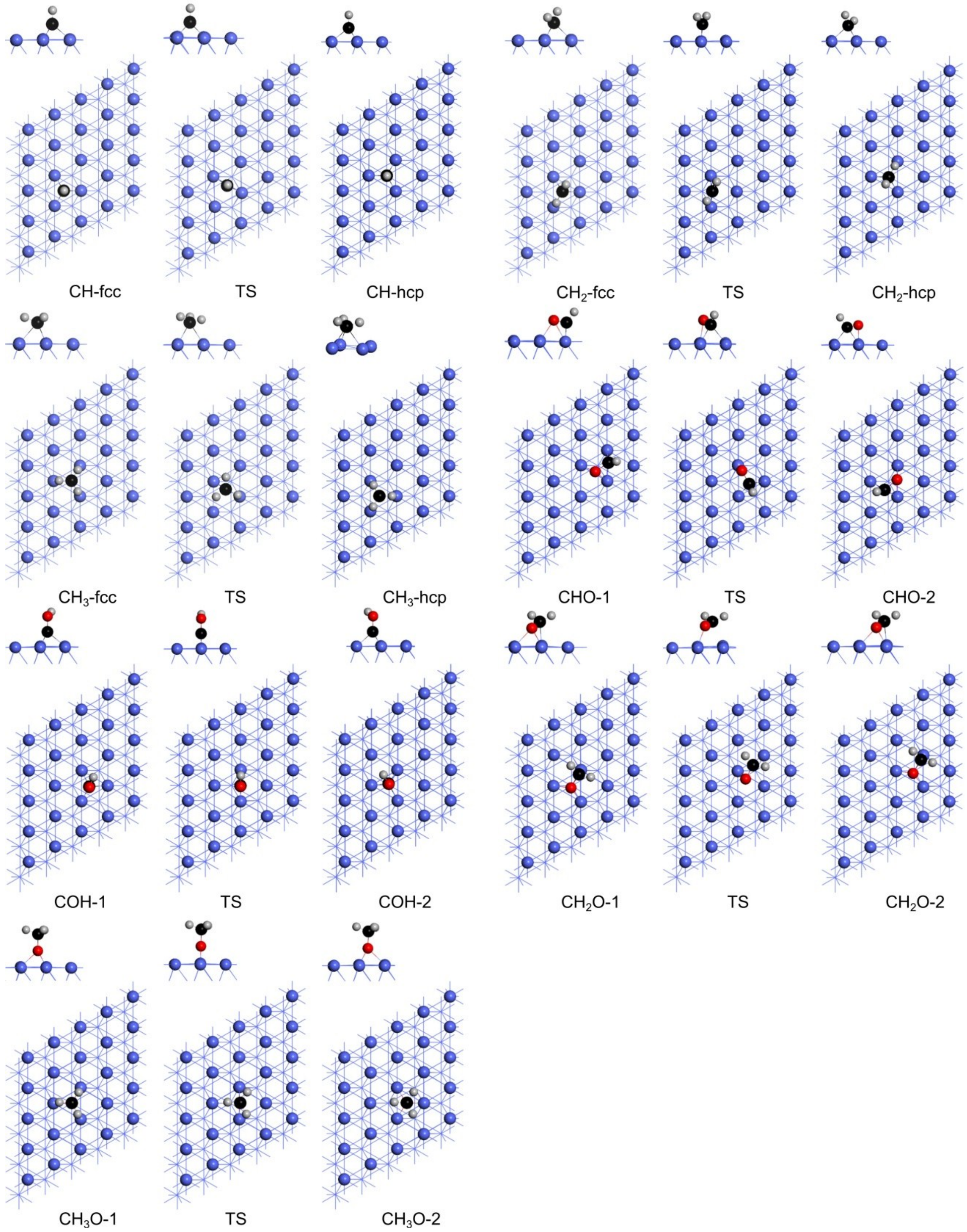


Figure S4. The geometries of the initial state and the final state as well as the transition state for the reactions starting from CO+H in the H-assisted pathway

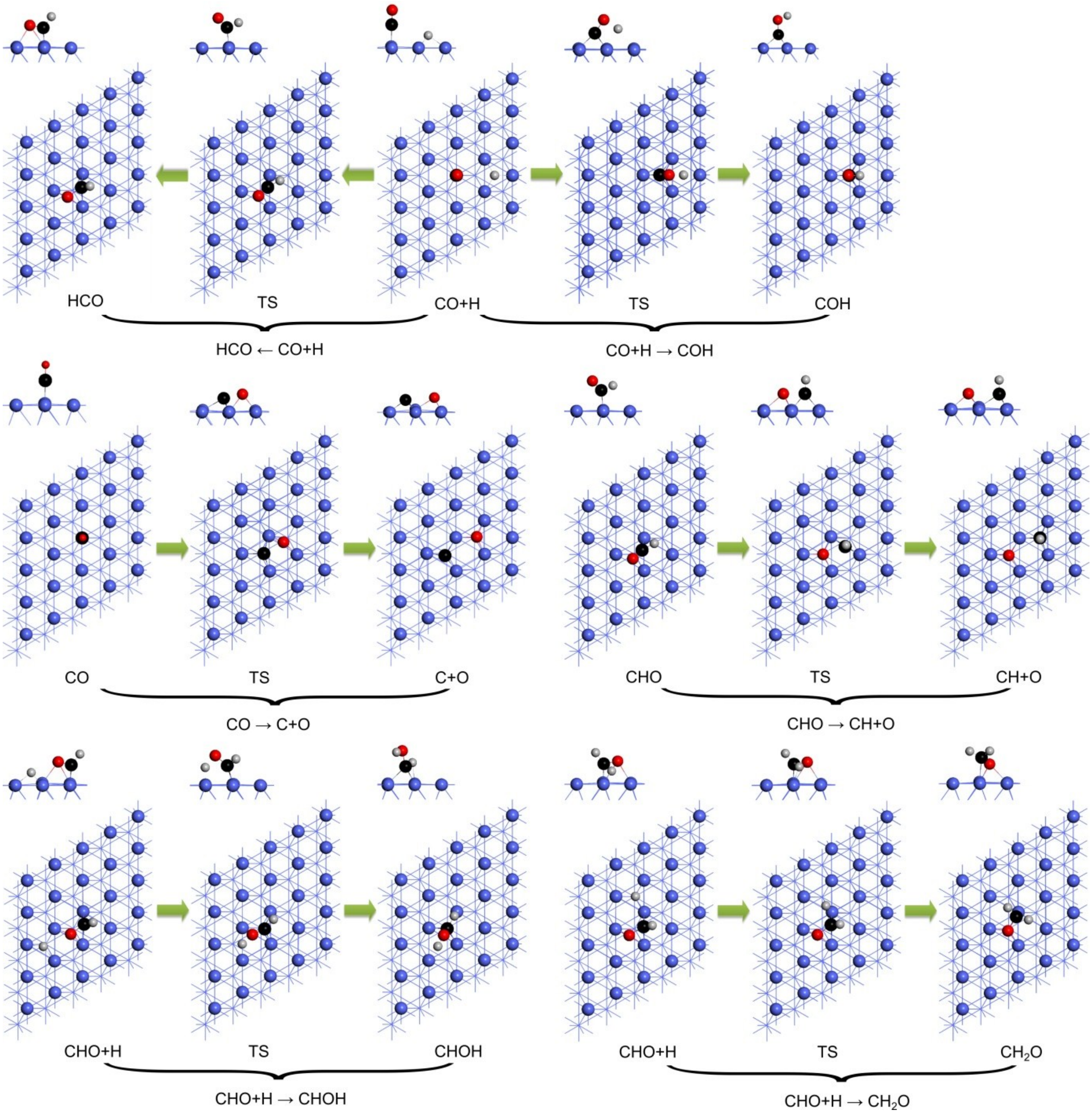


Figure S5. The geometries of the initial state and the final state as well as the transition state for the reactions starting from CH_2O in the H-assisted pathway

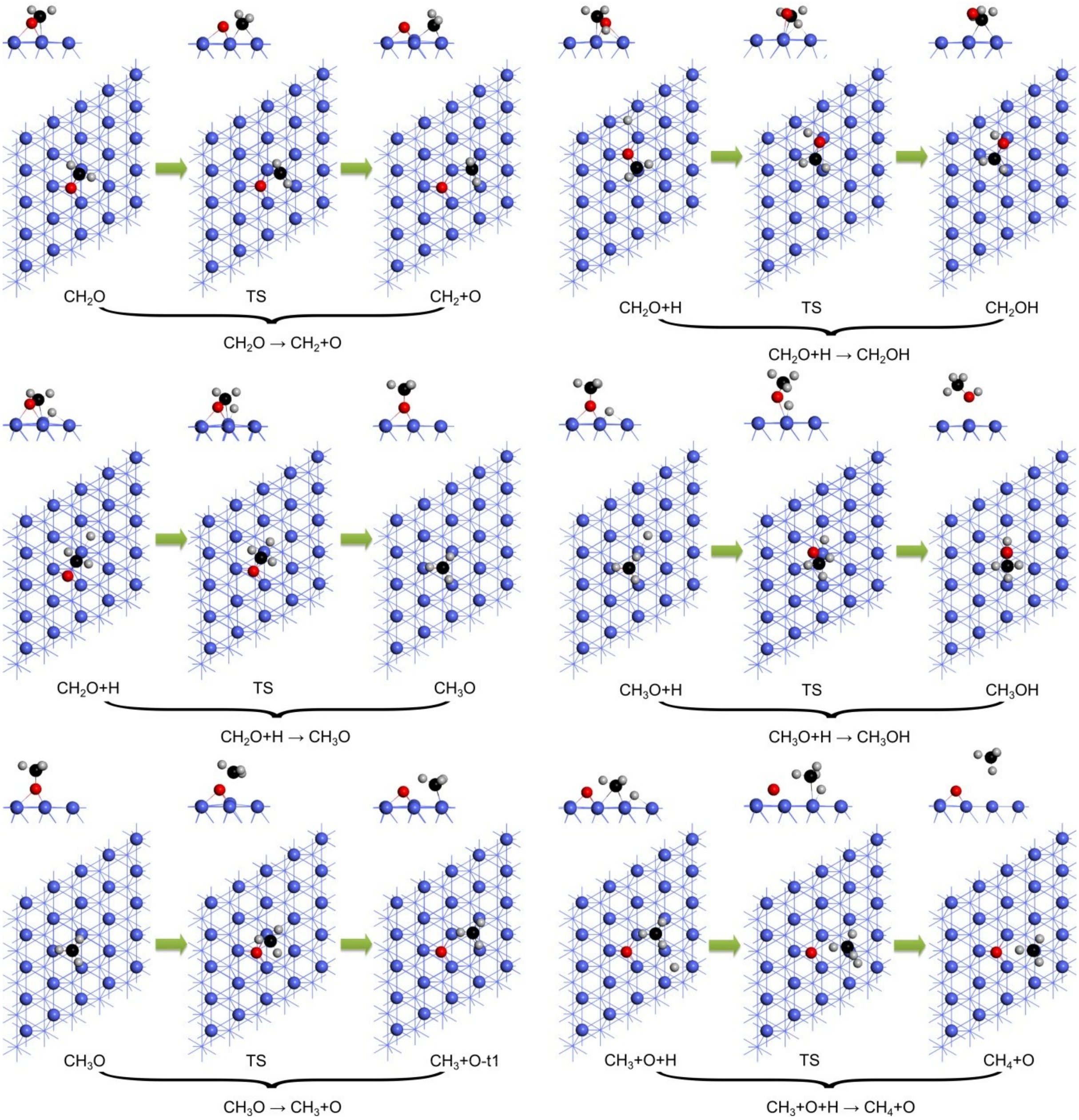


Figure S6. The geometries of the initial state and the final state as well as the transition state in the reaction of the coupling of CH_x (x=1-3) with H or CO

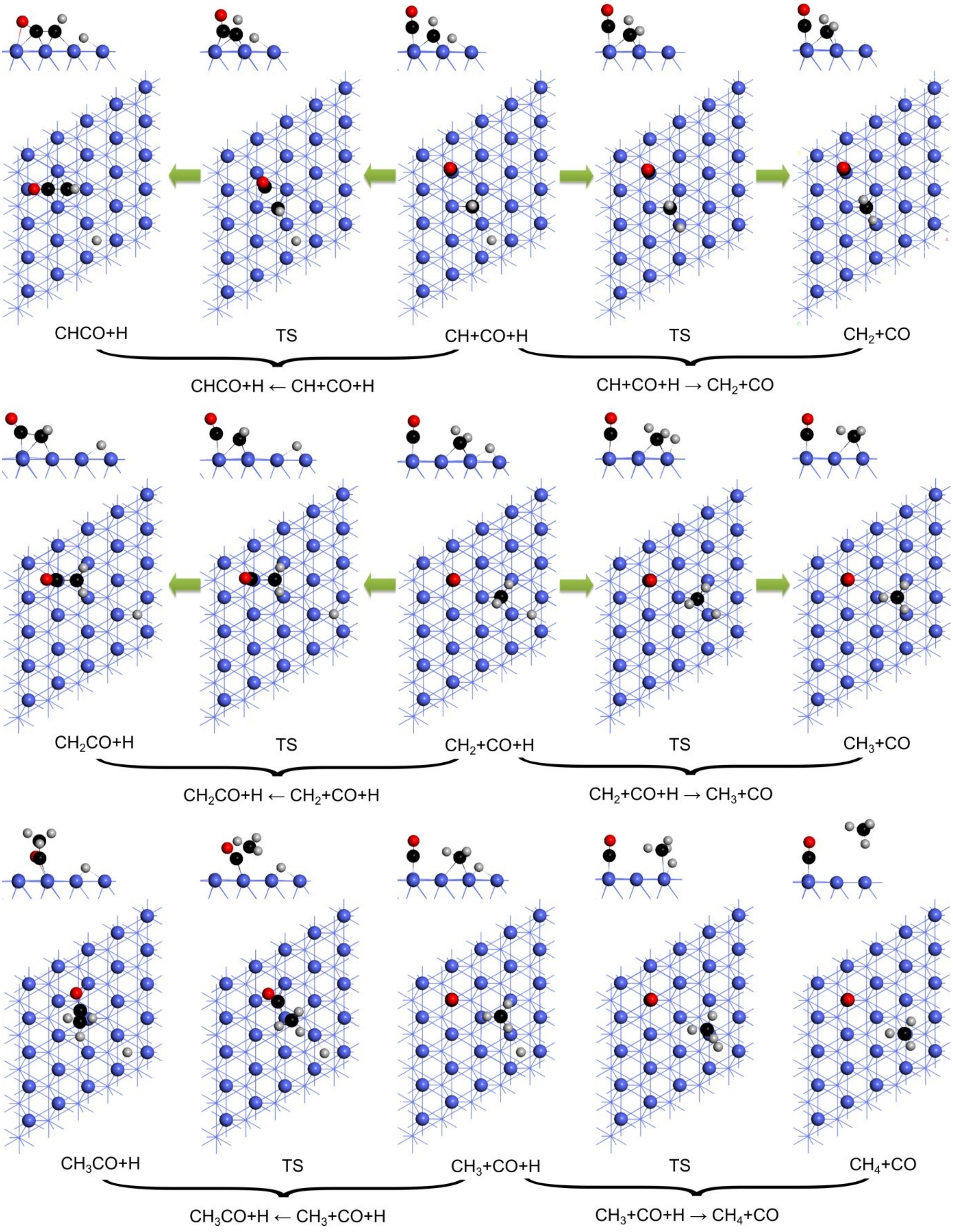


Figure S7. The geometries of the initial state and the final state as well as the transition state for the reactions starting from CO+OH in the OH-assisted pathway

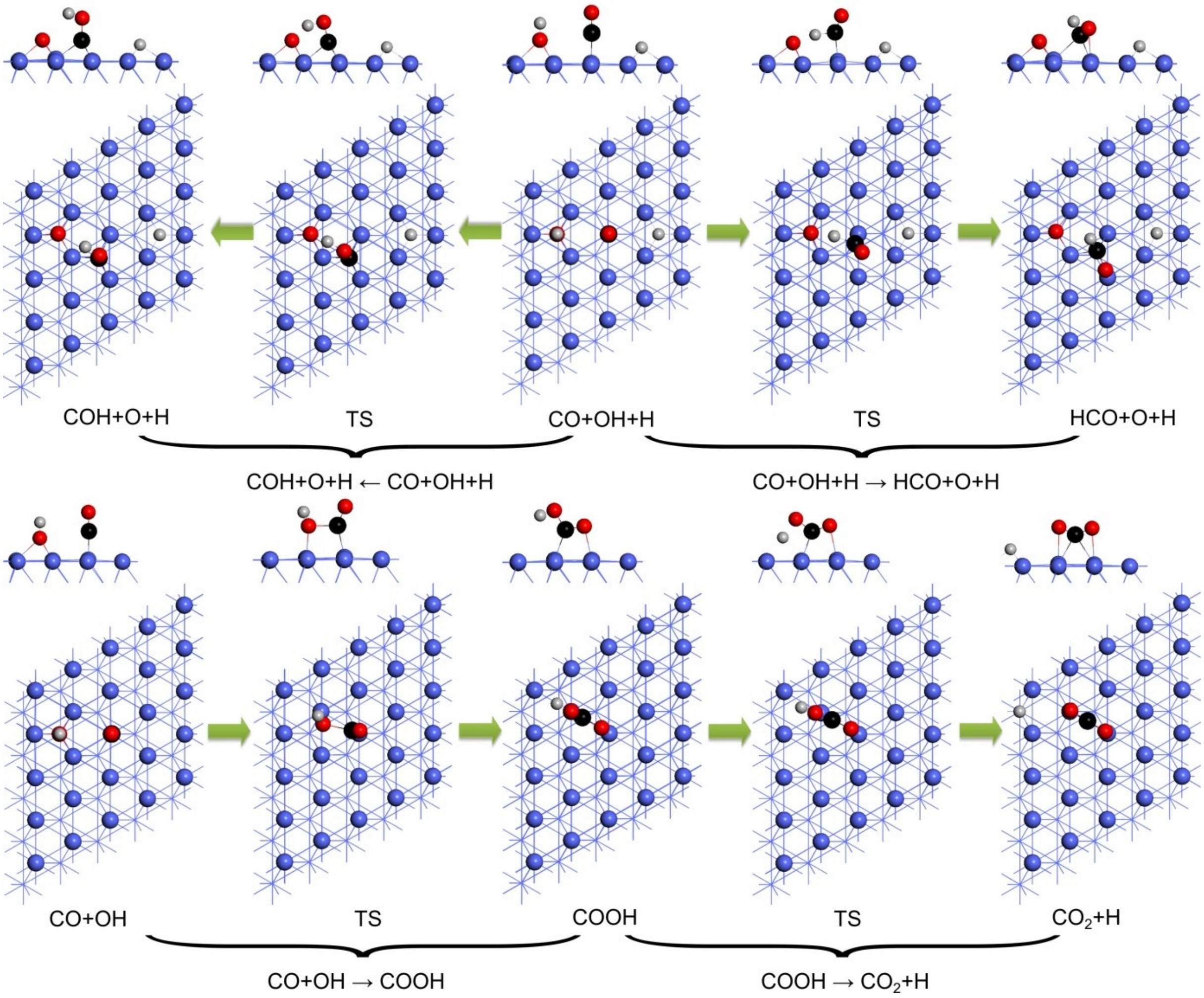
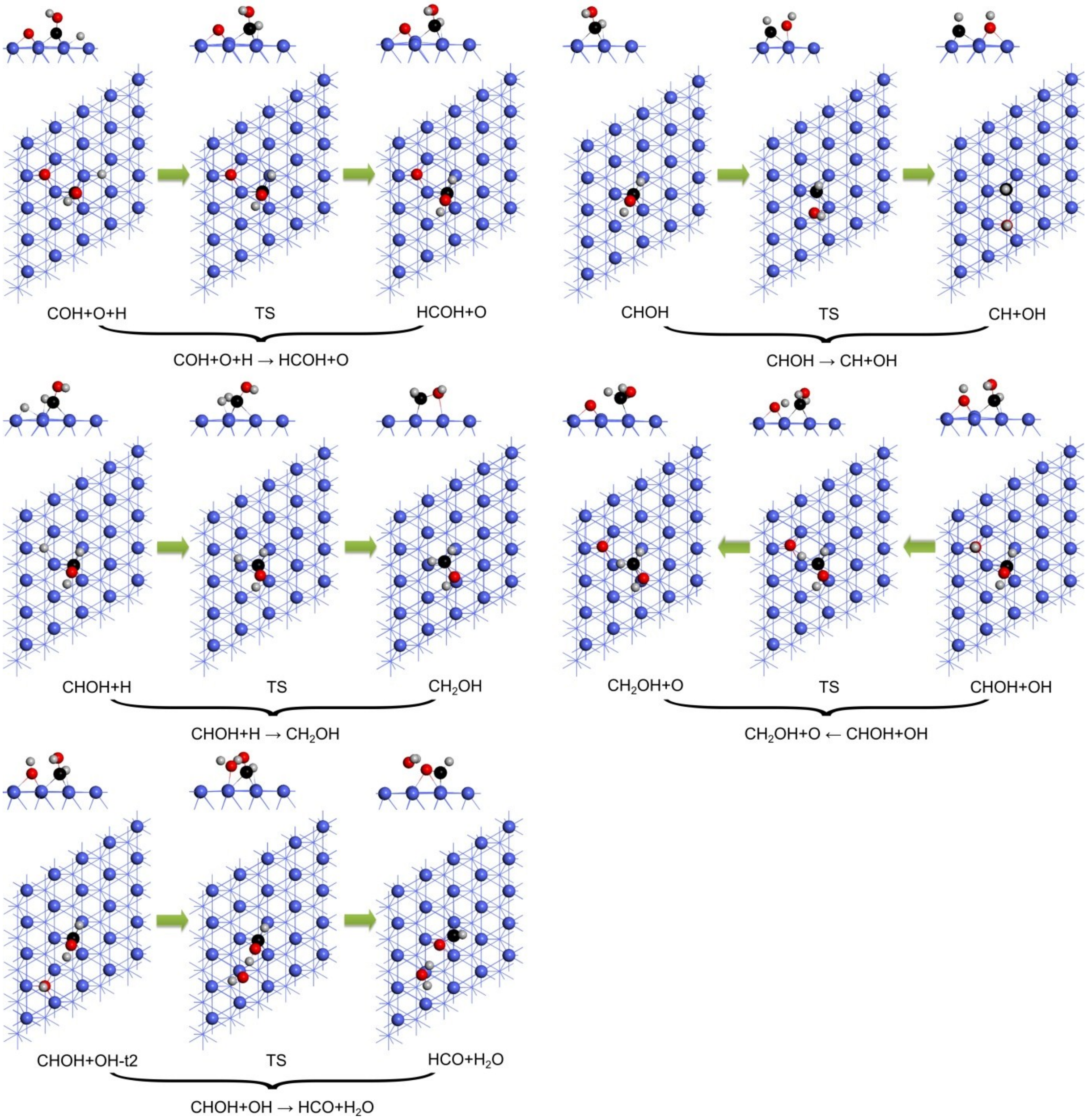


Figure S8. The geometries of the initial state and the final state as well as the transition state for the reactions starting from COH in the OH-assisted pathway



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