Supplementary Material

A new and different insight into the promotion mechanisms of Ga for carbon dioxide hydrogenation to methanol over Ga doped Ni(211) bimetallic catalyst

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Table S1. The activation barriers and reaction energies of elementary steps on Ni(211) and Ga-Ni(211) surfaces

No.	reaction	Ni(211)				Ga-Ni(211)				Ga_3Ni_5(111)			
		E_a	E_a^{ZPE}	ΔE	ΔE^{ZPE}	E_a	E_a^{ZPE}	ΔE	ΔE^{ZPE}	E_a	E_a^{ZPE}	ΔE	ΔE^{ZPE}
R1	H_2→H+H	0.10	0.00	-0.70	-0.72	0.02	-	-0.78	-0.76	0.03	-	-0.74	-0.73
R2	CO_2+H→*bi*-HCOO	0.78	0.85	-0.50	-0.35	0.56	0.64	-0.68	-0.55	0.56	0.63	-0.63	-0.47
R3	CO_2+H→*trans*-COOH	0.95	0.88	0.03	0.18	0.70	0.61	-0.12	0.02	0.69	0.65	-0.22	-0.06
R4	CO_2→CO+O	0.79	0.74	-0.72	-0.75	1.03	0.95	-0.27	-0.38	1.13	1.08	-0.79	-0.83
R5	*bi*-HCOO→*mono*-HCOO	0.71	0.70	0.66	0.69	0.73	0.66	0.63	0.58	0.66	0.62	0.57	0.53
R6	*bi*-HCOO→HCO+O	1.68	1.59	0.82	0.73	1.83	1.74	1.14	1.07	1.76	1.69	0.74	0.67
R7	*bi*-HCOO+H→H_2COO	1.72	1.75	1.02	1.15	1.90	1.88	1.02	1.08	1.59	1.59	0.91	1.00
R8	*bi*-HCOO+H→HCOOH	1.19	1.08	0.83	0.93	1.07	0.95	0.78	0.86	1.06	0.94	0.83	0.91
R9	H_2COO+H→H_2COOH	0.74	0.64	-0.15	-0.02	0.55	0.47	-0.49	-0.36	0.57	0.48	-0.58	-0.44
R10	HCOOH+H→H_2COOH	0.88	0.88	0.25	0.42	0.93	0.90	0.23	0.37	0.94	0.92	-0.04	0.13
R11	H_2COOH→H_2CO+OH	0.73	0.60	-0.28	-0.38	0.66	0.53	-0.01	-0.15	0.66	0.52	0.04	-0.07
R12	HCOOH→HCO+OH	0.91	0.87	-0.31	-0.38	0.58	0.65	-0.23	-0.31	0.49	0.47	-0.28	-0.38
R13	HCO+H→H_2CO	0.59	0.57	0.34	0.45	0.41	0.39	-0.29	-0.16	0.55	0.54	0.07	0.22
R14	H_2CO+H→CH_2OH	1.16	1.05	0.34	0.47	0.93	0.84	0.16	0.24	1.18	1.07	0.44	0.53
R15	H_2CO+H→CH_3O	0.49	0.46	-0.31	-0.19	0.44	0.39	-0.37	-0.25	0.43	0.42	-0.37	-0.27
R16	*trans*-COOH→*cis*-COOH	0.49	0.44	0.02	0.02	0.49	0.45	0.03	-0.02	0.51	0.45	0.01	0.01
R17	*cis*-COOH→CO+OH	1.04	0.93	-1.07	-1.15	0.95	0.92	-1.04	-1.05	0.99	0.87	-0.85	-0.92
R18	CO+H→COH	1.95	1.87	1.00	1.11	2.03	1.95	1.14	1.23	1.78	1.71	0.86	0.97
R19	CO+H→HCO	1.34	1.37	1.16	1.26	1.25	1.28	1.17	1.26	1.05	1.08	0.96	1.05
R20	*trans*-COOH+H→*t,t*-COHOH	0.53	0.45	-0.12	0.02	0.65	0.60	-0.25	-0.08	0.73	0.72	-0.09	0.08
R21	*t,t*-COHOH→*t,c*-COHOH	0.42	0.39	0.10	0.09	0.41	0.38	0.10	0.09	0.42	0.40	0.06	0.08

No.	reaction	Ni(211)				Ga-Ni(211)				Ga_3Ni_5(111)			
		E_a	E_a^{ZPE}	ΔE	ΔE^{ZPE}	E_a	E_a^{ZPE}	ΔE	ΔE^{ZPE}	E_a	E_a^{ZPE}	ΔE	ΔE^{ZPE}
R22	*t,c*-COHOH→*c,c*-COHOH	0.57	0.53	0.55	0.51	0.47	0.47	0.43	0.43	0.41	0.39	0.40	0.33
R23	*t,t*-COHOH→COH+OH	1.21	1.12	-0.47	-0.55	1.22	1.14	-0.43	-0.53	1.10	1.03	-0.34	-0.42
R24	*t,c*-COHOH→COH+OH	1.05	0.98	-0.72	-0.77	1.13	1.01	-0.57	-0.63	0.99	0.87	-0.43	-0.48
R25	*c,c*-COHOH→COH+OH	0.36	0.38	-1.09	-1.09	0.77	0.75	-0.92	-0.93	0.63	0.63	-0.78	-0.82
R26	COH+H→HCOH	0.62	0.64	0.29	0.48	0.58	0.56	0.02	0.17	0.53	0.52	0.17	0.30
R27	HCOH+H→CH_2OH	0.61	0.60	0.43	0.50	0.51	0.50	0.31	0.40	0.43	0.44	0.15	0.22
R28	CH_2OH+H→CH_3OH	0.66	0.62	0.00	0.15	0.57	0.60	0.11	0.26	0.30	0.25	-0.38	-0.26
R29	CH_3O+H→CH_3OH	1.44	1.37	0.58	0.72	1.45	1.41	0.67	0.81	1.30	1.27	0.58	0.74
R30	O+H→OH	1.26	1.19	-0.15	-0.04	1.27	1.20	-0.27	-0.20	1.16	1.10	-0.29	-0.19
R31	OH+H→H_2O	1.53	1.44	0.67	0.76	1.00	0.90	0.28	0.36	0.95	0.85	0.33	0.45

ZPE denotes zero point energy correction, E_a, E_a^{ZPE}, ΔE and ΔE^{ZPE} are in eV

Table S2. The reaction rate constants at the temperature of 500-600 K of elementary steps in the process of CO_2 hydrogenation to CH_3OH.

	Reactions	k/s^{-1}				
		500K	525K	550K	575K	600K
1	H_2→H+H	1.59E+13	1.57E+13	1.56E+13	1.54E+13	1.53E+13
2	CO_2+H→*bi*-HCOO	7.57E+06	1.61E+07	3.20E+07	5.99E+07	1.06E+08
3	CO_2+H→*trans*-COOH	2.53E+08	5.23E+08	1.02E+09	1.86E+09	3.26E+09
4	CO_2→CO+O	3.00E+03	9.05E+03	2.47E+04	6.20E+04	1.44E+05
5	*bi*-HCOO→*mono*-HCOO	8.93E+11	1.02E+12	1.15E+12	1.29E+12	1.44E+12
6	*bi*-HCOO→HCO+O	1.81E-05	1.30E-04	7.84E-04	4.05E-03	1.83E-02
7	*bi*-HCOO+H→H_2COO	2.01E-06	1.68E-05	1.16E-04	6.83E-04	3.46E-03
8	*bi*-HCOO+H→HCOOH	7.72E+03	2.31E+04	6.26E+04	1.56E+05	3.61E+05
9	H_2COO+H→H_2COOH	4.51E+08	7.92E+08	1.32E+09	2.12E+09	3.28E+09
10	HCOOH+H→H_2COOH	6.14E+03	1.74E+04	4.50E+04	1.07E+05	2.39E+05
11	H_2COOH→H_2CO+OH	1.08E+08	2.04E+08	3.65E+08	6.21E+08	1.01E+09
12	HCOOH→HCO+OH	4.89E+05	1.06E+06	2.14E+06	4.07E+06	7.37E+06
13	HCO+H→H_2CO	2.41E+08	3.89E+08	6.01E+08	8.98E+08	1.30E+09
14	H_2CO+H→CH_2OH	2.84E+04	7.57E+04	1.85E+05	4.19E+05	8.88E+05
15	H_2CO+H→CH_3O	4.48E+08	7.28E+08	1.13E+09	1.70E+09	2.47E+09
16	*trans*-COOH→*cis*-COOH	2.08E+08	3.60E+08	5.95E+08	9.43E+08	1.44E+09
17	*cis*-COOH→CO+OH	6.23E+03	1.81E+04	4.78E+04	1.16E+05	2.63E+05
18	CO+H→COH	1.58E-07	1.44E-06	1.07E-05	6.71E-05	3.62E-04
19	CO+H→HCO	1.10E+00	4.73E+00	1.79E+01	6.02E+01	1.83E+02
20	*trans*-COOH+H→*t,t*-COHOH	2.96E+06	6.05E+06	1.16E+07	2.11E+07	3.65E+07
21	*t,t*-COHOH→*t,c*-COHOH	3.27E+09	5.21E+09	7.98E+09	1.18E+10	1.69E+10
22	*t,c*-COHOH→*c,c*-COHOH	4.43E+08	7.72E+08	1.28E+09	2.04E+09	3.12E+09
23	*t,t*-COHOH→COH+OH	5.19E+01	1.93E+02	6.37E+02	1.90E+03	5.18E+03
24	*t,c*-COHOH→COH+OH	1.39E+03	4.47E+03	1.30E+04	3.44E+04	8.42E+04
25	*c,c*-COHOH→COH+OH	5.78E+05	1.39E+06	3.09E+06	6.43E+06	1.26E+07
26	COH+H→HCOH	2.41E+07	4.70E+07	8.65E+07	1.51E+08	2.52E+08
27	HCOH+H→CH_2OH	3.07E+07	5.62E+07	9.75E+07	1.62E+08	2.57E+08
28	CH_2OH+H→CH_3OH	4.16E+06	8.50E+06	1.63E+07	2.96E+07	5.13E+07
29	CH_3O+H→CH_3OH	2.55E-02	1.27E-01	5.47E-01	2.08E+00	7.08E+00
30	O+H→OH	1.81E+01	7.13E+01	2.48E+02	7.76E+02	2.21E+03
31	OH+H→H_2O	8.65E+03	2.47E+04	6.40E+04	1.53E+05	3.42E+05

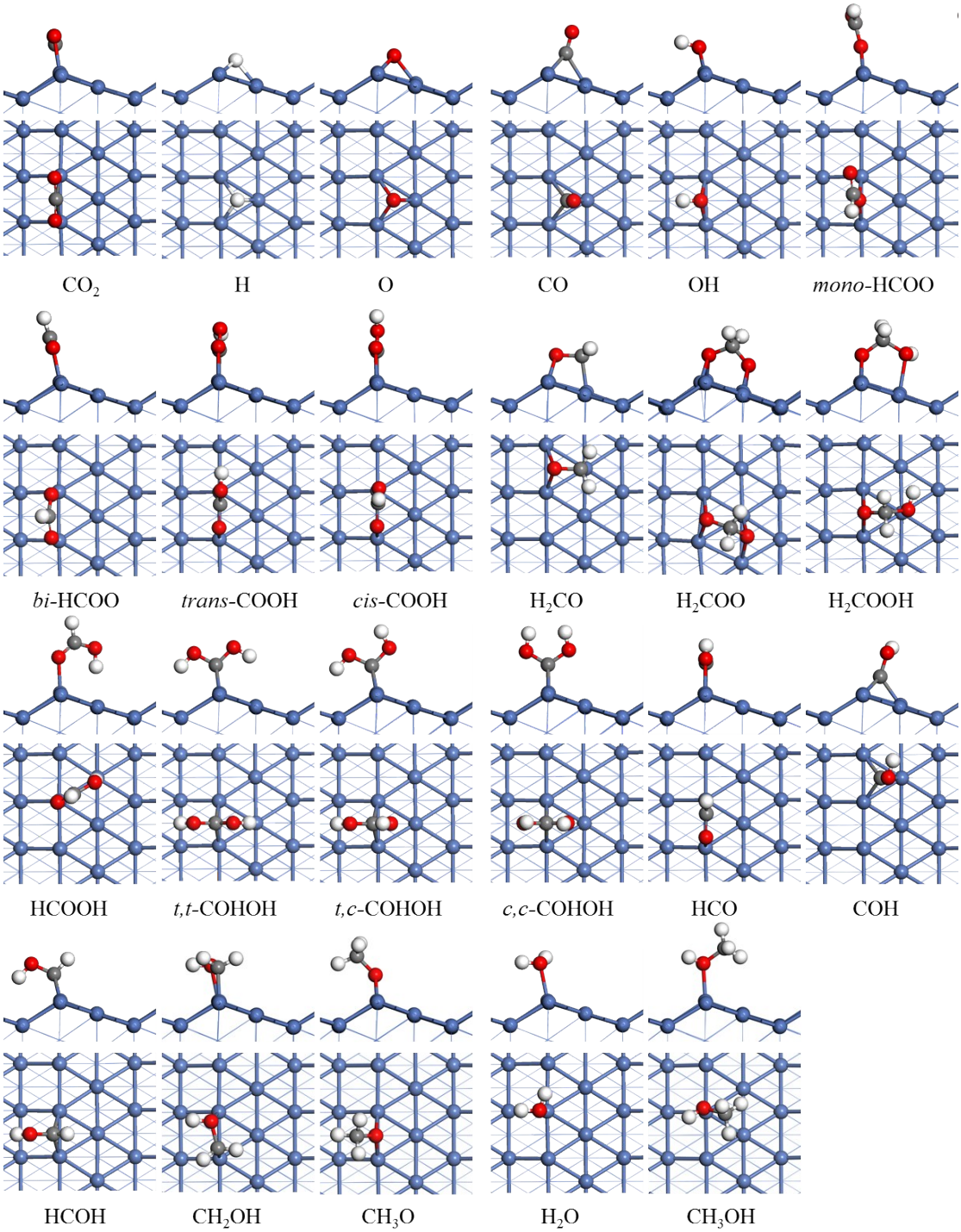

Figure S1. The side views (top) and top views (bottom) of optimized structures of potential intermediates in the process of CH_3OH synthesis on Ni(211) surface.

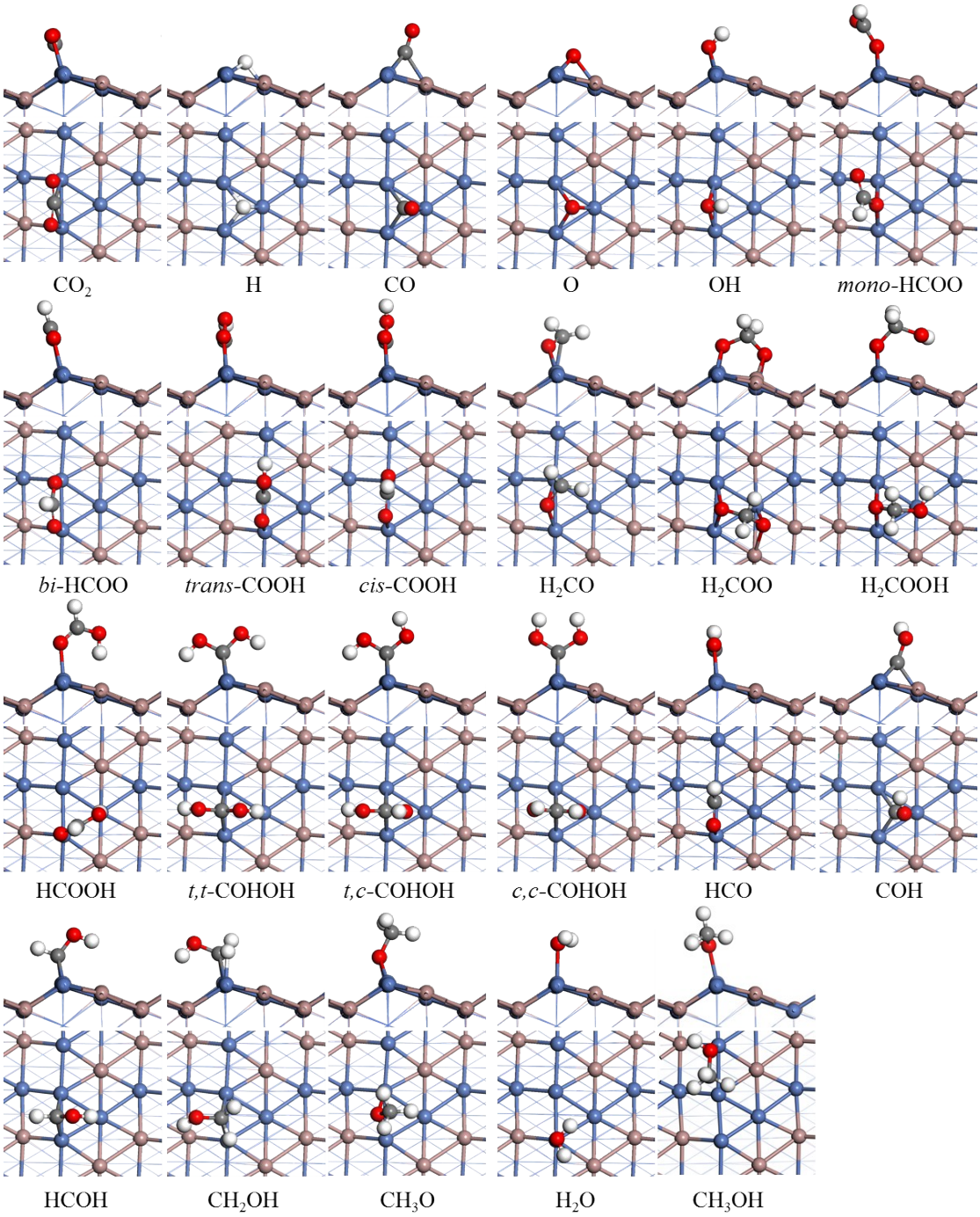

Figure S2. The side views (top) and top views (bottom) of the optimized structures of potential intermediates in the process of CH_3OH synthesis on Ga-Ni(211) surface.

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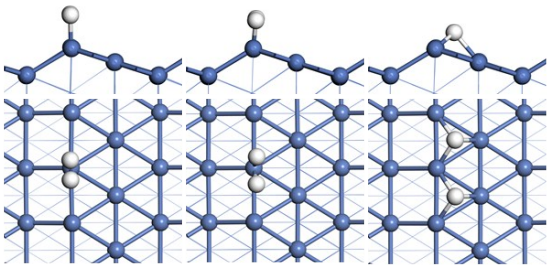
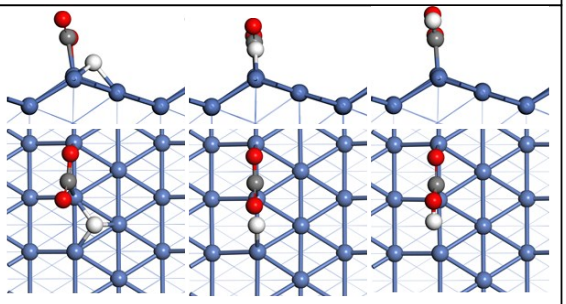
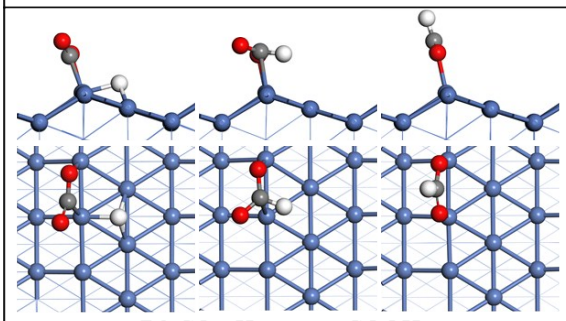
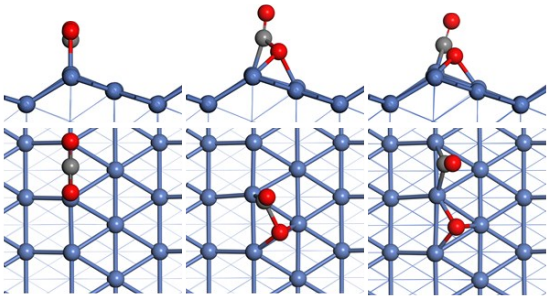
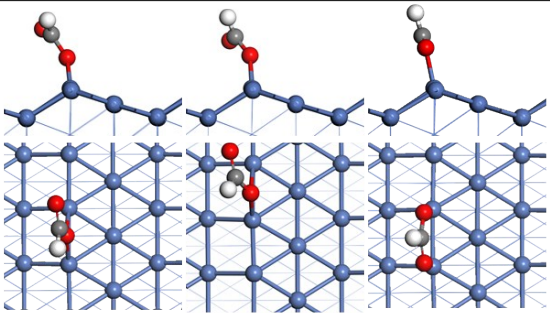
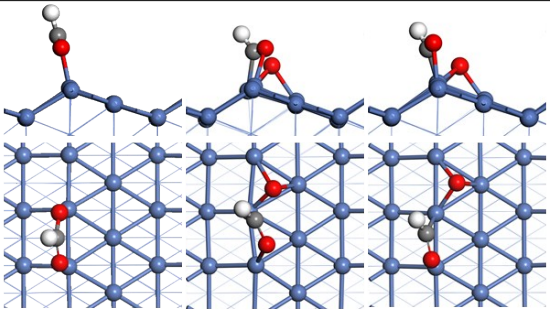
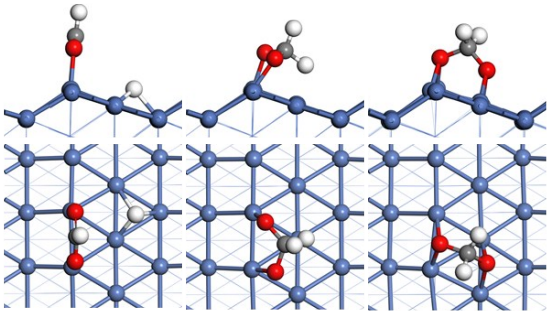
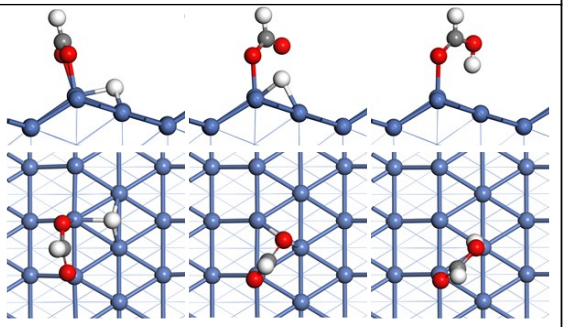
					
R1.H_2→H+H			R2.CO_2+H→*bi*-HCOO		
					
R3.CO_2+H→*trans*-COOH			R4.CO_2→CO+O		
					
R5.*mono*-HCOO→*bi*-HCOO			R6.*bi*-HCOO→HCO+O		
					
R7.*bi*-HCOO+H→H_2COO			R8.*bi*-HCOO+H→HCOOH		

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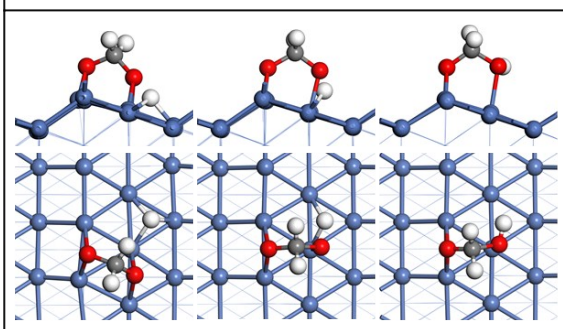
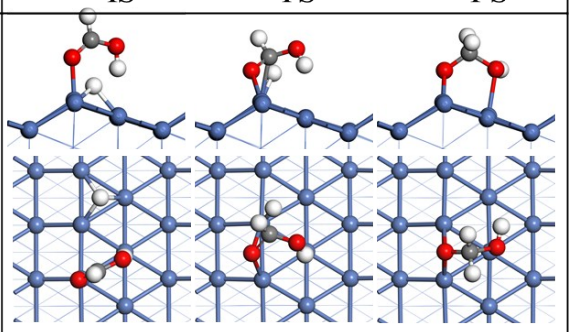
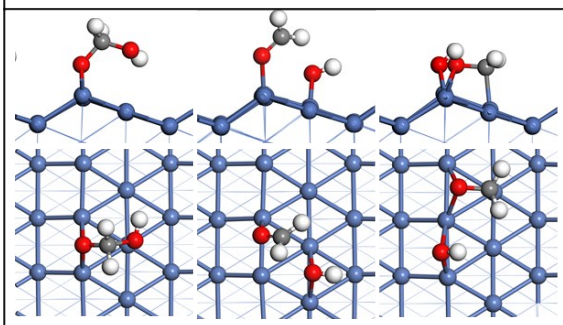
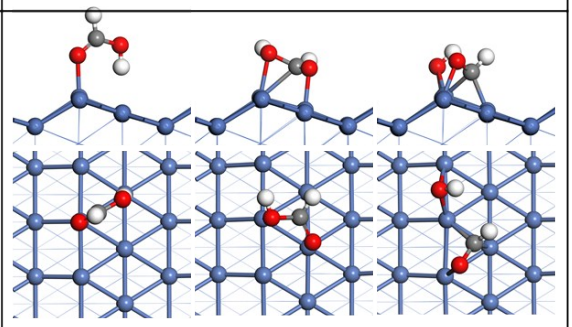
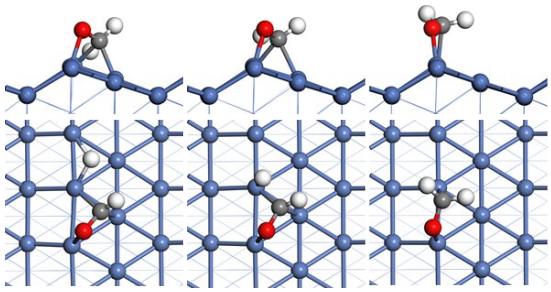
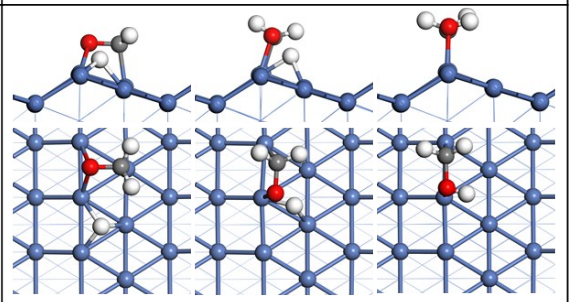
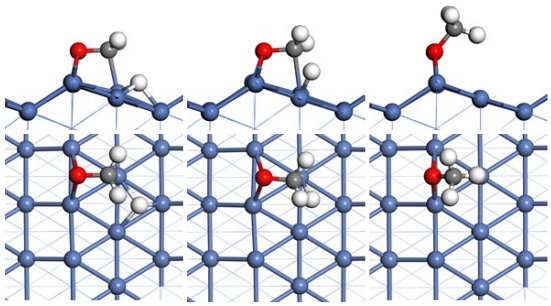
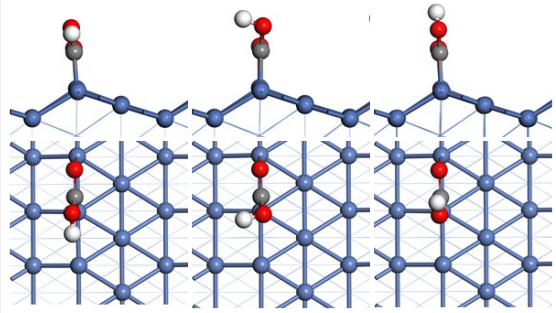
					
R9.$H_2COO+H \rightarrow H_2COOH$			R10.$HCOOH+H \rightarrow H_2COOH$		
					
R11.$H_2COOH \rightarrow H_2CO+OH$			R12.$HCOOH \rightarrow HCO+OH$		
					
R13.$HCO+H \rightarrow H_2CO$			R14.$H_2CO+H \rightarrow CH_2OH$		
					
R15.$H_2CO+H \rightarrow CH_3O$			R16.*trans*-COOH→*cis*-COOH		

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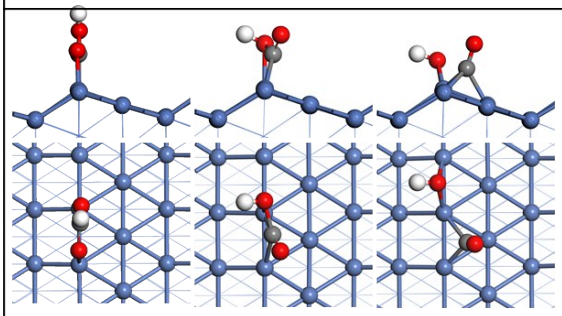
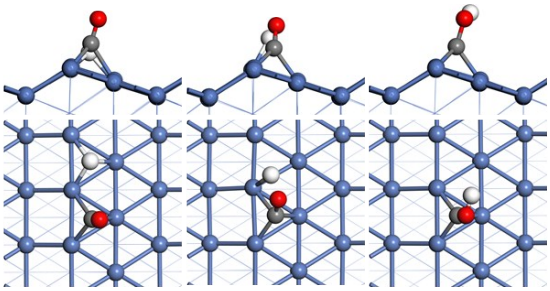
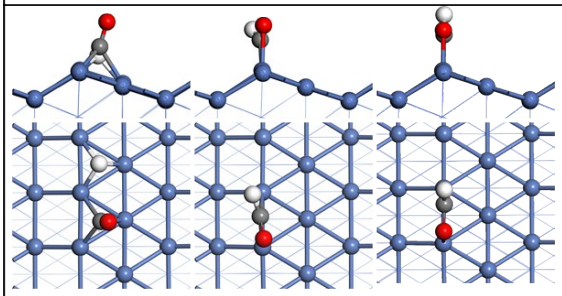
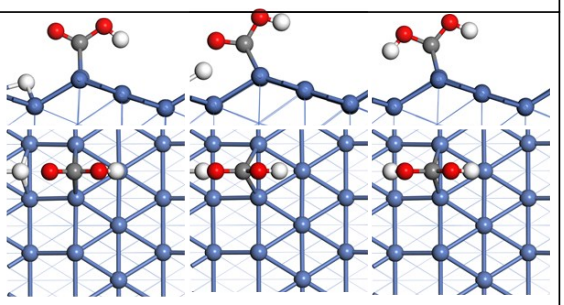
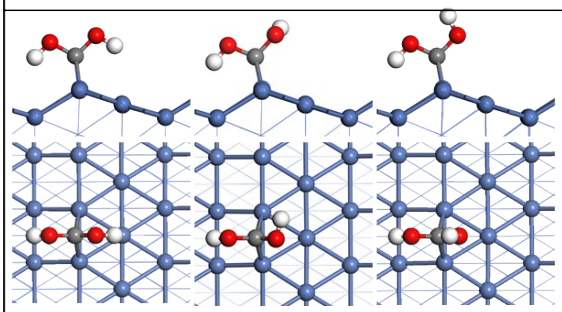
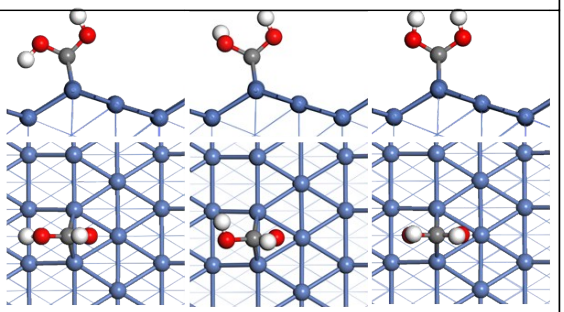
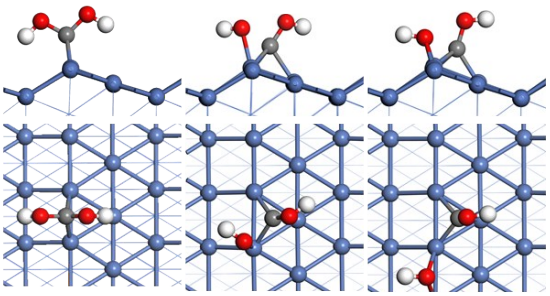
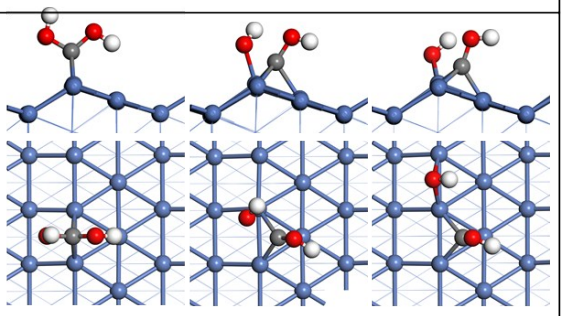
					
R17.*cis*-COOH→CO+OH			R18.CO+H→COH		
					
R19.CO+H→HCO			R20.*trans*-COOH+H→*t,t*-COHOH		
					
R21.*t,t*-COHOH→*t,c*-COHOH			R22.*t,c*-COHOH→*c,c*-COHOH		
					
R23.*t,t*-COHOH→COH+OH			R24.*t,c*-COHOH→COH+OH		

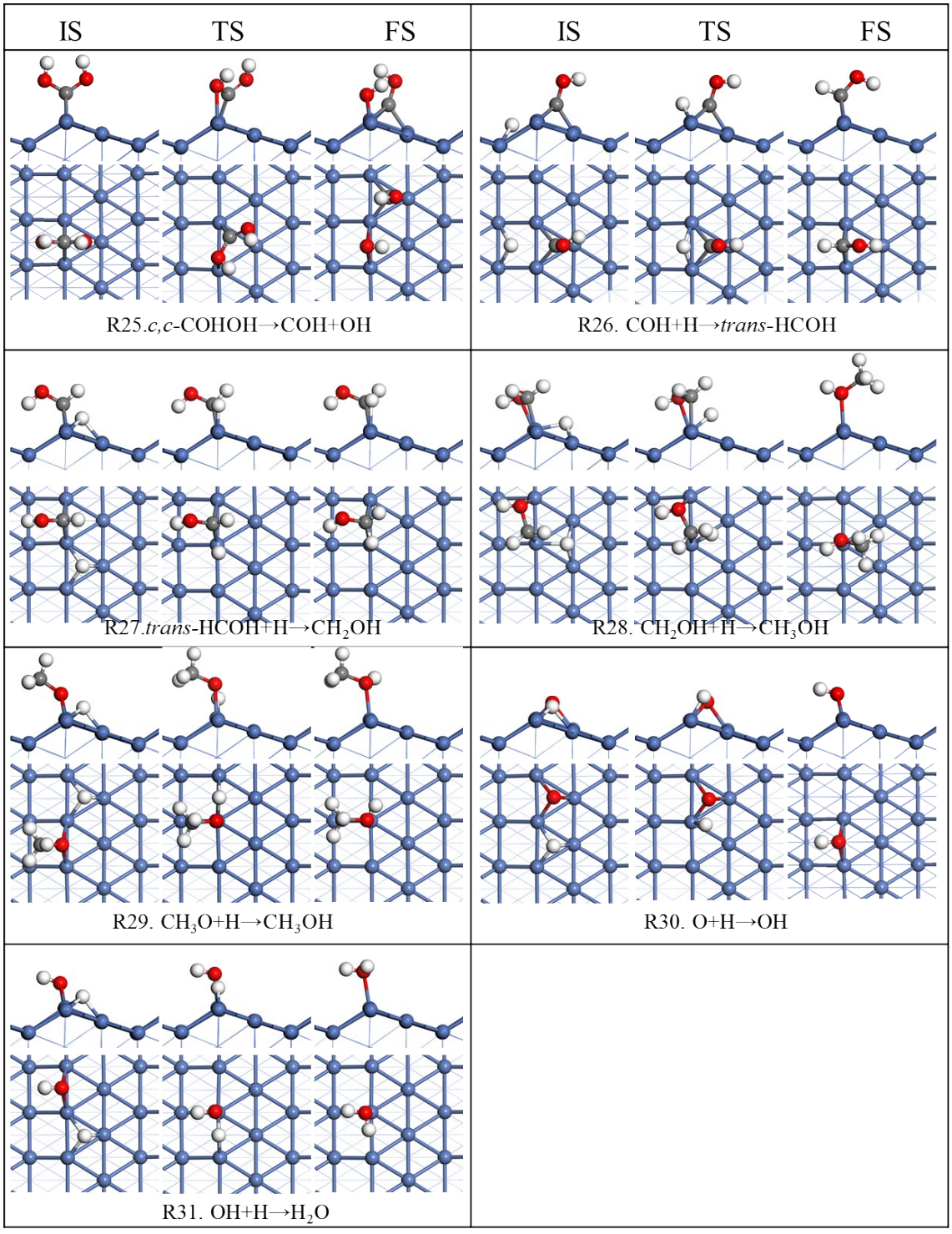
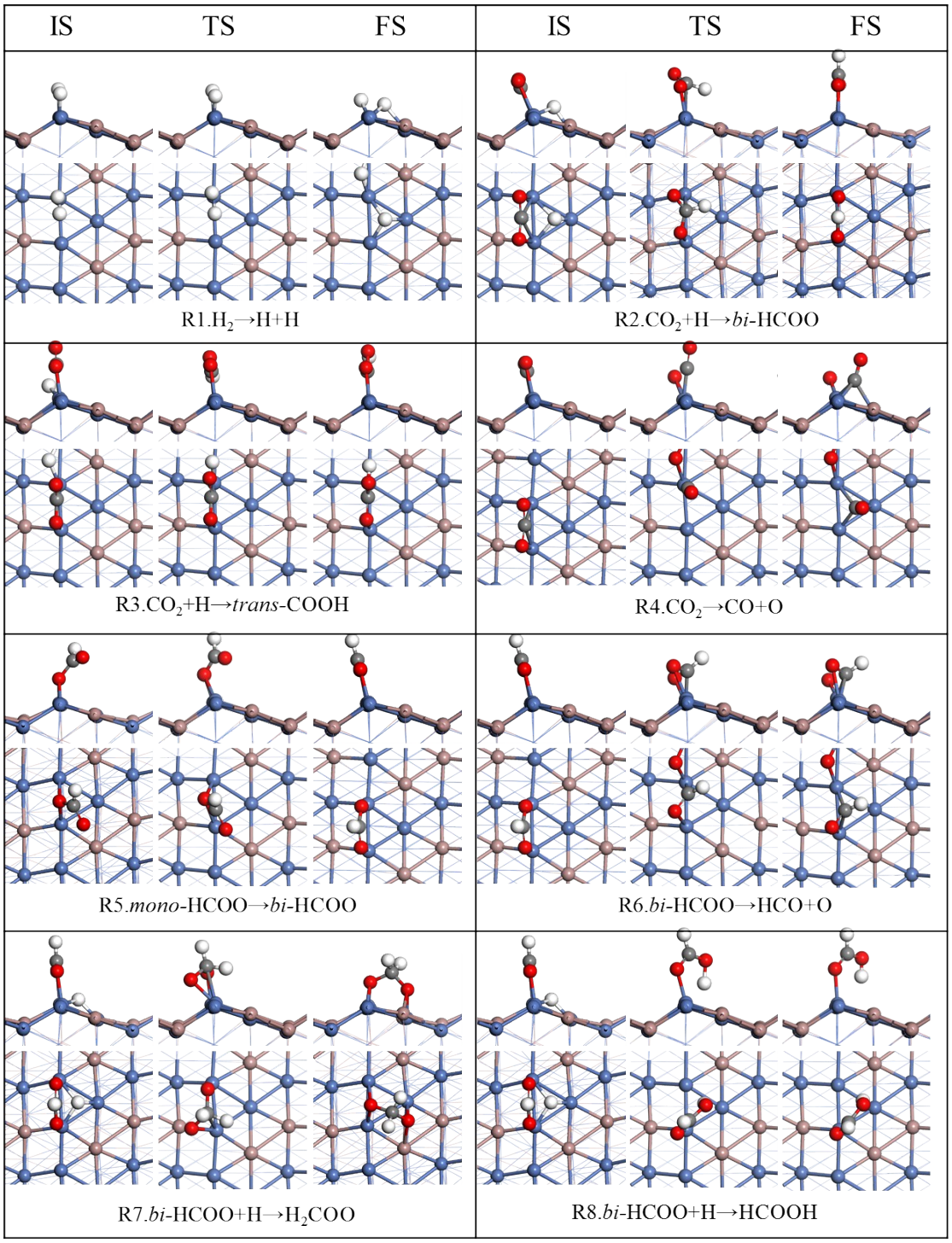
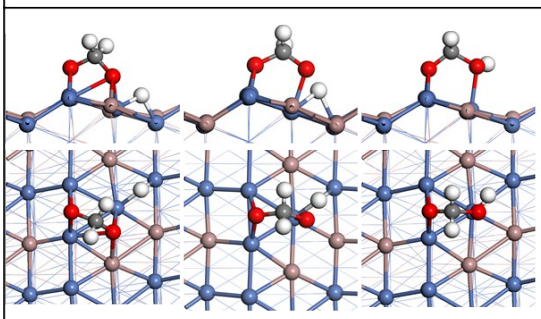
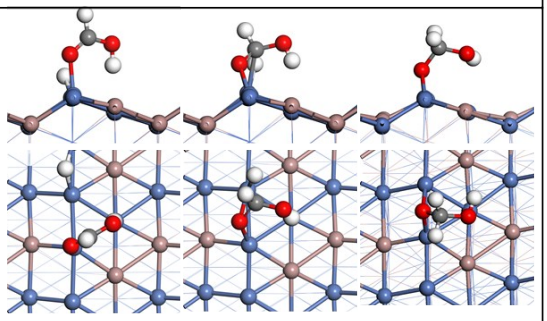
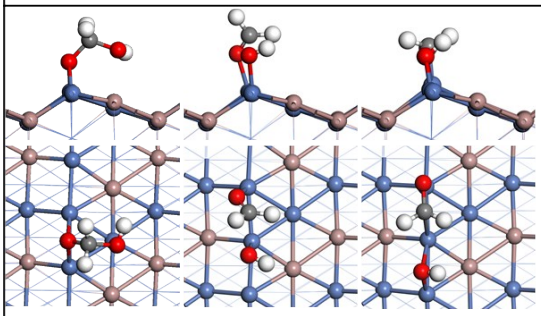
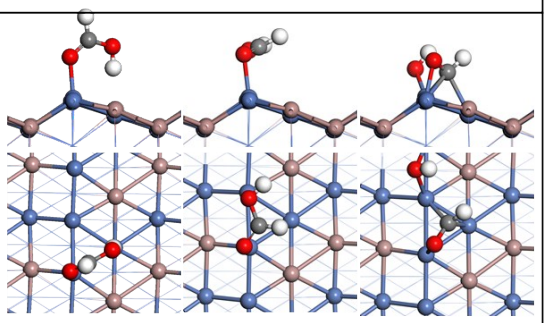
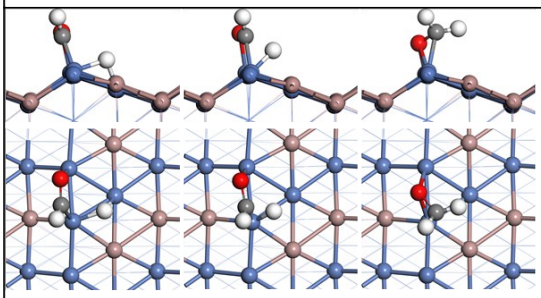
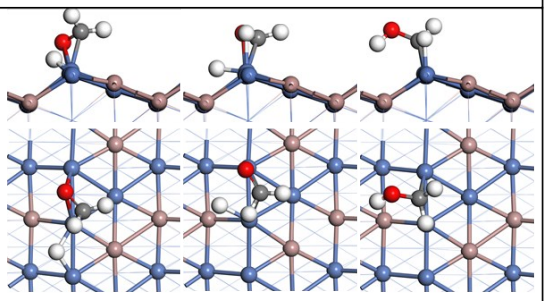
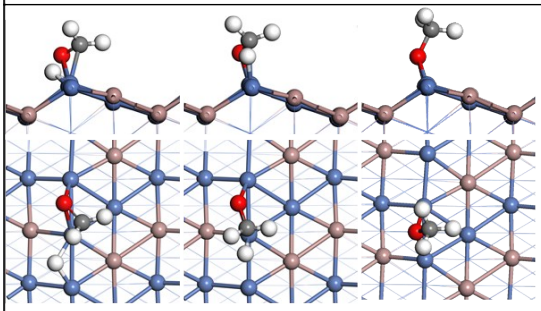
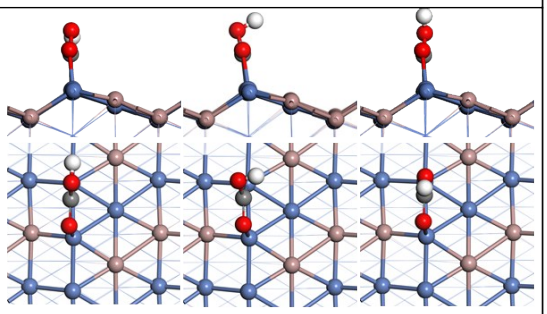
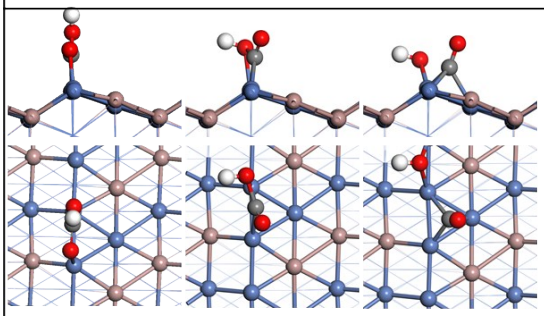
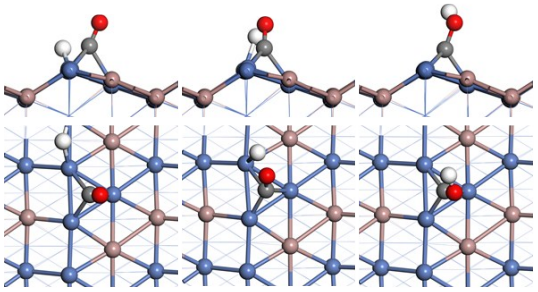
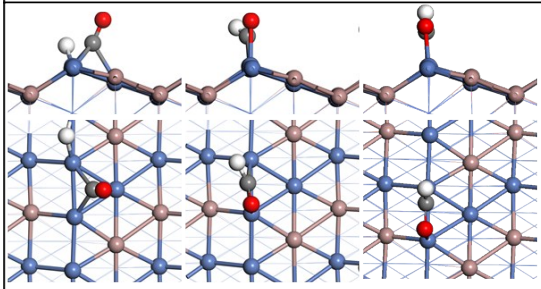
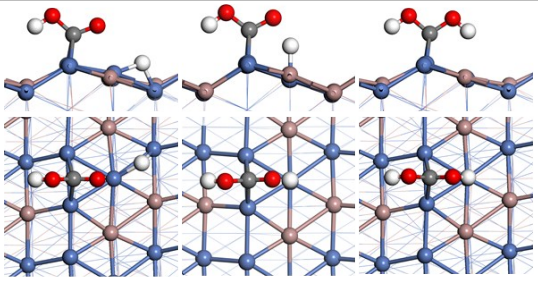
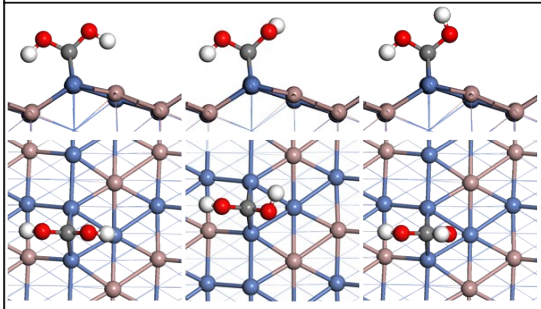
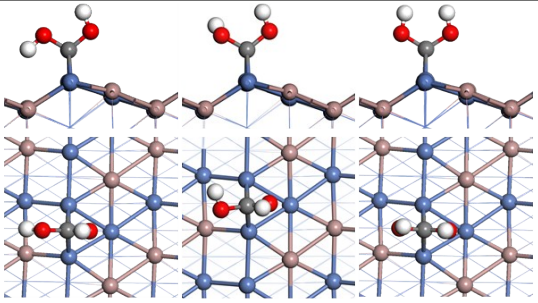
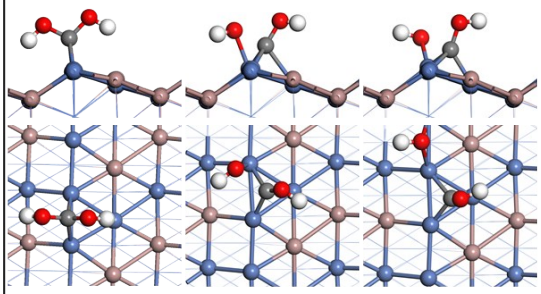
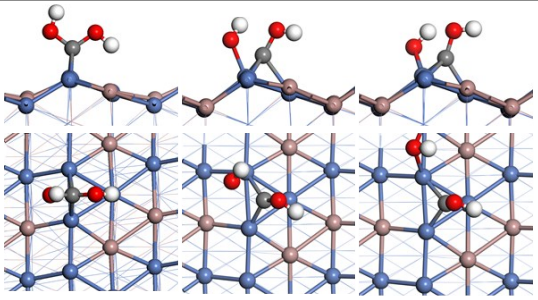


Figure S3. The side views (top one) and top views (bottom one) of ISs, TSs and FSs of all the elementary steps that are considered in the process of CO_2 hydrogenation to CH_3OH on Ni(211) surface.


IS
TS
FS
IS
TS
FS
R1.H_2→H+H
R2.CO_2+H→*bi*-HCOO
R3.CO_2+H→*trans*-COOH
R4.CO_2→CO+O
R5.*mono*-HCOO→*bi*-HCOO
R6.*bi*-HCOO→HCO+O
R7.*bi*-HCOO+H→H_2COO
R8.*bi*-HCOO+H→HCOOH

IS	TS	FS	IS	TS	FS
					
R9.$H_2COO+H \rightarrow H_2COOH$			R10.$HCOOH+H \rightarrow H_2COOH$		
					
R11.$H_2COOH \rightarrow H_2CO+OH$			R12.$HCOOH \rightarrow HCO+OH$		
					
R13.$HCO+H \rightarrow H_2CO$			R14.$H_2CO+H \rightarrow CH_2OH$		
					
R15.$H_2CO+H \rightarrow CH_3O$			R16.*trans*-COOH→*cis*-COOH		

IS	TS	FS	IS	TS	FS
					
R17.*cis*-COOH→CO+OH			R18.CO+H→COH		
					
R19.CO+H→HCO			R20.*trans*-COOH+H→*t,t*-COHOH		
					
R21.*t,t*-COHOH→*t,c*-COHOH			R22.*t,c*-COHOH→*c,c*-COHOH		
					
R23.*t,t*-COHOH→COH+OH			R24.*t,c*-COHOH→COH+OH		

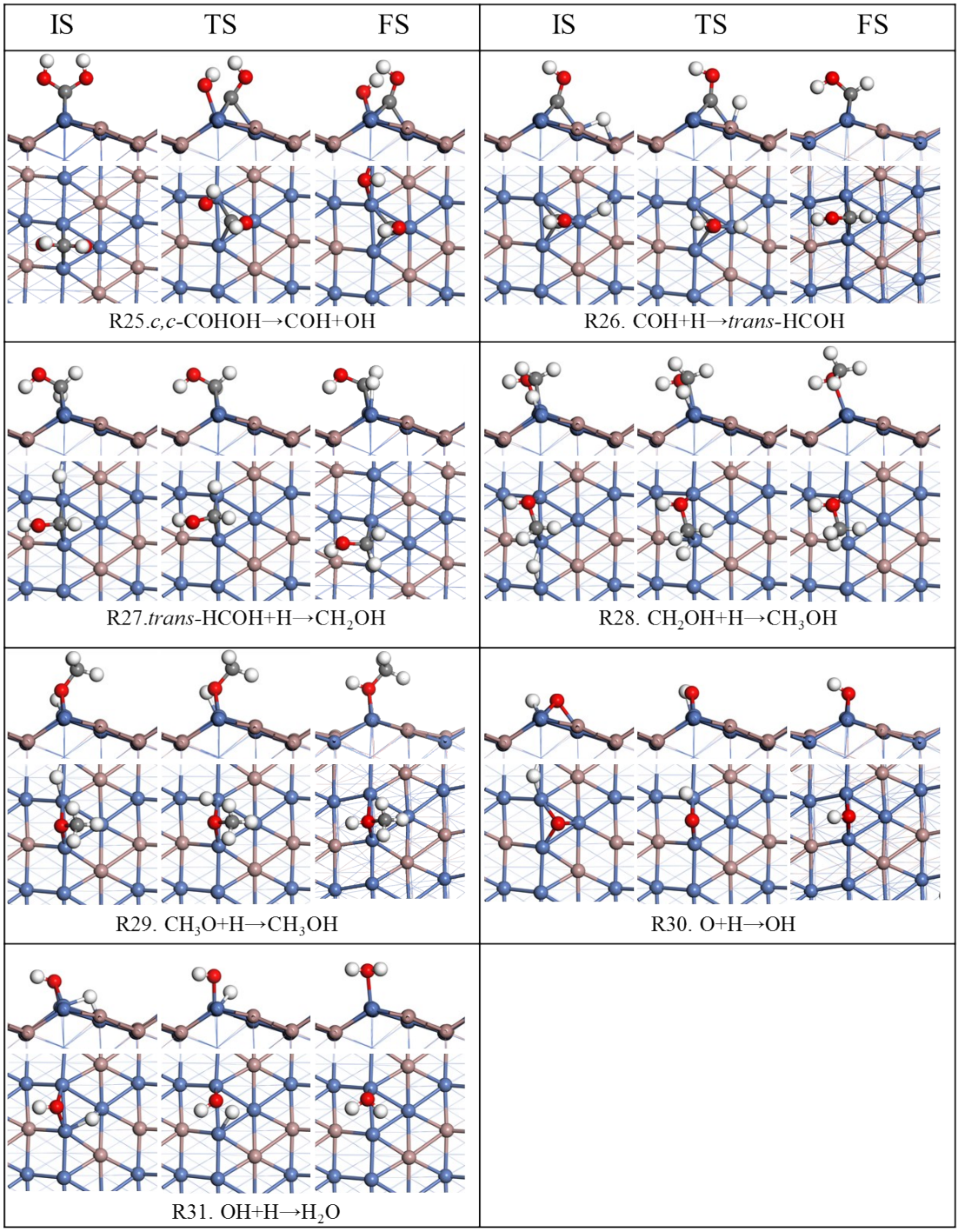


Figure S4. The side views (top one) and top views (bottom one) of ISs, TSs and FSs of all the elementary steps that are considered in the process of CO_2 hydrogenation to CH_3OH on Ga-Ni(211) surface.

Computational details of micro-kinetic modeling

The site balance of intermediates can be written in the coverage of the species.[1] Pseudo steady-state approximation[2] was used to describe the adsorbed surface species, based on the assumption that the production and consumption rate are equal for the species. In addition, the adsorptions of CO_2 and H_2 are assumed to be in equilibrium in the micro-kinetic modeling. The equations are displayed as follows:

$$\theta_{CO_2} + \theta_H + \theta_{trans-COOH} + \theta_{cis-COOH} + \theta_{OH} + \theta_{t,t-COHOH} + \theta_{t,c-COHOH} + \theta_{c,c-COHOH} + \theta_{HCOH} + \theta_{CH_2OH} + \theta^* = 1 \quad (1)$$

$$k_3 * \theta_{CO_2} * \theta_H - k_{16} * \theta_{trans-COOH} - k_{20} * \theta_{trans-COOH} * \theta_H = 0 \quad (2)$$

$$k_{17} * \theta_{cis-COOH} + k_{23} * \theta_{t,t-COHOH} + k_{24} * \theta_{t,c-COHOH} + k_{25} * \theta_{c,c-COHOH} - k_{31} * \theta_{OH} * \theta_H = 0 \quad (3)$$

$$k_{16} * \theta_{trans-COOH} - k_{17} * \theta_{cis-COOH} = 0 \quad (4)$$

$$k_{20} * \theta_{trans-COOH} * \theta_H - (k_{21} * \theta_{t.t-COHOH} + k_{23} * \theta_{t,t-COHOH}) = 0 \quad (5)$$

$$k_{21} * \theta_{t,t-COHOH} - (k_{22} * \theta_{t.c-COHOH} + k_{24} * \theta_{t,c-COHOH}) = 0 \quad (6)$$

$$k_{22} * \theta_{t,c-COHOH} - k_{25} * \theta_{c,c-COHOH} = 0 \quad (7)$$

$$k_{23} * \theta_{t,t-COHOH} + k_{24} * \theta_{t,c-COHOH} + k_{25} * \theta_{c,c-COHOH} - k_{26} * \theta_{COH} * \theta_H = 0 \quad (8)$$

$$k_{26} * \theta_{COH} - k_{27} * \theta_{HCOH} = 0 \quad (9)$$

$$k_{27} * \theta_{HCOH} - k_{28} * \theta_{CH_2OH} = 0 \quad (10)$$

$$\theta_{CO_2} = P_{CO_2} * k * \theta^* \quad (11)$$

$$\theta_H = \sqrt{P_{H_2} * k_1} * \theta^* \quad (12)$$

where θ_x represents the coverage rate of x. θ^* is the coverage of free site.

(1) Zhang, R.; Peng, M.; Wang, B. Catalytic selectivity of Rh/TiO_2 catalyst in syngas conversion to ethanol: probing into the mechanism and functions of TiO_2 support and promoter. *Catal. Sci. Technol.* **2017**, *7*, 1073-1085.

(2) Liu P.; Logadottir A.; Nørskov J. K. Modeling the electro-oxidation of CO and H_2/CO on Pt, Ru, PtRu and Pt_3Sn. *Electrochim. Acta*. **2003**, *48*, 3731-3742.