Supplemental Materials

DFT and DRIFTS Studies of Oxidative Carbonylation of Methanol over γ-Cu₂Cl(OH)₃: the Influence of Cl

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 Geometric and electronic character of γ-Cu₂Cl(OH)₃(021) before and after geometry optimized There are five kinds of atoms on γ-Cu₂Cl(OH)₃(021) after geometry optimization: one-coordinated H atoms; two-coordinated Cl atoms, three-coordinated O atoms, four-coordinated O atoms, and six-coordinated Cu atoms. Four Cl atoms (donated as Cl_A, Cl_B, Cl_C and Cl_D, shown in Fig. 2) are located at the top layer of the γ-Cu₂Cl(OH)₃(021).

Compared to the bulk structure, the γ -Cu₂Cl(OH)₃(021) reconstructed after relaxation. From Table S1, it is clear that after relaxation, the bond population of Cl_X-Cu_{X,1} (X indicates A, B, C or D) became smaller while the Cl_X-Cu_{X,2} became larger. The opposite tendency was observed on the distance of these Cl_X-Cu_{X,1} and Cl_X-Cu_{X,2} bond and except the Cl_D-Cu_{D,1}. Meanwhile, the charge of the top four Cl atoms were also reduced (Table S2).

Table S1 The overlap population and bond distances (Å) of the relative atoms at the γ -Cu₂Cl(OH)₃(021) before and after relaxation.

	Cl_A - $Cu_{A,1}$	Cl _A -Cu _{A,2}	Cl_B - $Cu_{B,1}$	Cl _B -Cu _{B,2}	Cl_C - $Cu_{C,1}$	Cl_C - $Cu_{C,2}$	Cl_D - $Cu_{D,1}$	Cl _D -Cu _{D,2}
Defere	2.626 Å	2.626 Å	2.836 Å	2.545 Å	2.864 Å	2.545 Å	2.864 Å	2.836 Å
Delote	0.14	0.14	0.09	0.23	0.09	0.25	0.08	0.10
A Gran	2.803 Å	2.354 Å	3.109 Å	2.322 Å	3.15 Å	2.328 Å	3.346 Å	3.008 Å
Alter	0.09	0.35	0.04	0.40	0.04	0.41	0.06	0.14

Table S2 The charge of the relative atoms at the γ -Cu₂Cl(OH)₃(021) before and after relaxation.

	C	l _A	С	l _B	С	l _C	С	l _D
Before	-0.	.47	-0.	.47	-0.	.47	-0.	.46
After	-0.	45	-0.	.46	-0.	.44	-0.	.42
	Cu _{A,1}	Cu _{A,2}	Cu _{B,1}	Cu _{B,2}	Cu _{C,1}	Cu _{C,2}	Cu _{D,1}	Cu _{D,2}
Before	0.80	0.80	0.79	0.77	0.76	0.75	0.75	0.79
After	0.92	0.75	0.90	0.70	0.82	0.73	0.76	0.88

2. Single CH₃OH substitution reaction on γ -Cu₂Cl(OH)₃(021)

2.1 Methoxide and HCl coadsorption on γ -Cu₂Cl(OH)₃(021)

The coadsorption configurations of methoxide and HCl (donated as X-Y, X indicates the different CH₃O adsorption sites, Y represents the different HCl adsorption sites; shown in Fig. S1~S4) were created as the product of the substitution reaction of singly adsorbed methanol. The top site of H/O atoms surround the adsorbed methoxide species were chosen as the adsorption sites of HCl. Around each surface methoxide, several adsorption configurations were calculated and the adsorption energies and key structural parameters are summarized in Table S3~S6.

After geometry optimized, the methoxide species adsorbed with its C-O axis is titled relative to the normal of the substrate about $13^{\circ} \sim 18^{\circ}$, which is agreed with the work of Amemiya et al.¹ and Gomes et al.² on the methoxide adsorption on Cu surface. Calculated C-O bond length, 1.391 Å~1.432 Å, is also in good agreement with the experimental results reported by Hofmann et al., 1.42 Å.³ All HCl species weakly adsorbed on the surface, their adsorption energies are lower than 0.45 eV, and most of them have a long distance from the surface. It indicates that the adsorption of HCl is weak and moveable, which can also explain the phenomenon of the leaching of Cl species observed from experimental measurements.⁴⁻⁸

Table S3 Adsorption energy and structure calculation for HCl adsorption on different sites in A-Y

system.

	A-H1	A-H2	A-H3	A-01	A-02
Adsorption Energy (eV)	-0.31	-0.28	-0.31	-0.43	-0.42
Distance from the surface* (Å)	4.423	2.871	3.605	0.620	0.851

	B- H1	B-H2	В-Н3	B-H4	B-O1
Adsorption Energy (eV)	-0.33	-0.39	-0.34	-0.31	-0.41
Distance from the surface* (Å)	2.982	2.158	3.254	4.752	0.608

Table S4 Adsorption energy and structure calculation for HCl adsorption on different sites in B-Y

Table S5 Adsorption energy and structure calculation for HCl adsorption on different sites in C-Y

system.

system.

	C-H1	C-H2	C-H3	C-01
Adsorption Energy (eV)	-0.22	-0.23	-0.24	-0.38
Distance from the surface* (Å)	3.610	2.812	3.193	1.752

Table S6 Adsorption energy and structure calculation for HCl adsorption on different sites in D-Y

system.

	D-H1	D-H2	D-H3	D-H4	D-H5	D-01	A-02
Adsorption Energy (eV)	0.27	0.14	0.25	0.24	0.34	0.29	0.27
Distance from the surface* (Å)	2.963	2.961	2.813	3.162	3.027	2.245	2.474

*Distance from the surface was set to be the normal distance between the bottle atom of HCl

species and the Cl atom at the top of the surface.



Fig. S1 The optimized structure of methoxide and HCl coabsorbed on γ -Cu₂Cl(OH)₃(021).



Fig. S2 The optimized structure of methoxide and HCl coabsorbed on γ -Cu₂Cl(OH)₃(021).



Fig. S3 The optimized structure of methoxide and HCl coabsorbed on γ -Cu₂Cl(OH)₃(021).



Fig. S4 The optimized structure of methoxide and HCl coabsorbed on γ -Cu₂Cl(OH)₃(021).

2.2. Reaction pathways

The PATH(X1/2-Y) (X indicates the corresponding methanol adsorption site, 1 and 2 represents the vertical and parallel adsorption of methanol, respectively; Y indicates the corresponding HCl adsorption site) started from single CH_3OH adsorption configurations (X1/2

configurations, Fig. 2) and end with the corresponding methoxide and HCl coadsorption configurations (X-Y configurations, Fig. S1~S4) have been established, and the MEP for the pathways were calculated.

In each PATH(X1/2-Y), one energy minimum state was located, and the corresponding configuration (denoted as Mid-X1/2-Y) is depicting in Fig. S5~S8. The calculated values of the distance and overlap population of the corresponding bonds are summarized in Table S7~S14.

From the Figures, it is clear that the Cl atom at the adsorption site escaped from the surface, while the Mulliken analysis shows that nearly all the overlap populations of Cl-Cu₁ bond and Cl-Cu₂ bond have dropped to zero. In addition, a weak Cl-H bond was found through the Mulliken analysis in each intermediate configuration. Meanwhile, the O-H bond is slightly weaker than in gaseous phase (0.970 Å, 0.54); and the other bonds of methanol are barely changed.

Table S7 The overlap population and distances of the relative bonds in the Mid-A1-Y configurations

	Cl-Cu ₁	Cl-Cu ₂	Cl-H	Н-О
A1-Mid-H1	5.123 Å	5.198 Å	2.180 Å	0.999 Å
	0	0	0.10	0.53
A1-Mid-H2	6.603 Å	4.194 Å	2.147 Å	0.994 Å
	0	0	0.09	0.53
A1-Mid-H3	5.240 Å	5.039 Å	2.338 Å	0.989 Å
	0	0	0.06	0.53 e
A1-Mid-O1	3.894 Å	4.804 Å	2.076 Å	1.007 Å
	0	0	0.13	0.53
A1-Mid-O2	4.198 Å	4.891 Å	2.241 Å	0.998 Å
	0	0	0.10	0.55

Table S8 The overlap population and distances of the relative bonds in the Mid-A2-Y configurations

Cl-Cu ₁	Cl-Cu ₂	Cl-H	Н-О

A2-Mid-H1	5.123 Å	5.198 Å	2.180 Å	0.999 Å
	0	0	0.10	0.52
A2-Mid-H2	6.329 Å	4.026 Å	2.080 Å	1.005 Å
	0	0	0.13	0.53
A2-Mid-H3	6.272 Å	3.978 Å	2.161 Å	0.992 Å
	0	0.04 e	0.08	0.50
A2-Mid-O1	3.919 Å	4.914 Å	2.104 Å	1.003 Å
	0	0	0.13	0.52
A2-Mid-O2	4.198 Å	4.891 Å	2.241 Å	0.998 Å
	0	0	0.10	0.54

Table S9 The overlap population and distances of the relative bonds in the Mid-B1-Y

configurations

	Cl-Cu ₁	Cl-Cu ₂	Cl-H	H-O
B1-Mid-H1	5.106 Å	3.833 Å	2.103 Å	1.000 Å
	0	0.03	0.11	0.51
B1-Mid-H2	3.764 Å	5.737 Å	2.146 Å	0.993 Å
	0.04	0	0.09	0.54
B1-Mid-H3	4.236 Å	6.401 Å	2.265 Å	0.991 Å
	0.01	0	0.09	0.54
B1-Mid-H4	4.679 Å	3.815 Å	2.093 Å	1.002 Å
	0	0.03 e	0.13	0.51
B1-Mid-O1	6.640 Å	7.170 Å	2.132 Å	0.996 Å
	0	0	0.10	0.50

Table S10 The overlap population and distances of the relative bonds in the Mid-B2-Y

	Cl-Cu	CLCus	CLH	H-O
D2 M: 1 111	<u> </u>	$\frac{\text{CI-CU}_2}{2.792 \text{ Å}}$		
B2-MIQ-HI	4.554 A	3./83 A	2.089 A	0.999 A
	0	0.04	0.11	0.51
B2-Mid-H2	4.226 Å	3.938 Å	2.060 Å	1.000 Å
	0.03	0.03	0.12	0.51
B2-Mid-H3	6.304 Å	7.143 Å	2.129 Å	0.997 Å
	0	0	0.10	0.50
B2-Mid-H4	6.571 Å	7.310 Å	2.100 Å	1.000 Å
	0	0	0.12	0.49
B2-Mid-O1	6.640 Å	7.170 Å	2.132 Å	0.996 Å
	0	0	0.10	0.50

configurations

Table S11 The overlap population and distances of the relative bonds in the Mid-C1-Y configurations

	Cl-Cu ₁	Cl-Cu ₂	Cl-H	Н-О
C1-Mid-H1	3.906 Å	4.641 Å	2.096 Å	0.994 Å
	0.02	0	0.10	0.51
C1-Mid-H2	6.128 Å	5.529 Å	2.220 Å	0.992 Å
	0	0	0.08	0.51
C1-Mid-H3	3.880 Å	4.646 Å	2.102 Å	0.996 Å
	0.02	0	0.11	0.52
C1-Mid-O1	4.734 Å	4.883 Å	2.089 Å	0.997 Å
	0	0	0.10	0.51

Table S12 The overlap population and distances of the relative bonds in the Mid-C2-Y

configurations

	Cl-Cu ₁	Cl-Cu ₂	Cl-H	H-O
C1-Mid-H1	3.561 Å	3.010 Å	1.848 Å	1.016 Å
	0.02	0.17	0.10	0.50
C1-Mid-H2	5.145 Å	4.465 Å	1.984 Å	1.010 Å
	0	0.02	0.10	0.50
C1-Mid-H3	3.962 Å	4.401 Å	2.017 Å	0.995 Å
	0.02	0	0.11	0.51
C1-Mid-O1	3.992 Å	4.553 Å	2.144 Å	0.994 Å
	0.02	0	0.09	0.52

Table S13 The overlap population and distances of the relative bonds in the Mid-D1-Y

configurations

	Cl-Cu ₁	Cl-Cu ₂	Cl-H	H-0
D1-Mid-H1	6.248 Å	4.425 Å	2.104 Å	0.996 Å
	0	0	0.10	0.50
D1-Mid-H2	6.189 Å	6.366 Å	2.243 Å	0.991 Å
	0	0	0.07	0.50
D1-Mid-H3	3.831 Å	5.762 Å	2.211 Å	0.993 Å
	0.03	0	0.07	0.51
D1-Mid-H4	4.041 Å	5.935 Å	2.302 Å	0.989 Å
	0.03	0	0.07	0.51
D1-Mid-H5	4.794 Å	5.746 Å	2.117 Å	0.995 Å
	0	0	0.09	0.50
D1-Mid-O1	5.790 Å	5.459 Å	2.158 Å	0.997 Å
	0	0	0.09	0.50
D1-Mid-O2	5.335 Å	6.237 Å	2.128 Å	1.000 Å
	0	0	0.09	0.50

Table S14 The overlap population and distances of the relative bonds in the Mid-D2-Y configurations

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	Cl-Cu ₁	Cl-Cu ₂	Cl-H	H-0
D2-Mid-H1	4.903 Å	3.965 Å	2.203 Å	0.992 Å
	0	0.02 e	0.07	0.52
D2-Mid-H2	5.324 Å	5.428 Å	2.248 Å	0.990 Å
	0	0	0.07	0.51
D2-Mid-H3	4.512 Å	7.280 Å	2.244 Å	0.990 Å
	0.01 e	0	0.07	0.51
D2-Mid-H4	5.970 Å	6.177 Å	2.341 Å	0.989 Å
	0	0	0.06	0.52
D2-Mid-H5	6.566 Å	7.250 Å	2.171 Å	0.994 Å
	0	0	0.09	0.50
D2-Mid-O1	6.027 Å	4.445 Å	2.237 Å	0.990 Å
	0	0	0.09	0.53
D2-Mid-O2	4.289 Å	6.931 Å	2.212 Å	0.993 Å
	0	0	0.08	0.52





Fig. S5 Structure of Mid-A1/2- Y_A configurations; A indicates that the methanol adsorbed at A site, 1 and 2 indicate the parallel and vertical adsorption of methanol, H1~O2 indicate the different HCl adsorption sites around A site.

Fig. S6 Structure of Mid-B1/2- Y_B configurations; B indicates that the methanol adsorbed at B site, 1 and 2 indicate the parallel and vertical adsorption of methanol, H1~O1 indicate the different HCl adsorption sites around B site.

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Fig. S7 Structure of Mid-C1/2-Y_C configurations; C indicates that the methanol adsorbed at C site, 1 and 2 indicate the parallel and vertical adsorption of methanol, H1 \sim O1 indicate the different HCl adsorption sites around C site.

Fig. S8 Structure of Mid-D1/2- Y_D configurations; D indicates that the methanol adsorbed at D site, 1 and 2 indicate the parallel and vertical adsorption of methanol, H1~O2 indicate the different HCl adsorption sites around D site.

Take the Mid-X1/2-Y configurations as the intermediate, the reaction pathways were rebuilt. The PATH (X1/2-Mid-Y) corresponds to the reaction paths have X1/2 configurations as reactant and Mid-X1/2-Y configurations as product, respectively. The PATH(Mid-X1/2-Y) corresponds to reaction paths have Mid-X1/2-Y configurations as reactant and X-Y configurations as product, respectively. The energy barriers and reaction energies for these paths as well as PATH(X1/2-Y) are all summarized in Table S15~S22 for comparison.

Table S15 Activation energies (Ea) and reaction energies (Er) for all the conceivable reaction paths of methoxide substitution reaction for A1 configuration.

Pathways	A1-H1	A1-H2	А1-Н3	A1-01	A1-02
Reactant	A1	A1	A1	A1	A1
Product	A-H1	A-H2	A-H3	A-01	A-O2
Ea	2.37	5.11	2.30	2.20	2.75
Er	0.74	0.77	0.75	0.62	0.63

Pathways	A1-Mid-H1	A1-Mid-H2	A1-Mid-H3	A1-Mid-O1	A1-Mid-O2
Reactant	A1	A1	A1	A1	A1
Product	Mid-A1-H1	Mid-A1-H2	Mid-A1-H3	Mid-A1-O1	Mid-A1-O2
Ea	1.11	1.84	1.11	1.11	1.17
Er	0.37	0.60	0.68	0.68	0.69
Pathways	Mid-A1-H1	Mid-A1-H2	Mid-A1-H3	Mid-A1-O1	Mid-A1-O2
Reactant	Mid-A1-H1	Mid-A1-H2	Mid-A1-H3	Mid-A1-O1	Mid-A1-O2
Product	A-H1	A-H2	A-H3	A-01	A-02
Ea	0.86	0.88	0.60	0.60	0.63
Er	0.38	0.17	0.07	-0.06	-0.06

Table S16 Activation energies (Ea) and reaction energies (Er) for all the conceivable reaction paths

of methoxide substitution reaction for A2 configuration.

Pathways	A2-H1	A2-H2	А2-Н3	A2-01	A2-O2
Reactant	A2	A2	A2	A2	A2
Product	A-H1	A-H2	A-H3	A-01	A-02
Ea	2.40	2.74	2.25	2.27	2.91
Er	0.71	0.74	0.71	0.59	0.60
Pathways	A2-Mid-H1	A2-Mid-H2	A2-Mid-H3	A2-Mid-O1	A2-Mid-O2
Reactant	A2	A2	A2	A2	A2
Product	Mid-A2-H1	Mid-A2-H2	Mid-A2-H3	Mid-A2-O1	Mid-A2-O2
Ea	1.00	1.40	1.36	1.17	1.29
Er	0.34	0.34	0.70	0.62	0.44
Pathways	Mid-A2-H1	Mid-A2-H2	Mid-A2-H3	Mid-A2-O1	Mid-A2-O2
Reactant	Mid-A2-H1	Mid-A2-H2	Mid-A2-H3	Mid-A2-O1	Mid-A2-O2
Product	A-H1	A-H2	A-H3	A-01	A-02
Ea	0.86	0.73	1.27	0.62	0.60
Er	0.38	0.40	0.00	0.08	0.16

Table S17 Activation energies (Ea) and reaction energies (Er) for all the conceivable reaction paths

of methoxide substitution reaction for B1 configuration.

Pathways	B1-H1	B1-H2	B1-H3	B1-H4	B1-O1
Reactant	B1	B1	B1	B1	B1
Product	B-H1	B-H2	B-H3	B-H4	B-O1
Ea	2.39	2.06	2.30	2.21	2.23
Er	0.94	0.88	0.93	0.95	0.75
Pathways	B1-Mid-H1	B1-Mid-H2	B1-Mid-H3	B1-Mid-H4	B1-Mid-O1
Reactant	B1	B1	B1	B1	B1
Product	Mid-B1-H1	Mid-B1-H2	Mid-B1-H3	Mid-B1-H4	Mid-B1-O1
Ea	0.98	0.83	0.86	1.38	1.21
Er	0.78	0.64	0.37	0.43	0.90
Pathways	Mid-B1-H1	Mid-B1-H2	Mid-B1-H3	Mid-B1-H4	Mid-B1-O1
Reactant	Mid-B1-H1	Mid-B1-H2	Mid-B1-H3	Mid-B1-H4	Mid-B1-O1
Product	B-H1	B-H2	B-H3	B-H4	B-O1
Ea	1.10	1.05	1.14	0.85	0.70

Er	0.16	0.23	0.56	0.52	0.05

Table S18 Activation energies (Ea) and reaction energies (Er) for all the conceivable reaction paths

Pathways	B2-H1	B2-H2	B2-H3	B2-H4	B2-O1
Reactant	B2	B2	B2	B2	B2
Product	B-H1	B-H2	B-H3	B-H4	B-O1
Ea	4.51	2.82	3.06	2.49	1.15
Er	0.89	0.83	0.88	0.90	0.71
Pathways	B2-Mid-H1	B2-Mid-H2	B2-Mid-H3	B2-Mid-H4	B2-Mid-O1
Reactant	B2	B2	B2	B2	B2
Product	Mid-B2-H1	Mid-B2-H2	Mid-B2-H3	Mid-B2-H4	Mid-B2-O1
Ea	1.26	1.33	1.27	1.21	1.19
Er	0.25	0.28	0.74	0.66	0.85
Pathways	Mid-B2-H1	Mid-B2-H2	Mid-B2-H3	Mid-B2-H4	Mid-B2-O1
Reactant	Mid-B2-H1	Mid-B2-H2	Mid-B2-H3	Mid-B2-H4	Mid-B2-O1
Product	B-H1	B-H2	B-H3	B-H4	B-O1
Ea	0.94	1.05	0.76	0.75	0.70
Er	0.64	0.55	0.14	0.24	-0.14

of methoxide substitution reaction for B2 configuration.

Table S19 Activation energies (Ea) and reaction energies (Er) for all the conceivable reaction paths

of methoxide substitution reaction for C1 configuration.

Pathways	C1-H1	С1-Н2	С1-Н3	C1-01
Reactant	C1	C1	C1	C1
Product	C-H1	C-H2	C-H3	C-H4
Ea	2.03	1.93	1.98	1.71
Er	0.92	0.89	0.92	0.78
Pathways	C1-Mid-H1	C1-Mid-H2	C1-Mid-H3	C1-Mid-O1
Reactant	C1	C1	C1	C1
Product	Mid-C1-H1	Mid-C1-H2	Mid-C1-H3	Mid-C1-O1
Ea	0.74	1.18	1.06	0.56
Er	0.40	0.47	0.14	0.52
Pathways	Mid-C1-H1	Mid-C1-H2	Mid-C1-H3	Mid-C1-O1
Reactant	Mid-C1-H1	Mid-C1-H2	Mid-C1-H3	Mid-C1-O1
Product	C-H1	C-H2	C-H3	C-H4
Ea	1.15	1.33	0.85	0.90
Er	0.52	0.42	0.78	0.26

Table S20 Activation energies (Ea) and reaction energies (Er) for all the conceivable reaction paths

of methoxide substitution reaction for C2 configuration.

Pathways	С2-Н1	С2-Н2	С2-Н3	C2-O1
Reactant	C2	C2	C2	C2

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Product Ea Er	C-H1 1.96 0.87	C-H2 2.56 0.84	C-H3 1.90 0.87	C-H4 1.73 0.73
Pathways	C2-Mid-H1	C2-Mid-H2	C2-Mid-H3	C2-Mid-O1
Reactant	C2	C2	C2	C2
Product	Mid-C2-H1	Mid-C2-H2	Mid-C2-H3	Mid-C2-O1
Ea	0.74	0.63	0.68	0.74
Er	0.35	0.59	0.28	0.21
Pathways	Mid-C2-H1	Mid-C2-H2	Mid-C2-H3	Mid-C2-O1
Reactant	Mid-C2-H1	Mid-C2-H2	Mid-C2-H3	Mid-C2-O1
Product	C-H1	C-H2	C-H3	C-H4
Ea	1.15	1.09	1.13	0.99
Er	0.52	0.25	0.58	0.52

Table S21 Activation energies (Ea) and reaction energies (Er) for all the conceivable reaction paths

	of	methoxide	e substitution	reaction	for D1	configuration
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Pathways	D1-H1	D1-H2	D1-H3	D1-H4	D1-H5	D1-01	D1-O2
Reactant	D1						
Product	D-H1	D-H2	D-H3	D-H4	D-H5	D-01	D-02
Ea	1.44	2.36	2.02	1.99	1.48	1.58	1.59
Er	0.77	0.97	0.77	0.78	0.78	0.79	0.94
Pathways	D1-Mid-H1	D1-Mid-H2	D1-Mid-H3	D1-Mid-H4	D1-Mid-H5	D1-Mid-O1	D1-Mid-O2
Reactant	D1						
Product	Mid-D1-H1	Mid-D1-H2	Mid-D1-H3	Mid-D1-H4	Mid-D1-H5	Mid-D1-O1	Mid-D1-O2
Ea	0.53	0.22	0.14	0.19	0.39	0.72	0.19
Er	-0.01	0.05	0.06	0.05	0.15	0.22	0.14
Pathways	Mid-D1-H1	Mid-D1-H2	Mid-D1-H3	Mid-D1-H4	Mid-D1-H5	Mid-D1-O1	Mid-D1-O2
Reactant	Mid-D1-H1	Mid-D1-H2	Mid-D1-H3	Mid-D1-H4	Mid-D1-H5	Mid-D1-O1	Mid-D1-O2
Product	D-H1	D-H2	D-H3	D-H4	D-H5	D-01	D-O2
Ea	0.96	1.17	1.33	1.04	1.00	0.85	0.84
Er	0.78	0.92	0.71	0.74	0.61	0.57	0.80

Table S22 Activation energies (Ea) and reaction energies (Er) for all the conceivable reaction paths

Pathway s	D2-H1	D2-H2	D2-H3	D2-H4	D2-H5	D2-O1	D2-O2
Reactant	D2						
Product	D-H1	D-H2	D-H3	D-H4	D-H5	D-01	D-O2
Ea	1.49	1.47	1.49	1.82	1.69	1.58	1.29
Er	0.87	1.06	0.87	0.88	0.87	0.88	1.03
Pathway	D2-Mid-H	D2-Mid-H	D2-Mid-H	D2-Mid-H	D2-Mid-H	D2-Mid-O	D2-Mid-O
S	1	2	3	4	5	1	2
Reactant	D2						
Product	Mid-D2-H1	Mid-D2-H2	Mid-D2-H3	Mid-D2-H4	Mid-D2-H5	Mid-D2-O1	Mid-D2-O2
Ea	0.15	0.26	0.63	0.59	0.74	0.38	0.84
Er	0.07	0.17	0.17	0.11	0.22	-0.06	0.08

of methoxide substitution reaction for D2 configuration.

S	1 2	3	4	5	1	2
Reactant Mid-I	D2-H1 Mid-D2-	H2 Mid-D2-H3	3 Mid-D2-H4	Mid-D2-H5	Mid-D2-O1	Mid-D2-O2
Product D-	H1 D-H2	D-H3	D-H4	D-H5	D-01	D-O2
Ea 1.	0.85	0.98	1.02	1.10	0.90	0.85
Er 0.	79 0.96	0.70	0.77	0.65	0.94	0.96

Through the investigation of these reaction paths, the activation energies for PATH(X1/2-Mid-Y) and PATH(Mid-X1/2-Y) are much lower compared to PATH (X1/2-Y), indicates that the new reaction paths built by using the new Mid-X1/2-Y configurations should be more suitable for describing the methoxide substitution reaction of methanol. Meanwhile, we also found that the methanol parallelly adsorbed at A site (A2 configuration), vertically adsorbed at B (B1 configuration), C (C1 configuration) and D (D1 configuration) site is more suitable for the substitution reaction at its adsorption site. On the other hand, the methanol at D site has the lowest activation energy among all these four sites.

3. Three/four CH₃OH coadsorption on γ -Cu₂Cl(OH)₃(021)

Fig. S9 demonstrates the optimized structures of three methanol coabsorbed on γ -Cu₂Cl(OH)₃(021). Adsorption energies, distances and overlap populations of relative bonds are also summarized in Table S23, the marks of the configurations indicate the three sites that methanol adsorbed on.

Based on our calculation results, the methanol in coadsorption has the similar stability as in single adsorption configurations; and the similar parameters of overlap population and bond distances indicate the similar activity of methanol in different configurations at the same adsorption site. Meanwhile, the same conclusion can be carried out from the calculated parameters of adsorption energy, geometric and electronic structure for four methanol coadsorbed configuration (Fig. S10, Table S24).

Fig. S9 The optimized structure of three methanol coabsorbed on γ -Cu₂Cl(OH)₃(021) surface

Fig. S10 The optimized structure of four methanol coabsorbed on γ-Cu₂Cl(OH)₃(021) surface

Table S23 The bond distance, overlap population and adsorption energy calculations for three

CH₃OH coadsorption on γ-Cu₂Cl(OH)₃(021)

	a(a	bc)	b(a	bc)	c(a	ıbc)	*E _{ad} (eV)	*Es (eV)
	R(H-O)	R(H-Cl)	R(H-O)	R(H-Cl)	R(H-O)	R(H-Cl)		
ADC	0.984 Å	2.287 Å	0.982 Å	2.300 Å	0.986 Å	2.312 Å	1.45	1 47
ADU	0.54	0.04	0.54	0.04	0.50	0.05	-1.43	-1.4/
	0.983 Å	2.351 Å	0.979 Å	2.417 Å	0.983 Å	2.351 Å	1.62	154
ADD	0.54	0.03	0.54	0.03	0.54	0.03	-1.02	-1.34
	0.983 Å	2.351 Å	0.981 Å	2.447 Å	0.992 Å	2.149 Å	1.60	1.62
ACD	0.54	0.03	0.54	0.04	0.53	0.07	-1.09	-1.05
BCD	0.983 Å	2.316 Å	0.985 Å	2.295 Å	0.991 Å	2.173 Å	1.65	1.57
вср	0.55	0.04	0.55	0.05	0.54	0.07	-1.03	-1.37

*E_{ad} was calculated as the total adsorption energy of three methanol;

 $*E_s$ was the plus of the adsorption energies of corresponding singly adsorbed methanol in Table 1.

Table S24 The bond distance, overlap population and adsorption energy calculations for four

	R(O-H)	R(H-Cl)	R(O-H)	R(H-Cl)	*E _{ad} (eV)	*Es (eV)
	1	A	Ι	3		
	0.984Å	2.280Å	0.983Å	2.299Å		
	0.54	0.04	0.54	0.04	2.11	2.09
ABCD	(С	Ι)	2.11	2.08
	0.985Å	2.323Å	0.992Å	2.147Å		
	0.54	0.05	0.53	0.07		

CH_3OH coadsorption on γ	$-Cu_2Cl(OH)_3(021)$
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*E_{ad} was calculated as the total adsorption energy of four methanol;

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 $*E_s$ was the plus of the adsorption energies of corresponding singly adsorbed methanol in Table 1.

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