Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Theoretical Study on The Electrocatalytic Carbon Dioxide Reduction over Copper with Copper-based Layered Double Hydroxides

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	site of CuAl-LDH, Cu@CuAl-LDH, Cu_2@CuAl-Cl-LDH, Td-Cu_4@CuAl-Cl-LDH and Pl-Cu_4@CuAl-Cl-LDH.
S7	The reaction formula and calculation equation for each elementary step over the surface of the CuAl-LDH, Cu@CuAl-LDH, Cu_2@CuAl-Cl-LDH, Td-Cu_4@CuAl-Cl-LDH and Pl-Cu_4@CuAl-Cl-LDH.

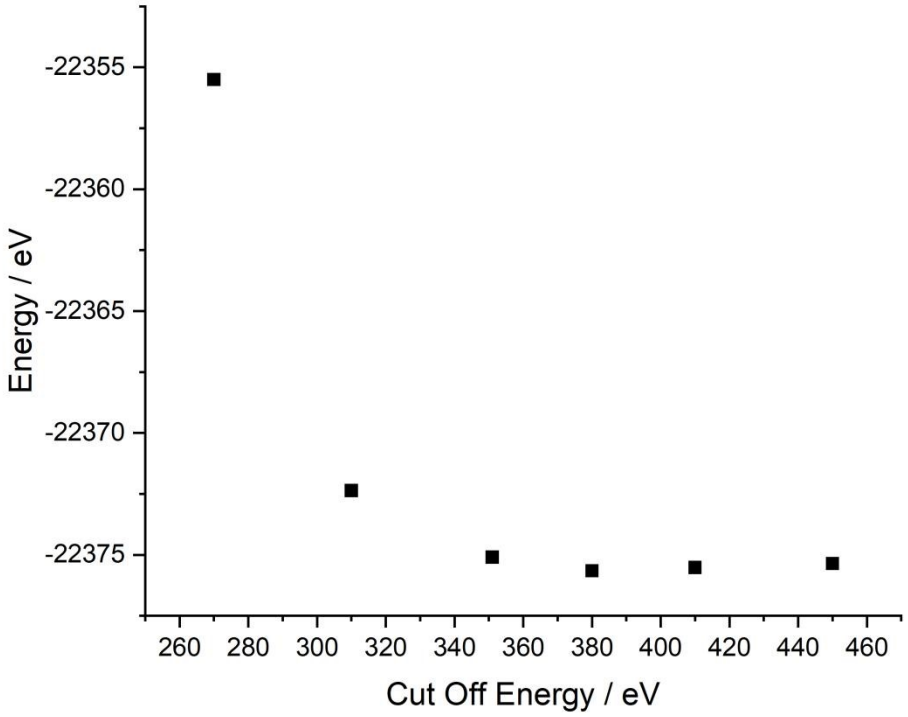


Figure S1. The calculated adsorption energies of COOH on CuAl-Cl-LDHs (001) under the cutoff energies ranging from 260 eV to 450 eV.

As shown in Fig. S1, the energy decreases with increasing cutoff energy, the inflection point is reached at a cutoff energy of 380 eV. Therefore, in this work, the cutoff energy of 380 eV is chosen.

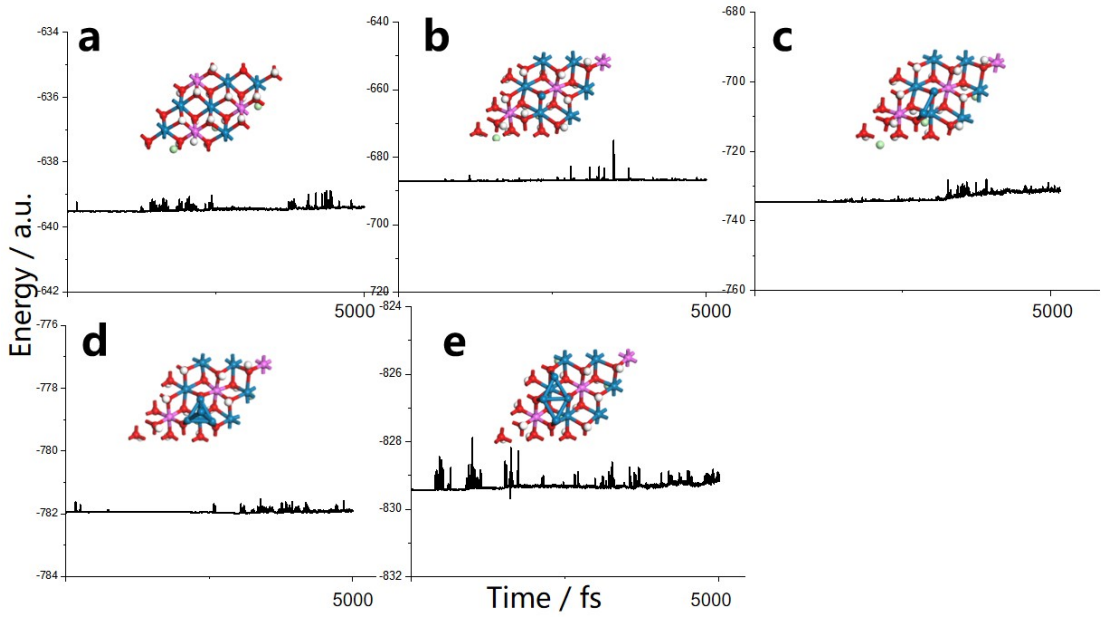


Figure S2. AIMD calculation of (a) CuAl-LDH, (b) Cu@CuAl-LDH, (c) Cu_2@CuAl-Cl-LDH, (d) Td-Cu_4@CuAl-Cl-LDH and (e) Pl-Cu_4@CuAl-Cl-LDH in 5000 fs.

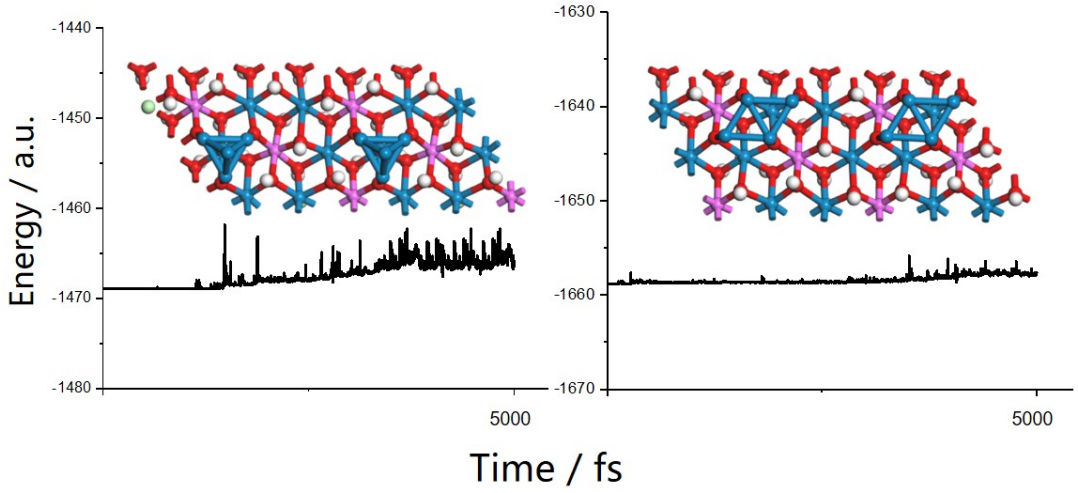


Figure S3. AIMD calculation of extended Cu cluster cell (a) Td-Cu_4@CuAl-Cl-LDH and (b) Pl-Cu_4@CuAl-Cl-LDH in 5000 fs.

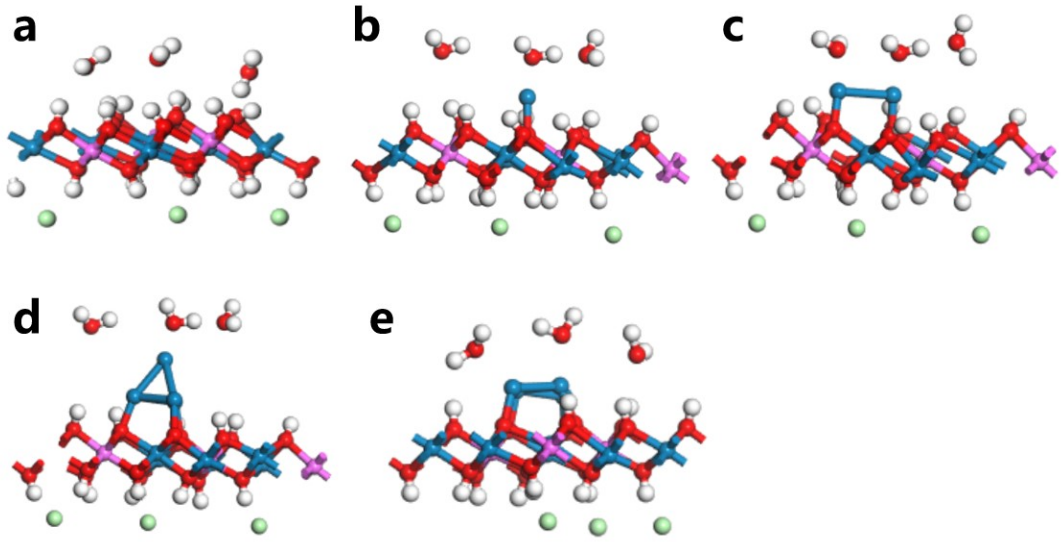


Figure S4. Structural optimization of (a) CuAl-LDH, (b) Cu@CuAl-LDH, (c) Cu_2@CuAl-Cl-LDH, (d) Td-Cu_4@CuAl-Cl-LDH and (e) Pl-Cu_4@CuAl-Cl-LDH in the H_2O system.

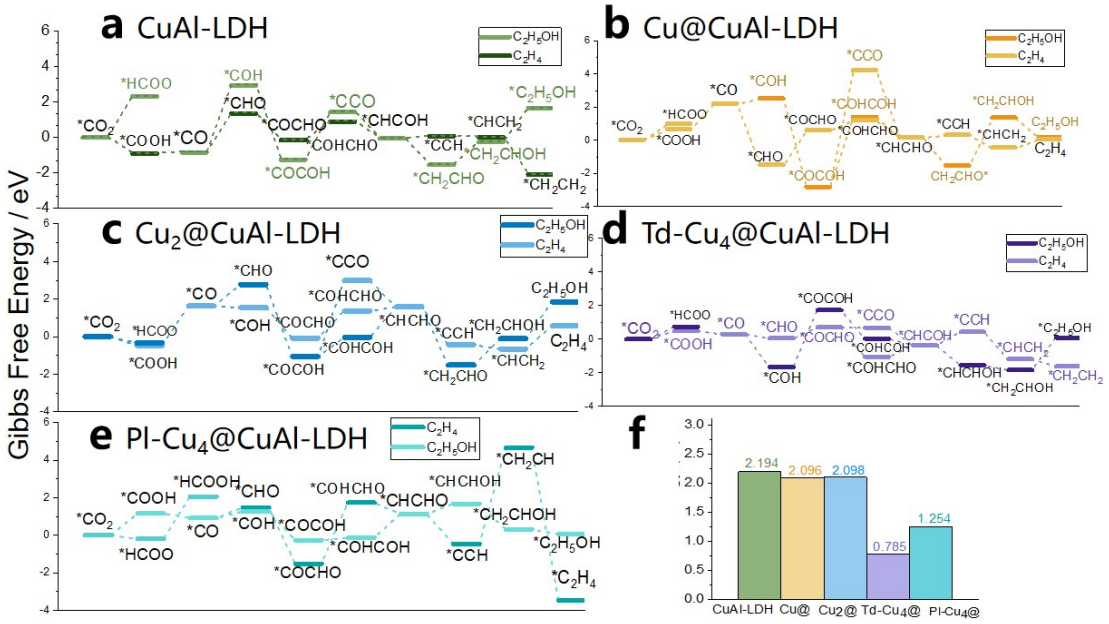


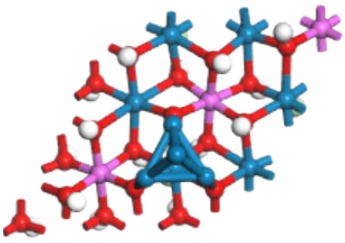
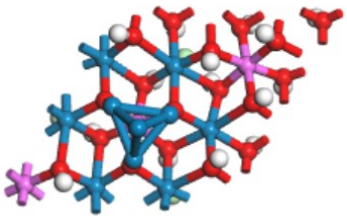
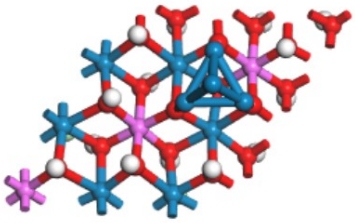
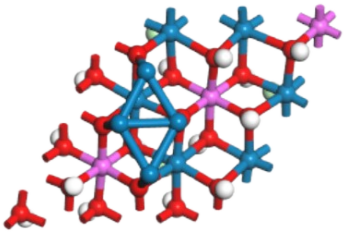
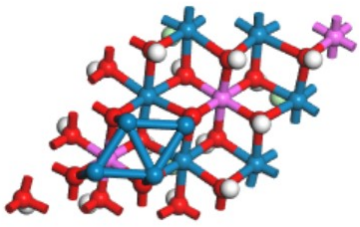
Figure S5. Standard free energy diagrams for the CO_2RR on (a) CuAl-LDH, (b) Cu@CuAl-LDH, (c) Cu_2@CuAl-Cl-LDH, (d) Td-Cu_4@CuAl-Cl-LDH and (e) Pl-Cu_4@CuAl-Cl-LDH and the potential energy determines step of five structures above (f).

Table S1. Formation energy of Cu@CuAl-LDH , Cu_2@CuAl-Cl-LDH, Td-Cu_4@CuAl-Cl-LDH and Pl-Cu_4@CuAl-Cl-LDH.

	$E_{(LDH+Cux)}$/eV	$E_{(LDH)}$/eV	$E_{(Cux)}$/eV	$E_{(f)}$/eV
Cu@CuAl-LDH	-19870.882	-18396.311	-1473.068	-1.503
Cu_2@CuAl-LDH	-21329.469	-18379.627	-2948.401	-1.441
Td-Cu_4@CuAl-LDH Cu	-24265.547	-18362.044	-5897.611	-5.892
Td-Cu_4@CuAl-LDH Al	-24265.450	-18362.468	-5897.611	-5.370
Td-Cu_4@CuAl-LDH O	-24264.914	-18362.187	-5897.611	-5.115
Pl-Cu_4@CuAl-LDH Cu O	-24247.442	-18344.266	-5898.604	-4.572
Pl-Cu_4@CuAl-LDH Al O	-24247.374	-18344.921	-5898.604	-3.849

Table S2 shows structure of Td-Cu_4@CuAl-Cl-LDH (Cu site) Cu site means orthotetrahedral Cu_4 cluster is at the top of Cu site on CuAl-Cl-LDH Pl-Cu_4@CuAl-Cl-LDH (Cu, O sites) which means planar Cu_4 cluster is at the top of Cu site and O site on CuAl-Cl-LDH, the other optimized structures of Cu_4@CuAl-Cl-LDHs (Td-Cu_4@CuAl-Cl-LDH (Al, O site), orthotetrahedral Cu_4 cluster is at the top of Al or O site on CuAl-Cl-LDH Pl-Cu_4@CuAl-Cl-LDH (Al, O sites) planar Cu_4 cluster is at the top of Al site and O site on CuAl-Cl-LDH)

Table S2. Screening of Cu_4@CuAl-Cl-LDH structural model.

		$E_{(DFT)}$/eV	$E_{(f)}$/eV	$E_{(ad)}CO_2$/ eV
Td-Cu_4@CuAl-LDH (Cu site)		-24265.547	-5.892	-1.114
Td-Cu_4@CuAl-LDH (Al site)		-24247.604	-5.370	1.302
Td-Cu_4@CuAl-LDH (O site)		-24264.914	-5.115	-0.864
Pl-Cu_4@CuAl-LDH (Cu, O site)		-24247.442	-4.572	-1.037
Pl-Cu_4@CuAl-LDH (Al, O site)		-24247.374	-3.849	-0.531

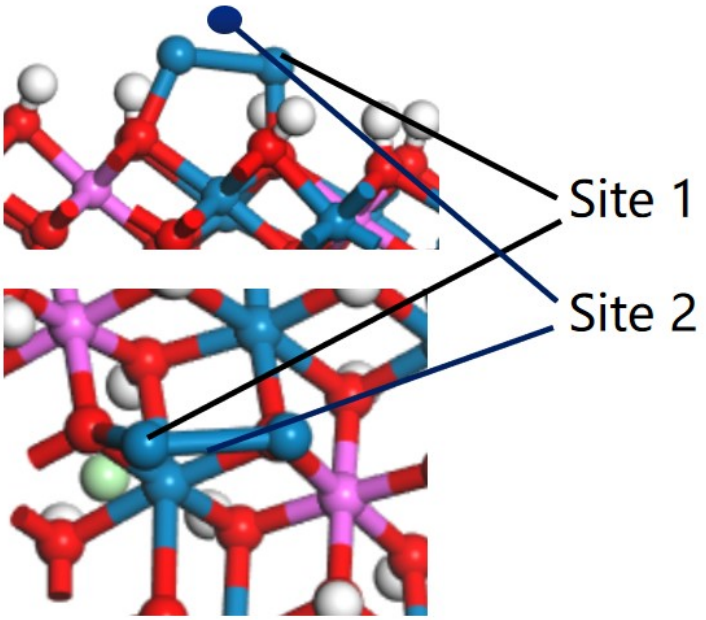
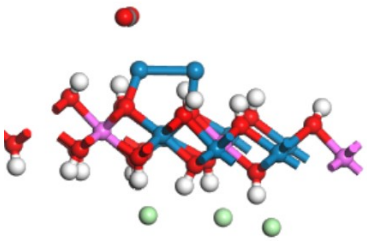
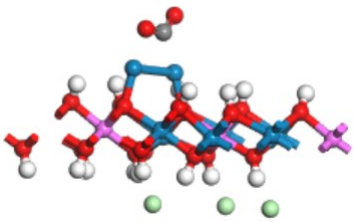
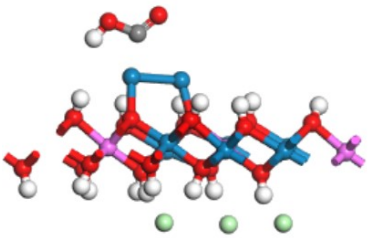
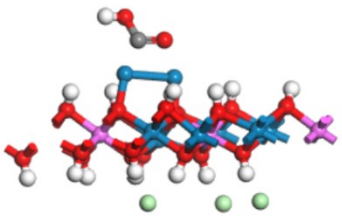
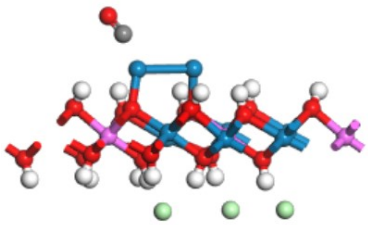
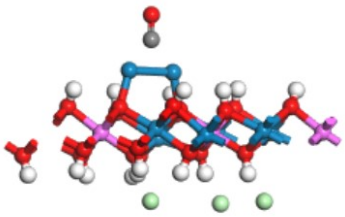
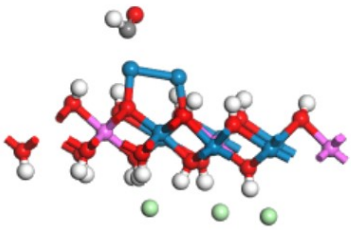
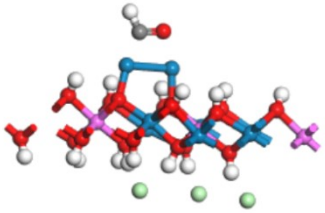
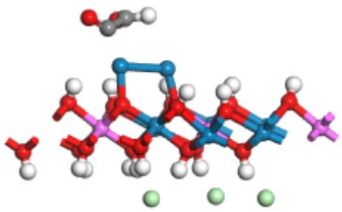
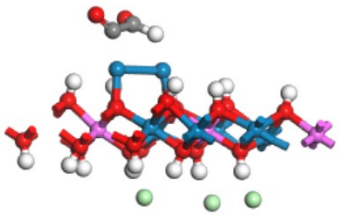
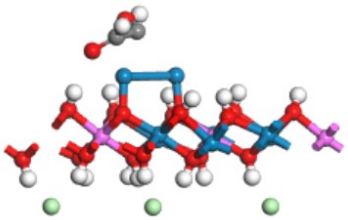
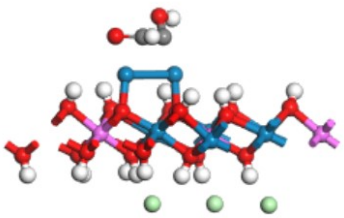
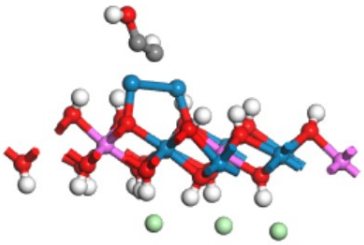
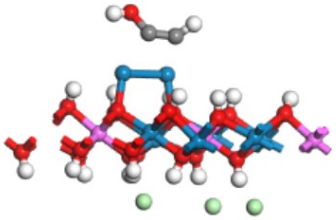
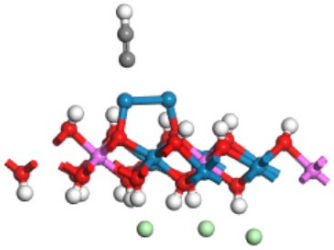
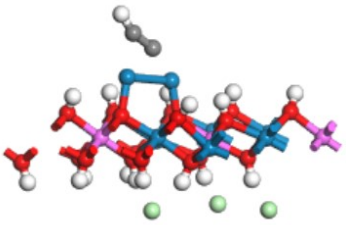
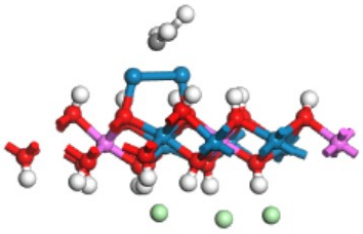
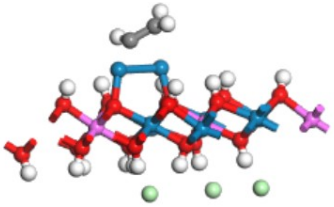
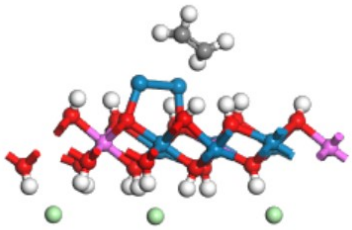
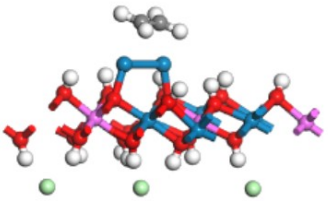


Figure S6. Schematic diagram of active site of Cu_2@CuAl-Cl-LDH.

The top and bottom diagrams represent the side and top views of Cu_2@CuAl-Cl-LDH, respectively, where the blue balls represent copper atoms

Table S3. Optimized geometries of electro catalyzed CO_2 reduction intermediates over two sites (site 1 and site 2) on Cu_2@CuAl-Cl-LDH and adsorption energy.

	Site 1	$E_{(ad)}$/ eV	Site 2	$E_{(ad)}$/ eV
*CO_2		-0.70		-1.73
*COOH		-4.30		-4.75
*CO		-3.22		-3.21
*CHO		-2.46		-3.53
*COCHO		-3.61		-3.44

*COHCHO		-3.96		-3.82
*CHCOH		-5.02		-3.37
*CCH		-6.80		-6.08
*CH_2CH		-5.24		-5.12
*CH_2CH_2		-2.01		-2.00

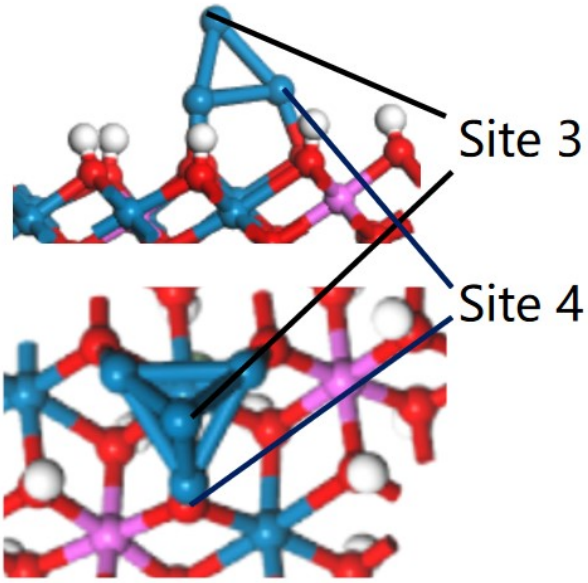
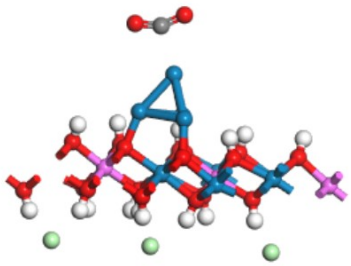
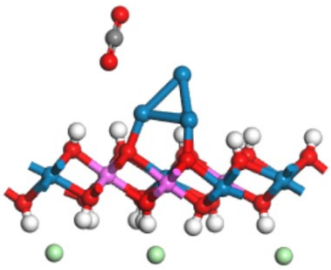
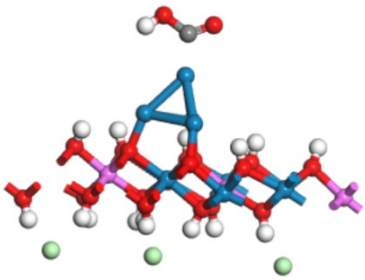
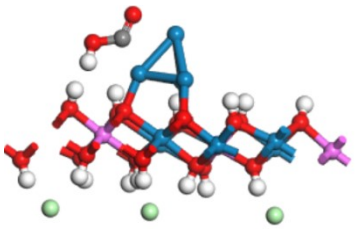
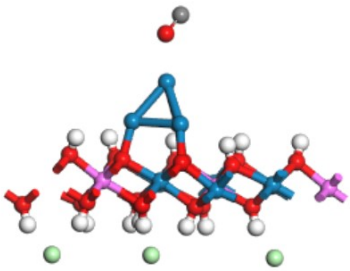
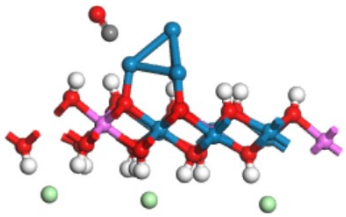
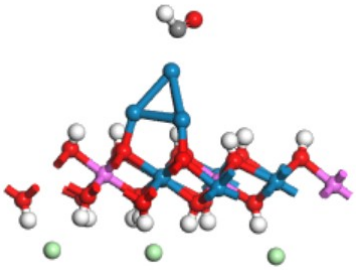
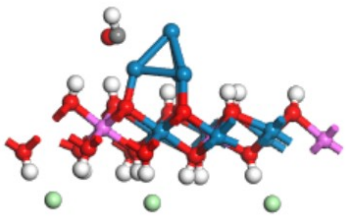
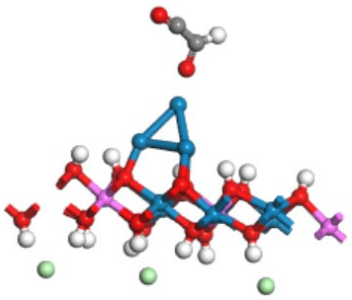
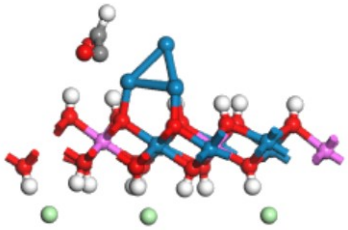
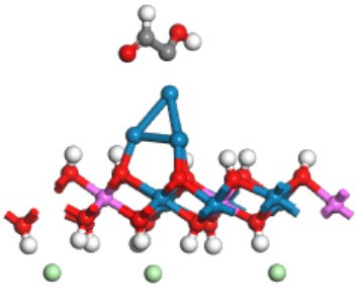
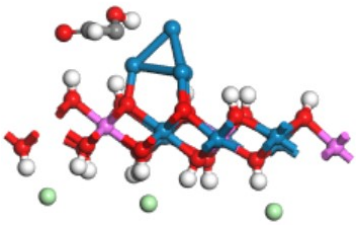
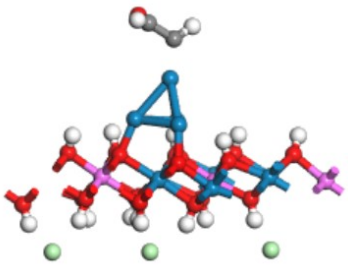
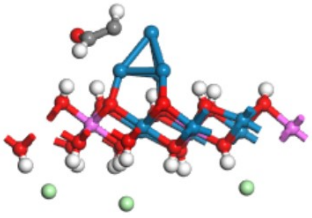
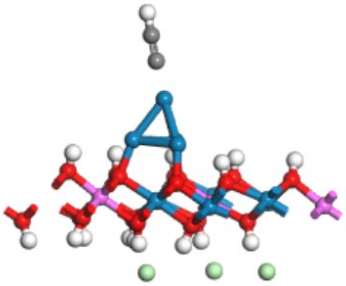
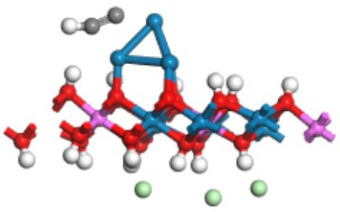
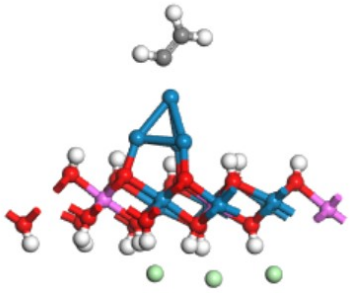
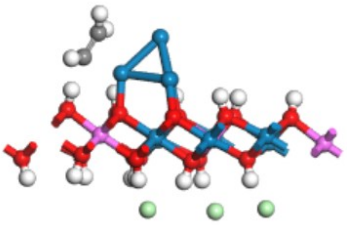


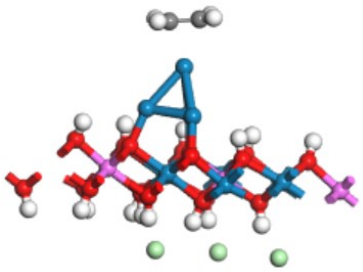
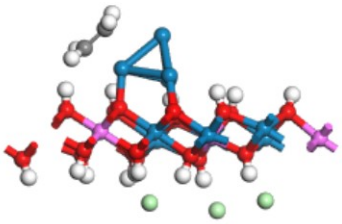
Figure S7. Schematic diagram of active site of Td-Cu_4@CuAl-Cl-LDH.

The top and bottom diagrams represent the side and top views of Td-Cu_4@CuAl-Cl-LDH, respectively, where the blue balls represent copper atoms

Table S4. Optimized geometries of electro catalyzed CO_2 reduction intermediates over two sites (site 3 and site 4) on Td-Cu_4@CuAl-Cl-LDH and adsorption energy..

	Site 3	$E_{(ad)}$/ eV	Site 4	$E_{(ad)}$/ eV
*CO_2		-1.11		-0.72
*COOH		-1.96		-1.53
*CO		-1.05		-0.99
*CHO		-1.16		-1.38

*COCHO		-0.78		-1.02
*COHCHO		-2.25		-2.06
*CHCHO		-1.26		-1.20
*CCH		-3.57		-4.25
*CH_2CH		-2.13		-1.71

*CH_2CH_2		-0.86		-0.61

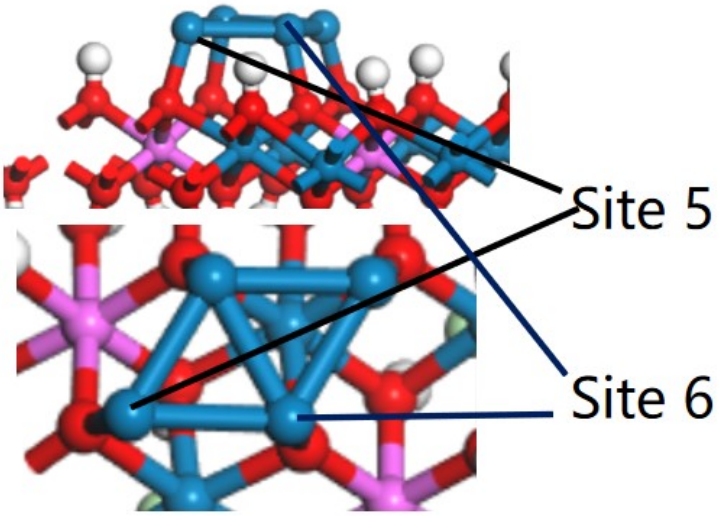
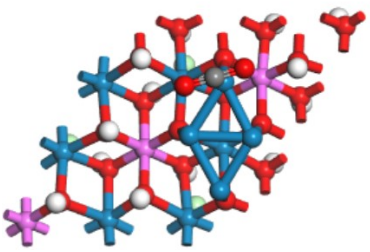
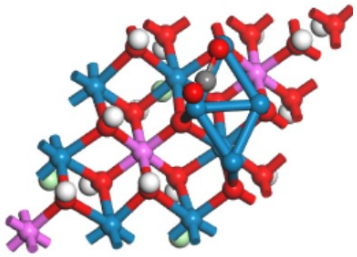
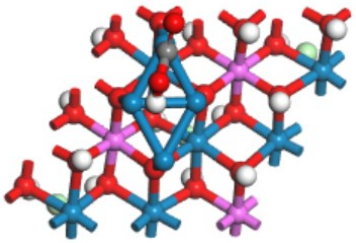
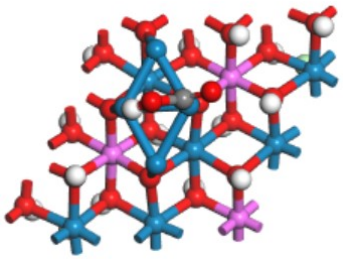
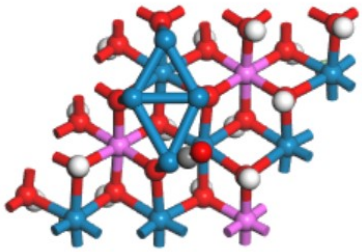
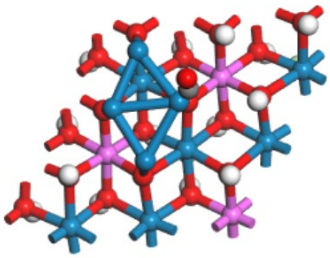
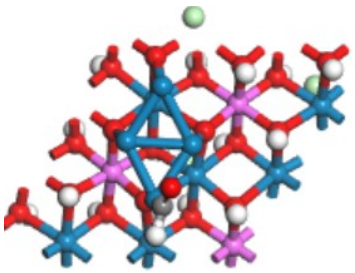
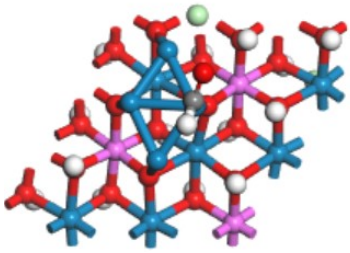
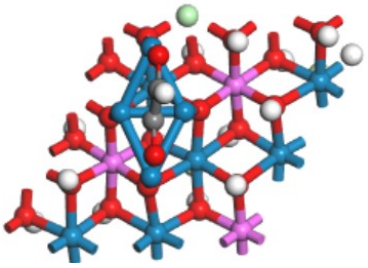
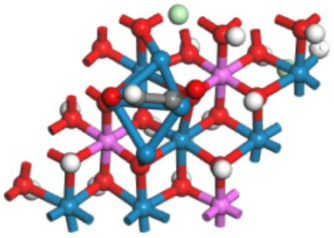
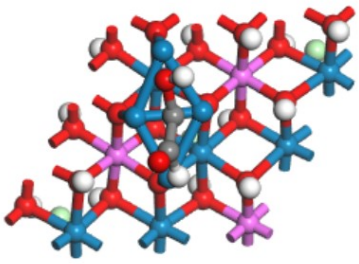
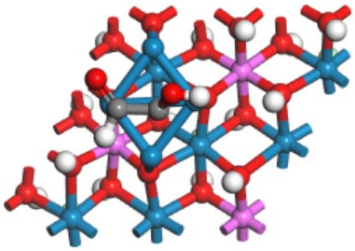
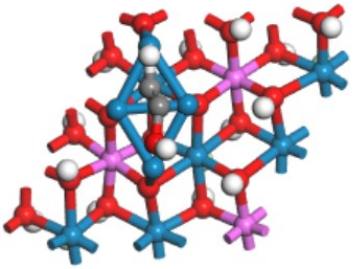
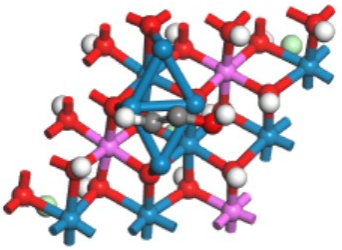
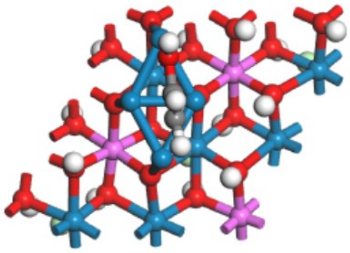
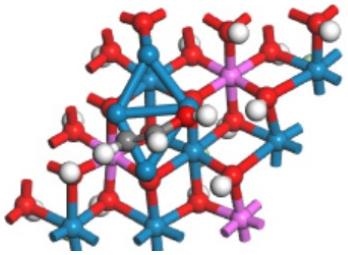
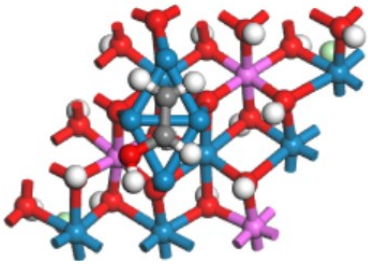
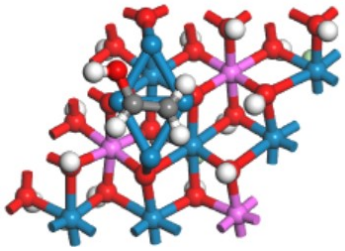
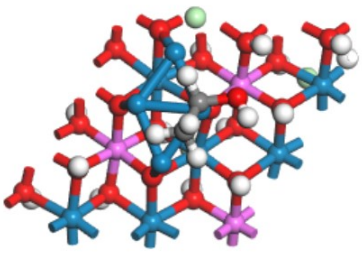
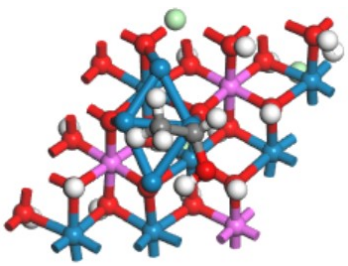


Figure S8 Schematic diagram of active site of Pl-Cu_4@CuAl-Cl-LDH.

The top and bottom diagrams represent the side and top views of Pl-Cu_4@CuAl-Cl-LDH, respectively, where the blue balls represent copper atoms

Table S5. Optimized geometries of electro catalyzed CO_2 reduction intermediates over two sites (site 5 and site 6) on Pl-Cu_4@CuAl-Cl-LDH and adsorption energy.

	Site 5	$E_{(ad)}$/ eV	Site 6	$E_{(ad)}$/ eV
*CO_2		-1.04		-1.27
*COOH		-3.08		-3.19
*CO		-2.71		-2.41
*CHO		-2.22		-1.99

*COCHO		-4.75		-4.03
*COHCHO		-4.43		-6.75
*CHCOH		-5.19		-5.28
*CHCHOH		-2.96		-4.27
*CH_2CHOH		-0.43		-0.41
*C_2H_5OH		-4.70		-1.27

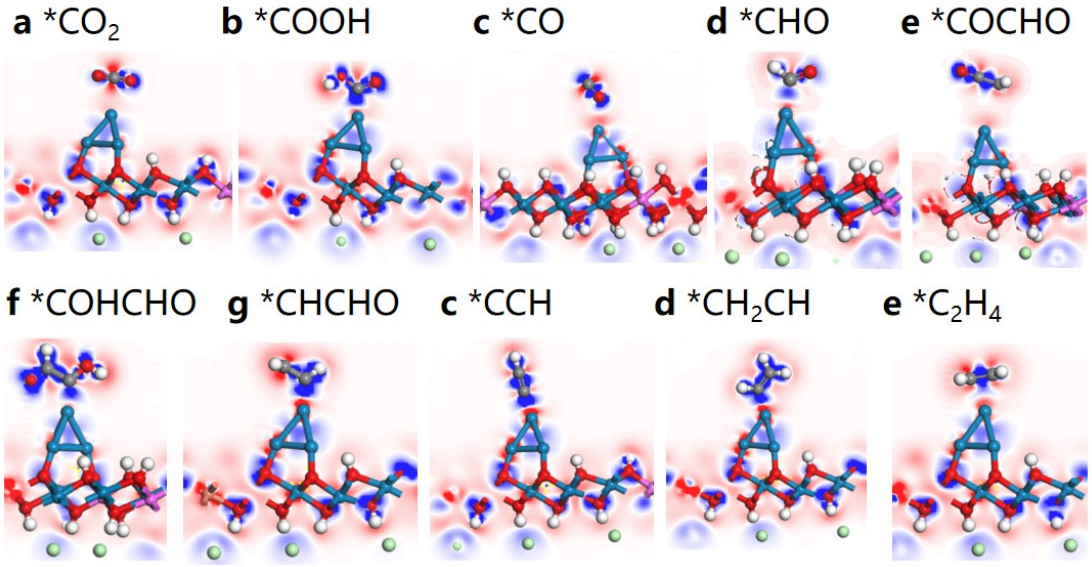
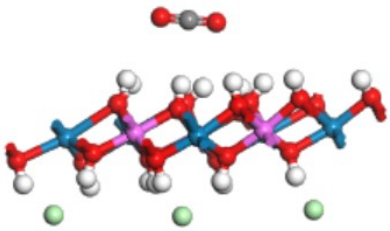
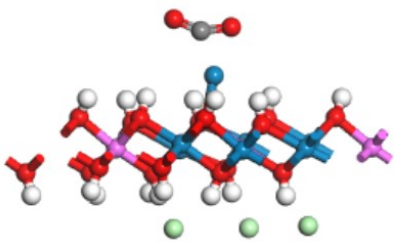
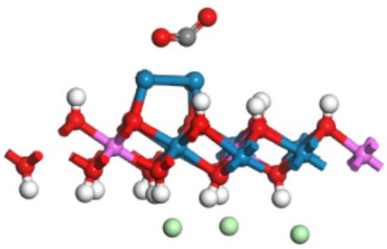


Figure S9. Differential charge density map of electrocatalytic CO_2 reduction intermediates over Td-Cu_4@CuAl-Cl-LDH

Table S6. The adsorption site of CO_2 and O-C-O bond angle on the active site of CuAl-LDH, Cu@CuAl-LDH, Cu_2@CuAl-Cl-LDH, Td-Cu_4@CuAl-Cl-LDH and Pl-Cu_4@CuAl-Cl-LDH.

model	∠O-C-O	Adsorption sites
	179.20°	C
	149.05°	C
	161.70°	C
	150.29°	C
	132.98°	C

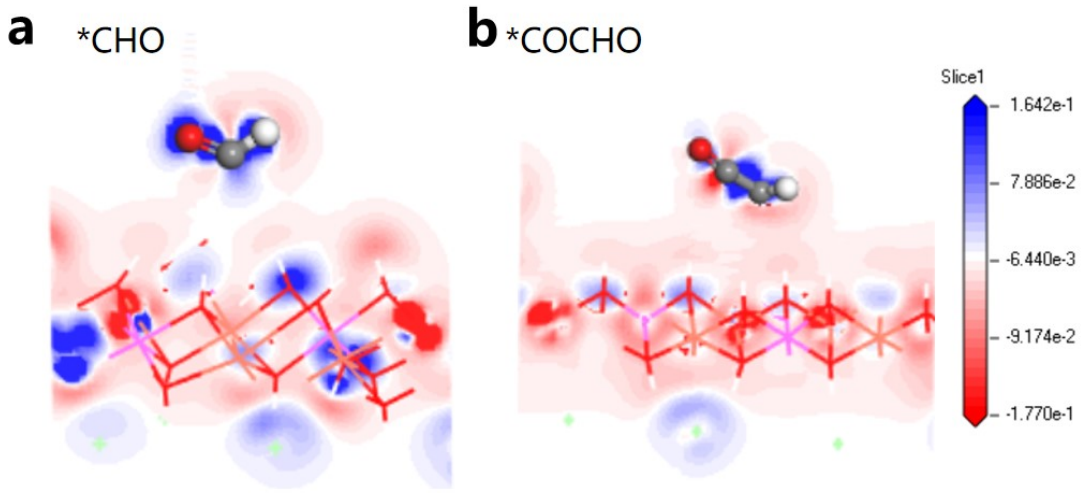


Figure S10. Differential charge density map of C-C coupling on CuAl-LDH (*CHO→*COCHO)

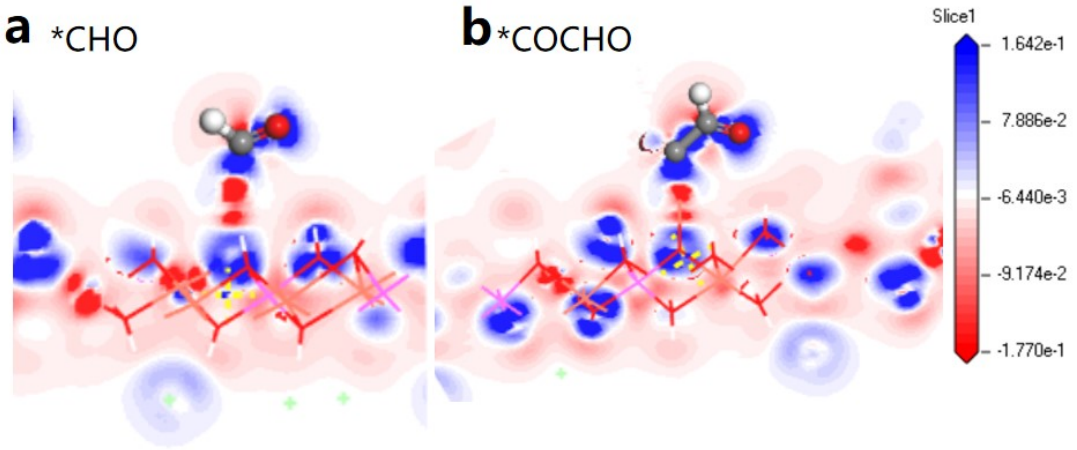


Figure S11. Differential charge density map of C-C coupling on Cu@CuAl-LDH (*CHO→*COCHO)

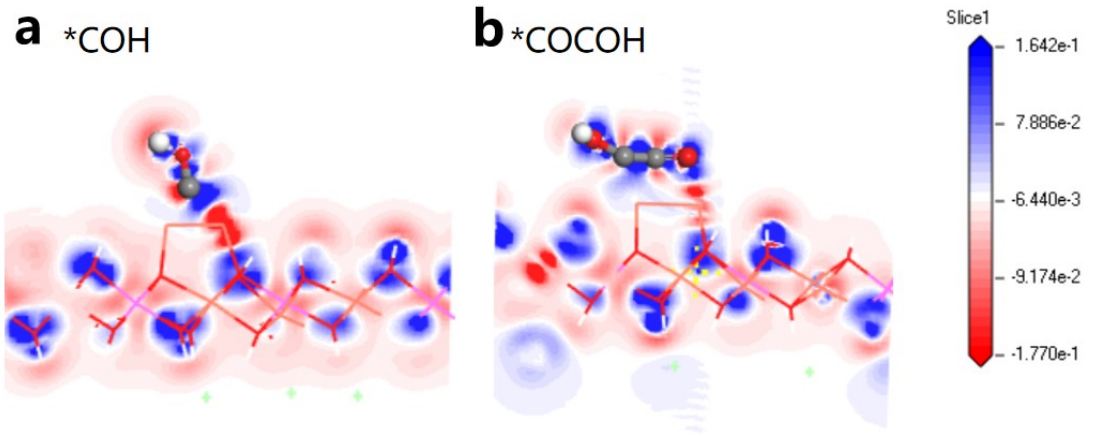


Figure S12. Differential charge density map of C-C coupling on Cu_2@CuAl-LDH (*COH→*COCOH)

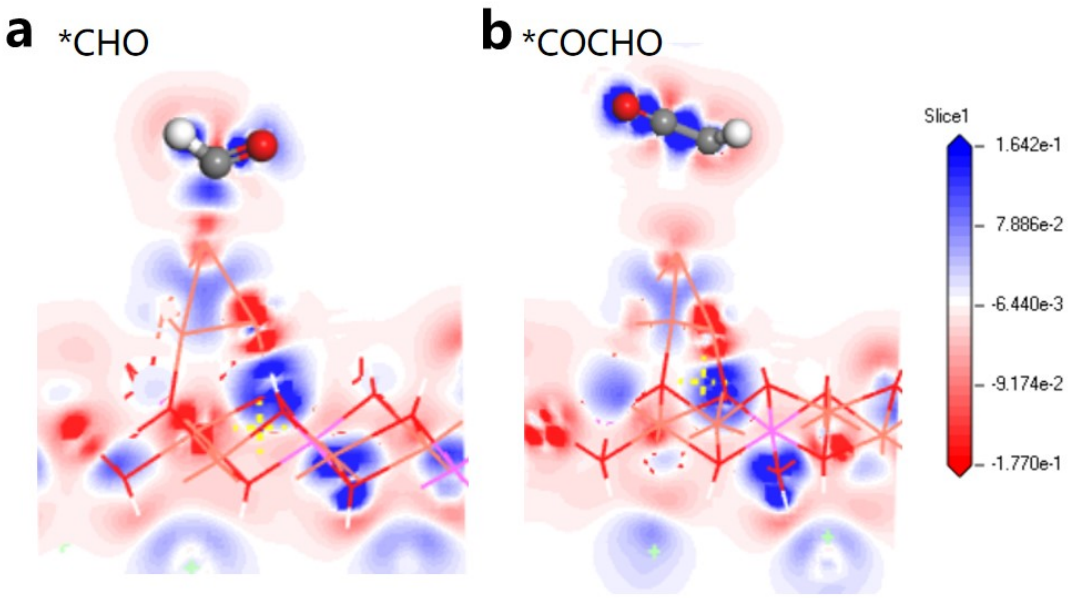


Figure S13. Differential charge density map of C-C coupling on Td-Cu_4@CuAl-LDH (*CHO→*COCHO)

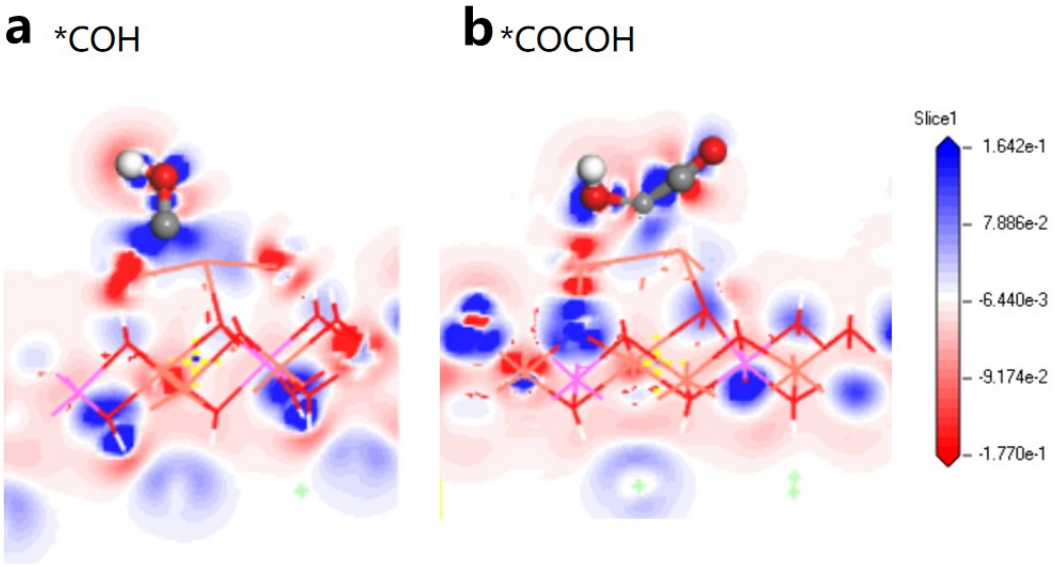


Figure S14. Differential charge density map of C-C coupling on Pl-Cu_4@CuAl-LDH (*COH→*COCOH)

Table S7. The reaction formula and calculation equation for each elementary step over the surface of the CuAl-LDH, Cu@CuAl-LDH, Cu_2@CuAl-Cl-LDH, Td-Cu_4@CuAl-Cl-LDH and Pl-Cu_4@CuAl-Cl-LDH.

	reaction	equation
R1	$*CO_2+H^++e^-\rightarrow *COOH$	$G_{*COOH}-G_{*CO2}-0.5G_{H2}+kT\ln10\cdot pH-eU$
R2	$*COOH+H^++e^-\rightarrow *CO$	$G_{*CO}-G_{*COOH}-0.5G_{H2}+kT\ln10\cdot pH-eU$
R3	$*CO+H^++e^-\rightarrow *COH$	$G_{*COH}-G_{*CO}-0.5G_{H2}+kT\ln10\cdot pH-eU$
R4	$*CO+H^++e^-\rightarrow *CHO$	$G_{*CHO}-G_{*CO}-0.5G_{H2}+kT\ln10\cdot pH-eU$
R5	$*COH+*CO\rightarrow *COCOH$	$G_{*COCOH}-G_{*CO}-G_{*COH}+kT\ln10\cdot pH-eU$
R6	$*CHO+*CO\rightarrow *COCHO$	$G_{*COCHO}-G_{*CO}-G_{*CHO}+kT\ln10\cdot pH-eU$
R7	$*COCOH+H^++e^-\rightarrow *COHCOH$	$G_{*COHCOH}-G_{*COCOH}-0.5G_{H2}+kT\ln10\cdot pH-eU$
R8	$*COCOH+H^++e^-\rightarrow *CCO+H_2O$	$G_{*CCO}+G_{H2O}-G_{*COCOH}-0.5G_{H2}+kT\ln10\cdot pH-eU$
R9	$*COCHO+H^++e^-\rightarrow *CCO+H_2O$	$G_{*CCO}+G_{H2O}-G_{*COCHO}-0.5G_{H2}+kT\ln10\cdot pH-eU$
R10	$*COCHO+H^++e^-\rightarrow *CHOCOH$	$G_{*COHCHO}-G_{*COCHO}-0.5G_{H2}+kT\ln10\cdot pH-eU$
R11	$*COHCOH^-+2H^++2e^-\rightarrow *CHCOH+H_2O$	$G_{*CHCOH}-G_{*COHCOH}-G_{H2}+G_{H2O}+kT\ln10\cdot pH-eU$
R12	$*CCO+2H^++2e^-\rightarrow *CHCOH$	$G_{*CHCOH}-G_{*CCO}-G_{H2}+kT\ln10\cdot pH-eU$
R13	$*CCO+2H^++2e^-\rightarrow *CHCHO$	$G_{*CHCHO}-G_{*CCO}-G_{H2}+kT\ln10\cdot pH-eU$
R14	$*CHOCOH^-+2H^++2e^-\rightarrow *CHCHO+H_2O$	$G_{*CHCHO}-G_{*CHOCOH}-G_{H2}+G_{H2O}+kT\ln10\cdot pH-eU$

R15	$*CHOCOH^{-}+2H^{+}+2e^{-}\rightarrow *CHCOH+H_2O$	$G_{*CHCOH}-G_{*CHOCOH}-G_{H2}+G_{H2O}+kT\ln10\cdot pH-eU$
R16	$*CHCOH+H^{+}+e^{-}\rightarrow *CH_2COH$	$G_{*CH2COH}-G_{*CHCOH}-0.5G_{H2}+kT\ln10\cdot pH-eU$
R17	$*CHCOH+H^{+}+e^{-}\rightarrow *CHCHOH$	$G_{*CHCHOH}-G_{*CHCOH}-0.5G_{H2}+kT\ln10\cdot pH-eU$
R18	$*CHCOH+H^{+}+e^{-}\rightarrow *CCH+H_2O$	$G_{*CCH}+G_{H2O}-G_{*CHCOH}-0.5G_{H2}+kT\ln10\cdot pH-eU$
R19	$*CHCHO+H^{+}+e^{-}\rightarrow *CH_2COH$	$G_{*CH2CHO}-G_{*CHCOH}-0.5G_{H2}+kT\ln10\cdot pH-eU$
R20	$*CHCHO+H^{+}+e^{-}\rightarrow *CHCHOH$	$G_{*CHCHO}-G_{*CHCHOH}-0.5G_{H2}+kT\ln10\cdot pH-eU$
R21	$*CHCHO+H^{+}+e^{-}\rightarrow *CCH+H_2O$	$G_{*CCH}+G_{H2O}-G_{*CHCHO}-0.5G_{H2}+kT\ln10\cdot pH-eU$
R22	$*CH_2COH+H^{+}+e^{-}\rightarrow *CH_2CHOH$	$G_{*CH2CHOH}-G_{*CH2COH}-0.5G_{H2}+kT\ln10\cdot pH-eU$
R23	$*CHCHOH+H^{+}+e^{-}\rightarrow *CH_2CHOH$	$G_{*CH2CHOH}-G_{*CHCHOH}-0.5G_{H2}+kT\ln10\cdot pH-eU$
R24	$*CCH+2H^{+}+2e^{-}\rightarrow *CHCH_2$	$G_{*CHCH2}-G_{*CCH}-G_{H2}+kT\ln10\cdot pH-eU$
R25	$*CH_2CHOH+2H^{+}+2e^{-}\rightarrow C_2H_5OH$	$G_{*C2H5OH}-G_{*CH2CHOH}-G_{H2}+kT\ln10\cdot pH-eU$
R26	$*CHCH_2+H^{+}+e^{-}\rightarrow *CH_2CH_2$	$G_{*CH2CH2}-G_{*CHCH2}-0.5G_{H2}+kT\ln10\cdot pH-eU$
R27	$*COH+*H^{+}+e^{-}\rightarrow *CHOH$	$G_{*CHOH}-G_{*COH}-0.5G_{H2}+kT\ln10\cdot pH-eU$
R28	$*CHO+*H^{+}+e^{-}\rightarrow *CHOH$	$G_{*CHOH}-G_{*CHO}-0.5G_{H2}+kT\ln10\cdot pH-eU$
R29	$*COH+*CO\rightarrow *COCOH$	$G_{*COCOH}-G_{*CO}-G_{*COH}+kT\ln10\cdot pH-eU$