

Supporting Information

Directing Selectivity of CO₂ Electroreduction to Target C₂ products via Non-metal Doping on Cu Surfaces

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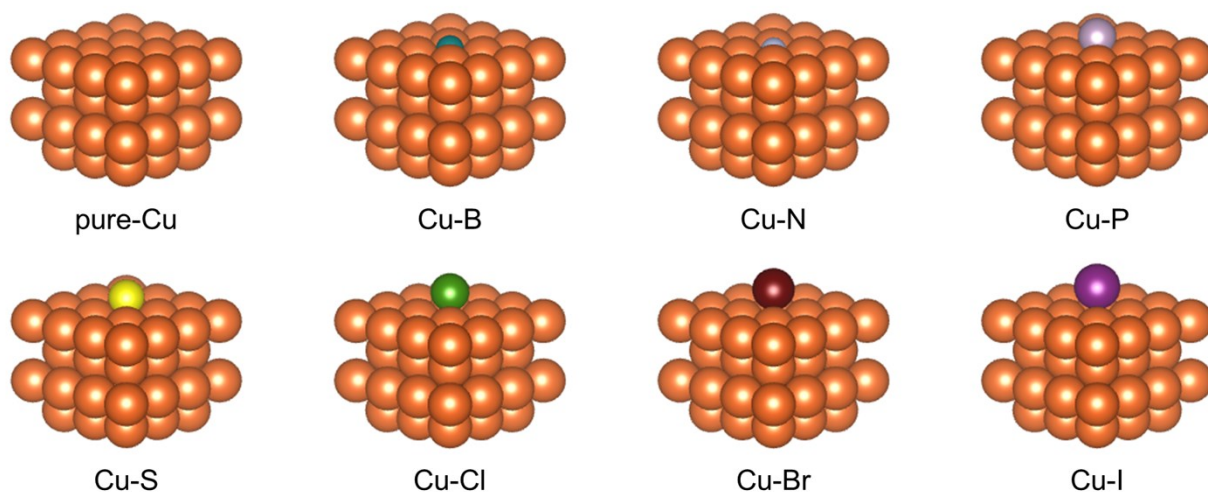


Figure S1. Optimized configurations of Cu-X, and pure Cu, surfaces. Copper atoms are shown as orange-spheres with other non-metal atoms labelled for each structure. Fluorine is not included as a doping element, because after geometry optimization of some reaction intermediates on the Cu-F model, the F atom move away from its original position, which indicates geometric instability of Cu-F model.

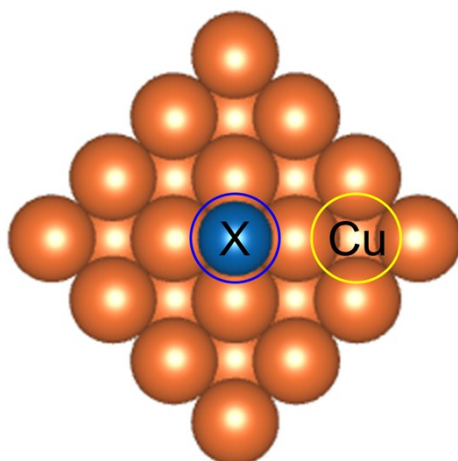


Figure S2. Dopant atom site (blue circle) and Cu site (yellow circle) used to rationalize oxygen affinities as descriptors for C_2 product selectivity on Cu-X catalysts.

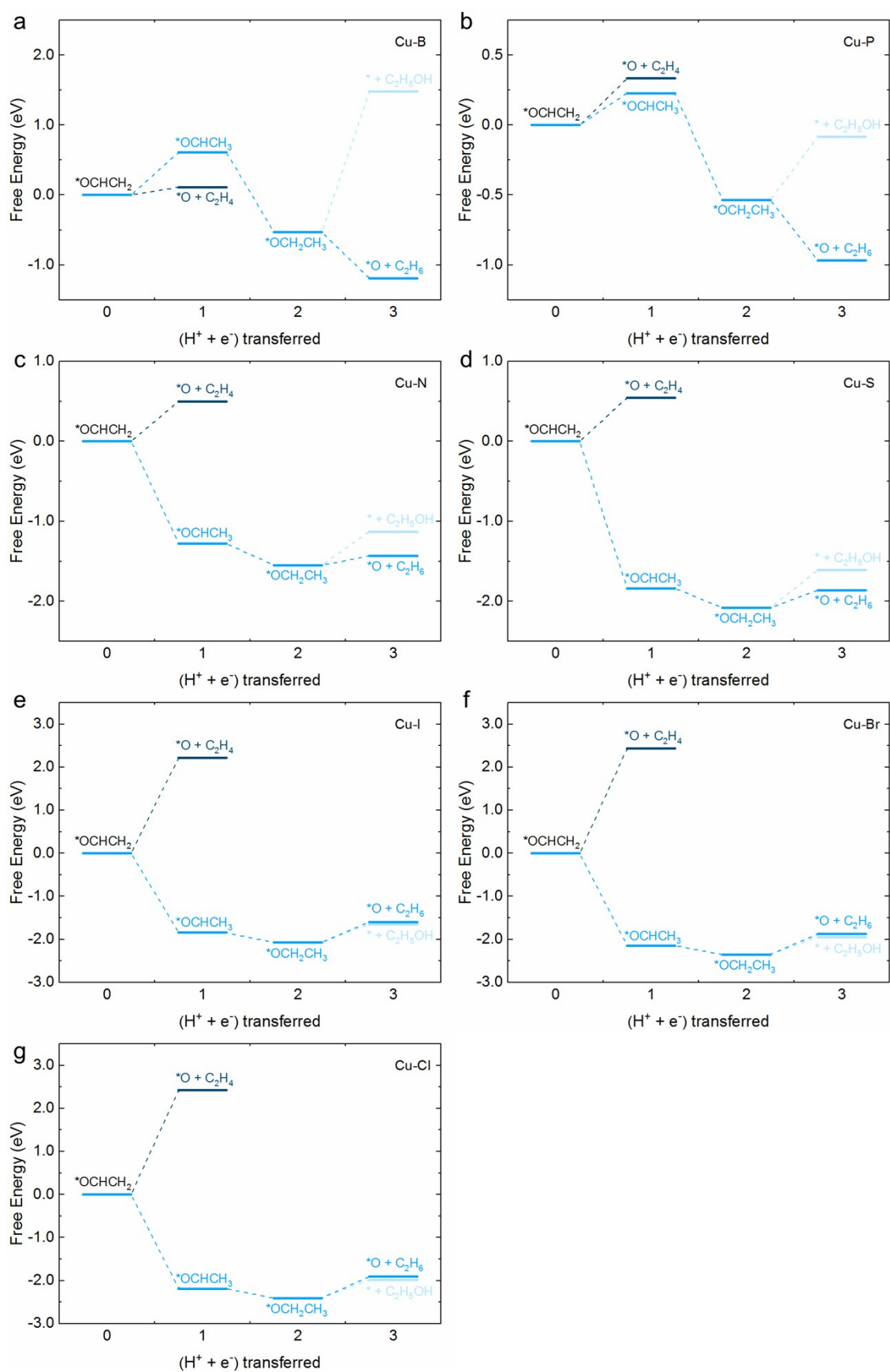


Figure S3. Free energy diagram starting from $*\text{OCHCH}_2$ intermediate adsorbed on the dopant atom site to ethylene (dark blue line), ethane (blue line) and ethanol (light blue line) for each Cu-X surface.

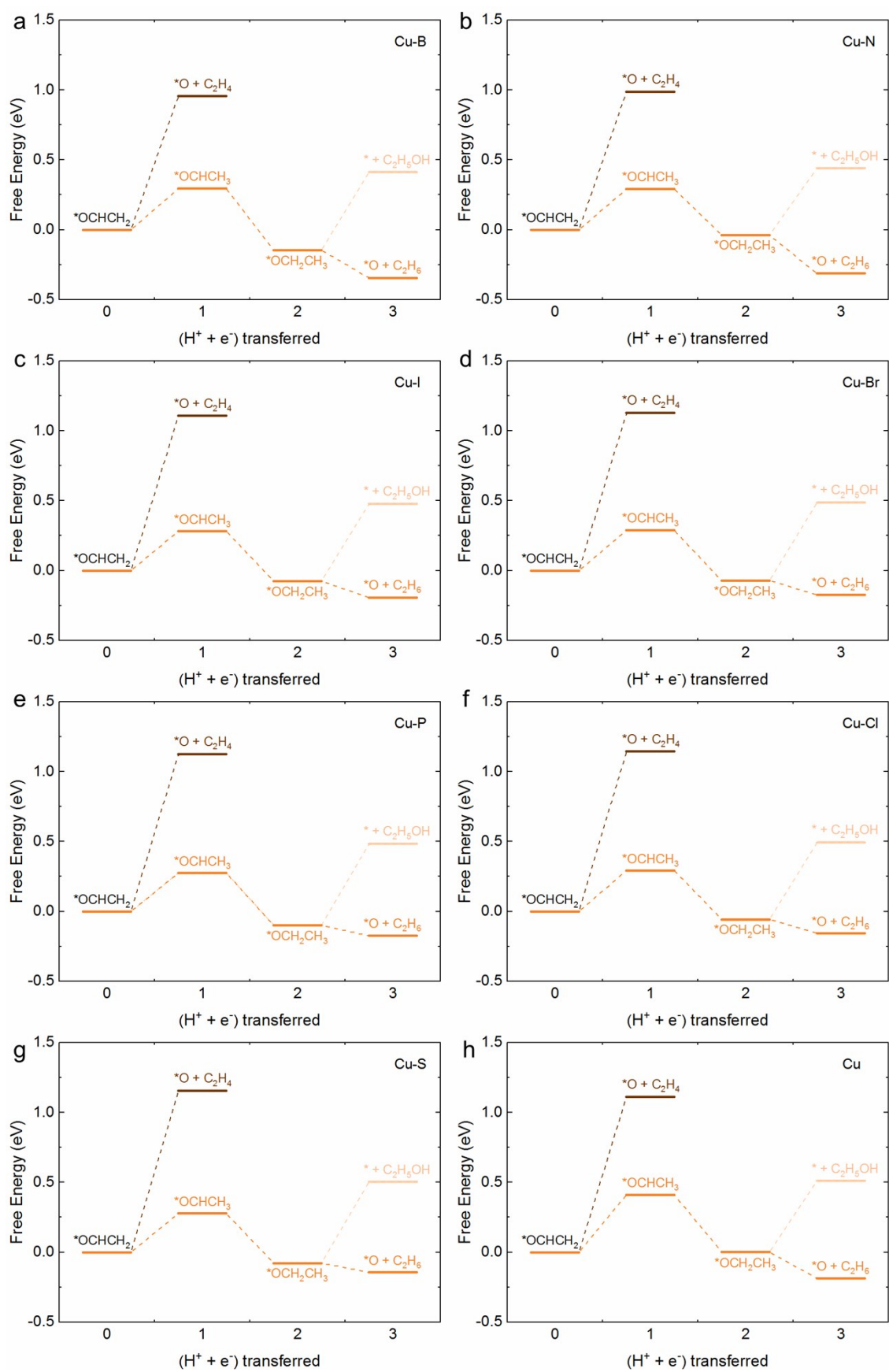


Figure S4. Free energy diagram starting from $*\text{OCHCH}_2$ intermediate adsorbed on the Cu site to ethylene (orange-brown line), ethane (orange line) and ethanol (light orange line) for each Cu-X surface and pure Cu surface.

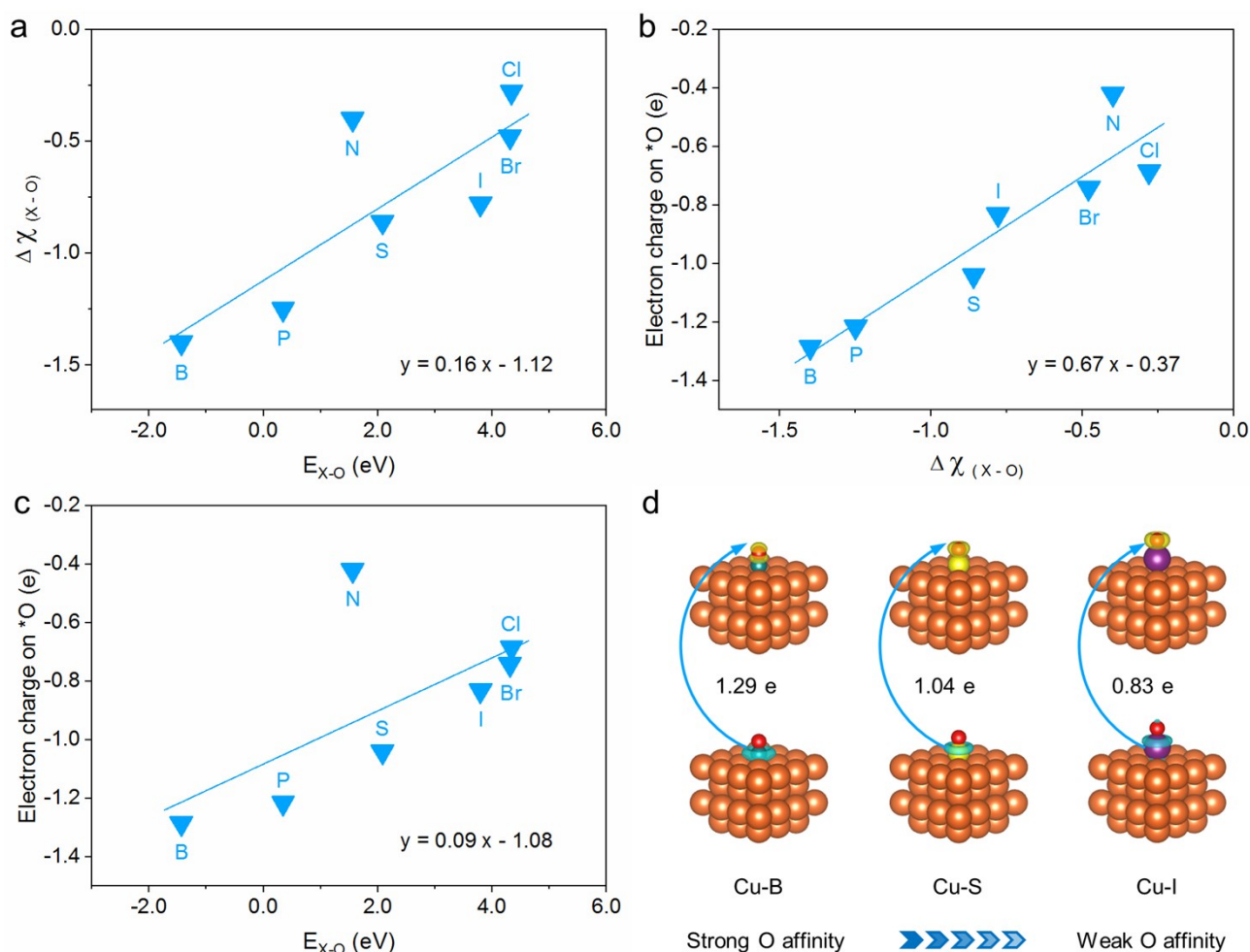


Figure S5. (a) Electronegativity difference between doping element and oxygen plotted against O affinity of the dopant atom site (E_{X-O}). (b) Electron charge on *O adsorbed on the dopant atom site plotted against the electronegativity difference between the doping element and oxygen. (c) Relationship between the electron charge on *O adsorbed on the dopant atom site and O affinity of the dopant atom site (E_{X-O}). (d) Electron charge transfer of *O adsorbed on the dopant atom site of Cu-B (left), Cu-S (middle), and Cu-I (right) with decreasing E_{X-O} . Yellow and cyan isosurface represents electron accumulation and electron depletion, respectively. The isosurface value is $2 \times 10^{-2} e \text{ \AA}^{-3}$.

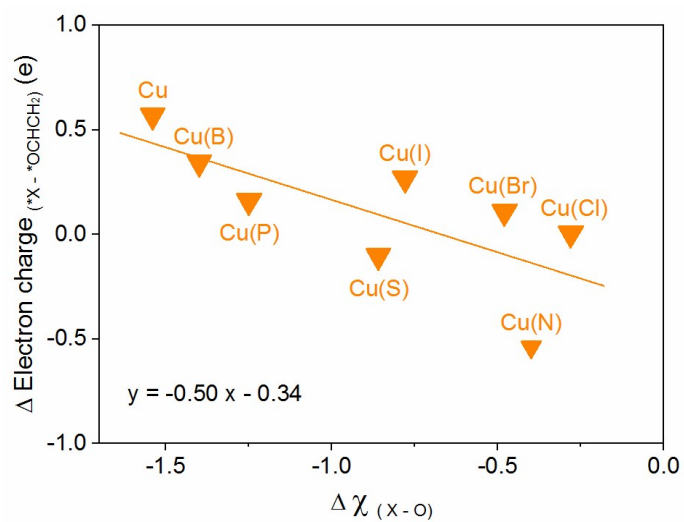


Figure S6. Difference in electron charge between dopant atom and *OCHCH_2 adsorbed on the Cu site plotted against electronegativity difference between doping element and oxygen.

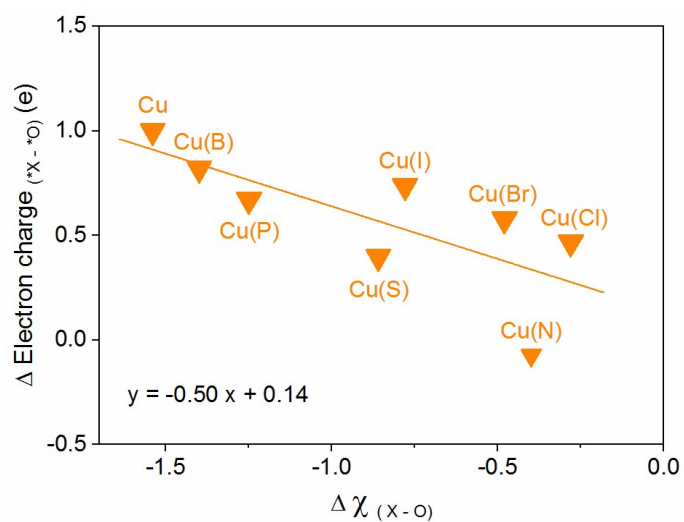


Figure S7. Difference in electron charge between dopant atom and *O adsorbed on the Cu site plotted against electronegativity difference between doping element and oxygen.

Table S1. Adhesion energy (in eV) of dopant atom X on a hollow site of Cu(100) surface.

Model catalyst	E_{ah}^a	E_{X}^b
Cu-B	0.715	-6.704
Cu-P	-1.288	-5.372
Cu-N	0.524	-8.312
Cu-S	-2.071	-4.126
Cu-I	-2.195	-1.316
Cu-Br	-2.168	-1.490
Cu-Cl	-2.194	-1.777

^a E_{ah} values were computed as $E_{\text{ah}} = E_{\text{Cu-X}} - E_{\text{Cu}} - E_{\text{X}}$, where $E_{\text{Cu-X}}$ is the energy of Cu-X surface, E_{Cu} is the energy of Cu(100) surface, and ^b E_{X} is the energy of X atom in its most stable format. For N, Cl, Br and I doped catalysts, the reference energies for E_{X} are based on calculated energies of N_2 , Cl_2 , Br_2 and I_2 gaseous molecules, respectively. For B, P and S doped catalysts, the reference energies for E_{X} are based on calculated energies of corresponding elementary substances, which are B_{12} , P_4 , and S_{32} .

Table S2. Adhesion energy (in eV) of dopant atom X on a bridge site or a top site of Cu(100) surface.

Model catalyst	E_{ah}^a (bridge site)	E_{ah}^a (top site)
Cu-B	2.317	3.168
Cu-P	-0.136	0.580
Cu-N	2.037	3.376
Cu-S	-1.146	-0.358
Cu-I	-1.940	-1.653
Cu-Br	-1.991	-1.682
Cu-Cl	-2.079	-1.743

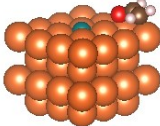
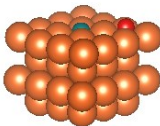
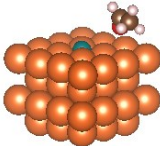
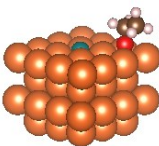
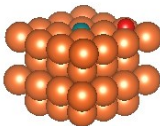
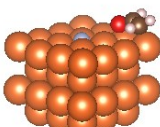
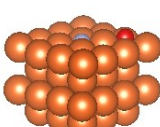
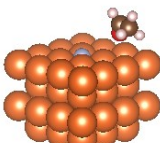
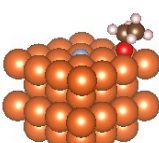
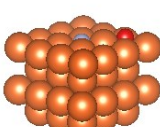
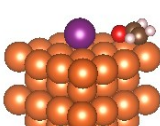
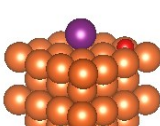
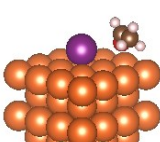
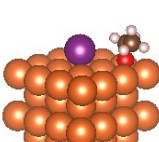
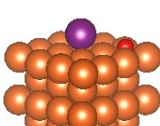
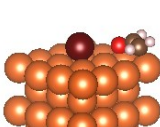
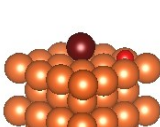
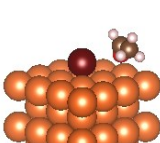
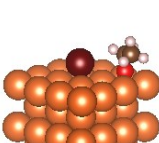
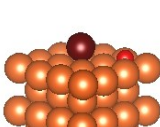
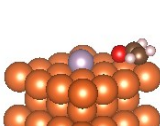
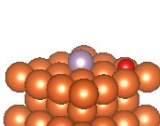
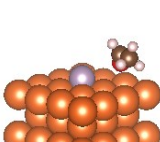
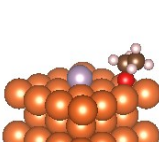
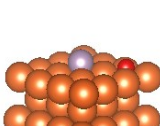
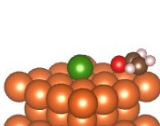
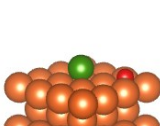
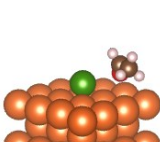
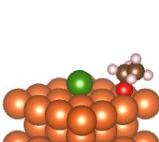
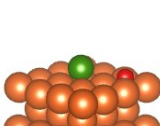
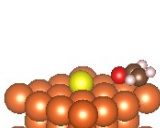
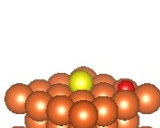
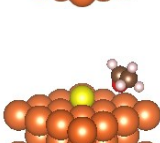
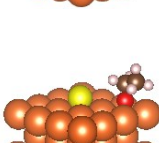
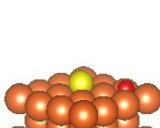

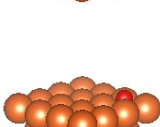
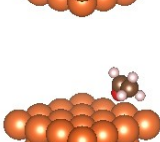
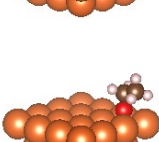
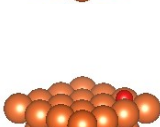
^a E_{ah} values were computed as $E_{\text{ah}} = E_{\text{Cu-X}} - E_{\text{Cu}} - E_{\text{X}}$, where $E_{\text{Cu-X}}$ is the energy of Cu-X surface, E_{Cu} is the energy of Cu(100) surface, and E_{X} is the energy of X atom. E_{X} values are the same as those listed in Table S1.

Table S3. Comparative summary of optimized configurations of key, C₂ reaction intermediates in this research, beginning with *OCHCH₂ adsorbed on the dopant atom site.

Model catalyst	*OCHCH ₂	*O ^a	*OCHCH ₃	*OCH ₂ CH ₃	*O ^b
Cu-B					
Cu-P					
Cu-N					
Cu-S					
Cu-I					
Cu-Br					
Cu-Cl					

^a Optimized *O adsorption configurations after ethylene desorption from *OCHCH₂. ^b Optimized *O adsorption configurations following ethane desorption from *OCH₂CH₃.

Table S4. Comparative summary of optimized configurations of key, C₂ reaction intermediates in this research, beginning with *OCHCH₂ adsorbed on the Cu site.

Model catalyst	*OCHCH ₂	*O ^a	*OCHCH ₃	*OCH ₂ CH ₃	*O ^b
Cu-B					
Cu-N					
Cu-I					
Cu-Br					
Cu-P					
Cu-Cl					
Cu-S					
Cu					

^a Optimized *O adsorption configurations after ethylene desorption from *OCHCH₂. ^b Optimized *O adsorption configurations after ethane desorption from *OCH₂CH₃.

Table S5. Thermodynamic energy corrections (in eV) for reaction intermediates.

Adsorbate	ZPE	-TS
*OCHCH ₂	1.200	-0.274
*OCHCH ₃	1.498	-0.310
*OCH ₂ CH ₃	1.837	-0.281

Table S6. Thermodynamic energy corrections (in eV) for gaseous molecules.

Gas molecule	ZPE	-TS
CO ₂	0.307	-0.661
C ₂ H ₄	1.356	-0.411
C ₂ H ₆	1.805	-0.519
C ₂ H ₅ OH	2.119	-0.572

Table S7. Solvation corrections (in eV) for reaction intermediates.

Adsorbate	Solvation Correction
*OCHCH ₂	0.38
*OCHCH ₃	0.10
*OCH ₂ CH ₃	0.00

Table S8. Free energy change (in eV) of *H adsorption on the dopant atom site of Cu-X surface.

Model catalyst	ΔG_{*H}
Cu-B	-0.473
Cu-P	0.036
Cu-N	-0.935
Cu-S	0.710
Cu-I	1.932 ^a
Cu-Br	1.914 ^a
Cu-Cl	1.874 ^a

^a Free energy change of *H adsorption on the dopant atom site of Cu-I, Cu-Br, and Cu-Cl was calculated with the dopant atom fixed in z direction.

For Cu-X catalysts with positive free energy change of *H adsorption on the dopant atom site, the hydrogen evolution reaction (HER) is not favorable. Regarding the Cu-X catalysts with negative free energy change of *H adsorption, the HER may have an effect on the full product distribution. In experimental studies, the hydrogen evolution also exhibits an inevitable Faradaic efficiency during the electrocatalytic CO₂ reduction [Nat. Chem., 2018, 10, 974-980]. However, for most Cu-X catalysts in this study, the HER is thermodynamically unfavorable.

Table S9. Free energy differences (in eV) between two states of acetaldehyde, i.e. adsorbed *OCHCH₃ and CH₃CHO molecule, with dopant atoms and Cu examined as active sites.

Model catalyst	ΔG_{-X}^a	ΔG_{-Cu}^b
Cu-B	-1.261	-0.509
Cu-P	-0.080	-0.599
Cu-N	-0.540	-0.541
Cu-S	-0.622	-0.617
Cu-I	-0.585	-0.587
Cu-Br	-0.592	-0.589
Cu-Cl	-0.592	-0.590
Cu	^c	-0.492

^a ΔG_{-X} is the free energy difference between adsorbed *OCHCH₃ on the dopant atom site and CH₃CHO molecule with catalyst substrate. ^b ΔG_{-Cu} is the free energy difference between adsorbed *OCHCH₃ on the Cu site and CH₃CHO molecule with catalyst substrate. ^c ΔG_{-X} value for pure Cu model catalyst is missing due to the absence of dopant atom site. The negative values of ΔG indicate favorable thermodynamics for *OCHCH₃ formation.

Table S10. Adsorption energy (in eV) of *OH intermediate on Cu-X and Cu surfaces

Model catalyst	E_{*OH}^a
Cu-B	-1.317
Cu-P	-0.180
Cu-N	-0.159
Cu-S	-0.196
Cu-I	-0.171
Cu-Br	-0.177
Cu-Cl	-0.180
Cu	-0.194

^a E_{*OH} values were obtained by optimizing the *OH adsorption on various active sites of Cu-X and Cu surfaces. The Cu-X catalysts that have very high O affinity to the dopant atom (e.g. Cu-B) exhibit limited efficiency for *OH removal. Along with decreasing O affinity to the dopant atom, the removal of *OH from Cu-X catalysts surfaces is likely to be facilitated.

Table S11. Electronegativity (χ) of doping element, copper and oxygen.

Atomic symbol	χ
B	2.04
P	2.19
N	3.04
S	2.58
I	2.66
Br	2.96
Cl	3.16
Cu	1.90
O	3.44