Supporting Information

Key to C₂ production: Selective C-C Coupling for Electrochemical CO₂ Reduction on Copper Alloy Surfaces

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Computational Methods

All computations were conducted using density functional theory (DFT) method. The Perdew-Burke-Ernzerhof (PBE) functional was applied for electron exchange correlation within the generalized gradient approximation (GGA), as implemented in the VASP code.^{1,2} The ionic cores were described by the projector-augmented wave (PAW) method.³ The parameter of 500 eV was used for the plane wave cutoff energy with a 0.18 eV width of the smearing.

The Cu(100) and Cu(111) surfaces were modelled with three-layer (3×3) supercells with 15 Å of vacuum space. The M@Cu models were simulated by substituting one Cu surface atom with one dopant metal atom M (M = Pt, Pd, Au), respectively. The adsorption energies were calculated on the Cu and M@Cu surfaces with the bottom two layers fixed. In order to evaluate the stability of the dopant metal atom on Cu alloy surfaces, the adhesion energy of the dopant metal atom M was calculated from the following:

 $E_{ad} = E_{M@Cu} - E_{Cu-v} - E_M$

where $E_{M@Cu}$ is the energy of M@Cu(100) or M@Cu(111) surface, E_{Cu-v} is the corresponding energy of Cu(100) or Cu(111) surface with one Cu surface atom vacancy, and E_M is the energy of M atom (Table S1).

Kinetic barriers for C-C coupling processes were evaluted by using the climbing-image nudged elastic band (NEB) method.^{4, 5} Transition state energies were calculated with the top layer relaxed and the rest constrained in the three-layer (3×3) supercells. Varied Gamma k-point grids were used for different C-C coupling steps. For calculating the activation barriers of OC-COH coupling, a ($4 \times 4 \times 1$) k-point grid was applied. As for OC-CHO coupling, a ($1 \times 1 \times 1$) k-point grid was used because it was computationally demanding to obtain the minimum energy paths with a ($4 \times 4 \times 1$) k-point grid. This also suggested the less favorable reaction kinetics of OC-CHO coupling compared to OC-COH coupling. Using denser k-point grid might change the activation barriers, but is unlikely to alter the variation trend of reaction energetics on the investigated Cu-based catalyst surfaces. All structures in geometry optimizations and transition state calculations were relaxed to forces less than 0.05 eV Å⁻¹.



Scheme S1. Reaction pathways of CO_2 reduction toward C_2 products via C-C coupling. The blue path represents the C_2 pathway via OC-CHO coupling; the orange path denotes the C_2 pathway via OC-COH coupling.



Figure S1. The reaction energies for C-C coupling of OC-COH, OC-CHO and OC-CO on Cu(100) and M@Cu(100) catalyst surfaces. A $(4 \times 4 \times 1)$ k-point grid is applied.



Figure S2. The reaction energies for C-C coupling of OC-COH, OC-CHO and OC-CO on Cu(111) and M@Cu(111) catalyst surfaces. A $(4 \times 4 \times 1)$ k-point grid is applied.



Figure S3. The minimum energy paths for OC-COH coupling on (a) Cu(111), (b) Pt@Cu(111), (c) Pd@Cu(111) and (d) Au@Cu(111) catalyst surfaces, respectively. Insets show the optimized structures of initial state (IS), transition state (TS) and final state (FS). Copper atoms are shown as blue-spheres with other metal atoms labelled for each catalyst surface. Carbon, oxygen and hydrogen atoms are brown, red and light pink, respectively. (e) Activation barriers and reaction energies for C-C association between adsorbed *CO and *COH on Cu(111) and M@Cu(111) surfaces. The inset shows the schematic configurations of the initial and final states for the corresponding C-C association reaction. Copper and the dopant metal atoms are blue and grey, respectively.



Figure S4. The minimum energy paths for OC-CHO coupling on (a) Cu(100), (b) Pt@Cu(100), (c) Pd@Cu(100) and (d) Au@Cu(100) catalyst surfaces, respectively. Insets show the optimized structures of initial state (IS), transition state (TS) and final state (FS). Copper atoms are shown as blue-spheres with other metal atoms labelled for each catalyst surface. Carbon, oxygen and hydrogen atoms are brown, red and light pink, respectively. A $(1 \times 1 \times 1)$ k-point grid is applied. (e) Activation barriers and reaction energies for C-C association between adsorbed *CO and *CHO on Cu(100) and M@Cu(100) surfaces. The inset shows the schematic configurations of the initial and final states for the corresponding C-C association reaction. Copper and the dopant metal atoms are blue and grey, respectively.



Figure S5. The minimum energy paths for OC-CHO coupling on (a) Cu(111), (b) Pt@Cu(111), (c) Pd@Cu(111) and (d) Au@Cu(111) catalyst surfaces, respectively. Insets show the optimized structures of initial state (IS), transition state (TS) and final state (FS). Copper atoms are shown as blue-spheres with other metal atoms labelled for each catalyst surface. Carbon, oxygen and hydrogen atoms are brown, red and light pink, respectively. A $(1 \times 1 \times 1)$ k-point grid is applied. (e) Activation barriers and reaction energies for C-C association between adsorbed *CO and *CHO on Cu(111) and M@Cu(111) surfaces. The inset shows the schematic configurations of the initial and final states for the corresponding C-C association reaction. Copper and the dopant metal atoms are blue and grey, respectively.



Figure S6. (a) Relationship between the charge distribution on C atom of adsorbed *CO in the initial state of OC-COH coupling and activation barriers for OC-COH coupling on Cu(111) and M@Cu(111) surfaces. (b) The density of states (DOS) of d-orbital for the nearby Cu atom and p-orbital for C atom of adsorbed *CO in the initial state of OC-COH coupling on Cu(111) and M@Cu(111) surfaces. The d-orbital DOS of the nearby Cu atom without adsorption is also shown in the dashed line. (c) The enlargement of the grey squares in (b).



Figure S7. The activation barriers for C-C bond dissociation of adsorbed *COCHO as a function of the corresponding reaction barriers. A $(1 \times 1 \times 1)$ k-point grid is applied.



Figure S8. The activation barriers for OC-CHO coupling as a function of the corresponding reaction barriers. A $(1 \times 1 \times 1)$ k-point grid is applied.

	E _{ad}	
	On Cu(100) surface	On Cu(111) surface
Pt	-1.04	-1.47
Pd	-0.96	-1.17
Au	-1.10	-1.31

Table S1. The adhesion energy (in eV) of metal atom M on Cu(100) and Cu(111) surfaces.

Table S2. Bond distance (in Angstrom) between C atom of *CO and C atom of *COH in the initial, transition and final states for the OC-COH coupling on Cu(100) and M@Cu(100) surfaces.

Catalyst surface	*CO + *COH → *COCOH			
	*CO + *COH	TS^a	*СОСОН	
Cu(100)	2.90	2.01	1.48	
Pt@Cu(100)	2.93	2.07	1.49	
Pd@Cu(100)	2.89	2.06	1.48	
Au@Cu(100)	2.83	2.05	1.48	

^{*a*} TS indicates transition state.

Table S3. Bond distance (in Angstrom) between C atom of *CO and C atom of *COH in the initial, transition and final states for the OC-COH coupling on Cu(111) and M@Cu(111) surfaces.

Catalyst surface	*CO + *COH → *COCOH		
	*CO + *COH	TS^a	*СОСОН
Cu(111)	2.83	1.91	1.45
Pt@Cu(111)	3.84	2.00	1.49
Pd@Cu(111)	3.85	2.03	1.47
Au@Cu(111)	2.91	1.84	1.45

^{*a*} TS indicates transition state.

Catalyst surface	*CO + *CHO → *COCHO			
	*CO + *CHO	TS^a	*СОСНО	
Cu(100)	3.82	2.02	1.49	
Pt@Cu(100)	3.79	1.97	1.52	
Pd@Cu(100)	3.70	1.91	1.55	
Au@Cu(100)	4.73	1.97	1.50	

Table S4. Bond distance (in Angstrom) between C atom of *CO and C atom of *CHO in the initial, transition and final states for the OC-CHO coupling on Cu(100) and M@Cu(100) surfaces.

^{*a*} TS indicates transition state.

Table S5. Bond distance (in Angstrom) between C atom of *CO and C atom of *CHO in the initial, transition and final states for the OC-CHO coupling on Cu(111) and M@Cu(111) surfaces.

Catalyst surface	*CO + *CHO → *COCHO		
	*CO + *CHO	TS^a	*COCHO
Cu(111)	3.54	1.88	1.51
Pt@Cu(111)	2.85	1.78	1.54
Pd@Cu(111)	3.11	1.54	1.54
Au@Cu(111)	4.40	1.55	1.55

^{*a*} TS indicates transition state.

References

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