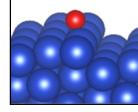
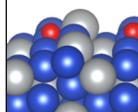
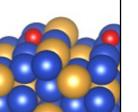
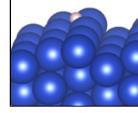
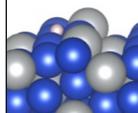
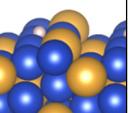
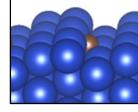
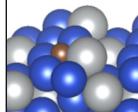
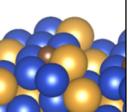
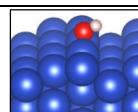
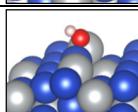
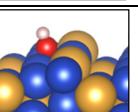
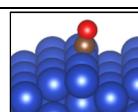
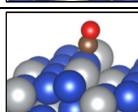
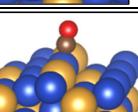
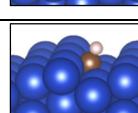
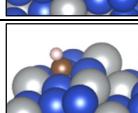
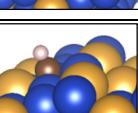
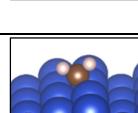
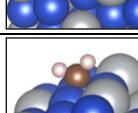
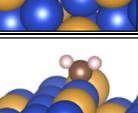
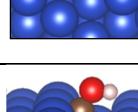
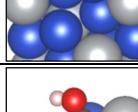
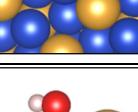


Supplementary Information for “Electroreduction of carbon dioxide to methane on copper, copper-silver and copper-gold catalysts: A DFT study”

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Table S1. Adsorption energy of intermediate species, *B.E*, on Cu(211), Cu₃Ag(211), and Cu₃Au(211) in eV.

species	Cu(211)		Cu ₃ Ag(211)		Cu ₃ Au(211)	
	configuration	<i>B.E</i>	configuration	<i>B.E</i>	configuration	<i>B.E</i>
O		0.77		0.88		1.13
H		-0.28		-0.19		-0.17
C		2.05		2.85		2.91
OH		-0.28		0.05		0.24
CO		0.93		1.05		1.12
CH		1.01		1.35		1.55
CH ₂		0.53		0.77		0.79
COH		1.91		2.00		2.12

	Cu(211)		Cu ₃ Ag(211)		Cu ₃ Au(211)	
species	configuration	B.E	configuration	B.E	configuration	B.E
HCO		1.43		1.51		1.45
HCOH		1.18		1.45		1.37
HOCO		1.04		1.26		1.51
CH ₃		-0.61		-0.39		-0.40
OCH ₂		0.83		1.06		1.01
OCH ₃		-0.27		0.07		0.16
^a CO* + H*		0.68		0.86		0.99
^a HCO* + H*		1.15		1.44		1.33
^a CH* + OH*		0.94		1.54		1.85

$$B.E = E_{total(C_xH_yO_z)} - E_{slab} - xE(C) - yE(H) - zE(O)$$

Where $E_{total(C_xH_yO_z)}$ is the total energy of the state, E_{slab} is the energy of the clean slab, $E(C)$ is energy of C atom referenced to graphene, $E(H)$ is the energy of H atom referenced to $1/2H_2$ and $E(O)$ is the energy of O atom referenced to $(H_2O - H_2)$

^a The adsorption energies corresponds to the co-adsorption of the two adsorbates.

Table S2. Calculated zero-point energy correction, enthalpic temperature and entropic corrections for adsorbed species.

adsorbed species	ZPE (eV)	$\int C_p dT$ (eV)	-TS (eV)	ZPE + $\int C_p dT - TS$ (eV)
H*	0.160	0.005	-0.007	0.158
O*	0.072	0.025	-0.038	0.059
C*	0.097	0.017	-0.025	0.089
OH*	0.364	0.046	-0.079	0.331
CO*	0.192	0.076	-0.153	0.115
HCO*	0.444	0.086	-0.184	0.346
COH*	0.451	0.068	-0.110	0.409
HOCO*	0.624	0.096	-0.178	0.542
HCOH*	0.765	0.068	-0.109	0.724
OCH ₂ *	0.758	0.091	-0.190	0.659
OCH ₃ *	1.108	0.093	-0.179	1.022
CH*	0.348	0.028	-0.039	0.337
CH ₂ *	0.589	0.049	-0.075	0.563
CH ₃ *	0.900	0.060	-0.096	0.864

Table S3. Calculated zero-point energy correction, enthalpic temperature and entropic corrections for gas-phase species taken from ref [1].

adsorbed species	ZPE (eV)	$\int C_p dT$ (eV)	-TS (eV)	ZPE + $\int C_p dT - TS$ (eV)
H ₂	0.27	0.09	-0.42	-0.06
CO ₂	0.31	0.10	-0.65	-0.24
H ₂ O	0.58	0.10	-0.65	0.03
CH ₄	1.20	0.10	-0.06	1.24

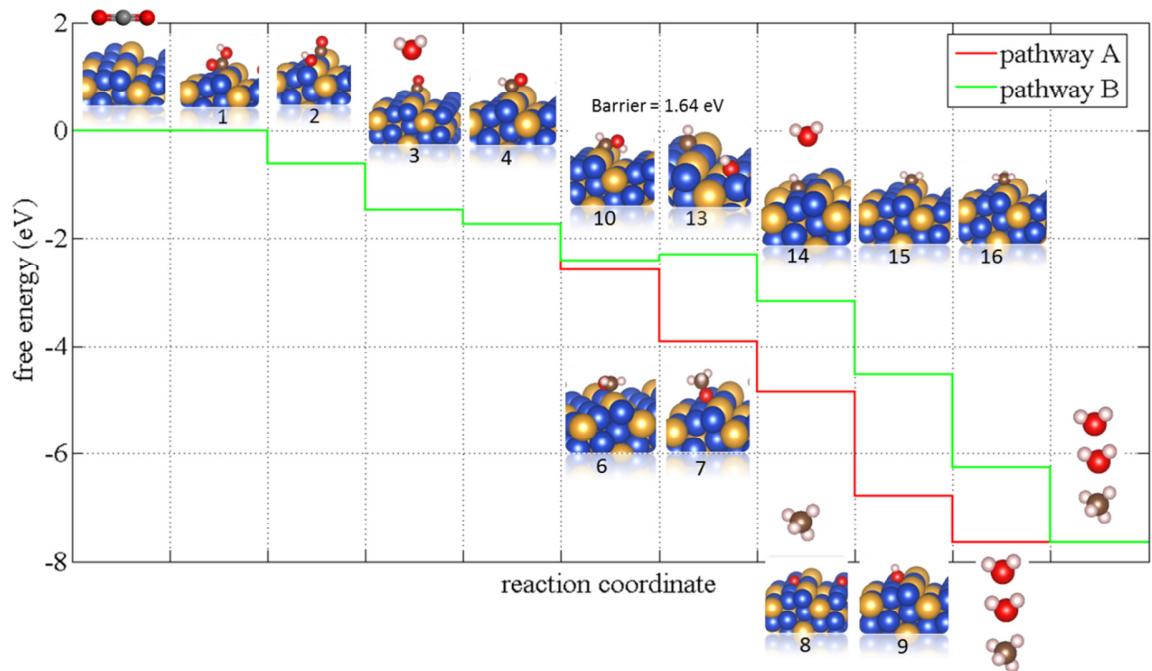


Figure S1. Cu₃Au(211) free energy diagram following reaction steps in pathway A and pathway B at limiting potential U = -0.86 V_{RHE}.

Table S4. Transition state structures corresponding to the calculated barrier energies shown in Table 1.

Elementary step	Cu(211)		Cu ₃ Ag (211)		Cu ₃ Au (211)	
	Ea		Ea		Ea	
H* + CO* → HCO*	+0.96		+0.48		+0.98	
HCO* + H* → OCH ₂ *	+0.66		+0.37		+0.66	
HCO* + H* → HCOH*	+0.60		+0.74		+0.72	
HCOH* → CH* + OH*	+1.37		+1.20		+1.64	

Reference

- Peterson, A.A., et al., *How copper catalyzes the electroreduction of carbon dioxide into hydrocarbon fuels*. Energy & Environmental Science, 2010. **3**(9): p. 1311-1315.