Supporting Information

Theoretical search for novel Au or Ag bimetallic alloys capable of transforming CO_2 into hydrocarbons

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Optimised configurations of key intermediates

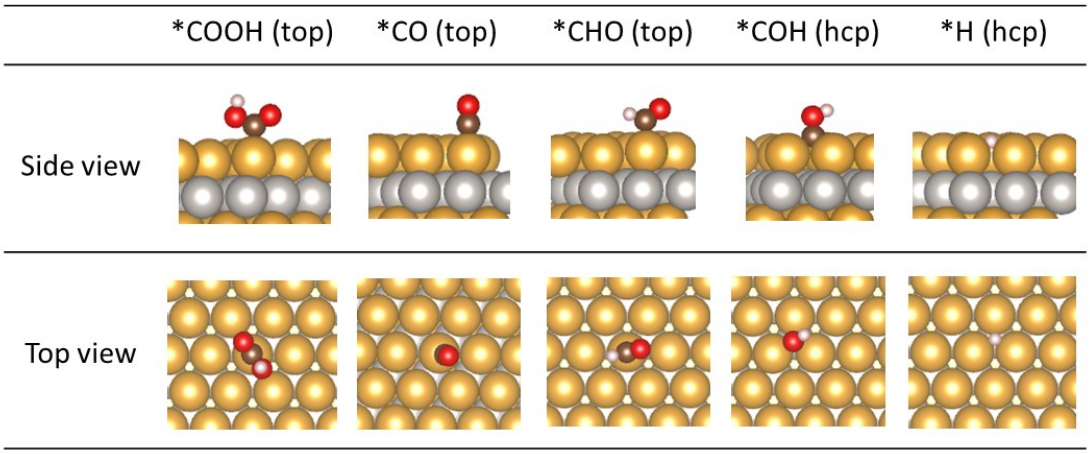

Figure S1. Optimized configurations (side view and top view) of intermediates *COOH, *CO, *CHO, *COH, *H on the (111) facet of metallic alloys.

Energetic calculations

The free energies (all refer to CO_2, H_2O and H_2) based on the computational hydrogen electrode model (CHE)[1] are defined as:

$$G_{*COOH} = G_{*COOH+slab} - G_{slab} - G_{CO_2} - 0.5 \times G_{H_2}$$

$$G_{*CO} = G_{*CO+slab} + G_{H_2O} - G_{slab} - G_{CO_2} - G_{H_2}$$

$$G_{*CHO} = G_{*CHO+slab} + G_{H_2O} - G_{slab} - G_{CO_2} - 1.5 \times G_{H_2}$$

$$G_{*COH} = G_{*COH+slab} + G_{H_2O} - G_{slab} - G_{CO_2} - 1.5 \times G_{H_2}$$

$$G_{*H} = G_{*H+slab} - G_{slab} - 0.5 \times G_{H_2}$$

The reaction free energies of key elementary steps are defined as:

$$\Delta G_{*COOH} = G_{*COOH+slab} - G_{slab} - G_{CO_2} - 0.5 \times G_{H_2}$$

$$\Delta G_{*CHO-*CO} = G_{*CHO+slab} - G_{*CO+slab} - 0.5 \times G_{H_2}$$

$$\Delta G_{*COH-*CO} = G_{*COH+slab} - G_{*CO+slab} - 0.5 \times G_{H_2}$$

$$\Delta G_{*H} = G_{*H+slab} - G_{slab} - 0.5 \times G_{H_2}$$

The free energy is derived from electronic energy:

$$\Delta G = \Delta E_{DFT} + \Delta ZPE - T\Delta S + \Delta \int C_p dT$$

The zero-point energies (ZPE) of intermediates and molecules were calculated from the vibrational frequencies obtained with in the harmonic oscillator approximation. All 3N degrees of freedom are treated as vibrational motions while neglecting the contributions from the material surfaces. Vibrational contributions to the entropy and heat capacity were considered for adsorbed species taken from standard thermodynamic tables at 298.15K and 101325 Pa. We take uniform frequency for all surfaces, i.e., randomly choose six surfaces to calculate their frequency and take the mean value of zero vibrational energy as the corrections for all surfaces. We calculated the ZPE for gas molecules according to the vibrational calculations, in consistence with the value in the reference,[2] corrections for TS and CpdT for gas molecules are directly obtained from the reference. In consideration of the aqueous environment, different adsorbates have different response toward water, we made an energetic correction referred to literature with the same PBE exchange-correlation functional,[3] the stabilization energies of solvation for *CO and *CO were -0.1 eV, and *COH and *COOH were -0.38 eV. All correlated thermodynamic energy corrections are shown in Tables SI,

Table S1. Thermodynamic energy corrections (in eV) for intermediates and gas molecules.

Unit / eV	CO	CHO	COH	COOH	H	CO_2	H_2	H_2O
ZPE	0.183	0.451	0.465	0.599	0.142	0.311	0.273	0.585
TS	0.153	0.184	0.140	0.178	0.007	0.65	0.39	0.65
$\int C_p dT$	0.076	0.086	0.079	0.096	0.005	0.1	0.09	0.1
Stabilization	-0.1	-0.1	-0.38	-0.38	0			

Table S2. Free energies of key intermediates *CO, *CHO, *COH, *COOH, *H on the (111) facet of Au or Ag alloys

Free energy/eV	CO	CHO	COH	COOH	H
Au/Pt/Au(111)	0.12	0.58	1.08	0.56	0.19
Au/Rh/Au(111)	0.15	0.72	1.29	0.66	0.29
Cu	0.16	1.07	1.14	0.86	-0.01
Au/Ni/Au(111)	0.23	0.76	1.54	0.73	0.36
Ag/Ir/Ag(111)	0.26	0.99	1.80	0.93	0.22

Ag/Rh/Ag(111)	0.28	1.02	1.91	0.87	0.23
Au/Pd/Au(111)	0.28	0.74	1.46	0.71	0.35
Ag/Pt/Ag(111)	0.34	1.05	1.73	0.78	0.22
Ag/Ni/Ag(111)	0.37	1.03	1.97	0.79	0.25
Ag/Pd/Ag(111)	0.42	1.12	1.98	0.80	0.32
Au/Cu/Au(111)	0.46	0.95	1.96	0.88	0.39
Ir/Ag(111)	0.52	1.16	2.08	0.91	0.28
Ir/Au(111)	0.55	0.70	1.46	0.74	0.42
Au	0.58	0.91	1.59	0.91	0.29
Rh/Au(111)	0.58	0.97	1.76	0.97	0.65
Pd/Ag(111)	0.60	1.31	2.32	1.06	0.46
Pt/Au(111)	0.60	0.98	1.87	0.97	0.52
Pt/Ag(111)	0.62	1.33	2.25	1.08	0.48
Au/Ag/Au(111)	0.62	1.03	1.77	0.98	0.30
Au/Ag(111)	0.64	1.31	2.18	1.09	0.36
Pd/Au(111)	0.64	1.03	1.98	1.00	0.57
Ag/Au(111)	0.66	1.10	1.83	1.08	0.35
Ag/Au/Ag(111)	0.68	1.36	2.23	1.14	0.38
Ag	0.68	1.43	2.34	1.15	0.42
Ag/Cu/Ag(111)	0.68	1.36	2.38	1.08	0.42
Rh/Ag(111)	0.73	1.38	2.31	1.14	0.47

Table S3. The reaction free energies and activation energies of key elementary steps

	ΔG_{*COOH} / eV	$\Delta G_{*CHO-*CO}$ / eV	ΔG_{*H} / eV	E_a / eV
Au/Pt/Au(111)	0.56	0.46	0.19	0.57
Au/Rh/Au(111)	0.66	0.57	0.29	0.62
Cu	0.86	0.91	-0.01	1.12
Au/Ni/Au(111)	0.73	0.54	0.36	0.64

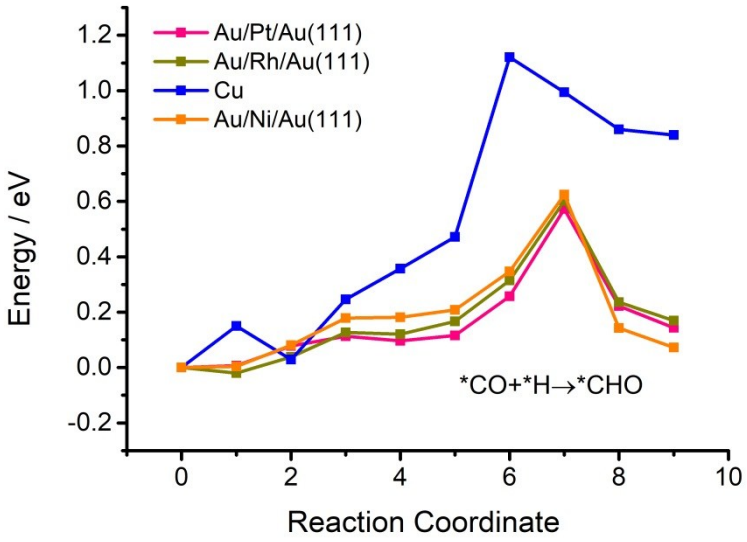

Figure S2. Energy profiles of *CO protonation to *CHO.

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3 F. Calle-Vallejo and M. T. Koper, Angewandte Chemie, 2013, 52, 7282-7285.