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

Electronic Supplementary Information

Enhancing C-C Bond Formation by the Surface Strain: Investigating the C2 and C3 Intermediate Formation on the Strained Cu Surfaces

Yu-Te Chan, I-Shou Huang, Ming-Kang Tsai*

Department of Chemistry, National Taiwan Normal University, Taipei, 11677, Taiwan.

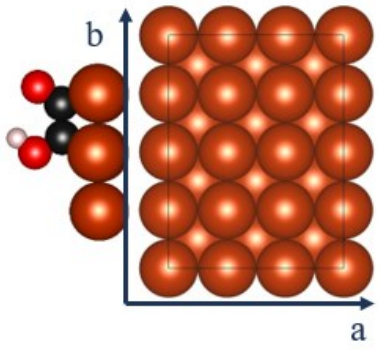
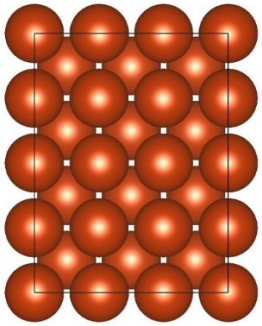
(a)	(b)
	

Figure S1. A set of 4×3 Cu(100) models (4 layers) are chosen, (a) top view of pristine model and (b) the schematic representation of N_a >0 and N_b > 0 model. In order to simulate the surface strain, a combination of compressed or elongated cell constant $\vec{a}$ and $\vec{b}$ scenarios are constructed. The choices of constant $\vec{a}$ corresponds to a 0 to 10 percent compression of a pristine cell (11 grids) and those of cell constant $\vec{b}$ corresponds to a 0 to 10 percent elongation (11 grids). There were totally 11×11 = 121 models being described by following equation:

$Cell\ constant_{strained} = (Cell\ constant_{pristine}) \times (100 + N)\%$

where $N_a = -10 \sim 0$ and $N_b = 0 \sim 10$, respectively. Notably, the C–C bond of C2 intermediates like *OCCOH lying along the *b*-axis. The bottom three layers were frozen during each optimization calculation.

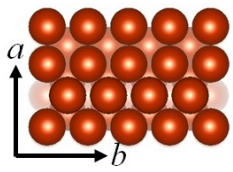
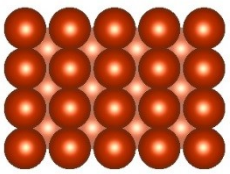
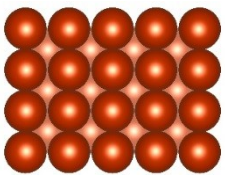
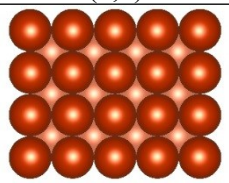
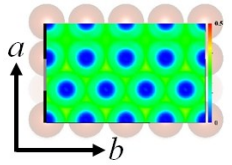
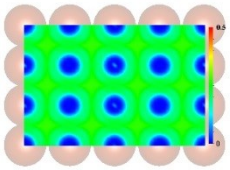
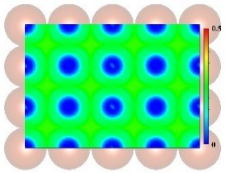
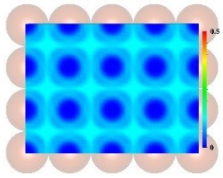
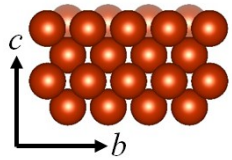
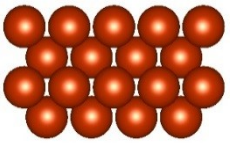
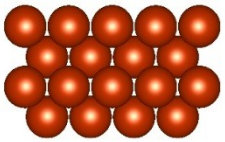
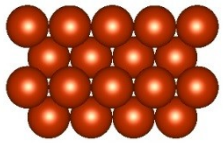
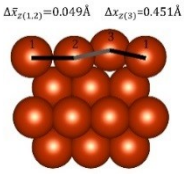
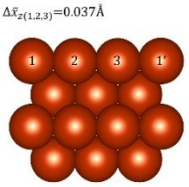
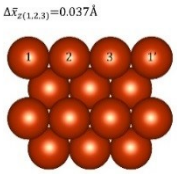
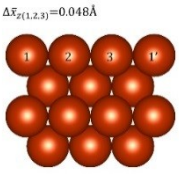
	(10,-10)	(-6,6)	(-3,3)	(0,0)
(a)				
(b)				
(c)				
(d)				

Figure S2. The schematic represenation of thevarious surface strain models (N_a, N_b) Cu(100) models where (a) top views, (b) electron localixation function maps, and (c) side vews. The $\Delta\bar{x}_{z(a,b,\ldots)}$ represent the average displacement of atoms (a, b, …) of each optimized slab model from the pristine bulk z coordinate.

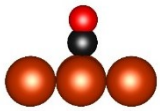
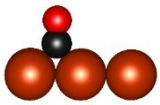
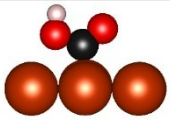
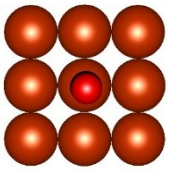
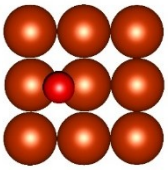
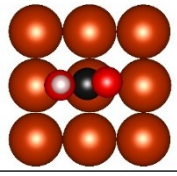
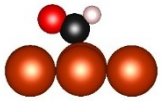
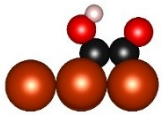
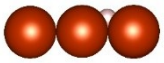
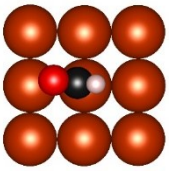
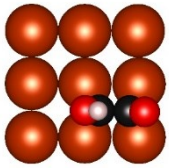
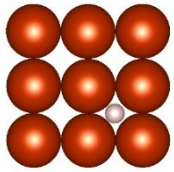
$^{*}CO_t$	$^{*}CO_b$	$^{*}COOH$
		
		
$^{*}CHO$	$^{*}OCCOH$	$^{*}H$
		
		

Figure S3. Schematic representations of top and side views of the selected intermediates along the CO_2RR/HER pathway on the Cu(100) surface: (a) $^{*}CO_{atop}$, (b) $^{*}CO_{bridge}$, (c) *COOH, (d) *CHO, (e) *OCCOH, (f) *H. Cu, C, O and H atoms are depicted as orange, black, red and white spheres.

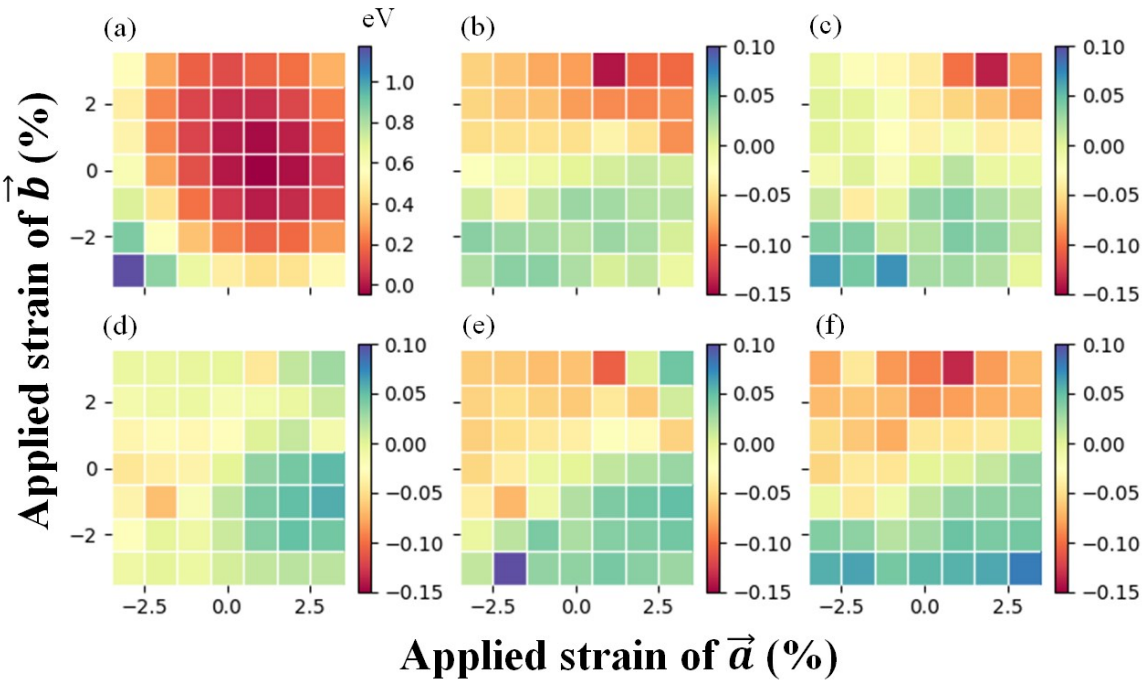


Figure S4. (a) The relative energy of bare Cu surface, (b) the relative formation energy (ΔE_{form}^{X}) *CO_{atop} , (c) *CHO, (d) *H, (e)*CO_{bridge} , (f) *OCCOH in color scale (in eV) in respect to the non-strain case – the central spot (0, 0). The numerical values – (x, y) of x-axis and y-axis denote the strained percentage along the lattice direction *a* and *b* of Cu(100) surface. For example, (1, -2) denotes the elongation and compression along the *a*- and *b*-direction by 1 and -2%, respectively.

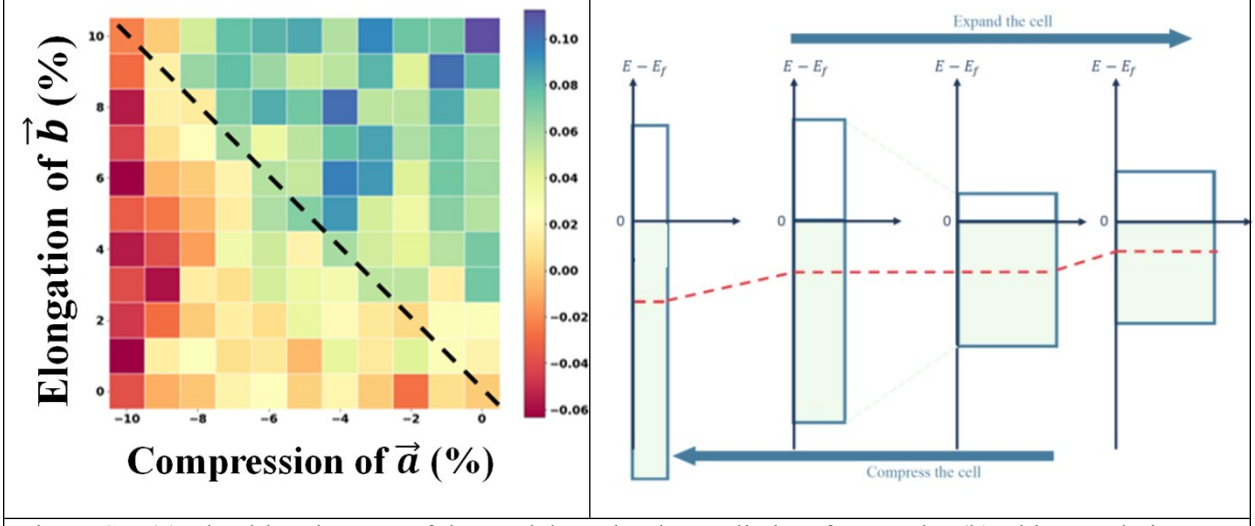
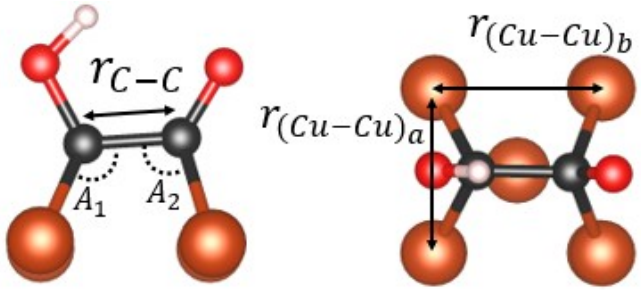


Figure S5. (a) The d-band center of the models under the applied surface strain; (b) This correlation between surface strain and d-band center elaborated by Mavrikakis et al.[1]

(a)



(b) Selected structural properties

Model	(0,0)	(-6,10)
A_1	117.84°	120.00°
A_2	103.05°	110.70°
r_{C-C}	1.477Å	1.493Å
$r_{(Cu-Cu)_b}$	2.61Å	2.93Å
$r_{(Cu-Cu)_a}$	2.55Å	2.40Å

(c) Color maps of the structural properties

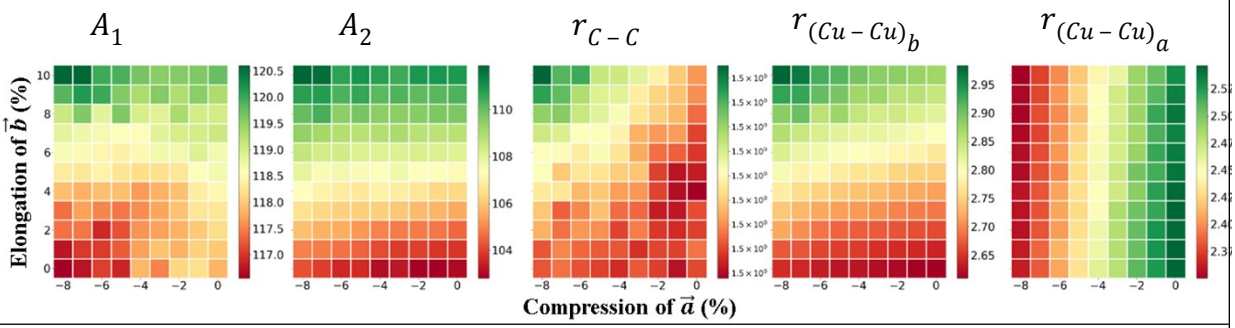


Figure S6. (a) Structural parameters of *OCCOH intermediate; (b) Comparison of the structural properties of (0,0) and (-6,10) models; (c) heat map of the absolute values of the aforementioned structural properties under applied strain conditions.

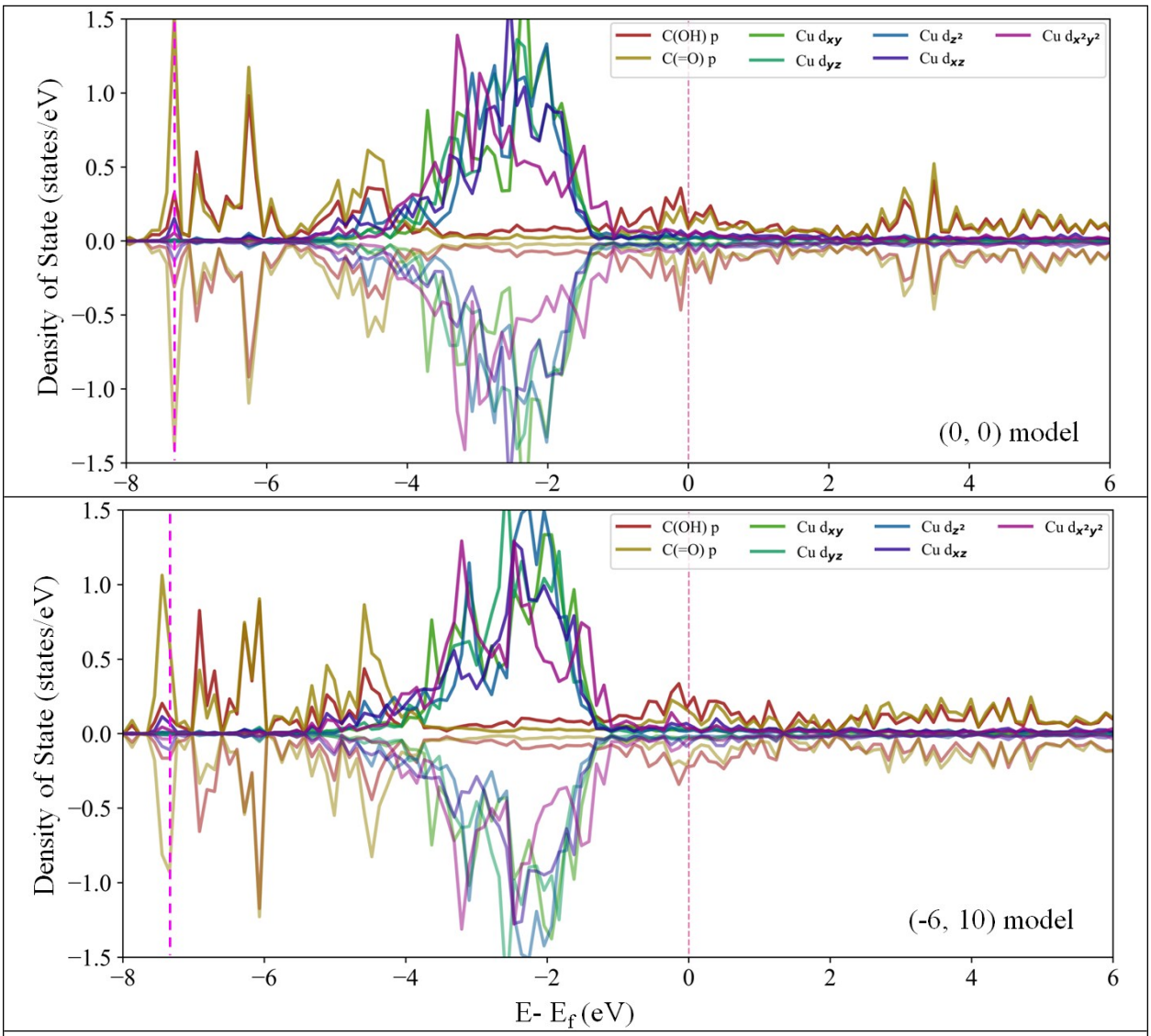


Figure S7. Partial density of states (PDOS) of carbon atoms in *OCCOH and the contacted four Cu atoms on surface. The pink dash line indicates the bonding orbital between C(=O) and Cu shift to lower energy under the strain condition.

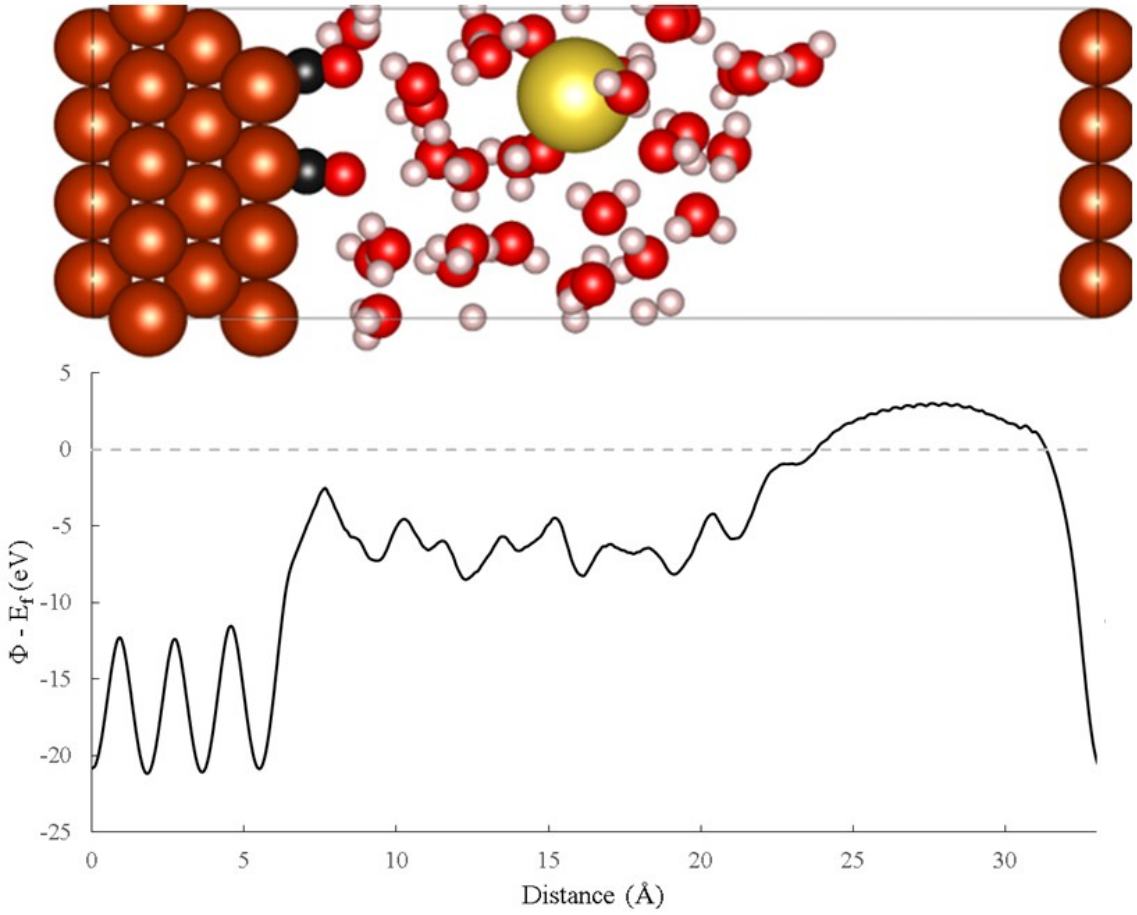


Figure S8. (top) Schematic representation of the explicit water solvation model; (down) the calculated electrostatic potential (in respect to Fermi energy) of the aforementioned two *CO absorbed on pristine Cu(100) surface.

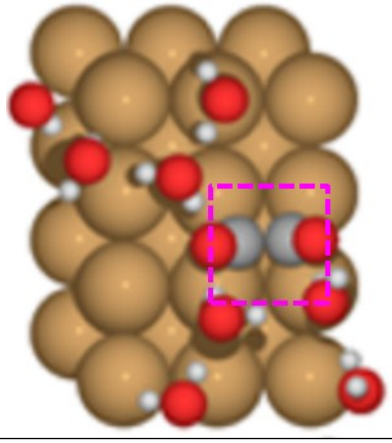
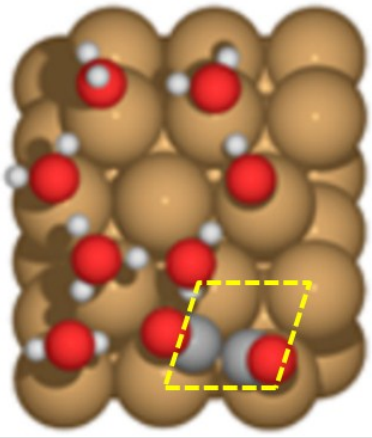
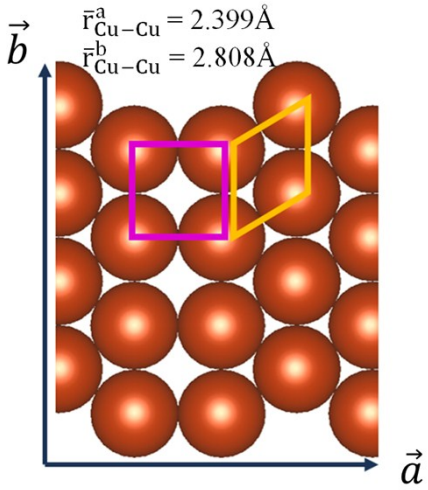
(a) Pristine Cu(100) from ref. 3	(b) Pristine Cu(111) from ref. 3
	
(c) (-6,10) model	
	

Figure S9. (a) and (b) denote the DFT models of Cu(111) and Cu(100) reported by Montoya et al., respectively;[2] (c) denote the current (-6,10) model containing adjacent rectangle and parallelogram morphology with the average Cu–Cu distance along $\vec{a}$ and $\vec{b}$.

Table S1. Correction terms calculated from frequencies for free energy calculations (in eV)

	E_{zpe}	-TS	Correction term
*OCCO_(-10,10)_32H_2O_INI	0.502	-0.269	0.233
*OCCO_(-10,10)_ 32H_2O_TS	0.466	-0.237	0.230
*OCCO_(-10,10)_ 32H_2O_FIN	0.493	-0.218	0.275
*OCCO_(-6,10)_ 32H_2O_INI	0.500	-0.273	0.227
*OCCO_(-6,10)_ 32H_2O_TS	0.464	-0.238	0.226
*OCCO_(-6,10)_ 32H_2O_FIN	0.499	-0.195	0.304
*OCCO_(0,0)_ 32H_2O_INI	0.496	-0.267	0.230
*OCCO_(0,0)_ 32H_2O_TS	0.461	-0.218	0.243
*OCCO_(0,0)_ 32H_2O_FIN	0.496	-0.202	0.294
*CCH_(-10,0)_ 32H_2O_INI	0.775	-0.229	0.546
*CCH_(-10,0)_ 32H_2O_TS	0.736	-0.305	0.431
*CCH_(-10,0)_ 32H_2O_FIN	0.820	-0.183	0.637
*CCH_(-10,10)_ 32H_2O_INI	0.770	-0.254	0.516
*CCH_(-10,10)_ 32H_2O_TS	0.745	-0.245	0.500
*CCH_(-10,10)_ 32H_2O_FIN	0.814	-0.191	0.623
*CCOH_(-10,0)_ 32H_2O_INI	0.930	-0.260	0.670
*CCOH_(-10,0)_ 32H_2O_TS	0.919	-0.286	0.633
*CCOH_(-10,0)_ 32H_2O_FIN	0.974	-0.273	0.702
*CCOH_(-10,10)_ 32H_2O_INI	0.901	-0.288	0.613
*CCOH_(-10,10)_ 32H_2O_TS	0.908	-0.267	0.642
*CCOH_(-10,10)_ 32H_2O_FIN	0.969	-0.257	0.711

Table S2. Calculated energies of reactant (INI), TS, and product (FIN) states for the C-C coupling processes of Figure 4.

	Model	INI	TS	FIN	ΔE(TS)	ΔE(rxn)
2CO	(-10,10)_1	-666.97	-666.48	-666.71	0.49	0.26
	(-10,10)_2	-667.32	-666.83	-666.87	0.49	0.45
	(-10,10)_3	-667.41	-666.59	-666.90	0.82	0.51
	(-10,10)_4	-666.89	-666.42	-666.76	0.47	0.13
	(-10,10)_5	-667.41	-666.82	-666.93	0.59	0.48
	(-6,10)_1	-669.82	-668.96	-669.51	0.86	0.31
	(-6,10)_2	-669.99	-669.41	-669.86	0.58	0.13
	(-6,10)_3	-669.90	-669.29	-669.83	0.61	0.07
	(-6,10)_4	-670.20	-669.36	-669.84	0.84	0.36
	(-6,10)_5	-669.98	-669.43	-669.87	0.55	0.11
	(0,0)_1	-673.29	-672.73	-673.08	0.56	0.21
	(0,0)_2	-673.31	-672.60	-672.98	0.71	0.33
	(0,0)_3	-673.43	-672.87	-673.09	0.56	0.34
	(0,0)_4	-673.35	-672.78	-673.07	0.57	0.28
	(0,0)_5	-673.28	-672.84	-673.05	0.44	0.23
CCH	(-10,0)_1	-672.48	-671.94	-672.42	0.54	0.06
	(-10,0)_2	-672.66	-672.10	-672.69	0.56	-0.03
	(-10,0)_3	-672.78	-672.17	-672.74	0.61	0.04
	(-10,0)_4	-672.68	-672.07	-672.58	0.61	0.10
	(-10,0)_5	-672.67	-672.14	-672.64	0.53	0.03
	(-10,10)_1	-671.21	-670.73	-671.02	0.48	0.19
	(-10,10)_2	-671.21	-670.71	-671.15	0.50	0.06
	(-10,10)_3	-670.77	-670.24	-670.79	0.53	-0.02
	(-10,10)_4	-671.18	-670.65	-671.13	0.53	0.05
	(-10,10)_5	-671.13	-670.54	-671.03	0.59	0.10
CCOH	(-10,0)_1	-679.23	-678.61	-679.31	0.62	-0.08
	(-10,0)_2	-679.31	-678.81	-679.52	0.50	-0.21
	(-10,0)_3	-679.04	-678.40	-679.24	0.64	-0.20
	(-10,0)_4	-679.30	-678.48	-679.17	0.82	0.13
	(-10,0)_5	-679.39	-678.61	-679.22	0.78	0.17

	(-10,10)_1	-677.54	-677.00	-677.84	0.54	-0.30
	(-10,10)_2	-678.00	-677.39	-678.24	0.61	-0.24
	(-10,10)_3	-678.09	-677.60	-678.40	0.49	-0.31
	(-10,10)_4	-678.42	-678.05	-678.66	0.37	-0.24
	(-10,10)_5	-678.48	-677.96	-678.85	0.52	-0.37

(1). The notation of model (x,y)_z denotes the strain condition (x,y) and the trial of AIMD calculations (z).
(2). ΔE(TS) and ΔE(rxn) denote the reaction barrier and reaction energy, respectively.
(3). All energy values are shown in eV.

Table S3. The statistical details of mean relative energetics, and standard deviations.

	Model	Term[1,2]	[3]INI	TS	FIN
2CO	(-10,10)	E(mean)	0.00	0.57	0.37
		STD	0.25	0.15	0.16
		ZPE-TΔS	0.23	0.23	0.28
		ΔG = Δ(E+ZPE-TS)	0.00	0.57	0.41
	(-6,10)	E(mean)	0.00	0.69	0.20
		STD	0.14	0.15	0.13
		ZPE-TΔS	0.23	0.23	0.30
		ΔG	0.00	0.69	0.27
	(0,0)	E(mean)	0.00	0.57	0.28
		STD	0.06	0.10	0.06
		ZPE-TΔS	0.23	0.24	0.29
		ΔG	0.00	0.58	0.34
CCH	(-10,0)	E(mean)	0.00	0.57	0.04
		STD	0.11	0.04	0.05
		ZPE-TΔS	0.55	0.43	0.64
		ΔG	0.00	0.45	0.13
	(-10,-10)	E(mean)	0.00	0.53	0.08
		STD	0.19	0.04	0.08
		ZPE-TΔS	0.52	0.50	0.62
		ΔG	0.00	0.51	0.18
CCOH	(-10,0)	E(mean)	0.00	0.67	-0.04

		STD	0.13	0.13	0.18
		ZPE-TΔS	0.67	0.63	0.70
		ΔG	0.00	0.63	-0.01
	(-10,-10)	E(mean)	0.00	0.51	-0.29
		STD	0.38	0.09	0.05
		ZPE-TΔS	0.61	0.64	0.71
		ΔG	0.00	0.53	-0.19

(1). E(mean) denotes the average energy of the five optimized solvated models.

(2). STD denotes the standard deviation using $$STD = \sqrt{\frac{1}{N-1}\sum_{i=1}^{N}(x-\bar{x})^2}$$

(3). STD of INI is calculated using the sampled electronic energy of INI configurations.

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