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Supplemental information for the article "Promoting effect of tungsten carbide on catalytic activity of Cu for CO_2 reduction"

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Table S1. Initial site and its location (SL), final site, adsorption energies (E_{ads}), adsorption energy on the same site of the corresponding pristine surface ($E_{ads,Cu}/E_{ads,WC}$), CO carbon–nearest surface atom distance (d (C-Surface)), shortest C–surface distance (d⊥ (C-Surface)), C-O bond length (d(CO)) and Bader charge for CO on Cu/WC(0001)

Surface	SL	Initial site	Final site[a]	E_{ads} (eV)	$E_{ads,Cu}/E_{ads,WC}$ (eV)	d (C-Surface) (A)°	$d_{\perp}$ (C-Surface) (A)°	d(C-O) (A)°	Q (*e*)
Cu_{ML}/C-WC	Cu	Top	Top	-1.48	-1.03	1.81	1.78	1.16	-0.14
		Bridge	E*hcp*	-1.22	-1.16	2.07	1.30	1.19	–
		C*hcp*	Top	-1.49	-1.03	1.81	1.78	1.16	–
		E*hcp*	E*hcp*	-1.22	-1.16	2.07	1.30	1.19	–
Cu_{ML}/W-WC	Cu	Top	Top	-1.66	-1.03	1.84	1.82	1.16	–
		Bridge	E*hcp*	-1.72	-1.16	2.08	1.45	1.19	–
		W*hcp*	W*hcp*	-1.52	-1.15	2.06	1.42	1.19	–
		E*hcp*	E*hcp*	-1.72	-1.16	2.08	1.45	1.19	-0.40
Cu_4/C-WC	Cu	Top	Top (DS)	-1.66	-1.03	1.79	1.79	1.16	–
		Bridge	Bridge (DS)	-1.41	-1.03	1.97	1.45	1.18	–
		C*hcp*	Top-C of WC	-2.15	-2.92	1.43	1.29	1.26	-0.45
		E*hcp*	Bridge (DS)	-1.44	-1.16	1.97	1.45	1.18	–
		4-fold	Top (DS)	-1.66	-1.03	1.79	1.79	1.16	–
	WC	Top-1	Top-1 (DS)	-2.76	-2.92	1.32	1.32	1.18	-0.30
		Top-2	Top-2 (DS)	-2.97	-2.92	1.31	1.31	1.18	–
		Bridge-1	Bridge-1 (DS)	-2.48	-1.95	1.46	0.70	1.44	–
		Bridge-2	W*hcp* (DS)	-3.39	-3.64	1.46	0.60	1.45	–
		Bridge-3	W*hcp* (DS)	-3.17	-3.64	1.51	0.66	1.44	–
		Bridge-4	W*hcp* (DS)	-3.39	-3.64	1.46	0.60	1.45	–
		W*hcp*	W*hcp* (DS)	-3.39	-3.64	1.46	0.60	1.45	-0.57
		E*hcp*	Bridge-2	-2.63	-1.95	1.52	0.91	1.23	–
Cu_4/W-WC	Cu	Top	Top	-1.35	-1.03	1.83	1.49	1.16	-0.13
		Bridge	Top	-1.35	-1.03	1.82	1.47	1.16	–
		W*hcp*	W*hcp*	-1.11	-1.15	1.97	1.40	1.19	–
		E*hcp*	E*hcp*	-1.32	-1.16	2.02	1.40	1.19	–
		4-fold	W*hcp*	-1.11	-1.15	1.97	1.40	1.19	–
	WC	Top-1	Top-1	-2.17	-2.12	2.04	2.04	1.17	–
		Top-2	E*hcp*	-2.02	–	2.06	1.42	1.34	–
		Bridge-1	Top-1 (DS)	-2.12	-2.12	2.04	1.41	1.26	–
		Bridge-2	E*hcp*	-2.02	–	2.06	1.42	1.34	–
		Bridge-3	Top-1	-2.20	-2.12	2.06	2.06	1.18	–
		Bridge-4	Bridge-4	-2.24	-2.39	2.06	1.40	1.24	-0.87
		C*hcp*	Top-1	-2.20	-2.12	2.06	2.06	1.18	–
		E*hcp*	E*hcp*	-2.02	–	2.06	1.42	1.34	–

[a]DS stands for significantly distorted geometry of the Cu particle

Table S2. Initial site and its location (SL), final site, adsorption energies (E_{ads}), adsorption energy on the same site of the corresponding pristine surface ($E_{ads,Cu}/E_{ads,WC}$), CO carbon–nearest surface atom distance (d (C-Surface)), shortest C–surface distance (d⊥ (C-Surface)), C-O bond length (d(CO)), O-C-O inner angle (∠ (O-C-O)) and Bader charge for CO_2 on Cu/WC(0001)

Surface	SL	Initial site	Final site[a]	Eads (eV)	$E_{ads,Cu}/E_{ads,WC}$ (eV)	d (C-Surface) (A)°	d⊥ (C-Surface) (A)°	d (C-O) (A)°	∠ (O-C-O)o	Q (e)
CuML/C-WC	Cu	Top	Desorption							
		Bridge	Desorption							
		Chcp	Chcp	-0.32	–	1.99	1.43	1.27	126.2	-0.80
		Ehcp	Desorption							
CuML/W-WC	Cu	Top	Bridge	-0.43	–	2.06	1.68	1.25	137.6	–
		Bridge	Bridge	-0.43	–	2.05	1.68	1.24	137.5	–
		Whcp	Whcp	-0.65	–	1.96	1.33	1.29	122.5	-1.00
		Ehcp	Ehcp	-0.62	–	1.94	1.27	1.29	119.1	–
Cu4/C-WC	Cu	Top	Desorption							
		Bridge	Bridge	-0.38	–	1.99	1.86	1.22	135.5	–
		Chcp	Top-C of WC	-2.16	–	1.50	1.50	1.30	118.2	-0.72
		Ehcp	Ehcp	-0.38	–	2.02	1.34	1.28	123.3	–
		4-fold	Top-C of WC	-2.16	–	1.49	1.49	1.31	117.8	–
	WC	Top-1	Top-1	-1.41	–	1.55	1.55	1.27	127.4	–
		Top-2	Top-2 (DS)	-2.19	–	1.49	1.47	1.29	117.7	-0.69
		Bridge-1	Desorption							
		Bridge-2	Desorption							
		Bridge-3	Desorption							
		Bridge-4	Top-2 (DS)	-1.91	–	1.52	1.51	1.29	119.2	–
		Whcp	Top-2 (DS)	-1.91	–	1.52	1.51	1.29	119.2	–
		Ehcp	Top-2 (DS)	-2.27	–	1.42	1.33	1.30	119.0	–
Cu4/W-WC	Cu	Top	Desorption							
		Bridge	Ehcp	-0.41	–	2.07	1.48	1.25	129.2	–
		Whcp	Whcp	-0.61	–	1.94	1.33	1.30	118.6	-1.03
		Ehcp	Ehcp	-0.41	–	2.06	1.48	1.25	128.9	–
		4-fold	Whcp	-0.61	–	1.94	1.31	1.30	118.6	–
	WC	Top-1	Dissociation							
		Top-2	Dissociation							
		Bridge-1	Bridge-1	-1.80	–	2.15	1.78	1.30	114.8	-1.34
		Bridge-2	Desorption							
		Bridge-3	Chcp	-1.63	-1.56	2.42	1.66	1.34	116.0	–
		Bridge-4	Chcp	-1.56	-1.56	2.26	1.65	1.33	116.2	–

		Chcp	Chcp	-1.62	-1.56	2.42	1.66	1.34	116.0	–
		Ehcp	Dissociation							

[a]DS stands for significantly distorted geometry of the Cu particle

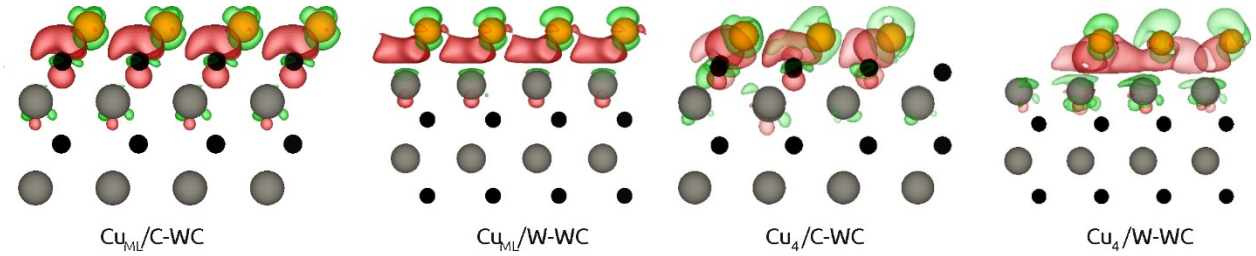

Figure S1. Charge density difference (CDD) plots for bare Cu/WC(0001) surfaces. Here green and red regions correspond to a charge loss (atoms become more positively charged) and charge accumulation (atoms become more negatively charged), respectively.

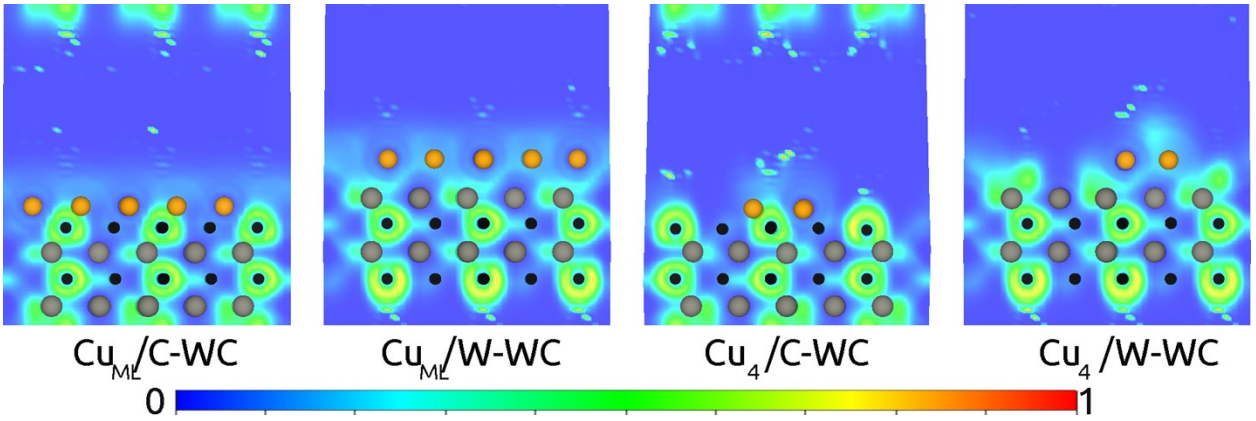

Figure S2. 2D plots of electron localization function (ELF) for bare Cu/WC(0001) surfaces. The probability of finding electron varies from 0 (blue) to 1 (red).

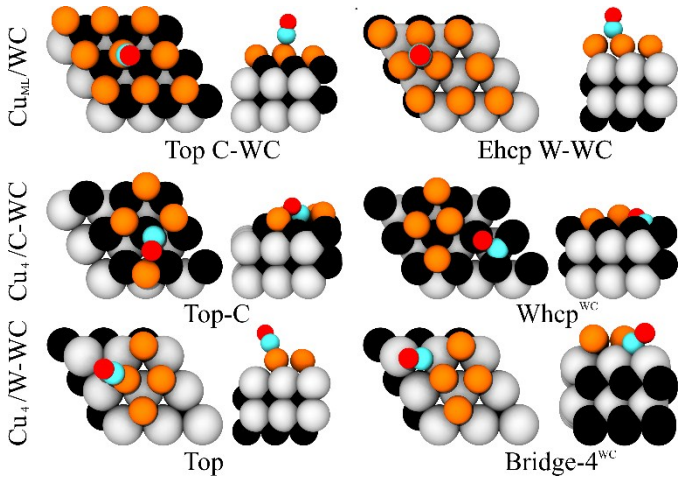

Figure S3. Top and side views of the most stable geometries for CO after its bonding on Cu/WC(0001) surfaces. The legend below each panel indicates the adsorption site. Sites located on the support are indicated with WC. CO carbon atoms are represented by cyan spheres, tungsten, carbon and copper atoms are represented by silver, black and orange spheres, respectively.

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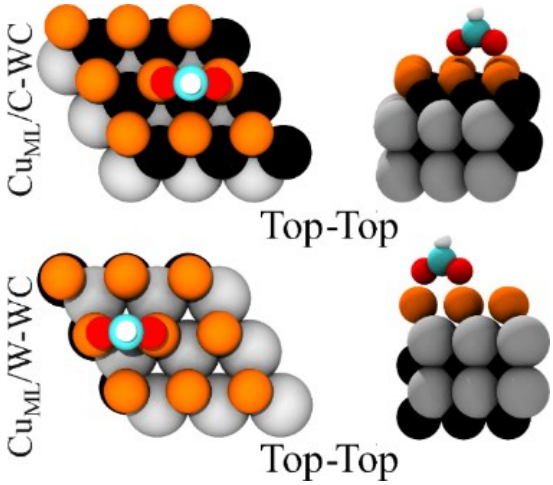

Figure S4. Top and side views for the most stable geometries of HCOO after its bonding on Cu_{ML}/WC(0001) surfaces. The legend below each panel indicates the adsorption site. HCOO carbon atoms are represented by cyan spheres, the rest of the atoms are indicated the same as on Figure S3.

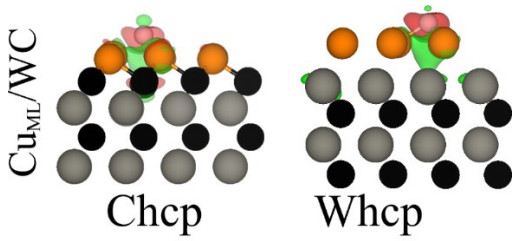

Figure S5. Charge density difference (CDD) plots for a H atom adsorbed on Cu_{ML}/WC(0001) surfaces. Hydrogen atoms are indicated by white spheres. Charge difference color code is the same as on Figure S1.

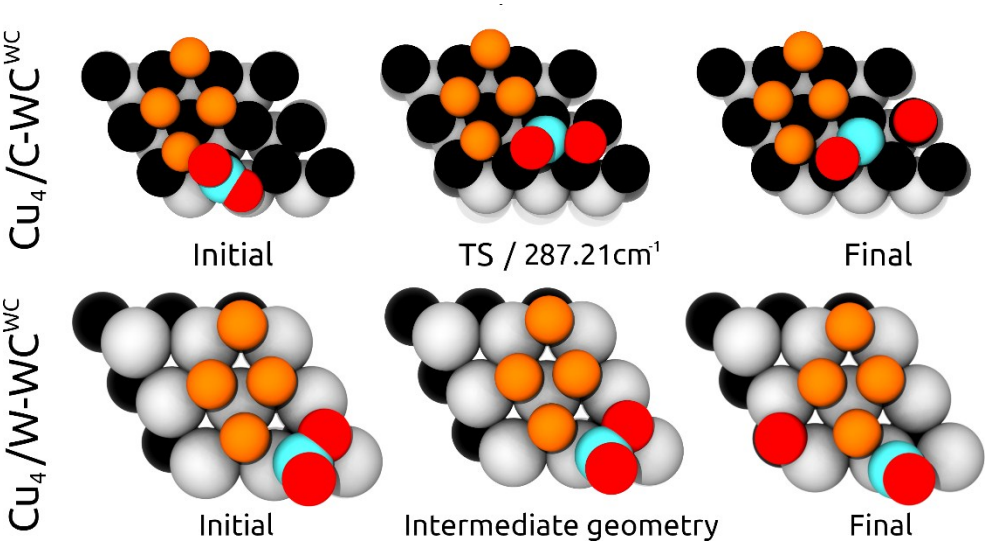

Figure S6. Initial, transition and final states geometries for direct CO2 dissociation on WC sites of Cu_4/WC surfaces. Carbon atoms of CO2 and CO are represented by cyan spheres; tungsten, carbon and copper atoms are represented by silver, black and orange spheres, respectively. Vibrational frequencies are given for the TS where possible.