

Supporting Information

Insight into the Confined Space Between Copper Nanoparticles for the Electrochemical CO₂ Reduction to CO

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KEYWORDS: Confined space catalysis • Electrochemical CO₂ reduction • Copper nanoparticles

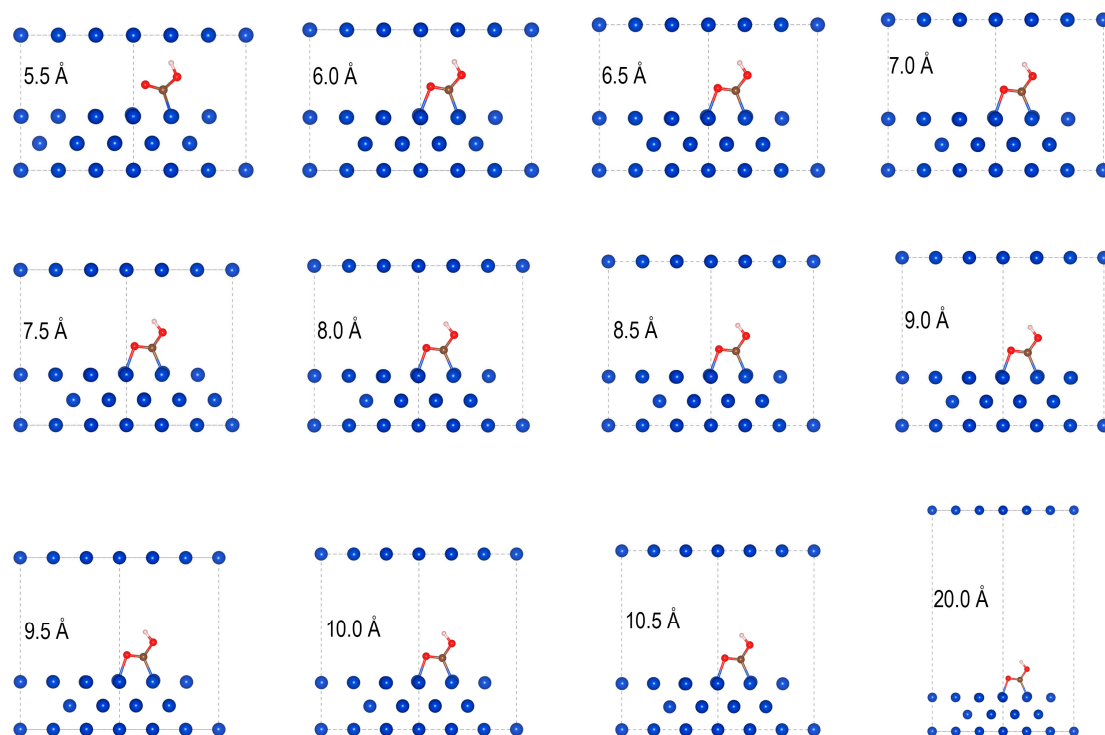


Figure S1. Adsorption structures of *COOH intermediates on $\text{Cu}(100)$ for different values of d_{Cu} .

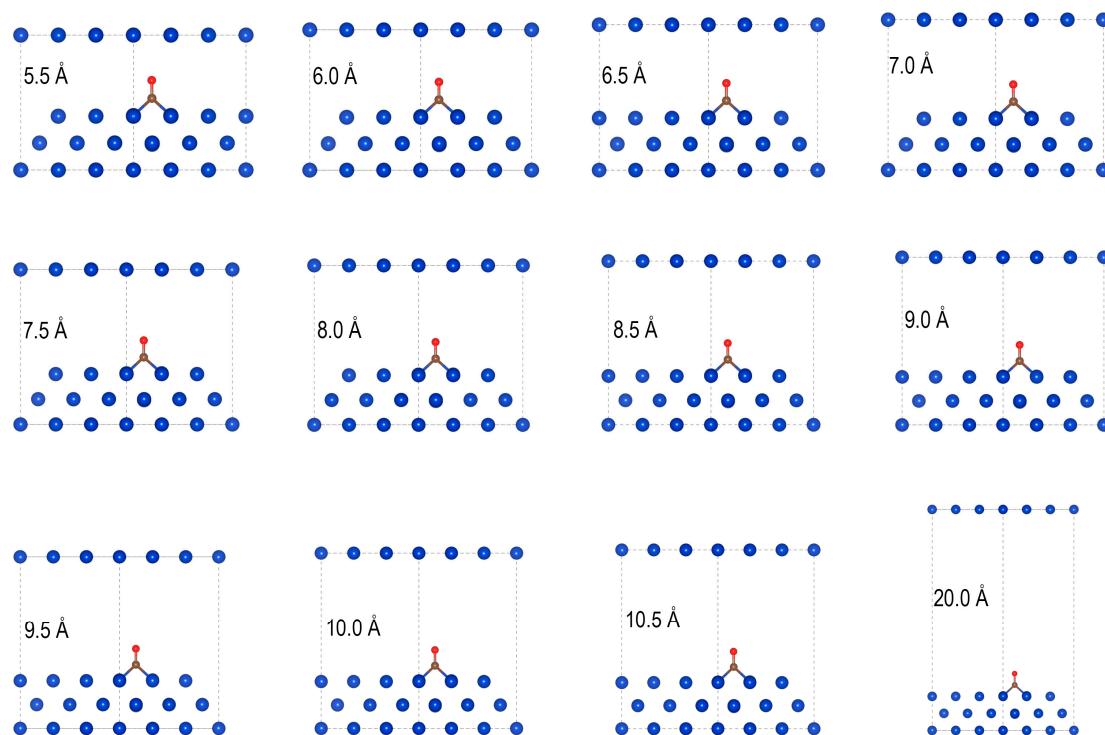


Figure S2. Adsorption structures of $^*\text{CO}$ intermediates on Cu(100) for different values of d_{Cu} .

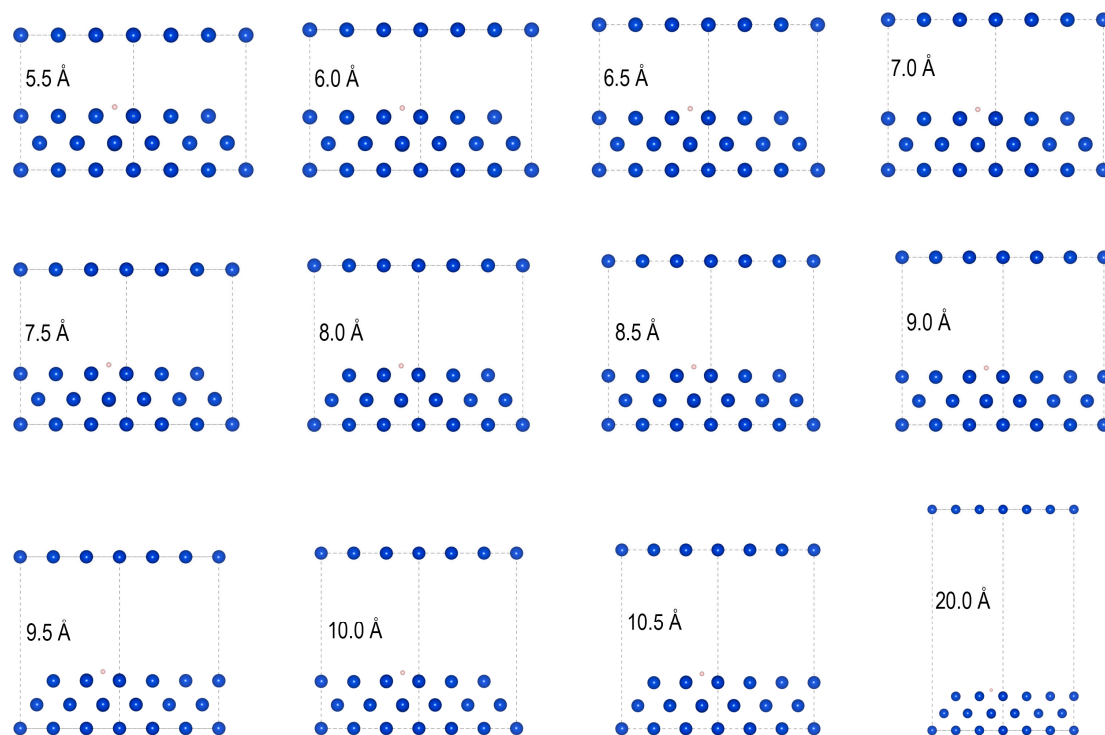


Figure S3. Adsorption structures of $*H$ intermediates on Cu(100) for different values of d_{Cu} .

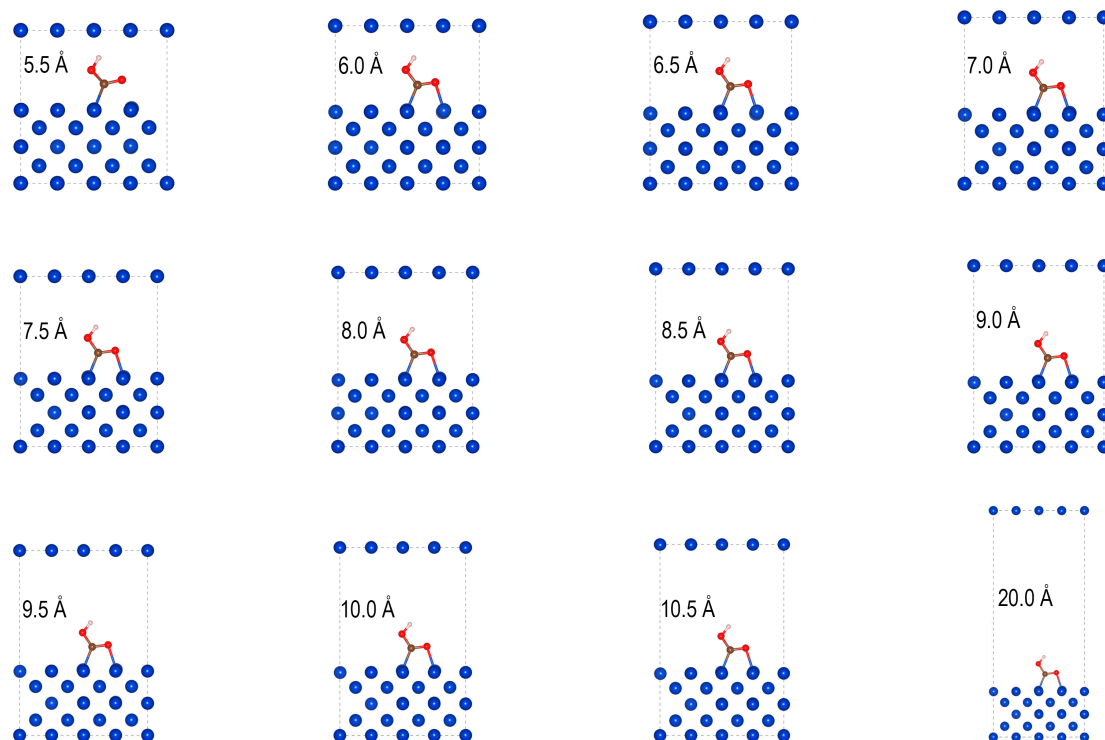


Figure S4. Adsorption structures of $\ast\text{COOH}$ intermediates on Cu(110) for different values of d_{Cu} .

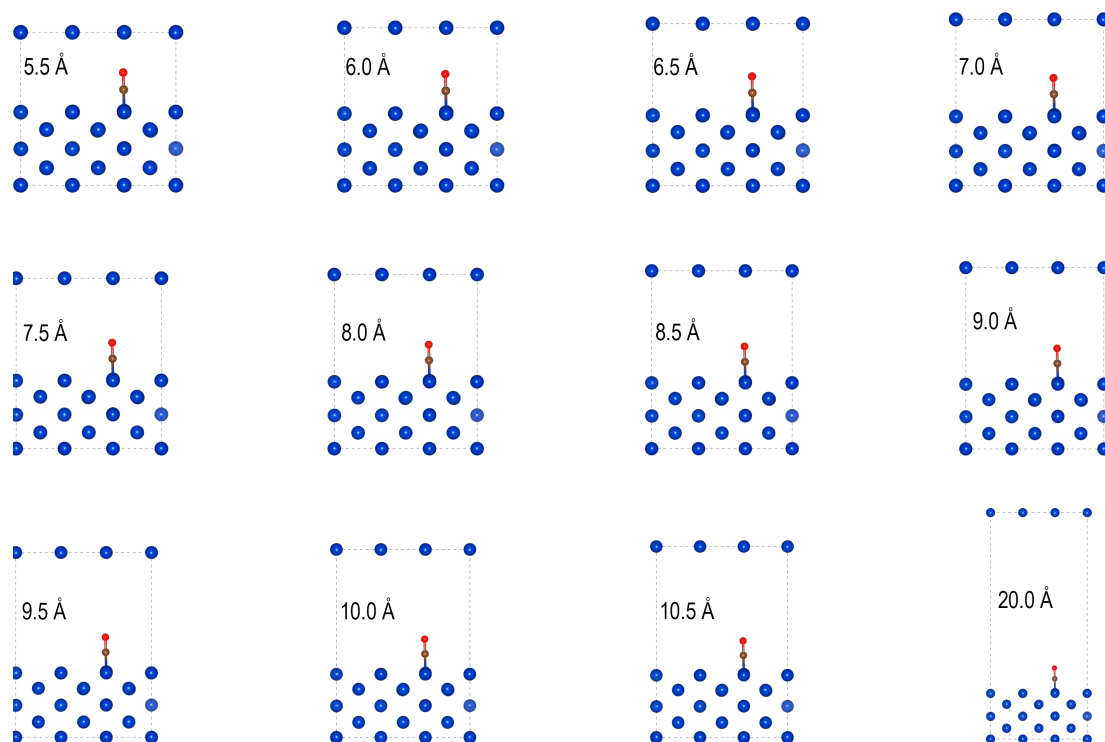


Figure S5. Adsorption structures of $^*\text{CO}$ intermediates on Cu(110) for different values of d_{Cu} .

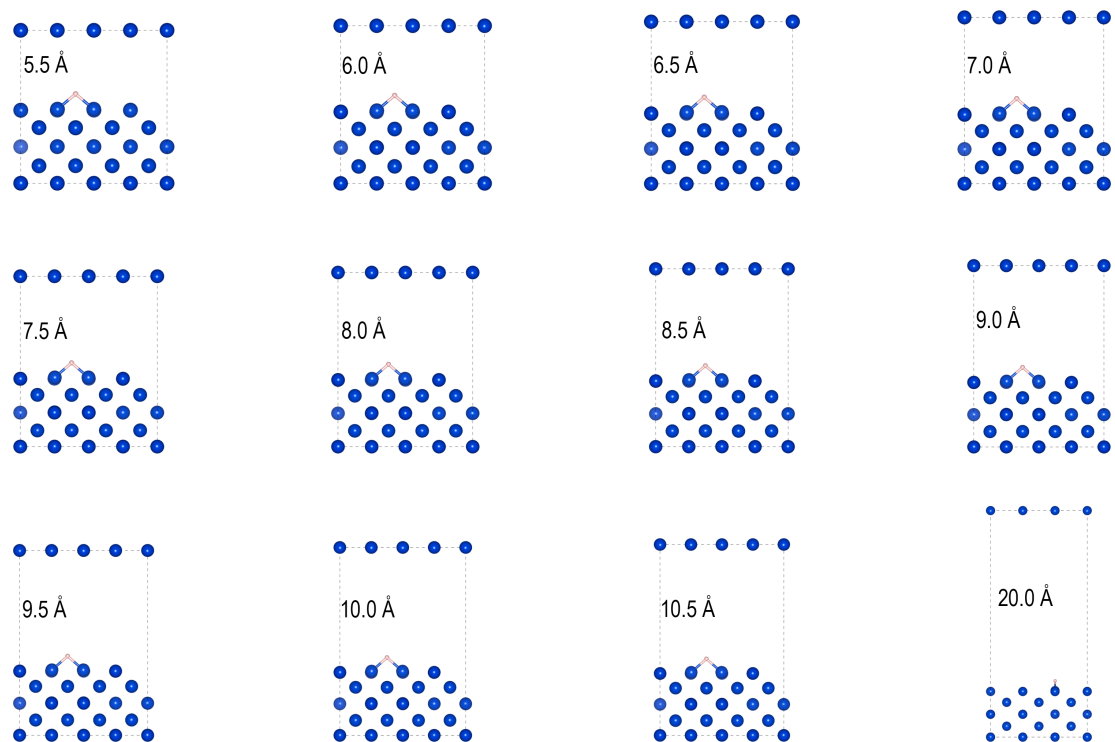


Figure S6. Adsorption structures of $*\text{H}$ intermediates on $\text{Cu}(110)$ for different values of d_{Cu} .

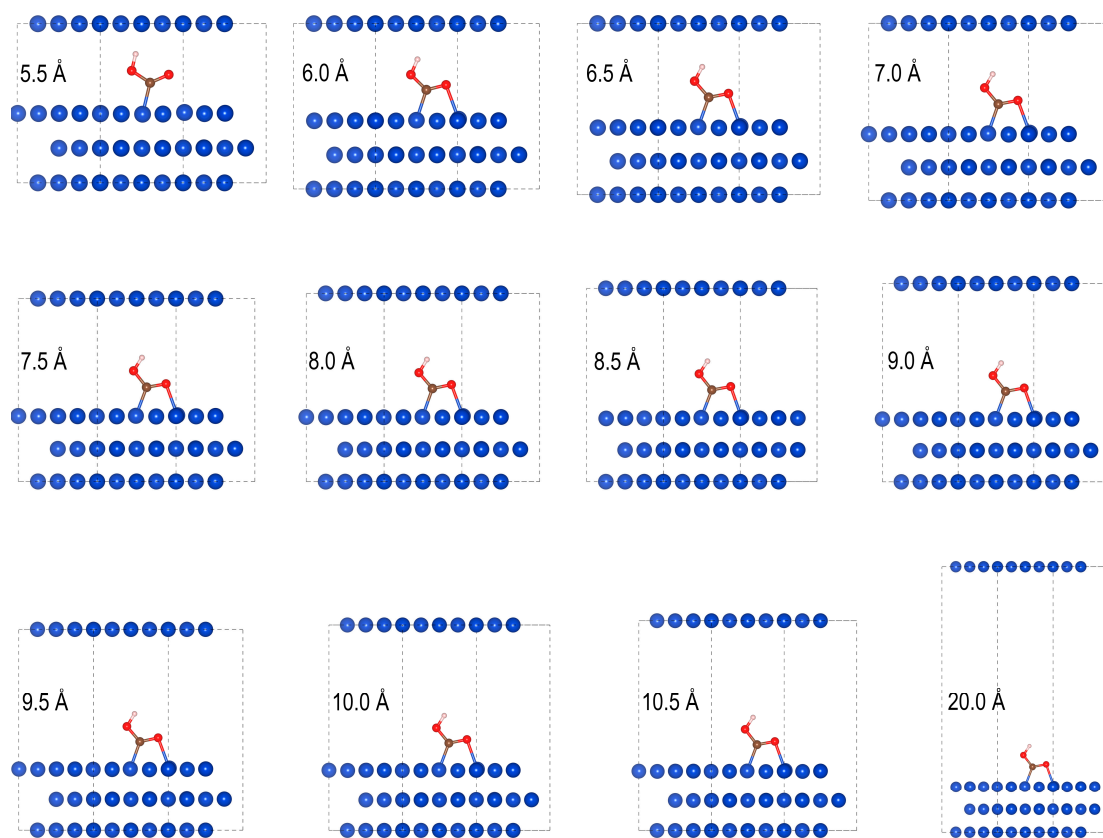


Figure S7. Adsorption structures of $\ast\text{COOH}$ intermediates on Cu(111) for different values of d_{Cu} .

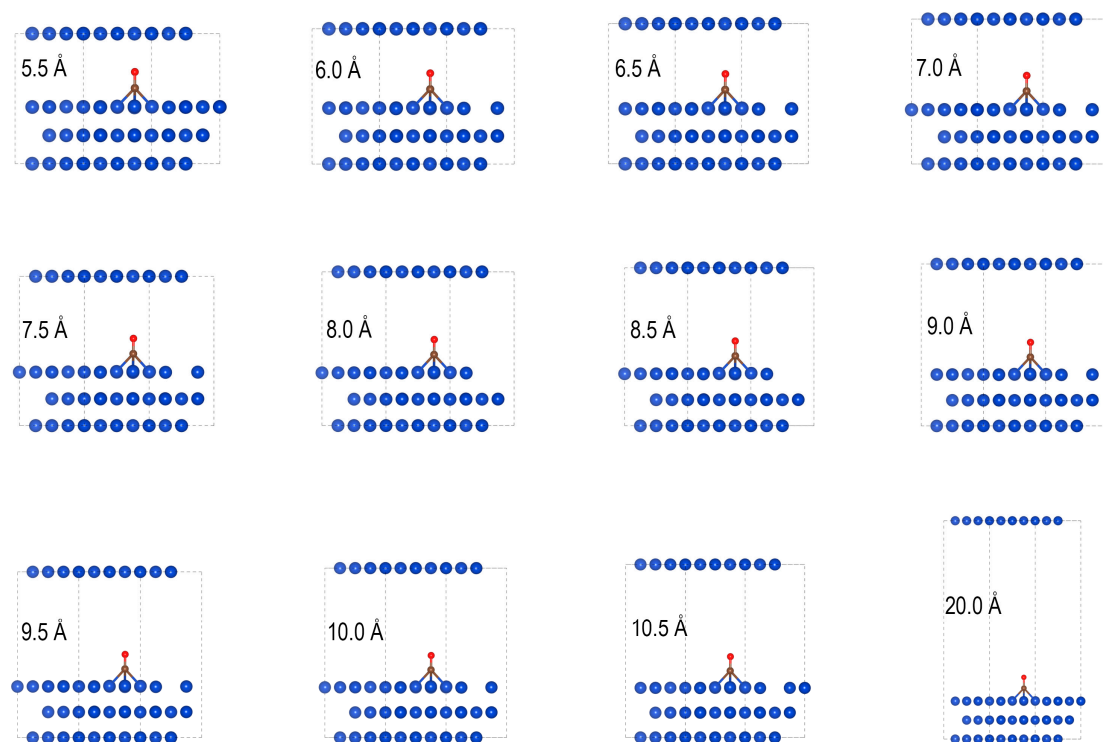


Figure S8. Adsorption structures of $^*\text{CO}$ intermediates on Cu(111) for different values of d_{Cu} .

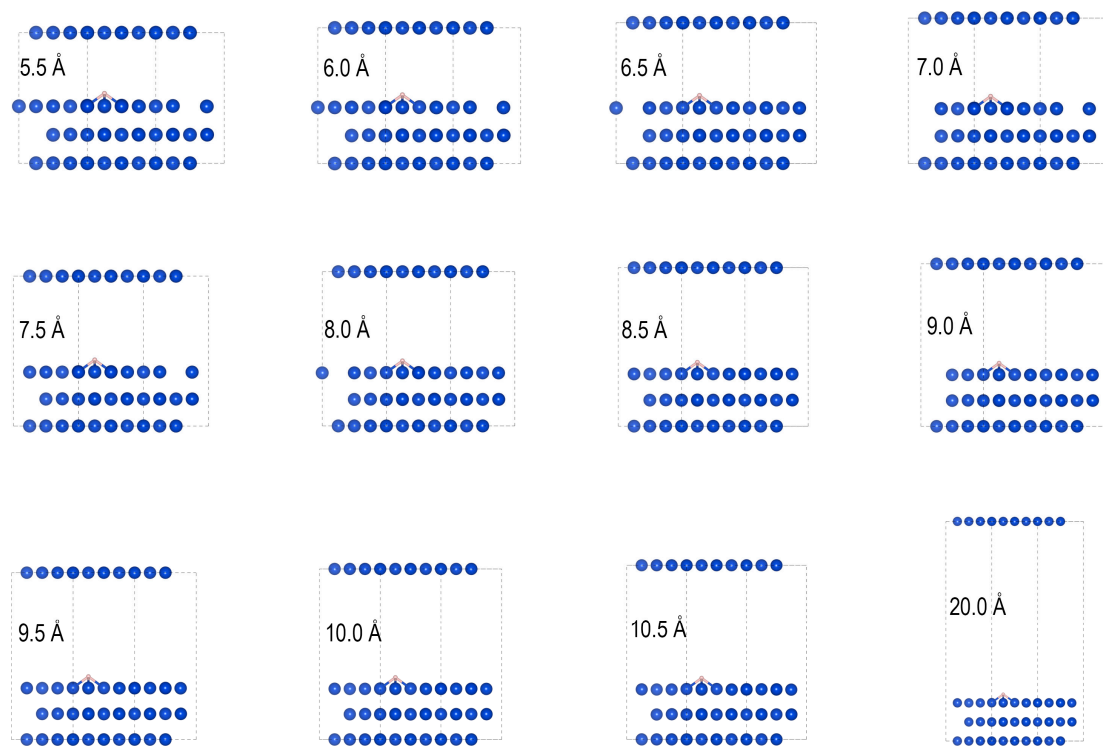


Figure S9. Adsorption structures of $^*\text{H}$ intermediates on Cu(111) for different values of d_{Cu} .

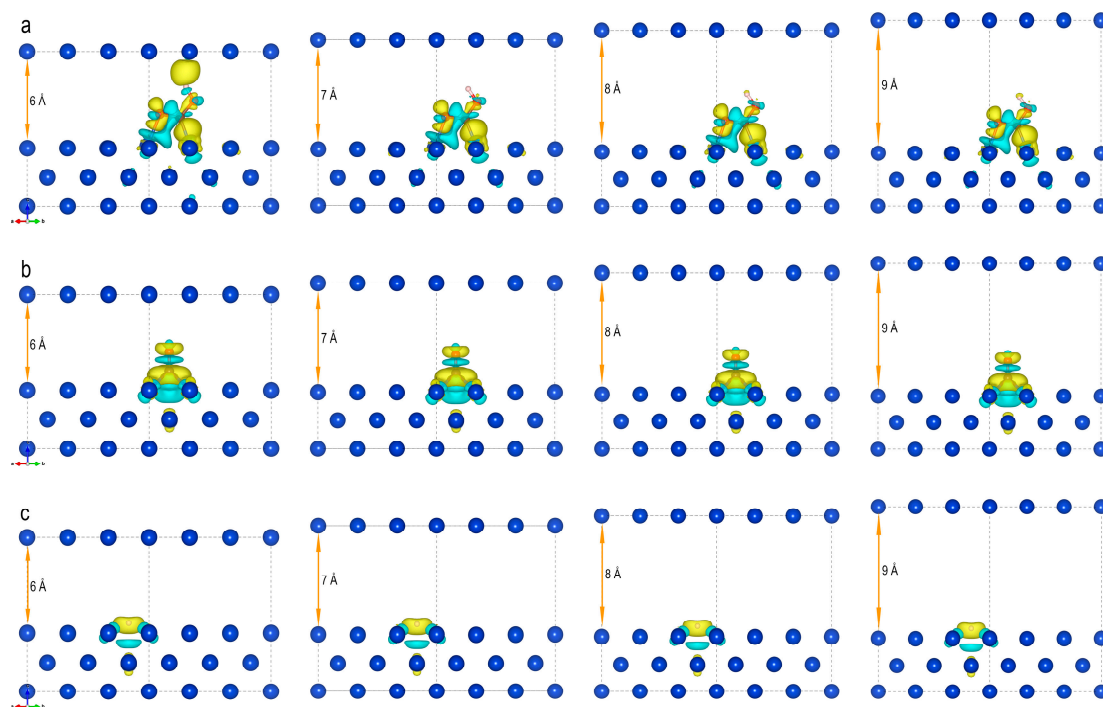


Figure S10. The charge density difference of (a) *COOH, (b) *CO, and (c) *H on c-sCu(100) with d_{Cu} varying from 6 Å to 9 Å, respectively. The isosurface level was set to $0.002 \text{ e}/\text{\AA}^3$. The yellow and blue parts of charge density indicate the electron accumulation and depletion, respectively.

Table S1. The most stable adsorption sites for *COOH, *CO, and *H on different surfaces of Cu.

Surface	*COOH	*CO	*H
Cu(100)	Bridge site	Hollow site	Hollow site
Cu(110)	Bridge site	Bridge site	Bridge site
Cu(111)	Bridge site	fcc site	fcc site

Table S2. Bader charge analysis of CO₂RR and HER intermediates.

Species	20 Å	6 Å
*COOH	0.44	0.46
*CO	0.48	0.51
*H	0.25	0.23

Table S3. Adsorption free energies of all CO₂RR and HER intermediates in Cu(100).

d_{Cu}	*COOH	*CO	*H
5.5	0.219568226	-0.235299729	0.04463713
6	0.178830986	-0.196498039	0.05001646
6.5	0.244392366	-0.147140179	0.04467251
7	0.321304516	-0.128517009	0.03818031
7.5	0.378437326	-0.122444299	0.03742673
8	0.395838456	-0.140497059	0.02231646
8.5	0.442982536	-0.107769379	0.02655278
9	0.450500736	-0.113868639	0.02396672
9.5	0.453928216	-0.120706899	0.02462285
10	0.474696486	-0.105639269	0.02447666
10.5	0.486239666	-0.104846599	0.02608613
11	0.479608636	-0.109497559	0.02751974
20	0.504958636	-0.085423309	0.02968354

Table S4. Adsorption free energies of all CO₂RR and HER intermediates in Cu(110).

d_{Cu}	*COOH	*CO	*H
5.5	0.200298066	-0.057627669	0.21886791
6	0.204983966	-0.088607339	0.21047823
6.5	0.223107756	-0.107979149	0.1890975
7	0.289301476	-0.088855349	0.19414949
7.5	0.319743616	-0.090624739	0.18999645
8	0.334161186	-0.086777629	0.18836295
8.5	0.356074026	-0.081746409	0.18916451
9	0.363112766	-0.078612389	0.18778843
9.5	0.363960306	-0.080303909	0.1872374
10	0.371557206	-0.072520109	0.18754675
10.5	0.373794956	-0.074110419	0.18687802
11	0.379850886	-0.063793299	0.18386066
20	0.383239256	-0.065652929	0.18773999

Table S5. Adsorption free energies of all CO₂RR and HER intermediates in Cu(111).

d_{Cu}	*COOH	*CO	*H
5.5	0.284541906	-0.283482739	-0.04104145
6	0.283305526	-0.275354709	-0.06191839
6.5	0.350782856	-0.272161839	-0.07373933
7	0.391737086	-0.297178639	-0.08455302
7.5	0.488314776	-0.263628149	-0.07541056
8	0.544152306	-0.230343609	-0.06332255
8.5	0.565418806	-0.234032249	-0.06048139
9	0.573612216	-0.238712279	-0.06290716
9.5	0.602280486	-0.211509029	-0.05877589
10	0.596731496	-0.223969219	-0.05985992
10.5	0.568126946	-0.258313279	-0.06430195
11	0.612007196	-0.218356759	-0.05773118
20	0.620363936	-0.216466259	-0.05913793

Table S6. The optimized geometries of *COOH in Cu(100) with $d_{\text{Cu}} = 6 \text{ \AA}$.

*COOH in Cu(100)

10.693899999999993	0.0000000000000000	0.0000000000000000
0.0000000000000000	10.693899999999993	0.0000000000000000
0.0000000000000000	0.0000000000000000	9.5646000000000004

H	C	O	Cu
1	1	2	54

Selective dynamics

Direct

0.3265947979082738	0.6302599415217657	0.7725515560259489
0.3625885969834073	0.6160137346334207	0.5736042002112908
0.4476931973211907	0.5376203158939791	0.5961390326888716
0.2971922194106772	0.6648525578368006	0.6788425624197849
0.6666700000000034	0.6666700000000034	0.0000000000000000
-0.0009713356579819	0.0008701211697297	0.3770966443160626
0.1666700000000034	0.1666700000000034	0.0000000000000000
0.5000000000000000	0.1666700000000034	0.0000000000000000
0.0000000000000000	0.0000000000000000	0.0000000000000000
0.3309074207695495	0.3295019958611649	0.3737366079878264
0.3328119803977817	0.0005470361034068	0.3744482705965750
0.1664704530830273	0.3337508779740046	0.1881124118948775
0.5000000000000000	0.5000000000000000	0.0000000000000000
0.1651768744209526	0.4991514643520710	0.3761196401507790
0.3333299999999966	0.3333299999999966	0.0000000000000000
0.5002034177172975	0.0001807765957524	0.1879139916011021
0.6666700000000034	0.0000000000000000	0.0000000000000000
0.4990149735360970	0.6650941615091718	0.1910795985369021
0.3333299999999966	0.6666700000000034	0.0000000000000000
0.1677482237877538	0.6665959058197178	0.1881744340914453
-0.0002201283669446	0.8334174951372822	0.1874265049076052
0.8334869151866044	0.9998164863133003	0.1876102397177870
0.0000000000000000	0.3333299999999966	0.0000000000000000
0.9991406378965495	0.6670912206885218	0.3743740950701566
0.1666700000000034	0.8333299999999966	0.0000000000000000
0.6697242459969019	0.6692037869313939	0.3742026028905769
0.8333299999999966	0.8333299999999966	0.0000000000000000
0.8341661647178221	0.8347937553257354	0.3765076681148706
0.6663489958540105	0.8334791530754133	0.1878909682444470
0.8332200746174506	0.4998008263268224	0.3756410545421880
0.6647979741227726	0.4996940940281822	0.1908108762227964
0.6706857703196313	0.3291888251673771	0.3767354610908627
0.8333299999999966	0.5000000000000000	0.0000000000000000
0.5004087183109986	0.3349588392086764	0.1906250005247612

0.6666700000000034	0.3333299999999966	0.0000000000000000
0.8332884822203511	0.6663882985662086	0.1868114341934988
0.8338167571582925	0.3330725222303829	0.1878124339369005
0.0000000000000000	0.6666700000000034	0.0000000000000000
0.3333299999999966	0.0000000000000000	0.0000000000000000
0.1665831554489762	0.0002392313213396	0.1874195570782833
0.8333299999999966	0.1666700000000034	0.0000000000000000
0.6678046316280855	0.0003876290713753	0.3774335285794788
0.6670925791765161	0.1661239906438131	0.1878371412717254
0.8351776073326255	0.1650097972162622	0.3774585006584050
0.3335447825533725	0.1663912751850412	0.1867874486481852
0.5003383077432120	0.1663843073081088	0.3755993857045469
0.0001339551410472	0.1665070095459097	0.1875693647586553
0.1649768150509972	0.1657540379813355	0.3765296061932628
0.3347693642167779	0.5006538781986412	0.1905520570765513
0.3290339907098663	0.6702773229611402	0.3834440047353658
0.5000000000000000	0.8333299999999966	0.0000000000000000
0.5008506303845602	0.8351161584354732	0.3759802590347169
-0.0001651072342122	0.4998420774442261	0.1881672300916589
0.9996256155260692	0.3324937136629152	0.3775972284919735
0.1666700000000034	0.5000000000000000	0.0000000000000000
0.5064150532882600	0.4940223198528181	0.3900675439497365
0.3333896338748353	0.8317581099115993	0.1888118845325568
0.1636105048281142	0.8362743452877125	0.3759521589865202

Table S7. The optimized geometries of *COOH in Cu(110) with $d_{\text{Cu}} = 6 \text{ \AA}$.

*COOH in Cu(110)

10.693899999999993	0.0000000000000000	0.0000000000000000
0.0000000000000000	10.0823000000000000	0.0000000000000000
0.0000000000000000	0.0000000000000000	11.0411000000000001

H	C	O	Cu
1	1	2	60

Selective dynamics

Direct

0.6317676591527285	0.5457858513224286	0.7958018949117711
0.6487191843689969	0.5715582505405326	0.6241476349178423
0.6413324577169029	0.4905265909230503	0.7204375597080696
0.6445447059321187	0.6948304986989078	0.6412891358876921
0.3333299999999966	0.7500000000000000	0.0000000000000000
0.0000708968174786	0.7496017275907204	0.4542350452937640
0.1662093399008031	0.3746020983743891	0.3455649205782589
0.4997952703537499	0.3748720751769189	0.1075549066680159
0.1664502459783166	0.1246073116504268	0.3457229650728080
0.1663209487923299	0.1244988750762281	0.1082093960793905
0.9995575302313717	0.9994870533827281	0.4553603361434794
0.1665912478055071	0.3750072793531664	0.1079230176578574
0.0000000000000000	0.0000000000000000	0.0000000000000000
0.0003562247137880	0.2497538956386413	0.2269366562170448
0.0000000000000000	0.2500000000000000	0.0000000000000000
0.9997155026222961	0.9996691008941588	0.2277198575344017
0.3329053852675876	0.4997903189708496	0.2268879619418473
0.3333299999999966	0.5000000000000000	0.0000000000000000
0.3322044174834552	0.4996847264123661	0.4540443622759792
0.3330339683042375	0.7503812987569041	0.2271630430466155
0.6660949735070376	0.4980941107032558	0.4615712812486846
0.3333299999999966	0.2500000000000000	0.0000000000000000
0.5000631215743282	0.8750001045741430	0.3452272111558786
0.5006669520212830	0.6252109606283637	0.1074955667432030
0.4986665616251343	0.6251567534768726	0.3437317421362451
0.5003685109414849	0.8748636020872529	0.1079275780931893
0.6662521471753252	0.7556491249621242	0.4630284282772555
0.0000000000000000	0.7500000000000000	0.0000000000000000
0.9999380222152860	0.4998432383916471	0.2271385540890196
0.1666641300178224	0.6251491233951219	0.1080533920297842
0.3330504794049544	0.9998761366149753	0.2275043575383991
0.8330345556429148	0.6251993996255437	0.1079518605493639
0.8325555118799074	0.8746776061194078	0.3457718520917836
0.8334973176472750	0.6250388640631305	0.3448761625856981

0.1661478467221253	0.6246033122209843	0.3453331165961404
0.9998925158169732	0.7502155459732257	0.2272482782667669
0.9996805221261312	0.4994254968576374	0.4546603571216108
0.6661911893174709	0.2487425831133725	0.4541476193133269
0.0000000000000000	0.5000000000000000	0.0000000000000000
0.8328811181558264	0.8748658725724259	0.1080927779081095
0.6665291367652765	0.5001868344893594	0.2303165240777392
0.1663376605921524	0.8752315096239649	0.3457028444937477
0.1664917486899126	0.8752546479710913	0.1077684818543234
0.9996613576150403	0.2498339466221241	0.4545941263504071
0.4993462336956825	0.3747286873467668	0.3445210200294591
0.3325082315590527	0.2495892883877011	0.2268190933923213
0.3333299999999966	0.0000000000000000	0.0000000000000000
0.3321153260358636	0.7497887433868863	0.4538419872643754
0.3333185784943566	0.9996216479738002	0.4551162192736622
0.6667948981936728	0.7496230836358694	0.2321265999870699
0.6666700000000034	0.5000000000000000	0.0000000000000000
0.5000740997123253	0.1249616959630413	0.1078643329988183
0.4990624789124676	0.1253409158108360	0.3450017740842086
0.6664052153571082	0.2502958235468853	0.2276144253090170
0.6663527865178295	0.0026069203678201	0.4529673874036859
0.3330192018599084	0.2498634172283508	0.4545459996728781
0.6666700000000034	0.0000000000000000	0.0000000000000000
0.8330002165100555	0.1250287091827576	0.1082481587307946
0.8328672445734464	0.3751172021751303	0.3449446967827455
0.8335075532802682	0.3749804421287721	0.1079791164633460
0.8339596793917524	0.1253300916776047	0.3451209325524087
0.6666700000000034	0.7500000000000000	0.0000000000000000
0.6666700000000034	0.2500000000000000	0.0000000000000000
0.6665285593874319	0.0001056751623343	0.2271636080495500

Table S8. The optimized geometries of *COOH in Cu(111) with $d_{\text{Cu}} = 6 \text{ \AA}$.

*COOH in Cu(111)

10.0823000000000000	0.0000000000000000	0.0000000000000000
-5.0411500000000000	8.7315279300000004	0.0000000000000000
0.0000000000000000	0.0000000000000000	10.1160999999999994

H	C	Cu	O
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1	1	48	2
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Selective dynamics

Direct

0.5169484605020441	0.5200731941820476	0.7834125935595199
0.5652670460174861	0.5081619757117473	0.5994596601012324
0.0035284902002150	0.4997004471006650	0.4129872654960270
0.1674675515402370	0.8327706086982714	0.2056914148838668
0.3333299999999966	0.6666700000000034	0.0000000000000000
0.7521048226914245	0.0006919224652416	0.4134050763066375
0.9179392255100824	0.3333054227257820	0.2062375860984251
0.5833299999999966	0.1666700000000034	0.0000000000000000
0.7521832281418569	0.2481053455074964	0.4118026158654382
0.9174200868973786	0.0829280416745769	0.2067450143142936
0.1675501423609077	0.5834462067771582	0.2059196041568181
0.3333299999999966	0.9166700000000034	0.0000000000000000
0.5017654452153841	0.0003218498162022	0.4126413910319401
0.8333299999999966	0.4166700000000034	0.0000000000000000
0.8333299999999966	0.1666700000000034	0.0000000000000000
0.4999053365420383	0.2465540815248039	0.4104868648877134
0.5833299999999966	0.4166700000000034	0.0000000000000000
0.6669880682302597	0.8330156666995305	0.2056704549814835
0.6676624734942146	0.0837808794783164	0.2061404831188453
0.0833299999999966	0.1666700000000034	0.0000000000000000
0.4184148904059672	0.3347286599115858	0.2068189961545634
0.2516436992098170	-0.0001167492472488	0.4124829467794930
0.8333299999999966	0.6666700000000034	0.0000000000000000
0.0833299999999966	0.6666700000000034	0.0000000000000000
0.4177209687650819	0.8335921486872661	0.2059159370885269
0.4183224452250933	0.5827951532233225	0.2070911187778852
0.2522948108941474	0.7504401433555026	0.4120361178676319
0.0038421046345461	0.7517347369881727	0.4123375186612666
0.0833299999999966	0.9166700000000034	0.0000000000000000
0.5010812287410099	0.5008533968053053	0.4156887716685967
0.2493989824938052	0.4999284123802268	0.4120296918178851
0.1681726666885465	0.3334360932540943	0.2066652012894026
0.3333299999999966	0.1666700000000034	0.0000000000000000
0.3333299999999966	0.4166700000000034	0.0000000000000000

0.0017048160750188	0.0000529595233551	0.4126859696580385
0.0021262443464939	0.2494132075727117	0.4132090065955839
0.1678319098758080	0.0832180264802132	0.2060253541508379
0.6678427650888652	0.3353884886679256	0.2085842282826175
0.0833299999999966	0.4166700000000034	0.0000000000000000
0.2504587288214601	0.2487266863135764	0.4116231409424104
0.4174493070262602	0.0834258018157271	0.2057790800633647
0.8333299999999966	0.9166700000000034	0.0000000000000000
0.6682823381435951	0.5834422739505037	0.2082160970386515
0.5021526159064547	0.7522271092153252	0.4111959406569674
0.5833300000000037	0.9166700000000034	0.0000000000000000
0.9156489276953771	0.5822187051013485	0.2097768514398594
0.7533299497367371	0.7536608419532327	0.4098961615699238
0.5833300000000037	0.6666700000000034	0.0000000000000000
0.9179664232788535	0.8329931592550371	0.2060383642053552
0.7578003395086208	0.4995656177246842	0.4220648338989311
0.4764847029425950	0.5195530938120934	0.6914269288258568
0.6813557520556156	0.5003497732783333	0.6295608555613244