Electronic Supplementary Material (ESI) for ChemComm. This journal is © The Royal Society of Chemistry 2021

Electronic Supplementary Information

Potential-dependent C-C coupling mechanism and activity of C₂ formation in the electrocatalytic reduction of CO₂ on defective Cu(100) surfaces

Hong Liu and Bo Yang*

School of Physical Science and Technology, ShanghaiTech University, Shanghai

201210, China

Email: yangbo1@shanghaitech.edu.cn

Computational Methods

Spin-polarized density functional theory calculations were performed employing the Vienna Ab initio Simulation Package (VASP) code¹ with projector augmented wave (PAW) method.²⁻⁵ All the calculations were based on the generalized gradient approximation (GGA) with revised Perdew-Burke-Ernzerhof (RPBE) exchangecorrelation functional.^{6, 7} The plane wave cut-off energy was 500 eV and the convergence criteria were 0.05 eV/Å for force and 1×10^{-4} eV for energy. The transition states were located with the constrained minimization method.⁸⁻¹⁰

Four-layer slab with 4×4 supercells were used for calculations based on the original Cu(100) surface structure, which is named as Cu(100)_{ori}. Through removing one row of surface Cu atoms from Cu(100)_{ori}, a new defect Cu(100) structure could be constructed, namely Cu(100)_{one}. Similarly, the Cu(100)_{two} slab was constructed through further removing one row of surface Cu atoms from Cu(100)_{one}, and the Cu(100)_{three} slab was constructed through removing one column of surface Cu atoms from Cu(100)_{two}, and the Cu(100)_{four} slab was constructed though further removing one column of surface Cu atoms from Cu(100)_{three}. The configurations of all surfaces are shown in Fig. S1. The Cu atoms of bottom two layers were fixed during optimizations and the vacuum region of higher than 12 Å was employed in all models. The Monkhorst–Pack mesh k-point grids were $2 \times 2 \times 1$ for all slabs.

In order to include the solvent effect, we used the VASPsol method for an implicit model with the relative permittivity set as 80^{11} The free energy change of the elementary steps involving electrochemical proton-electron transfer was obtained according to the computational hydrogen electrode (CHE) model.¹² As suggested by Nørskov and co-workers, the field effect on CO adsorption was ignored here.¹³

The elementary steps considered here include:

$$CO^* + CO^* \rightarrow OCCO^* + *$$

 $CO^* + H^+ + e^- \rightarrow CHO^*$

~ ~

 $CO^* + CHO^* \rightarrow OCCHO^* + *$

 $CO^* + H^+ + e^- \rightarrow COH^*$

 $CO^* + COH^* \rightarrow OCCOH^* + *$

	Potential/V _{RHE}	OCCO	ОССНО	ОССОН
Cu(100) _{ori}	0	0.91	1.53	1.73
	-0.79	0.91	0.73	0.94
	-0.89	0.91	0.73	0.84
	-1.2	0.91	0.73	0.84
Cu(100) _{one}	0	0.74	1.35	1.80
	-0.64	0.74	0.71	1.16
	-0.95	0.74	0.71	0.85
	-1.2	0.74	0.71	0.85
Cu(100) _{two}	0	0.64	1.37	1.80
	-0.66	0.64	0.71	1.14
	-0.90	0.64	0.71	0.90
	-1.2	0.64	0.71	0.90
Cu(100) _{three}	0	0.71	1.40	1.82
	-0.71	0.71	0.69	1.11
	-0.99	0.71	0.69	0.84
	-1.2	0.71	0.69	0.84
Cu(100) _{four}	0	0.84	1.40	1.94
	-0.69	0.84	0.70	1.25
	-0.91	0.84	0.70	1.03
	-1.2	0.84	0.70	1.03

Table S1. Values of effective free energy barriers (in eV) determined at different

 potentials applied. These values are also included in Fig. 3 in the main text.

If we take a look at the charge of CO over different surfaces considered in this work (Table S2), the difference between the values of the same adsorption configuration over different surfaces is rather small. This strongly suggests that, even the possible valency change between IS and TS is considered, the trend obtained in the current work would be unchanged.

	Cu(100) _{ori}	Cu(100) _{one}	Cu(100) _{two}	Cu(100) _{three}	Cu(100) _{four}
hollow	0.64	0.57	0.56	0.58	0.57
bridge	0.34	0.32	0.32	0.32	0.33
top	0.17	0.17	0.15	0.13	0.13

Table S2. Net charge of adsorbed CO at different surface sites over Cu(100) surfaces.



Fig. S1 Side and top view of our Cu(100) models. Cu(100)_{ori} is the original Cu(100) slab, and others are defect and under-coordinated slabs. Colour code: orange, bulk Cu; yellow, surface Cu.



Fig. S2 Top view of optimal configurations of the transition states of three different C-C coupling processes in different slabs. $Cu(100)_{ori}$ is the original Cu(100) slab, and others are defect and under-coordinated slabs. Colour code: orange, bulk Cu; yellow, surface Cu; red, oxygen; grey, carbon; white, hydrogen.



Fig. S3 Top view of configurations of the transition states of three different C-C coupling processes at the interface sites in different slabs. The values (in eV) shown here are the transition state energies with respect to the corresponding most stable ones shown in Fig. S2.



Fig. S4 Top view of optimal adsorption configurations of CO on different surfaces.

References

- 1. J. Hafner, J. Comput. Chem., 2008, 29, 2044.
- 2. P. E. Blöchl, *Phys. Rev. B*, 1994, **50**, 17953-17979.
- 3. G. Kresse and J. Furthmüller, *Phys. Rev. B*, 1996, **54**, 11169-11186.
- 4. G. Kresse and J. Furthmüller, *Comput. Mater. Sci.*, 1996, 6, 15-50.
- 5. G. Kresse and D. Joubert, *Phys. Rev. B*, 1999, **59**, 1758-1775.
- 6. B. Hammer, L. B. Hansen and J. K Nørskov, *Improved adsorption energetics* within density-functional theory using revised Perdew-Burke-Ernzerhof functionals, 1999.
- J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh and C. Fiolhais, *Phys. Rev. B*, 1992, 46, 6671-6687.
- A. Alavi, P. Hu, T. Deutsch, P. L. Silvestrelli and J. Hutter, *Phys. Rev. Lett.*, 1998, 80, 3650-3653.
- 9. Z.-P. Liu and P. Hu, J. Am. Chem. Soc., 2003, 125, 1958-1967.
- A. Michaelides, Z. P. Liu, C. J. Zhang, A. Alavi, D. A. King and P. Hu, J. Am. Chem. Soc., 2003, 125, 3704-3705.
- K. Mathew, R. Sundararaman, K. Letchworth-Weaver, T. A. Arias and R. G. Hennig, J. Chem. Phys., 2014, 140, 084106.
- J. K. Nørskov, J. Rossmeisl, A. Logadottir, L. Lindqvist, J. R. Kitchin, T. Bligaard and H. Jónsson, J. Phys. Chem. B, 2004, 108, 17886-17892.
- P. Liu, A. Logadottir and J. K. Nørskov, *Electrochim. Acta*, 2003, 48, 3731-3742.