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

Supporting Information

Mechanistic Study on Cu-Catalyzed CO_2 Electroreduction into CH_4 at the Simulated Low Overpotentials Based on an Improved Electrochemical Model

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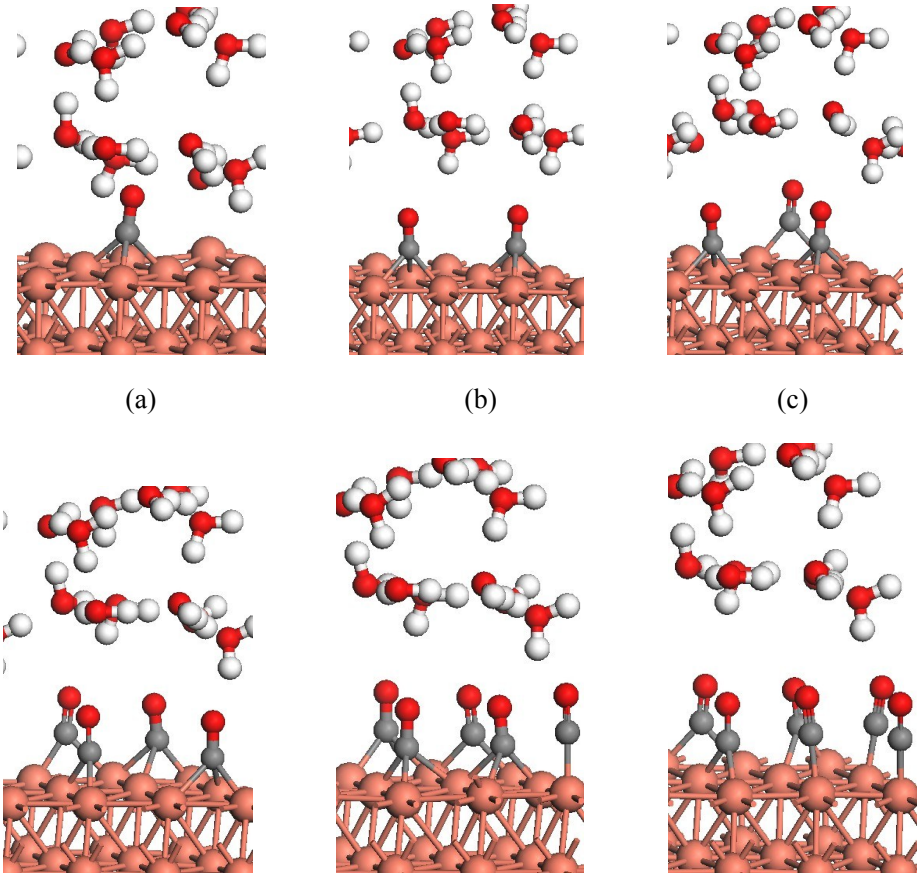

(a) (b) (c)

(d) (e) (f)

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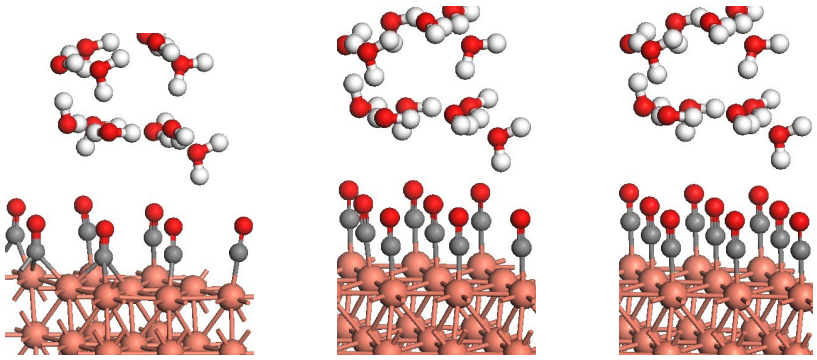


(g) (h) (i)

Figure S1. Various possible surface CO adsorption configurations on Cu(111) at different CO coverage: (a) 1/9 ML; (b) 2/9 ML; (c) 1/3 ML; (d) 4/9 ML; (e) 5/9 ML; (f) 2/3 ML; (g) 7/9 ML; (h) 8/9 ML; (i) 1ML.

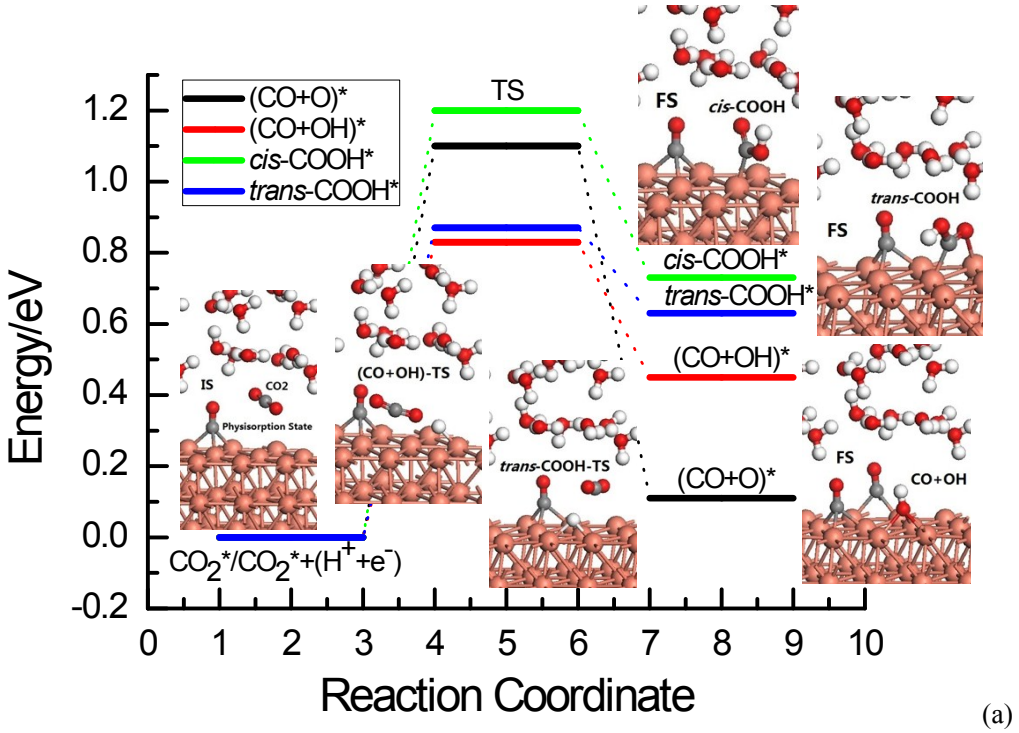
Table S1. Activation Barriers (ΔE_{act}, eV) and Reaction Free Energies (ΔG_{reac}, eV) for the Possible Elementary Reaction Steps for CO_2 Electroreduction on Cu(111) in Aqueous Phase at the Present Simulated low Overpotential

Reactions	ΔE_{act}, eV[a]	ΔG_{reac}, eV
$CO_2^* \rightarrow (CO + O)^*$	1.10	0.99
$CO_2^* + (H^+ + e^-) \rightarrow (CO + OH)^*$	0.83	0.45
$CO_2^* + (H^+ + e^-) \rightarrow COOH^*$	0.87	0.63
$COOH^* + (H^+ + e^-) \rightarrow CO^* + H_2O$	0.20	-1.00
$CO^* + (H^+ + e^-) \rightarrow CHO^*$	0.85	0.65
$CO^* + (H^+ + e^-) \rightarrow COH^*$	1.39	1.09
$CHO^* \rightarrow (CH + O)^*$	1.67	1.42
$CHO^* + (H^+ + e^-) \rightarrow CH_2O^*$	0.45	-0.27
$CHO^* + (H^+ + e^-) \rightarrow CHOH^*$	0.43	0.07
$CH_2O^* \rightarrow (CH_2 + O)^*$	1.36	0.83
$CH_2O^* + (H^+ + e^-) \rightarrow CH_2OH^*$	0.32	-0.22
$CH_2O^* + (H^+ + e^-) \rightarrow CH_3O^*$	0.23	-0.98
$CHOH^* \rightarrow (CH + OH)^*$	0.73	0.31
$CHOH^* + (H^+ + e^-) \rightarrow CH_2OH^*$	0.38	-0.55
$CHOH^* + (H^+ + e^-) \rightarrow CH^* + H_2O$	0.19	0.09

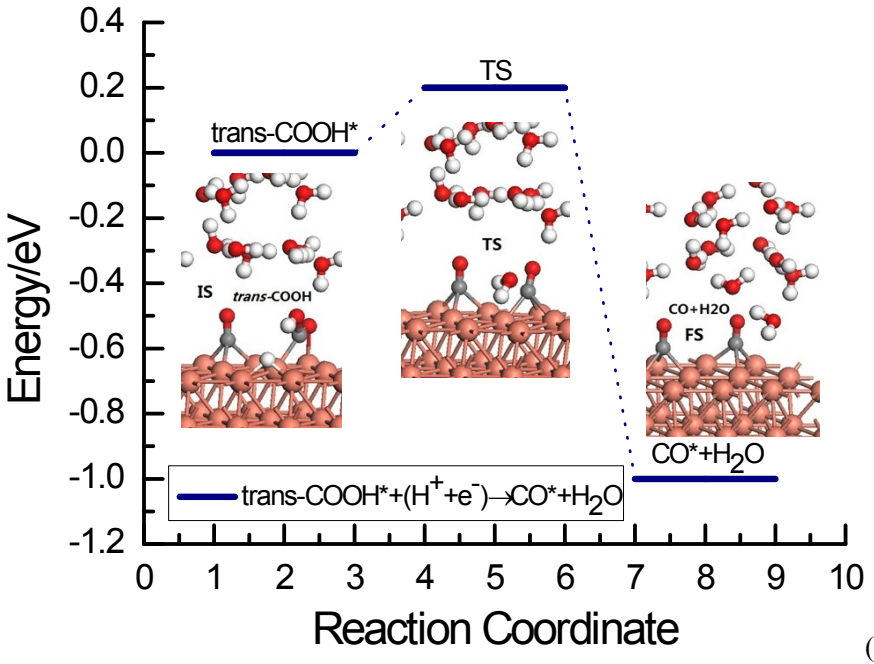
$CH_2OH^* \rightarrow (CH_2 + OH)^*$	1.02	0.23
$CH_2OH^* + (H^+ + e^-) \rightarrow CH_2^* + H_2O$	0.07	-0.34
$CH_2OH^* + (H^+ + e^-) \rightarrow CH_3OH^*$	0.36	-0.94
$CH_3O^* \rightarrow (CH_3 + O)^*$	2.29	0.74
$CH_3O^* + (H^+ + e^-) \rightarrow CH_3OH^*$	0.69	-0.33
$CH^* + (H^+ + e^-) \rightarrow CH_2^*$	0.33	-0.80
$CH_2^* + (H^+ + e^-) \rightarrow CH_3^*$	0.32	-1.04
$CH_3^* + (H^+ + e^-) \rightarrow CH_4^*$	1.31	-0.88

The asterisk (*) indicates that the species is adsorbed on Cu(111).

[a]In the calculations, the entropies obtained from the literature of Nørskov and coworkers are considered for gaseous molecules,[1, 2] whereas the entropies of the adsorbed species are ignored. The DFT calculated zero point energies (*ZPE*) for all species are included in the activation barrier and reaction free energy calculations.



(a)



(b)

Figure S2. The MEP analysis of (a) the first elementary step of CO_2 electroreduction and (b) subsequent *trans*-COOH electroreduction into CO and H_2O on Cu(111) at the present simulated low overpotential (an asterisk * indicates adsorption to the Cu surface; IS represents Initial State, TS represents Transition State, FS represents Final State).

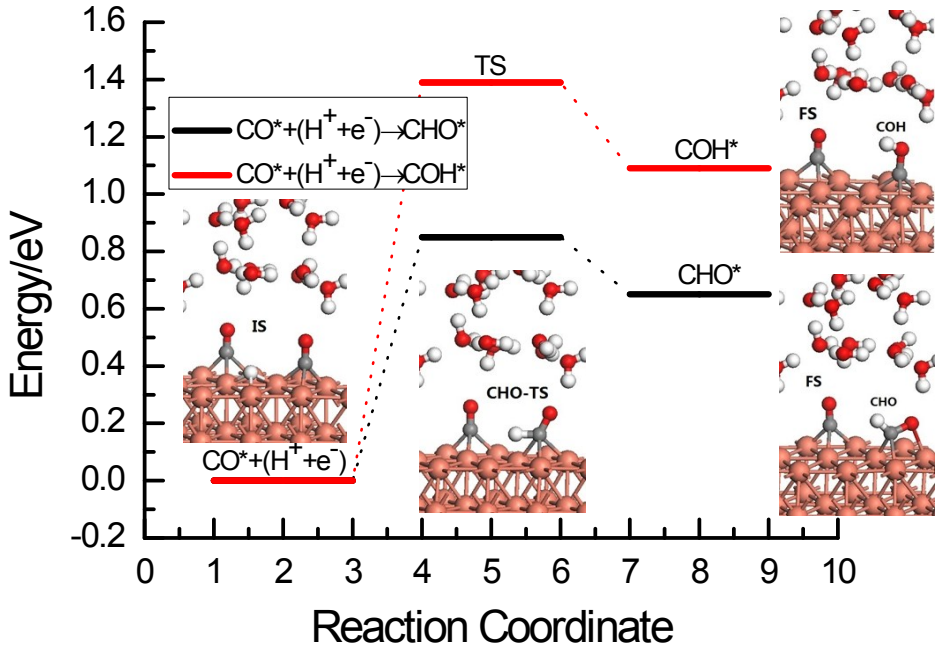


Figure S3. The MEP analysis of CO electroreduction into CHO and COH intermediates on Cu(111) at the present simulated low overpotential (an asterisk * indicates adsorption to the Cu surface; IS represents Initial State, TS represents Transition State, FS represents Final State).

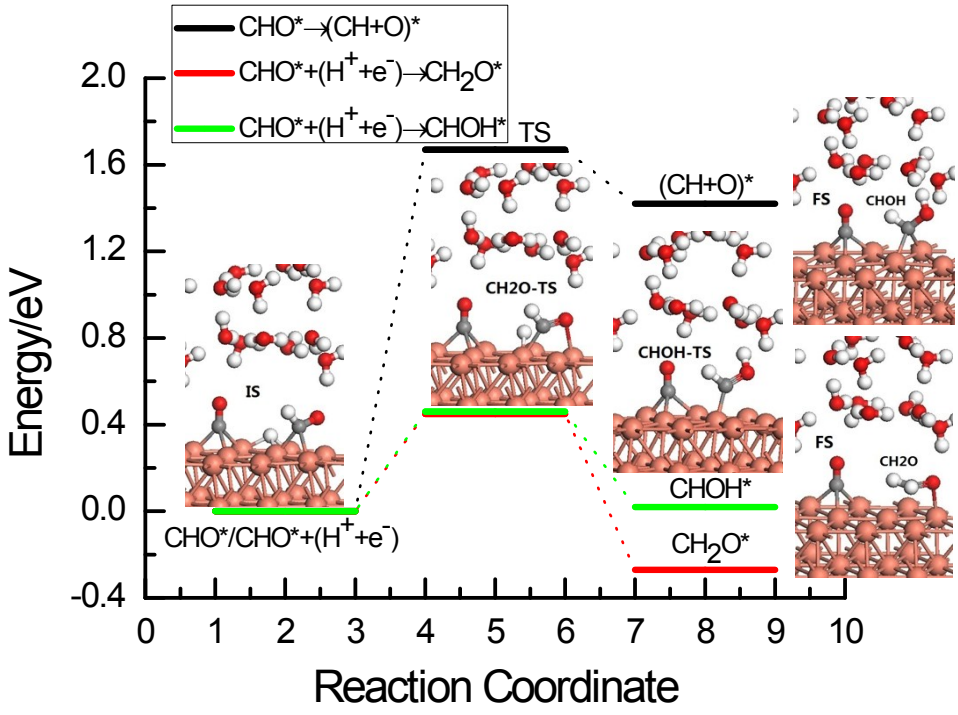


Figure S4. The MEP analysis of CHO electroreduction into CH_2O and CHOH intermediates on Cu(111) at the present simulated low overpotential (an asterisk * indicates adsorption to the Cu surface; IS represents Initial State, TS represents Transition State, FS represents Final State).

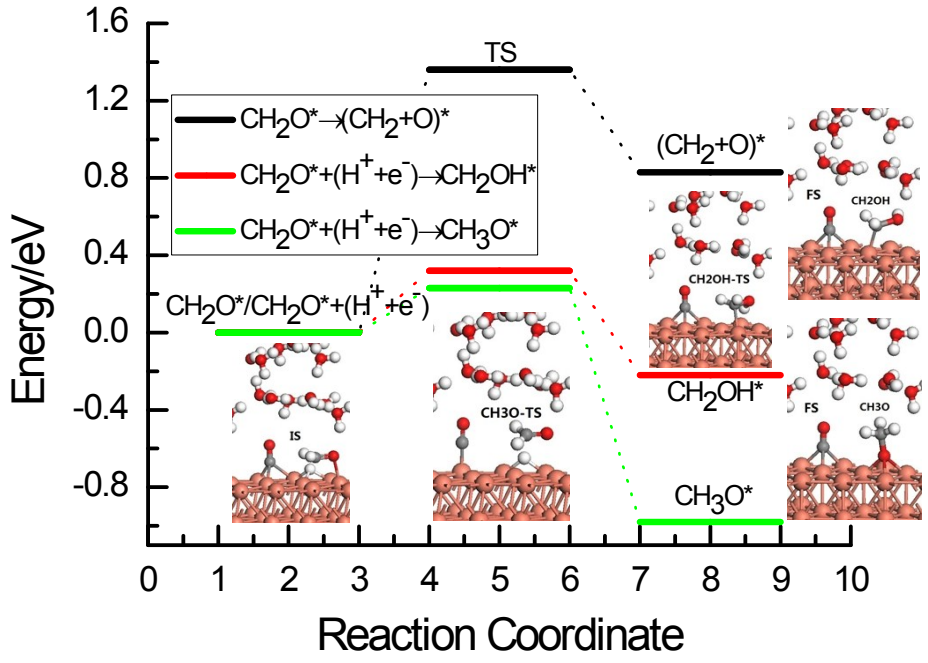


Figure S5. The MEP analysis of CH_2O electroreduction into CH_2OH and CH_3O intermediates on Cu(111) at the present simulated low overpotential (an asterisk * indicates adsorption to the Cu surface; IS represents Initial State, TS represents Transition State, FS represents Final State).

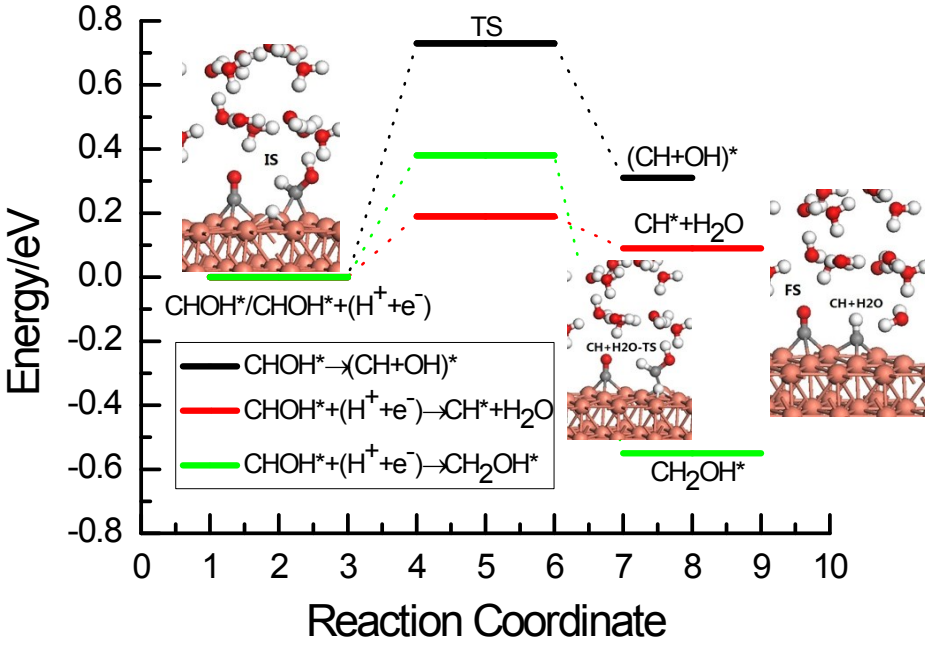


Figure S6. The MEP analysis of CHOH electroreduction into CH_2OH and CH intermediates on Cu(111) at the present simulated low overpotential (an asterisk * indicates adsorption to the Cu surface; IS represents Initial State, TS represents Transition State, FS represents Final State).

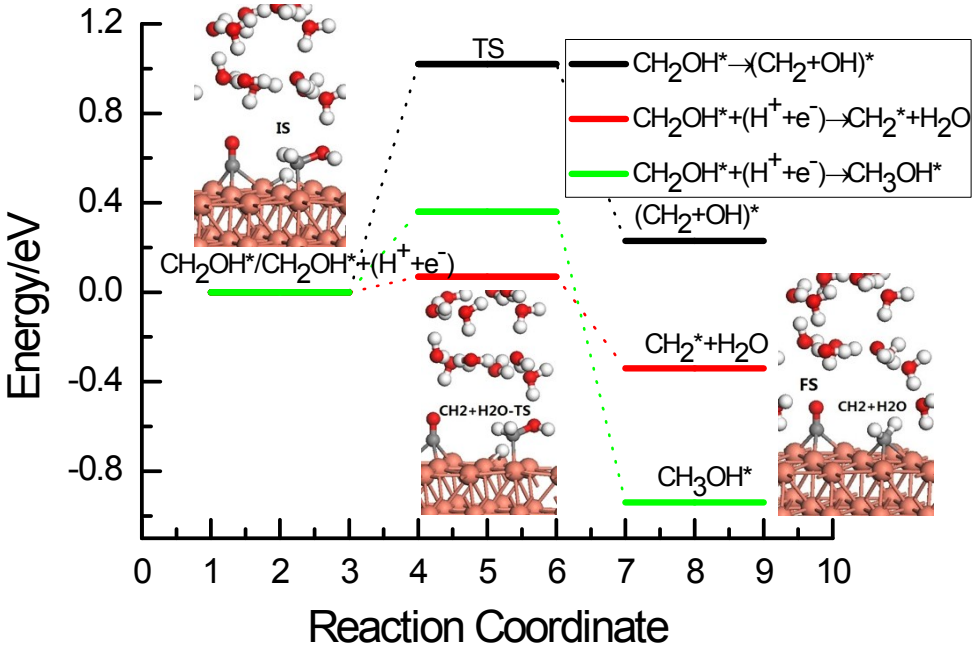


Figure S7. The MEP analysis of CH_2OH electroreduction into CH_2 intermediate and CH_3OH production on Cu(111) at the present simulated low overpotential (an asterisk * indicates adsorption to the Cu surface; IS represents Initial State, TS represents Transition State, FS represents Final State).

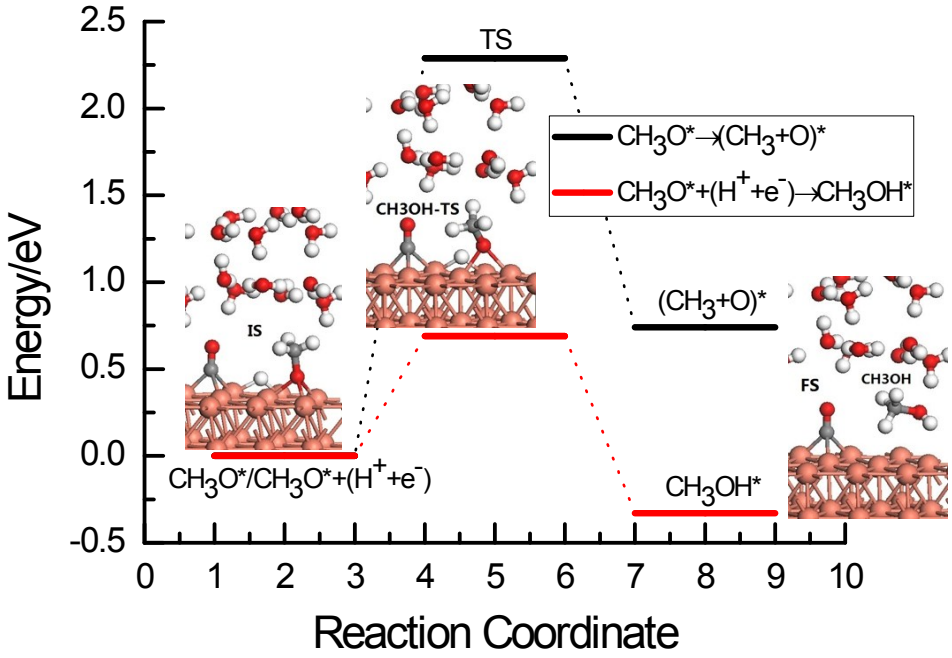


Figure S8. The MEP analysis of CH_3O electroreduction into CH_3OH production on Cu(111) at the present simulated low overpotential (an asterisk * indicates adsorption to the Cu surface; IS represents Initial State, TS represents Transition State, FS represents Final State).

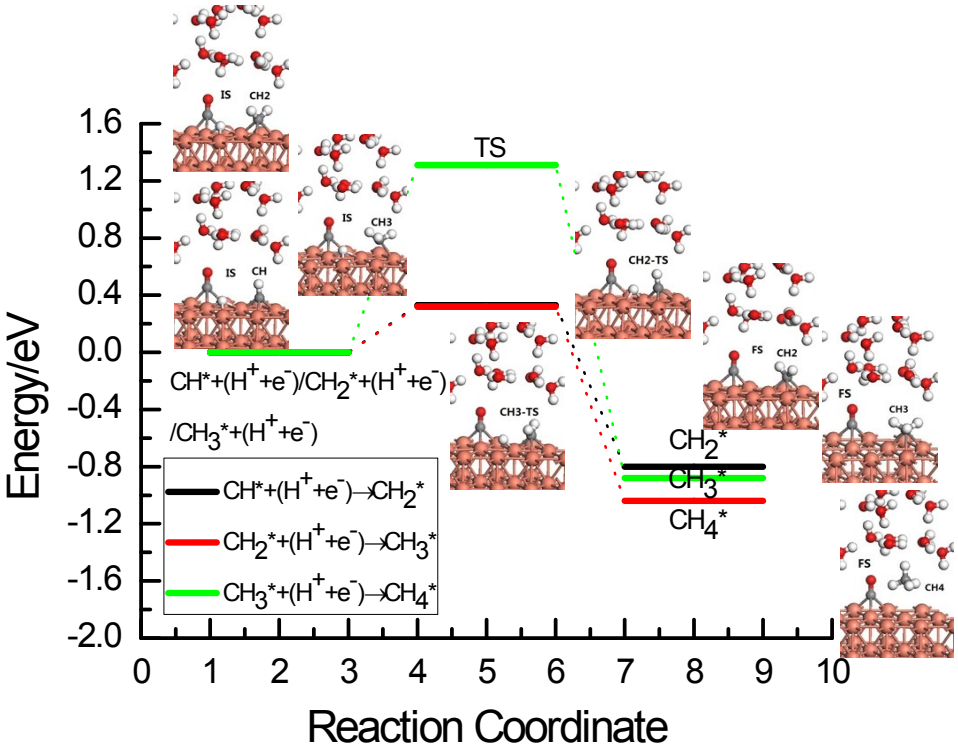


Figure S9. The MEP analysis of CH electroreduction into CH_2, CH_2 electroreduction into CH_3 and CH_3 electroreduction into CH_4 on Cu(111) at the present simulated low overpotential (an asterisk * indicates adsorption to the Cu surface; IS represents Initial State, TS represents Transition State, FS represents Final State).

References

1 A. A. Peterson, F. Abild-Pederson, F. Studt, J. Rossmeisl and J. K. Nørskov, How Copper Catalyzes the Electroduction of Carbon Dioxide into Hydrocarbon Fuels, *Energy Environ. Sci.*, 2010, **3**, 1311-1315.

2 W. J. Durand, A. A. Peterson, F. Studt, F. Abild-Pederson and J. K. Nørskov, Structure Effects on the Energetics of the Electrochemical Reduction of CO_2 by Copper Surfaces, *Surf. Sci.*, 2011, **605**, 1354-1359.