Supplementary Material

Mechanistic exploration of syngas conversion at the interface of graphene/Cu(111): Identifying the effect of promoted electron transfer on the product selectivity

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The details of the thermodynamic corrections

The shomate gas equation[1] was used for the free energy correction of gaseous species:

$$G(T) = H(T) - TS(T) \qquad (a)$$

$$H(T) = E_{\text{elec}} + E_{\text{ZPE}} + \int C_P \mathrm{d}T \qquad (b)$$

$$E_{ZPE} = \frac{1}{2}\sum h_i \omega_i \qquad (c)$$

$$C_P = A + B \times t + C \times t^2 + D \times t^3 - \frac{E}{t^2} \qquad (d)$$

$$S = A \times \ln(t) + B \times t + \frac{C \times t^2}{2} + \frac{D \times t^3}{3} - \frac{E}{2 \times t^2} + G \qquad (e)$$

where E_{elec} is the DFT energy, E_{ZPE} is the zero point energy, the parameter from A to G for different gas species can be obtained from the National Institute of Standards and Technology (NIST) website.

The harmonic approximation method was used to calculate the Gibbs free energy of adsorbates[2]:

$$G(T) = H(T) - TS(T) \qquad (f)$$

$$H(T) = E_{elec} + E_{ZPE} + \sum \frac{\varepsilon_i}{e^{\varepsilon_i/k_B} - 1} \qquad (g)$$

$$\varepsilon_i = h\omega_i \qquad (h)$$

where ε_i is harmonic energy, ω_i is angular frequency, k_B is Boltzmann constant, T is reaction temperature, and h is plank constant. The entropy of the surface intermediate was calculated by the following equation:

$$S(T) = k_B \sum_{i}^{harmDOF} \frac{\varepsilon_i}{k_B T (e^{\varepsilon_i/k_B} - 1)} - \ln(1 - e^{-\varepsilon_i/k_B} - 1) \qquad (i)$$

Fig. S1 Top and side view of the most stable adsorption configurations of possible species involved in syngas conversion at the graphene/Cu(111) interface.
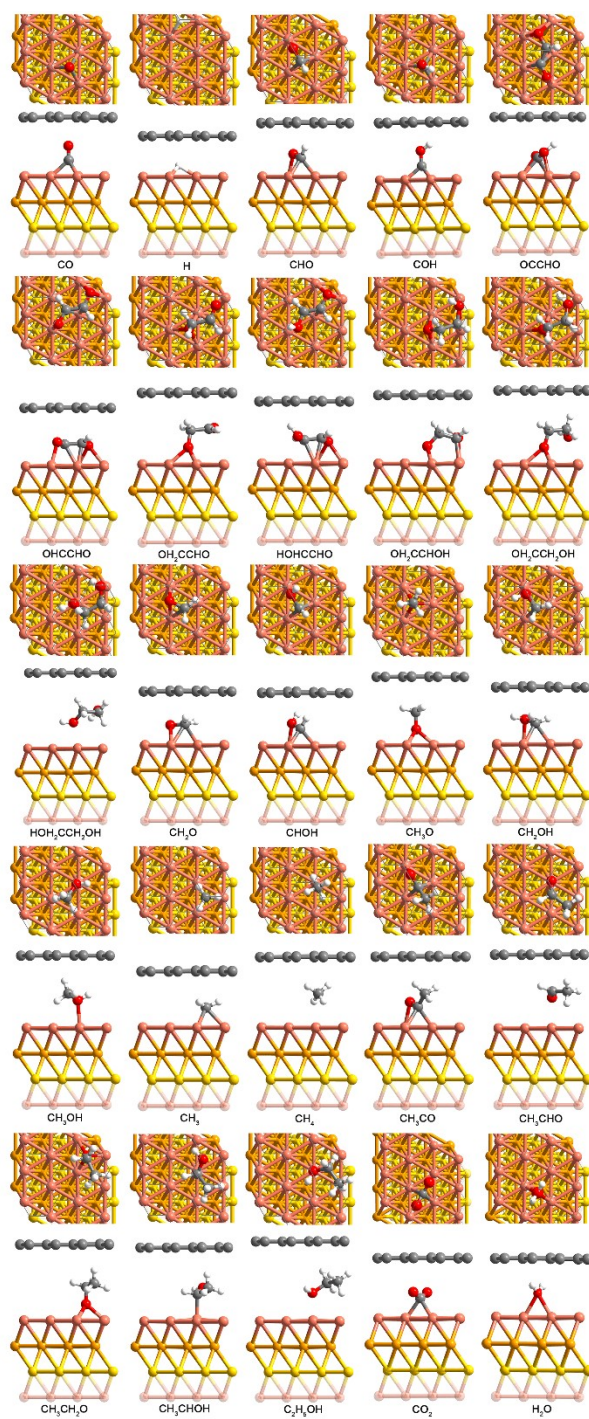
Table S1 Adsorption energy (eV) and key geometrical parameters (Å) of reactants, possible intermediates and products involved in syngas conversion at the graphene/Cu(111) interface.

	Species	E_{ads}/eV	Configuration	$d_{graphene/Cu}$/Å	Key parameters/Å
1	H	-3.68 (-2.43[ref50], -3.77[ref51])	fcc *via* H	3.334	Cu - H: 1.728
2	CO	-0.03 (-0.86 [ref50],-1.09[ref51])	hcp *via* C	4.802	Cu - C: 1.987
3	CHO	-1.24 (-1.18[ref50], -1.99[ref51])	fcc *via* bridge-CO	4.381	Cu - C: 2.023; Cu-O: 2.045
4	COH	-2.64 (-2.57[ref50], -3.77[ref51])	hcp *via* C	4.886	Cu - C: 1.916
5	OCCHO	-0.84	bridge-OCCO	4.945	Cu - C(HO): 2.163; Cu - C(O): 2.067 Cu - O(HO):2.132; Cu - O(O):2.071
6	OHCCHO	-0.14	bridge-OCCO	4.858	Cu - C$_I$:: 2.269; Cu - C$_{II}$: 2.118 Cu-O$_I$:2.029; Cu-O$_{II}$:2.121
7	OH$_2$CCHO	-1.56	hcp *via* O	5.758	Cu - O: 2.054
8	HOHCCHO	-0.80	bridge-CCO	5.009	Cu - O: 2.170; Cu – C : 2.218
9	OH$_2$CCHOH	-0.93	bridge-OCCO	5.473	Cu - C: 2.019; Cu - O: 2.044
10	OH$_2$CCH$_2$OH	-1.90	hcp *via* O	6.085	Cu - O: 2.028
11	HOH$_2$CCH$_2$OH	0.57	no bond	6.607	/
12	CH$_2$O	0.39 (-0.06[ref50], -0.35[ref51])	fcc *via* bridge-CO	4.395	Cu - C: 2.167; Cu - O: 2.113
13	CHOH	-1.27 (-1.85[ref50], -2.27[ref51])	fcc *via* bridge-CO	4.434	Cu - C: 1.961; Cu - O: 2.091
14	CH$_3$O	-1.90 (-2.45[ref50], -3.04[ref51])	fcc *via* O	5.644	Cu - O:2.010
15	CH$_2$OH	-1.07 (-0.84[ref50], -1.68[ref51])	fcc *via* bridge-CO	4.613	Cu - C: 2.132; Cu - O: 2.140
16	CH$_3$OH	0.73 (-0.28[ref50], -0.32[ref51])	top *via* O	5.925	Cu - O: 2.233
17	CH$_3$	-1.72 (-2.24[ref52])	fcc *via* C	4.491	Cu - C: 2.163
18	CH$_4$	1.13 (-0.05[ref52])	no bond	5.646	/
19	CH$_3$CO	-0.72 (-1.88[ref52])	fcc *via* bridge-CO	5.704	Cu - C: 2.132; Cu - O: 2.168
20	CH$_3$CHO	0.82 (-0.16[ref52])	no bond	6.004	/
21	CH$_3$CH$_2$O	-1.85	fcc *via* O	6.221	Cu - O: 2.018
22	CH$_3$CHOH	-0.49	top *via* C	6.106	Cu - C: 2.084
23	C$_2$H$_5$OH	0.93	no bond	6.559	/
24	CO$_2$	1.40 (-0.08[ref50])	bridge *via* C	4.869	Cu - C: 2.129
25	H$_2$O	0.42 (-0.21[ref50], -0.24[ref51])	bridge *via* O	4.618	/

Table S2 Possible elementary reactions involved in syngas conversion at the interface of graphene/Cu(111) with the imaginary frequency of the transition state are tabulated.

	Reaction	v/cm^{-1}
(R1)	$CO + H \rightarrow CHO$	$697i$
(R2)	$CO + H \rightarrow COH$	$1590i$
(R3)	$CHO + H(1) \rightarrow CH_2O$	$1285i$
(R4)	$CHO + H(2) \rightarrow CHOH$	$1266i$
(R5)	$CHO + H(1) \rightarrow CH_2 + O$	$348i$
(R6)	$CHO + CHO \rightarrow OHCCHO$	$45i$
(R7)	$CHO + CO \rightarrow OCCHO$	$357i$
(R8)	$CHO + CO \rightarrow CH + CO_2$	$372i$
(R9)	$OHCCHO + H \rightarrow OH_2CCHO$	$472i$
(R10)	$OHCCHO + H \rightarrow HOHCCHO$	$1187i$
(R11)	$OHCCHO \rightarrow OHCCH + O$	$207.7i$
(R12)	$OH_2CCHO + H \rightarrow OH_2CCHOH$	$1329i$
(R13)	$OH_2CCHO + H \rightarrow OH_2CCH_2O$	$78i$
(R14)	$OH_2CCHOH + H \rightarrow OH_2CCH_2OH$	$1223i$
(R15)	$OH_2CCH_2OH + H \rightarrow HOH_2CCH_2OH$	$1222i$
(R16)	$OH_2CCH_2OH \rightarrow H_2CCH_2OH + O$	$376.3i$
(R17)	$CH_2O + H \rightarrow CH_3O$	$390i$
(R18)	$CH_2O + H(2) \rightarrow CH_2OH$	$1196i$
(R19)	$CH_2O + H(1) \rightarrow CH_3 + O$	$837i$
(R20)	$CH_2O \rightarrow CH_2 + O$	$165i$
(R21)	$CH_2O + H(2) \rightarrow CH_2 + OH$	$1094i$
(R22)	$CH_3O + H \rightarrow CH_3 + OH$	$119i$
(R23)	$CH_3O + H \rightarrow CH_3OH$	$1159i$
(R24)	$CH_3O \rightarrow CH_3 + O$	$241i$
(R25)	$CH_3 + H \rightarrow CH_4$	$91i$
(R26)	$CH_3 + CHO \rightarrow CH_3CHO$	$442i$
(R27)	$CH_3 \rightarrow CH_2 + H$	$838i$
(R28)	$CH_3 + CO \rightarrow CH_3CO$	$517i$
(R29)	$CH_3 + CH_3 \rightarrow C_2H_6$	$521i$
(R30)	$CH_3CHO + H \rightarrow CH_3CHOH$	$1261i$
(R31)	$CH_3CHO + H \rightarrow CH_3CH_2O$	$1691i$
(R32)	$CH_3CHOH + H \rightarrow C_2H_5OH$	$350i$
(R33)	$CH_3CH_2O + H \rightarrow C_2H_5OH$	$1139i$
(R34)	$CO + O \rightarrow CO_2$	$369i$
(R35)	$OH + H \rightarrow H_2O$	$1345i$

Table S3 The comparison of activation barriers (E_a/eV) and reaction energies (ΔE/eV) of the key elementary reactions on the graphene/Cu(111), Cu(111), Cu(211) and Cu_1/graphene catalysts .

	reaction	graphene/Cu(111) (this work)		Cu_1/graphene (Ref.15)		Cu(111) (Ref.50)		Cu(111) (Ref.51, Ref.52)		Cu(211) (ref.58)	
		ΔE/eV	E_a/eV	ΔE/eV	E_a/eV	ΔE/eV	E_a/eV	ΔE/eV	E_a/eV	ΔE/eV	E_a/eV
R1	$CO+H \rightarrow CHO$	0.55	1.03	0.96	1.16	0.78	0.99	0.85	1.10	0.16	1.20
R2	$CO+H \rightarrow COH$	1.11	2.06	3.03	/	1.15	2.26	1.01	2.42	0.87	2.87
R3	$CHO+H \rightarrow CHOH$	0.33	0.89	-0.50	0.04	0.09	0.91	-0.04	0.92	0.35	1.43
R4	$CHO+H \rightarrow CH_2O$	-0.20	0.37	-0.22	/	−0.40	0.47	-0.23	0.52	-0.50	0.93
R5	$CH_2O+H \rightarrow CH_2OH$	-0.03	1.00	-0.04	0.99	−0.06	0.82	0.04	0.93	0.28	1.37
R6	$CH_2O+H \rightarrow CH_3O$	-0.49	0.31	-0.66	1.12	−1.02	0.24	-0.91	0.36	-0.62	1.46
R7	$CH_3O+H \rightarrow CH_3OH$	-0.01	1.38	/	/	−0.23	1.17	0.16	1.20	0.20	2.02
R8	$CHO+CHO \rightarrow OHCCHO$	-1.15	0.13	-0.48	0.61	/	/	/	/	/	/
R9	$CHO+CO \rightarrow OCCHO$	0.29	1.46	-0.56	0.69	/	/	/	/	/	/
R10	$CH_3+CHO \rightarrow CH_3CHO$	-0.64	0.92	-1.15	0.51	/	/	-1.04[ref.52]	0.51[ref.52]	-0.94	0.91
R11	$CH_3+H \rightarrow CH_4$	-0.04	0.59	-0.78	0.54	/	/	-0.67[ref.52]	0.80[ref.52]	-0.23	1.34
R12	$CH_3CHO+H \rightarrow CH_3CHOH$	0.22	0.93	0.18	1.35	/	/	/	/	-0.12	2.73
R13	$CH_3CHO+H \rightarrow CH_3CH_2O$	-0.66	2.45	-0.68	0.60	/	/	/	/	-0.83	1.39
R14	$CH_3CHOH+H \rightarrow CH_3CH_2OH$	-1.05	0.15	-0.58	1.98	/	/	/	/	/	/
R15	$CH_3CH_2O+H \rightarrow CH_3CH_2OH$	-0.17	1.22	0.06	1.60	/	/	/	/	0.23	1.93

Fig. S2 The optimized configurations of (a) Cu(111) and (b) graphene/Cu(111), respectively. (Cu atom: pink, C atom : grey)
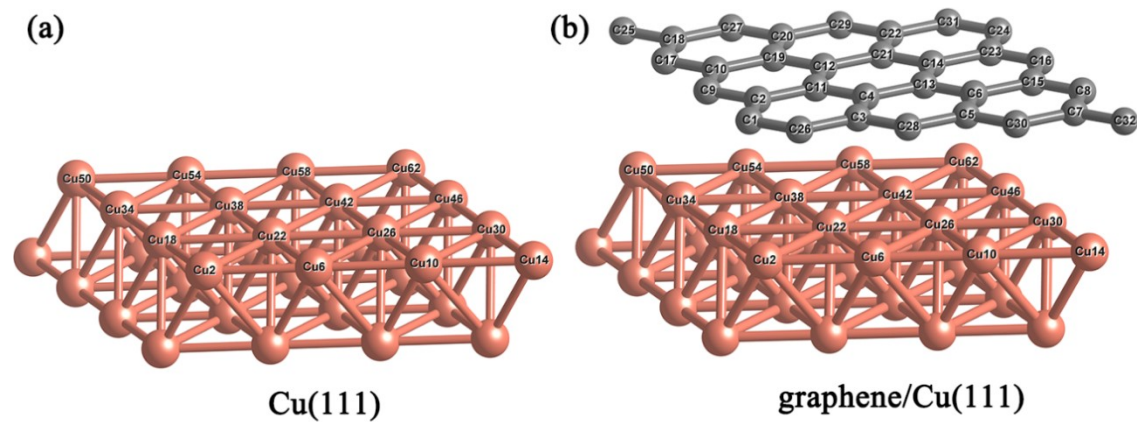
Table S4 Comparison of Bader charge distribution between Cu(111) and graphene/Cu(111) based on the labelled atoms in Fig. S2.

Aotm	Bader charge	
	Cu(111)	graphene/Cu(111)
Cu 2	-0.0102	-0.0190
Cu 6	-0.0106	-0.0198
Cu 10	-0.0109	-0.0208
Cu 14	-0.0100	-0.0199
Cu 18	-0.0101	-0.0194
Cu 22	-0.0101	-0.0193
Cu 26	-0.0099	-0.0199
Cu 30	-0.0107	-0.0199
Cu 34	-0.0105	-0.0195
Cu 38	-0.0107	-0.0197
Cu 42	-0.0106	-0.0203
Cu 46	-0.0099	-0.0199
Cu 50	-0.0105	-0.0192
Cu 54	-0.0102	-0.0195
Cu 58	-0.0105	-0.0194
Cu 62	-0.0099	-0.0197
C1	\	0.0699
C2	\	-0.0779
C3	\	0.0701
C4	\	-0.0777
C5	\	0.0697
C6	\	-0.0779
C7	\	0.0696
C8	\	-0.0783
C9	\	0.0698
C10	\	-0.0779
C11	\	0.0704
C12	\	-0.0778
C13	\	0.0704
C14	\	-0.0774
C15	\	0.0700
C16	\	-0.0778
C17	\	0.0700
C18	\	-0.0784
C19	\	0.0695
C20	\	-0.0784
C21	\	0.0701
C22	\	-0.0784

C23	\	0.0699
C24	\	-0.0781
C25	\	0.0695
C26	\	-0.0780
C27	\	0.0695
C28	\	-0.0781
C29	\	0.0695
C30	\	-0.0783
C31	\	0.0698
C32	\	-0.0784

References

[1] P. Atkins, J. De Paula, Atkins' Physical Chemistry, 2006.

[2] E.B. Wilson, J.C. Decius, P.C. Cross, Molecular Vibrations: The Theory of Infrared and Raman Vibrational Spectra, Dover Publications, 1980.