Supplementary information
On the nature of Cu-carbon interaction by N-modified for enhanced ethanol synthesis from syngas and methanol

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The details of the thermodynamic corrections

To calculate the free energy of gaseous states, we use the shomate gas equation [1]:

$$G(T) = H(T) - TS(T) \tag{a}$$

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

$$E_{ZPE} = \frac{1}{2}\sum h_i \omega_i \tag{c}$$

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

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

From the National Institute of Standards and Technology (NIST) website, the parameters for different gas species can be obtained from A to G, and Eelec is the DFT energy, EZPE is the zero point energy .

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

$$G(T) = H(T) - TS(T) \tag{f}$$

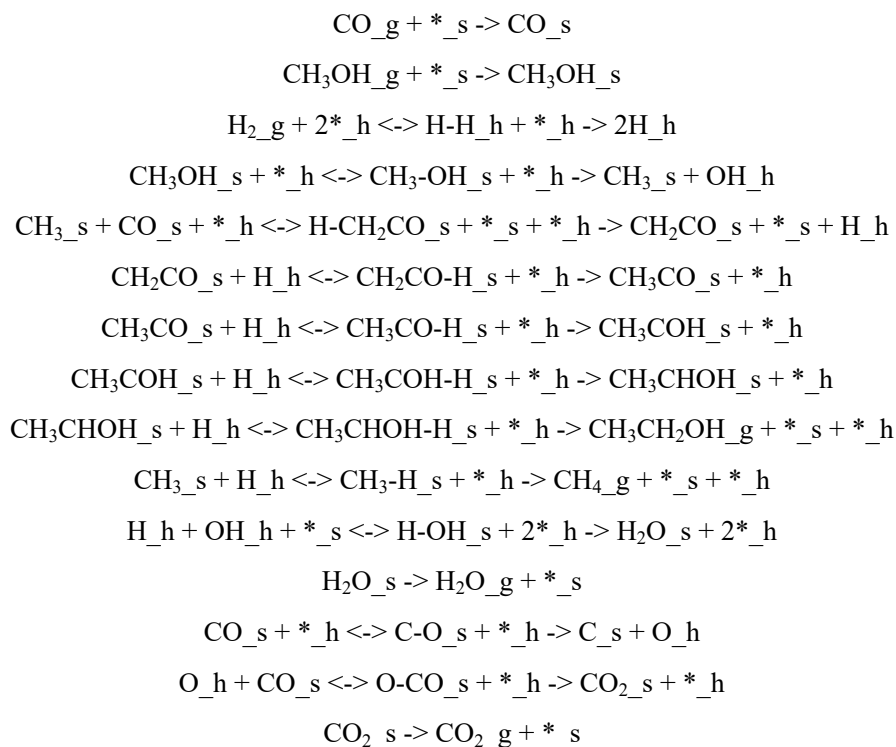$$H(T) = E_{\text{elec}} + E_{\text{ZPE}} + \sum \frac{\varepsilon_i}{e^{\varepsilon_i / k_B} - 1} \tag{g}$$

$$\varepsilon_i = h\omega_i \tag{h}$$

This equation contains four important variables: 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. As a result of the following equation, the entropy of the surface intermediate can be calculated:

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

Elementary reactions

All elementary steps involved in the microkinetic modelling for C1 and C2 products formation are listed below. Adsorption and desorption reactions are shown as A → B. Activated reactions are described as A + B ↔ A-B → AB. A-B represents for the transition state.

$$CO\_g + *\_s \rightarrow CO\_s$$

$$CH_3OH\_g + *\_s \rightarrow CH_3OH\_s$$

$$H_2\_g + 2*\_h \longleftrightarrow H\text{-}H\_h + *\_h \rightarrow 2H\_h$$

$$CH_3OH\_s + *\_h \longleftrightarrow CH_3\text{-}OH\_s + *\_h \rightarrow CH_3\_s + OH\_h$$

$$CH_3\_s + CO\_s + *\_h \longleftrightarrow H\text{-}CH_2CO\_s + *\_s + *\_h \rightarrow CH_2CO\_s + *\_s + H\_h$$

$$CH_2CO\_s + H\_h \longleftrightarrow CH_2CO\text{-}H\_s + *\_h \rightarrow CH_3CO\_s + *\_h$$

$$CH_3CO\_s + H\_h \longleftrightarrow CH_3CO\text{-}H\_s + *\_h \rightarrow CH_3COH\_s + *\_h$$

$$CH_3COH\_s + H\_h \longleftrightarrow CH_3COH\text{-}H\_s + *\_h \rightarrow CH_3CHOH\_s + *\_h$$

$$CH_3CHOH\_s + H\_h \longleftrightarrow CH_3CHOH\text{-}H\_s + *\_h \rightarrow CH_3CH_2OH\_g + *\_s + *\_h$$

$$CH_3\_s + H\_h \longleftrightarrow CH_3\text{-}H\_s + *\_h \rightarrow CH_4\_g + *\_s + *\_h$$

$$H\_h + OH\_h + *\_s \longleftrightarrow H\text{-}OH\_s + 2*\_h \rightarrow H_2O\_s + 2*\_h$$

$$H_2O\_s \rightarrow H_2O\_g + *\_s$$

$$CO\_s + *\_h \longleftrightarrow C\text{-}O\_s + *\_h \rightarrow C\_s + O\_h$$

$$O\_h + CO\_s \longleftrightarrow O\text{-}CO\_s + *\_h \rightarrow CO_2\_s + *\_h$$

$$CO_2\_s \rightarrow CO_2\_g + *\_s$$

Where *s represents the surface site, and *h represents the hydrogen storage site.

Table S1 Adsorption energy (eV) and key geometrical parameters (Å) of reactants, possible intermediates, and products involved in syngas conversion on the C_{13}/Cu(111) surface.

|	Species	E_{ads}/eV	Configuration	Key parameters/Å
1	H_2	-0.31	*no bond*	/
2	CO	-1.56	bridge C *via* C2 and Cu10	C2—C: 1.486; Cu10—C: 2.017
3	CO_2	-1.18	bridge O-C-O *via* C2, Cu5, Cu9, and Cu10	C2—C: 1.507; Cu10—C: 2.228; Cu5—O: 2.063; Cu9—O: 2.128
4	H_2O	-0.74	O *via* Cu9	Cu9—O: 2.233
5	CHO	-4.01	bridge C-O *via* C2, Cu9, and Cu10	C2—C: 1.456; Cu10—C: 2.203; Cu9—O: 2.213
6	COH	-4.86	bridge C *via* C2, Cu5, and Cu10	C2—C: 1.470; Cu5—C: 2.050; Cu10—C: 2.119
7	CH_3OH	-0.94	O *via* Cu5	Cu5—O: 2.156
8	CH_3OCH_3	-0.47	O *via* C2	C2—O: 1.606
9	CH_3	-4.71	C *via* C3	C3—C: 1.484
10	CH_4	-0.44	*no bond*	/
11	CH_3CH_3	-0.62	*no bond*	/
12	CH_3CO	-4.59	bridge C-O *via* C4 and Cu3	C4—C: 1.451; Cu3—O: 2.063
13	CH_3CHO	-2.55	bridge C-O *via* C4, Cu2, and Cu3	C4—C: 1.523; Cu2—O: 1.997; Cu3—O: 1.975
14	CH_3COH	-5.40	C *via* C4	C4—C: 1.387
15	CH_3CHOH	-4.52	C *via* C4	C4—C: 1.514
16	C_2H_5OH	-0.99	O *via* Cu3	Cu3—O: 2.140
17	COOH	-4.94	bridge C-O *via* C3 and Cu2	C3—C: 1.464; Cu2—O: 2.083
18	HCOOH	-1.56	bridge O-C-O *via* C3, Cu2, and Cu3	C3—C: 1.554; Cu2—O: 1.922; Cu3—O: 2.173
19	CH_3COOH	-1.22	bridge C-O *via* C4, Cu2, and Cu3	C4—C: 1.528; Cu2—O: 2.007; Cu3—O: 1.994
20	HOOCCOOH	-1.46	bridge C-O *via* C3 and Cu2	C3—C: 1.536; Cu2—O: 1.917

Table S2 The comparison of activation barriers (E_a/eV) and reaction energies (ΔE/eV) of the key elementary reactions on the C_{13}/Cu(111), graphene/Cu(111), Cu_1/graphene, Cu(111), and Cu(211) catalysts.

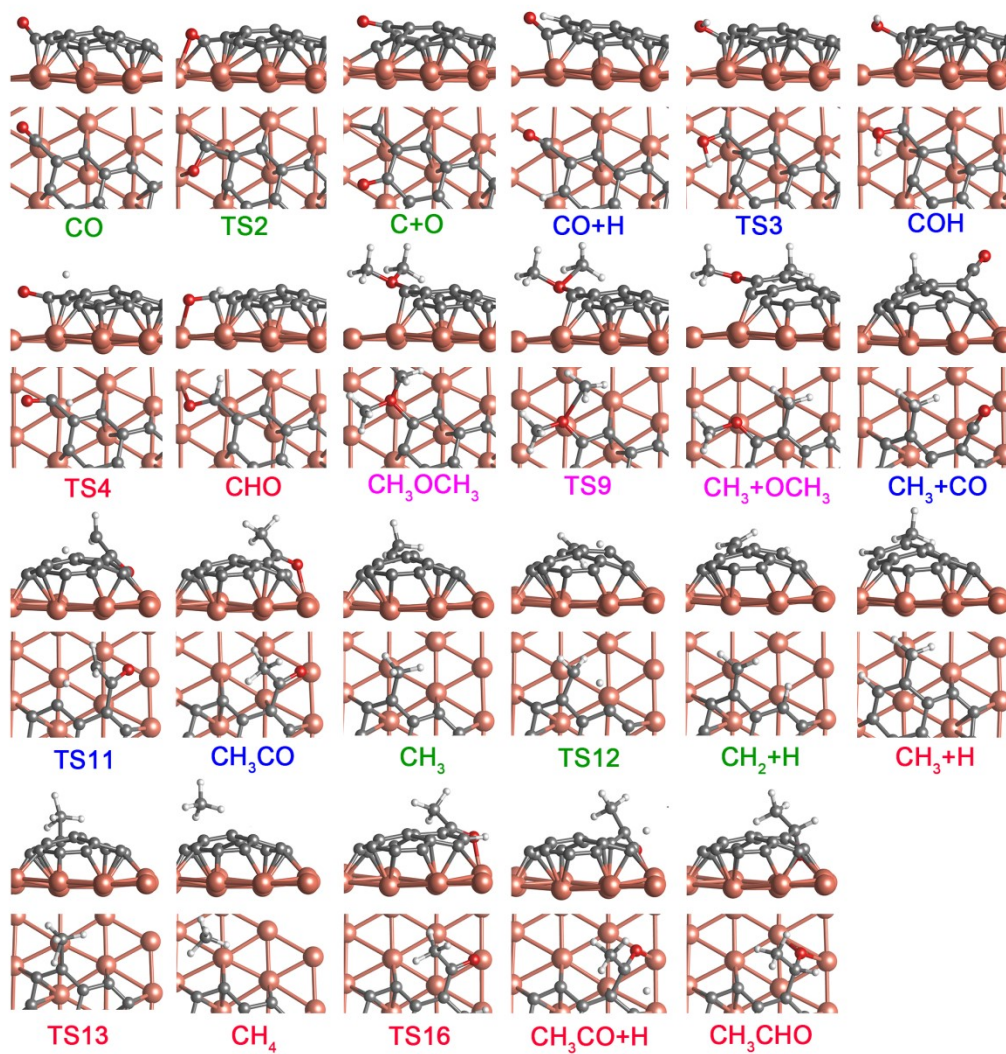| Reaction	C_{13}/Cu(111) (this work)		gra/Cu(111) (Ref.17)		Cu_1/graphene (Ref.15)		Cu(111) (Ref.59)		Cu(211) (Ref.58)	
	E_a/eV	ΔE/eV	E_a/eV	ΔE/eV	E_a/eV	ΔE/eV	E_a/eV	ΔE/eV	E_a/eV	ΔE/eV
$CH_3OH \rightarrow CH_3+OH$	0.61	-1.89	/	/	0.52	-0.04	/	/	1.73	-0.22
$CH_3+CHO \rightarrow CH_3CHO$	/	/	0.92	-0.64	0.51	-1.15	0.51	-1.04	0.91	-0.94
$CH_3+CO \rightarrow CH_2CO+H$	1.05	0.26	/	/	/	/	/	/	/	/
$CH_3CHOH+H \rightarrow C_2H_5OH$	3.19	2.78	0.15	-1.05	1.98	-0.58	/	/	/	/
$H+OH \rightarrow H_2O$	1.09	0.88	1.16	0.29	/	/	1.18	-0.21	/	/
$CO+O \rightarrow CO_2$	1.54	0.46	0.66	-0.34	/	/	0.65	-1.12	/	/
$CH_3+H \rightarrow CH_4$	4.08	2.50	0.59	-0.04	0.54	-0.78	0.80	-0.67	1.34	-0.23

Fig S1 Optimized configurations of three carbon skeletons of (a) phenalenyl, (b) anthracene, and (c) phenanthrene as different graphene fragments loaded on the Cu(111) surface. Calculated Bader charge of carbon atoms and its surrounding Cu atoms are labeled.
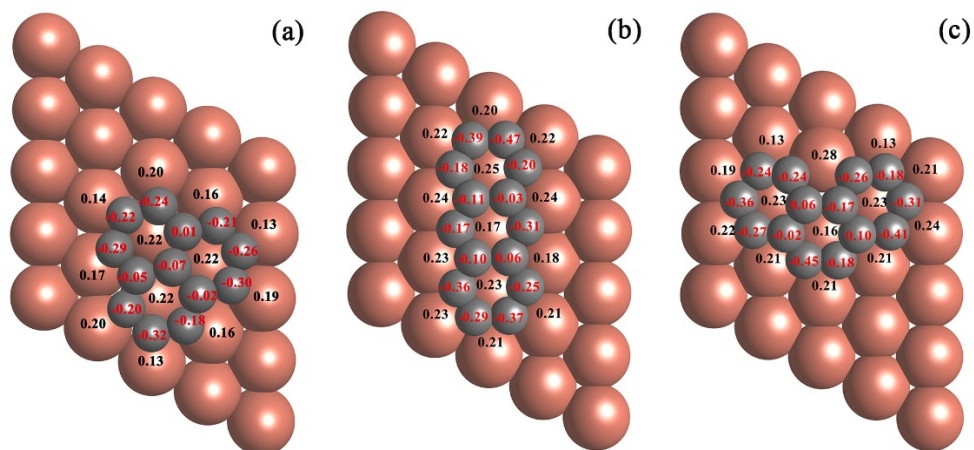
Fig. S2 Top and side views of the most stable adsorption configurations of possible species involved in syngas conversion over C_{13}/Cu(111) catalyst. Red and white spheres represent O and H atoms, respectively.
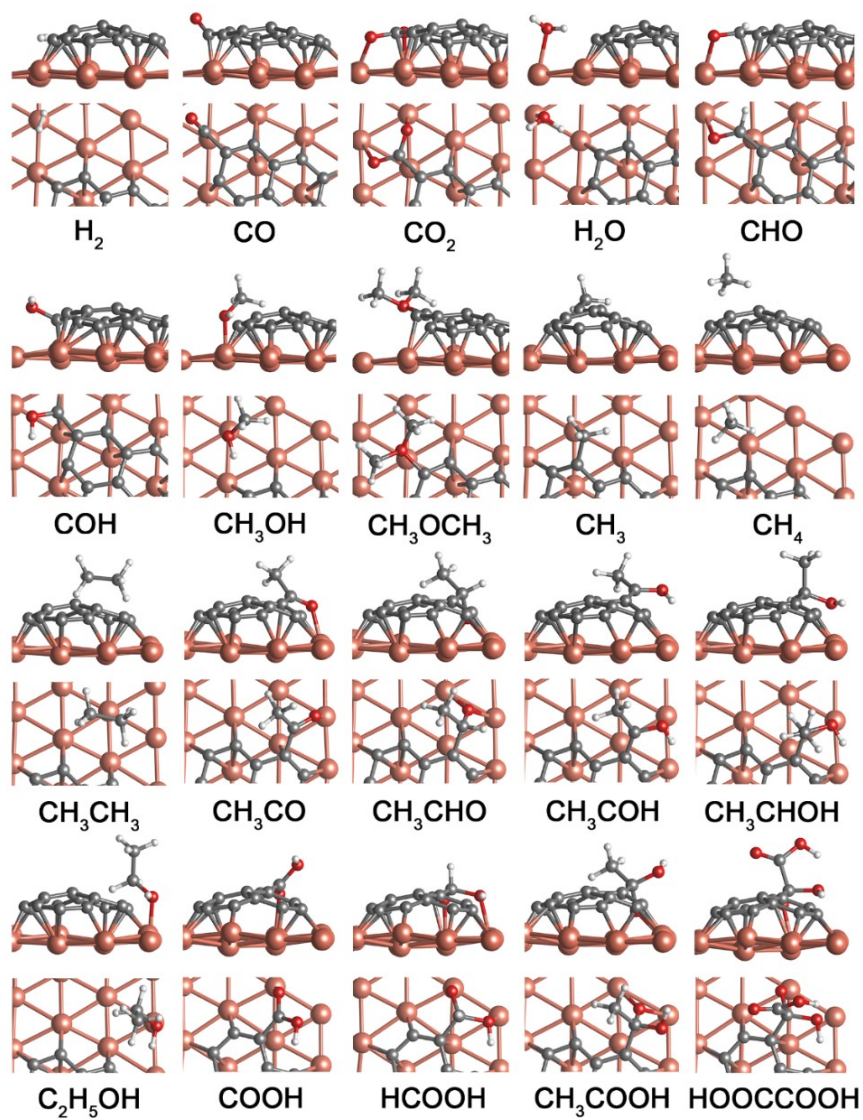
Fig. S3 The structures of IS TS and FS in the other possible competitive pathways in Fig. 3.

CO　　TS2　　C+O　　CO+H　　TS3　　COH

TS4　　CHO　　CH_3OCH_3　　TS9　　CH_3+OCH_3　　CH_3+CO

TS11　　CH_3CO　　CH_3　　TS12　　CH_2+H　　CH_3+H

TS13　　CH_4　　TS16　　CH_3CO+H　　CH_3CHO

Fig. S4 Simulated STM images for the closed-shell (a) C_{13}/Cu(111) and (b) $C_{11}N_2$/Cu(111) systems at a bias of V=-0.6 V. The wireframe structures are overlapped to the simulated STM images.
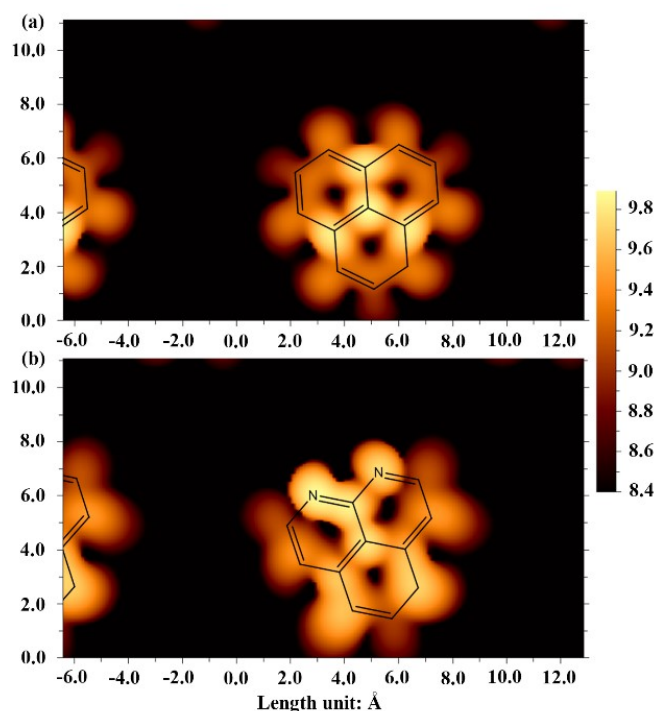
Based on the Tersoff–Hamann approximation[3], we further simulated the STM images in the Fig. S4 for the closed-shell C_{13}/Cu(111) and $C_{11}N_2$/Cu(111) catalyst models by the Multiwfn software[4]. The STM tip is scanned above the measured C_{13}/Cu(111) and $C_{11}N_2$/Cu(111) catalysts. When the catalyst is close enough to the tip and a bias voltage (V) is applied, tunneling current (I) is formed between them due to the tunneling effect. STM image is formed according to the I (x,y,z) function, so I is different when the tip is in different positions. When V is negative, electrons flow from the catalyst to the tip, and when V is positive, electrons flow from the tip to the catalyst.

Here the images were obtained at a negative bias V = -0.6 V which had been used in the STM experiment for the synthesized unsubstituted phenalenyl radical on Au(111) surface.[27] The bright features because of the obvious tunneling current in the simulated STM image are associated to the C_{13} and $C_{11}N_2$ fragments, while the dark features due to negligible tunneling current correspond to the Cu(111) surfaces. Note that in Fig. 9 the orange color of four C atoms in the center of C_{13} is brighter, however, the color of

four atoms including two N and two C atom at the edge of $C_{11}N_2$ is brighter, both of the brighter regions are associate with higher electron density. The simulated STM images could provide a support in favor of experimental synthesis of N-doped graphene fragment on the metal surface in the future.

References:

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

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

[3] J. Tersoff and D. R. Hamann, Phys. Rev. Lett., 1983, 50, 1998–2001.

[4] T. Lu and F. Chen, J. Comput. Chem., 2012, 33, 580–592.