Electronic Supplementary Information for

Cu supported on polymeric carbon nitride for selective CO_2 reduction into CH_4: a combined kinetics and thermodynamics investigation

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Table of Context

Figures:

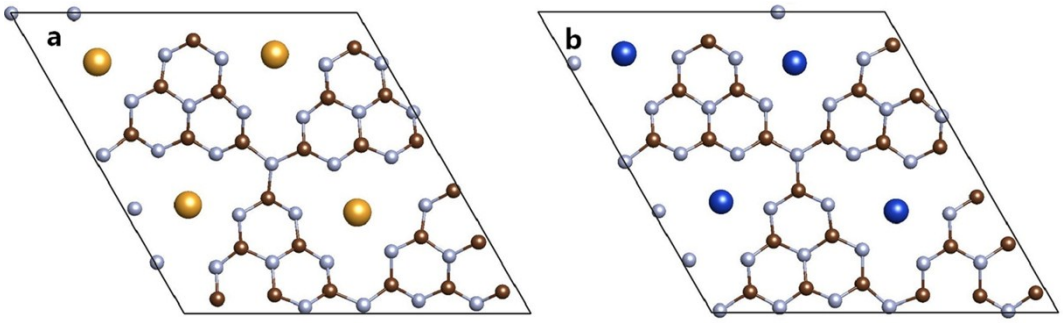

Figure S1. Constructed calculation models of Au/CN (a) and Cu/CN (b). Brown, grey, yellow and blue spheres refer to C, N, Au and Cu atoms respectively.

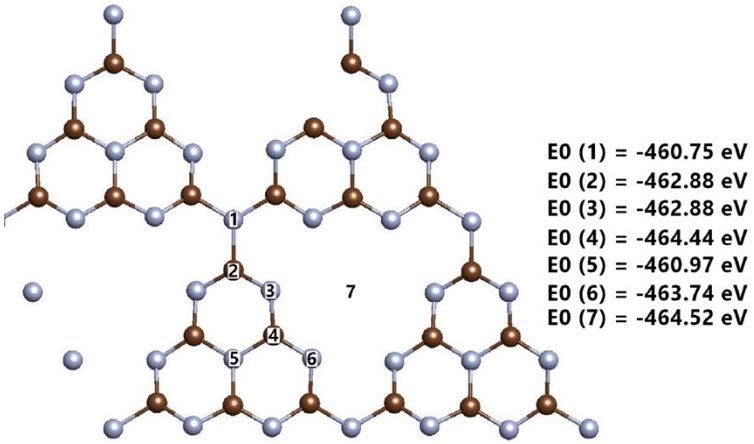

Figure S2. Site tests for Au atom loading into CN.

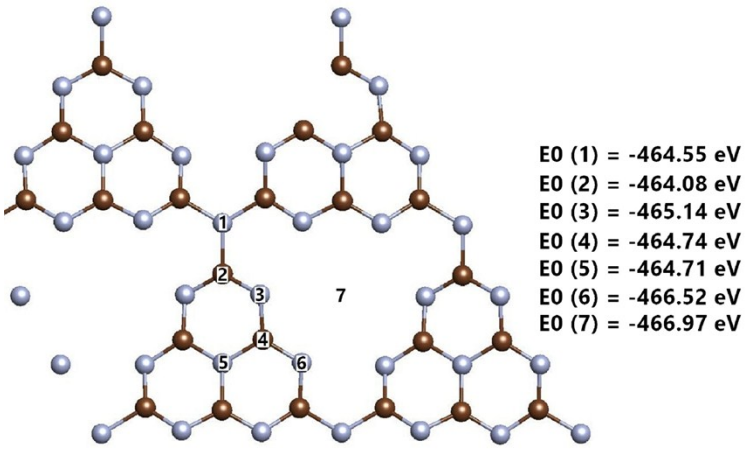

Figure S3. Site tests for Cu atom loading into CN.

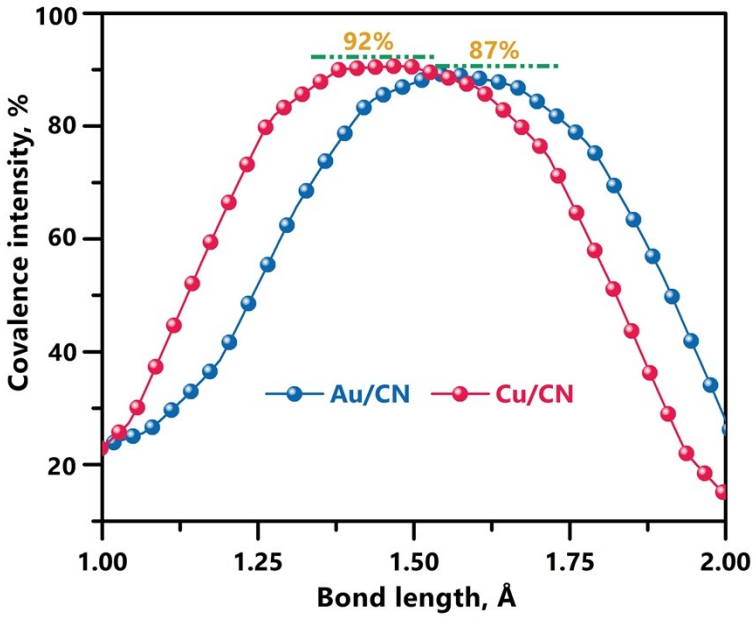

Figure S4. Line profile of the electronic localization function (ELF) calculations for Au/CN and Cu/CN.

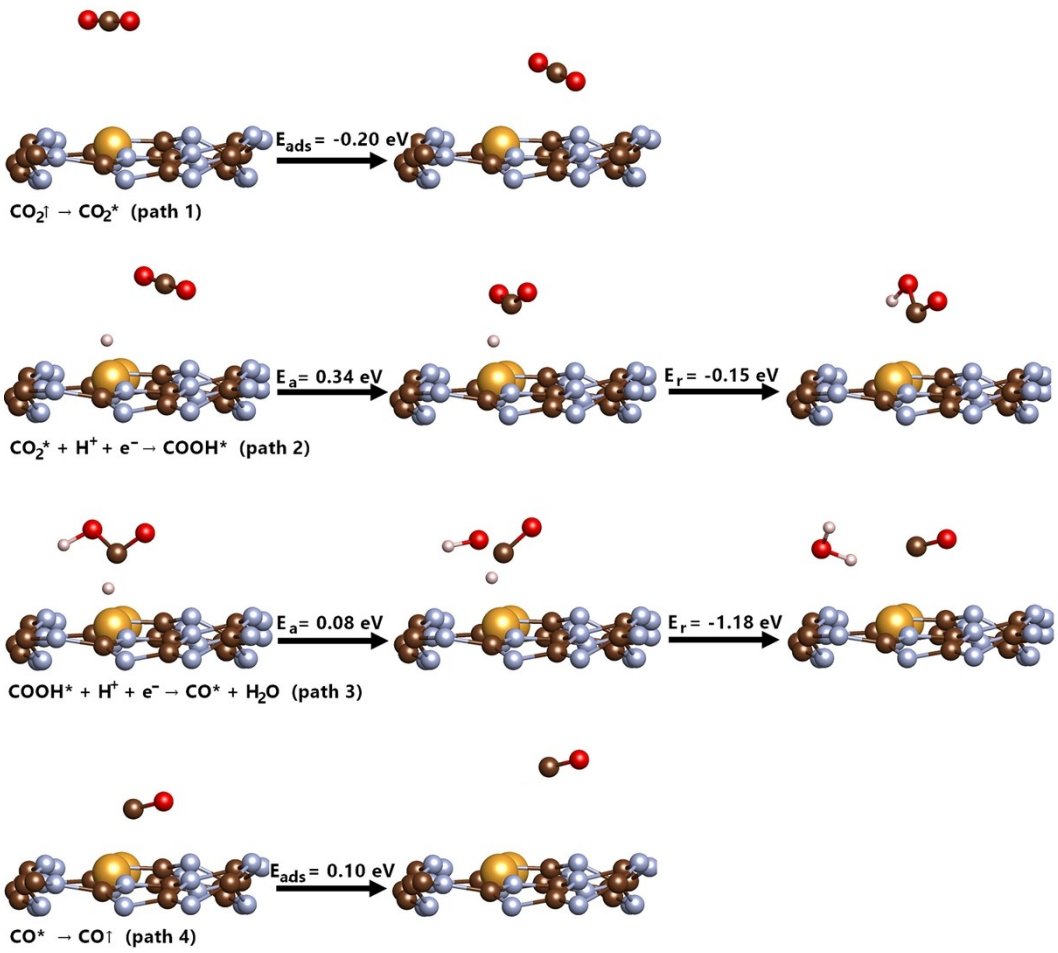

Figure S5. CO_2RR MEPs for the primary reaction pathways on Au/CN (part one). The blue, brown, gold, red and pink spheres refer to N, C, Au, O and H atoms respectively. The positive and negative of energies depict energy absorption and release respectively.

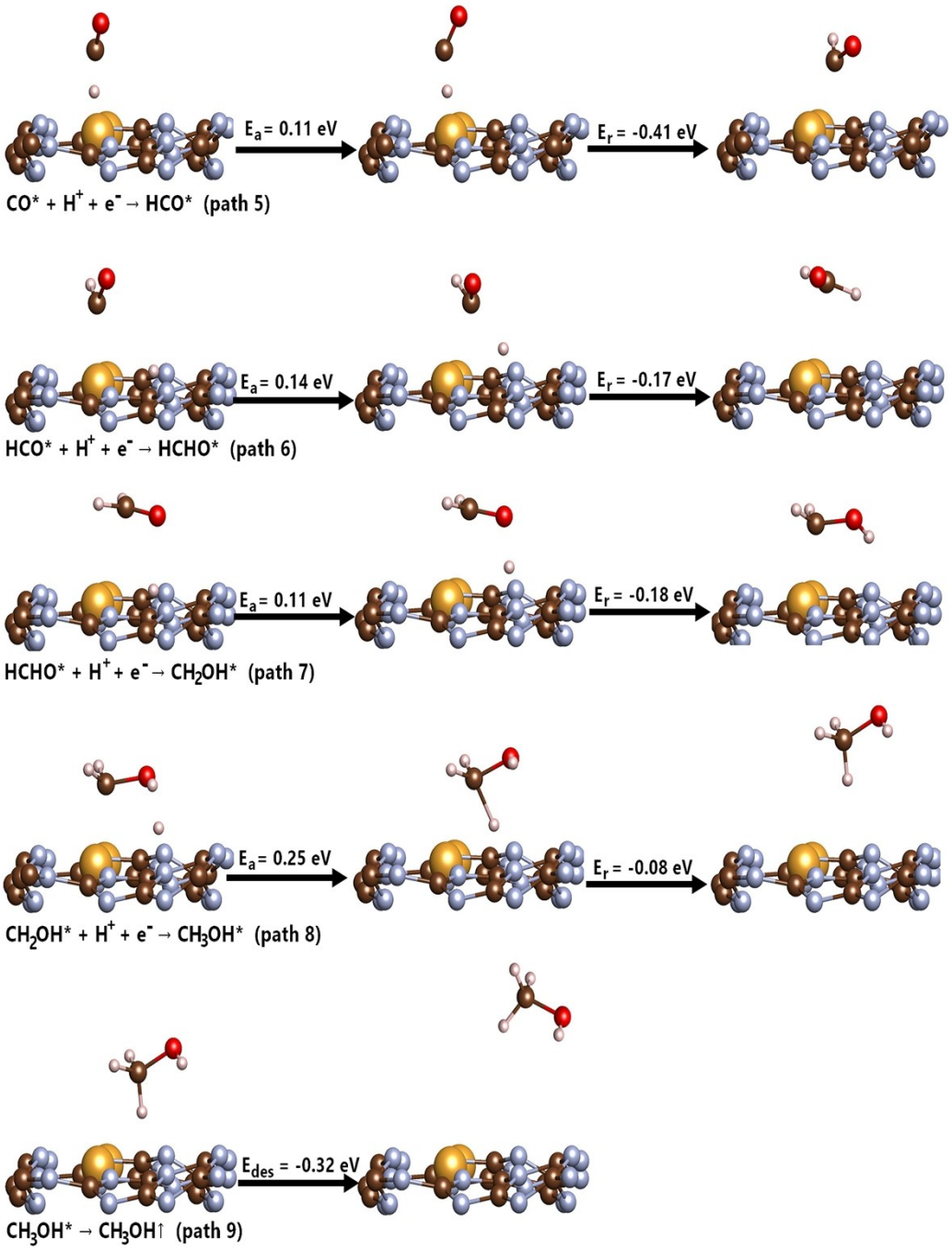

Figure S6. CO_2RR MEPs for the primary reaction pathways on Au/CN (part two). The blue, brown, gold, red and pink spheres refer to N, C, Au, O and H atoms respectively. The positive and negative of energies depict energy absorption and release respectively.

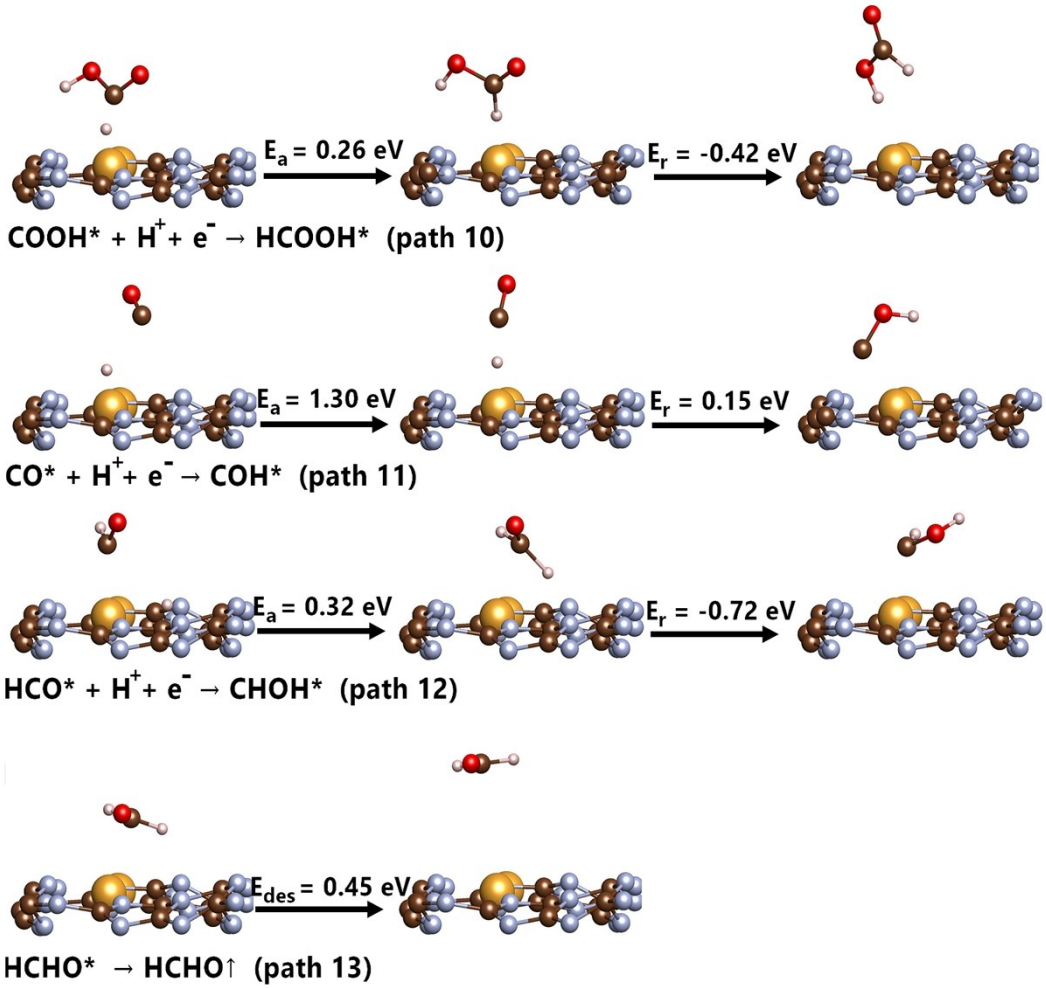

Figure S7. CO_2RR MEPs for the secondary reaction pathways on Au/CN (part one). The blue, brown, gold, red and pink spheres refer to N, C, Au, O and H atoms respectively. The positive and negative of energies depict energy absorption and release respectively.

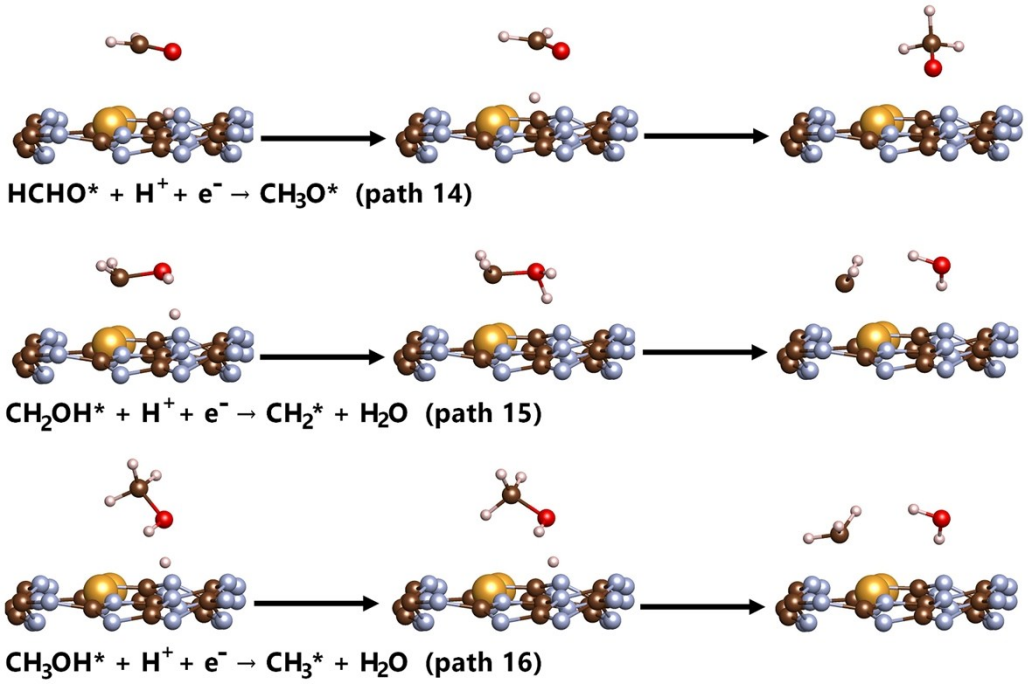

Figure S8. CO_2RR MEPs for the secondary reaction pathways on Au/CN (part two). The blue, brown, gold, red and pink spheres refer to N, C, Au, O and H atoms respectively. The positive and negative of energies depict energy absorption and release respectively.

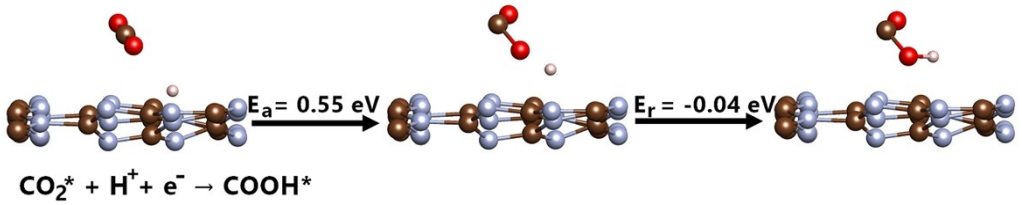

Figure S9. MEP for the path 2 on pristine CN. The blue, brown, red and pink spheres refer to N, C, O and H atoms respectively. The positive and negative of energies depict energy absorption and release respectively.

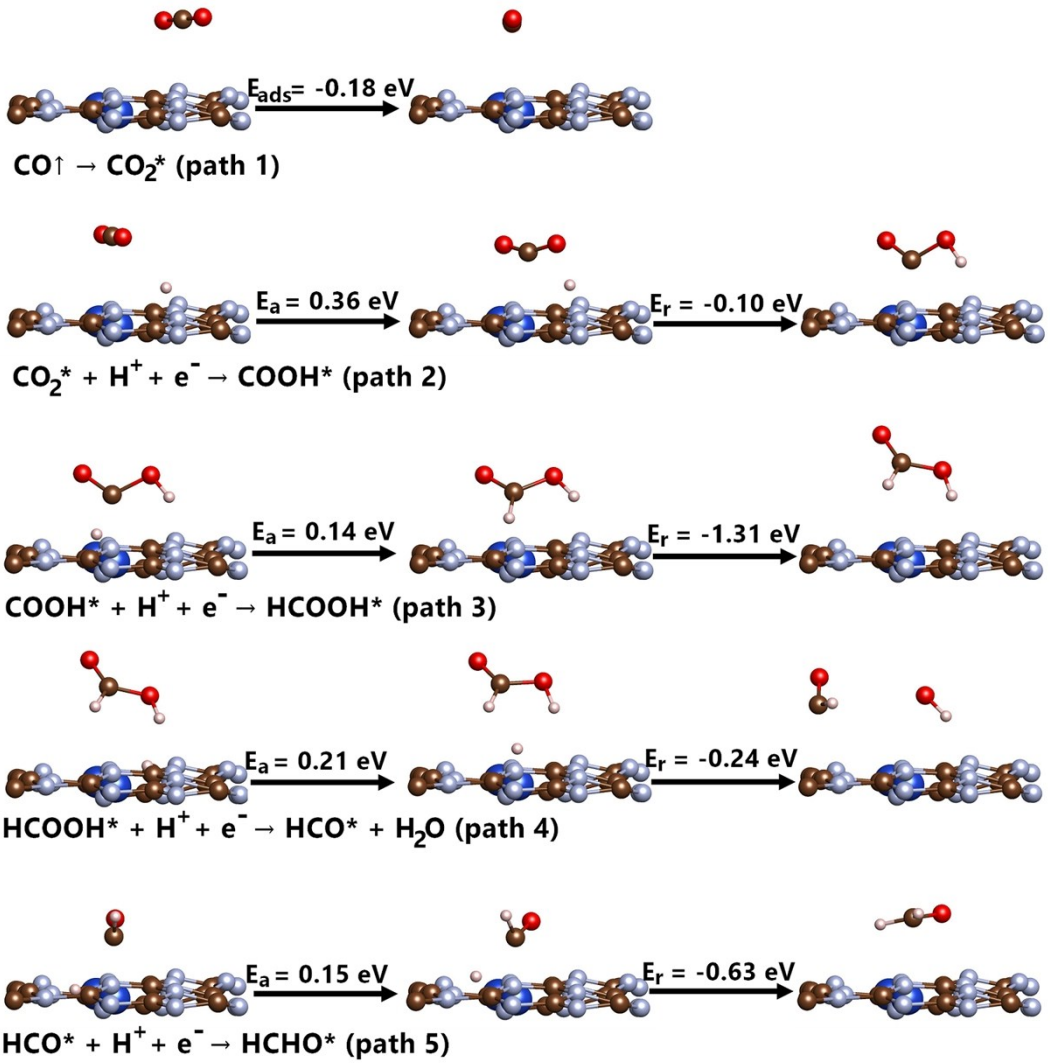

Figure S10. CO_2RR MEPs for the primary reaction pathways on Cu/CN (part one). The light blue, brown, blue, red and pink spheres refer to N, C, Cu, O and H atoms respectively. The positive and negative of energies depict energy absorption and release respectively.

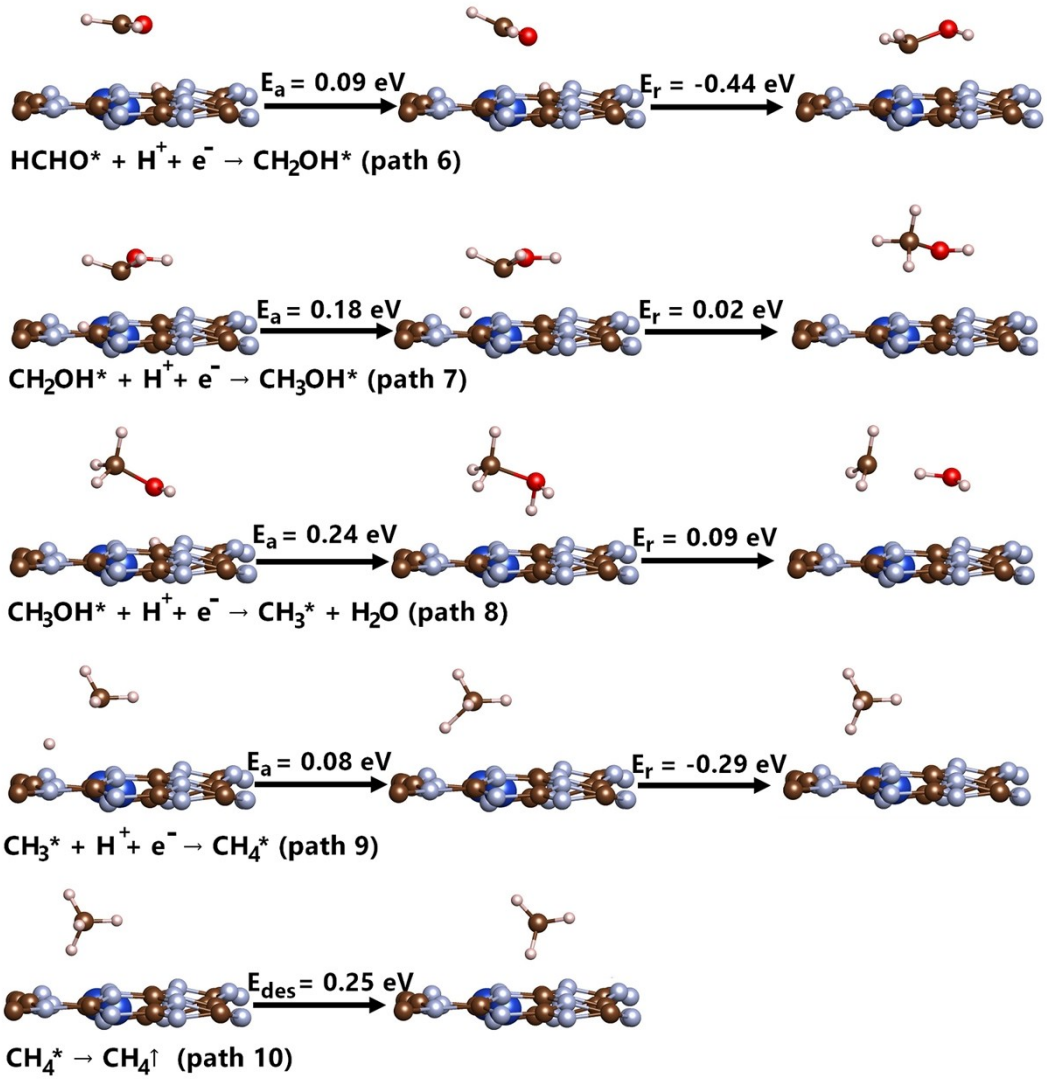

Figure S11. CO_2RR MEPs for the primary reaction pathways on Cu/CN (part two). The light blue, brown, blue, red and pink spheres refer to N, C, Cu, O and H atoms respectively. The positive and negative of energies depict energy absorption and release respectively.

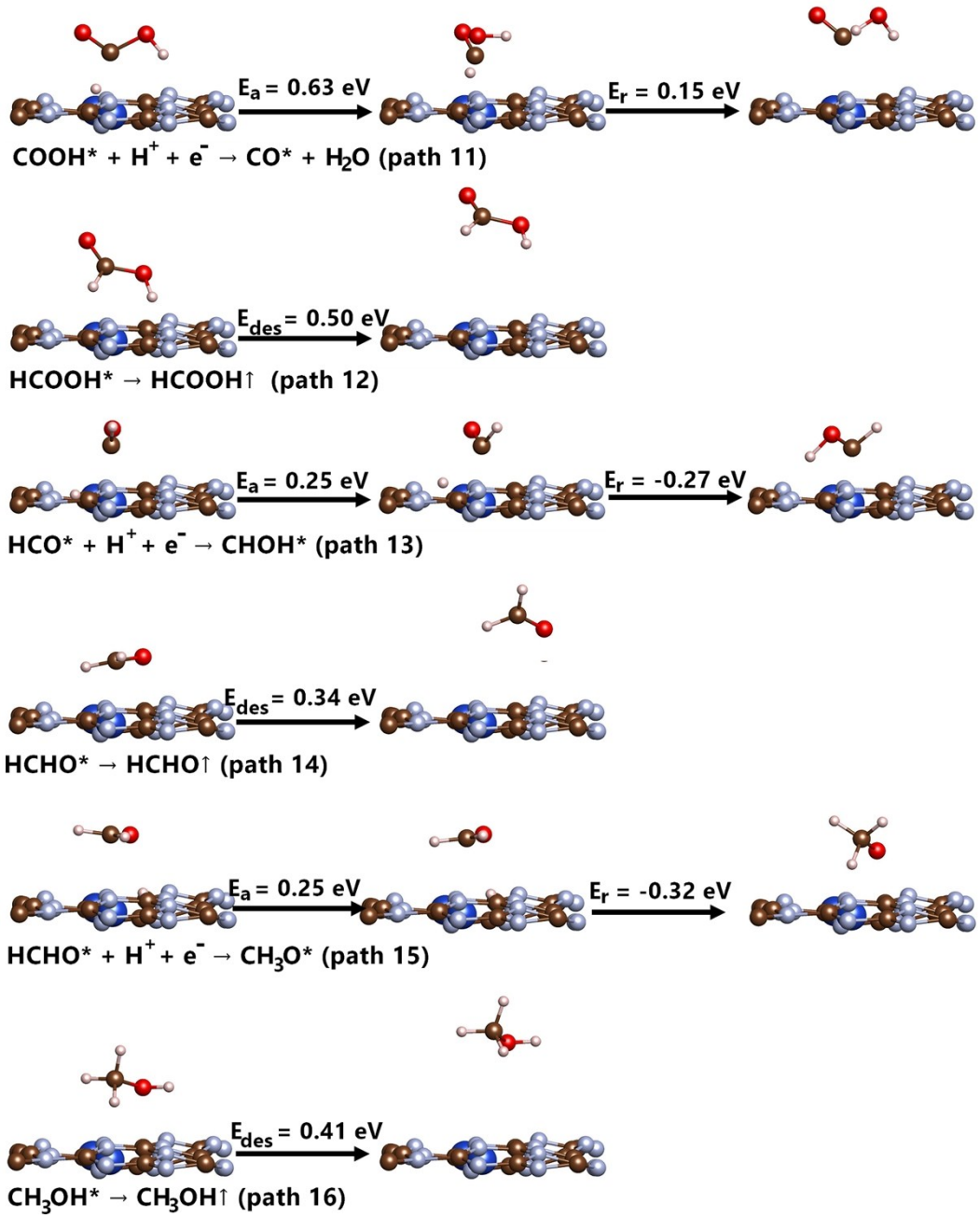

Figure S12. CO_2RR MEPs for the secondary reaction pathways on Cu/CN. The light blue, brown, blue, red and pink spheres refer to N, C, Cu, O and H atoms respectively. The positive and negative of energies depict energy absorption and release respectively.

Tables:

Table S1. Summary of calculated results for the primary reaction pathways on Au/CN.

	ΔG_{ads}, eV	ΔG_a, eV	ΔG_r, eV	ΔG_{des}, eV	*f/i*, cm^{-1}
path 1	-0.19	/	/	/	/
path 2	/	0.34	-0.16	/	401
path 3	/	0.08	-1.17	/	205
path 4	/	/	/	0.11	/
path 5	/	0.12	-0.39	/	145
path 6	/	0.15	-0.16	/	247
path 7	/	0.17	-0.10	/	198
path 8	/	0.23	-0.11	/	332
path 9	/	/	/	-0.32	/

ΔG_{ads}, ΔG_a, ΔG_r, ΔG_{des} and *f/i* depict the adsorption free energy, activation free energy, reaction free energy, desorption free energy and imaginary frequency, respectively. Positive and negative of the energies refer to energy absorption and release respectively.

Table S2. Summary of calculated results for the secondary reaction pathways on Au/CN.

	ΔG_a, eV	ΔG_r, eV	ΔG_{des}, eV	*f/i*, cm^{-1}
path 10	0.28	-0.44	/	357
path 11	1.30	0.15	/	542
path 12	0.32	-0.72	/	264
path 13	/	/	0.45	/
path 14	0.92	-0.09	/	574
path 15	1.34	0.47		
path 16	0.99	0.15	/	662

ΔG_a, ΔG_r, ΔG_{des} and *f/i* depict the activation free energy, reaction free energy, desorption free energy and imaginary frequency, respectively. Positive and negative of the energies refer to energy absorption and release respectively.

Table S3. Summary of calculated results for the primary reaction pathways on Cu/CN.

	ΔG_{ads}, eV	ΔG_a, eV	ΔG_r, eV	ΔG_{des}, eV	*f/i*, cm^{-1}
path 1	-0.18	/	/	/	/
path 2	/	0.37	-0.11	/	224
path 3	/	0.13	-1.28	/	111
path 4	/	0.22	-0.22	/	254
path 5	/	0.17	-0.68	/	191
path 6	/	0.10	-0.46	/	209
path 7	/	0.18	0.02	/	275
path 8	/	0.24	0.09	/	176
path 9	/	0.08	-0.27	/	254
path 10	/	/	/	0.25	/

ΔG_{ads}, ΔG_a, ΔG_r, ΔG_{des} and *f/i* depict the adsorption free energy, activation free energy, reaction free energy, desorption free energy and imaginary frequency, respectively. Positive and negative of the energies refer to energy absorption and release respectively.

Table S4. Summary of calculated results for the secondary reaction pathways on Cu/CN.

	ΔG_a, eV	ΔG_r, eV	ΔG_{des}, eV	*f/i*, cm^{-1}
path 11	0.64	0.18	/	499
path 12	/	/	0.51	/
path 13	0.26	-0.29	/	287
path 14	/	/	0.33	/
path 15	0.25	-0.30	/	195
path 16	/	/	0.41	/

ΔG_a, ΔG_r, ΔG_{des} and *f/i* depict the activation energy, reaction energy, desorption energy and imaginary frequency, respectively. Positive and negative of the energies refer to energy absorption and release respectively.

Reaction pathways:

Secondary reaction pathways on Au/CN

$COOH^* + H^+ + e^- \rightarrow HCOOH^*$	path 10 (Au/CN)
$CO^* + H^+ + e^- \rightarrow COH^*$	path 11 (Au/CN)
$HCO^* + H^+ + e^- \rightarrow CHOH^*$	path 12 (Au/CN)
$HCHO^* \rightarrow HCHO\uparrow$	path 13 (Au/CN)
$HCHO^* + H^+ + e^- \rightarrow CH_3O^*$	path 14 (Au/CN)
$CH_2OH^* + H^+ + e^- \rightarrow CH_2^* + H_2O$	path 15 (Au/CN)
$CH_3OH^* + H^+ + e^- \rightarrow CH_3^* + H_2O$	path 16 (Au/CN)

Secondary reaction pathways on Cu/CN

$$COOH^{*} + H^{+} + e^{-} \rightarrow CO^{*} + H_2O \qquad \text{path 11 (Cu/CN)}$$

$$HCOOH^{*} \rightarrow HCOOH\uparrow \qquad \text{path 12 (Cu/CN)}$$

$$HCO^{*} + H^{+} + e^{-} \rightarrow CHOH^{*} \qquad \text{path 13 (Cu/CN)}$$

$$HCHO^{*} \rightarrow HCHO\uparrow \qquad \text{path 14 (Cu/CN)}$$

$$HCHO^{*} + H^{+} + e^{-} \rightarrow CH_3O^{*} \qquad \text{path 15 (Cu/CN)}$$

$$CH_3OH^{*} \rightarrow CH_3OH\uparrow \qquad \text{path 16 (Cu/CN)}$$