Supplementary information

Neighbouring Cu-B_6 electron reservoirs in α-borophene promote long-range C–C coupling to generate C_2 products from CO_2

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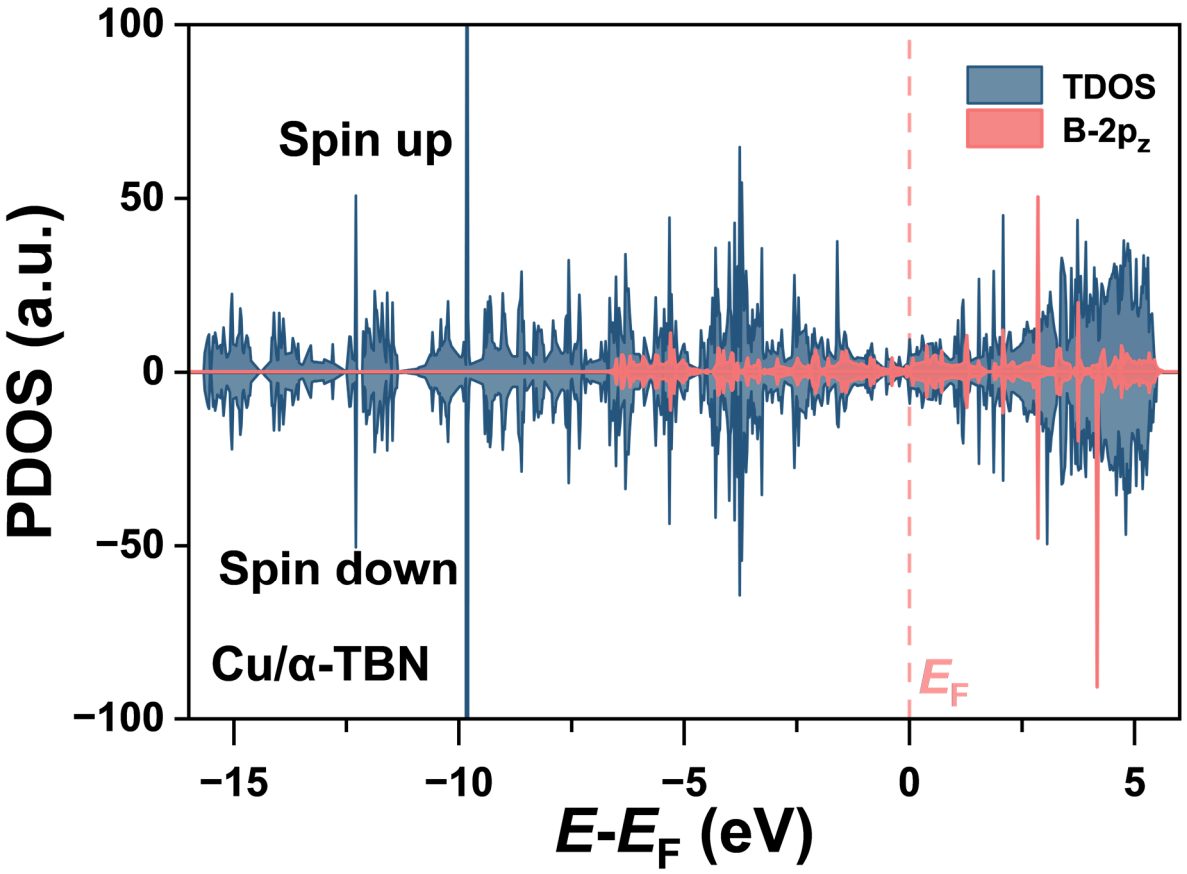

Fig. S1 The PDOS diagram of Cu/α-TBN.

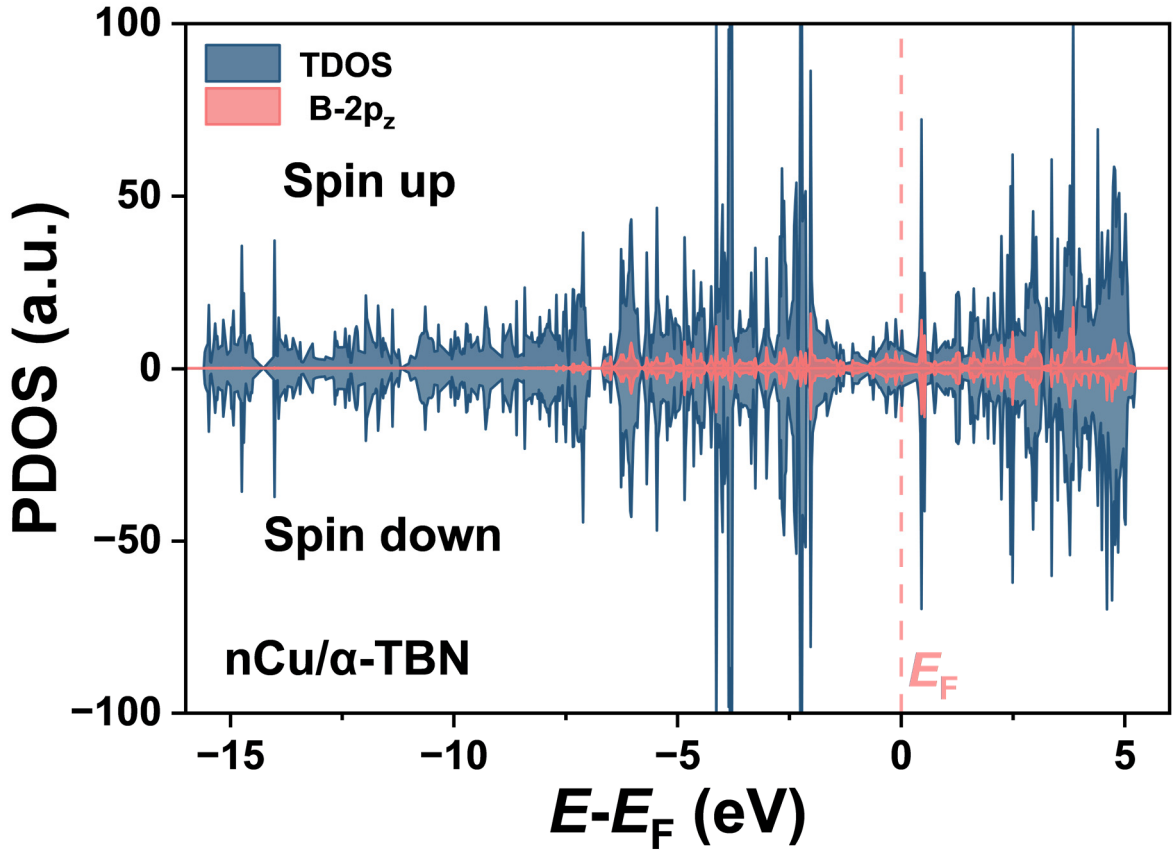

Fig. S2 The PDOS diagram of nCu/α-TBN.

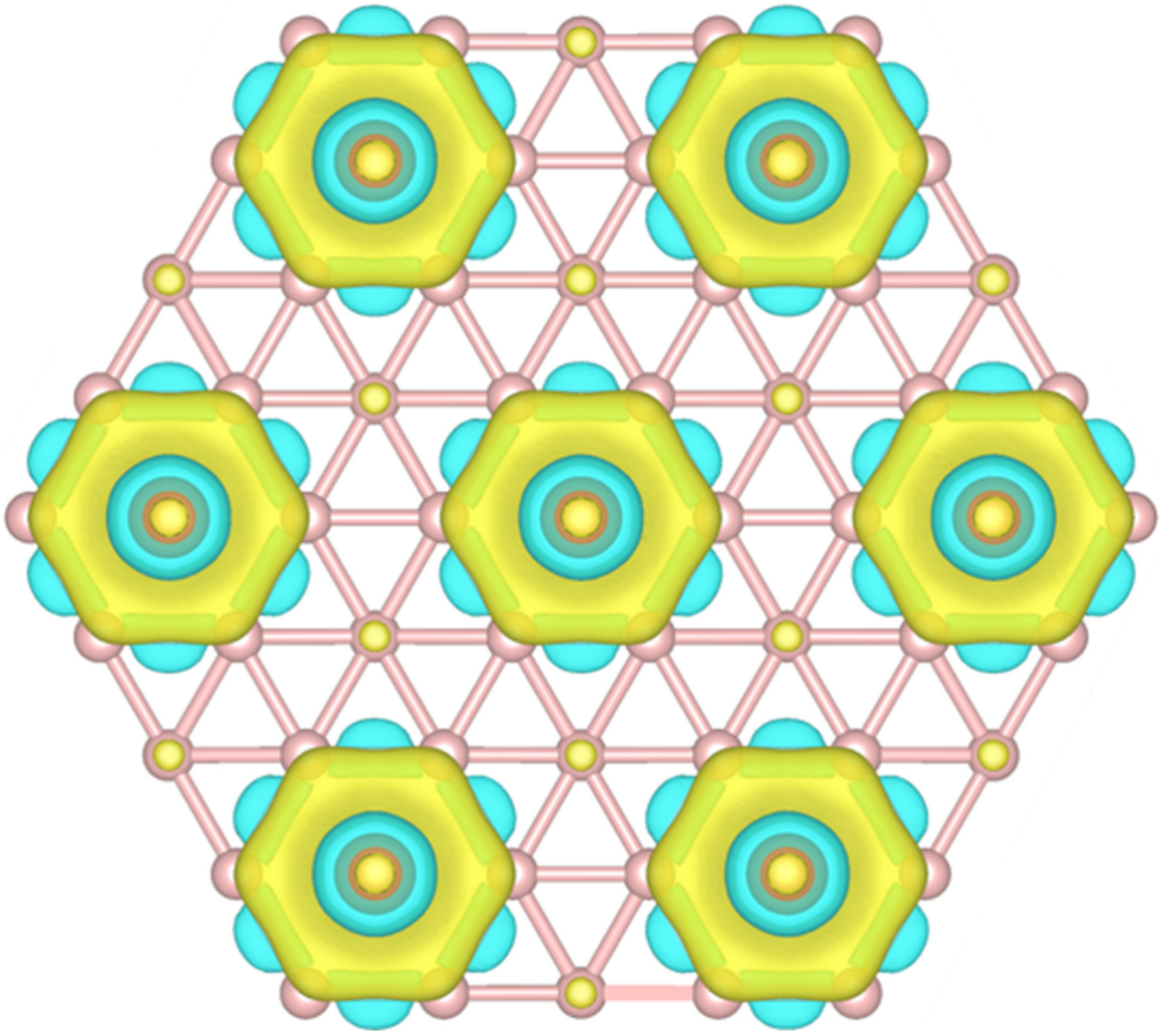

Fig. S3 The CDD diagram of nCu/α-TBN, showcasing the Cu-B_6 electron reservoirs.

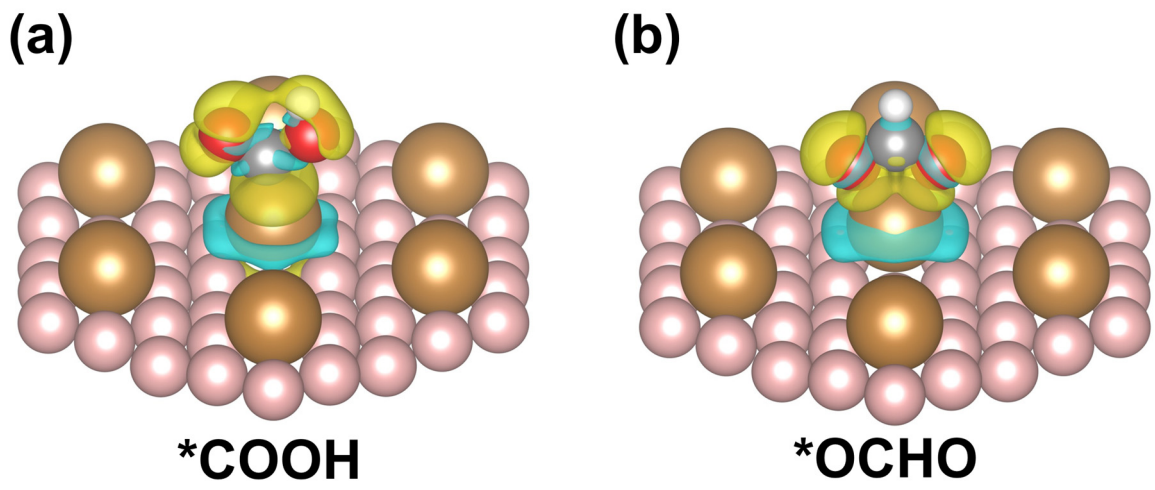

Fig. S4 The CDD diagrams of (a) *COOH and (b) *OCHO on nCu/α-TBN.

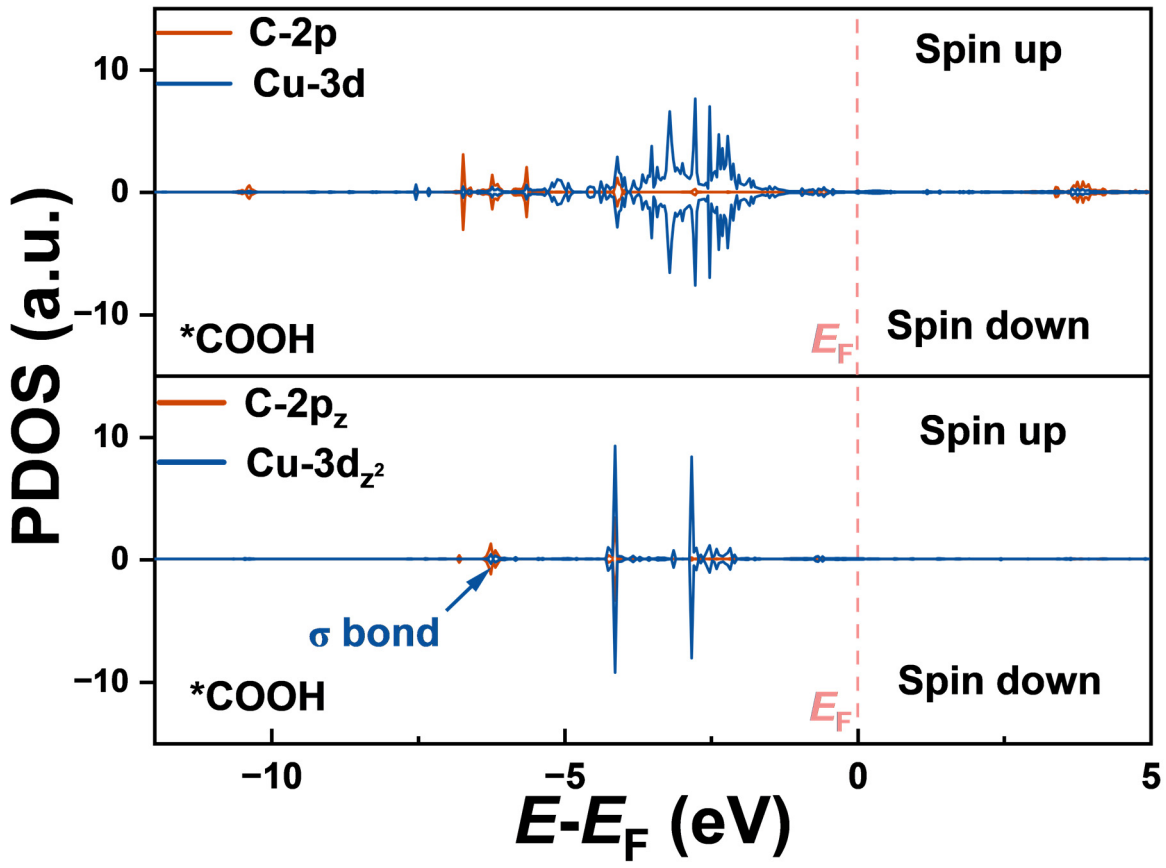

Fig. S5 The PDOS diagram of *COOH on nCu/α-TBN.

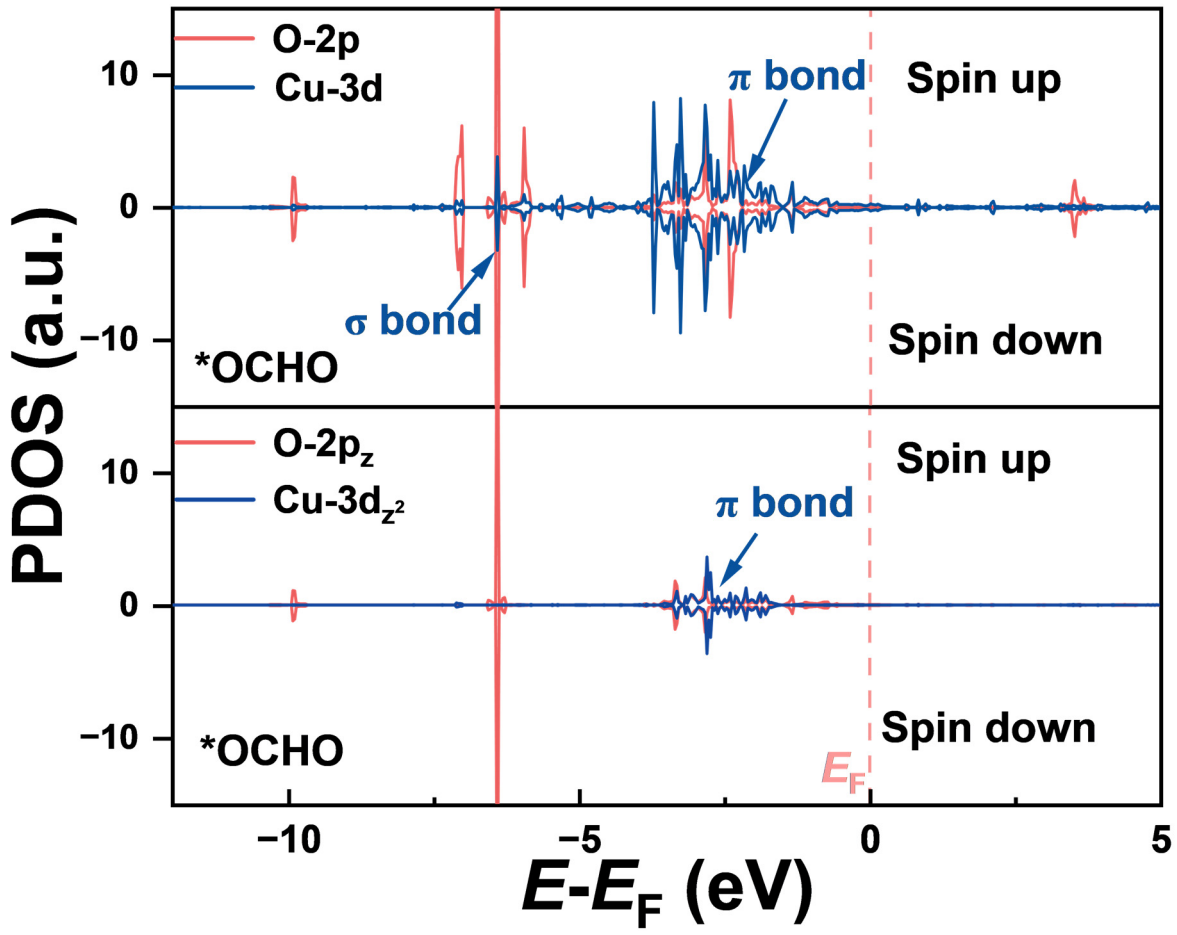

Fig. S6 The PDOS diagram of *OCHO on nCu/α-TBN.

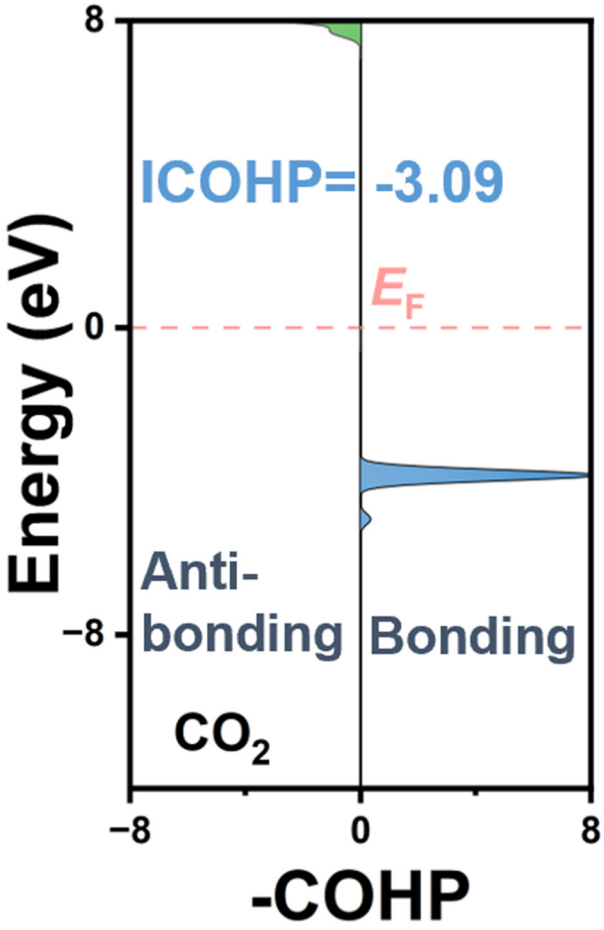

Fig. S7 The COHP diagram and ICOHP values for bonding between the C and O atoms in a CO_2 molecule.

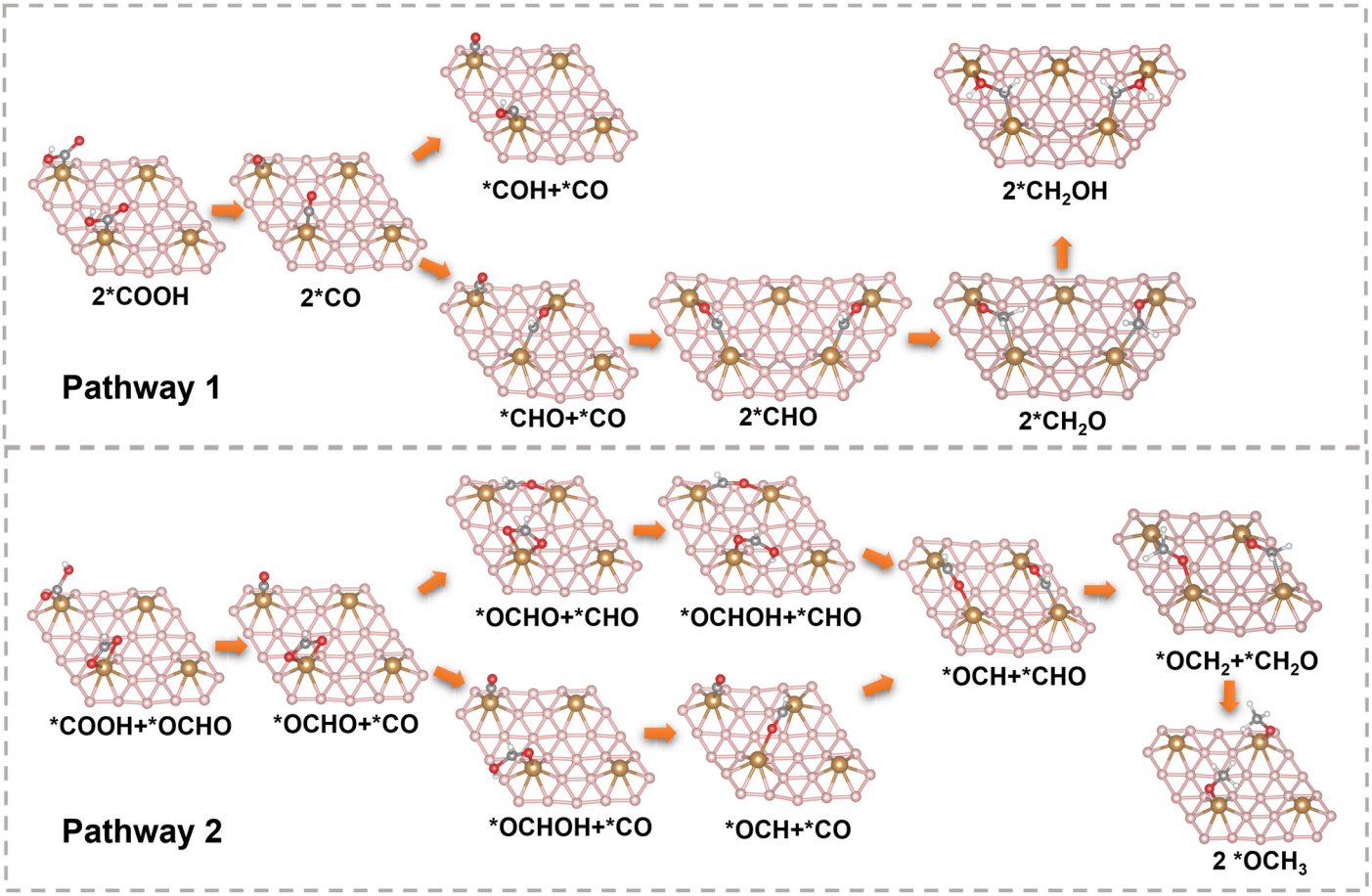

Fig. S8 The model structures of a series of intermediates that may appear in Pathway 1 (upper diagram) and Pathway 2 (lower diagram).

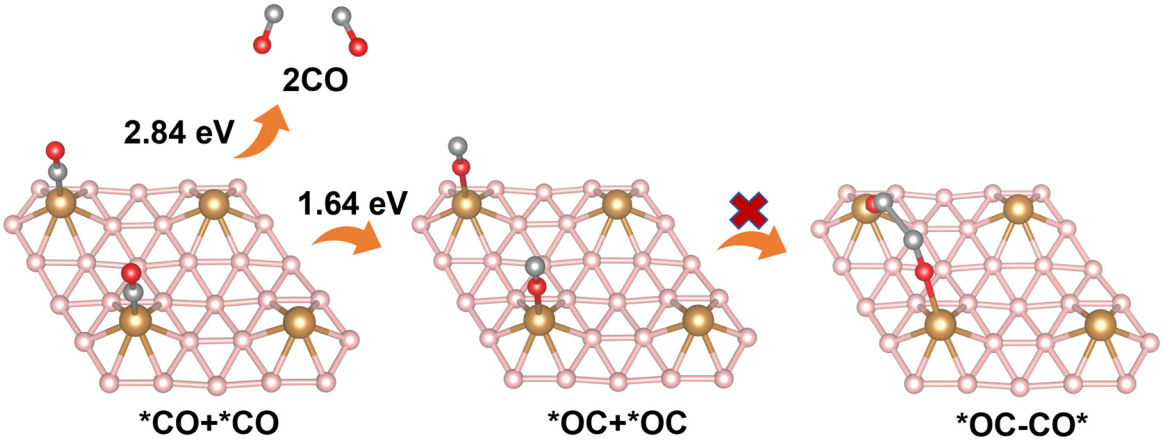

Fig. S9 The model structures showing the dimerization of *CO to *OCCO*.

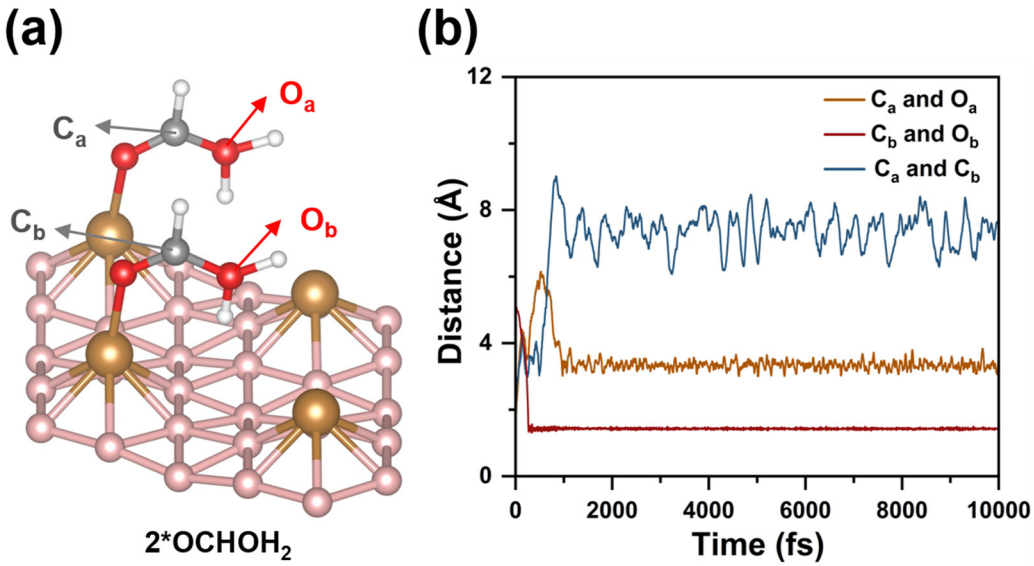

Fig. S10 (a) The model structure of 2*OCHOH$_2$ (the positions of C_a, C_b, O_a and O_b are also marked). (b) The curve of distance between C_a and C_b, C_a and O_a, C_b and O_b of 2*OCHOH$_2$→*OCHCHO+2H$_2$O from 0 to 10 ps based on the AIMD simulations.

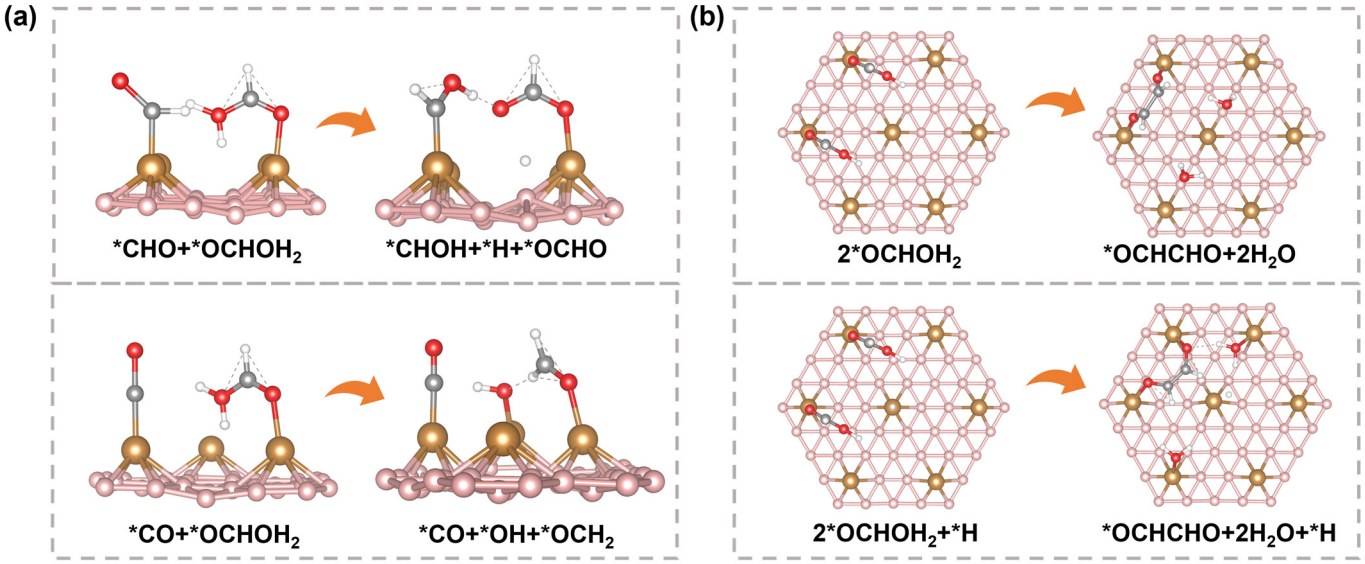

Fig. S11 (a) The model structures of *$OCHOH_2$ affected by the neighbouring *CHO and *CO. (b) Schematic of the C–C coupling processes affected by the neighbouring *H.

Table S1 Bader charges of Cu/α-TBN and nCu/α-TBN as well as the *COOH and *OCHO intermediates.

Structure	Bader charge (e)	Structure	Bader charge (e)
Cu of Cu/α-TBN	–0.27	Cu of nCu/α-TBN	–0.24
Cu-B_6 of Cu/α-TBN	0.71	Cu-B_6 of nCu/α-TBN	0.52
Cu of Cu/α-TBN-*OCHO	–0.62	Cu of Cu/α-TBN-COOH	–0.37
*OCHO of Cu/α-TBN-*OCHO	0.69	*COOH of Cu/α-TBN-COOH	0.40
Cu of nCu/α-TBN-*OCHO	–0.59	Cu of nCu/α-TBN-COOH	–0.34
*OCHO of nCu/α-TBN-*OCHO	0.72	*COOH of nCu/α-TBN-COOH	0.52

Table S2 The binding energies of Cu/α-TBN and nCu/α-TBN.

Structure	*E* (eV)	Structure	*E* (eV)
Cu/α-TBN	–459.07	nCu/α-TBN	–482.41
α-TBN	–456.29	α-TBN	–456.29
Cu	–0.25	nCu	–2.22
E_{b1}	–2.54	E_{b2}	–2.66

Table S3 The Gibbs free energies of *COOH and *OCHO on Cu/α-TBN.

Model	$E_{(DFT+sol)}$ (eV)	G_{corr} (eV)	E_{ads} (eV)	G (eV)	$\triangle G$ (eV)
Cu/α-TBN	–459.07	0.00	–459.07	–509.62	——
*COOH	–486.04	0.45	–485.59	–509.40	0.22
*OCHO	–486.58	0.47	–486.11	–509.93	–0.31

Note: $E_{(DFT+sol)}$ represents the energy of DFT calculations and solvation correction; G_{corr} represents the frequency correction value; $E_{ads} = E_{(DFT+sol)} + G_{corr}$; G is the Gibbs free energy; $\triangle G$ is Gibbs free energy change.

Table S4 The Gibbs free energies of *COOH and *OCHO on nCu/α-TBN.

Model	$E_{(DFT+sol)}$ (eV)	G_{corr} (eV)	E_{ads} (eV)	G (eV)	$\triangle G$ (eV)
nCu/α-TBN	–482.41	0.00	–482.41	–569.89	□□
*COOH	–509.80	0.45	–509.35	–570.10	–0.21
*OCHO	–510.27	0.47	–509.80	–570.55	–0.66

Table S5 The Gibbs free energies for the production of CH_3OH on nCu/α-TBN via Pathway 1.

Model	$E_{(DFT+sol)}$ (eV)	G_{corr} (eV)	E_{ads} (eV)	G (eV)	$\triangle G$ (eV)
nCu/α-TBN	–482.41	0.00	–482.41	–569.89	——
2*COOH	–536.91	1.04	–535.87	–569.89	0.00
2*CO	–514.99	0.28	–514.71	–571.00	–1.11
*CO+*CHO	–518.10	0.50	–517.59	–570.49	0.51
*CO+*COH	–516.31	0.59	–515.72	–568.62	2.39
2*CHO	–521.30	0.81	–520.50	–569.99	0.50
2*CH_2O	–528.94	1.34	–527.60	–570.29	–0.30
2*CH_2OH	–536.60	2.03	–534.57	–570.45	–0.17
*+2CH_3OH	–482.41	0.00	–482.41	–571.04	–0.59

Table S6 The Gibbs free energies for the production of CH_4 on nCu/α-TBN via Pathway 1.

Model	$E_{(DFT+sol)}$ (eV)	G_{corr} (eV)	E_{ads} (eV)	G (eV)	$\triangle G$ (eV)
nCu/α-TBN	–482.41	0.00	–482.41	–583.50	□□
2*COOH	–536.91	1.04	–535.87	–583.50	0.00
2*CO	–514.99	0.28	–514.71	–584.61	–1.11
*CO+*CHO	–518.10	0.50	–517.59	–584.10	0.51
*CO+*COH	–516.31	0.59	–515.72	–582.23	2.39
2*CHO	–521.30	0.81	–520.50	–583.60	0.50
2*CH_2O	–528.94	1.34	–527.60	–583.89	–0.30
2*CH_2OH	–536.60	2.03	–534.57	–584.06	–0.17
2*CH_2	–512.41	1.03	–511.38	–583.14	0.92
2*CH_3	–523.18	1.72	–521.46	–586.42	–3.28
*+2CH_4	–482.41	0.00	–482.41	–587.21	–0.79

Table S7 The Gibbs free energies for the production of CH_3OH on nCu/α-TBN via Pathway 2.

Model	$E_{(DFT+sol)}$ (eV)	G_{corr} (eV)	E_{ads} (eV)	G (eV)	$\triangle G$ (eV)
nCu/α-TBN	–482.41	0.00	–482.41	–569.89	——
*OCHO+*COOH	–537.38	1.01	–536.37	–570.40	–0.50
*OCHO+*CO	–526.48	0.61	–525.86	–571.02	–0.63
*OCHO+*CHO	–529.54	0.85	–528.70	–570.46	0.57
*OCHOH+*CHO	–532.76	0.93	–531.83	–570.18	0.27
*OCH+*CHO	–521.17	0.79	–520.38	–569.87	0.31
OCH_2+CH_2O	–529.09	1.34	–527.75	–570.44	–0.57
2*OCH_3	–537.12	1.83	–535.29	–571.17	–0.73
2*$HOCH_3$	–545.19	2.61	–542.58	–571.66	–0.49
*+2CH_3OH	–482.41	0.00	–482.41	–570.34	1.32

Table S8 The Gibbs free energies for the production of CH_4 on nCu/α-TBN via Pathway 2.

Model	$E_{(DFT+sol)}$ (eV)	G_{corr} (eV)	E_{ads} (eV)	G (eV)	$\triangle G$ (eV)
nCu/α-TBN	–482.41	0.00	–482.41	–583.50	——
*OCHO+*COOH	–537.38	1.01	–536.37	–584.01	–0.50
*OCHO+*CO	–526.48	0.61	–525.86	–584.63	–0.63
*OCHOH+*CO	–529.78	0.70	–529.08	–584.45	0.18
*OCH+*CO	–518.10	0.50	–517.59	–584.06	0.35
*OCH+*CHO	–521.05	0.78	–520.27	–584.10	0.72
OCH_2+CH_2O	–529.09	1.34	–527.75	–583.79	–0.57
2*OCH_3	–537.12	1.83	–535.29	–583.48	–0.73
2*$HOCH_3$	–545.19	2.61	–542.58	–584.05	–0.49
2*OH+2CH_4	–505.23	0.79	–504.44	–584.78	–1.69
*+H_2O	–482.41	0.00	–482.41	–587.21	–0.24

Table S9 The Gibbs free energies for the production of HCOOH on nCu/α-TBN via Pathway 3.

Model	$E_{(DFT+sol)}$ (eV)	G_{corr} (eV)	E_{ads} (eV)	G (eV)	$\triangle G$ (eV)
nCu/α-TBN	–482.41	0.00	–482.41	–542.68	□□
2*OCHO	–537.86	0.95	–536.92	–543.72	–1.05
2*OCHOH	–544.53	1.59	–542.94	–542.94	0.79
*+2HCOOH	–482.41	0.00	–482.41	–541.88	1.06

Table S10 The Gibbs free energies for the production of CH_2CH_2 on nCu/α-TBN via Pathway 3.

Model	$E_{(DFT+sol)}$ (eV)	G_{corr} (eV)	E_{ads} (eV)	G (eV)	$\triangle G$ (eV)
nCu/α-TBN	–482.41	0.00	–482.41	–569.89	□□
2*OCHO	–537.86	0.95	–536.92	–570.94	–1.05
2*OCHOH	–544.53	1.59	–542.94	–570.16	0.79
*OCHCHO	–522.75	0.92	–521.83	–571.33	–1.17
*OCHCHOH	–526.08	1.24	–524.85	–570.94	0.39
*$OCHCH_2OH$	–529.64	1.48	–528.16	–570.84	0.09
*$OCHCH_2$	–518.91	1.06	–517.85	–571.67	–0.83
*$OHCHCH_2$	–522.35	1.35	–521.00	–571.42	0.25
*OH+CH_2CH_2	–493.95	0.25	–493.70	–571.94	–0.52
*+H_2O	–482.41	0.00	–482.41	–571.79	0.15

Table S11 The Gibbs free energies for the production of CH_3CH_3 on nCu/α-TBN via Pathway 3.

Model	$E_{(DFT+sol)}$ (eV)	G_{corr} (eV)	E_{ads} (eV)	G (eV)	$\triangle G$ (eV)
nCu/α-TBN	–482.41	0.00	–482.41	–576.70	——
2*OCHO	–537.86	0.95	–536.92	–577.75	–1.05
2*OCHOH	–544.53	1.59	–542.94	–576.96	0.79
*OCHCHO	–522.75	0.92	–521.83	–578.13	–1.17
*OCHCHOH	–526.08	1.24	–524.85	–577.74	0.39
*$OCHCH_2OH$	–529.64	1.48	–528.16	–577.65	0.09
*$OCHCH_2$	–518.91	1.06	–517.85	–578.48	–0.83
*$OCHCH_3$	–522.88	1.33	–522.88	–578.77	–0.29
*$OHCHCH_3$	–526.75	1.69	–526.75	–578.88	–0.11
*$OHCH_2CH_3$	–530.73	1.99	–530.73	–579.16	–0.28
*OH+CH_3CH_3	–493.95	0.25	–493.95	–579.36	–0.19
*+H_2O	–482.41	0.00	–482.41	–579.20	–0.32

Table S12 The Gibbs free energies for the production of CH_3CHO on nCu/α-TBN via Pathway 3.

Model	$E_{(DFT+sol)}$ (eV)	G_{corr} (eV)	E_{ads} (eV)	G (eV)	$\triangle G$ (eV)
nCu/α-TBN	–482.41	0.00	–482.41	–563.09	□□
2*OCHO	–537.86	0.95	–536.92	–564.14	–1.05
2*OCHOH	–544.53	1.59	–542.94	–563.35	0.79
*OCHCHO	–522.75	0.92	–521.83	–564.52	–1.17
*OCHCHOH	–526.08	1.24	–524.85	–564.13	0.39
*$OCHCH_2OH$	–529.64	1.48	–528.16	–564.04	0.09
*$OCHCH_2$	–518.91	1.06	–517.85	–564.87	–0.83
*$OCHCH_3$	–522.88	1.33	–522.88	–565.16	–0.29
*+CH_3CHO	–482.41	0.00	–482.41	–563.96	1.20

Table S13 The Gibbs free energies for the production of CH_3CH_2OH on nCu/α-TBN via Pathway 3.

Model	$E_{(DFT+sol)}$ (eV)	G_{corr} (eV)	E_{ads} (eV)	G (eV)	$\triangle G$ (eV)
nCu/α-TBN	–482.41	0.00	–482.41	–569.89	□□
2*OCHO	–537.86	0.95	–536.92	–570.94	–1.05
2*OCHOH	–544.53	1.59	–542.94	–570.16	0.79
*OCHCHO	–522.75	0.92	–521.83	–571.33	–1.17
*OCHCHOH	–526.08	1.24	–524.85	–570.94	0.39
*$OCHCH_2OH$	–529.64	1.48	–528.16	–570.84	0.09
*$OCHCH_2$	–518.91	1.06	–517.85	–571.67	–0.83
*$OCHCH_3$	–522.88	1.33	–522.88	–571.97	–0.29
*OCH_2CH_3	–526.75	1.69	–526.75	–572.08	–0.11
*$OHCH_2CH_3$	–530.73	1.99	–528.74	–572.36	–0.28
*+CH_3CH_2OH	–482.41	0.00	–482.41	–571.82	0.54