Supporting Information

In Silico Design of Dual-doped Nitrogenated Graphene (C_2N) Applied to Electrocatalytic Reduction of Carbon Monoxide to Ethylene

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Complement to Computational Detail

The Gibbs reaction free energy change (ΔG) of each elementary step during the CO reduction process was calculated by using the computational hydrogen electrode model, as pioneered by Nørskov et al[1]. The ΔG value can be obtained by the formula: $\Delta G = \Delta E + \Delta E_{ZPE} - T\Delta S + \Delta G_{pH} +$, where ΔE is the calculated electronic total energy difference. ΔE_{ZPE} and ΔS calculated from the vibrational frequencies, are the zero-point energy corrections and entropy between the reactant and products at 298.15 K, respectively. The pH value was set to be zero in this work for simplicity; U was the applied potential. The Gibbs free energy of C_2H_4 under the pressure of one bar and the temperature of 298.15 K, which be obtained from the CRC handbook[2]. The average CO adsorption energy is calculated refer to Zhou et al.[3], the equation can be expressed as $E_{ad_{avg}} = \frac{E_{ad}(CO_{1st}) + E_{ad}(CO_{2nd})}{2}$. The adsorption energy of each molecule (Mol) on the surface (Sur) can be expressed as $E_{ad} = E_{Total} - E_{Sur} - E_{Mol}$.

Table S1. Calculated electronic total energy (E_{DFT}), zero point energies (E_{ZPE}), and entropy of different adsorption species, where the * denotes the adsorption site.

Adsorbed species	E_{DFT} (eV)	E_{ZPE} (eV)	TS (eV)
*COCO	-705.51	0.91	0.12
*COHCO	-709.16	1.52	0.13
*COCOH	-709.07	1.52	0.12
*COHCOH	-713.19	2.17	0.12
*COC	-696.86	0.68	0.06
*CCO	-699.37	0.75	0.09
*COHCHOH	-716.05	2.75	0.11
*CHOHCOH	-716.05	2.71	0.13

*COHC	-701.00	1.32	0.07
*CCOH	-701.64	1.31	0.08
*CHOHCHOH	-720.82	3.39	0.12
*CC	-690.53	0.50	0.02
*COHCH	-706.73	1.97	0.07
*CHCOH	-706.67	1.94	0.08
*CHOHCH	-709.38	2.46	0.08
*CHCHOH	-710.42	2.55	0.09
*CCH	-695.03	1.08	0.02
*CHC	-694.30	1.05	0.03
*CHOHCH2	-714.47	3.19	0.07
*CH2CHOH	-714.58	3.21	0.07
*CHCH	-699.94	1.73	0.03
*CHCH2	-703.24	2.32	0.03
*CH2CH	-703.04	2.23	0.04
*CHCH2	-703.54	2.29	0.07
*CH2CH2	-708.21	2.95	0.02

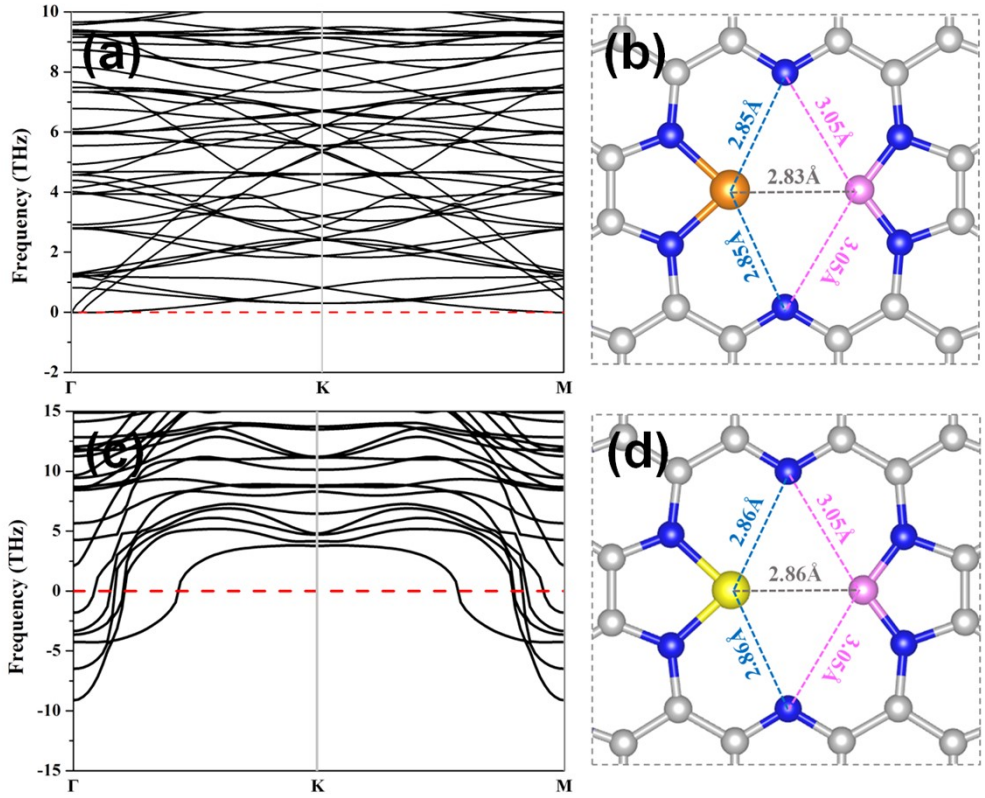


Fig. S1, The calculated phonon dispersion of (a) B&P/C_2N and (c) B&S/C_2N monolayer along the high symmetry lines in the first Brillouin zone. (b) B&P/C_2N and (d) B&S/C_2N structure and the relevant distances are given.

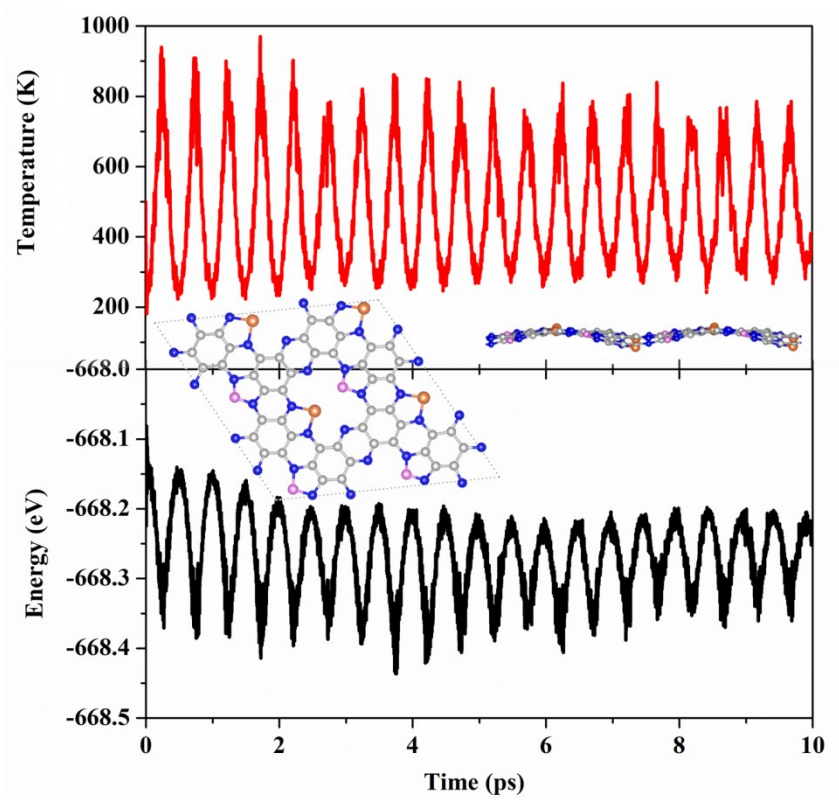
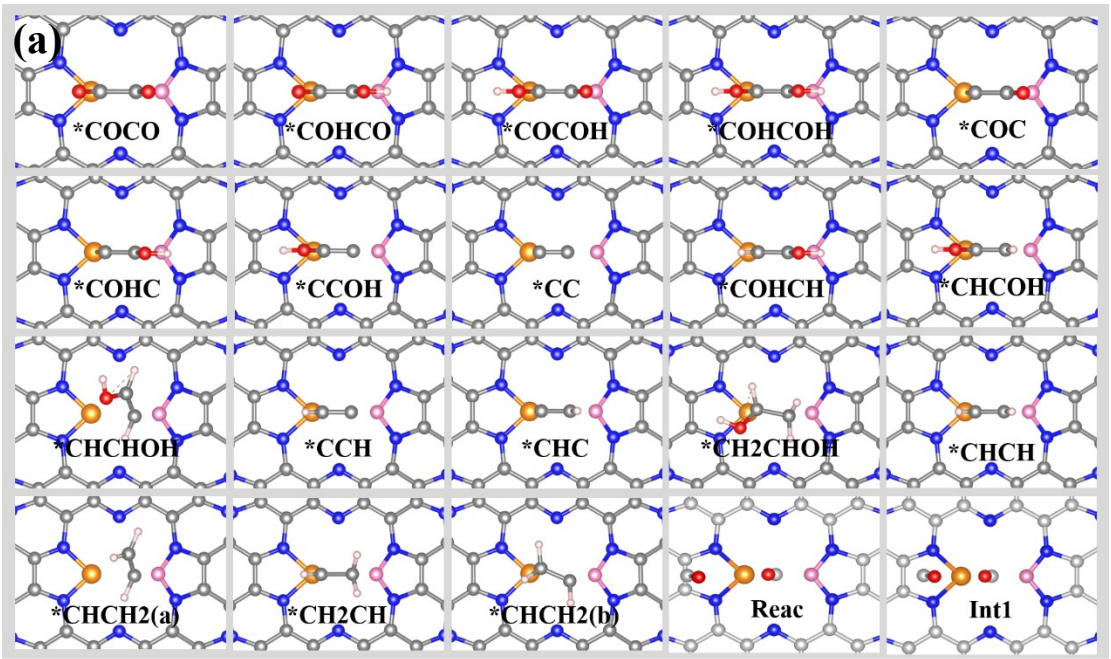


Fig. S2, Variations of temperature and energy versus the time for AIMD simulations of B&P/C_2N.



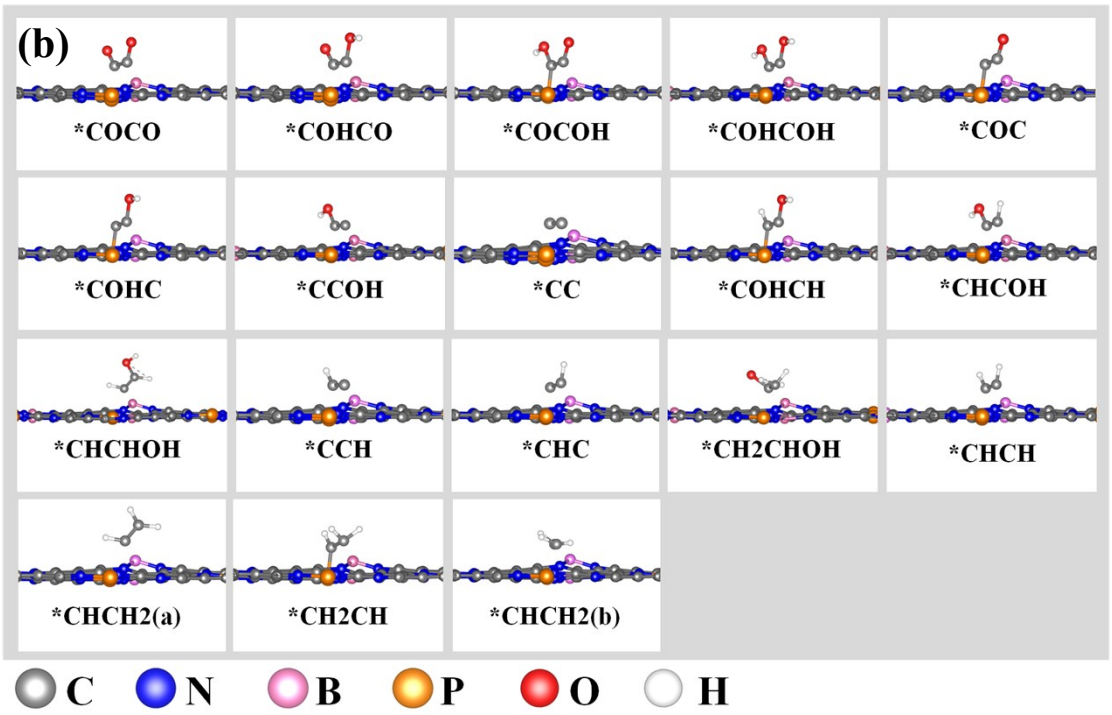


Fig. S3, Schematic illustration of crystal structures in the reaction path. (a) top view and (b) side view.

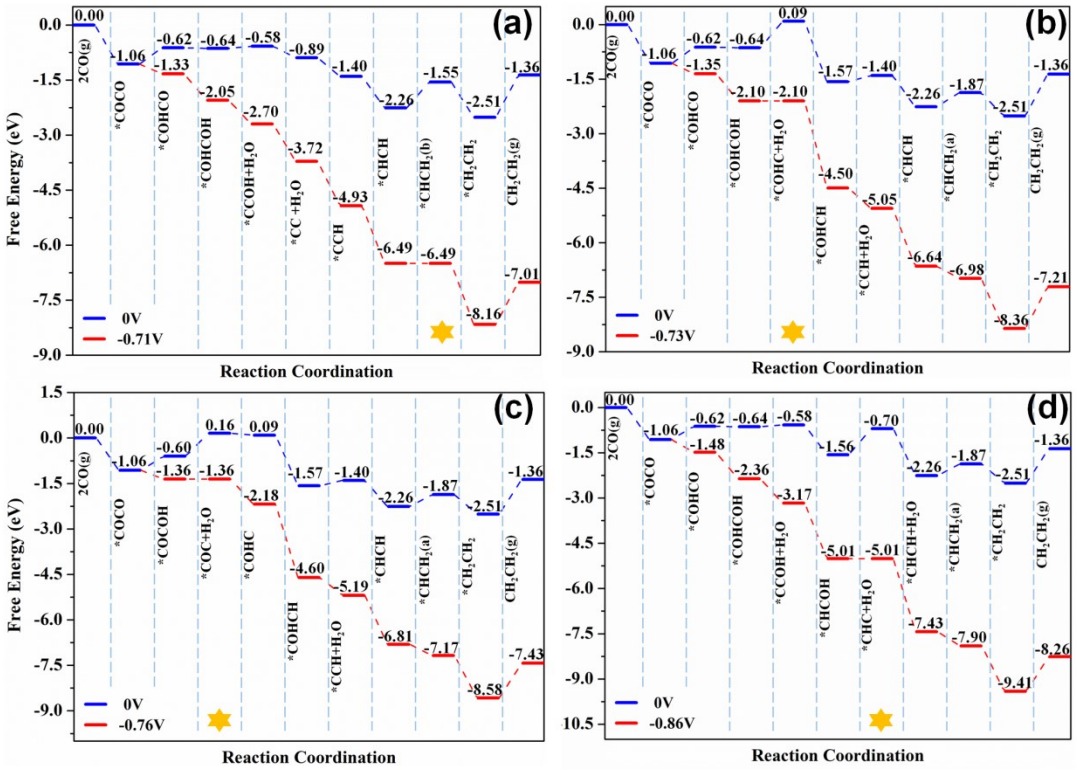


Fig. S4, Gibbs free energy diagrams for CO reduction to C_2H_4.

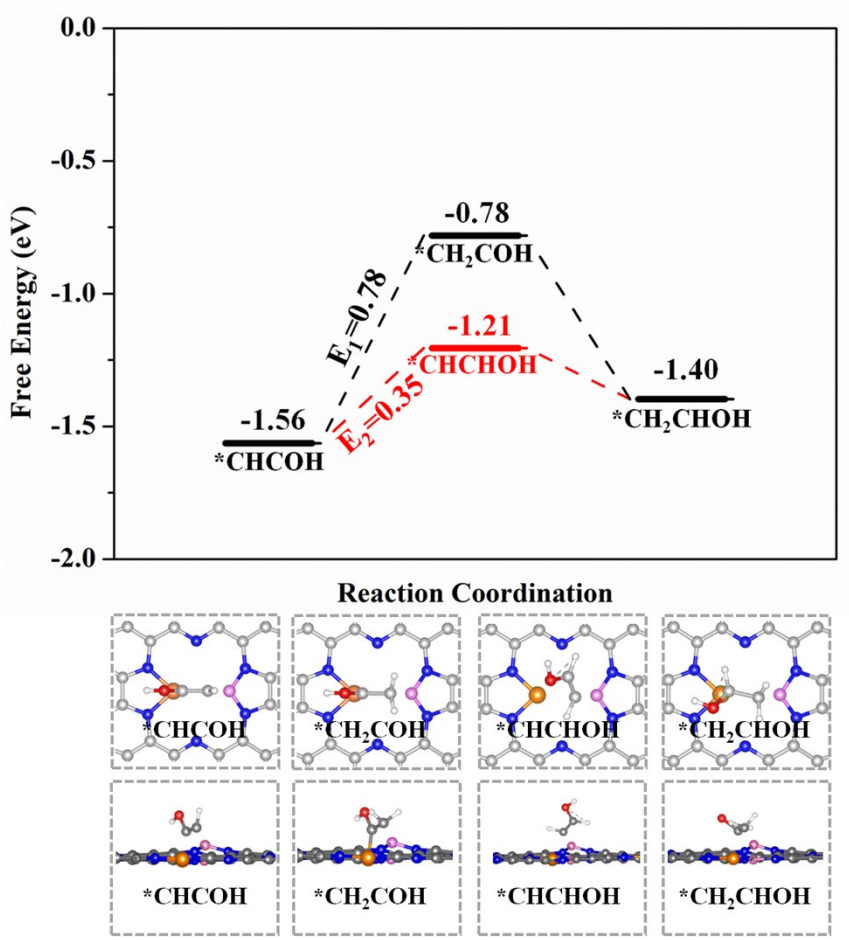


Fig. S5, The calculated free energy diagrams of the *CHCOH hydrogenation to CH_2CHOH. The structures of corresponding reaction intermediates are given in the lower panel.

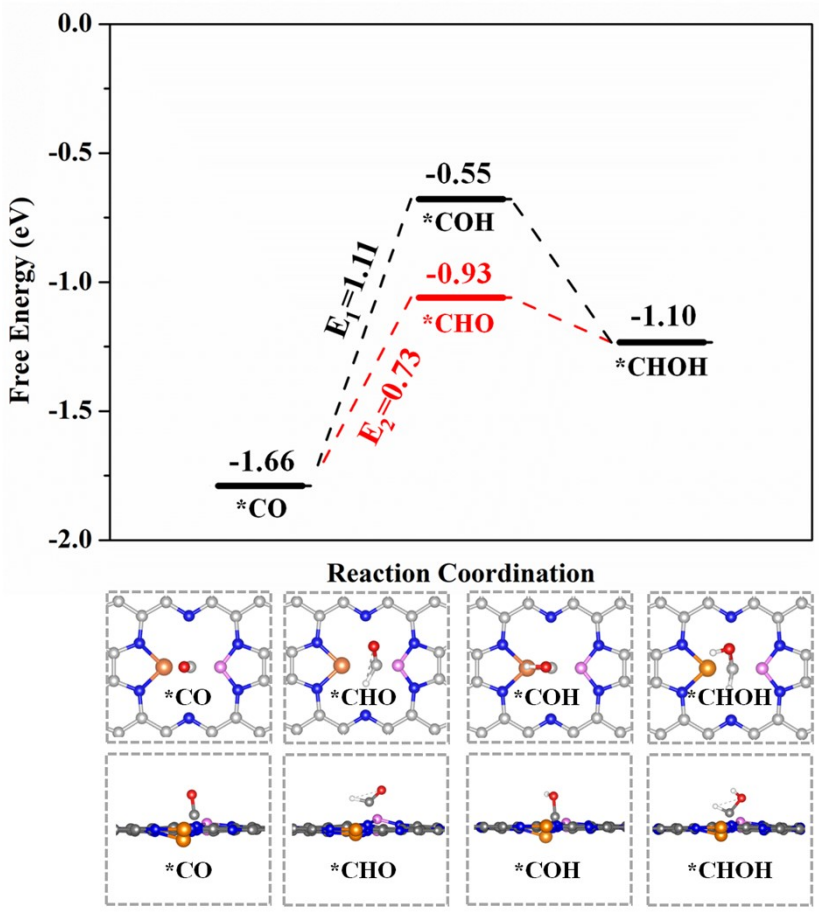


Fig. S6, The calculated free energy diagrams of the CO hydrogenation to *CHOH. The structures of corresponding reaction intermediates are given in the lower panel.

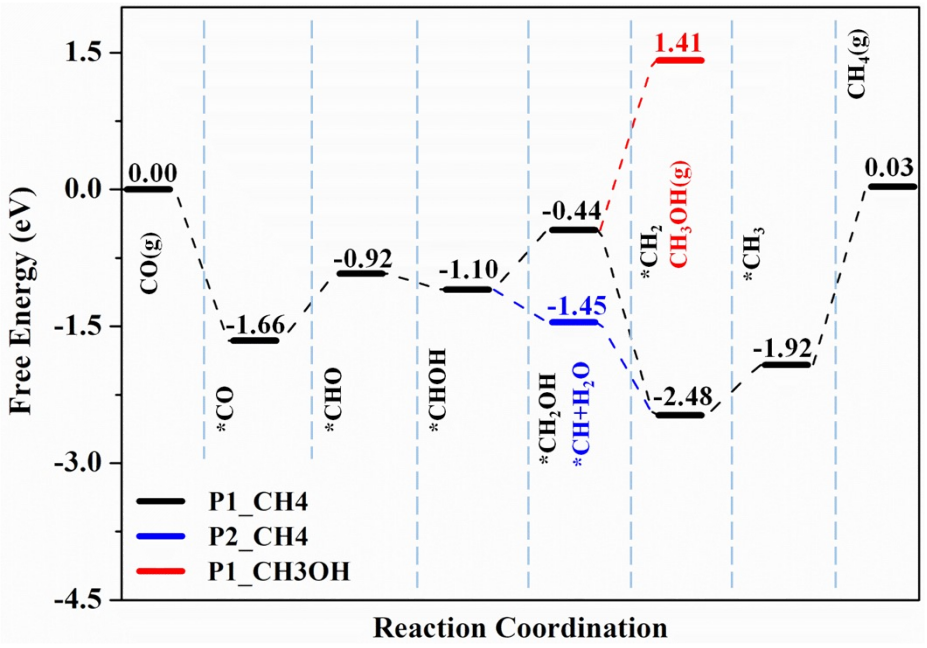


Fig. S7, Gibbs free energy diagrams for CO reduction to C_1 chemicals.

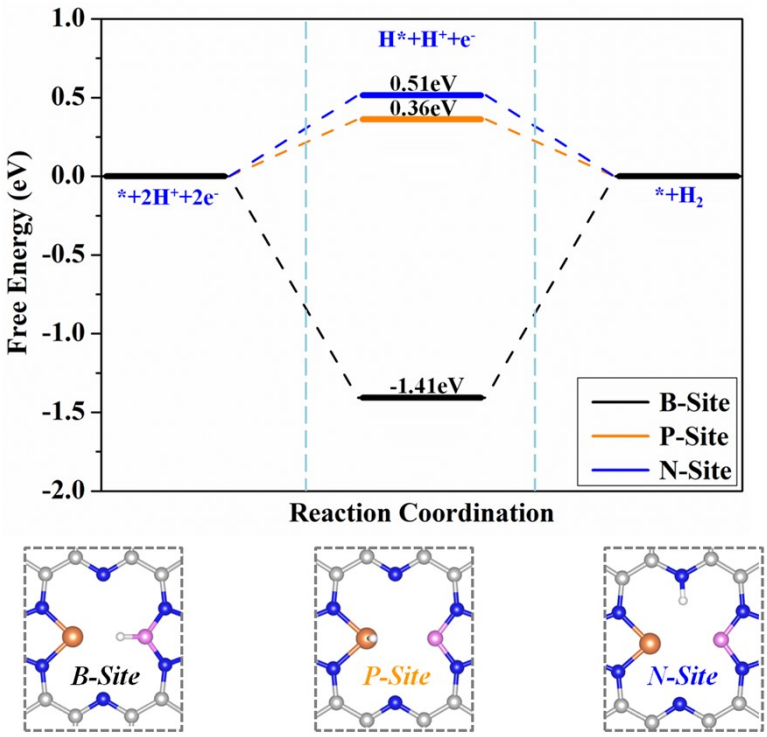


Fig. S8, Gibbs free energy diagrams of HER on B&P/C_2N with different active sites. The corresponding reaction intermediates are given in the lower panel.

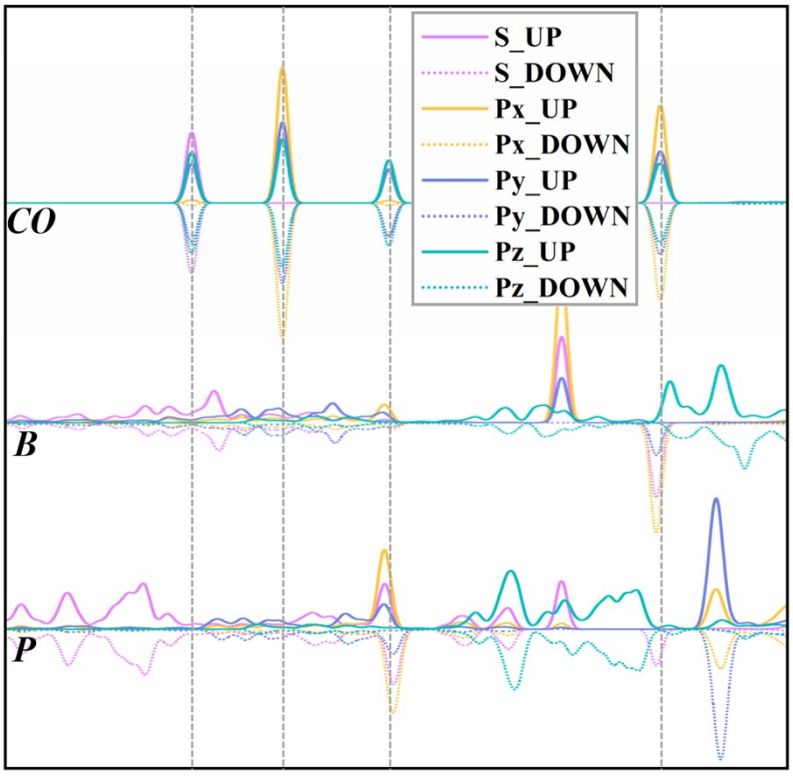


Fig. S9, The calculated projected density of states (PDOS) of B&P/C_2N. The Fermi level energy was set to be zero.

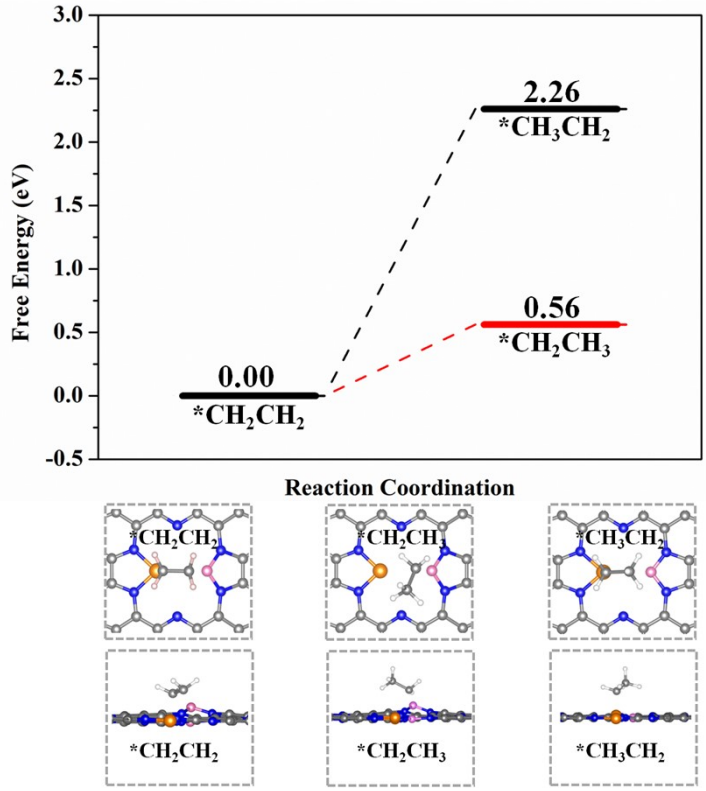


Fig. S10, The calculated free energy diagrams of the *C2H4 hydrogenation. The structures of corresponding reaction intermediates are given in the lower panel.

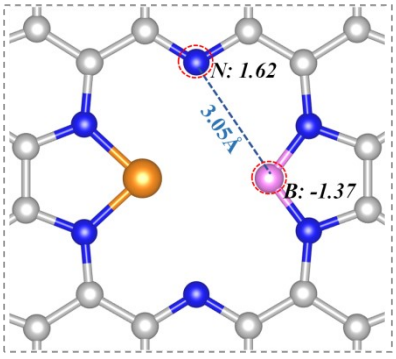


Fig. S11, Relevant distances and bader charge for B and N atom

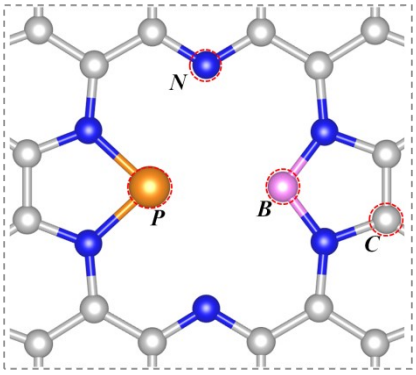


Fig. S12, structure of B&P/C2N and the atom has been listed in Table S4

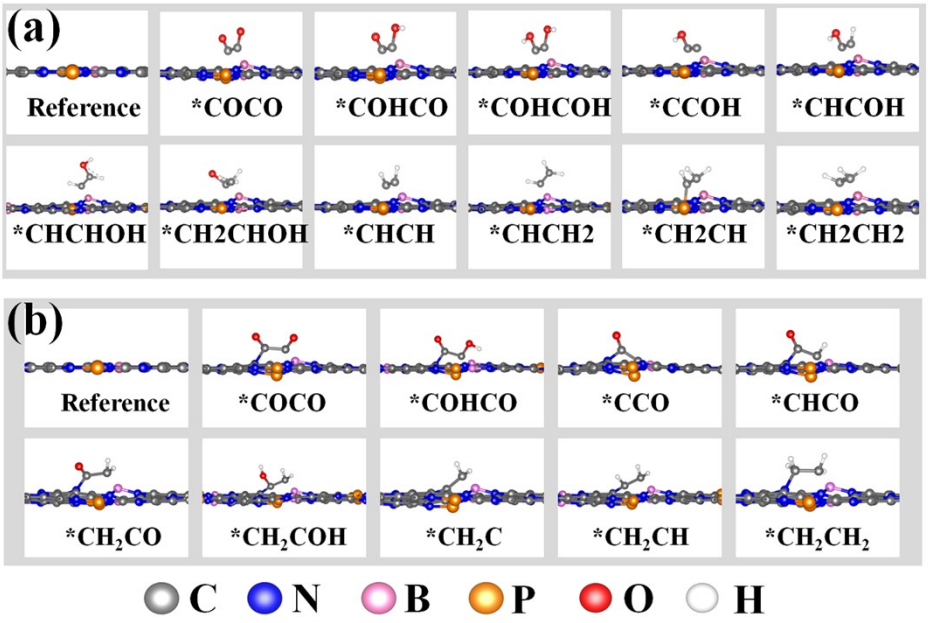


Fig. S13, Side views for Fig.5 (a) and Fig.7 (b) in the manuscript.

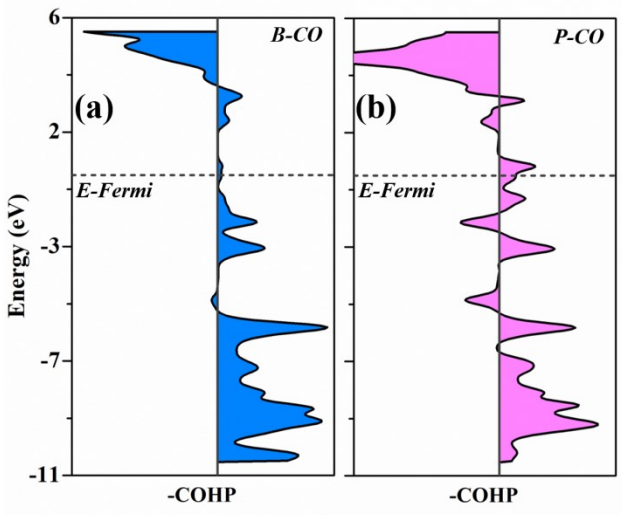


Fig. S14. The crystal orbital Hamilton populations of (a) B-2CO and (b) P-2CO.

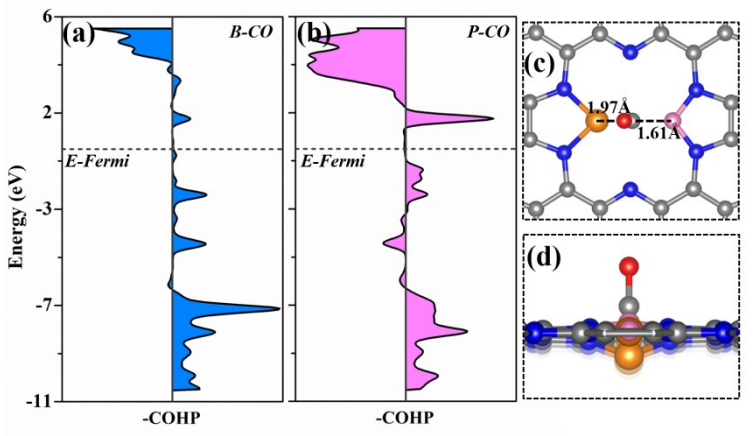


Fig. S15. The crystal orbital Hamilton populations of (a) B-CO and (b) P-CO and the top (c) and side (d) views of CO molecule were captured by B&P/C_2N.

Table S2. The structural information and bader charge of B&P/C2N unit.

Lattice parameters				
	8.405	0.221	0.014	
	-4.011	6.949	0.007	
	0.035	0.045	23.095	
Atom	X	Y	Z	Charge
C	0.674	0.159	0.501	0.405
C	0.841	0.512	0.501	0.548
C	0.515	0.344	0.501	0.353
C	0.320	0.841	0.501	0.465
C	0.154	0.486	0.501	0.506
C	0.481	0.654	0.501	0.353
C	0.154	0.669	0.501	0.530
C	0.481	0.828	0.501	0.412
C	0.320	0.480	0.501	0.459
C	0.841	0.330	0.501	0.598
C	0.515	0.172	0.501	0.413
C	0.674	0.516	0.501	0.395
N	0.658	0.979	0.501	-1.384
N	-0.004	0.677	0.501	-1.168
N	0.336	0.313	0.501	-1.471
N	0.336	0.023	0.501	-1.496
N	0.996	0.320	0.501	-1.184
N	0.658	0.680	0.501	-1.385
B	0.217	0.109	0.501	1.378
P	0.833	0.917	0.501	1.272

Table S3. The information of B and P simple substances, unit of energy is eV.

	Atom_Number	Energy_Total	Energy_Atom
mp-157	4	-22.87	-5.72
mp-1198724	42	-240.21	-5.72
mp-160	12	-82.99	-6.92
mp-161	105	-721.41	-6.87

Table S4. The exact electron charge accumulation and depletion for CO and atoms in B&P/C_2N

	CO	B	P	N	C
B-P Center	1.06	-0.56	-0.21	0.00	-0.13
B-N Center	0.77	-0.59	-0.01	-0.09	-0.07

References

1. J. K. Nørskov; J. Rossmeisl; A. Logadottir; L. Lindqvist; J. R. Kitchin; T. Bligaard; Jónsson, H., Origin of the Overpotential for Oxygen Reduction at a Fuel-Cell Cathode. *J. Phys. Chem. B* **2004,** *108* (46), 17886-17892.
2. Haynes, W. M., CRC handbook of chemistry and physics. *CRC press* **2014**.
3. Zhou, Y.; Che, F.; Liu, M.; Zou, C.; Liang, Z.; De Luna, P.; Yuan, H.; Li, J.; Wang, Z.; Xie, H.; Li, H.; Chen, P.; Bladt, E.; Quintero-Bermudez, R.; Sham, T. K.; Bals, S.; Hofkens, J.; Sinton, D.; Chen, G.; Sargent, E. H., Dopant-induced electron localization drives CO2 reduction to C2 hydrocarbons. *Nat. Chem.* **2018,** *10* (9), 974-980.