Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Reduction reaction of carbon dioxide on precise number of Fe atoms anchored on two-dimensional biphenylene

Na Xing[a], Ziyang Liu[a], Zhongwei Wang[a], Yan Gao*[,a], Qingfang Li*[,b] and Haifeng Wang*[,a]

[a]*Department of Physics, College of Science, Shihezi University, Xinjiang 832003, China*

[b]*School of Physics & Optoelectronic Engineering, Nanjing University of Information Science & Technology, Nanjing 210044, China*

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Fig. S11 Calculated free energy profiles for HCOOH desorption and further hydrogenation on Fe_2@BP.

Fig. S12 Calculated free energy profiles for HCOOH desorption and further hydrogenation on Fe_3@BP.

Fig. S13 (a) Adsorption energies of reaction molecules on Fe_2@BP and (b) free energy diagram of CO_2 reduction on Fe_2@BP by considering an implicit solvent model.

Table S1 The adsorption energies, Zero-point energy (ZPE), entropic corrections (TS) at T = 298 K to the free energies and $(\mathrm{ZPE} - TS)$ values of the gas-phase. The Zero-point energy (ZPE) and entropic corrections (TS) at T = 298 K to the free energies values were taken from NIST-JANAF thermodynamic table.[2]

Table S2 The adsorption energy, Zero-point energy (ZPE), entropic corrections (TS) at T = 298 K to the free energies and (ZPE − *TS*) values of the adsorbed species (with*). The Zero-point energy (ZPE) and entropic corrections (TS) at T = 298 K to the free energies values were obtained by calculating the vibration frequency of the reaction intermediate.

Table S3 The free energy values of Fe_n (n = 1–3) doped BP sheet in Fig. 5a,c,e.

* Corresponding authors. Email: gaoy@shzu.edu.cn, qingfangli@nuist.edu.cn or whfeng@shzu.edu.cn.

Consideration of electrochemical proton-electron transfer

In this work, we employed the computational hydrogen electrode (CHE) model to include the electrode potential correction to the free energy of each state, by considering the electrochemical proton-electron transfer being a function to the applied electrical potential.[1] The protons and electrons are in equilibrium with hydrogen at 0 V, all pH values and 1 atm of pressure. The reaction is used as the reference potential at any pH:

$$\frac{1}{2}H_{2(g)} \leftrightarrow H^{+}_{(aq)} + e^{-}, \quad (1)$$

Under this conditions, the chemical potential (μ) of 1/2H_2 (g) is equivalent to that of a proton-electron pair in aqueous solution. Therefore, the energetics of H_2 (g) is used as electrochemical reference. The effect of an external potential over this equilibrium can be included as a term eU in the following way, where U is the electrode potential:

$$\frac{1}{2}\mu(H_2) - eU = \mu(H^{+} + e^{-}), \quad (2)$$

Consideration of the solvent effect on the catalytic behavior

The electroreduction of CO_2 usually takes place in the aqueous condition, to simulate the reaction in $Fe_{1\text{-}3}$@BP catalysts, we employed the self-consistent continuum solvation model incorporated implicitly with the Poisson-Boltzmann model as implemented in VASPsol.[2,3] The relative dielectric constant corresponding to the medium is selected as $\varepsilon_r = 78.4$,[4] which corresponds to the value of pure water.

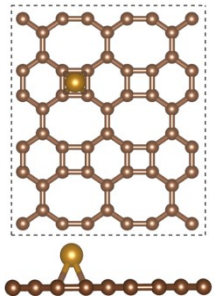
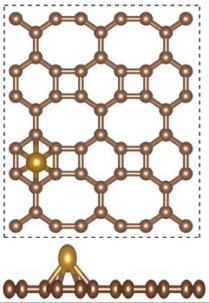
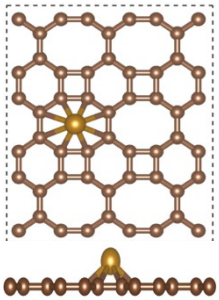
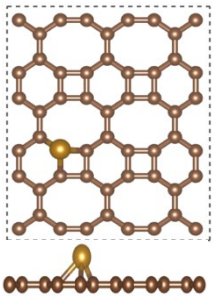
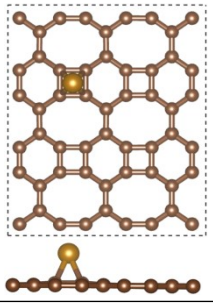
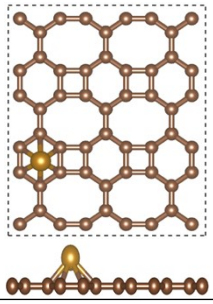
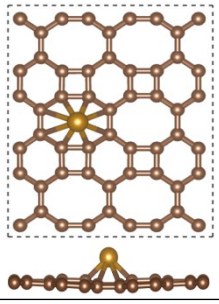
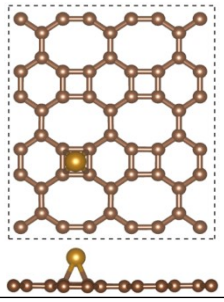
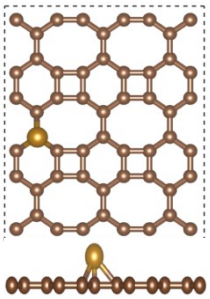
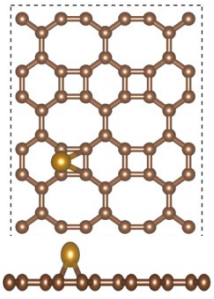
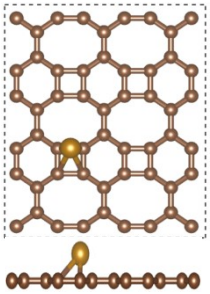
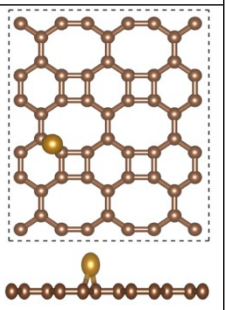
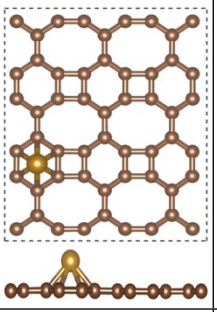
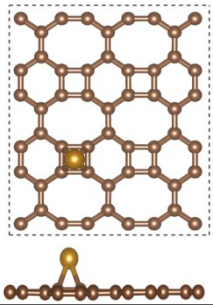
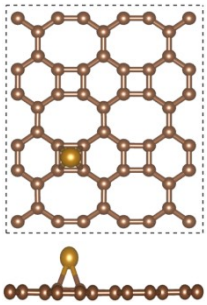
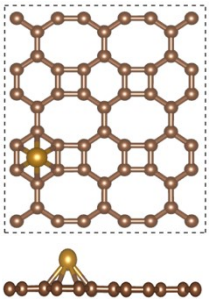
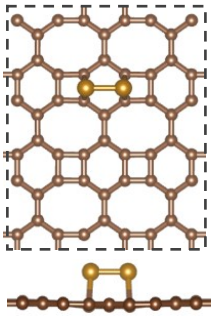
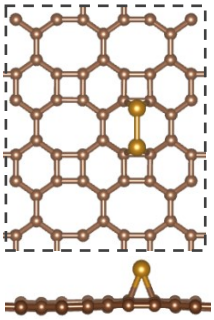
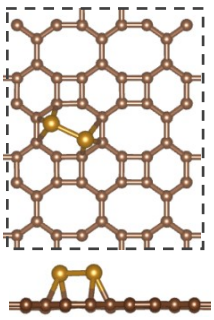
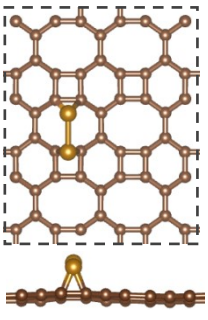
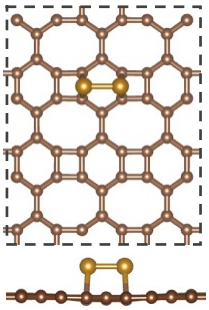
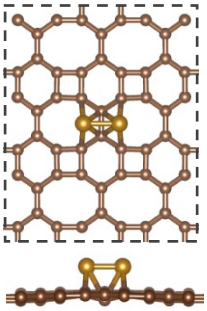
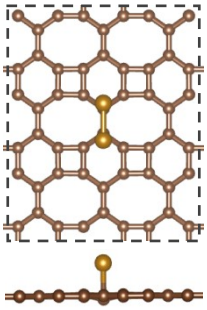
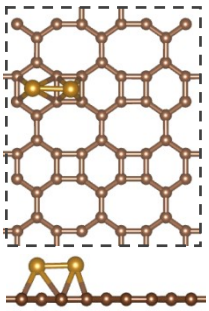
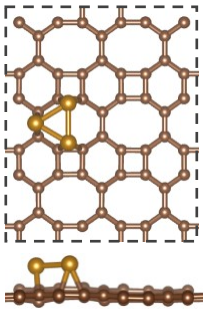
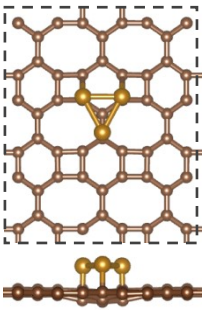
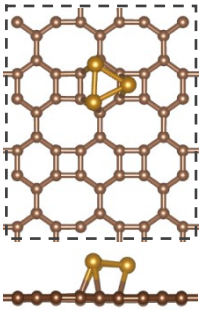
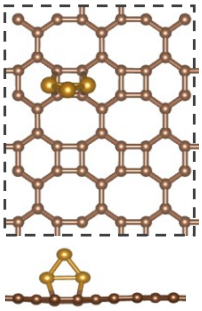
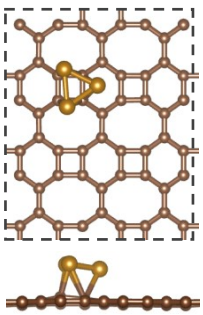
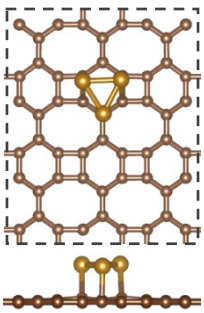
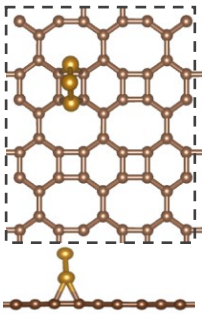
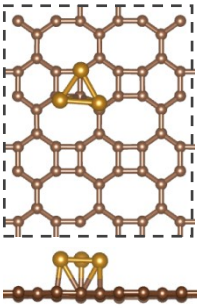
	H_1	H_2	H_3	T_1
Initial				
Final				
Relative energy/eV	0□	0.09	0.45	0.01
	T_2	B_1	B_2	B_3
Initial				
Final				
Relative energy/eV	0.09	0.01	0.01	0.09

Fig. S1 The eight different stable adsorption configurations and relative energies of single Fe atom embedded on the BP monolayer.

Fe_2@BP				
Relative energy/eV	0	0.04	0.96	0.59
Fe_2@BP				
Relative energy/eV	0.57	1.02	0.29	0.57
$Fe_{3@}$BP				
Relative energy/eV	0	0.49	0.50	0.87
Fe_3@BP				
Relative energy/eV	1.04	0.62	1.18	0.87

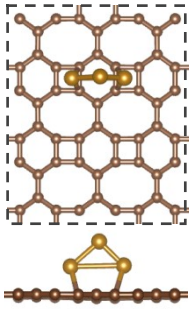
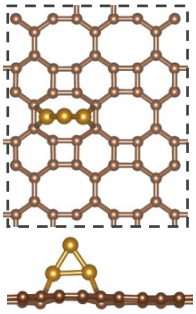
Fe_3@BP				
Relative energy/eV	1.43	3.03		

Fig. S2 The optimized structures and relative energies of Fe_{2-3} anchored on BP sheet.

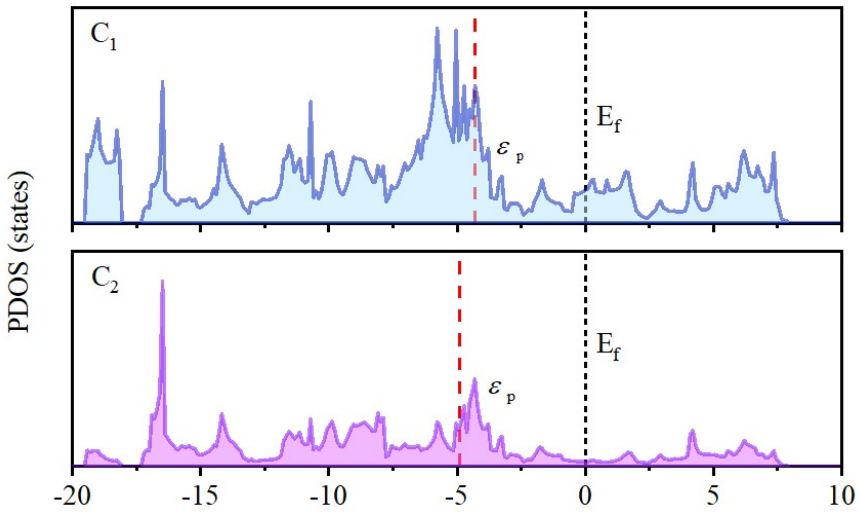


Fig. S3 Partial density of states (PDOS) of the active C sites of 2D BP monolayer with the corresponding *p*-band center (ε_p).

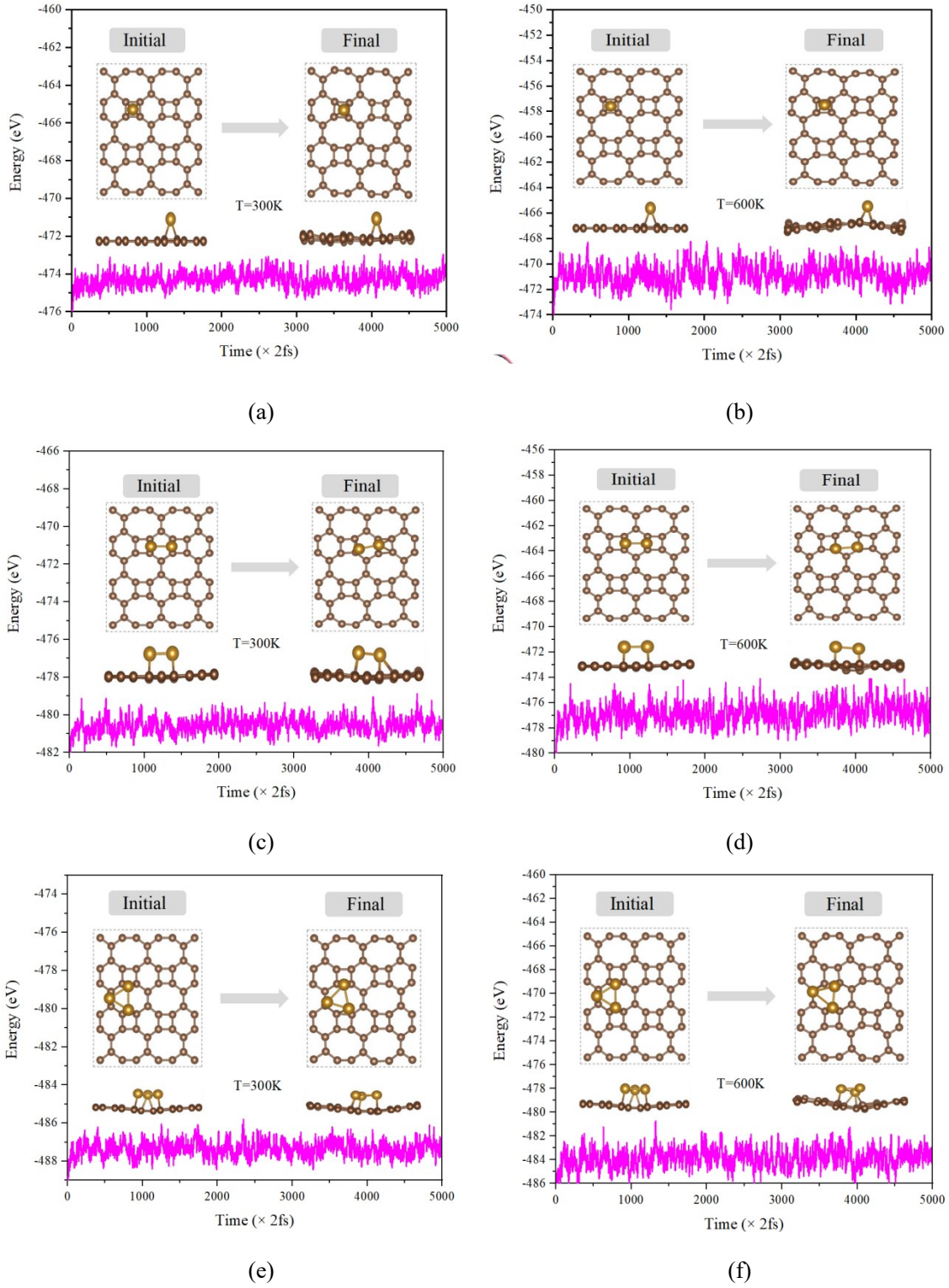


Fig. S4 Evolution of the total energy of ab initio molecular dynamics (AIMD) simulation for Fe_n (n = 1−3) doped BP sheet at 300 and 600 K. The inset are snapshot structures of Fe_{1-3}@BP catalysts at 10 ps.

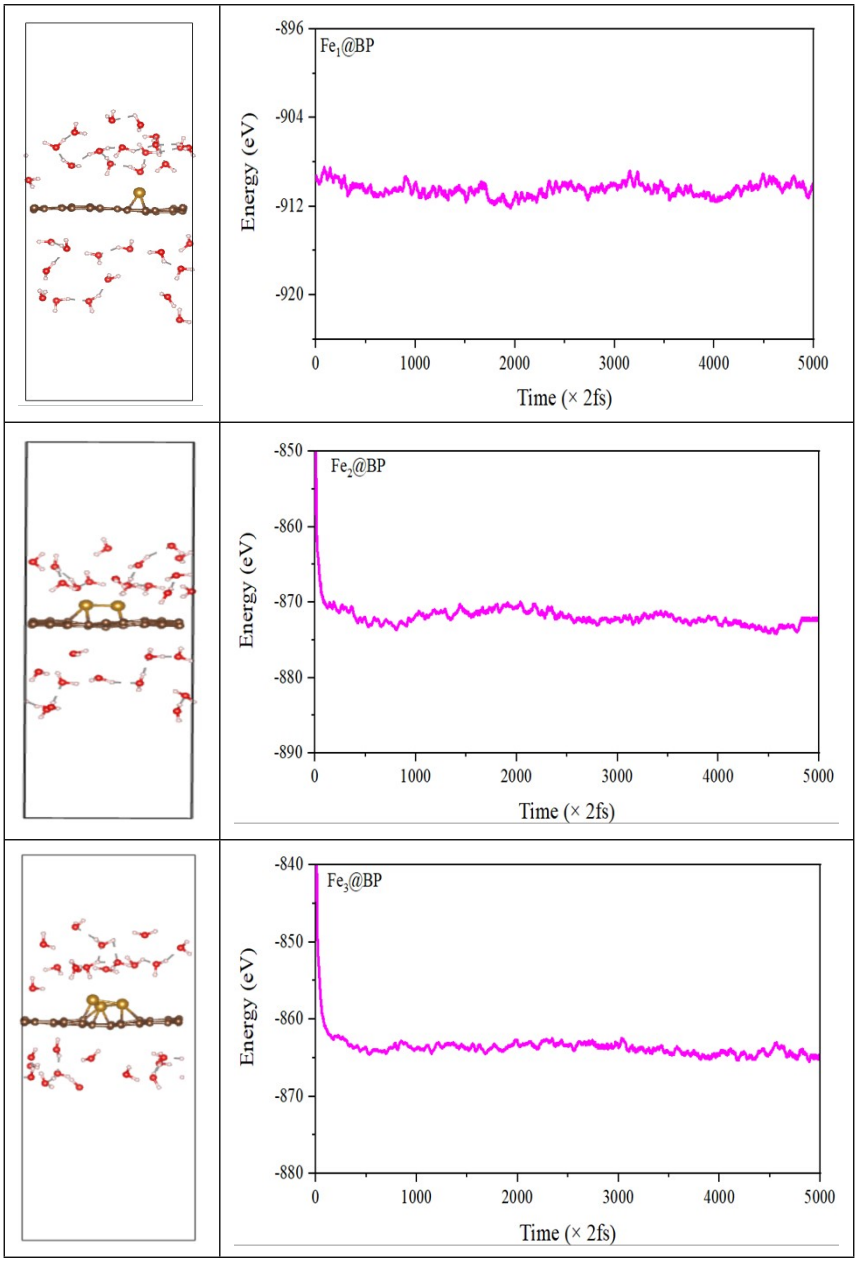
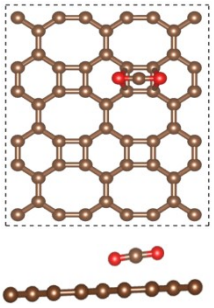
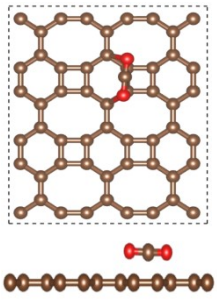
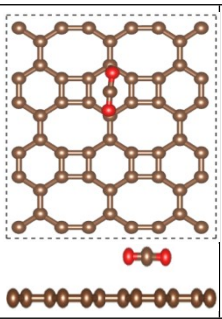
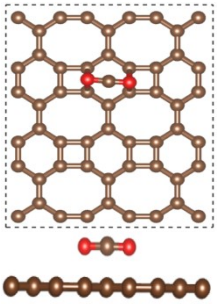
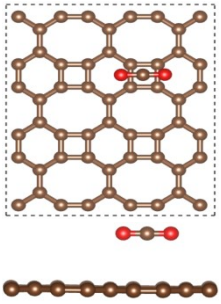
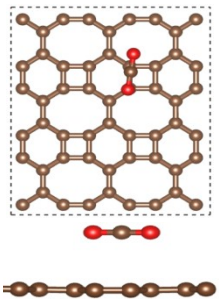
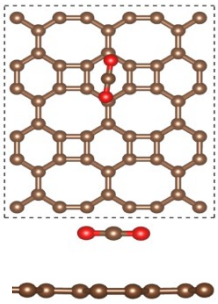
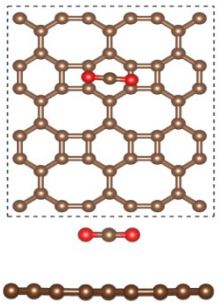
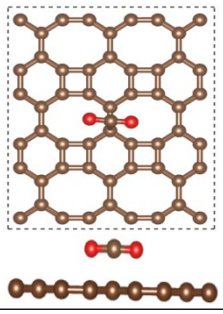
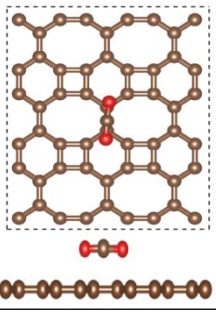
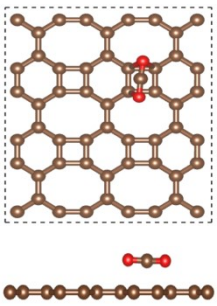
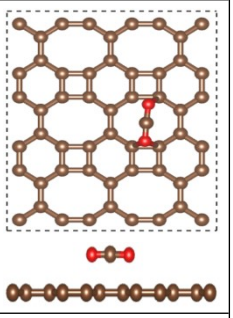
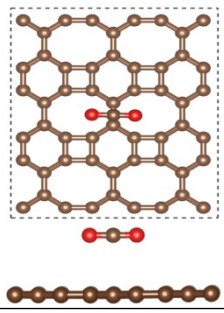
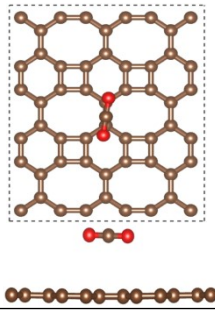
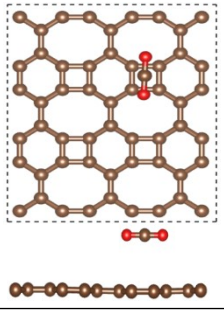
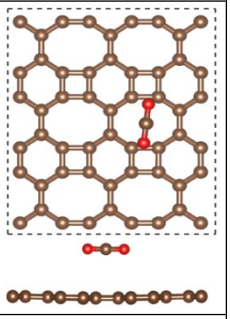


Fig. S5 Structures of Fe_n (n = 1−3) doped BP sheet in a water enviroment after AIMD simulaions at 300K for 10 ps and variations of temperature with simulation time for Fe_{1-3}@BP catalysts.

Initial				
O–C–O (°)	180°	180°	180°	180°
L (Å)	1.84	1.42	1.71	1.82
Final				
O–C–O (°)	179.76°	179.96°	179.79°	179.71°
L(Å)	3.39	3.29	3.32	3.33
E_{ads} /eV	−0.42	−0.42	−0.41	−0.41
Initial				
O–C–O (°)	180°	180°	180°	180°
L(Å)	1.80	1.75	1.87	1.93
Final				
O–C–O (°)	179.56°	179.72°	179.87°	179.92°
L(Å)	3.46	3.30	3.39	3.34
E_{ads} /eV	−0.42	−0.41	−0.43	−0.42

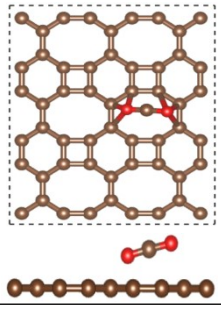
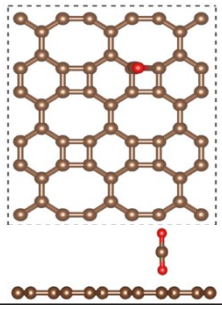
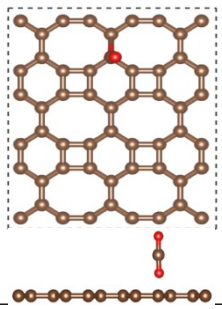
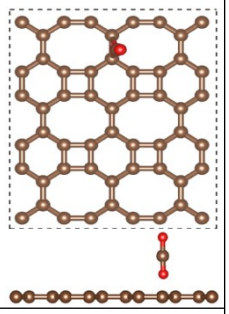
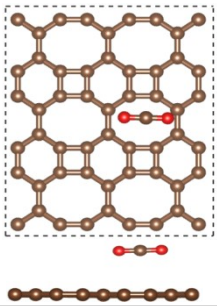
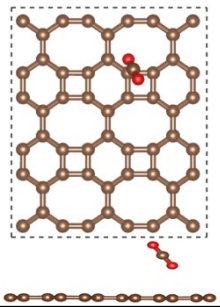
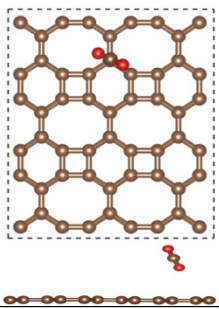
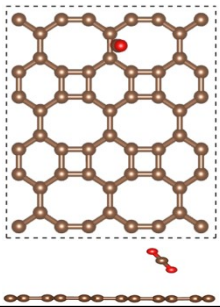
Initial				
O–C–O (°)	180°	180°	180°	180°
L(Å)	1.69	1.41	1.39	1.59
Final				
O–C–O (°)	179.73°	179.89°	179.96°	179.87°
L (Å)	3.45	3.22	3.29	3.26
E_{ads} /eV	−0.41	−0.41	−0.43	−0.41

Fig. S6 Structures before and after CO_2 adsorption on pure BP sheet, the distances between CO_2 and BP substrate, the adsorption energies and the bond angles of the O−C−O for each system are also given. The C, O atoms are shown in brown, red colors, respectively.

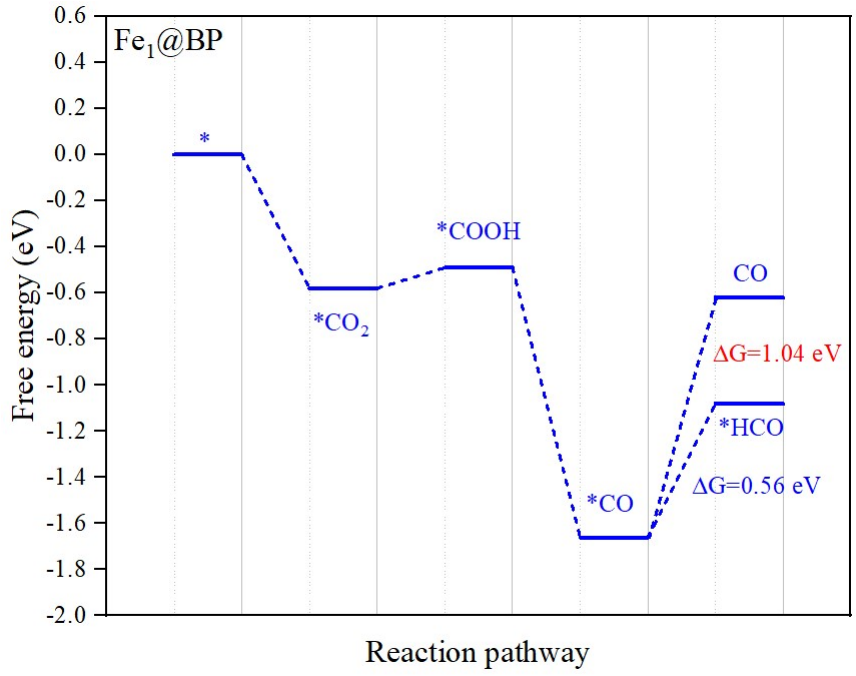


Fig. S7 Calculated free energy profiles for CO desorption and further hydrogenation on Fe_1@BP.

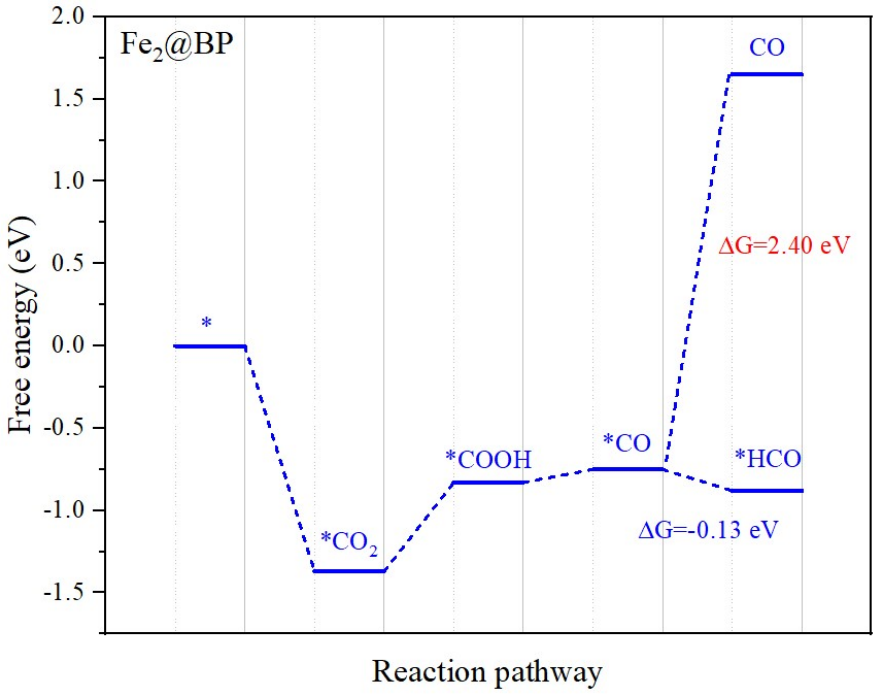


Fig. S8 Calculated free energy profiles for CO desorption and further hydrogenation on Fe_2@BP.

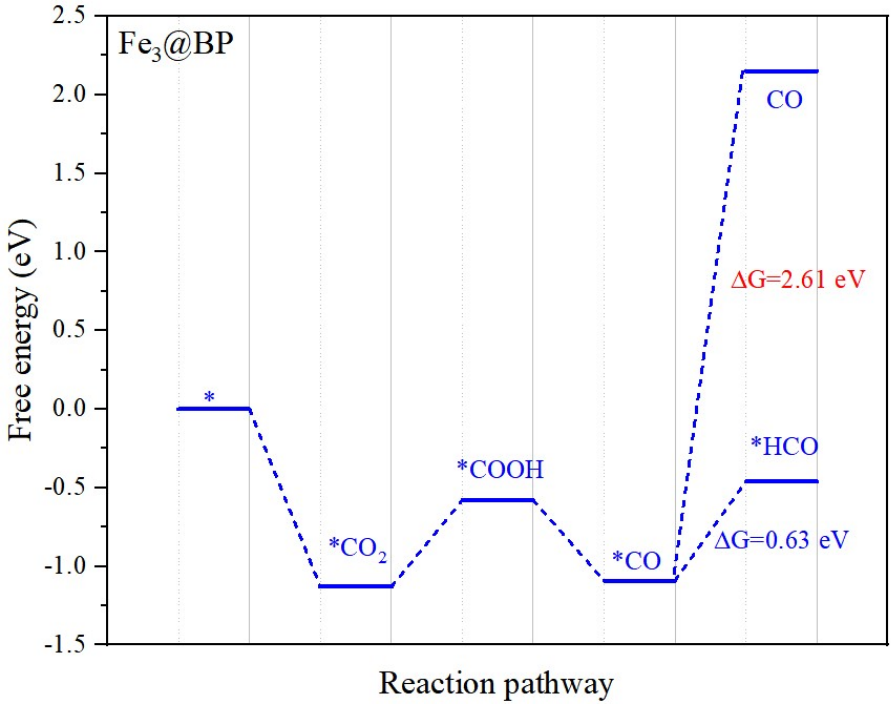


Fig. S9 Calculated free energy profiles for CO desorption and further hydrogenation on Fe_3@BP.

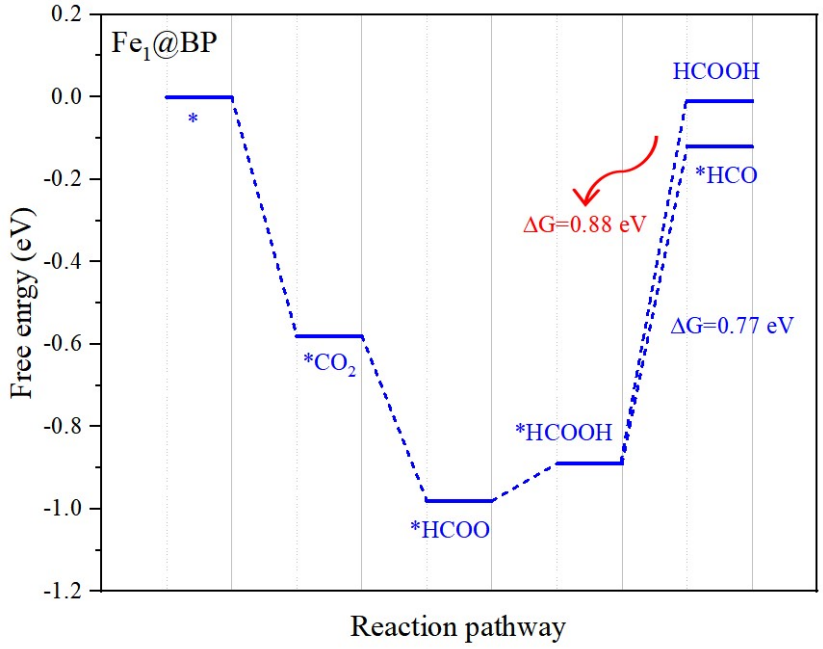


Fig. S10 Calculated free energy profiles for HCOOH desorption and further hydrogenation on Fe_1@BP.

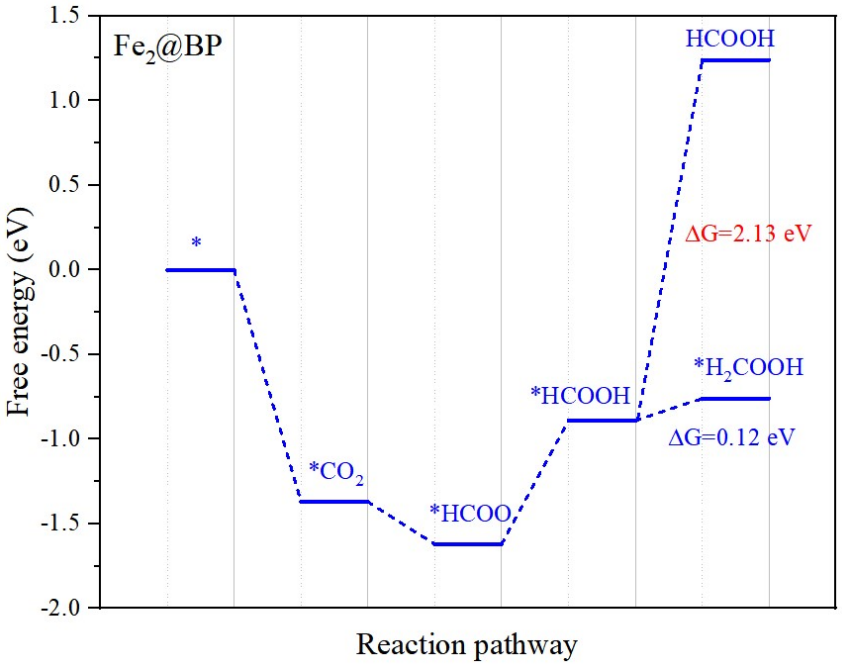


Fig. S11 Calculated free energy profiles for HCOOH desorption and further hydrogenation on Fe_2@BP.

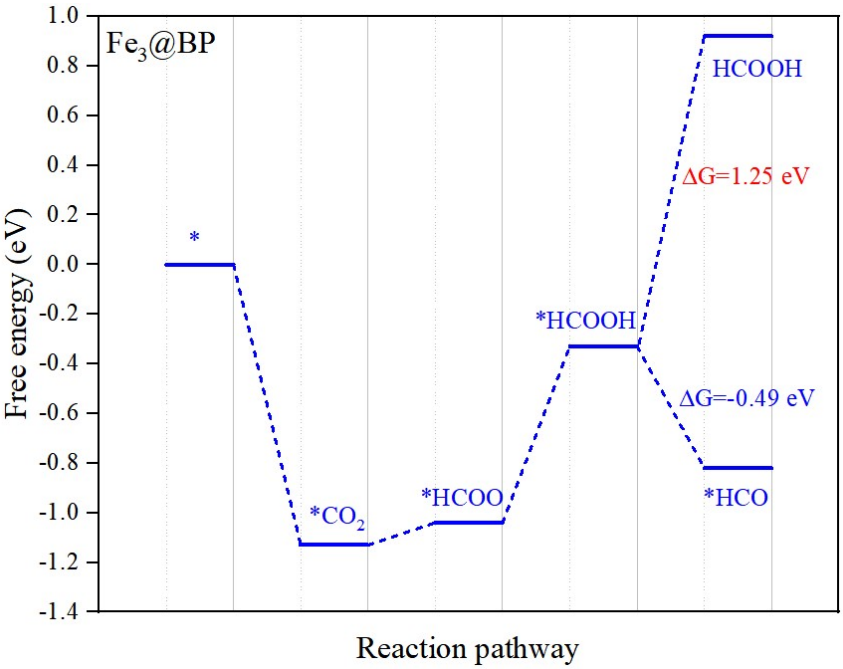
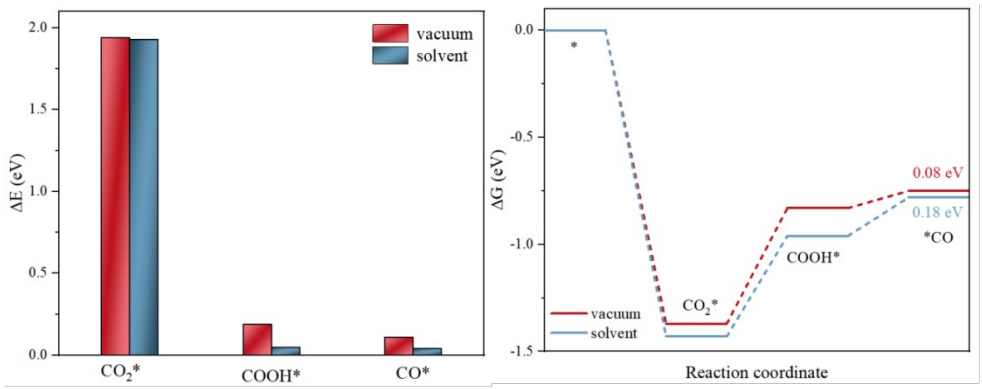


Fig. S12 Calculated free energy profiles for HCOOH desorption and further hydrogenation on Fe_3@BP.



(a) (b)

Fig. S13 (a) Adsorption energies of reaction molecules on Fe_2@BP and (b) free energy diagram of CO_2 reduction on Fe_2@BP by considering an implicit solvent model.

Table S1 The adsorption energies, Zero-point energy (ZPE), entropic corrections (TS) at T = 298 K to the free energies and $(\mathrm{ZPE} - TS)$ values of the gas-phase. The Zero-point energy (ZPE) and entropic corrections (TS) at T = 298 K to the free energies values were taken from NIST-JANAF thermodynamic table.[5]

species	E_{ads} (eV)	ZPE (eV)	*TS* (eV)	ZPE – *TS* (eV)
H_2	–6.77	0.27	0.42	–0.15
H_2O	–14.22	0.58	0.65	–0.07
CO_2	–22.95	0.31	0.65	–0.34
CO	–14.77	0.14	0.67	–0.53
HCOOH	–29.88	0.90	1.02	–0.12
H_2CO	–22.13	0.70	0.66	0.04
CH_3OH	–30.22	1.35	0.79	0.56
CH_4	–24.04	1.20	0.60	0.60

Table S2 The adsorption energy, Zero-point energy (ZPE), entropic corrections (TS) at T = 298 K to the free energies and (ZPE − *TS*) values of the adsorbed species (with*). The Zero-point energy (ZPE) and entropic corrections (TS) at T = 298 K to the free energies values were obtained by calculating the vibration frequency of the reaction intermediate.

Fe_1@BP	E_{ads} (eV)	ZPE (eV)	*TS* (eV)	ZPE – *TS* (eV)
*CO_2	–503.64	0.51	0.28	0.23
*COOH	–507.18	0.67	0.26	0.41
*CO	–512.15	1.12	0.37	0.75
*HCO	–500.36	0.50	0.16	0.34
*H_2CO	–503.48	0.79	0.15	0.64
*H_2COH	–507.21	1.11	0.18	0.93
*CH_3OH	–512.10	1.29	0.34	0.95
Fe_1@BP	E_{ads} (eV)	ZPE (eV)	*TS* (eV)	ZPE – *TS* (eV)
*CO_2	–503.64	0.52	0.28	0.24
*HCOO	–507.80	0.79	0.26	0.53
*HCOOH	–511.31	0.96	0.29	0.67
*HCO	–514.03	1.14	0.43	0.71
*H_2CO	–504.33	0.82	0.18	0.64
*H_3CO	–508.24	1.12	0.21	0.91
*O	–511.27	1.45	0.23	1.22
*OH	–492.12	0.36	0.16	0.20
*H_2O	–495.13	0.67	0.24	0.43
Fe_2@BP	E_{ads} (eV)	ZPE (eV)	*TS* (eV)	ZPE – *TS* (eV)
*CO_2	–510.99	0.38	0.30	0.08
*COOH	–514.18	0.70	0.34	0.36
*CO	–517.68	0.87	0.39	0.48
*HCO	–506.72	0.53	0.31	0.22
*H_2CO	–510.64	0.85	0.25	0.60
*H_2COH	–513.87	1.16	0.30	0.86

*CH_3OH	–518.83	1.37	0.38	0.99
Fe_2@BP	E_{ads} (eV)	ZPE (eV)	*TS* (eV)	ZPE – *TS* (eV)
*CO_2	–510.99	0.38	0.30	0.08
*HCOO	–514.94	0.68	0.35	0.33
*HCOOH	–517.95	0.98	0.36	0.62
*H_2COOH	–521.67	1.30	0.30	1.00
*H_2CO	–524.82	1.46	0.37	1.09
*H_3CO	–514.69	1.20	0.36	0.84
*O	–518.90	1.38	0.41	0.97
*OH	–498.65	0.44	0.22	0.22
*H_2O	–500.55	0.77	0.26	0.51
Fe_3@BP	E_{ads} (eV)	ZPE (eV)	*TS* (eV)	ZPE – *TS* (eV)
*CO_2	–517.74	0.43	0.39	0.04
*COOH	–520.89	0.71	0.43	0.28
*CO	–525.07	0.98	0.49	0.49
*HCO	–513.29	0.57	0.40	0.17
*H_2CO	–517.13	0.82	0.39	0.43
*H_2COH	–520.36	1.16	0.44	0.72
*CH_3OH	–525.64	1.37	0.49	0.88
Fe_3@BP	E_{ads} (eV)	ZPE (eV)	*TS* (eV)	ZPE – *TS* (eV)
*CO_2	–517.74	0.43	0.39	0.04
*HCOO	–521.44	0.79	0.42	0.37
*HCOOH	–524.37	0.97	0.42	0.55
*HCO	–528.64	1.26	0.39	0.87
*H_2CO	–517.01	0.87	0.42	0.45
*H_3CO	–520.53	1.21	0.42	0.79
*O	–523.65	1.49	0.40	1.09
*OH	–504.59	0.45	0.40	0.05
*H_2O	–508.04	0.75	0.39	0.36

Table S3 The free energy values of Fe_n (n = 1–3) doped BP sheet in Fig. 5a, c, e.

Fe_1@BP	ΔG (eV)	Uphill potentials (V)
*H	–0.68	–0.68
*COOH	–0.49	
*CO	–1.66	
CO	–0.62	–1.04
*HCO	–1.08	–0.58
*H_2CO	–0.53	–0.55
*H_2COH	0.10	–0.63
*CH_3OH	–1.29	
CH_3OH	–0.70	–0.59
Fe_1@BP	ΔG (eV)	U_L (V)
*H	–0.68	–0.68
*HCOO	–0.98	
*HCOOH	–0.89	–0.09
HCOOH	–0.01	–0.88
*HCO	–0.12	–0.77
*H_2CO	–1.32	
*H_3CO	–1.49	
*O	–0.77	–0.72
*O+CH_4	–1.12	0.35
*OH	–2.27	
*H_2O	–1.93	
H_2O	-1.68	–0.25
Fe_2@BP	ΔG (eV)	U_L (V)
*H	–0.89	–0.89
*COOH	–0.83	

*CO	–0.75	–0.08
CO	1.65	–2.40
*HCO	–0.88	
*H_2CO	–0.96	
*H_2COH	–0.48	–0.48
*CH_3OH	–1.84	
CH_3OH	–1.39	–0.45
Fe_2@BP	ΔG (eV)	U_L (V)
*H	–0.89	–0.89
*HCOO	–1.62	
*HCOOH	–0.89	–0.73
HCOOH	1.24	–2.13
*H_2COOH	–0.76	–0.13
*H_2CO	–0.36	–0.40
*H_3CO	–1.32	
*O	–1.93	
*O+CH_4	–2.01	0.07
*OH	–2.41	
*H_2O	–2.57	
H_2O	–2.47	–0.10
Fe_3@BP	ΔG (eV)	U_L (V)
*H	–0.93	–0.93
*COOH	–0.58	
*CO	–1.09	
CO	2.15	–2.61
*HCO	–0.46	–0.63
*H_2CO	–0.58	
*H_2COH	–0.06	–0.52
*CH_3OH	–1.73	

CH_3OH	–1.21	–0.52
Fe_3@BP	ΔG (eV)	U_L (V)
*H	–0.93	–0.93
*HCOO	–1.04	
*HCOOH	–0.33	–0.71
HCOOH	0.92	–1.25
*HCO	–0.82	
*H_2CO	–0.45	–0.37
*H_3CO	–0.17	–0.28
*O	0.49	–0.66
*O+CH_4	–1.78	2.27
*OH	–1.49	
*H_2O	–1.17	–0.32
H_2O	–0.54	–0.63

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