Supplementary Information

Methane activation on Fe- and FeO-embedded graphene and boron nitride sheet: role of atomic defects in catalytic activities

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Table S1 Electronic energies for Fe-BN, Fe-GP, FeO-BN, and FeO-GP catalysts from PBE calculations.

System	Spin multiplicity	*Relative energy (kcal mol^{-1})
Fe-BN	Doublet	0.0
	Quartet	17.0
	Sextet	50.3
	Octet	111.4
Fe-GP	Singlet	0.0
	Triplet	7.9
	Quintet	40.2
	Septet	74.6
FeO-BN	Doublet	9.2
	Quartet	0.0
	Sextet	39.5
	Octet	104.2
FeO-GP	Singlet	0.1
	Triplet	0.0
	Quintet	31.1
	Septet	78.5

*Relative energy compared to the most stable state

Table S2 Calculated adsorption energies for methane (CH_4) adsorption on perfect boron nitride (BN) sheet and perfect graphene (GP).

System	Adsorption energy (kcal mol^{-1})	
	PBE/DNP	PBE+D2//PBE/DNP
CH_4/BN at B atom	–0.7	–3.9
CH_4/BN at N atom	–0.7	–4.0
CH_4/GP	–0.5	–2.9

Table S3 Adsorption energies (kcal mol^{-1}) of methane adsorbed on Fe-BN and Fe-GP catalysts at various fashions of methane interacted to the Fe active center calculated by PBE+D2//PBE/DNP. η^1 and η^3 fashions on Fe-BN was not found.

Fashion of methane	CH_4/BN	CH_4/GP
η^1	-	–5.2 (–2.9)
η^2	–14.4 (–11.1)	–11.6 (–8.1)
η^3	-	–10.5 (–7.0)

Table S4 Structural parameters for CH_4/Fe-BN system. Bond distances are in Å.

Parameter	CH_4/Fe-BN system			
	Isolate state	Adsorption	Transition state	Product
Fe–B1	1.90	1.93	1.95	2.02
Fe–B2	1.90	1.92	1.92	1.93
Fe–B3	1.90	1.90	1.95	1.98
Fe–H_m	-	1.88	1.51	1.54
Fe–C_m	-	2.24	1.99	1.96
C_m–H_m	1.10	1.13	1.63	2.46
C_m–$H_m^{'}$	1.10	1.12	1.11	1.11
B1–H_m	-	2.95	2.04	1.42

Table S5 Structural parameters for CH_4/Fe-GP system. Bond distances are in Å.

Parameter	CH_4/Fe-BN system			
	Isolate state	Adsorption	Transition state	Product
Fe–C1	1.77	1.78	1.86	1.90
Fe–C2	1.77	1.78	1.78	1.78
Fe–C3	1.77	1.78	1.78	1.78
Fe–H_m	-	1.96	1.48	1.58
Fe–C_m	-	2.37	1.98	1.98
C_m–H_m	1.10	1.12	1.85	2.40
C_m–$H_m^{'}$	1.10	1.11	1.10	1.10
C1–H_m	-	2.78	1.73	1.23

Table S6 Structural parameters for CH_4/FeO-BN system (only the lowest spin state of each reaction step). Bond distances are in Å.

Parameters	CH_4/FeO-BN system							
	Isolated state	ADS_CH_4	TS1	INT_radical	INT_ nonradical	TS2_radical	TS2_ nonradical	PROD_ CH_3OH
Fe–B1	1.99	1.99	1.97	1.98	1.96	1.96	1.92	1.92
Fe–B2	2.00	2.00	1.95	1.98	2.07	1.96	1.98	1.91
Fe–B3	1.99	1.99	2.00	1.94	1.98	1.96	1.93	1.91
Fe–O	1.63	1.63	1.72	1.77	1.77	1.84	1.87	2.03
O–H_m	-	2.46	1.10	0.97	0.97	0.98	0.98	0.98
C_m–H_m	1.10	1.10	1.48	1.09	1.10	1.09	1.10	-
Fe–C_m	-	-	-	-	1.97	2.46	2.41	-
O–C_m	-	-	-	3.20	3.29	1.98	1.88	1.46

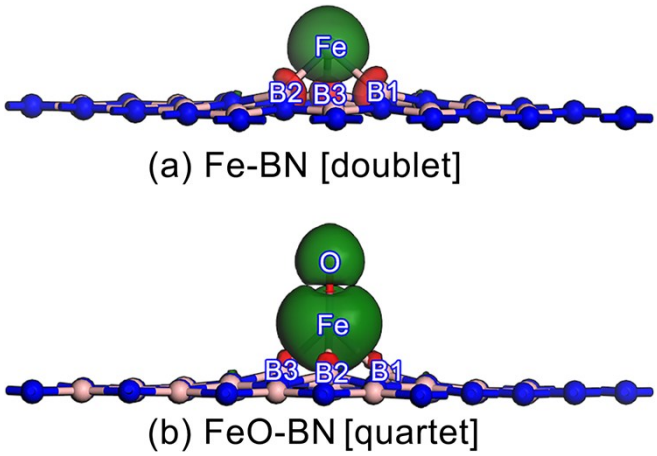


Fig. S1 Spin density for (a) Fe-BN [doublet state] and (b) FeO-BN [quartet state]. The green and red regions illustrate α-electron and β-electron density. The isosurface value is ±0.03 e $Å^{-3}$.

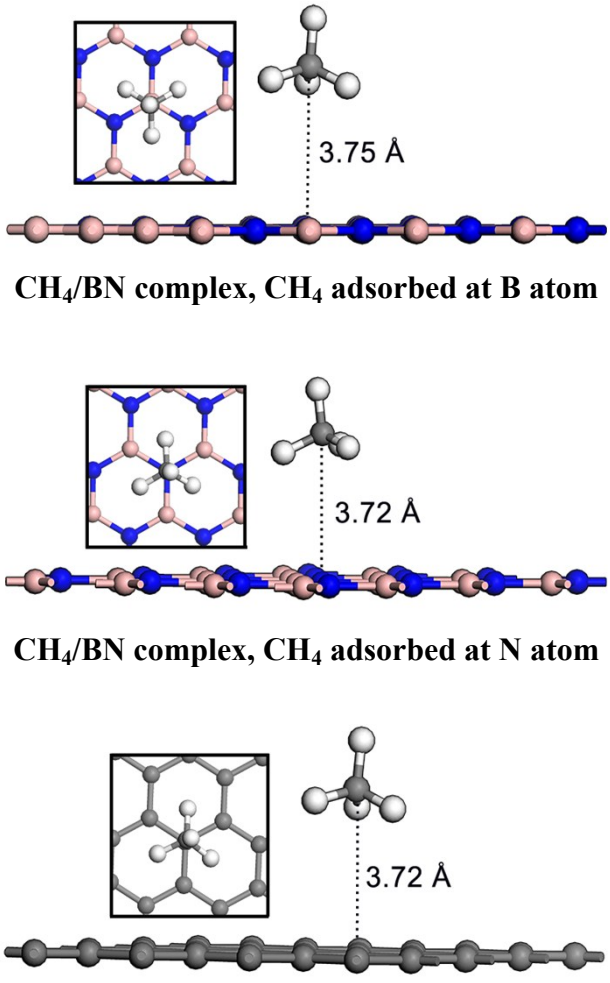


Fig. S2 Optimized structures of methane (CH_4) adsorbed on perfect boron nitride (BN) and perfect graphene (GP) sheet.

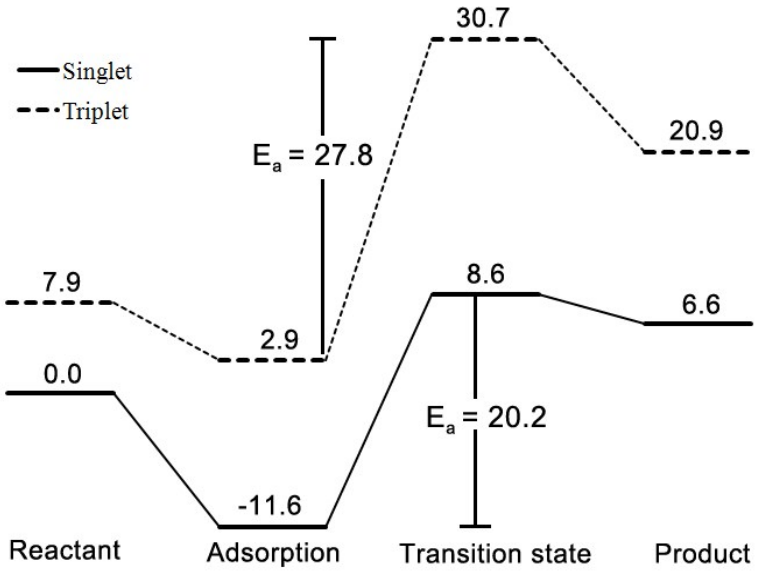


Fig. S3 Energy profiles for methane activation over Fe-GP calculated at PBE-D2. Energies are in kcal mol^{-1}.

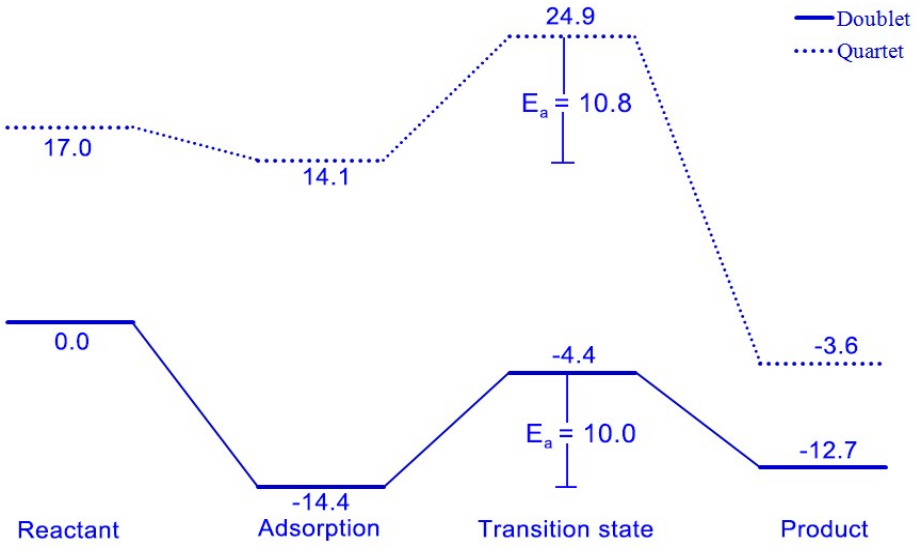


Fig. S4 Energy profiles for methane activation over Fe-BN calculated at PBE-D2. Energies are in kcal mol^{-1}.

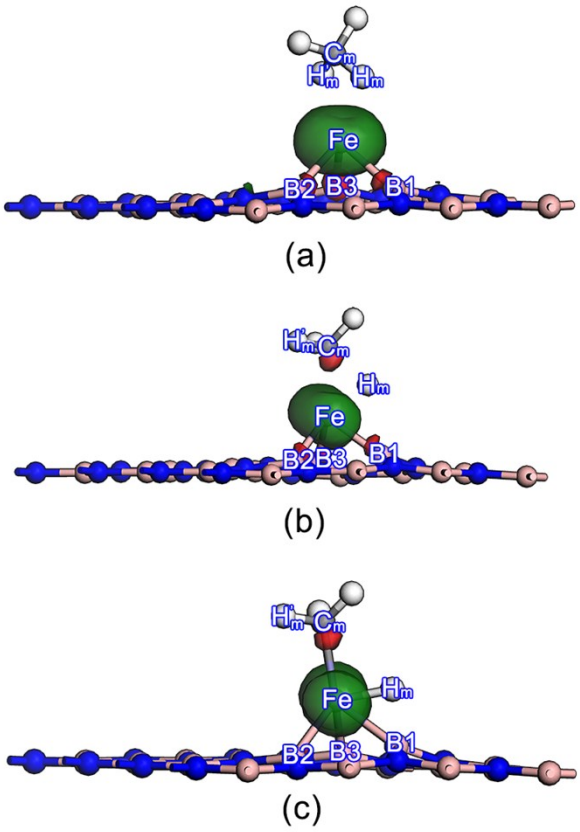


Fig. S5 Spin density for methane activation over Fe-BN on doublet potential energy surface: (a) Adsorption, (b) Transition state, and (c) Product. The green and red isosurfaces stand for α-electron and β-electron density and the isosurface plotted at ±0.03 e $Å^{-3}$.

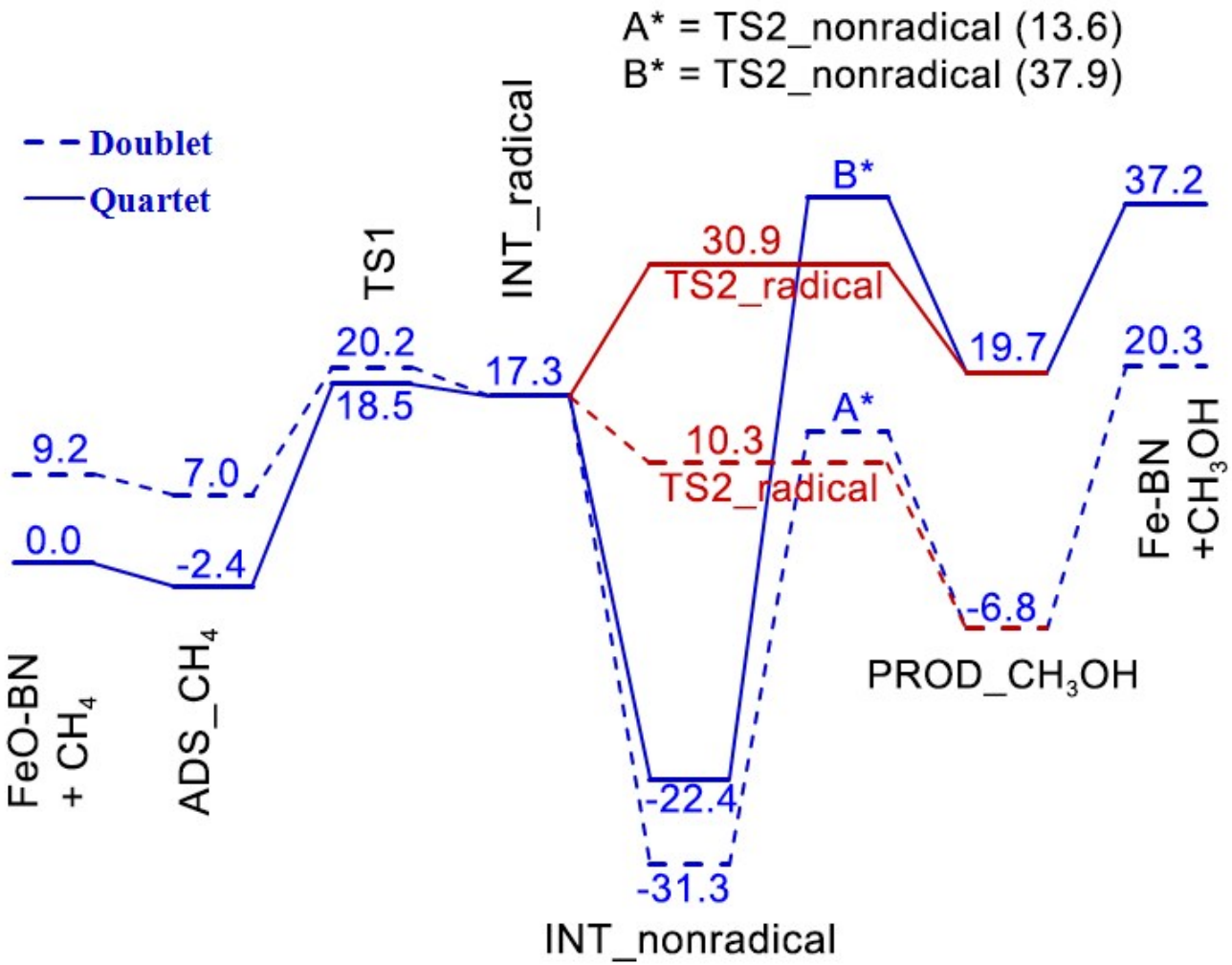


Fig. S6 Energy profiles for methane oxidation over FeO-BN calculated at PBE-D2. Energies are in kcal mol^{-1}.

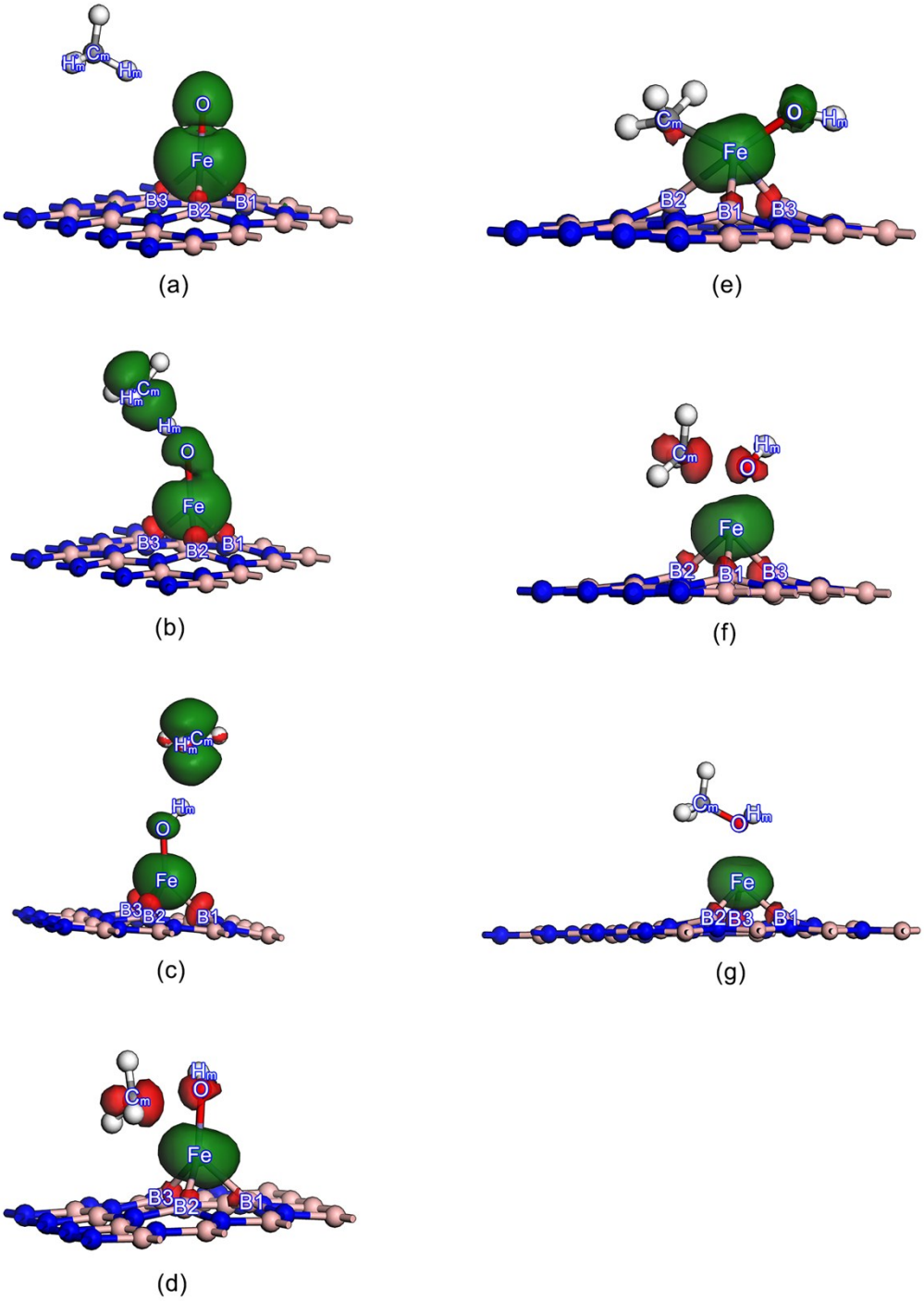


Fig. S7 Spin density for methane oxidation over FeO-BN: (a) Methane adsorption (ADS_CH_4) (b) Transition state C–H bond cleavage (TS1), (c) Intermediate radical (INT_radical), (d) Transition state radical methanol formation (TS2_radical), (e) Intermediate nonradical (INT_nonradical), (f) Transition state nonradical methanol formation (TS2_nonradical), and (g) methanol product adsorption (PROD_CH_3OH). The green isosurface represents α-electron and the red one represents β-electron density. The isosurface value is ±0.03 e $Å^{-3}$.

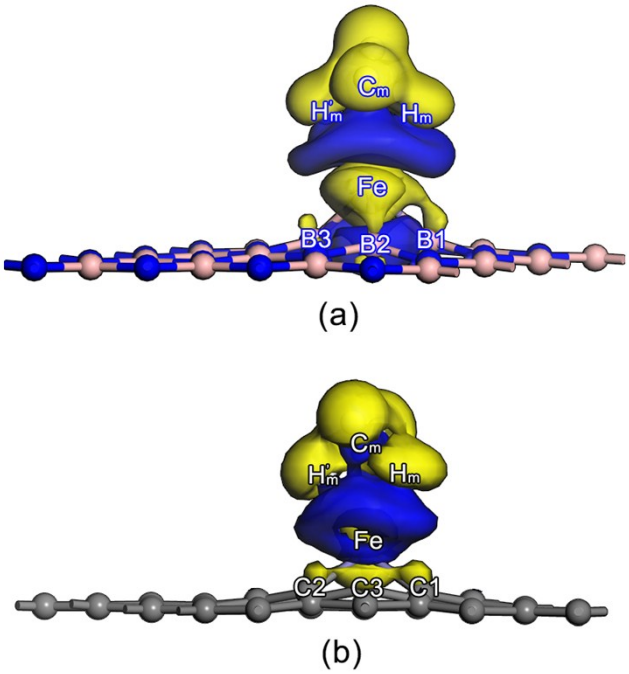


Fig. S8 Electron density difference map for methane adsorption over (a) Fe-BN and (b) Fe-GP. The blue and yellow colors indicate the region of electron accumulation and depletion, respectively. The isosurface value is ±0.005 e Å^{-3}.

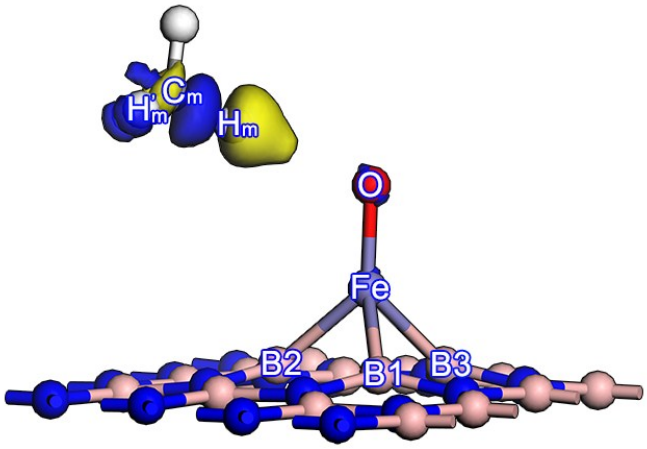
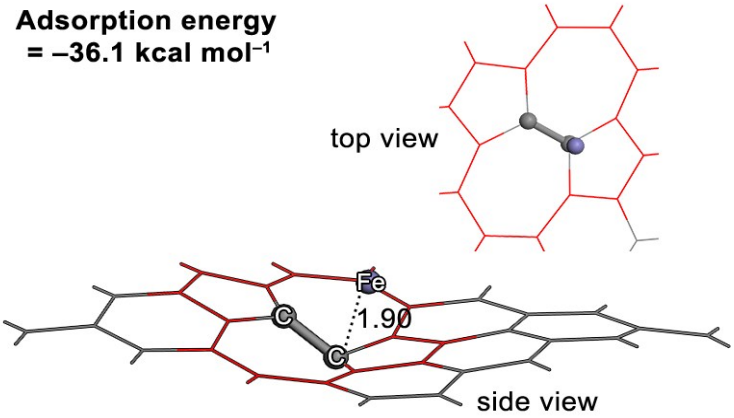
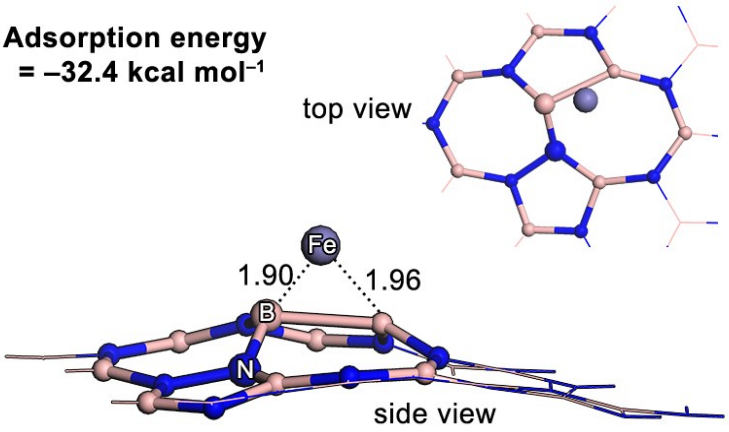


Fig. S9 Electron density difference map for methane adsorption over FeO-BN. The blue and yellow colors indicate the region of electron accumulation and depletion, respectively. The isosurface value is ±0.005 e Å^{-3}.



Fe-GP (SW) at the most stable configuration



Fe-BN (SW) at the most stable configuration

Fig. S10 Optimized structures of Fe adsorbed over Stone-Wales defect (SW) graphene (GP) and boron nitride (BN) sheet.