

Electronic Supplementary Information

Competitive adsorption of binary CO₂/CH₄ mixture in nanoporous carbons:

Effect of edge-functionalization

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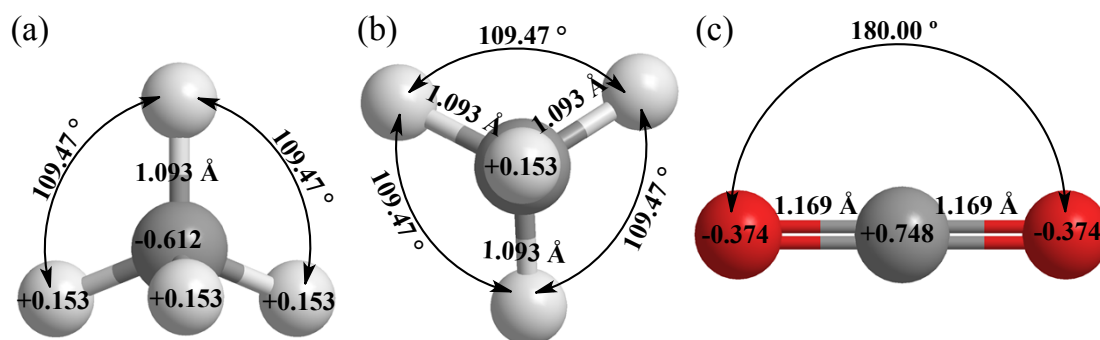
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Fig. S1 DFT optimization on molecular structures of CH₄ (a: side view, b: top view), and (c) CO₂.



As shown in Fig. S1, atomic partial charge and geometrical structural parameters of gas molecule are used in present GCMC simulations. The atomic partial charges on C and H atoms in CH₄ are -0.612 e and 0.153 e, respectively; the C-H bond length is 1.093 Å and an H-C-H bond angle of 109.47°. The atomic partial charges on C and O atoms in CO₂ are 0.748 e and -0.374 e, respectively. The CO₂ molecule has a C=O bond length of 1.169 Å and an O=C=O bond angle of 180.00°.

Calibration of computational methodology

(1) Pore topology and morphology

Accessible surface area of NPC is determined to be 3580 m²/g by CH₄ probe molecule, consistent well with the previous calculation result of 3610 m²/g¹ (within an error of 0.84%).

(2) Mulliken charge analysis

For the Mulliken charge used in the present work, the values of atomic partial charges in the functional groups agree well with the results of Kandagal *et al.*,² as shown in Table S1.

Table S1 Mulliken charge analysis.

Functional group	C	O	N	H
-OH	--	-0.739 ~ -0.548 (-O)	--	0.404 ~ 0.456
	--	-0.700 (-O) ^a	--	0.435 ^a
-COOH	-0.407 ~ 0.743	-0.455 ~ -0.251	--	0.370 ~ 0.404
	0.520 ^a	-0.440 (=O), -0.530 (-O) ^a	--	0.450 ^a
-NH ₂	--	--	-0.879 ~ -0.577	0.267 ~ 0.367
	--	--	-0.900 ^a	0.360 ^a

^a Results from Ref. 2.

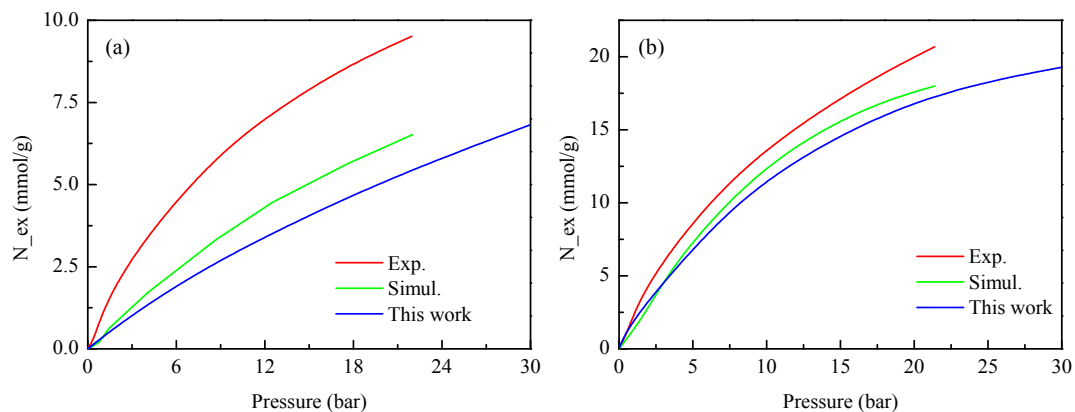
(3) Density functional theory (DFT)

The adsorption energy of the most stable configuration of CH₄ (B1) and CO₂ (B4)⁴ on coronene is 56.98 and 49.90 meV (see Figs. S5l and S6i), respectively. The adsorption energy of CO₂ is consistent well with the DFT result (~ 50 meV) by Liu⁵ *et al.* For CH₄, it is between the LDA (122.3 meV) and GGA (13.6 meV) results of CH₄ on graphene by Yang⁶ *et al.* As well, the equilibrium distance is optimized to be 3.176 and 3.659 Å for CH₄ (B1) and CO₂ (B4), consistent well with corresponding results of 3.14 and 3.31 Å⁴. The difference of the CH₄ adsorption energy might originate from the fact that the local density approximation (LDA) tends to overestimate the adsorption energy and underestimate the equilibrium distance.⁶⁻⁹

(4) Grand canonical Monte Carlo (GCMC) simulation

The excess adsorption isotherm of CH₄ and CO₂ in NPC at 298 K is chosen to compare with the results by Sarkisov *et al.*³ There is a minor difference in adsorption isotherms for CH₄-NPC systems, as shown in Fig. S2.

Fig. S2 The simulated and experimental excess adsorption isotherms of (a) CH₄ and (b) CO₂ in NPC at 298 K.



The agreement of our result with previous theoretical observations demonstrates the reliability of our model and levels of theory, including structure characterization analysis, Mulliken charge analysis, GCMC simulations, and DFT calculations.

Computational method of the pore volume by molecular simulation

Molecular simulation of He in a porous material is carried to calculate the absolute adsorption amount, N_{abs} . Excess adsorption amount, N_{ex} , can be determined by:

$$N_{ex} = N_{abs} - V_p \cdot \rho_{bulk} \quad (1)$$

where V_p is the specific pore volume (m^3/uc), and ρ_{bulk} is gas-phase bulk density at the specific temperature and pressure. For He, $N_{ex} = 0$,

$$V_p = N_{abs} / \rho_{bulk} \quad (2)$$

At sufficiently low pressures, He can be assumed to follow the ideal gas law:

$$V_p = N_{abs} \cdot kT / p \quad (3)$$

where k is the Boltzmann's constant, 1.38065×10^{-23} J/K.

The second virial coefficient, B_{abs} and B_{ex} , can be calculated:

$$B_{abs} = kT \lim_{p \rightarrow 0} (dN_{abs}/dp) \quad (4)$$

$$B_{ex} = kT \lim_{p \rightarrow 0} (dN_{ex}/dp) \quad (5)$$

Combining equations (1), (4), and (5):

$$B_{ex} = B_{abs} - V_p \quad (6)$$

For He, $B_{ex} = 0$, so V_p can be determined in the simulations by:

$$V_p = B_{abs} \approx kT(\Delta N_{abs} / \Delta p) = kTK \quad (7)$$

where K is the slope of the quasi-linear helium adsorption isotherm as $P \rightarrow 0$.

As shown in Fig. S3, the pore volume of NPCs is calculated as follows:

$$\begin{aligned} V_p &= kTK = 1.38065 \times 10^{-23} \times 298 \times 8.43 \times 10^{-6} (\text{m}^3/\text{uc}) \\ &= 3.47 \times 10^{-26} (\text{m}^3/\text{uc}) = 3.47 \times 10^4 (\text{\AA}^3/\text{uc}) \end{aligned} \quad (8)$$

Fig. S3 Total (absolute) adsorption amount of He in NPC at 298 K and low pressures.

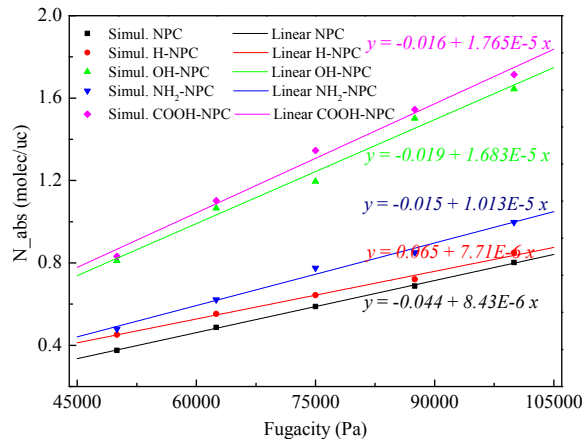


Fig. S4 The calculated atomic partial charge: (a) NPC basis unit; (b) coronene; (c) NH_2 -basis unit; (d) COOH -basis unit.

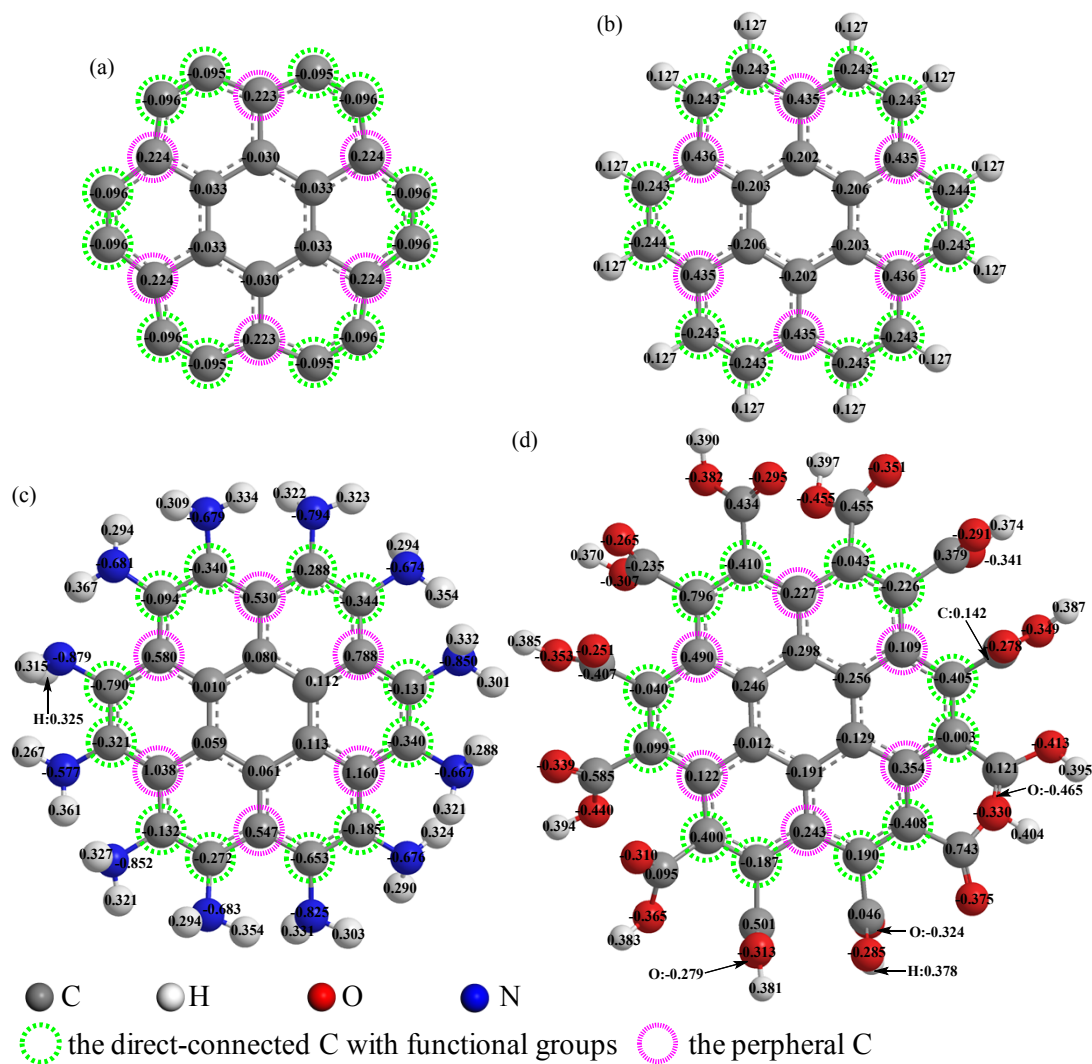
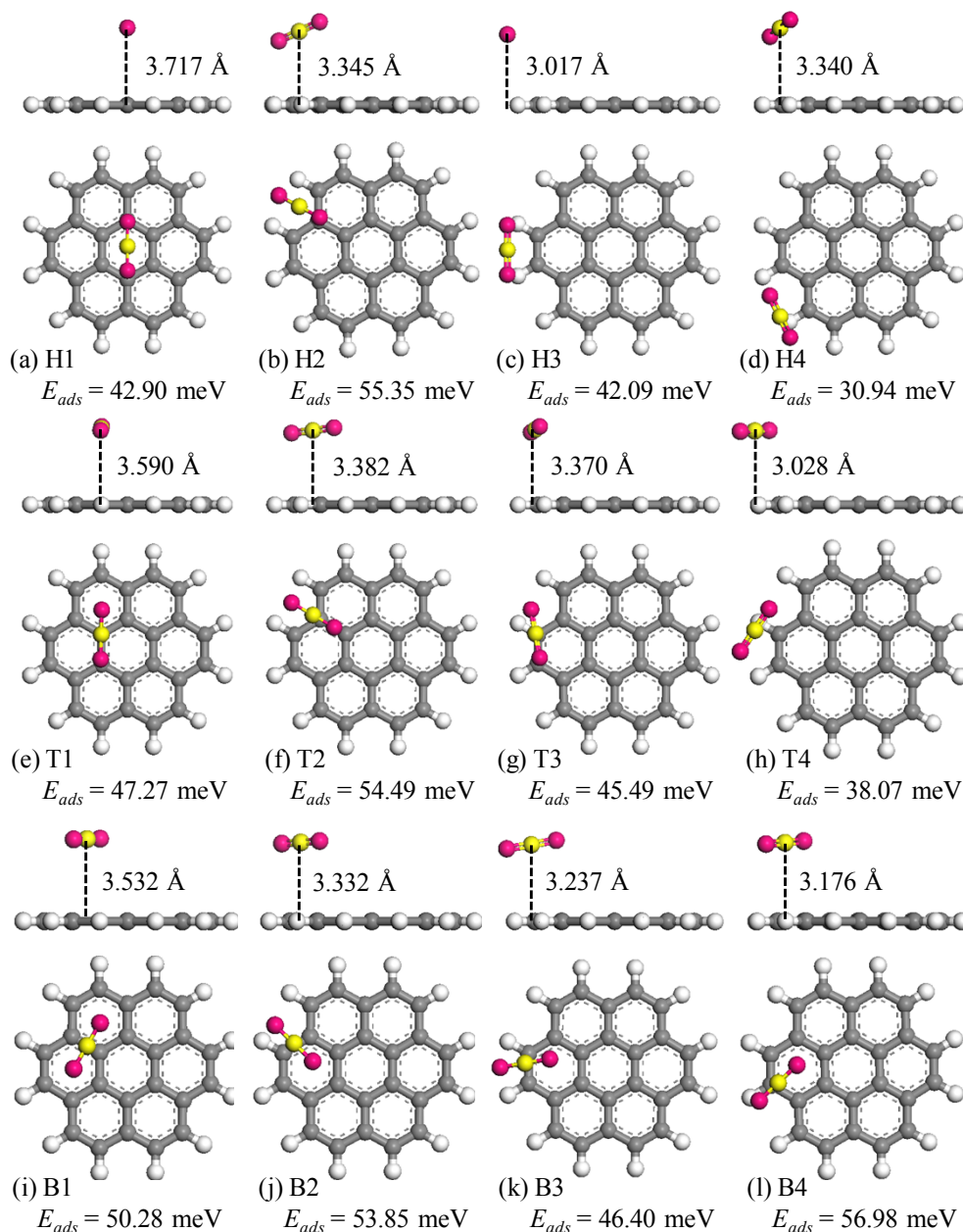
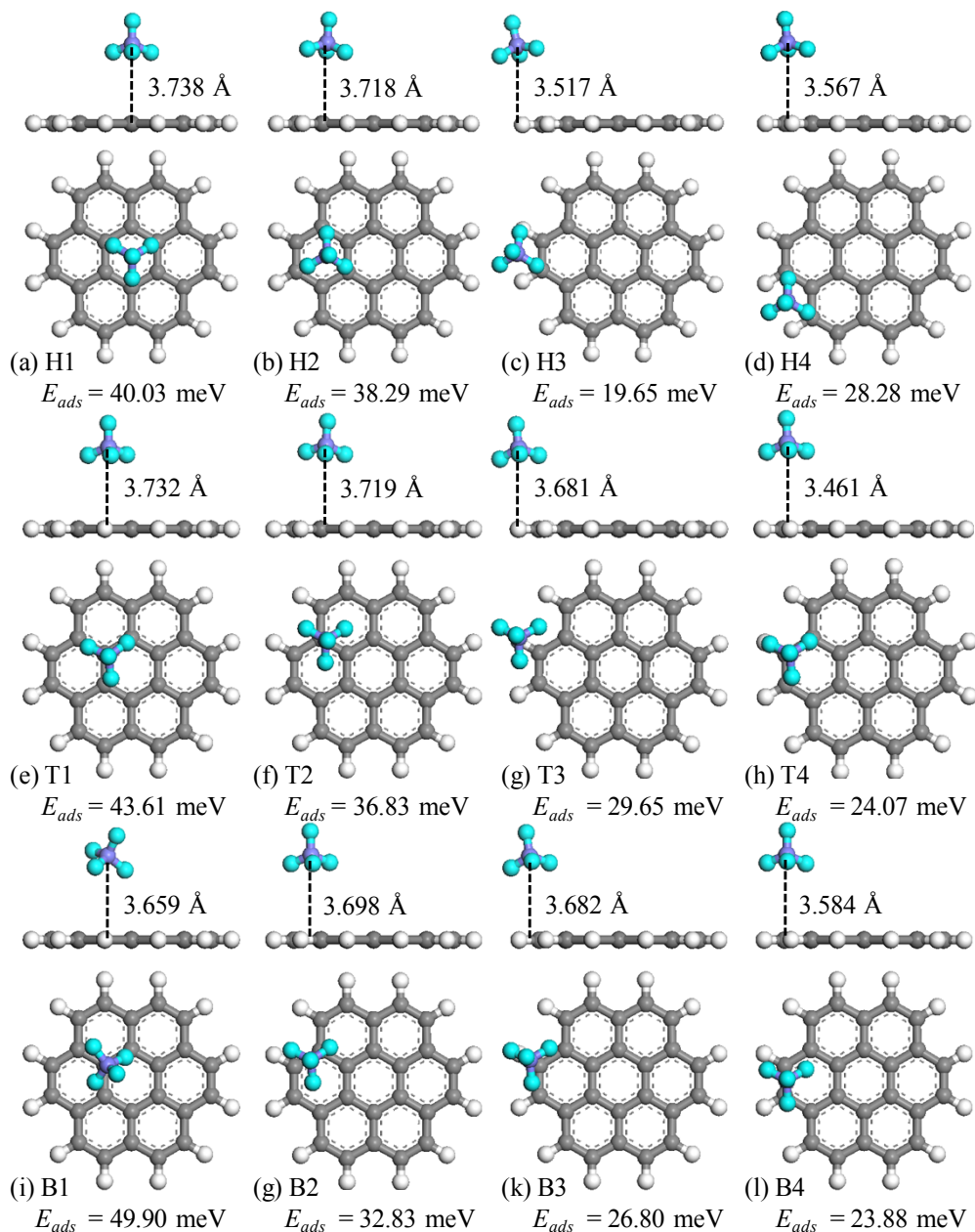


Fig. S5 Stable adsorption configurations of CO₂ on coronene from different directions (up, side view; down, top view): (a-d) H direction; (e-h) T direction; (i-l) B direction. Color code: gray, C; white, H; yellow, C (CO₂); deep pink, O (CO₂).



Notes: Adsorption energy and equilibrium distance (defined as the distance from the gas molecular centre-of-mass to the coronene plane) are labelled correspondingly.

Fig. S6 Stable adsorption configurations of CH₄ on coronene from different directions (up, side view; down, top view): (a-d) H direction; (e-h) T direction; (i-l) B direction. Color code: gray, C; white, H; violet, C (CH₄); cyan, H (CH₄).



Notes: Adsorption energy and equilibrium distance (defined as the distance from the gas molecular centre-of-mass to the coronene plane) are labelled correspondingly.

Fig. S7 Absolute adsorption isotherms of CO_2 and CH_4 from an equimolar CO_2/CH_4 mixture in all the edge-functionalized NPCs with atomic partial charges at temperatures of (a) 298 K; (b) 313 K; (c) 373 K.

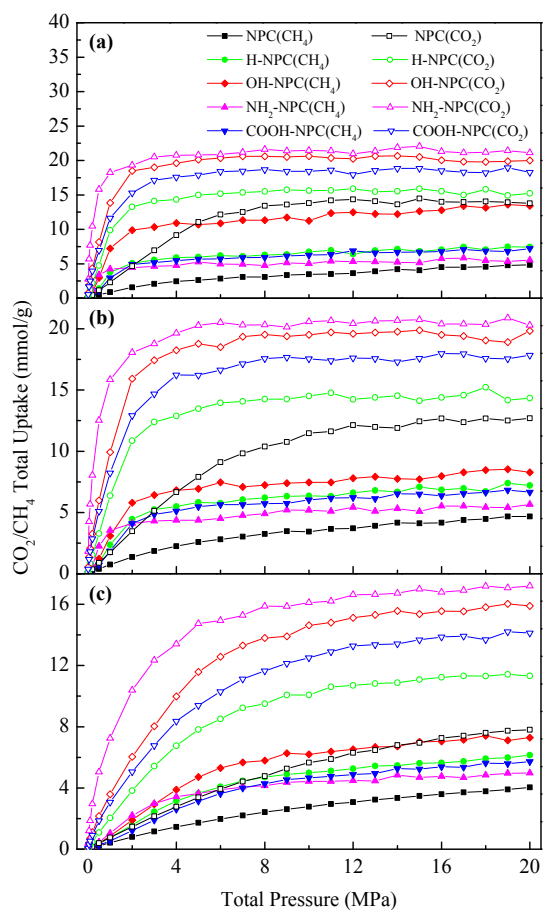
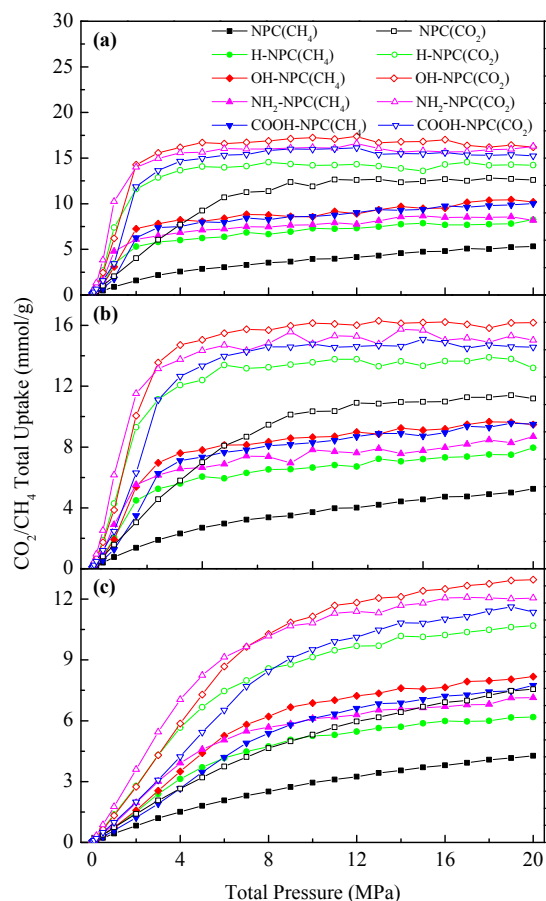


Fig. S8 Absolute adsorption isotherms of CO_2 and CH_4 from an equimolar CO_2/CH_4 mixture in all the edge-functionalized NPCs without atomic partial charges at temperatures of (a) 298 K; (b) 313 K; (c) 373 K.



Notes and references

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