Theoretical study on the edge-functionalization effect on nanoporous carbons for adsorption capacity and selectivity of CO\textsubscript{2} over N\textsubscript{2}

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Abstract. The adsorption and separation of CO\textsubscript{2}/N\textsubscript{2} mixture in the edge-functionalized nanoporous carbons (NPCs) were investigated by grand canonical Monte Carlo simulation. Results demonstrated that edge-functionalization effectively improved the pore structure characteristics of NPCs. The edge-functionalization can enhance the uptake of CO\textsubscript{2}/N\textsubscript{2} and the selectivity of CO\textsubscript{2} over N\textsubscript{2} in NPCs. The isosteric heat and radial distribution functions confirmed that temperature had a negative effect on the single-component adsorption of CO\textsubscript{2}/N\textsubscript{2} whereas pressure had a positive effect before adsorption reaches a stable equilibrium state. Overall, this work highlighted the effects of edge-functionalization on the adsorption and separation of CO\textsubscript{2}/N\textsubscript{2} in NPCs, and provided an effective strategy for designing and selecting solid adsorbents for carbon capture and storage.

1. Introduction
Carbon capture and storage (CCS) has received widespread concerns as a promising strategy to alleviate excessive emissions of CO\textsubscript{2} into the atmosphere [1]. One of the crucial issues for CCS technology is to screen adsorbent materials with excellent CO\textsubscript{2} adsorption capacity and selectivity, low regeneration energy, and good tolerance in equipment corrosion [2]. Nanoporous carbon materials exhibit remarkable advantages because of their lightweight property, high surface area and porosity, easy regeneration [3]. Apart from intrinsic advantages of carbon materials, chemical functionalization is extensively used to enhance carbon materials of CO\textsubscript{2} capture and selectivity [4].

The separation of CO\textsubscript{2} from N\textsubscript{2} is research focus because post-combustion processes in fuel-based power plants often release CO\textsubscript{2}/N\textsubscript{2} mixture gas. Xiang et al. [5] successfully incorporated –OH, –NH\textsubscript{2}, and –SO\textsubscript{2}Cl functional groups into one phase for porous organic materials and observed that functionalized covalent organic polymers exhibited considerably higher selectivity for CO\textsubscript{2} over N\textsubscript{2} than initial structures. Babarao et al. [6] indicated that the introduction of O- and N-containing functional groups on porous aromatic frameworks could enhance the adsorption capacity of CO\textsubscript{2} and selectivity of CO\textsubscript{2} over N\textsubscript{2}. Despite these findings, the in-depth theoretical investigations on the effects of edge-functionalization on the adsorption and separation of CO\textsubscript{2}/N\textsubscript{2} in NPCs materials have not been convincingly elucidated. In this work, the density functional theory (DFT) and grand canonical Monte Carlo (GCMC) was performed to explore the adsorption and separation behaviour of CO\textsubscript{2}/N\textsubscript{2} mixtures in the edge-functionalized NPCs.

2. Model and computing methodology
Coronene-shaped graphene build non-functionalized NPC. Four functional groups, –H, –OH–NH₂, and–COOH, are used to passivate the edge of NPC to form the edge-functionalized NPCs, as shown in Figure 1. Atomic partial charge was calculated after the geometry optimization by using the B3LYP functional and incorporating the 6-31+g(d, p) basis set in Gaussian 09 package [7]. The LJ potential parameters for both molecules were from the TraPPE model [8]. For NPC frameworks, the universal force field (UFF) was adopted to set atomic LJ potential parameters. More informations can be found in previous works [9]. Calculations on the adsorption uptake and selectivity of CO₂ over N₂ were performed by GCMC in MuSiC [10].

![Figure 1. Initial configurations of NPCs with different functional groups, and snapshots of CO₂/N₂ adsorption](image)

3. Results and discussions

3.1. Pore topology and morphology

Pore physical characteristics are critical factors for the gas adsorption and separation. Table 1 lists the pore topology and morphology of the frameworks evaluated by Sarkisov [11] and Duren [10] methods and Poreblazer v3.0 procedure [8]. The Φ of the edge-functionalized NPCs ranges from 68.48% to 76.50% relative to 66.58% for the unmodified NPC. The porosity of the edge-functionalized NPCs is smaller than that of some PAFs (84.46%–91.22%) [12] but larger than that of HKUST-1 (72%) [13]. The accessible surface area of the edge-functionalized NPCs fluctuates from 3006.17 to 3548.36 m² g⁻¹, and these values are larger than those of microporous MOFs (600-2858 m² g⁻¹) [14]. Figure 2 displays the geometric pore size distributions (PSDs). Miniscule ultramicropores (< 7.00 Å) and numerous micropores (7.00–20.00 Å; 84.50%–96.80% of the total) are observed in the edge-functionalized NPCs in accordance with the IUPAC classification [15]. In summary, edge-functionalization improves the effective accessible surface area and increases the pore spaces and diameters, and facilitates the creation of a favorable environment for gas adsorption in gas-framework systems.
Table 1. Physical characteristics and isosteric heat of NPCs with different functional groups. (Gas probe molecule = He).

| Parameters                | None | H– | OH– | NH₂– | COOH– |
|---------------------------|------|----|-----|------|-------|
| V_p (cm³/g)               | 1.30 | 1.26 | 1.41 | 1.33 | 1.36  |
| D_s (Å)                   | 7.06 | 8.33 | 11.90 | 8.19 | 8.52  |
| D_m (Å)                   | 12.87 | 11.26 | 17.99 | 12.44 | 16.97 |
| Porosity, Φ (%)           | 66.58 | 68.48 | 76.54 | 71.78 | 71.53 |
| Microporosity (%)          | 84.9 | 84.5 | 96.8 | 88.1 | 95.0  |
| Surface area (m²/g)       | 3191 | 3091.31 | 3006.17 | 3492.48 | 3548.30 |
| Q_st of CO₂ (kJ mol⁻¹)    | 24.63 | 27.26 | 30.339 | 34.252 | 30.704 |
| Q_st of N₂ (kJ mol⁻¹)     | 8.388 | 12.176 | 14.180 | 13.129 | 12.996 |

3.2. Single-component adsorption of CO₂/N₂

Figure 3a presents the absolute adsorption isotherms of CO₂ at 298 K. The uptake of CO₂ in the edge-functionalized NPCs are significantly higher than that of the unmodified NPC. At low pressures (0-2 MPa), the uptake of CO₂ follows the sequence of NH₂–NPC > COOH–NPC > OH–NPC > H–NPC > NPC. That is, a functional group with large electronegativity increases the adsorption at low pressures. At high pressures (2-10 MPa), the saturated uptake of CO₂ follow the sequence of OH–NPC > NH₂–NPC > COOH–NPC > H–NPC > NPC. This finding is attributed to the combined effect of pore size and porosity [16]. Figure 3d delineates the absolute adsorption isotherms of N₂ in the edge-functionalized NPCs at 298 K. Edge-functionalization significantly enhances the uptake of N₂. The uptake of N₂ follows the sequence of OH–NPC > NH₂–NPC > H–NPC > COOH–NPC > NPC. The effects of temperature on the adsorption of CO₂/N₂ are presented in Figure 3a–c and 3d–f. The results show that the uptake of CO₂/N₂ in the edge-functionalized NPCs decreases with the increase of temperature due to the exothermic nature of the adsorption process. Overall, the adsorption of CO₂/N₂ in the edge-functionalized NPCs exhibits type–I Langmuir adsorption behavior [17]. This result indicates that edge-functionalization can improve the ability of NPCs to separate CO₂ from N₂.
Figure 3. Absolute adsorption isotherms of CO$_2$ (a-c) and N$_2$ (d-f) in the edge-functionalized NPCs at 298 K, 313 K, and 373 K

3.3. Effect of functional groups on adsorption

We calculated the average isosteric heats (Qst) and radial distribution functions (RDFs, g(r)) to obtain the gas adsorption strength and distribution, as shown in Table 1 and Figure 4. Isosteric heat is a good indicator exhibiting the affinity of gas molecules toward porous adsorbents [18]. The Qst of CO$_2$ remains basically constant (24.630 kJ mol$^{-1}$) in NPC, whereas the Qst of CO$_2$ increases to 27.276-34.252 kJ mol$^{-1}$ in the edge-functionalized NPCs due to the introduction of functional groups. The isosteric heat of CO$_2$ in NPCs is in good consistence with that of CO$_2$ uptake at low pressure. The sequence of Qst of N$_2$ agrees well with the sequence of N$_2$ uptake. For both CO$_2$ and N$_2$, the isosteric heat analyses clearly show that the adsorption capacity of gases depends on the strength of the gas-framework interaction. Comparatively, the isosteric heat of CO$_2$ is larger than the corresponding value of N$_2$ in NPCs, and this result is attributed to the stronger interactions in CO$_2$-frameworks.

To estimate the influence of functional groups on gas distribution, we calculated the RDFs of CO$_2$/N$_2$ around the heteroatoms in functional groups. As shown in Figure 4a, the strongest peak occurs at r = ~3.75 Å due to the strong interaction between the CO$_2$ and electronegative N atoms in the framework. For COOH–NPC, the g(r) presents two evident peaks. The first peak represents the adsorbed phase, and the second peak represents the equilibration phase. The RDFs of N$_2$ are shown in Figure 4b. The g(r) of N$_2$ in the edge-functionalized NPCs presents weak first peaks, indicating that the functional groups have minimal effects on N$_2$ adsorption. This is ascribed to the weak quadrupole moment of N$_2$ and the resulting weak interaction between N$_2$ and heteroatoms in the edge-functionalized NPCs. These CO$_2$/N$_2$ radial distribution functions are consistent with the corresponding isosteric heat values. Therefore, both isosteric heat and RDFs analyses can explain why the functional groups exert a better effect on the adsorption of CO$_2$ than that of N$_2$. 
Figure 4. Radial distribution functions of CO$_2$ (a) N$_2$ (b) around N in NH$_2$–NPC, O in COOH–NPC, O in OH–NPC, and H in H–NPC for CO$_2$/N$_2$ mixture at 10 MPa. (c) Selectivity of CO$_2$ over N$_2$ in the edge-functionalized NPCs at 298 K with the equal mixture ratio.

3.4. Selectivity of CO$_2$ over N$_2$ with equal molar fraction

Selectivity of CO$_2$ over N$_2$, $S_{CO_2/N_2} = (x_{CO_2}/x_{N_2})/(y_{CO_2}/y_{N_2})$, is an excellent indicator of the ability of certain species to separate from its mixed gases. Figure 4c shows the selectivity of CO$_2$ over N$_2$ with equal molar fraction in the edge-functionalized NPCs at 298 K. The selectivity of CO$_2$ over N$_2$ declines sharply initially, and then flattens out to a constant value with the increase in pressure. Functional groups improve the selectivity of CO$_2$ over N$_2$, especially at low pressures. Consistent with the results of isosteric heat and RDFs analyses, the selectivities demonstrate the positive effect of functional groups. At low pressures, the adsorption of CO$_2$ is prior to that of N$_2$ due to the strong attractive interactions between CO$_2$ and the framework, leaving N$_2$ to fill the void space and thus forms a high selectivity of CO$_2$ over N$_2$. With the increase in pressure, the increasing repulsion between the gas molecules weakens the attraction between the gas molecules and the framework and then renders adsorption reaching an equilibrium state. Thus, the selectivity of CO$_2$ over N$_2$ tends to be a constant value. This finding further highlights the positive effect of functional groups on the separation of CO$_2$ from N$_2$.

4. Summary

The edge-functionalization effects on adsorption and selectivity of CO$_2$/N$_2$ gas in NPCs were investigated by DFT and GCMC simulations. Edge-functionalization creates a favorable environment for the adsorption of CO$_2$/N$_2$. The results of isosteric heat and radial distribution function confirm that the uptake of CO$_2$ is more significantly enhanced by edge functionalization than that of N$_2$, indicating the enhanced selectivity of CO$_2$ over N$_2$. Temperature has a negative effect on the uptake of CO$_2$/N$_2$ in the edge-functionalized NPCs. This work highlights edge-functionalization effects on the adsorption and separation of CO$_2$/N$_2$ in NPCs, and provides an effective strategy for designing and selecting solid adsorbents for carbon capture and storage.

5. References

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