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Full Length Article

Edge-functionalized nanoporous carbons for high adsorption capacity and selectivity of CO_2 over N_2

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ABSTRACT

Single-component adsorption and competitive behavior of binary CO_2/N_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 topology and morphological characteristics of NPCs. Evaluation of adsorption capacity and analyses of the isosteric heat and radial distribution functions confirmed that edge-functionalization can evidently enhance the single-component adsorption of CO_2/N_2. Temperature had a negative effect on the single-component adsorption of CO_2/N_2 whereas pressure had a positive effect before adsorption reaches a stable equilibrium state. Edge-functionalization can significantly increase the selectivity of CO_2 over N_2 in NPCs, which demonstrate the following sequence according to selectivity: NH_2—NPC > COOH—NPC > OH—NPC > H—NPC > NPC. The increased CO_2 molar fraction in the binary CO_2/N_2 mixture decreased the selectivity and saturation pressure to reach a stable equilibrium state. Overall, this work highlighted the effects of edge-functionalization on the adsorption and separation of CO_2/N_2 in NPCs, and provided an effective strategy for designing and screening adsorbent materials for carbon capture and separation.

1. Introduction

Carbon capture and storage (CCS) has received widespread concerns as a promising strategy to allow the continued use of fossil fuels whilst alleviating excessive emissions of CO_2 into the atmosphere [1,2]. On the basis of this strategy, a large number of adsorbent materials with high CO_2 adsorption capacity and selectivity have emerged [3–7]. Nanoporous carbon materials exhibit remarkable advantages as feasible gas adsorbents because of their lightweight property, high surface area and porosity, easy regeneration, low-cost preparation, chemical stability, and low sensitivity to humidity [8–10]. Apart from the intrinsic advantages of carbon materials, some advanced modification approaches are currently adopted to enhance CO_2 capture and selectivity, such as topological structure design, chemical doping, chemical functionalization, and open/unsaturated metal sites [11]. Among these approaches, chemical functionalization can change the packing pattern of the adsorbate and increase the interactions between gases and frameworks; thus, chemical functionalization is extensively used in carbon adsorbent materials in experimental research and several industries [12,13].

In industrial operations, the adsorption and separation of CO_2 are accompanied by the competitive adsorption of N_2. For instance, post-combustion processes in fuel-based power plants often release CO_2/N_2 mixture gas at a ratio of 15:85 [14]. Thus, investigation on the selectivity of CO_2 from N_2 is of great significance. Xiang et al. [15] successfully incorporated —OH, —NH_2, and —SO_2Cl functional groups into one phase for porous organic materials and observed that functionalized covalent organic polymers (COPs) exhibited considerably higher selectivity for CO_2 over N_2 than COPs without functional groups. Babarao et al. [16] indicated that the introduction of O— and N-containing functional groups on porous aromatic frameworks (PAFs) could enhance the adsorption capacity of CO_2 ($10\,\mathrm{mmol\,g^{-1}}$ at 298 K and 1 bar) and selectivity of CO_2 over N_2. Dasgupta et al. [3] explored the effects of functionalized graphene nanoribbon bilayer on the adsorption and selectivity of CO_2/N_2 mixture gas through grand canonical Monte Carlo (GCMC) simulations. They found that edge-functionalization can increase the adsorption capacity and selectivity, especially for —COOH graphene nanoribbons which increased by 28% in selec-

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tivity. Despite these findings, the effects of edge-functionalization, temperature, pressure, and adsorbate molar fraction difference on the adsorption and selectivity of CO_2/N_2 mixture gas in NPCs materials have not been convincingly elucidated.

In this work, we investigate the competitive adsorption behavior of CO_2/N_2 mixture gas in the edge-functionalized NPCs with —H, —OH, —NH_2, and —COOH passivated basic units. First, density functional theory (DFT) is employed to optimize the geometry and calculate the atomic partial charge as the basic input parameters in molecular simulation; then, the pore topology and morphological characteristics of the edge-functionalized NPCs are explored; next, the single-component adsorption of CO_2/N_2 is calculated with the consideration of the temperature and pressure effects; subsequently, the isosteric heats and radial distribution functions are analyzed to determine the effects of edge-functionalization on the adsorption strength and gas distribution; finally, the selectivities of CO_2 from N_2 in mixture gases with equal and non-equal molar ratios are investigated to determine the effects of various compositions. Our results highlighted the potential use of the edge-functionalized NPCs in CCS for high adsorption capacity and selectivity of CO_2 over N_2.

2. Model and computing methodology

Coronene-shaped graphene was adopted as a substrate to build non-functionalized NPC. Four functional groups, hydrogen (—H), hydroxyl (—OH), amine (—NH_2), and carboxyl (—COOH), are used to passivate the edge of substrate of NPC to form four substrates of the edge-functionalized NPCs, as shown in Fig. 1. After building these five substrates, we performed DFT calculations to optimize structure and analyze atomic charge. The B3LYP/6–31 + g(d,p) basis set in Gaussian 09 package was chosen with the consideration of the balance between efficiency and accuracy on the structural optimization and atomic charge analysis [17,18]. Next, the frameworks of the edge-functionalized NPCs were composed by collecting the optimized substrates, as shown in Fig. S1 (see Supporting Information). The mass density of all edge-functionalized NPCs was kept as $0.542\ \mathrm{g\,cm^{-3}}$. Atomic partial charges of NPCs were adopted as input parameters in GCMC simulations to describe the electrostatic interaction.

Since CO_2 and N_2 are rigid linear molecules, three charged LJ interaction sites were chosen for N_2 and CO_2. The LJ potential parameters for both molecules were from the TraPPE model reported by Potoff and Siepmann [19]. For NPC frameworks, the universal force field (UFF) was adopted to set atomic LJ potential parameters, which has been extensively applied to similar NPC systems [8], open–metal–site metal organic frameworks (MOFs) [20], and Zeolites [21], *ect*. The Van der Waals interaction was described by the LJ (12, 6) model, and the electrostatic interaction was calculated by the Coulomb law. Information of LJ potential parameters of NPC frameworks and atomic partial charge were described in detail in previous work [22].

GCMC simulations were employed to calculate the adsorption of single-component CO_2, N_2, and their binary mixture in these five models. For each state point, the GCMC simulation run 1×10^7 steps to achieve the thermodynamics properties. All these GCMC simulations were performed by using an object–oriented multipurpose simulation code (MuSiC) [23].

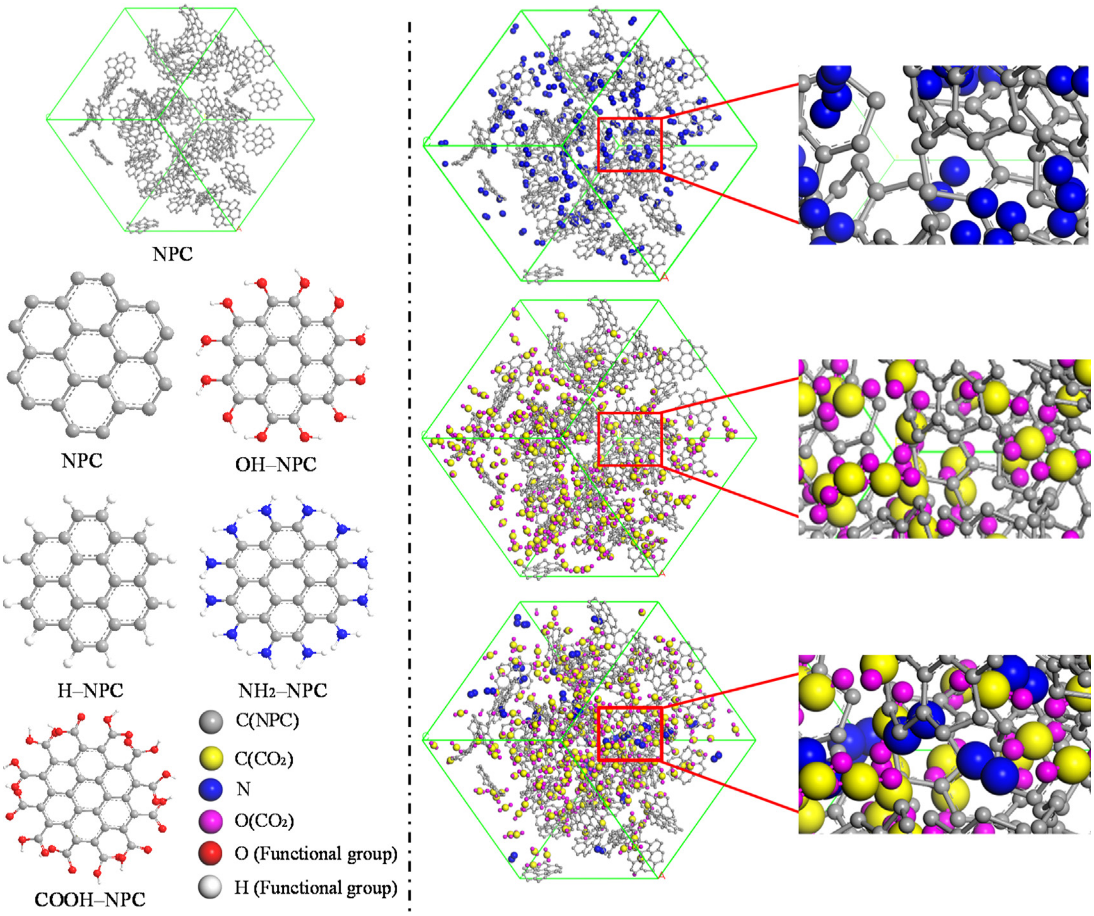

Fig. 1. Initial configurations of NPCs with different functional groups, and snapshots of CO_2/N_2 adsorption.