Simulation study on the effect of pore structure and surface curvature of activated carbon on the adsorption and separation performance of CO\textsubscript{2} /N\textsubscript{2}

Weihua Chen  
Changzhou University

Weiqiu Huang (hwq213@cczu.edu.cn) 
Changzhou University

Lipei Fu  
Changzhou University

Xufei Li  
Changzhou University

Xinya Wang  
Changzhou University

Yongyin Zheng  
Changzhou University

Yilong Zhang  
China University of Mining and Technology (Beijing)

Jiahui Zhu  
Changzhou University

Bing Zhu  
Changzhou University

Research Article

Keywords: Activated carbon, Pore structure, Surface curvature, Grand Canonical Monte Carlo (GCMC), Adsorption, Separation

Posted Date: May 11th, 2022

DOI: https://doi.org/10.21203/rs.3.rs-1593775/v1

License: This work is licensed under a Creative Commons Attribution 4.0 International License. Read Full License
Abstract

In this paper, the Grand Canonical Monte Carlo (GCMC) method was used to explore the effects of four pore structures (disordered pore, wedge pore, carbon nanotube and slit pore structures) and surface curvature of activated carbon on the adsorption and separation of $\text{CO}_2/\text{N}_2$. On the whole, carbon nanotubes have the greatest selectivity for $\text{CO}_2$, followed by disordered pores, wedge pores and slit pores. The effect of pore structure on the interaction energy of gas molecules is similar to that of selectivity, in which the fluid-solid potential energy between adsorbates and adsorbents plays an important role. Due to the different affinity between adsorbate molecules and activated carbon, $\text{CO}_2$ with high affinity is more sensitive to the change of pore size. Therefore, under high pressure, the density of $\text{CO}_2$ in the slit pore is greater than that in the wedge pore. However, $\text{N}_2$ with poor affinity is limited by the surface area, resulting in the density of it in the wedge pore is always higher than that in the slit pore. Although the existence of non-six membered corannulene rings in activated carbon can't always cause the increase of specific surface area, the surface curvature of activated carbon caused by it can increase strong energetically adsorption sites. Hence, the surface curvature plays a positive role in the adsorption density, interaction energy and $\text{CO}_2$ selectivity. The discovery of $\text{CO}_2/\text{N}_2$ adsorption and separation at the molecular level is expected to provide valuable insights.

1. Introduction

The increase of greenhouse gases (GHG), especially carbon dioxide ($\text{CO}_2$, whose concentration in the air has reached an alarming 400 ppm volume [1]) has a serious impact on the global economy and ecosystem, such as sea-level rise, drought, which make the capture and storage of $\text{CO}_2$ imperative. In recent years, governments are also aim to have $\text{CO}_2$ emissions peak and achieve carbon neutrality. $\text{CO}_2$ is mainly contributed by the flue gas from steel plants, power plants and petrochemical industries burning carbon-based fossil fuels. The flue gas contains mainly $\text{N}_2$ and $\text{CO}_2$, of which $\text{CO}_2$ accounts for about 12–15% [2]. Although post-combustion capture technology (capturing $\text{CO}_2$ from flue gas) is widely used, the conventional chemical absorption technology based on amine solution (such as mono-ethanolamine) requires 25–40% of the energy of power plant, and the consumption of regeneration process accounts for more than 60% of the total energy demand [3]. Therefore, new $\text{CO}_2$ capture processes need to be not only technically feasible, but also cost-effective.

Among the technologies such as absorption, membrane separation, low-temperature distillation and adsorption, adsorption based on porous materials is of great interest because of its efficiency and economy. Typical adsorbents include Metal-Organic Framework (MOF) materials, zeolites, clays, and activated carbon (AC) [4–7], among which AC is competitive due to its large specific surface area, easy modification, and adjustable pore size (such as the mesoporous carbon synthesized by template method) [8, 9]. The adsorption and separation experiments of AC for $\text{CO}_2/\text{N}_2$ have been widely carried out. For examples, Shen et al. [10] demonstrated that bitumen-based AC beads have significant adsorption for
CO₂ than N₂ and the latter diffuses faster at the same temperature. Similarly, Yi et al. [11] reported that microwave assisted AC has a high separation factor for CO₂/N₂.

However, due to the technical challenges of experimental measurements of multicomponent adsorption in AC [12], the selectivity of CO₂ is usually obtained by the ideal adsorption solution theory (IAST), but the method has its own limitations [13]. What's more, because of the complex internal structure of AC, the high adsorption capacity and selectivity of CO₂ in the experiment are attributed to many factors [11]. It is difficult to investigate the effects of AC properties such as pore structure, surface curvature and surface chemistry, especially the first two, because they are difficult to be controlled and verified by experiments. It is here that molecular simulation is introduced to study the effects of various properties of AC on CO₂/N₂ adsorption and separation by explicitly considering the interaction between gas molecules and pore wall.

Generally, AC is established as slit pore structure in simulation, but experiments show that the pores are generally composed of curved surfaces or non-parallel graphene planes [14], which means that it is insufficient to study adsorption only through the classical slit model. Therefore, the wedge model [15] or disordered model [16] further improved on the slit model and the nanotube model with cylindrical structure [17] are of great significance to study the adsorption and separation of gases on AC. With the same idea, previous studies by Liu et al. [12] and Kumar et al. [18] showed that the pore structure of AC had a significant impact on the adsorption and separation of mixing gases. Specifically, the fluid-solid potential energy plays a decisive role in the selectivity of mixed gases. In the disordered structure, the nanotube structure and the foam like structure, nanotube structure with strong energy effect has the best separation performance for CH₄/CO₂ and CH₄/H₂. Their findings are very instructive, but the wedge pores are not considered, and other factors such as pore size are not constrained.

In addition, the evidences from TEM [19] and simulation [20] show that there are five membered rings and seven membered rings in non-graphitized porous carbon, and their existence leads to the generation of surface curvature. It is proved by ab initio quantum mechanics (QM) that the surface curvature will produce stronger binding energy for gas. Nguyen et al. [21] and Di et al. [22] obtained similar conclusions, and the AC with non-six membered rings has better adsorption capacity for CO₂. The result is caused by the special hybridization of carbon between sp² and sp³ [23], in other words, the AC with non-six membered ring produces stronger energetically adsorption sites than graphite. However, previous studies have often used C60 fullerenes and carbon nanotubes to explore the influence of surface curvature [24, 25], but it is not applicable to the disordered structure, because the surface curvature in this structure is caused by non-six membered rings [26]. In addition, researchers pay more attention to the change of adsorption energy and ignore its overall impact on adsorption and separation [24].

In this paper, it aims to study the effects of four representative structures of AC (slit pores, wedge pores, nanotube pores and disordered pores) and surface curvature on CO₂/N₂ adsorption and separation from a micro perspective. The changes of adsorption density, interaction energy and CO₂ selectivity were discussed in detail by GCMC simulation.
2. Methodology

2.1 Models

Four different pore structures and four models with different surface curvature are constructed, as shown in Fig. 1 and Fig. 2 below. Among the four pore structures, the disordered pore structure is composed of basic structural units (BSUs), and the model refers to the work of Bahamon et al. [27] and Li et al [28]. Using the Amorphous module in Materials Studio software, various BSUs are filled in the box to construct AC. The BSUs are shown in Fig. S1. Only some of the BSUs are shown in the figure, and more than 10 different shapes of BSUs were considered for the construction. Besides, in the disordered pore model, some atoms were randomly deleted to construct defects [29], and five membered rings and seven membered rings were introduced into the model [30]. In order to make the disordered pore model as close to the experimental material as possible, the specific surface area, pore volume and skeleton density are limited. The parameters of four pore structures and experimental material are shown in Table 1.

| Type                  | Surface area (m²·g⁻¹) | Pore volume (cm³·g⁻¹) | Skeletal density (g·cm⁻³) | Size of simulation box (x*y*z, Å) |
|-----------------------|-----------------------|-----------------------|---------------------------|----------------------------------|
| Experimental material | 1306.4                | 0.46                  | 1.850                     |                                  |
| Disordered model      | 1319.1                | 0.47                  | 1.810                     | 40.2*40.2*40.2                   |
| Wedge model           | 917.5                 | 0.60                  | 2.192                     | 39.4*126.5*40.0                  |
| Nanotube model        | 767.6                 | 0.35                  | 1.949                     | 39.4*39.4*44.5                   |
| Slit model            | 890.7                 | 0.59                  | 2.293                     | 39.4*38.3*47.0                   |

The wedge pore model refers to the work of Zeng et al. [15] and Fan et al. [14] The pore wall of the model is composed of three layers of graphene, and the length (L) and the deflection angle (α) of the model are 10 nm and 5°, respectively. Gas reservoirs are connected at both ends of the model to maintain the balance between molecules in the pore and the surroundings [14]. For comparing the effects of different pore structures on adsorption and separation, the pore sizes of four pore structures were constructed as 1.67 nm. The disordered pore model adopts the average pore size of the experimental material, and the average pore size is 1.67 nm; the pore size of the wedge pore model is the average distance between the two ends; the pore size of nanotube pores is the diameter of the nanotube pore, and only the adsorption inside the nanotube pore was considered; the pore size of the slit pore model is the distance in the innermost graphite sheets.
The construction of four different surface curvature models is composed of BSUs (five membered corannulene rings, six membered corannulene rings and seven membered corannulene rings, and the models are referred to as AC1, AC2, AC3 and AC4 according to the number of five membered corannulene rings and seven membered corannulene rings from less to more). The change of surface curvature depends on the number of five membered corannulene rings and seven membered corannulene rings. In order to better compare the impact of surface curvature, the density of the four models is maintained at 0.8 g·cm$^{-3}$. Models including the five membered corannulene ring, the six membered corannulene ring and the seven membered corannulene ring are shown in Fig. 2. In this paper, all AC models use periodicity in the x, y and z directions. Sizes of simulation boxes of four different surface curvature models are 39.1*39.1*39.1 Å.

The energy and structure of CO$_2$ and N$_2$ were optimized by Dmol3 module. The optimization method refers to the work of An et al. [32] and Liao et al. [33] The generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) function [34] was selected to calculate. The electrostatic potential (ESP) fitting method was used to obtain atomic charges. The optimized models are shown in Fig. 3, in which the length of C-O bond is 1.175 Å, and the atomic charges of C and O atoms are +0.596 e and −0.298 e respectively, and the length of N-N bond is 1.108 Å. The models of CO$_2$ and N$_2$ in this paper are close to the common physical models [35, 36].

2.2 Grand canonical Monte Carlo simulation

The GCMC method was used to calculate the adsorption data of AC for CO$_2$ and N$_2$ within 1000 kPa. In the simulation, the molecule was regarded as rigid, and the volume (V), the chemical potential (µ), and the temperature (T) remained constant, where the temperature was maintained at 293K. All GCMC simulations first performed 5×10$^6$ equilibrium steps, and then performed 5×10$^6$ production steps to obtain the average adsorption capacity. Besides, the interaction between adsorbent and adsorbate was calculated by the sum of the van der Waals and the electrostatic energy. The van der Waals force was calculated based on the atom-based method, and the electrostatic force was calculated based on the Ewald and group method. The cutoff radius of molecular interaction energy was 15.5 Å. The Lennard Jones (LJ) parameters of AC, CO$_2$ and N$_2$ were taken from the Dreiding force field [37]. For different kinds of interatomic interaction parameters, they were obtained by Lorentz–Berthelot mixing rules. The equation of interaction energy and LJ parameters of atoms are shown in Support Information.

In order to compare the absolute adsorption capacity $N_{\text{abs}}$ obtained by simulation with the experimental data, the simulation data was converted into excess adsorption capacity $N_{\text{excess}}$ through Eq. (1).

$$ N_{\text{excess}} = N_{\text{abs}} - V \times \rho_g \quad (1) $$

where, $V$ is the free volume of AC, and $\rho_g$ is the density of the gas at a certain temperature and pressure.
Adsorption density $\rho_{\text{abs}}$ can be obtained by the Eq. (2).

$$\rho_{\text{ads}} = \frac{N}{V_{\text{acc}}} \quad (2)$$

In Eq. (2), $N$ and $V_{\text{acc}}$ are the average number of adsorbed molecules and the accessible volume of the cell, respectively.

For exploring separation performance, the selectivity of CO$_2$ ($S$) is calculated by the following formula.

$$S = \frac{\left( \frac{x_1}{y_1} \right)_{\text{pore}}}{\left( \frac{x_2}{y_2} \right)_{\text{bulk}}} \quad (3)$$

where $x_1$ and $y_1$ represent the mole fractions of CO$_2$ and N$_2$ in the adsorbed phase, and $x_2$ and $y_2$ represent the mole fractions of CO$_2$ and N$_2$ in the bulk phase.

3. Results And Discussion

3.1 Impact of pore structure on adsorption and separation

In this section, the accuracy of the disordered pore model is verified by comparing its excess adsorption capacity with the experimental material data [31]. Then, the effects of different pore structures on the adsorption density, interaction energy of adsorbates and the CO$_2$ selectivity are explored. Furthermore, the differences of adsorption in different pore structures are intuitively displayed through adsorption snapshots.

3.1.1 Comparison of adsorption density of pore structures

As shown in Fig. 4, the adsorption isotherms of N$_2$ obtained by simulation and experiment basically coincide, and there is only a slight difference between the adsorption isotherms of CO$_2$. It is worth noting that the disordered pore model in this paper only includes carbon atoms, other atoms such as nitrogen, hydrogen and oxygen do not exist. But nitrogen-containing functional groups can improve the adsorption of CO$_2$ [38], as CO$_2$ is considered as Lewis acid and the introduction of nitrogen can increase the basicity of carbon framework, which increases the affinity of AC for CO$_2$ [39]. Therefore, it can be explained that the CO$_2$ adsorption capacity of simulation is less than that of the experiment in a pressure range before 600 kPa. Moreover, since the accessible volume of the disordered pore model is larger than that of the experimental material, the CO$_2$ adsorption capacity of the former is larger at 1000 kPa. In short, the simulation results are in good agreement with the experimental data, which verifies the rationality of the disordered pore model.
Figure 5 shows that at low pressure, the adsorption density of CO\textsubscript{2} follows the sequence of the nanotube pore, the disordered pore, the wedge pore and the slit pore model. Because the curved wall has the strongest fluid-solid potential energy with CO\textsubscript{2}, the adsorption density of CO\textsubscript{2} in the nanotube pore is the largest. While the adsorption density of CO\textsubscript{2} in disordered pore and wedge pore is larger than that in the slit pore as they have small pore size. Under low pressure, it is difficult to distinguish the adsorption density of N\textsubscript{2} in the four structures. The reason for the phenomenon is that the quadrupole moment and polarizability of CO\textsubscript{2} are higher than that of N\textsubscript{2}, resulting in more van der Waals force between CO\textsubscript{2} and carbon chain [40], therefore, the change of fluid-solid potential energy caused by pore structure can be captured by CO\textsubscript{2}. Moreover, in the early stage of adsorption, the adsorption density of CO\textsubscript{2} increases with pressure much faster than that of N\textsubscript{2}, which also proves the conclusion.

In high pressure, the adsorption density of adsorbates in nanotube pores is much higher than that in other pore structures. Because of the curved structure and small pore volume of nanotube pores, the fluid-solid potential energy and fluid-fluid potential energy of adsorbates in the pore are the strongest. Among other three pore structures, the adsorbates in the disordered pore have a higher adsorption density. The reason lies on that the structure has a wide pore size distribution, especially with pores smaller than 1.67 nm, so the adsorbate is subjected to stronger fluid-solid potential energy. Compared with CO\textsubscript{2} adsorbed more in the slit pore than in the wedge pore, the adsorption density of N\textsubscript{2} in the two pore structures is very similar or even slightly higher in the wedge pore, which means that the adsorption performance of CO\textsubscript{2} is very different from that of N\textsubscript{2}. The former may be limited by the pore size (the pore size of the slit pore is more uniform than that of the wedge pore, so the CO\textsubscript{2} in slit pore is subjected to stronger fluid-solid and fluid-fluid potential energy at high pressure), while the latter will be limited by the specific surface area (it can be seen from Table 1 that the specific surface area of wedge pore is slightly larger than that of slit pore), since N\textsubscript{2} has a weaker affinity for AC, and only monolayer adsorption may have occurred on the pore wall of AC.

### 3.1.2 Adsorption processes in different pore structures

To get a clearer perspective on the difference in CO\textsubscript{2} and N\textsubscript{2} adsorption by pore structures, Fig. 6 gives snapshots of adsorption at 10 kPa, 100 kPa, 300 kPa, 500 kPa, 700 kPa, and 1000 kPa (only snapshots of N\textsubscript{2} in the nanotube pore and the wedge pore are shown in the figure, other snapshots are shown in the Fig. S2-Fig. S5).

As can be seen from Fig. 6 that the molecules of N\textsubscript{2} are adsorbed near the pore wall in nanotube pores at the beginning of adsorption, but with the increase of pressure, the pore center is gradually filled with N\textsubscript{2} molecules, resulting in multilayer adsorption. Different from nanotube pores, N\textsubscript{2} molecules are adsorbed near the pore wall of wedge pores and monolayer adsorption occurs. In addition, there is no significant filling at the smaller end of the pore size, which corresponds to the fact that the adsorption of N\textsubscript{2} is easily limited by the specific surface area rather than the pore size.

### 3.1.3 Change of interaction energy of pore structure
Intermolecular interaction can reflect the affinity between adsorbate and adsorbent [32], so it is necessary to explore the effect of pore structure on intermolecular interaction energy.

As shown in Fig. 7 that the interaction energy of the four pore structures displays different order with the increase of pressure. The interaction energy of disordered pores is the largest at the beginning, but as the pressure increasing, the interaction energy of nanotube pores is the highest. Except for the disordered pore, the interaction energy of other pore structures fluctuates slightly or remains in a stable state, because the shapes of the three pore structures are more regular. Although the small pore size, defects and surface curvature in the disordered pore provide strong energetically adsorption sites, when these strong energetically adsorption sites are occupied, the fluid-solid potential energy of adsorbates decreases significantly. Thus, the interaction energy decreases rapidly at low pressure.

Different from the influence of wedge pore and slit pore on the adsorption density of adsorbates, the interaction energy of wedge pore is always higher than that in slit pore, which is due to the strong fluid-solid potential energy brought by the small pore end of wedge pore. And, the fluid-fluid potential energy of two pore structures is close. Therefore, the gap between the corresponding interaction energy curves in the figure only slightly changes with the increase of pressure.

### 3.1.4 Difference in CO$_2$ selectivity between pore structures

For exploring the effect of pore structure on CO$_2$ separation performance, in this paper, the mole fractions of CO$_2$/N$_2$ in the bulk phase is maintained at 0.15/0.85, which is the typical proportion of in flue gas [41]. It has been observed from Fig. 8 that the disordered pore structure has the strongest selectivity for CO$_2$ within a pressure range at the beginning of adsorption, but it decreases rapidly. Because with the increase of pore size filled by gas mixture, the impact of pore size on selectivity becomes weaker and weaker, and finally tends to be stable. The selectivity of CO$_2$ in nanotube pores is generally high and stable, but local fluctuations remain. The increase of selectivity for CO$_2$ can be attributed to cooperative interactions between CO$_2$ molecules [42], while the decrease of selectivity for CO$_2$, especially in the pressure range of 700–1000 kPa is caused by the packing effect [43] (which means that smaller molecules are conducive to being filled in the pores created by adsorbed molecules under high pressure). For better understanding, Fig. 9 show the adsorption snapshot of the mixed gas at 1000 kPa. It can be clearly seen from Fig. 9 that N$_2$ molecules with smaller size are adsorbed in the pores created by CO$_2$ molecules under high pressure. The selectivity of the wedge pore and the slit pore to CO$_2$ is stable, which is maintained at about 14 and 10.5, respectively. Compared with the slit pore, the wedge pore has greater selectivity for CO$_2$. This can also be seen from the isosteric heat of adsorbed molecules in pores, because CO$_2$ molecules in the wedge pore have stronger fluid-solid potential energy.

From the competitive adsorption of CO$_2$/N$_2$ in different pore structures in Fig. 10, it can be seen that the adsorption capacity of CO$_2$ is the key to determining the selectivity. The adsorption density of N$_2$ in different pore structures is very close overall, but the adsorption density of CO$_2$ in nanotube pores far
exceeds that in other pores, because the ring structure will significantly increase the adsorption energy between CO$_2$ and AC.

In order to analyze the adsorption process of binary mixture from the perspective of energy, stable adsorption structures are established by using Dmol3 module, as shown in Fig. 11. The figure shows the adsorption structure of AC when CO$_2$ or N$_2$ is adsorbed after one CO$_2$ molecule is preferentially adsorbed. The corresponding adsorption energy $E_{ads}$ is as follows.

$$E_{ads} = E_{two} - E_{single} - E_{adsorbate}$$

Where, $E_{two}$ is the energy of AC with two adsorbates, $E_{single}$ is the energy of AC with CO$_2$, $E_{adsorbate}$ is the energy of CO$_2$ or N$_2$.

It is difficult to explore all possible adsorption structures. Therefore, considering the high affinity between CO$_2$ and AC, this paper totally constructed 24 stable structures in the same plane, above the side and above after preferentially adsorbing one CO$_2$ molecule. All constructed adsorption structures are shown in Fig. S6 and Fig. S7. Only four adsorption structures are shown in Fig. 11 because they are the most stable. After adsorbing CO$_2$, the adsorption energy of adsorbing N$_2$ molecules is higher than that of adsorbing CO$_2$. The former can be achieved $-5.58$ kJ·mol$^{-1}$ and the latter can be achieved $-4.42$ kJ·mol$^{-1}$. Therefore, from the perspective of energy, N$_2$ molecules are more likely to be adsorbed near the adsorption site where CO$_2$ molecules have been adsorbed. This phenomenon should be more pronounced at high pressure, as evidenced by the fact that the selectivity to CO$_2$ of the four pore structures shown in Fig. 8 has a certain downward trend at high pressure.

### 3.2 Impact of surface curvature on adsorption and separation

In this section, the effect of the surface curvature of AC on adsorption and separation performance was studied. The surface curvature of AC is controlled by the number of five membered corannulene rings and seven membered corannulene rings in models. The changes of AC structure, adsorption density, interaction energy and CO$_2$ selectivity caused by surface curvature are as follows.

#### 3.2.1 Influence of surface curvature on structure

Table 2 and Fig. 12 show the physical properties of four models with different surface curvature. The surface area, pore volume and density of the model are obtained by Materials Studio software, and the pore size distribution is obtained by Poreblazer program [44]. It can be seen from Table 2 that the pore volume and density of the four models are basically the same. And the surface areas of the four models are close. Although the addition of five membered corannulene rings and seven membered corannulene rings does not always cause the increase of surface area, the surface areas of AC3 and AC4 increase
compared with AC1, because the presence of non-six membered rings will lead to the bending of carbon pore wall and is likely to lead to the increase of specific surface area.

The pore size distribution of the four models has changed greatly. The change of it has no obvious relationship with the type and number of corannulene rings, as the corannulene rings were packed in random positions and directions in the cell. The pore size of AC1 is mainly distributed between 11.5–17.5 Å, the pore size of AC2 is mainly distributed between 12 and 16.5 Å, the pore size of AC3 is mainly distributed between 9.5–17.5 Å, and the pore size of AC4 is mainly distributed between 11.5–16.5 Å.

Table 2
Physical parameters of four models with different surface curvature

| Structure | Surface area (m²·g⁻¹) | Pore volume (cm³·g⁻¹) | Density (g·cm⁻³) | Number of corannulene rings |
|-----------|------------------------|-----------------------|-----------------|-----------------------------|
|           |                        |                       |                 | Five membered               |
|           |                        |                       |                 | Six membered                |
|           |                        |                       |                 | Seven membered              |
| AC1       | 1287.78                | 0.60                  | 0.8             | 0                           | 100 | 0 |
| AC2       | 1234.26                | 0.59                  | 0.8             | 13                          | 75  | 12|
| AC3       | 1341.65                | 0.59                  | 0.8             | 25                          | 50  | 25|
| AC4       | 1365.52                | 0.60                  | 0.8             | 38                          | 25  | 37|

3.2.2 Comparison of adsorption density in models with different surface curvatures

Figure 13 displays that the density of adsorbates in AC1 is the lowest among the four models, and the density of adsorbates in AC4 is the highest. The high density of adsorbates in AC4 can be attributed to the combined action of large surface area and surface curvature. And, the reason why the density of adsorbates in AC2 ranks second is also due to the surface curvature, as the surface area of AC2 is smaller than that of AC1 and AC3, and the pore sizes distribution of AC1 and AC3 is more abundant. The existence of surface curvature can significantly improve the density of adsorbates in AC2 by providing strong energetically adsorption sites. When the pressure is higher than 700 kPa, the density of CO₂ in AC2 is close to that in AC3, which is attributed to the existence of more small pores in AC3. Whereas, since N₂ is less affected by the fluid-solid potential energy brought by the pore size and more affected by the fluid-solid potential energy caused by the pore wall, the density of N₂ in AC2 with more strong energy adsorption sites is consistently greater than that in AC3.

3.2.3 Change of interaction energy in models with different surface curvatures
It can be seen from Fig. 14 that the interaction energy in the four models is in order: AC4 > AC2 > AC3 > AC1. The difference between the interaction energy curves is due to the difference of surface curvature and pore size, especially the former. At the initial stage of adsorption, the small pore size and surface curvature in the four models provide strong energy adsorption sites for the adsorbate. With the increase of pressure, these adsorption sites are occupied, and the fluid-solid potential energy decreases, resulting in the decrease of interaction energy. This change is particularly obvious in AC4 and AC2 models. After reaching a certain pressure, the change of fluid-solid potential energy and fluid-fluid potential energy reach equilibrium, so the interaction energy also tends to be stable.

### 3.2.4 Difference in CO\textsubscript{2} selectivity in models with different surface curvatures

Figure 15 shows that under the same pressure, the selectivity of CO\textsubscript{2} in four models is in order: AC4 > AC2 > AC3 > AC1, which is similar to the effect of surface curvature on the intermolecular interaction energy. The selectivity of CO\textsubscript{2} in AC4 and AC2 is higher than that in AC1 and AC3, indicating that the surface curvature has a positive effect on the selectivity of CO\textsubscript{2}. Additionally, the four models possess disordered pore structure and complex pore size distribution, resulting in the local influence of CO\textsubscript{2} selectivity. Therefore, the selectivity of CO\textsubscript{2} in the four models fluctuates locally and is the decreasing function of pressure.

Figure 16 and Fig. 17 respectively show the adsorption density distribution and the adsorption density of CO\textsubscript{2} and N\textsubscript{2}. It can be seen from Fig. 16 that the adsorption sites of CO\textsubscript{2} and N\textsubscript{2} are consistent, indicating that there is competition between CO\textsubscript{2} and N\textsubscript{2}, which is caused by the fact that their adsorption mainly depends on fluid-solid potential energy. Therefore, in Fig. 17, the sharp decline of CO\textsubscript{2} adsorption density is attributed to the decrease of adsorption pressure on the one hand and the competition of N\textsubscript{2} on the other hand. During competitive adsorption, the adsorption density of CO\textsubscript{2} and N\textsubscript{2} in AC2 and AC4 are higher than those in AC1 and AC3, and CO\textsubscript{2} will be occupied preferentially, which explains the high selectivity of CO\textsubscript{2} caused by AC2 and AC4 in Fig. 15 above.

### 4. Conclusion

The adsorption and separation of CO\textsubscript{2}/N\textsubscript{2} on AC with different pore structures and surface curvature were studied in detail through GCMC simulation. Studies have found that the adsorbates in nanotube pores possess the strongest interaction energy and the largest density on the whole. The interaction energy of adsorbates in the disordered pore are the decreasing function of pressure, while the interaction energy in other pore structures changes little. Due to the difference of affinity between gas molecules and AC, CO\textsubscript{2} is easy to be affected by the pore size, while N\textsubscript{2} is more sensitive to the specific surface area. So, although the interaction energy of adsorbates in the wedge pore is stronger than that in the slit pore, the density of CO\textsubscript{2} in the slit pore is greater than that in the wedge pore under high pressure due to the
smaller pore size. The selectivity of CO\textsubscript{2} is mainly affected by the fluid-solid potential energy and the adsorption capacity of CO\textsubscript{2}. The nanotube pores with closed structure have the highest selectivity of CO\textsubscript{2}, followed by the disordered pore, the wedge pore and the slit pore. Furthermore, the existence of non-six membered rings leads to the generation of surface curvature, which has positive impacts on the adsorption density, interaction energy of adsorbates and selectivity of CO\textsubscript{2} by providing strong energy adsorption sites. Because the four models with different surface curvature are the disordered pore structures and have wide pore size distribution, the selectivity of CO\textsubscript{2} in the four models is a decreasing function of pressure and presents local fluctuation.

**Declarations**

**Acknowledgements**

This work was supported by the National Natural Science Foundation of China (No. 52174058 and No. 51804045), the Key Research and Development Program of Jiangsu Province (Industry Foresight and Common Key Technology, No. BE2018065), and the Postgraduate Research & Practice Innovation Program of Jiangsu Province (No. KYCX21_2869, No. KYCX21_2790, and No. SJCX21_1208).

**Competing interests**

The authors declare no competing interests.

**Availability of data and materials**

The data that support the findings of this study are available from the corresponding author on reasonable request.

**Authors' contributions**

Conceptualization: Weiqiu Huang and Weihua Chen

Funding acquisition: Weiqiu Huang, Lipei Fu and Xufei Li

Methodology: Weiqiu Huang, Lipei Fu and Xufei Li

Writing - original draft: Weihua Chen and Xinya Wang

Formal analysis: Yongyin Zheng, Xinya Wang and Weihua Chen

Software and data curation: Yilong Zhang

Supervision: Jiahui Zhu and Bing Zhu

**References**
1. S. Mukherjee, N. Sikdar, D. O’Nolan, D.M. Franzvictoria, V. Gascon, A. Kumar, N. Kumar, H.S. Scott, D.G. Madden, P.E. Kruger, B. Space, M.J. Zaworotko, Sci. Adv. 5, eaax9171 (2019). https://doi.org/10.1126/sciadv.aax9171

2. E.J. Kim, R.L. Siegelman, H.Z.H. Jiang, A.C. Forse, J.H. Lee, J.D. Martell, P.J. Milner, J.M. Falkowski, J.B. Neaton, J.A. Reimer, S.C. Weston, J. R Long. Science 369, 392 (2020). https://doi.org/10.1126/science.abb3976

3. W. Gao, S. Liang, R. Wang, Q. Jiang, Y. Zhang, Q. Zheng, B. Xie, C.Y. Toe, X. Zhu, J. Wang, L. Huang, Y. Gao, Z. Wang, C. Jo, Q. Wang, L. Wang, Y. Liu, B. Louis, J. Scott, A.C. Roger, R. Amal, H. He, S.E. Park, Chem. Soc. Rev. 49, 8584 (2020). https://doi.org/10.1039/D0CS00025F

4. A. Bhatnagar, W. Hogland, M. Marques, M. Sillanpää, Chem. Eng. J. 219, 499 (2013). https://doi.org/10.1016/j.cej.2012.12.038

5. X. Li, B. Yan, W. Huang, H. Bian, X. Wang, J. Zhu, S. Dong, Y. Wang, W. Chen, Chem. Eng. J. 428, (2022). https://doi.org/10.1016/j.cej.2021.132501

6. R. Taddeo, S. Prajapati, R. Lepistö, J. Porous Mat. 24, 1545 (2017). https://doi.org/10.1007/s10934-017-0394-1

7. Y. Chu, M.A. Khan, S. Zhu, M. Xia, W. Lei, F. Wang, Y. Xu, J. Chem. Technol. Biot 94, 3585 (2019). https://doi.org/10.1002/jctb.6162

8. L. Fu, J. Zhu, W. Huang, J. Fang, X. Sun, X. Wang, K. Liao, Processes 8, 372 (2020). https://doi.org/10.3390/pr8030372

9. C. Tran, V. Kalra, J. Power Sources 235, 289 (2013). https://doi.org/10.1016/j.jpowsour.2013.01.080

10. C. Shen, C.A. Grande, P. Li, J. Yu, A.E. Rodrigues, Chem. Eng. J. 160, 398 (2010). https://doi.org/10.1016/j.cej.2009.12.005

11. H. Yi, F. Li, P. Ning, X. Tang, J. Peng, Y. Li, H. Deng, Chem. Eng. J. 215, 635 (2013). https://doi.org/10.1016/j.cej.2012.11.050

12. L. Liu, D. Nicholson, S.K. Bhatia, Chem. Eng. Sci. 121, 268 (2015). https://doi.org/10.1016/j.ces.2014.07.041

13. K.V. Kumar, F. Rodríguez-Reinoso, RSC Adv. 2, 9671 (2012). https://doi.org/10.1039/C2RA20775C

14. C. Fan, D.D. Do, D. Nicholson, Ind. Eng. Chem. Res. 52, 14304 (2013). https://doi.org/10.1021/ie402549z

15. Y. Zeng, P. Phadungbut, D.D. Do, D. Nicholson, J. Phys. Chem. C 119, 25853 (2015). https://doi.org/10.1021/acs.jpcc.5b06085

16. S.K. Bhatia, Langmuir 33, 831 (2017). https://doi.org/10.1021/acs.langmuir.6b03459

17. S. Agnihotri, J.P.B. Mota, M. Rostam-Abadi, M.J. Rood, Langmuir 21, 896 (2005). https://doi.org/10.1021/la047662c

18. K.V. Kumar, E.A. Müller, F. Rodriguez-Reinoso, J. Phys. Chem. C 116, 11820 (2012). https://doi.org/10.1021/jp302749t
19. Z. Zhang, R. Brydson, Z. Aslam, S. Reddy, A. Brown, A. Westwood, B. Rand, Carbon **49**, 5049 (2011). https://doi.org/10.1016/j.carbon.2011.07.023

20. M. Acharya, M.S. Strano, J.P. Mathews, S.J.L. Billinge, V. Petkov, S. Subramoney, H.C. Foley, Philos. Mag B **79**, 1499 (1999). https://doi.org/10.1080/13642819908218318

21. T.X. Nguyen, N. Cohaut, J.S. Bae, S.K. Bhatia, Langmuir **24**, 7912 (2008). https://doi.org/10.1021/la800351d

22. B.E. Di, S.L. Carbon 64, 262 (2013). https://doi.org/10.1016/j.carbon.2013.07.061

23. M. Wiśniewski, K. Werengowska-Ciećwierz, A.P. Terzyk, Chem. Phys. Lett. **619**, 219 (2015). https://doi.org/10.1016/j.cplett.2014.11.024

24. J.B. Klauda, J. Jiang, S.I. Sandler, J. Phys. Chem. B **108**, 9842 (2004). https://doi.org/10.1021/jp037897h

25. K. Balamurugan, E.R.A. Singam, V. Subramanian, J. Phys. Chem. C **115**, 8886 (2011). https://doi.org/10.1021/jp110898r

26. P.J.F. Harris, J. Mater. Sci. **48**, 565 (2013). https://doi.org/10.1007/s10853-012-6788-1

27. D. Bahamon, A.E. Ogungbenro, M. Khaleel, M.R.M. Abu-Zahra, L.F. Vega, Ind. Eng. Chem. Res. **59**, 7161 (2020). https://doi.org/10.1021/acs.iecr.9b05542

28. S. Li, K. Song, D. Zhao, J.R. Rugarabamu, R. Diao, Y. Gu, Micropor. Mesopor. Mat. **302**, 110220 (2020). https://doi.org/10.1016/j.micromeso.2020.110220

29. S.M.P. Lucena, C.A.S. Paiva, P.F.G. Silvino, D.C.S. Azevedo, C.L.C. Jr, Carbon **48**, 2554 (2010). https://doi.org/10.1016/j.carbon.2010.03.034

30. J.M. Leyssale, J.P.D. Costa, C. Germain, P. Weisbecker, G.L. Vignoles, Carbon **50**, 4388 (2012). https://doi.org/10.1016/j.carbon.2012.05.015

31. Y. Park, D.K. Moon, Y.H. Kim, H. Ahn, C.H. Lee, Adsorption **20**, 631 (2014). https://doi.org/10.1007/s10450-014-9608-x

32. Y. An, Q. Fu, D. Zhang, Y. Wang, Z. Tang, Chemosphere **227**, 9 (2019). https://doi.org/10.1016/j.chemosphere.2019.04.011

33. P.Q. Liao, W.X. Zhang, J.P. Zhang, X.M. Chen, Nat. Commun. **6**, 1 (2015). https://doi.org/10.1038/ncomms9697

34. J.P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996). https://doi.org/10.1103/PhysRevLett.77.3865

35. J.G. Harris, K.H. Yung, J. Phys. Chem. **99**, 12021 (1995). https://doi.org/10.1021/j100031a034

36. K. Makrodimitris, G.K. Papadopoulos, D.N. Theodorou, J. Phys. Chem. B **105**, 777 (2001). https://doi.org/10.1021/jp002866x

37. S.L. Mayo, B.D. Olafson, W.A. Goddard, J. Phys. Chem. **94**, 8897 (1990). https://doi.org/10.1021/j100389a010

38. K.V. Kumar, K. Preuss, L. Lu, Z.X. Guo, M.M. Titirici, J. Phys. Chem. C **119**, 22310 (2015). https://doi.org/10.1021/acs.jpcc.5b06017
39. A. Mukherjee, J.A. Okolie, A. Abdelrasoul, C. Niu, A.K. Dalai, J. Environ. Sci. 83, 46 (2019).
   https://doi.org/10.3390/pr8030372

40. S.M. Hong, S.W. Choi, S.H. Kim, K.B. Lee, Carbon 99, 354 (2016).
   https://doi.org/10.1016/j.carbon.2015.12.012

41. S. Zhuo, Y. Huang, J. Hu, H. Liu, Y. Hu, J. Jiang, J. Phys. Chem. C 112, 11295 (2008).
   https://doi.org/10.1021/jp083428n

42. B. Liu, B. Smit, J. Phys. Chem. C 114, 8515 (2010). https://doi.org/10.1021/jp101531m

43. B. Smit, T.L.M. Maesen, Chem. Rev. 108, 4125 (2008). https://doi.org/10.1021/cr076063j

44. L. Sarkisov, A. Harrison, Mol. Simulat 37, 1248 (2011).
   https://doi.org/10.1080/08927022.2011.592832

**Figures**
Figure 1
Four different pore structure models (disordered pore (a), nanotube pore (b), wedge pore (c) and slit pore (d))

Figure 2
Four different surface curvature models (a-d are AC1, AC2, AC3 and AC4, respectively)
Figure 3

Molecular structure models including CO$_2$ (a) and N$_2$ (b), and their surface electrostatic potential

(grey: carbon atoms; blue: nitrogen atoms; red: oxygen atoms)
Figure 4

Comparison of experimental data and simulated adsorption capacity of CO$_2$ and N$_2$ (Sim: simulation data, Exp: experimental data measured by Park et al. [31])
Figure 5

Adsorption density of CO₂ (a) and N₂ (b) for four pore structures

Figure 6

Adsorption snapshots of N₂ in nanotube pores (a1-a6) and wedge pores (b1-b6) at 10 kPa, 100 kPa, 300 kPa, 500 kPa, 700 kPa and 1000 kPa
Figure 7

Interaction energy of CO$_2$ (a) and N$_2$ (b) for four pore structures
Figure 8

Selectivity of CO$_2$ in four pore structures
Figure 9

Adsorption snapshot of nanotube pores at 1000 kPa

Figure 10

Competitive adsorption of CO$_2$/N$_2$ in four pore structures
Figure 11

Stable adsorption configurations of CO2 (a, b) and N2 (c, d) on AC adsorbed with CO2 from different directions, (a) and (b): top view and front view, (c) and (d): side view and front view.

Figure 12

Pore size distribution of four different surface curvature models.
Figure 13

Adsorption density of CO$_2$ (a) and N$_2$ (b) in four different surface curvature models

Figure 14

Interaction energy of CO$_2$ (a) and N$_2$ (b) in four different surface curvature models
Figure 15

Selectivity of CO₂ in four different surface curvature models

Figure 16

Adsorption density distribution of CO₂ (green) and N₂ (red) in the AC4 at 1000 kPa
Figure 17

Competitive adsorption of CO$_2$/N$_2$ in four different surface curvature models

Supplementary Files
This is a list of supplementary files associated with this preprint. Click to download.

- SupportInformation.docx