

# The Adsorption and Separation of CO<sub>2</sub>/CH<sub>4</sub> Mixtures with Nanoporous Adsorbents by molecular simulation

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## Abstract

We report a grand canonical Monte Carlo simulation study focused on the adsorption of CO<sub>2</sub>/CH<sub>4</sub> mixtures in different nanopore models that include pristine mesoporous carbons, carbon foams, carbon nanotubes (CNTs) and nanopore models modified with hydrophilic carboxylic groups. We report and discuss the selectivity of the different adsorbent morphologies under a wide range of temperature and pressure. Results show that the foam structures have the highest adsorption capacity of all pristine structures studied because of its special architecture. The selectivity enhanced markedly after modification especially at low pressures, and modified CNTs have highest selectivity. We report the effect of temperature and pressure and note the selectivity change trends of modified nanopore models are contrary to that of pristine ones. The results suggest that the separation performance in carbon nanopores is greatly affected by the nature of the architecture and of the heterogeneity of the materials. Results could be beneficial in conventional pressure swing adsorption processes and as parts of mixed polymer membranes. We review some guidelines for the design of nanoporous structures for the optimal separation of CO<sub>2</sub>/CH<sub>4</sub> mixture.

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## **1. Introduction**

There is a renewed interest in energy-efficient process for the separation of the carbon dioxide/methane (CO<sub>2</sub>/CH<sub>4</sub>) gaseous mixture. On one hand, the control of global warming in the short term relies on the capture and sequestration of CO<sub>2</sub> in viable underground reservoirs. The pumping of CO<sub>2</sub> in unmineable coal seams is hence an option; however, coal seams are saturated with CH<sub>4</sub> and the understanding of the selective adsorption of the CO<sub>2</sub>/CH<sub>4</sub> is a prerequisite to perform the large scale modeling of these processes considered achievable near-term methods of reducing emissions of this greenhouse gas[1]. On the other hand, shale gas and marsh gases are evolving as a replacement for more conventional fossil fuels only after CH<sub>4</sub> is separated and purified. The injection of CO<sub>2</sub> into coal seams with the purpose of enhancing the desorption of coalbed methane (a process called enhanced coalbed methane recovery (ECBM)) has been known to be a feasible process[2][3]. Amongst the low energy consumption alternatives for separation of the mixture we encounter adsorption on carbons and/or purification using nanoporous carbon-based membranes[4]. In this latter cases, the selectivity and flux of membrane is crucially related to the pore architecture and chemical composition of membrane materials in a very non-intuitive way.

Adsorption of CO<sub>2</sub> has been studied experimentally for many decades[5]. Most experiments performed to date have been performed at low pressure (usually below ambient) and sometimes at very low temperatures. The experimental work is hindered by the problem of characterizing the pore structure of coal, due to a swelling of the porous matrix. Furthermore, the interpretation of the data is not universal, mainly due to the lack

of detailed knowledge on the underlying physical phenomena. Therefore, the development of an understanding of the adsorption properties of CO<sub>2</sub> and CH<sub>4</sub> is vital for the optimum development of techniques to recover CH<sub>4</sub> while sequestering CO<sub>2</sub>. Molecular modeling of atomistically resolved structures allow the determination of the underlying mechanisms of selectivity and serve to explain in detail the relationship between pore architecture and function. Molecular simulation poses an advantage over experiments in allowing the systematic and controlled study of the various relevant variables.

Some simulation researches for adsorptions of CH<sub>4</sub>, CO<sub>2</sub> and/or their mixtures were performed in recent years. Lim predicted adsorption isotherms and diffusivities of CO<sub>2</sub> in the slit pore by GCMC and found the permeability within the slit pore is more strongly influenced by adsorption isotherms than by diffusion[6]. Vanin studied the adsorption of methane in carbon pores with rectangular, square, triangular, and circular cross sections by the Monte Carlo method in a grand canonical ensemble to research the forming of monolayer of methane molecules in different structure pores[7]. Kwalczyk use Grand canonical Monte Carlo (GCMC) simulation for the systematic investigation of the supercritical methane adsorption at 273 K on an open graphite surface and in slitlike micropores of different sizes. The effect of the pore size on the maximum surface excess and isosteric enthalpy of adsorption for methane storage at 273 K is discussed[8]. Zhang[9] found that the adsorption of methane in smaller SWNTs, whose diameters are 1.22 nm and 1.632 nm, exhibits "pore filling" behavior. In contrast, for the SWNTs of diameter larger than 2.04 nm, capillary condensation takes place. By simulation of isotherm and energies of adsorption Bojan reported the adsorption of methane in a

number of model porous solids at 300 K. The solids are made up of graphite basal planes arranged to make either parallel-walled slit pores or pores of triangular cross section[10]. Yang[11] simulated adsorption characteristics of carbon dioxide in slit graphite pores, The simulation results show that the minimum pore width for the adsorption of CO<sub>2</sub> is 0.57 nm, the maximum adsorption occurs at pore width. H = 2.43 nm and pressure P = 2.56-3.41 MPa. Peng[12] performed a molecular simulation study on methane and carbon dioxide storage in carbon nanoscrolls, and found that the adsorption of gases on pristine carbon nanoscrolls is relatively low. However, once the interlayer spacing is expanded, both adsorption capacities of methane and carbon dioxide exhibit a significant improvement. Density Functional Theory (DFT) and Grand Canonical Monte Carlo (GCMC) were used to simulate the adsorption of carbon dioxide, methane and the mixture, and the results with two methods were compared[13]. The adsorption of pure-component and binary mixtures of methane and carbon dioxide in a specific activated carbon was predicted[14]. These research work show the temperature, pressure and pore size affect the adsorption behavior of CO<sub>2</sub>, CH<sub>4</sub> or their mixtures. Although many researchers used adsorbents with different structure, few researchers consider the effect of pore architecture. Then Palmer et. al. researched the adsorptive behavior of CO<sub>2</sub>, CH<sub>4</sub> and their mixtures in four types of nanoporous carbons, which are examined as adsorbents for the separation of CO<sub>2</sub>/CH<sub>4</sub> mixtures at ambient temperature and pressures up to 10 MPa. They found both the pore morphology and size are the key variables[15]. But the reason should be studied in detail, and then we can give more specific prediction for industry process design.

It is known that CNTs can be chemically functionalized at their ends or outer walls

with various functional groups. Using carboxyl acid ( $-\text{COOH}$ ) groups, the successful modification on the ends of CNTs has already been reported experimentally.[16]-[18]. Beckstein and co-workers found that a closed hydrophobic pore can be switched to an open state for water permeation by introducing the hydrophilic character.[19][20]. Zheng and co-workers anchored  $-\text{COOH}$  groups onto the inner wall of a CNT to alter the hydrophobic surface into a hydrophilic one and carried out the dual-control-volume grand canonical molecular dynamics simulations to study the transport of water and methanol mixtures through the modified CNTs[21]. Huang et al.[22] found that the incurvature or excurvature configurations of  $-\text{COOH}$  groups on the mouths of CNT could control the flow direction of water molecules. Zhu et.al. [23]found the  $-\text{COOH}$  groups on the inner wall of the central region have a slight effect on the axial density distribution of the water molecules near the tube mouths, but a strong impact on that of water molecules inside the CNTs. Since  $-\text{COOH}$  groups can affect the behavior of water confine in CNTs, the adsorption of  $\text{CO}_2$  could be affect by modify the porous carbon adsorbent.

In this work, in order to investigate the effects of pore architecture and chemical modification the adsorption of  $\text{CO}_2/\text{CH}_4$  mixtures in different nanopore models that include pristine mesoporous carbons, carbon foams, carbon nanotubes (CNTs) and nanopore models modified with hydrophilic carboxylic groups will be performed by grand canonical Monte Carlo simulation.

## **2. Simulation Details and potential models**

### **2.1 Simulation Details**

GCMC simulations of equimolar  $\text{CO}_2/\text{CH}_4$  mixtures adsorption in different nanopore models were performed with Music 4.0 code. MC moves were attempted randomly with

probability of 50% for translation/rotation and 50% each for creation and deletion, and 33% each for translation creation and deletion for CH<sub>4</sub>. The maximum displacement step size was adjusted during equilibration to achieve approximately a 50% acceptance ratio for combined translation and rotation moves. The periodic boundary condition was imposed in x, y and z axis directions. And nanopore models were treated as rigid and fixed during the whole simulation process. For every state,  $2 \times 10^7$  configurations were generated. The former  $10^7$  configurations were discarded to guarantee equilibration, and the latter  $10^7$  configurations were used to average the desired ensemble properties.

## **2.2 The porous structure and molecular Models**

In the simulations six nanoporous carbon models with different structures were considered (figure 1), they are pristine carbon nanotubes, mesoporous carbon, carbon foam and their modified counterparts. The pore sizes of the studied structures are all about 1nm. The carbon nanotubes studied are (14,0) single walled CNTs and modified single walled (14,0) CNTs. The foam structure are made of by welding CNT(14,0) and CNT(8,8), and the mesoporous carbon is made of by making hole on graphite layers.

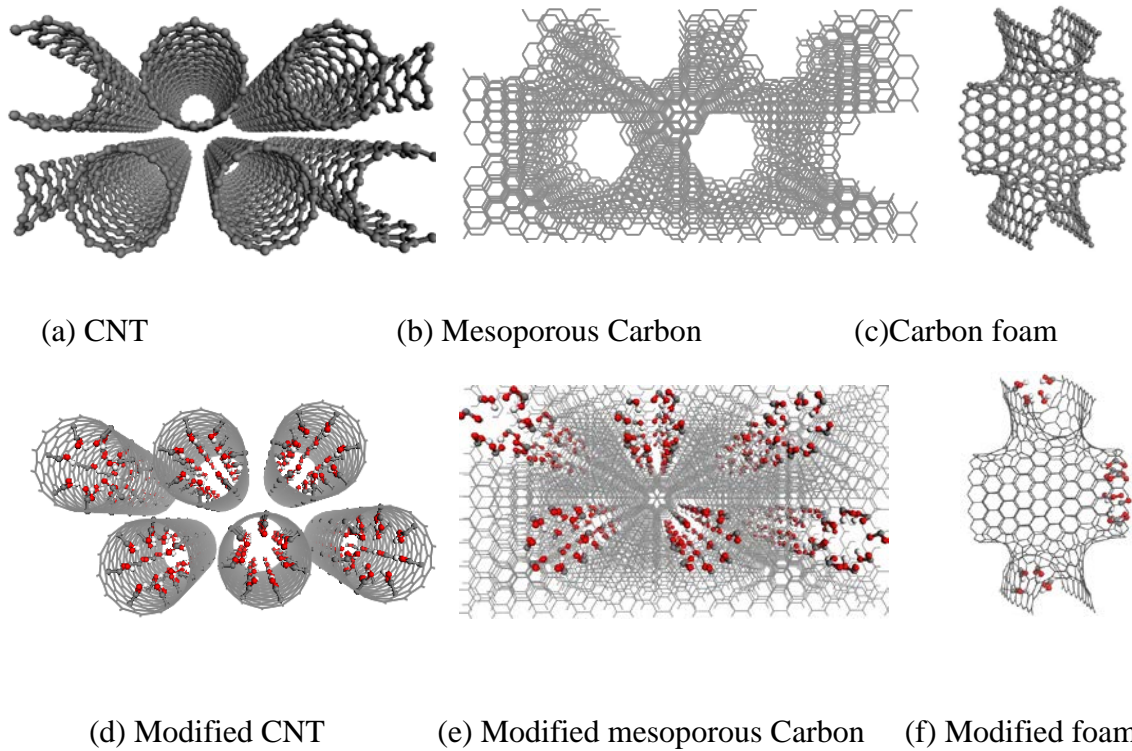


Figure1 The structure models for the adsorbents

The  $\text{CH}_4$  molecules were modeled using spherical model, which provides accurate representation of binary adsorption of  $\text{CO}_2/\text{CH}_4$  mixtures on activated carbons[14]. The  $\text{CO}_2$  molecule was described as a 3-centre LJ (EPM2) which include electrostatic interaction[25]. The intermolecular interaction between two sites was described by a Lennard-Jones potential. All the Lennard-Jones potential parameters used in this work are given in Table 1, where  $\sigma$  is the length parameter in the unit of  $\text{\AA}$  and  $\epsilon$  is energy parameter such that  $\epsilon/k_B$  is in the unit of K, where  $k_B$  is the Boltzmann constant.  $q_c$  is the charge on the site. Lorentz- Berthelot combining rules were used for all cross interactions. The cutoff radius for all interactions was  $12.0 \text{ \AA}$ . The bond length of C-O of  $\text{CO}_2$  is  $1.149 \text{ \AA}$  and the bond bending parameter is  $294.29 \text{ kcal/mol}$ [25].

Table 1 The Lennard-Jones parameter and partial charges for CO<sub>2</sub>, CH<sub>4</sub>,-COOH group and Carbon of adsorbents

site	$\sigma(\text{\AA})$	$\epsilon/k_B$ (K)	$q_c(e)$	ref
CH <sub>4</sub>	3.73	147.99	0	26
C(CO <sub>2</sub> )	2.757	28.129	0.6512	25
O(CO <sub>2</sub> )	3.033	80.507	-0.3256	25
C(Carbon structure)	3.55	35.26	0	22
C(-COOH)	3.75	52.64	0.55	22
O(-CO-)	2.96	105.28	-0.5	22
O(-OH)	3.00	85.24	-0.58	22
H	0	0	0.45	22
C(-C- COOH )	3.55	35.26	0.08	22

### 3. Results and Discussion

The adsorption capacity of an adsorbent at different temperature and pressure conditions is important; it can be estimated from the sorption isotherm. And detailed knowledge of the sorption isotherms for a CO<sub>2</sub>/CH<sub>4</sub> mixture is required in practical operations. The temperature, pressure, and pore size play an important role in the adsorption process. In our former research, we have considered the effects of temperature, pressure, and pore size, and we found the variations of temperature and pressure exert littler effects on the adsorption, and the effect of temperature and pressure is not very remarkable comparing to the effect of pore size. However, for the molecules at nanoscale confinement, we lack understanding on what architecture and heterogeneity exert their influence on the adsorption process in the nanopores. In this work, we firstly investigate



the adsorption behaviors of a CO<sub>2</sub>/CH<sub>4</sub> mixture inside different nanopores carbon with different architecture, then study the effect of chemical modification with –COOH.

As to separation process, the most interesting and important is the selectivity of the adsorption adsorbent. The selectivity of CO<sub>2</sub>/CH<sub>4</sub> mixture is also important for separation and purification process. Certainly, the experimental measurements are time-consuming and expensive. In the process of separation, the norm to estimate the selectivity of adsorbent is the relative selectivity of this adsorbent[27].

In this work, The adsorption selectivity,  $S_i$ , towards CO<sub>2</sub> was defined as follows:

$$S_{CO_2} = \frac{(x_{CO_2}/x_{CH_4})_{pore}}{(x_{CO_2}/x_{CH_4})_{bulk}} \quad (1)$$

where  $x_i$  denotes the molar fraction of component  $i$ , and  $(\dots)_{pore}$  and  $(\dots)_{bulk}$  refer to the pore and bulk quantities, respectively. A selectivity value of  $S_i > 1$  denotes that there is preferential adsorption for the fluid component  $i$  over the other fluid in the binary mixture.

The adsorption selectivity of CO<sub>2</sub> in an equimolar mixture with methane in different nanopore models that include pristine mesoporous carbons, carbon foams, carbon nanotubes (CNTs) and nanopore models modified with hydrophilic carboxylic groups were determined.

### 3.1 Isotherms and selectivity of pristine porous carbon

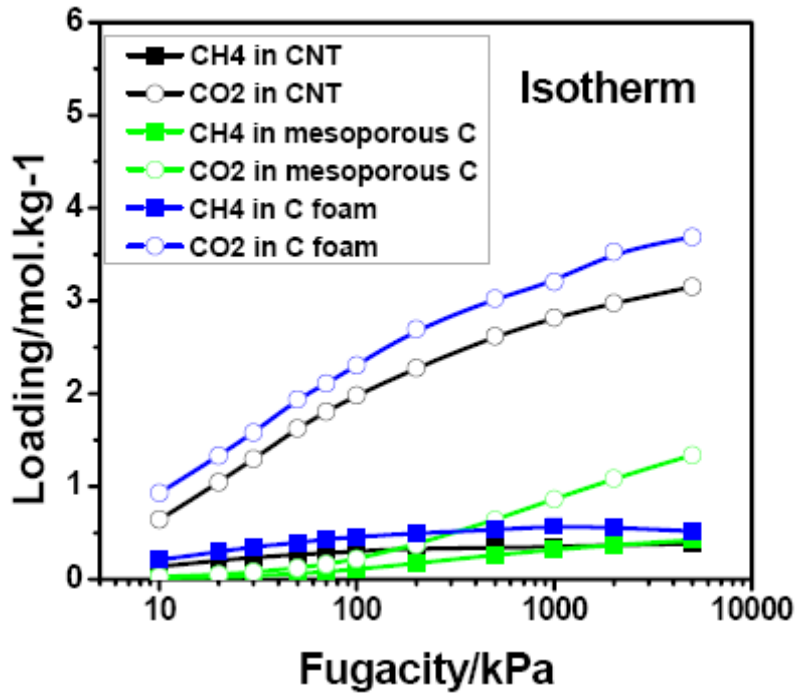


figure 2 The isotherms of CO<sub>2</sub>/CH<sub>4</sub> in pristine porous carbon adsorbents

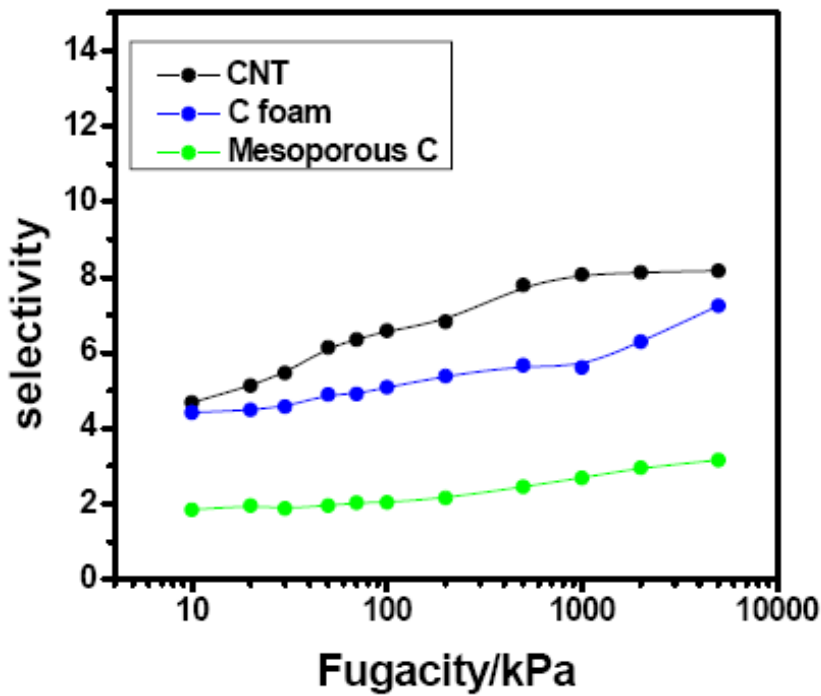


figure 3 The selectivities of CO<sub>2</sub>/CH<sub>4</sub> in pristine porous carbon adsorbents

According to the adsorption isotherms of CO<sub>2</sub>/CH<sub>4</sub> in pristine mesoporous carbons, carbon foams, carbon nanotubes (CNTs)(figure 2),The foam structures have the highest adsorption capacity of all structures studied especially at high pressure. From the results of the selectivity (figure 2) CNTs have higher selectivity at the range of studied pressures. Because CNTs are one dimension nano tube, it has high confining property. Although there are also nano pores in porous graphite carbon, they are more opening compare to CNTs due to the spaces between graphite layers. Foam structure still remain parts of confinement property because it is made of by welding CNT(14,0) and CNT(8,8), but it is not so confining as CNTs because the intercrossing pores at the junction of CNT(14,0) and CNT(8,8).

Foam structure has higher pore volume comparing to other two adsorbents, so it has highest adsorption capacity. The pores in form structure are still confining and the free pore volume is large at the same time. CNTs is most confining structure, it make it has most selectivity for CO<sub>2</sub>/CH<sub>4</sub> mixtrue. The pores of mesographite are more open due to the spaces between the layers, so the pore is not very confining, the adsorption amount and the selectivity in the mesographite are all lower. From the results, we can conclude that high confining property get high selectivity, but high adsorption capacity needs lager pore volume.

### 3.2 Isotherms and selectivity of modified porous carbon

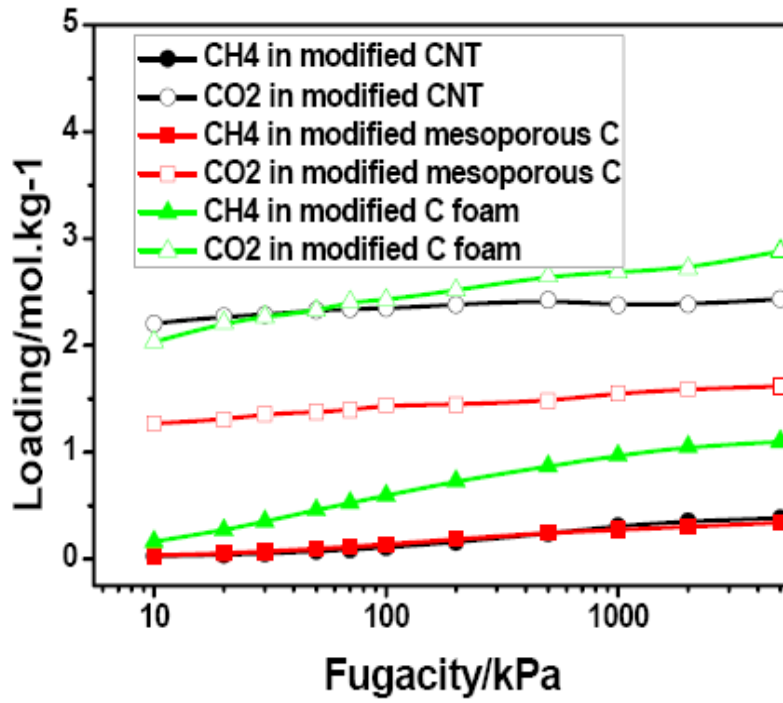


figure 4 The isotherms of  $\text{CO}_2/\text{CH}_4$  in modified porous carbon adsorbents

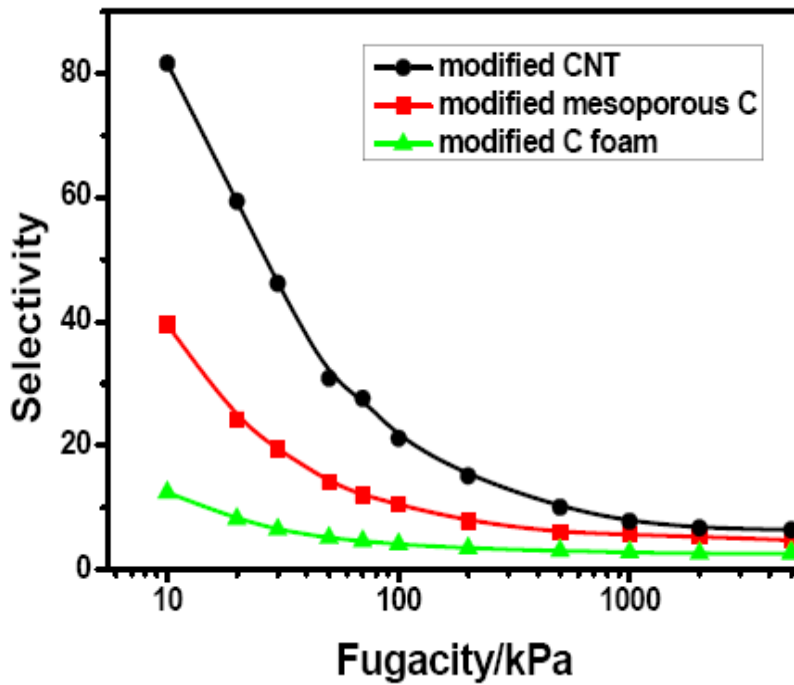


figure 5 The selectivities of  $\text{CO}_2/\text{CH}_4$  in modified porous carbon adsorbents

The separation of CO<sub>2</sub>/CH<sub>4</sub> mixtures in the modified CNTs are markedly different from that in the pristine ones, it has very high selectivity at low pressure. Although the selectivity of modified CNTs decreases with increasing pressure, their selectivity are still high with the value of 21.2 at 100kPa and 350K. This is because the –COOH(carboxyl) groups have strong electrostatic attractive force to CO<sub>2</sub> even at the low pressure. It makes the modified adsorption prefer to adsorb CO<sub>2</sub> molecules to CH<sub>4</sub> molecules, thus the selectivity for CO<sub>2</sub> increase. But the adsorption of CO<sub>2</sub> reach the saturated adsorption amount with increasing pressure, and then the CH<sub>4</sub> molecules are push into pores, it induces the selectivity decrease with increasing pressure. From these phenomena we can get the conclusion that the effect of chemical modification is stronger than that of pressure.

From figure 4, the adsorption amounts of the mixture in modified foam structure is the highest at a majority of range of pressure. The mesoporous graphite carbon has the lowest adsorption capacity. The adsorption amounts of CO<sub>2</sub>/CH<sub>4</sub> mixtures in modified structures do not change dramatically comparing to pristine structures. This is because strong electrostatic attractive force to CO<sub>2</sub> of the –COOH(carboxyl) groups make the adsorption reached saturated adsorption amount, then there is no more space to adsorb more molecule although the pressure increasing.

The selectivities of the modified structures are high especially at low pressure, but decrease dramatically with pressure increasing. This is because the –COOH(carboxyl) groups make the CO<sub>2</sub> adsorption reached saturated adsorption at low pressure, when the pressure increase, only spherical CH<sub>4</sub> can enter the pore. And it induces the selectivity to CO<sub>2</sub> decreased.

### 3.3 Comparison of pristine CNTs and modified CNTs

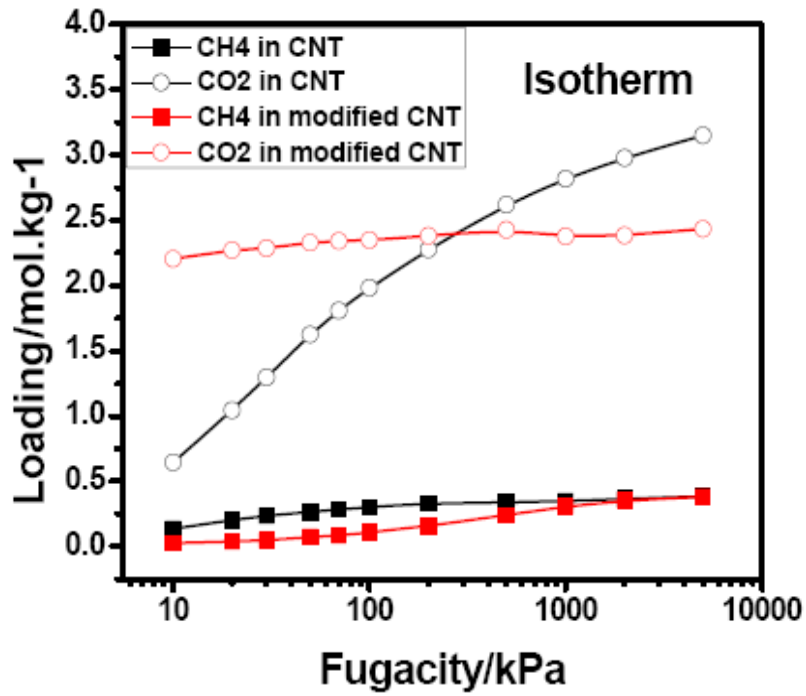


figure 6 The isotherms of CO<sub>2</sub>/CH<sub>4</sub> in pristine CNTs

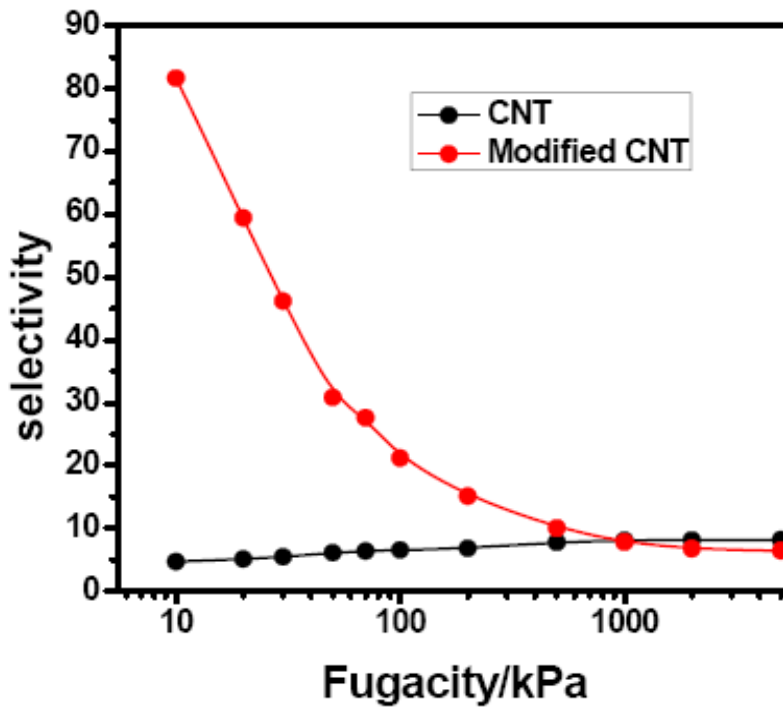


figure 7 The selectivities of CO<sub>2</sub>/CH<sub>4</sub> in modified CNTs

We compared the adsorption isotherms and selectivities of pristine CNTs and modified CNTs. From figure 6,7, the adsorption amount is more changeless with pressure increasing in modified CNTs. The selectivity of adsorbent increased after modification. Although the selectivity decreases dramatically with pressure increasing the selectivity is high up to 40 at 400K and 100kPa, and 178 at 10kPa. CH<sub>4</sub> could desorb at low pressure to purify mixture and then CO<sub>2</sub> can be release by heating.

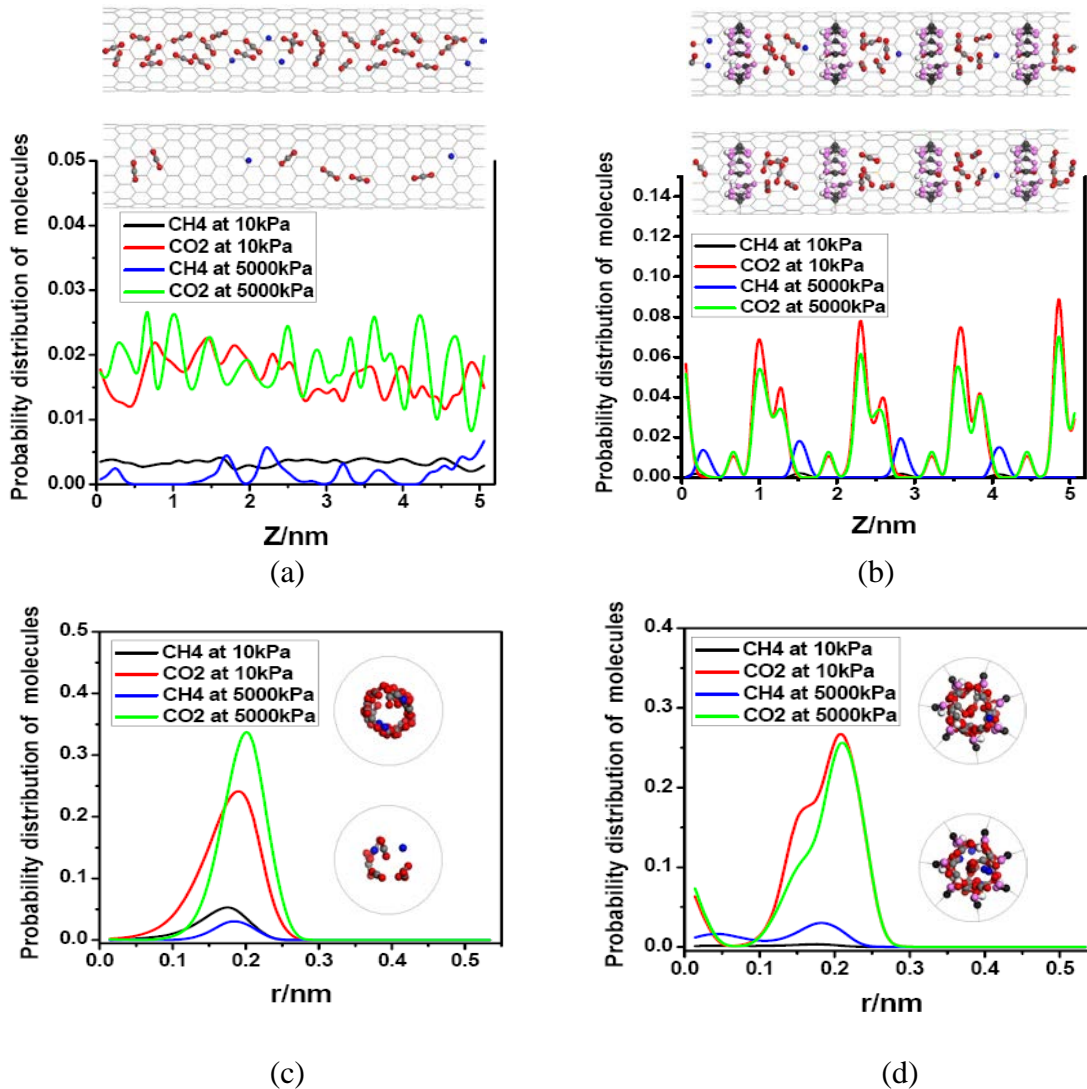


Figure 8 The probability distribution of CO<sub>2</sub>/CH<sub>4</sub> in Z direction (a,b) and radial direction (c,d) of CNTs and modified CNTs.

From figure 8 we can see the adsorption location of CO<sub>2</sub> and CH<sub>4</sub> molecules. The CO<sub>2</sub>/CH<sub>4</sub> molecules are preferred to locate in the sites which do not occupied by carboxylic groups in modified CNT. CO<sub>2</sub> molecules prefer to locate near the carbonyl group and CH<sub>4</sub> molecules prefer to locate near the hydroxyl group (Fig 8b). From the probability distribution in radial direction, there is a extra peak at the center of the modified tube (Fig 3d), it is the CO<sub>2</sub> molecule which is surrounded and confined by the circle of the carboxylic groups.

### 3.4 The effect of temperature

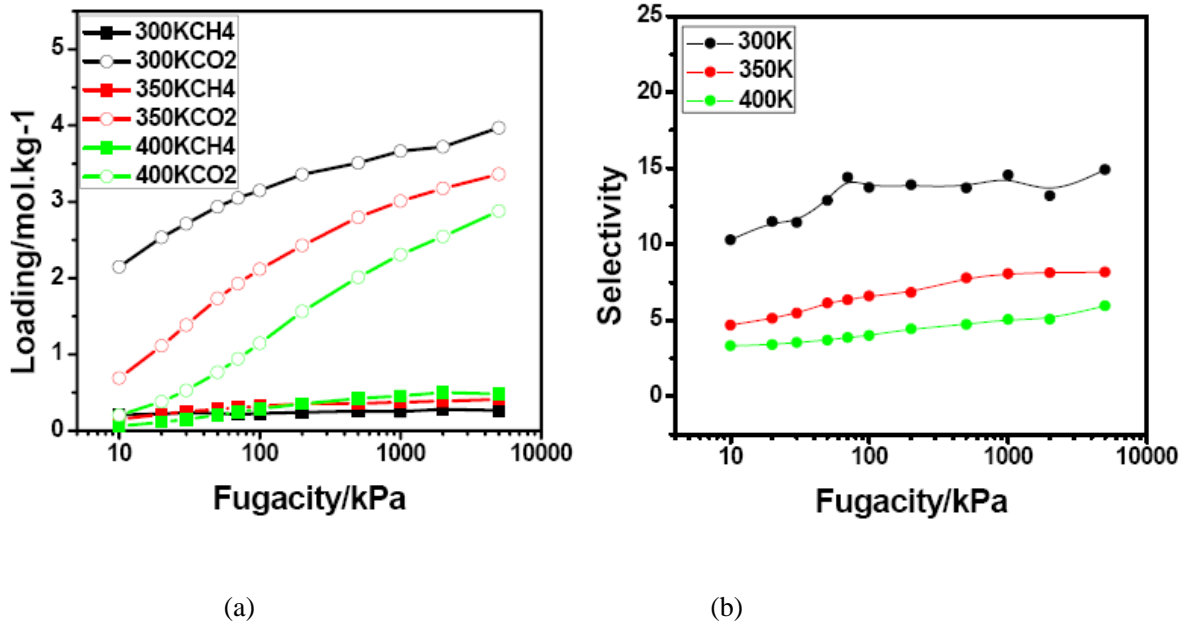


Figure 9 The isotherms(a) and selectivities(b) of CO<sub>2</sub>/CH<sub>4</sub> in CNTs at different temperature

The selectivity of CNTs increase with increasing temperature (Fig 9b) but The selectivity of CNTs decrease with increasing temperature (Fig 10b), and the adsorption amounts of CO<sub>2</sub> do not change markedly (figure 10a) it is different from general adsorbents. That could be beneficial in temperature swing adsorption processes.



From the results of modified CNTs, it is possible to find an appropriate function group, adsorb CO<sub>2</sub> with high selectivity by modifying porous-material using this function group. We can perform Swing pressure adsorption in modified porous material. Because the selectivity is high up to 40 at 400K and 100kPa, and 178 at 10kPa in modified CNTs. CH<sub>4</sub> could desorb at low pressure to purify mixture and then CO<sub>2</sub> can be released by heating. If we perform Swing temperature adsorption, the selectivity can be 20 at lower temperature (300K, 100kPa), the selectivity is enhanced by increasing temperature.(eg.400K) , CH<sub>4</sub> could be desorbed in priority. These processes could be performed at moderate temperature and pressure. It is not very hard to equipment.

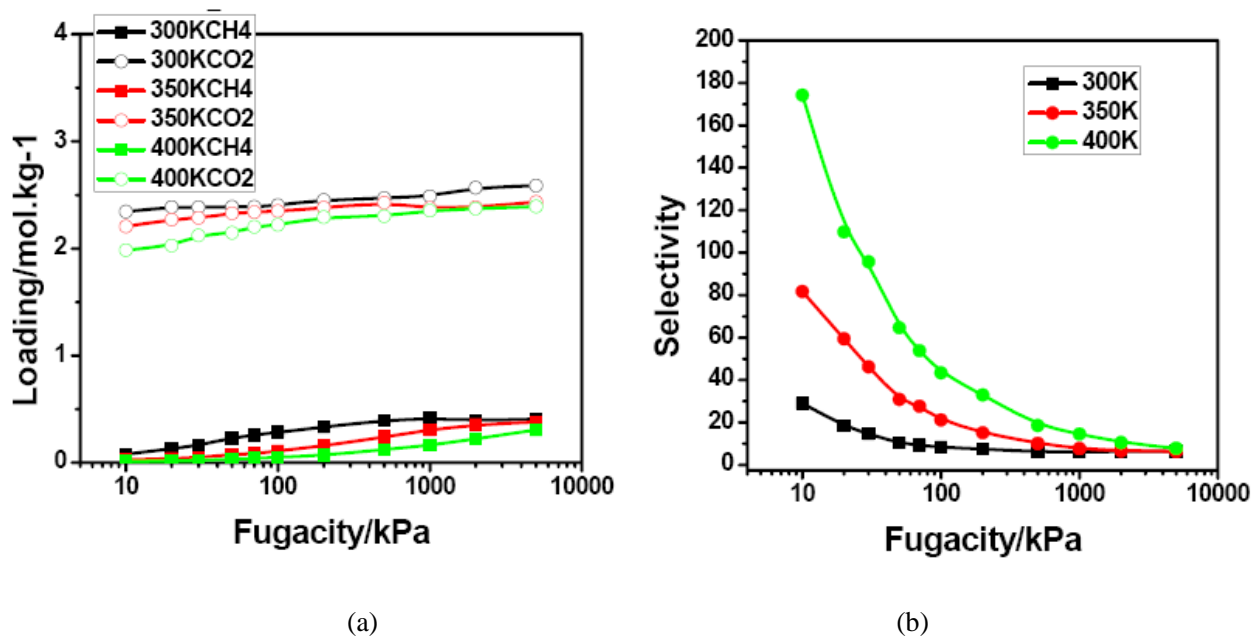


Figure 10 The isotherms(a) and selectivities(b) of CO<sub>2</sub>/CH<sub>4</sub> in modified CNTs at different temperature

## **4. Conclusions**

The adsorption of CO<sub>2</sub>/CH<sub>4</sub> mixtures in different nanopore models that include pristine mesoporous carbons, carbon foams, carbon nanotubes (CNTs) and nanopore models modified with hydrophilic carboxylic groups were researched using grand canonical Monte Carlo simulation study. The foam structures have the highest adsorption capacity of all pristine structures studied because of its special architecture. The selectivity enhanced markedly after modification especially at low pressures, and modified CNTs have highest selectivity. The effect of temperature and pressure and note the selectivity change trends of modified nanopore models are contrary to that of pristine ones. The results show the pore architecture and chemical modification do affect the adsorption behaviour of CO<sub>2</sub>/CH<sub>4</sub> in porous materials.

The results suggest that the separation performance in carbon nanopores is greatly affected by the nature of the pore architecture and of the heterogeneity of the materials. Results could be beneficial in conventional pressure swing adsorption processes and as parts of mixed polymer membranes. It could be guidelines for the design of nanoporous structures for the optimal separation of CO<sub>2</sub>/CH<sub>4</sub> mixture.

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