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Modeling the adsorptive selectivity of carbon nanotubes for effective separation of CO_2/N_2 mixtures

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Abstract Canonical Monte Carlo (CMC) simulations were carried out to investigate the behavior of CO_2 and N_2 mixtures upon adsorption on single walled carbon nanotubes (CNTs). In the simulation, all the particle–particle interactions between CO_2, N and C were modeled using Lennard-Jones (LJ) potential. To provide deep insight into the effect of pore width, temperature, pressure and bulk composition on the adsorption behavior of CO_2 /N_2 mixtures, five different CNTs [(6,6), (7,7), (8,8) (9,9) and (10,10) CNT] with diameters ranging from 0.807 to 1.35 nm, three temperatures (300 323 and 343 K), six pressures (0.15, 2, 4, 6, 8 and 10 MPa), and three bulk mole compositions of carbon dioxide (0.3 0.5 and 0.7) were tested. The results from all the simulation conditions investigated in this work show that CNTs preferentially adsorb carbon dioxide relative to nitrogen in a binary mixture. The results are consistent with the hypothesis that stronger interaction of one component with the nanotube surface results in a higher adsorption capacity compared to the other component. An optimized pore size of D= 8.07 nm corresponding to (6, 6) CNT, at T=300 K and P=0.15 MPa at a bulk mole composition of y_{CO2} =0.3 was identified in which carbon nanotubes demonstrate the greatest selectivity for separation of carbon dioxide relative to nitrogen. In addition, it is worth pointing out that, under similar simulation conditions, CNTs exhibit higher selectivity compared to other carbon-based materials [carbon membrane polyimide (PI) and PI/multi-wall carbon nanotubes (MWCNTs)] for CO_2 adsorption. As a prototype, the selectivity of an equimolar mixture of CO_2 /N_2 for adsorption on (6, 6) CNTs at 300 K and 0.15 MPa reaches 9.68, which is considerably larger than that reported in carbon membrane. Therefore, it can be concluded that carbon nanotubes can act as a capable adsorbent for adsorption/desorption of CO_2 in comparison with other carbon-based materials in the literature.

Introduction

Since the beginning of the industrial age, the effect of increasing the concentration of atmospheric carbon dioxide (CO_2—a greenhouse gas) from 280 to 380 parts per million (ppm) has been recognized as a significant environmental issue that human beings must face [1–3]. Rising CO_2 emissions have been accepted as a contributory factor to the global climate change commonly known as the "greenhouse effect" causing global warming [4, 5].

The increased CO_2 emissions are due to fuel combustion activities, industrial processes, and natural gas processing. By far the largest CO_2 emissions result from the oxidation of carbon when fossil fuels are burned. These emissions are associated with fossil fuel combustion in power plants oil refineries and large industrial facilities. Fuel composition, the chosen combustion system, and operating conditions are the major factors affecting the composition of greenhouse gases. The main components of fuel gases are CO_2

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and N_2 as well as O_2 and trace pollutant gases such as NO_x, SO_x, etc. [6].

If we are to continue to use fossil fuels as a main source of global energy supply, it is crucial to investigate potential approaches to reduce and remove CO_2 emissions, and this is considered an extremely important issue in finding ways to suppress the greenhouse effect. In the transition towards a reduction in CO_2 emissions, the efficiency of energy utilization and increasing the use of low-carbon energy sources are considered as potential methods [7]. Recently CO_2 capture and separation have received significant attention, and developing techniques for the effective capture and separation of CO_2 and optimizing currently used techniques should be considered as one of the main concerns in the field of carbon sequestration. Adsorption membrane separation technology has been accepted as a cost-effective technique for the separation of gases due to the low energy requirement, cost advantages, and simplicity of application over a relatively wide range of temperatures and pressures. In this context, the search for suitable adsorbents in order to obtain high CO_2 adsorption and selectivity is of vital importance for researchers.

A number of studies have provided good data for adsorption and separation of CO_2/N_2 mixtures. As previously mentioned, membrane adsorption is an effective and reasonable technology used to adsorb and separate CO_2 from gas mixtures. Several previous investigations on CO_2 separation focused on membrane technology such as ZSM-5 [8] and other types of zeolites (mordenite, faujasite, chabazite) [6], [8, 9]; microporous metal-organic frameworks [9, 10]; capillary-type facilitated transport membranes [11]; "molecular basket" adsorbents (MCM-41-PEI-50) [12]; C_{168} Schwarzite [6] and some carbon-based materials, e.g., carbon membrane [13]; nanoporous carbon (NPC) membrane [14, 15]; and polyimide (PI), PI/multi-wall carbon nanotubes (MWCNTs) [16].

Some recent studies have investigated adsorption of pure CO_2 [17] and N_2 [18] and their mixtures [19] on carbon-based materials, whereas, to the best of our knowledge, there are no recent reports on the basis of CO_2 separation on these materials.

Carbon nanotubes (CNTs) are one of the most important carbon-based materials that have been extensively studied in this context because of their unique structures and remarkable electronic, transport, magnetic, optical, chemical and mechanical properties [20]. In addition, the distinct shape and size of CNTs, as well as economic considerations, make them suitable for gas separation under extreme conditions [21]. Some previous investigations have shown that CNTs are promising candidates for the potential separation of gas mixtures such as CO_2/CH_4 [21], H_2/CO [22], N_2/O_2 [23, 24], He/H_2 [25], and so on. As a consequence, by choosing the right pore width and optimum conditions of pressure and temperature, CNTs can act as capable adsorbents for gas sequestration.

Therefore, in this present work, we intended to study the capability of CNTs to separate CO_2/N_2 binary mixtures using (N, V, T) canonical Monte Carlo (CMC) simulation, and compare the magnitude of CNT selectivity for CO_2/N_2 with other carbon-based materials in the literature [13, 16] to see whether CNTs are better candidates for CO_2/N_2 separation than other carbon-based materials or not. In order to gain extensive and comprehensive insight into the simulation results, the Virial equation of state obtained from experimental measurements was investigated. The main objective of this study was to evaluate the effect of different factors such as temperature, pressure, pore size, and bulk composition on the adsorption and separation performance of the CNTs with the intention of determining the optimum conditions for adsorption and separation of a CO_2/N_2 mixture. We provide detailed descriptions of the CMC Simulations details. In the Results and discussion, we present the effects of CNT size, temperature, pressure, and bulk mole composition in simulation results for adsorption isotherms and relative selectivity of CO_2 and N_2. The Conclusion summarises some of the most important arguments that arose as a result of this work.

Simulation details

Canonical Monte Carlo simulation

A standard CMC simulation was carried out at a fixed volume, temperature, and sum of the species for the adsorption of CO_2/N_2 mixture on the CNTs. In this method, the standard procedure of Metropolis sampling with the periodic boundary condition was applied. The cut-off radius was 2.5 times the collision diameter. For every state 5×10^7 configurations were generated. The first 2×10^7 configurations were discarded to guarantee equilibration, and the remaining 3×10^7 were used to assemble average values for thermodynamic properties. The simulation box ($100.0\,\text{Å} \times 100.0\,\text{Å} \times 45.0\,\text{Å}$) contained one single-walled (SW)CNT.

It was assumed that the nanotubes had a rigid structure. In all the computations, CO_2 and N_2 molecules were modeled as structureless particles that interact with each other using the Lennard-Jones (LJ) 12-6 potential [26]:

$$\phi_{LJ}(r) = 4\varepsilon_{ff}\left[\left(\frac{\sigma_{ff}}{r}\right)^{12} - \left(\frac{\sigma_{ff}}{r}\right)^{6}\right] \quad (1)$$

Where r is the distance between two interacting fluid molecules, σ_{ff} denotes the LJ fluid–fluid collision diam-

eter (nm), and ε_{ff} is the LJ fluid–fluid potential well depth (K).

The total interactions between fluids and SWCNTs were represented using the following interaction potential:

$$\phi_{fw} = 4\varepsilon_{fw} \sum_{i=1}^{N_f} \sum_{j=1}^{N_{carbon}} \left[\left(\frac{\sigma_{fw}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{fw}}{r_{ij}} \right)^{6} \right] \quad (2)$$

Where r_{ij} is the distance between fluid molecules and carbon atoms in the nanotube, σ_{fw} denotes the LJ fluid-carbon collision diameter, and εf_w is the LJ fluid-carbon potential well depth. Lorentz-Berthelot combining rules were used for interactions between unlike pair molecules.

$$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j} \quad , \quad \sigma_{ij} = \left(\sigma_i + \sigma_j \right)/2 \quad (3)$$

The LJ parameters for each species are listed in Table 1.

Virial equation of state

The Virial equation of state with second and third viral coefficients for a mixture of real gases was used [26] to estimate the number of fluid molecules at different temperatures and pressures. The investigated number of molecules of a natural gas system as a function of temperature and pressure is represented by the following equation of state [27]:

$$\frac{PV}{NRT} = 1 + B'_{mix}P + C'_{mix}P^2 \quad (4)$$

$$B'_{mix} = \frac{B_{mix}}{RT} \quad , C'_{mix} = \frac{\left(C_{mix} - B^2_{mix} \right)}{\left(RT \right)^2} \quad (5)$$

Where B_{mix} and C_{mix} are the mixture of the second and third Virial coefficients, which are functions of temperature and composition and are expressed as the following relationships [27]:

$$B_{mix} = \sum_i \sum_j x_i x_j B_{ij} \quad (6)$$

$$C_{mix} = \sum_i \sum_j \sum_k x_i x_j x_k C_{ijk} \quad (7)$$

Table 1 Lennard-Jones (LJ) potential parameters [13]

Species	ε / k_B (K)	σ (Å)
CO_2 -CO_2	225.3	3.91
N_2-N_2	71.4	3.798
C-C	28.2	3.4

In Eqs. 2 and 3, x_i x_j and x_k are the mole fractions of the i_{th} j_{th} and k_{th} components of the mixture. B_{ij} and C_{ijk} are the interaction second and third Virial coefficients, respectively, which depend only on temperature [27]:

$$B_{ij} = b_{ij,0} + \frac{b_{ij,1}}{T} + \frac{b_{ij,2}}{T^2} \quad (8)$$

$$C_{ijk} = c_{ijk,0} + \frac{c_{ijk,1}}{T} + \frac{c_{ijk,2}}{T^2} \quad (9)$$

The values of the coefficients in Eqs. 8 and 9 have been reported by Estela-Uribe et al. [26] and are listed in Tables 2 and 3.

Results and discussion

Adsorption isotherms

For the sequestration process of carbon dioxide, having a detailed knowledge of the adsorption capacity of a sorbent under optimal conditions of pressure and temperature is important. Pressure, temperature, pore size, and bulk mole composition are all known to play important roles in the adsorption process. Therefore, in this work, to investigate the adsorption behavior of CO_2 /N_2 adsorption on CNTs with diameters varying from 0.807 nm to 1.356 nm under a pressure range of 0.15 to 10 MPa, three different temperatures (300 323 and 343 K) and three different bulk mole compositions of carbon dioxide (0.3 0.5 and 0.7) were chosen in order to understand how these parameters exert their effects on the adsorption process. The results show that the adsorption capacity increases as a function of pressure for all CNTs, with a greater magnitude of CO_2 adsorption relative to N_2 (Fig. 1). A stronger interaction of carbon dioxide with the nanotube surface results in higher adsorption capacity compared to that of nitrogen. The results are consistent with experimental adsorption measurements [28]. Additionally, from this figure, it is clear that while the effect of pore size on the adsorption capacity of carbon dioxide is significant, pore size has hardly any influence on the adsorption capacity of nitrogen, especially at y_{CO2} =0.3. Therefore, the adsorption capacity of nitrogen seems to be invariant with changing pore width. The reason why CO_2 adsorption capacity is a decreasing function of pore width is due to the volume capacity of this work (n/V), where n denotes the total number of carbon dioxide and nitrogen molecules adsorbed in CNTs, and V indicates the inner volume of the CNT. Therefore, smaller CNTs with smaller volume have greater volumetric density compared to larger CNTs. Moreover, Fig. 1 shows that the effect of pore width on the adsorption capacity is more significant at high pressures.

Table 2 Coefficients of temperature correlation for pure and mixed component second Virial coefficients [27]

Interaction	b_{ij0} (dm^{3}mol^{-1})	b_{ij1} (dm^{3}Kmol^{-1})	b_{ij2} (dm^{3}K^{2}mol^{-1})
CO$_2$ -CO$_2$ [a]	2.383567×10^{-3}	9.428195	-1.397999×10^4
N$_2$-N$_2$ [a]	3.810890×10^{-2}	-8.569905	-1.273455×10^3
N$_2$–CO$_2$ [b]	2.594179×10^{-2}	-5.395662	-4.355663×10^3

[a] Coefficients of temperature correlation for pure-component second Virial coefficients

[b] Coefficients of temperature correlation for interaction second Virial coefficients fitted to binary-mixture compression factors

Figure 2 presents the dependence of adsorption capacity of an equimolar mixture of carbon dioxide and nitrogen on temperature when the pressure is P=0.15 MPa. It is clear that the adsorption capacity is a decreasing function of temperature for both CO$_2$ and N$_2$ components. From this figure, we can see that the dependence of adsorption capacity on temperature is more significant with narrower CNTs. In addition, there is a greater effect of temperature on the adsorption capacity of carbon dioxide compared to nitrogen.

Selectivity

In order to estimate the effectiveness of CNTs on separation processes, we elucidated the adsorption selectivity of CO$_2$ relative to N$_2$ as follows:

$$S_{CO2/N2} = \frac{x_{CO2}/y_{CO2}}{x_{N2}/y_{N2}} \qquad (10)$$

Where x and y represent the bulk mole fraction of components at adsorbed and bulk phases, respectively.

To gain further insight into the discrepancies between the adsorption behaviors of CO$_2$ and N$_2$ molecules in different CNTs, we investigated the effects of pressure, temperature, pore size, and bulk mole composition on selectivity. The simulation results reveal that there is an optimum pore size of D=8.45 nm in which the CNTs show maximum adsorption of gases, and therefore we used D=8.45 for

investigating the effects of other factors on the adsorption behavior of gasses.

Effect of pressure on the selectivity of CO$_2$ /N$_2$

The selectivity of CNTs as a function of pressure was studied. Figure 3 depicts the adsorption selectivities for carbon dioxide and nitrogen with an increase in pressure from 0.15 MPa to 10 MPa when the pore width is D=0.807 nm. This figure indicates that the selectivity of CNTs over carbon dioxide and nitrogen declines with increasing pressure. This is attributable to the packing effect, which becomes key in the adsorption behavior of gases along with increasing pressure [22]. At higher pressures, the smaller molecules are more likely to pack into the tube. This behavior is similar to that found in carbon membrane [13]. In addition, we can see from Fig. 3a that the selectivity of carbon dioxide over nitrogen increases when the temperature falls. This is because, when the temperature increases, the behaviors of the two gasses become close to ideality and the preference of CNTs for one over the other of the two gases decreases due to the decrease in the interaction between the two gases and CNTs. It can also be concluded from Fig. 3b that, for all simulation conditions, selectivity is always better at smaller pore width of CNTs and lower temperatures and pressures. In addition, it is worth pointing out that selectivity is greater than unity under all simulation conditions. These results are consistent with the fact that CNTs exhibit a greater adsorption preference for carbon dioxide, and are in

Table 3 Coefficients of temperature correlation for pure and mixed component third Virial coefficients [27]

| Interaction	c_{ij0} (dm^{6}mol^{-2})	c_{ij1} (dm^{6}Kmol^{-2})	c_{ij2} (dm^{6}K^{2}mol^{-2})
CO$_2$ –CO$_2$ –CO$_2$ [a]	-2.364433×10^{-2}	1.521827×10^1	-1.992773×10^3
N$_2$–N$_2$–N$_2$ [a]	3.059600×10^{-3}	-1.125719	1.951933×10^2
CO$_2$ –CO$_2$ –N$_2$ [b]	-2.099037×10^{-2}	1.027488×10^1	-9.653652×10^2
N$_2$–N$_2$–CO$_2$ [b]	-1.714910×10^{-3}	2.611379	-4.339614×10^2

[a] Coefficients of temperature correlation for pure-component third Virial coefficients

[b] Coefficients of temperature correlation for independent double-interaction third Virial coefficients fitted to binary-mixture compression factors

Fig. 1 Adsorption capacity isotherms of (a) carbon dioxide (b) nitrogen in carbon nanotubes (CNTs) with different pore size at 323 K and different bulk mole composition y_{CO_2}
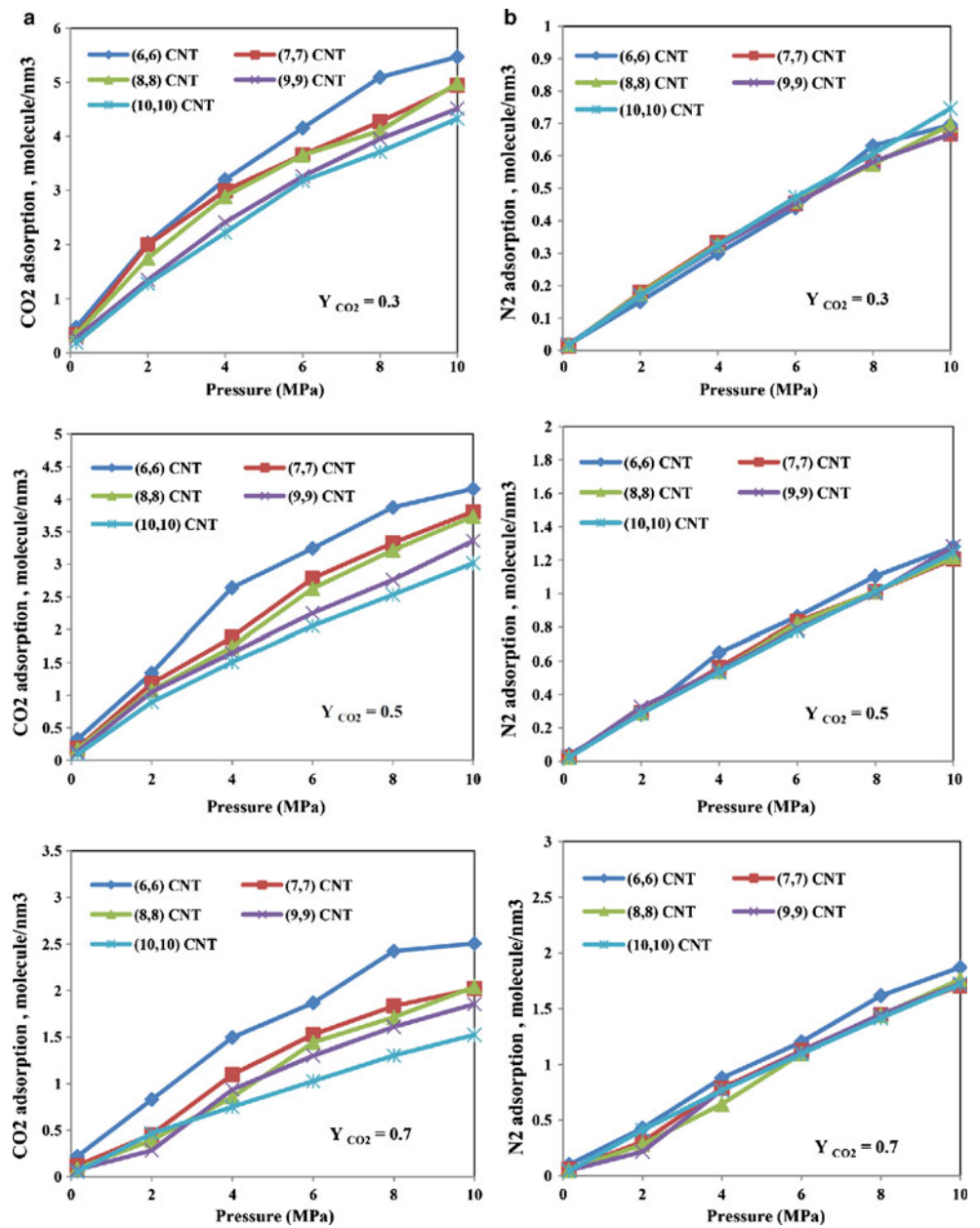
Fig. 2 Adsorption capacity isotherms of (a) carbon dioxide (b) nitrogen versus pore width at P=0.15 MPa and y_{CO_2} =0.5
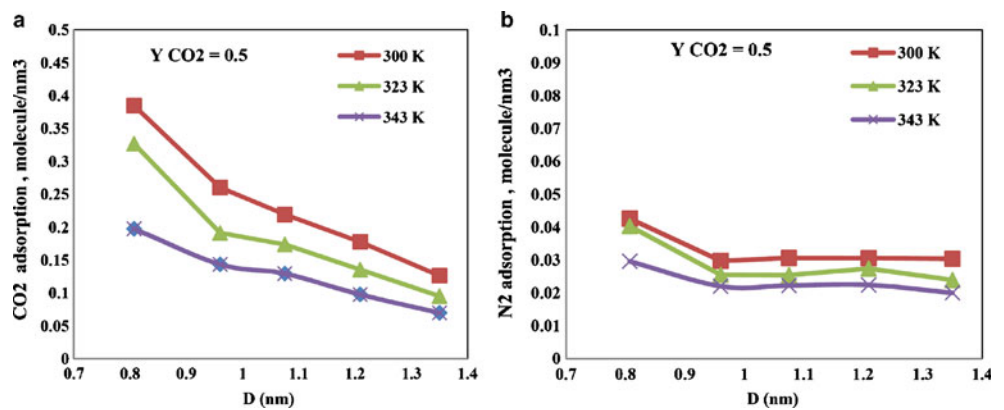
Fig. 3 Selectivity of carbon dioxide relative to nitrogen at various pressures at bulk composition of carbon dioxide y_{CO_2} =0.3, 0.5, or 0.7 (**a**) at pore size of D=0.807 nm, and three temperatures (**b**) T=323 and different CNT pore sizes
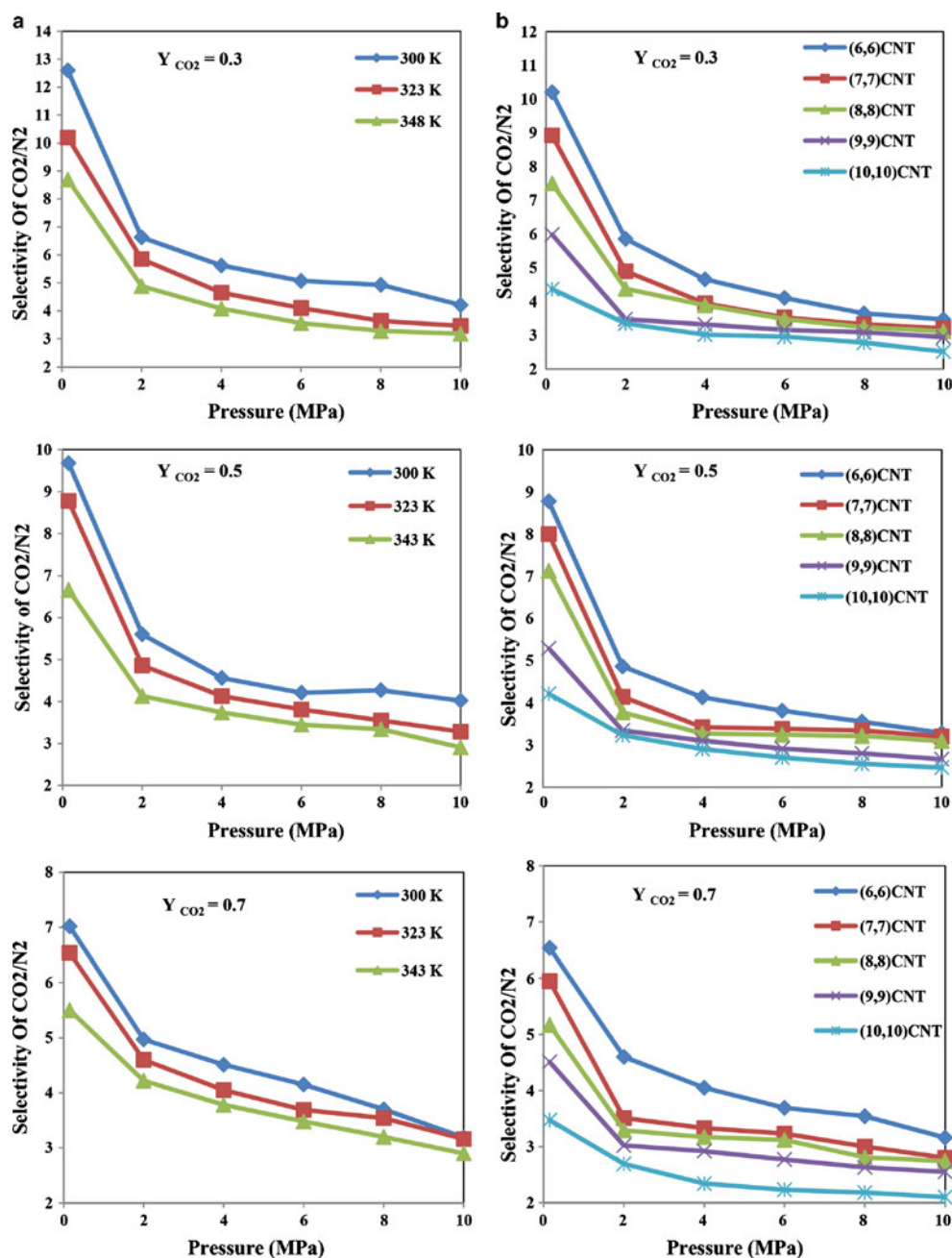
agreement with the adsorption isotherm of each species in Fig. 1. It is noteworthy that the magnitude of selectivity of CNTs for an equimolar mixture of CO_2 /N_2 at T=300 K and P=0.15 MPa is in the range of 11 to 4, which is ten times greater than the magnitude of selectivity (S<1) for carbon membrane. Moreover, recent experimental studies carried out by Tseng and co-workers [16] gave a selectivity of 2.7–4.2 in PI and PI/MWCNTs, respectively, which is considerably lower than that found in the CNTs used in this work. For the purposes of comparison, the results of separation performance for the mixture of CO_2 /N_2 with other carbon-based sorbents are listed in Table 4.

Effect of bulk mole fraction of CO_2 and CNT pore size on selectivity of CO_2/N_2

Figure 4a shows the dependence of selectivity on bulk mole fraction of CO_2 at different pressures, when the pore width is 8.07 nm and the temperature is 323 K. It can clearly be seen that selectivity is a decreasing function of bulk mole fraction of CO_2. It should be mentioned that, at a pressure of 0.15 MPa, selectivity falls drastically with an increase in the bulk mole fraction of CO_2, while at pressures higher than 2 MPa, selectivity changes only slightly with an increase in the bulk mole fraction of CO_2. Selectivity

Table 4 Comparison of selectivity of carbon nanotube (CNT) for the mixture of CO_2 /N_2 with other sorbents in the literature [13, 16]. *PI* Polyimide, *MWCNT* multi-wall carbon nanotubes

Adsorbent	T (K)	P (MPa)	y_{CO2}	Selectivity
PI	299	0.1	-	2.7
PI/MWCNTs	299	0.1	-	4.2
Carbon membrane	300	0.15	0.5	<1
Optimum size of carbon nanotube (this work)	300	0.15	0.5	9.68

decreases as pressure increases. Thus, an optimum pressure of 0.15 MPa in which the CNTs exhibit a strong adsorption preference for carbon dioxide over the whole range of y_{CO2} can be observed. Furthermore, with the pressures and bulk compositions used here, a variation in pressure from 2 to 10 MPa exerts little effect on the selectivity of carbon dioxide with y_{CO2} higher than 0.5, which indicates that selectivity seems to be invariant. In addition, at a range of y_{CO2} less than 0.5, selectivity has a distinct dependence on pressure at 2 and 4 MPa.

Figure 4b presents the effect of pore width on selectivity when the temperature is 323 K. It can be concluded from this figure that the selectivity has a direct falling trend with changes in y_{CO2}. As shown in Fig. 4b, (6, 6) (7, 7) and (8, 8) CNTs with diameters less than 1.1 nm have a clear dependence on the bulk mole fraction of carbon dioxide, whereas the bulk mole fraction of carbon dioxide has little effect on the larger (9, 9) and (10, 10) CNTs. Thus, it is worth pointing out that the selectivity in narrower CNTs with diameters less than 1.1 nm is sensitive to gas composition, while selectivity toward bulk mole fraction for larger CNTs does not change much. The effect of pore width on selectivity is also more understandable at low mole fractions of carbon dioxide. As a result, selectivity is very sensitive to variation in the bulk mole fraction of CO_2, especially at lower values, and an increase in the bulk mole fraction of carbon dioxide reduces the dependence of selectivity on pressure and pore width. Consequently, in the conditions used here to test selectivity, the optimal parameters are a pore size of D=8.07 nm, P=0.15 MPa, and y_{CO2}=0.1, in

which selectivity can reach a value of 12, which represents the preferential adsorption of carbon dioxide over nitrogen in the mixture. Accordingly, CNTs can be considered as a capable sorbents for separating CO_2 from CO_2 /N_2 gas mixtures compared to other carbon-based materials used for this purpose.

Figure 5a shows the dependence of selectivity on pore width of carbon nanotubes at the pressure range of 0.15 to 10 MPa. For all cases, with increase in the pore width, the selectivity of carbon dioxide falls. The effect of pore width on the selectivity can be considered as being essentially greater at lower pressures, especially at 0.15 MPa, and selectivity is very sensitive to pore width at lower pressures. As can be seen from Fig. 5a, the behavior of selectivity as a decreasing function of pore width is different at various pressures. At low pressure of 0.15 MPa, the slope of selectivity declines drastically with an increase in pore width, whereas it decreases slightly when the pressure ranges from 2 to 10 MPa. As expected, the magnitude of selectivity depends on the bulk mole fraction of carbon dioxide. Therefore, narrower CNTs and lower y_{CO2} exhibit higher selectivity.

At low pressure of 0.15 MPa, selectivity declines drastically with increased pore width, whereas it decreases slightly when the pressure ranges from 2 to 10 MPa. As expected, the magnitude of selectivity depends on bulk mole fraction of carbon dioxide. In addition, it is obvious from Fig. 5a that the dependence of selectivity on pressure is more significant in narrower CNTs and lower y_{CO2}.

Figure 5b depicts the dependence of selectivity of CNTs of different pore widths for the separation of carbon dioxide

Fig. 4 Selectivity of carbon dioxide relative to nitrogen versus bulk composition of carbon dioxide at T=323 changing with (**a**) pressures at pore width D=0.807 nm, and (**b**) pore width and P=0.15 MPa
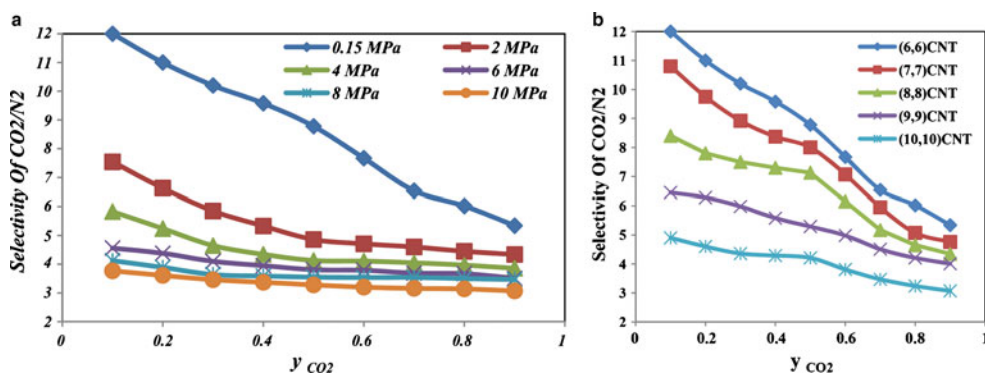
Fig. 5 Selectivity of carbon dioxide relative to nitrogen versus pore width of CNT changing with (**a**) pressures at T=323 K, and (**b**) temperature at P=0.15 MPa
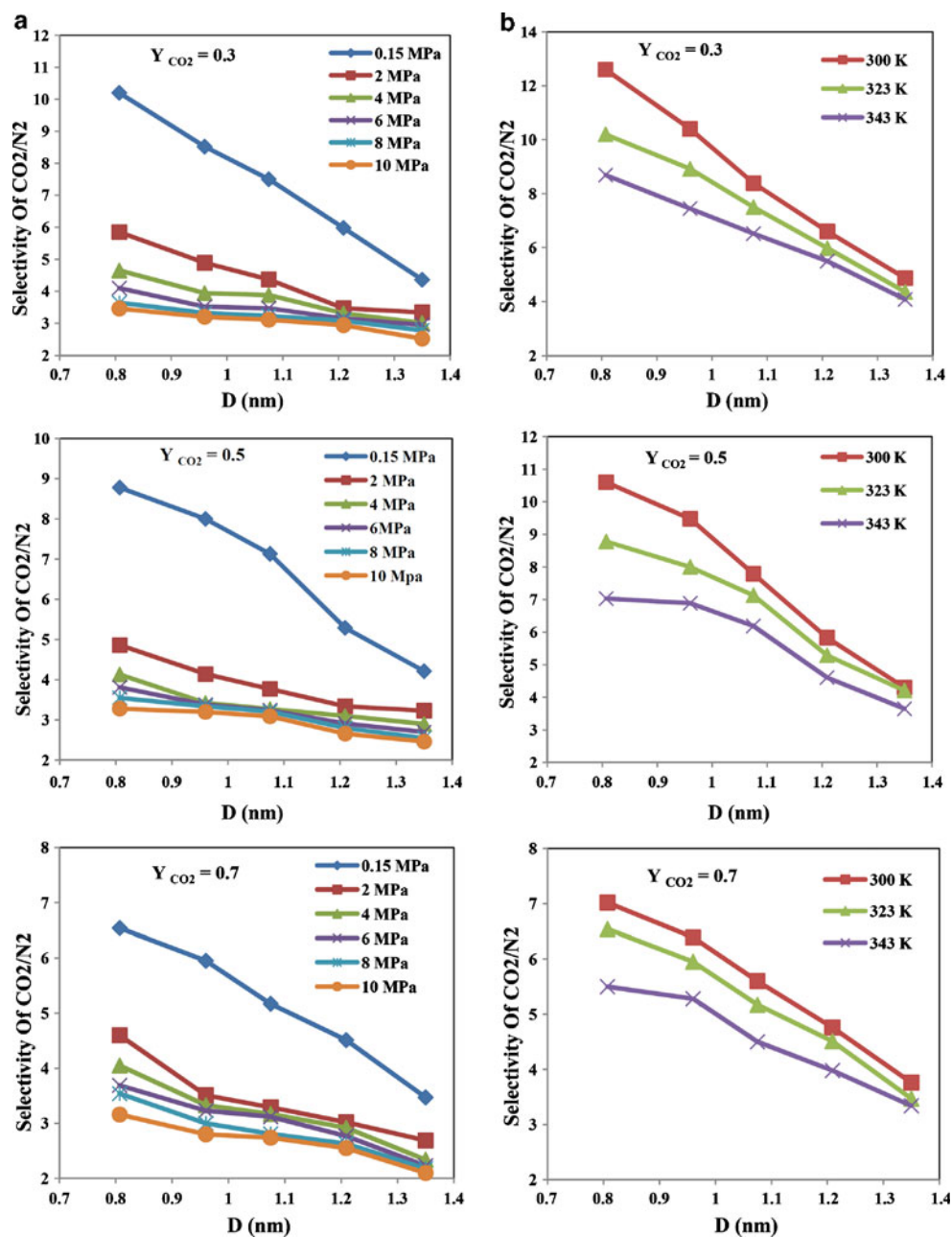
and nitrogen at three different temperatures (300, 323 and 343 K). Basically, in different bulk composition, the behavior of selectivity versus variation of pore width is the same, and selectivity decreases as pore width increases. The only difference at different y_{CO_2} is the magnitude of selectivity. Basically, in all cases, the selectivity is the same and the only difference is the magnitude of selectivity. In all cases, selectivity decreases as pore width increases. In addition, decreasing the temperature results in an increase in the extent of selectivity. Although temperature has no significant effect on the selectivity of carbon dioxide over nitrogen at larger CNTs, it has a considerable effect on narrower CNTs.

Overall, the optimum conditions for maximum selectivity of CNT are P=0.15 MPa, T=300 K and y_{CO_2} =0.3.

Conclusions

Canonical Monte Carlo simulation was used to investigate the adsorption and separation behaviors of CO_2 and N in CNTs. The effects of temperature, pressure, pore width, and bulk mole fraction of CO_2 on adsorption and separation behavior of CNTs were explored. The simulation results revealed that all adsorption isotherms exhibited a Langmuir isotherm shape (type I). Moreover, the results indicate that

CO_2 is preferentially adsorbed over N_2 on CNTs due to the structure of the adsorbate and packing effects. The adsorption amount is a decreasing function of pore width for (6, 6) to (10, 10) CNTs with a diameter range of 0.807 to 1.35 nm. Changing pore width plays an important role in the adsorption amount of CO_2, while the adsorption amount of nitrogen seems to be insensitive to variations in pore width. Studying the dependence of the adsorption capacity of the two gases on temperature indicated that the magnitude of gas adsorption decreases with increasing temperature. Additionally, the decrease in magnitude of adsorption capacity along with falling temperature is greater with narrow CNTs. Selectivity is a decreasing function of bulk mole composition. At a specified y_{CO2}, increasing the pressure and pore width results in decreased selectivity. The effect of increasing pressure and pore width on selectivity is clearer at low mole fraction of carbon dioxide. In addition, the slope of selectivity is steeper at lower pressure and narrower pore width.

The selectivity of CO_2 over N versus pore width was investigated at three different temperatures. The results indicated that selectivity is a decreasing function of temperature. This is understandable because when temperature increases, the properties of the two components seem to become closer compared to at lower temperatures. The decrease in selectivity along with increasing temperature is greater with narrower than with wider CNTs. As a result, optimum selectivity is achieved in narrow CNTs with a diameter of 0.807 nm and T=300 K when the pressure is 0.15 MPa and y_{CO2} =0.1. It is interesting to note that the selectivity obtained in this work at T=300 K p=0.15 MPa and y_{CO2} =0.5 reaches 9.68 in (6, 6) CNTs, which is noticeably greater than the magnitude of selectivity reported for carbon membrane (S < 1) PI (S=2.7) and PI/MWCNTs (S=4.2). Therefore, CNTs can be considered as a better material for separation of CO_2 from binary mixtures of CO_2/N_2 compared to other carbon-based materials so far reported in the literature.

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