

Experimental Evaluation of CO₂/N₂ Mixture Separation by Multi-multi-walled Carbon Nanotube

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In order to examine the ability of multi-multi-walled carbon nanotube for CO₂ separation from flue gas, uptakes of CO₂ and N₂ were measured at temperatures of 288 K, 298 K and 308 K over the pressure range 1 to 40 bar using volumetric method. The experimental data was fitted by the Langmuir and Freundlich model isotherms. The same shape of isotherms introduced a common mechanism of adsorption but the amount of CO₂ adsorbed on multi-multi-walled carbon nanotube was 2.5 times higher than N₂ adsorption which indicated the possibility of CO₂ removal from flue gases using adsorption process with multi-multi-walled carbon nanotube as the adsorbent. Isothermic heat of adsorption was evaluated from a set of isotherms based on the Clausius–Clapeyron equation.

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1. Introduction

Human activities, such as the combustion of fossil fuels have increased CO₂ concentrations in the atmosphere. CO₂ is one of the major greenhouse gases responsible for global warming [1]. Several technologies have been proposed to capture CO₂ including chemical absorption, cryogenic separation, physical adsorption, and membrane separation. Among these chemical absorption with aqueous solution is the most famous one [2]. But disadvantages of this method cause that physical adsorption plays an important role in the adsorption of CO₂ [3, 4]. Since the discovery of carbon nanotube (CNT) by Iijima in 1991, because of their unique properties such as uniform porosity, high effective surface area and low mass density, many researches were done on these new kinds of porous adsorbents [5]. In this study the potential of multi-multi-walled carbon nanotube (MWCNT) as an adsorbent for CO₂ removal from flue gas (mixture of CO₂ and N₂) was studied. Also experimental results of CO₂ and N₂ adsorption by MWCNT at equilibrium state were described by the Langmuir and Freundlich isotherms. Isothermic heat of adsorption was evaluated considering the Clausius–Clapeyron equation.

2. Apparatus

The amounts of gas adsorbed on the MWCNT were measured by using a volumetric method (Fig. 1). The apparatus used consisted of two pressure and adsorption cells that were put in a water bath to maintain the temperature constant. Before each test, the adsorbent was degassed at 473 K for 24 h and the system was evacuated by vacuum pump to 0.1 mbar. Prior the MWCNT was introduced into the adsorption cell; the setup was leak tested using air for 24 h to ensure that there was no pressure drop at the different operating pressures. Also the He gas was used to determine the dead volume. The amounts of gases adsorption were obtained by Soave–Redlich–Kwong (SRK) equation of state and the material balance before and after each test.

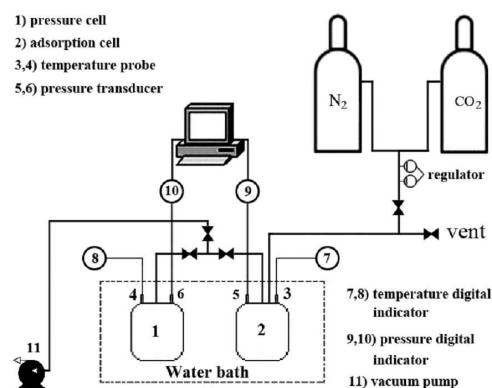


Fig. 1. Schematic diagram of the volumetric adsorption apparatus.

3. Result and discussion

The MWCNT used in this work were purchased from Alpha Nanotechnologies Company, Ltd (China) which was synthesized with chemical vapour deposition (CVD) method. The Brunauer–Emmett–Teller (BET) surface area, pore diameter and pore volume of MWCNT was obtained as 324 m²/g, 9.36 nm, and 0.76 cm³/g respectively. The N₂ adsorption and desorption isotherms is shown in Fig. 2a. The SEM image for MWCNT (Fig. 2b) demonstrate that due to their very short length, pristine-MWCNTs showed a little degree of entanglement. There are gray fragments in the structure of MWCNT, which indicates that MWCNTs contain some impurities as almost amorphous carbon. The adsorption experiments were carried out at range of 288–308 K. By increasing pressure and decreasing temperature, uptake of gases increased (Fig. 3a).

Results indicated that temperature had much less effect on the adsorption of N₂ on MWCNT than adsorption of CO₂. Also the amount of CO₂ adsorption on MWCNT was about three times higher than N₂ adsorption that may be attributed to this fact that the mean pore diameter of this sample is almost higher than N₂ molecule size compared to CO₂ molecule.

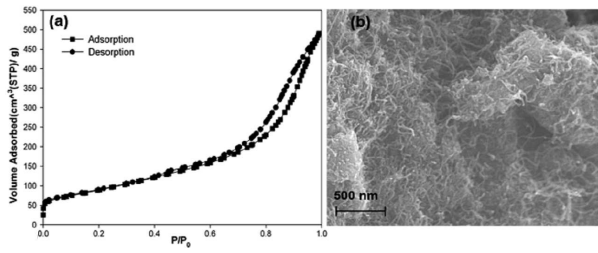


Fig. 2. N₂ adsorption/desorption isotherms (a) and SEM image (b) of MWCNT.

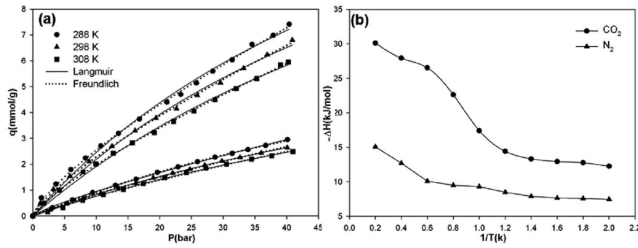


Fig. 3. Nonlinear fit of experimental uptake data (a) and variation of the ΔH_{st} with q_e (b).

Langmuir and Freundlich isotherm constants for adsorption of CO₂ and N₂ on MWCNT.

TABLE

| T [K] | CO ₂ | | | | | | N ₂ | | | | | |
|-------|-----------------|--------|--------|------------|------|--------|----------------|--------|--------|------------|--------|--------|
| | Langmuir | | | Freundlich | | | Langmuir | | | Freundlich | | |
| | q_m | K_L | R^2 | K_F | n | R^2 | q_m | K_L | R^2 | K_F | n | R^2 |
| 288 | 19.9 | 0.0141 | 0.9946 | 0.4454 | 1.31 | 0.9990 | 9.95 | 0.0103 | 0.9998 | 0.1448 | 1.2235 | 0.9994 |
| 298 | 18.94 | 0.0131 | 0.9955 | 0.3885 | 1.30 | 0.9993 | 9.67 | 0.0094 | 0.9999 | 0.1241 | 1.2000 | 0.9990 |
| 308 | 18.24 | 0.0117 | 0.9969 | 0.3226 | 1.27 | 0.9995 | 9.61 | 0.0086 | 0.9992 | 0.1087 | 1.7730 | 0.9972 |

These results suggested that the adsorption of the both gases on these sorbent is more favorable at low temperature. The trend of changes for CO₂ and N₂ adsorption on MWCNT were the same which approve similarity in adsorption mechanism for these gases. Heat of adsorption reflects the enthalpy variation before and after adsorption which is defined by the Clausius–Clapeyron equation:

$$\Delta H_{st} = R \frac{d \ln p}{d(1/T)} \Big|_{q_e} \quad (3)$$

The plot of $\ln p$ versus $1/T$ gives the isosteric heat of adsorption. A rule of thumb in adsorption is that heat of adsorption of 80 kJ/mol or more confirms chemisorption and smaller values is representative of physisorption [6]. The obtained amounts of ΔH_{st} indicated that the process of adsorption was physisorption. By increasing q_e , ΔH_{st} decreased, because in lower pressure gas molecules can come into direct contact with the MWCNT. This causes a stronger interaction between gases and MWCNT. The occupation of pores at higher gas pressure caused a weak interaction between gases and MWCNT. Hence, the ad-

The Langmuir isotherm is given in the following equation:

$$q_e = q_m \frac{K_L P}{1 + K_L P} \quad (1)$$

The Freundlich isotherm is given by

$$q_e = k_F P^{\frac{1}{n}} \quad (2)$$

Figure 3a shows the comparison of experimental adsorption data to predicted values by the Langmuir and Freundlich isotherm models. By inspecting the R -squared values (regression correlation coefficients) (Table), parameters obtained demonstrated that both models give good fit with experimental data. The maximum gas capacity (q_m) for adsorption and K_L values decreased with increasing temperature. These represent that the affinity between CO₂ and N₂ MWCNT had an inverse relationship with temperature and represent an exothermic reaction. The K_F value of the gas adsorbed by the MWCNT decreased when the temperature increased.

sorption enthalpy decreased. A comparison between ΔH_{st} (Fig. 3b) revealed that the heat of adsorption of CO₂ was higher compared with N₂ at all surface coverages. This showed that CO₂ was adsorbed more strongly on MWCNT. Since the molecular mass of CO₂ is higher than N₂, this caused increase of Van der Waals forces between CO₂ molecules and adsorbent.

4. Conclusion

The equilibrium uptake of CO₂ and N₂ by multi-multi-walled carbon nanotube adsorbent was measured. The experimental isotherm data confirmed that the affinity between CO₂ and N₂ on MWCNT had an inverse relationship with temperature. In conclusion, the general results obtained indicated that MWCNTs is a promising adsorbent for CO₂ removal from flue gas (mixture of CO₂ and N₂).

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