STUDY OF THE EFFECT OF FUNCTIONALIZATION OF CARBON NANOTUBES ON GAS SEPARATION

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(Submitted: June 22, 2018 ; Revised: January 3, 2019 ; Accepted: February 2, 2019)

Abstract - In order to improve the adsorption capacity and selectivity of CO₂/CH₄ and CO₂/N₂, we have functionalized multi-walled carbon nanotubes (MWCNT) with 3-aminopropyltriethoxysilane (APTES). The functionalized MWCNT was characterized by Fourier transform infrared (FT-IR), energy dispersive X-ray spectroscopy (EDX) and BET analysis. CO₂, CH₄ and N₂ adsorption at two different temperatures and P < 5 bar on the functionalized MWCNTs was investigated by the volumetric method. The selectivity of the functionalized MWCNTs for CO₂/CH₄ and CO₂/N₂ was studied and compared with MWCNTs. The functionalized MWCNTs show higher adsorption capacity of CO₂ and selectivity of CO₂/CH₄ and CO₂/N₂ in comparison with the MWCNTs at different pressures. The highest CO₂/CH₄ and CO₂/N₂ selectivities for the functionalized MWCNTs were 6.78 and 26.14, respectively, at a pressure of 0.2 bar and at 298 K. Two of the most common adsorption models, the Langmuir and Sips isotherms, were used to correlate the experimental data of CO₂ and CH₄ adsorption on the adsorbents. The results confirm that the functionalized MWCNTs are promising materials for the separation and purification of gases.

Keywords: Carbon nanotubes; Functionalization; Adsorption isotherm; Gas separation.

INTRODUCTION

The continuous use of fossil fuels has led to emission of greenhouse gases and global warming, which is one of the most important environmental issues facing human beings. Two ways can decrease the emission of CO₂: (1) carbon capture and storage (CCS) and (2) use of clean and renewable energy sources. An ideal replacement for fossil fuels is natural gas because it releases less greenhouse gases (Chong et al., 2016; Lajunen et al., 2016). Natural gas is mainly composed of methane, but contains impurities such as CO₂, H₂S and H₂O, which decrease the energy content and corrode pipelines (Campos et al., 2016; Faramawy et al., 2018; Kajama et al., 2018). Therefore, removing these components from natural gas is important in its industrial application. In order to separate the gas mixtures into their component parts, a variety of methods have been proposed such as solvent absorption, membrane separation, adsorptive separation, and chemical conversion. Among the gas separation methods, adsorptive separation appears to be important for gas separation/purification and storage technology owing to its simplicity, low cost, ease of control, and high energy performance (Peng et al., 2006; Babarao et al., 2009; Li et al., 2009).

A lot of porous materials, such as zeolites (Cavenati et al., 2004; Su et al., 2010), activated alumina (Luebbe et al., 2006; Carreon et al., 2008), metal organic frameworks (MOFs) (Belmabkhout et al., 2009; Xiang et al., 2010) and carbonaceous materials (Przepiórski et al., 2004; Lu et al., 2008; Budaeva et al., 2010; Palmer et al., 2011; Lei et al., 2014) have been utilized in gas adsorption/separation processes. Recently, there is a lot of interest in utilizing CNTs for CO₂ adsorption due to their distinctive chemical and physical properties, high thermal and chemical stability and also the reversible nature of the CO₂ adsorption process upon increasing...
the temperature (Su et al., 2009; Shen et al., 2010; Khoerunnisa et al., 2014; Wang et al., 2016).

Investigation of the effect of surface functional groups on the textural properties of carbonaceous materials such as surface area and pore size distribution and also on the adsorption/separation of gases has shown that modification of the surface of carbonaceous materials could cause selective adsorption of one molecule over another (Bezerra et al., 2011; Su et al., 2011; Hu et al., 2017; Keller et al., 2018). The functionalization of CNTs can be performed with a wide range of functional groups including oxygen- and nitrogen-containing groups. Incorporation of nitrogen-containing groups enhances the basicity of CNTs and thus can improve capacity and selectivity of carbonaceous materials in adsorption of acidic gases such as CO\(_2\) and SO\(_2\) (Fatemi et al., 2011; Gui et al., 2013; Khalili et al., 2013; Irani et al., 2017; Zhou et al., 2017).

A large number of experimental studies on single gas adsorption in carbon nanotubes have been reported in literature, but experimental studies on the gas compounds and separation of their mixtures, especially on CNTs, are seldom found. Therefore, further studies are needed to improve the performance of CNTs for gas separation. In this work, a kind of multiwall carbon nanotubes (MWCNT) is functionalized by 3-aminopropyltriethoxysilane (APTES) and its application for CO\(_2\) separation studied. The adsorption isotherms for pure components are obtained at two temperatures. The adsorption capacity and selectivity of the MWCNTs are investigated at 298 K and 348 K.

**EXPERIMENTAL SECTION**

**Materials**

Commercial MWCNTs (Neutrino Corporation) with inner diameter 5-10 nm and 95% purity were used in this study. Nitric acid 65% (HNO\(_3\)), sulfuric acid 95–97% (H\(_2\)SO\(_4\)) and APTES were obtained from E. Merck (Germany). The solvent used in this work was ethanol obtained from Merck. The CO\(_2\), CH\(_4\) and N\(_2\) gas cylinders with purity > 99.999 used in adsorption experiments, were supplied by Sepehr Gas Kavian Co.

**Preparation of adsorbent**

Acid pre-treatment of MWCNTs was performed to achieve two aims: (1) removal of metal catalyst particles from the pristine MWCNTs and (2) carboxylation of the MWCNTs to introduce carboxyl groups on the MWCNT surface prior to amine functionalization. The oxidized MWCNT (MWCNT-COOH) was prepared by adding 500 mg of the calcined MWCNTs to 80 mL of a mixture of H\(_2\)SO\(_4\)/HNO\(_3\) (3:1 v/v) via sonication for 1 h. Then the solution was stirred with a magnetic stirrer, at room temperature for 24 h. The mixture was filtered with distilled water and filtered through a 0.2 μm fiber filter and washed with distilled water several times until the pH increased to neutral (pH 7). The carboxylated MWCNT were then dried in a vacuum drying oven at 100 °C for 4 h (Anbia et al., 2012).

The amine functionalization was then carried out on the pretreated MWCNTs using APTES. The pre-treated MWCNTs were dispersed into bottles containing APTES solution (10 mL of 97% APTS + 90 mL of ethanol) and continuously stirred with a magnetic stirrer at room temperature for 72 h. The mixture was filtered through a 0.2 μm fiber filter and washed repeatedly with ethanol and deionized water to remove excess APTES. Finally the filtered solid was dried in an oven at 100 °C for 6 h and denoted as N-MWCNT.

**Characterization**

The surface functional groups of the modified sorbents were evaluated by FTIR spectra obtained with a FT-IR DIGILAB FTS 7000 spectrometer. The chemical composition of N-MWCNT was studied by energy dispersive X-ray spectroscopy (EDX). The specific surface area and the pore diameter of the adsorbents were obtained by N\(_2\) adsorption–desorption isotherms at 77 K with a volumetric sorption analyzer.

**Gas adsorption measurement**

To evaluate the CO\(_2\), CH\(_4\) and N\(_2\) adsorption capacity of adsorbents at two different temperatures, a laboratory setup based on the volumetric method was used, which is schematically shown in Fig. 1. At first, 0.5 g of adsorbent was poured into the adsorption reactor and then attached to the system. To ensure that there is no leak in the connections, the system was checked with the inert Helium gas flow. In order to degas the system, the valves 6, 7, 8, 9 were opened and other valves closed; then, the system was evacuated with the vacuum pump for 1.5 h at 120°C. After degassing the adsorption system, temperature was decreased to ambient temperature. To perform the adsorption test, we opened the valves 1, 3, 5, 6, 7 and 8 while other valves were closed. The pressure drop observed during the process was the result of gas adsorption and some dead volumes in the reactor. We could exactly measure...
Study of the Effect of Functionalization of Carbon Nanotubes on Gas Separation

Brazilian Journal of Chemical Engineering, Vol. 36, No. 04, pp. 1613 - 1620, October - December, 2019

pressure reduction relevant to the gas adsorption by measuring the dead volumes via helium test. The CO$_2$, CH$_4$ and N$_2$ used for the experiment were of 99.99% purity (Jin et al., 2015; Li et al., 2016; Jin et al. 2018).

RESULT AND DISCUSSION

Adsorbents characterization

Fig. 2 shows the FTIR spectra of calcined and amine modified MWCNTs. In the calcined MWCNT spectrum, the peak at 1630 cm$^{-1}$ is attributed to C=C bonds of nanotubes. The peak at 3432 cm$^{-1}$ is associated with hydroxyl groups (−OH) on the surface of the adsorbents. The IR spectrum of N-MWCNT shows significant bands at 3439, 2850-2960, 1743, 1355-1488, 1030-1100 and 803 cm$^{-1}$ which are associated with CH stretching from CH$_2$CH$_2$CH$_2$ groups, N-H stretch, N-H$_2$ deformation of hydrogen-bonded amine group (Chang et al., 2003; Huang et al., 2003), Si-O-Si(C) and O-Si-O vibrations (Jing et al., 2002; Zhang et al., 2005), respectively. The presence of these peaks confirms the incorporation of APTES on the surface of MWCNTs.

In order to confirm the incorporation of APTES on the surface of MWCNTs, an EDX experiment was performed with a LN (Liquid Nitrogen) free Energy Dispersive detector (SAMx SDD detector) attached to a SEM (Philips XL-30). The results of EDX elemental microanalysis of the N-MWCNT are listed in Table 1.

Figs. 3 and 4 show the N$_2$ adsorption/desorption isotherms and the BJH pore size distribution of MWCNT and N-MWCNT. It is seen that the modified MWCNTs have less adsorption capacity of N$_2$, because a smaller amount of porosity is retained after the incorporation of APTES on the modified MWCNT surface. The textural properties of the adsorbents are given in Table 1. It is seen that the surface area has decreased but the average pore diameter has increased. The decrease of the surface area could be explained by the blockage of pore entrances due to the formation of the amine groups on the surface of N-MWCNT and the increase of the average pore diameter is due to the removal of the amorphous carbon and the catalysts during the purification process by acidic solution (Ioannatos et al., 2010; Su et al., 2009).

Adsorption measurement

Fig. 5 shows the pure CO$_2$, CH$_4$ and N$_2$ adsorption isotherms on MWCNT and N-MWCNT at 298 K. The CO$_2$, CH$_4$ and N$_2$ adsorption capacities of MWCNT and N-MWCNT at 298 K and 348 K and P = 1 bar are given in Table 2.

As expected, adsorption capacity of the three gases was enhanced after amine modification of MWCNTs.
However, as seen in Fig. 5, the N-MWCNT presents a significant increase in the adsorption capacity of CO$_2$ in comparison with CH$_4$ and N$_2$ which may be due to the reaction between the surface amine groups with the CO$_2$ molecules and also because of the high quadrupole moment of CO$_2$ molecules. Chemical reactions between amine groups and CO$_2$ produce the carbamate species according to Eq. (1):

$$\text{CO}_2 + 2\text{RNH}_2 \leftrightarrow \text{RNH}_3^+ + \text{RNHCOO}^- \quad (1)$$

$$\text{RNHCOO}^- + \text{H}_2\text{O} \leftrightarrow \text{RNH}_2 + \text{HCO}_3^- \quad (2)$$

However, as seen in Table 2, the CO$_2$ and N$_2$ adsorption capacity decreases with increasing temperature. The decrease of adsorption capacity with rising temperature implies that the adsorption process is exothermic.

Two of the most common adsorption models, the Langmuir (Garnier et al., 2011) and Sips (Foo et al., 2010) isotherms, were used to correlate the experimental data of CO$_2$ and CH$_4$ adsorption on MWCNT and N-MWCNT at 298 K. The values of model parameters are given in Table 3. The Langmuir isotherm corresponds to homogeneous adsorbent surfaces (Purna Chandra Rao et al., 2006). The Langmuir isotherm is represented by the following equation:

$$q = q_m \frac{bP}{1 + bP} \quad (3)$$

where $q$ is the adsorbed capacity (mmol g$^{-1}$) at equilibrium pressure $P$, $q_m$ (mmol g$^{-1}$) and $b$ (KPa$^{-1}$) are the maximum amount of gas adsorbed (mmol g$^{-1}$) and the Langmuir constant, respectively.

The Sips isotherm is the combined formula of the Langmuir and Freundlich equations, which is given by Eq.(4):

$$q = q_m \left( \frac{bP}{1 + bP} \right)^{1/n} \quad (4)$$

where $q$ (mmol g$^{-1}$) is the amount of gas adsorbed at equilibrium pressure of $P$ (KPa), $q_m$ (mmol g$^{-1}$) is the maximum adsorption capacity, $b$ (KPa$^{-1}$) is the adsorption equilibrium constant which shows the adsorbate affinity for the surface of adsorbent, and $n$ is the heterogeneity parameter (Do, 1998).

The fitting accuracy of the proposed model for the experimental data was estimated by an error function based on the average percent deviation calculated according to:

$$\text{ARE} \% = 100 \left( \frac{1}{N} \sum_{i=1}^{N} \left| \frac{q_{\text{exp}} - q_{\text{cal}}}{q_{\text{exp}}} \right| \right) \quad (5)$$

where ARE (%) is the average percent deviation, $N$ is the number of data points available in the adsorption equilibrium isotherms, and $q_{\text{exp}}$ and $q_{\text{cal}}$ are the experimental and calculated amounts adsorbed (mmol/g), respectively.

As shown in Table 3, between the two isotherms mentioned above, the Sips isotherm with high correlation coefficients ($R^2 > 0.99$) and an average percent deviation value of less than 3% provides the best model for adsorbents, and presents the excellent agreement between the model parameters and the experimental data, which indicates the heterogeneous nature of the adsorbent surface.

Comparisons of the CO$_2$ adsorption capacities of the adsorbents used in this study and other porous materials are given in Table 4.

Table 2. Gas adsorption capacities of MWCNT and N-MWCNT at two temperatures and 1 bar.

| Adsorbent | CO$_2$ | CH$_4$ | N$_2$ | CO$_2$ | CH$_4$ | N$_2$ |
|-----------|--------|--------|-------|--------|--------|-------|
| MWCNT     | 1.19   | 0.63   | 0.17  | 1.02   | 0.2    | 0.09  |
| N-MWCNT   | 2.26   | 0.71   | 0.2   | 1.99   | 0.17   | 0.17  |

Figure 5. Adsorption isotherms of CO$_2$, CH$_4$ and N$_2$ on MWCNT and N-MWCNT at 298 K.

Table 3. Langmuir and Sips isotherm parameters for the adsorption of gases on adsorbents at 298K.

| Adsorbent | CO$_2$ | CH$_4$ | CO$_2$ | CH$_4$ |
|-----------|--------|--------|--------|--------|
| MWCNT     | 1.19   | 2.30   | 0.614  | 0.731  |
| N-MWCNT   | 1.18   | 2.34   | 0.617  | 0.729  |

| Adsorbent | N-MWCNT | N-MWCNT | N-MWCNT | N-MWCNT |
|-----------|----------|----------|----------|----------|
| Sips      | 0.595    | 1.76     | 2.53     | 2.95     |
| Langmuir  | 0.71     | 2.33     | 0.671    | 0.779    |

Brazilian Journal of Chemical Engineering
Adsorption selectivity for gases

The pure component selectivity for gases was obtained from their adsorption isotherms. By applying Eq. (6) (Pawar et al., 2009), the adsorption selectivity of gas 1 over gas 2 can be calculated, where \( V_1 \) and \( V_2 \) are the volumes of gases 1 and 2 adsorbed at a certain temperature and pressure, respectively.

\[
A_{1/2} = \frac{V_1}{V_2 \cdot T \cdot P}
\]  

(6)

The adsorption selectivities of \( \text{CO}_2/\text{CH}_4 \) on MWCNT and N-MWCNT at 1 bar pressure and 298 K are 1.9 and 3.18, respectively. As is clear, the N-MWCNT has higher selectivity to \( \text{CO}_2 \) than MWCNT. This is due to the increase of the cationic surface of carbon nanotubes which is produced by amine groups and also because of the high quadrupole moment of \( \text{CO}_2 \) molecules.

Fig. 6 shows the adsorption selectivities of \( \text{CO}_2/\text{CH}_4 \) and \( \text{CO}_2/\text{N}_2 \) on MWCNT and N-MWCNT at different pressures and 298 K. The \( \text{CO}_2/\text{CH}_4 \) selectivity decreases with increasing pressure. At high pressures, the adsorption of \( \text{CH}_4 \) becomes more significant than that of \( \text{CO}_2 \). The smaller and flat molecules of \( \text{CO}_2 \) can easily diffuse through the pore mouths of nanotubes at lower pressures, whereas large molecules of \( \text{CH}_4 \) require higher pressure to enter the pores (Fatemi et al., 2011).

The selectivity of \( \text{CO}_2/\text{N}_2 \) on N-MWCNT is higher than on MWCNT. According to the quadrupole moment of \( \text{CO}_2 \) and \( \text{N}_2 \) molecules as well as the size of the molecules, this is justified. These results suggest that N-MWCNT is a promising candidate for separation and purification of \( \text{CO}_2 \) from various gas mixtures by an adsorptive process.

CONCLUSION

The gas adsorption capacities on the functionalized MWCNT have been studied. The adsorption capacity of \( \text{CO}_2 \), \( \text{CH}_4 \) and \( \text{N}_2 \) is enhanced after amine modification of MWCNTs. However, the N-MWCNT presents a significant increase in the adsorption capacity of \( \text{CO}_2 \) in comparison with \( \text{CH}_4 \) and \( \text{N}_2 \). The \( \text{CO}_2/\text{CH}_4 \) and \( \text{CO}_2/\text{N}_2 \) selectivities were improved for N-MWCNT at 298 K. Selectivity of N-MWCNT for a \( \text{CO}_2/\text{CH}_4 \) mixture (6.78) at 298 K and \( p = 0.2 \) bar was higher than that of MWCNT (4.99), because \( \text{CO}_2 \) molecules have high quadrupole moment while \( \text{CH}_4 \) molecules do not have a quadrupole moment. Selectivities of N-MWCNT and MWCNT for the \( \text{CO}_2/\text{N}_2 \) mixture at \( p = 0.2 \) bar and 298 K were 26.14 and 19.96, respectively. It is concluded that N-MWCNT is a promising material for \( \text{CO}_2 \) capture from gas mixtures.

ACKNOWLEDGMENTS

The authors are grateful to the Research Council of Iran University of Science and Technology (Tehran) and Islamic Azad University, Kerman branch for the financial support of this project.
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