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A Study on Adsorption Equilibrium for Oxygen and Nitrogen into Carbon Nanotubes

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Abstract. In this work, it was investigated adsorption equilibria of pure oxygen and nitrogen in carbonaceous materials such as an activated carbon (AC), single-walled nanotubes (SWNTs), and Multi-walled nanotubes (MWNTs). The microporous structure of AC was a slit-shaped pore while carbon nanotubes (CNTs) were cylindrical structure. This different pore structure and pore size distribution may be led to difference in selectivity of oxygen to nitrogen. The adsorption capacity of oxygen and nitrogen was in the order AC $>$ SWNTs $>$ MWNTs, while the selectivity of oxygen to nitrogen was SWNTs $>$ MWNTs $>$ AC.

Keywords: adsorption, air separation, carbon nanotubes, kinetic separation

1. Introduction

The separation of oxygen and nitrogen from air is usually carried out by either of two methods: cryogenic distillation or pressure swing adsorption (PSA). There have been efforts to separate useful gases from air since the first attempt in Europe in the 19th century, and in the 1970s PSA technique (Yang, 1987) is established, which is a representative process of air separation at normal temperature using an absorbent instead of liquefying it. In small to medium size plants, PSA is more economical than cryogenic method in the separation of air to produce oxygen and nitrogen. Furthermore, with the development of new adsorbents and the improvement of the adsorption process, PSA process is expected to have competitive advantage even in large-quantity production (Carter and Wyszynski, 1983).

Zeolites are used for the production of oxygen because they preferentially adsorb nitrogen. While for the production of nitrogen, carbon molecular sieves (CMS) are the preferred adsorbent. The CMS does not show the difference in equilibrium adsorption capacities between oxygen and nitrogen. However, oxygen is adsorbed faster than nitrogen, leading to a kinetic selectivity. The PSA technique based on the difference between the kinetics of adsorption of oxygen and nitrogen with oxygen adsorption being faster than nitrogen adsorption is able to be adopted as a process to produce nitrogen from air. Several theoretical and experimental studies of a kinetically controlled PSA separation have been reported (Yang and Doong, 1985; Hassen et al., 1987; Farooq and Ruthven, 1991; LaCava and Lemcoff, 1996; Shirley and Lemcoff, 1997, 2002). From these results, it showed that CMS gave a higher yield than the zeolite in the low-purity region. Another example of PSA technique using CMS as an adsorbent is oxygen and argon separation from a typical O_2 product stream

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of air separation unit (Rege and Yang, 2000). To produce high purity O_2, it is needed to remove impurity such as Ar from the O_2 product stream of air separation process.

Although carbon nanotubes (CNTs) have been recently discovered (Iijima, 1991), they have been attracting a great deal of scientific interest due to their potential application in areas such as adsorbents and composite materials. Since the discovery of CNTs numerous studies have been conducted on their synthesis, treatment, and physical properties. There has been a good deal of experimental and theoretical studies in the possibility of hydrogen storage in carbon materials (Chambers et al., 1998; Yin et al., 2000; Gu et al., 2002; Hou et al., 2003; Sudan et al., 2003). However, only a limited number of studies have been made on the adsorption of other fluids in CNTs (Ohba et al., 2001; Kim et al., 2003). The aim of this work is to provide basic information for the kinetically controlled processes of air separation using carbonaceous materials as an adsorbent. In this work the adsorption of nitrogen and oxygen in single-walled nanotubes (SWNTs) and multi-walled nanotubes (MWNTs) synthesized by an arc-discharged method and chemical vapor decomposition (CVD) method, respectively.

2. Experimental

2.1. Carbon Nanotubes

According to the number of graphite sheets in the tube wall, there are two types of CNTs, i.e., SWNTs and MWNTs. Real CNTs can be as long as several hundred microns. There are several methods of synthesizing CNTs including arc-discharge, pyrolysis, laser vaporization, catalytic decomposition, and CVD. The commercial SWNTs and MWNTs used in this work were supplied by Iljin Nanotech Co Ltd., South Korea. And the activated carbon (BPL4 × 10) supplied by Calgon Carbon Corporation, USA was used to compare adsorption amount of gases. Surface area and pore size analysis of the carbon materials were characterized using a Micrometritics ASAP 2010 by nitrogen at 77 K. The total surface area was determined by the BET method. The pore size distribution was determined from nitrogen desorption data by the BJH method. The samples were degassed at 623 K in high vacuum before the measurements.

The purity of MWNT produced through CVD process was over 95%, which was higher than 40–50%, the purity of SWNTs produced through arc-discharge method. The CNTs were purified using following procedure. As-prepared CNTs (AP-CNTs) were first treated in air at 673 K for 2 hr to remove amorphous carbon. An aqua regia (royal water, $HCl:HNO_3 = 3:1$) were diluted 1:1 with deionized water. The sample was then ultrasonicated in the aqua regia solution at 313 K for 12 hr to remove the metallic catalyst. Finally the sample was rinsed with deionized water and dried (PU-CNTs).

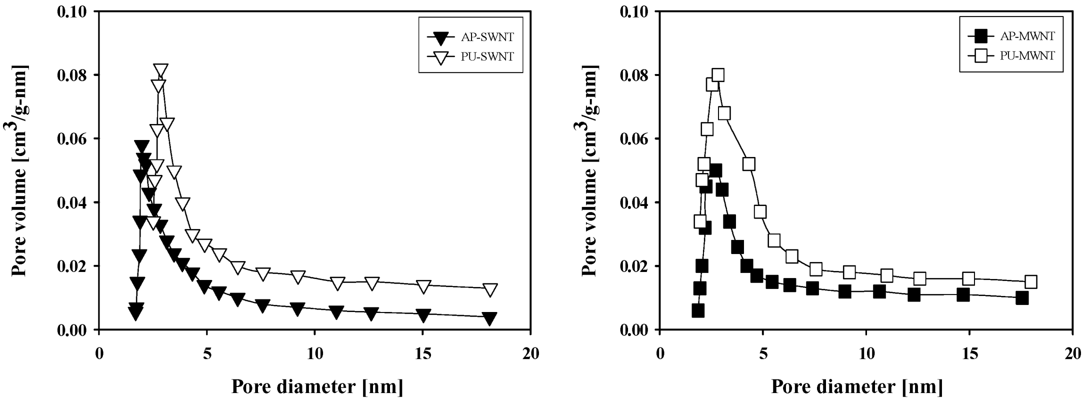
Table 1. The physical properties of carbon nanotubes and activated carbons.

	Adsorbents		
Properties	SWNTs	MWNTs	Activated carbon
BET surface area	AP: 365 m^2/g PU: 1045 m^2/g	AP: 269 m^2/g PU: 431 m^2/g	1483 m^2/g
Process	Arc-discharge	CVD	Steam activation
Length	2–20 μm	10–50 μm	

Table 1 shows the physical properties of adsorbents used in this study. The surface area of SWNTs appeared to be relatively larger than that of MWNTs. However, their surface area was very smaller than that of activated carbon (AC) used in this work. The surface area of purified CNTs was increased about 1.6 fold for MWNTs and 2.8 fold for SWNTs as compare AP-CNTs, respectively. Because the purity of SWNTs was low, the surface area after purification was remarkably increased, but the resultant material was very small. This caused substantial increase of surface and PSD change after rinsing and drying.

2.2. Measurement of Adsorption

The adsorption isotherms were measured by a conventional volumetric technique. The gases used were N_2 (high-purity grade 99.99%) and O_2 (high-purity grade 99.99%). All gases were supplied by Praxair Ltd., South Korea. Each gas was first passed through a bed of gas purifier supplied by Alltech, USA in order to remove water vapor and trace impurities. Prior to the measurements, the adsorbents were outgassed at 523 K under a vacuum better than 10^{-5} torr using turbo molecular pump (Edwards, England) for over 4 hr. The amount of gas was evaluated from measurements of pressure and temperature. The nonideality of gas phase was corrected by use of the second virial coefficients.



(a) SWNTS

(b) MWNTS

Figure 1. Pore size distribution of CNTs before and after purification.

MKS Baratron gauges and readout system were used to measure and record pressures.

3. Results and Discussion

3.1. Characterization

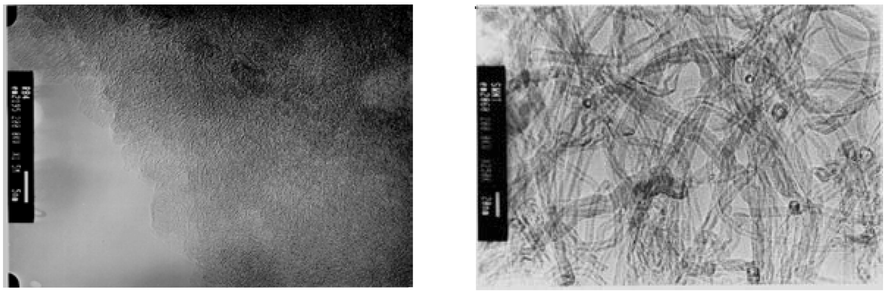
Figure 1(a) shows a pore size distribution determined from N_2 desorption data by the BJH method. The all carbon nanotubes had micropore and mesopore size distribution with maximum at 2 to 3 nm. This is quite consistent with the TEM results. The purified CNTs show higher portion at around peak and a larger pore size thane AP-CNTs, possibly due to the removal of some the graphite layer near the opened tip. This caused the increment of surface area of CNTs after purification.

Figure 2 shows TEM images of the AC and CNTs taken with JEM 2010 (Jeol Co., Japan). The TEM images shown in Fig. 2 demonstrate the formation of amorphous carbon around elongated catalyst particles. The composition of the sample has been dramatically changed after purifying with thermal treatment and ulstrasonicating in aqua regia. Most of the elongated catalyst particles covered by amorphous carbon have disappeared. The pore size and the shape are the most important properties in selective adsorption application. The pore structure of AC is very difficult to define. The pore structure of AC originates from the void spaces between distorted graphitic lamellae, which are highly irregular (Burchell, 1999). Therefore, the microporous structure of AC is slit-shaped pores while CNTs clearly are cylindrical structure, as shown in Fig. 2.

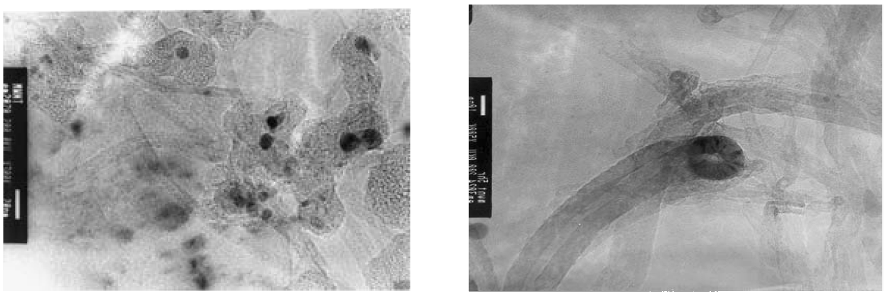
3.2. Equilibrium Isotherms in Activated Carbon and Carbon Nanotubes

Figure 3 shows the adsorption isotherms of pure oxygen and nitrogen in AC and SWNTs. All of the isotherms display Type I adsorption which corresponds to unimolecular adsorption. As shown in Fig. 3(a), the adsorbed amounts of oxygen and nitrogen are almost identical, and oxygen preferentially adsorbed in AC at low temperature (such as our temperature of 283 K). In general, zeolites have ability to separate a strongly quadrupolar species from a weakly quadrupolar species. The quadrupole moment of nitrogen is approximately four times that of oxygen. Therefore, the N_2 molecule adsorbs more strongly with zeolites than O_2 because of its larger quadrupole moment. On the other hand, carbonaceous materials can adsorb nonpolar and weakly polar molecules more strongly than other adsorbents because of chemically inert nature of the graphite surface.

Adsorption capacity is simply defined as the quantity of adsorbate adsorbed per unit weight of adsorbent. Of all characteristics, adsorption capacity is the most important factor because it describes the key economic factor in the adsorption process. The surface area of an adsorbent is usually related to adsorption capacity. Therefore, it is no wonder to show the higher adsorption capacity in AC than SWNTS and MWNTs.

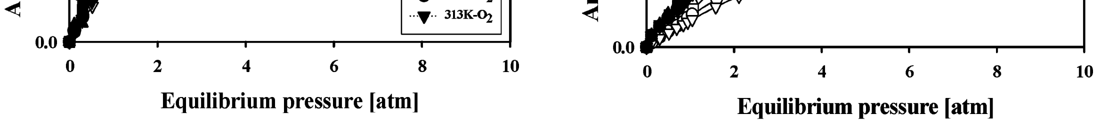


(a) Activated carbon (b) AP-SWNTs



(c) AP-MWNTs (d) PU-MWNTs

Figure 2. TEM images of activated carbon (a), single-walled carbon nanotubes (b) and Multi-walled carbon nanotubes (c and d).

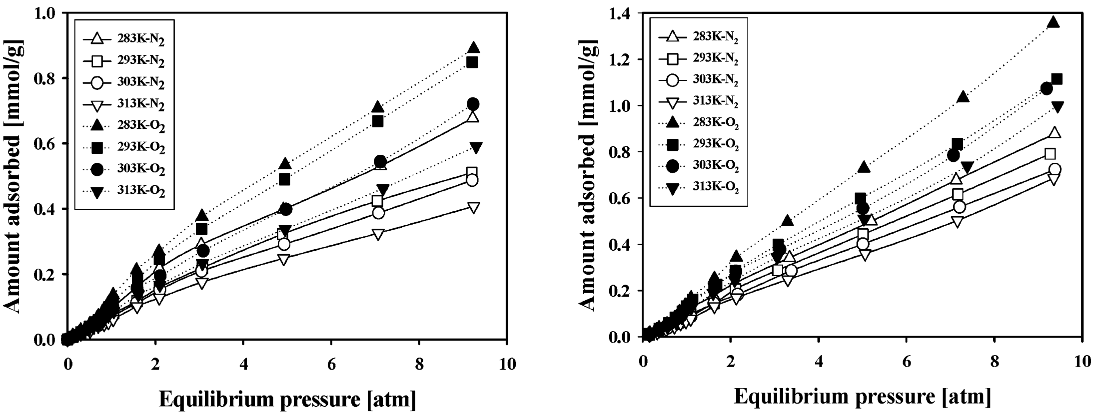


(a) Activated carbon (b) SWMTs

Figure 3. Equilibrium isotherms of pure oxygen and nitrogen on activated carbons and SWNTs.

From the point of view in the selective separation from a mixed gas, the selectivity becomes more important factor. O_2:N_2 selectivity of AC was approximately 1.1:1 at 1atm and 293 K, while 1.6 for SWNTs and 1.4 for MWNTs, respectively. The selectivity of purified MWNTs was increased to 1.5:1. To compare adsorptive selectivity of nitrogen and oxygen for air separation, we simply defined a separation factor, S, as a ratio of adsorbed amount of nitrogen at 600 mmHg to that of oxygen at 160 mmHg, which corresponded partial pressures of air composition, respectively.

$$S = \frac{\text{adsorbed amount of } N_2\ \left(\mathrm{P}_{\mathrm{N}_2} = 600\ \text{mmHg}\right)}{\text{adsorbed amount of } \mathrm{O}_2\ \left(\mathrm{P}_{\mathrm{O}_2} = 160\ \text{mmHg}\right)} \quad (1)$$



(a) As-prepared MWNTs

(b) Purified MWNTs

Figure 4. Equilibrium isotherms of pure oxygen and nitrogen in multi-walled carbon nanotubes.

If separation factor is 3.76 which corresponds the molar ratio of nitrogen and oxygen in air composition, no separation of nitrogen and oxygen has been accomplished. If $S < 3.76$, it means that the adsorbent adsorbs oxygen preferentially to nitrogen. The lower value in separation factor means the more favorable for oxygen. The separation factor in AC was 3.6, while 1.6 for SWNTs, 3.4 for AP-MWNTs, and 3.2 for PU-MWNTs, respectively.

4. Conclusions

In this work, it was carried out adsorption equilibria of pure oxygen and nitrogen in an activated carbon (AC), single-walled nanotubes (SWNTs), and Multi-walled nanotubes (MWNTs) as a carbonaceous adsorbent. The microporous structure of AC was a slit-shaped pore while carbon nanotubes (CNTs) were cylindrical structure. This different pore structure and pore size distribution may be led to difference in selectivity of oxygen to nitrogen. Adsorption capacity of oxygen and nitrogen was in the order AC > SWNTs > PU-MWNTs > AP-MWNTs. The selectivity was SWNTs > PU-MWNTs > AP-MWNTs > AC. The performance of purified MWNTs was improved about 10%.

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