Cryogenic Adsorption of Nitrogen and Carbon Dioxide in Activated Carbon

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Abstract. Activated carbon have been used for a long time at low temperature for cryogenic applications. The knowledge of adsorption characteristics of activated carbon at cryogenic temperature is essential for some specific applications. However, such experimental data are very scare in the literature. In order to measure the adsorption characteristics of activated carbon under variable cryogenic temperatures, an adsorption measurement device was presented. The experiment system is based on the commercially available PCT-pro adsorption analyzer coupled to a two-stage Gifford McMahon refrigerator, which allows the sample to be cooled to 4.2K. Cryogenic environment can be maintained steadily without the cryogenic liquid through the cryocooler and temperature can be controlled precisely between 5K and 300K by the temperature controller. Adsorption measurements were performed in activated carbon for carbon dioxide and nitrogen and the adsorption isotherm were obtained.

1. Introduction

All gases can be condensed easily except helium and hydrogen at cryogenic temperature of about 4K. The cryosorption pumps used for creating high vacuum for these gases are characterized by high pumping speed, brilliant storage capacity and low end pressure. \cite{[1]} Adsorption isotherms are strongly needed for the design of these kind of applications. However, such experiment data are very scare in the literatures. \cite{[2]}

Resulting from the high porosity, activated carbons are characterized by large inner pore surface area. For this reason, activated carbons are widely used in the integration of cryogenic devices for their adsorption properties, especially in the pumping of gases such as helium and hydrogen and their isotopes for some special applications. \cite{[3],[4]}

An adsorption measurement device was built in this paper which allow us systematically measure the adsorption characteristics of chosen adsorbent-adsorbate pairs. The experiment system is based on the commercially available PCT-pro adsorption analyzer coupled to a two-stage Gifford McMahon refrigerator, which allows the sample to be cooled to 4.2K. Nitrogen and mercury porosimetry facilities were used for testing the characterization of the samples. The adsorption isotherms are obtained by home built adsorption measurement device, including adsorption isotherms for CO\textsubscript{2} at 300K and 217K and N\textsubscript{2} at 220K and 170K.
2. Experimental Setup

2.1 Carbon Dioxide
Carbon dioxide has been widely used in cryogenic application for its large inner pore surface. For this reason, carbon dioxide has been selected as sorbent in this paper. In consideration of its high adsorption capacity, high hardness and wide grain size range, we choose PICACTIF TA 60, a kind of regenerable granular microporous activated carbon, as sample used in our experiment. Nitrogen and mercury porosimetry facilities were used for testing the characterization of the samples. Nitrogen and mercury porosimetry facilities were used for testing the characterization of the samples. Table 1 presents the porosity characterization of the activated carbon used in experiment.

| Property                        | Value          |
|--------------------------------|----------------|
| Surface area (m²/g)             | 1376.91        |
| Pore volume (cc/g)              | 0.547          |
| Apparent density (g/cm³)        | 0.45-0.53      |
| Humidity as packed (% min)      | 5              |
| CCl4 index (% min)              | 60-70          |

2.2 Gases used
As BET has become a recognized way to establish standards in the characterization of porous materials, experiments with nitrogen were carried out in our experiment. [5] With more attentions have been paid to the green house effects and their impacts, carbon dioxide were used as adsorptives in this paper, too. The nitrogen and carbon dioxide gases were used in a purity of 99.9999 vol.%.

The core parameters used in this paper were listed in table 2.

| Gas   | T (K) | p₁ (kPa) | p₀ (kPa) | M (g/mol) |
|-------|-------|----------|----------|-----------|
| N₂    | 126.19| 3397.80  | 101.35(77.35) | 28.0134   |
| CO₂   | 304.41| 7386.60  | 53.065(217)  | 44.0095   |

2.3 Experiment principle
The adsorption measurement device mentioned in this paper use a ‘Sieverts apparatus’ way to measure the solubility of gases in the sample. [6]

![Figure 1. The schematic diagram of ‘Sieverts apparatus’](image)
When we use ‘Sieverts apparatus’ to measure the adsorption characteristics, sample at known pressure and volume will be connected to a reservoir volume and pressure through an isolation valve. When valve is closed, reservoir is filled and equilibrated. Then we open the isolation valve, gases will diffuse until the new equilibrium establish. Sample pressure is equilibrated and measure in this moment. Through this way, gas adsorption can be calculated by formula 1 based on the conservation of mass.

\[
\Delta n = \left( \frac{P_s (m-1) \cdot V_s}{Z_s \cdot R \cdot T_s} + \frac{P_r (m) \cdot V_s}{Z_r \cdot R \cdot T_r} \right) - \left( \frac{P_s (m) \cdot V_s}{Z_s \cdot R \cdot T_s} + \frac{P_r (m) \cdot V_r}{Z_r \cdot R \cdot T_r} \right)
\]

- \( n \): the amount of gas adsorption
- \( P_s (m-1) \): the pressure of the sample reservoir in (m-1) moment
- \( P_r (m) \): the pressure of the expansion reservoir in (m-1) moment
- \( V_s \): the volume of the sample reservoir
- \( V_r \): the volume of the expansion reservoir
- \( T_s \): the temperature of the sample reservoir
- \( T_r \): the temperature of the expansion reservoir
- \( Z_s \): the compressibility factor of gas in the sample reservoir
- \( Z_r \): the compressibility factor of gas in the expansion reservoir

2.4 Experimental Setup

The adsorption measurement device mentioned in this paper is made up of three main parts: a commercially available PCT-pro adsorption analyzer, a sample chamber to accept the samples and a two-stage Gifford McMahon refrigerator for creating cryogenic testing environment. With the refrigerator unit integrated with the PCT-pro adsorption analyzer, we can study the sample to the temperature between 4.2K and 300K.

PCT-pro adsorption analyzer is a fully automated Sieverts instrument for measuring gas adsorption properties of materials. It is designed for precision measurements over a broad range of pressures, temperatures, and sample sizes. This instrument hosts a number of advanced features including PID controlled gas pressure, temperature regulated gas handling system, different calibrated volumes, automatic high and low-range pressure switching and sophisticated measurement and process.

![Home built adsorption measurement device](image)

**Figure 2.** Home built adsorption measurement device

Instead of using liquid nitrogen (77K as a minimum) or liquid helium (4.2K as a minimum) to cool the sample, the home built adsorption measurement device mentioned in this paper use a Gifford McMahon refrigerator as the cooling source. The refrigerator includes three main parts: a two-stage cold head, two transfer line and a compressor.

The sample chamber was installed on the cold head and connected to the PCT-pro adsorption analyzer by means of gas transfer line.
The cold head can attain temperature down to 30K at the first stage and 4.2K at the second stage based on the heat input. A radiation shield was installed in the first stage to reduce the thermal load of the second stage. A vacuum recipient was installed to maintain the vacuum environment. In order to control the testing temperature concisely, we choose a temperature controller made by model 32B to adjust the temperature and 150W heater was attached to the second stage.

![Image](image.png)

**Figure 3.** Radiation shield and sample chamber of experimental setup

### 3. Experimental Procedure and results

#### 3.1 Experimental Procedure

The whole adsorption testing experiment can be divided into three main parts: preparation of the sample, set of the testing environment and measurement of the sample.

In the first step of preparing the sample, we should put the sample into the vacuum oven and heat the sample in 400K at least 24 hours. After the sample being totally heated and vacuum, the sample should be weighed.

There are two environment condition we should set up to guarantee the experiment to run well: vacuum condition and temperature condition. In order to creating vacuum environment, we should put a copper shim into the gap between the two side of the chamber room after put the sample into the sample chamber room, then close the sample chamber room, the radiation shield and the vacuum recipient. Immediately afterwards, start to vacuum the vacuum recipient and the radiation shield at least 24 hours by the vacuum pump. After the vacuum condition is reached, the cryocooler is turned on and temperature controller can start to work to acquire the temperature condition.

Until the temperatures are reached equilibrium in the sample chamber, the radiation shield and the cold head, we can start the adsorption measurement experiment.

The first step of adsorption measurement experiment is evacuating the whole system, then calibrating the volume of the sample chamber. After the volume was obtained, the appropriate point on the menu can be used to start the adsorption measurement experiment. In this time, we should input the parameter we need to the computer. Then, the experiment start and the data can be recorded by the computer automatically.

#### 3.2 Experiment Results

The adsorption measurements were carried out with CO$_2$ and N$_2$. Adsorption isotherms were obtained for CO$_2$ as adsorbate at 300K and 220K and nitrogen as adsorbate at 217K and 170K. From figure 4 and figure 5, we can tell the isotherms of CO$_2$ belong to Type-I adsorption isotherm and the isotherms of N$_2$ are Type-II isotherms according to IUPAC.
4. Conclusion
An adsorption measurement device has been designed and built in a temperature range of 4.2K to 300K. The cryogenic adsorption measurements were carried out with CO$_2$ and N$_2$ as adsorbate. The porosity characterization of the activated carbon and the core parameters of gases used in the experiment were studied. Adsorption isotherms were obtained for CO$_2$ and N$_2$ at specific temperature.

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