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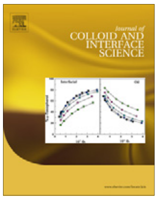

Determination of the optimal pore size for improved CO_2 adsorption in activated carbon fibers

Seul-Yi Lee, Soo-Jin Park *

Korea CCS R&D Center, Korea Institute of Energy Research, 152 Gajeong-ro, Yuseoung-gu, Daejeon 305-343, South Korea
Department of Chemistry, Inha University, 100 Inharo, Nam-gu, Incheon 402-751, South Korea

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ABSTRACT

Commercially available activated carbon fibers (ACFs) were modified further by a chemical activation method to obtain superior CO_2 adsorption capacity. The relationship between the pore structure of the modified ACF and the CO_2 adsorption behaviors was investigated. Chemical activation (with KOH at a fixed activation temperature of 900 °C for 1 h and various KOH/ACF weight ratios ranging from 1 to 4) of ACF increased the total pore volume and specific surface area to 1.124 $cm^3\ g^{-1}$ (KOH/ACF weight ratio of 2) and 2318 $m^2\ g^{-1}$ (KOH/ACF weight ratio of 4), respectively. Compared to ACF, the total pore volume and specific surface area were improved by factors of 2.5 and 2.3, respectively. Interestingly, the highest CO_2 adsorption capacity of 250 $mg\ g^{-1}$ at 298 K and 1 bar was observed at a KOH/ACF weight ratio of 3. The modified ACF had the narrowest microporosity ranging from 0.5 to 0.7 nm. Therefore, the increase in CO_2 adsorption capacity after chemical activation is closely related to the narrower pore size distribution rather than the total or micropore volume and specific surface area.

1. Introduction

Recently, the growing environmental concerns for global warming and climate change have motivated significant research activities, such as separation, capture and storage of greenhouse gases, particularly carbon dioxide (CO_2), which will be increasingly important in the future world economy.

The Intergovernmental Panel on Climate Change (IPCC)'s fourth assessment report [1] stated that the global atmospheric CO_2 concentration has increased from a preindustrial value of ~280 ppmv to 379 ppmv in 2005 and ~390 ppmv currently. Most of the CO_2 emissions into atmosphere might originate from the combustion of fossil fuels (~80% in global annual CO_2 emissions of approximately 38 Gt in 2004, as published in the IPCC report [2]).

Most of the huge amounts of CO_2 emission are closely related to large stationary emission sources, such as power plants, gas processing industries, refineries, chemical and petrochemical industries, iron and steel industries, and cement industries [3]. Therefore, the mitigation of CO_2 emission to achieve potential benefits including reduced air pollution and improvements to a healthy environment has become even more challenging.

Carbon capture and sequestration (CCS) has been identified as a solution that can save the Earth. CCS includes four primary steps: CO_2 capture, compression, transport, and storage. Cost-effective capture technology is important for the economical mitigation of CO_2 from fossil-fuel based power plants, because the capture processing costs comprise approximately ~70% of the whole CCS process.

Adsorption processes, which are an economic and promising alternative capture technique to other methods, such as absorption, cryogenics, and membranes have attracted increasing interest [4,5]. In this respect, a range of possible adsorbents including porous carbon [6–8], porous silicas [9–12], metal–organic frameworks (MOFs) [13–15], or organic–inorganic hybrid sorbents [16] have been considered potential candidates for CO_2 capture.

Among of the many well-known adsorbents, activated carbon-related materials are a class of adsorbents with a range of applications, such as catalyst supports, selective adsorption agents, and energy storage devices [17–19]. These activated carbon materials offer several advantages in terms of cost with rapid adsorption kinetics, availability, large surface area and easy-to-design pore structure, surface functionalization, hydrophobicity, reversibility, and low energy requirements for regeneration.

In particular, activated carbons fibers (ACFs) are considered promising materials based on their nano-structure, abundant micrometer porosity, and properties, such as high specific surface area and narrow pore size distribution. The fibrous shape of ACFs has the advantage of easy handling compared to granular and powdered adsorbents [20,21].

In this work, highly porous activated carbon fibers were prepared and the CO_2 adsorption behavior was examined as a function

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* Corresponding author. Fax: +82 32 860 8438.
E-mail address: sjpark@inha.ac.kr (S.-J. Park).

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of the KOH/ACF weight ratio. The relationship between the pore structure of modified ACF and the CO_2 adsorption behavior was also investigated.

2. Experimental

2.1. Materials and sample preparation

Commercially available chopstick-like activated carbon fibers (ACFs) with a diameter of 10–20 μm and a length of 100–1000 μm were used (Fig. 1). Prior to use, the crude ACFs underwent chemical treatments by immersion in concentrated nitric acid for 2 h at 60 °C to oxidize the ACF surfaces and remove the organic or metallic impurities from their synthesis. Subsequently, the ACF was treated with a KOH solution at 60 °C overnight. The KOH to ACF mass ratio ranged from 1:1 to 4:1. The prepared KOH/ACF mixtures were then transferred to an alumina boat in a furnace under an ultra-pure N_2 gas flow of 200 mL min^{-1}. The samples were heated to 900 °C for 1 h. The ramps for the heating and cooling steps were set to 2 °C min^{-1}. After cooling, the resulting products were washed consecutively with dilute hydrochloric acid and distilled water until a neutral pH was reached. The samples were finally dried in a vacuum oven at 120 °C for 24 h to obtain chemically heat-treated ACF. The chemically further activated carbon fiber samples are labeled according to the KOH ratios: ACFK-0, ACFK-1, ACFK-2, ACFK-3, and ACFK-4.

2.2. Characterization and CO_2 adsorption measurements

X-ray diffraction (XRD) was performed on a Bruker-AXS D2 Phaser Desktop X-ray Diffractometer with a Lynx-Eye detector using Cu Kα radiation at 30 kV and 10 mA (λ = 1.5406 Å). The surface morphology and feature of the sample were observed by scanning electron microscopy (SEM, Model S-4300, Hitachi Co., Ltd.) at an acceleration voltage of 15 kV. The samples were placed on a standard aluminum SEM holder and platinum-coated.

The porous textural characterization was analyzed at 77 K with a N_2 adsorption isotherm using a BEL Co., Ltd.'s, Model BEL-SORP. All samples were out-gassed at 573 K overnight prior to the measurements. The specific surface areas (S_{BET}) were calculated using the Brunauer–Emmett–Teller (BET) equation with a relative pressure of 0.01–0.15. The total pore volume (V_{Total}) was obtained at a relative pressure of 0.99. The micropore volume (V_{Micro}) was determined using the Dubinin–Radushkevitch (D–R) equation. The mesopore volume (V_{Meso}) was obtained by subtracting the micropore volume from the total pore volume. The micropore size distribution was calculated using the Harvath–Kawazoe (H–K) method.

Finally, the CO_2 adsorption experiment was conducted three times to provide an average reading by a pressure swing analysis. In each experiment, approximately 0.5 g of the sample was loaded into a glass tube. Prior to the measurements, the system was evacuated for 12 h while the sample tube was heated to 573 K. After cooling the sample tube to room temperature, ultra-high purity grade (99.9999%) CO_2 gas was introduced from 10^{-3} to 1 bar. The CO_2 adsorption capacity was determined using a volumetric measurement method.

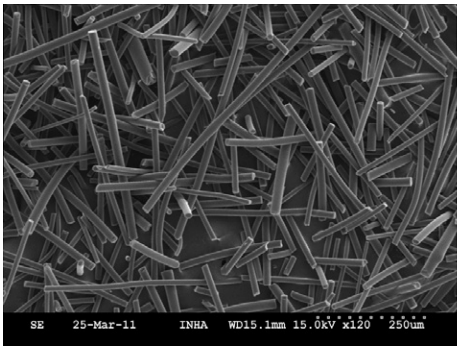

Fig. 1. SEM image of commercially available chopstick-like ACF used in this study.

3. Results and discussion

3.1. Characterization

Fig. 1 shows a SEM image of chopsticks-like ACF (ACFK-0) used in this study. Fig. 2 presents SEM images at 18,000 and 40,000× magnification. After the KOH heat-treatments, the samples maintained their original textile shapes and a width similar to ACFK-0, that is, there were no structural changes including broken or cut off. A very smooth surface was clearly identifiable for ACFK-0, as shown in the inset in Fig. 2a. On the other hand, the morphological features of ACFK-3 showed distinct patterns (in the inset of Fig. 2b). The KOH heat-treated ACF (ACFK-3) had a highly cracked and collapsed surface, indicating a high surface area and the creation of pores.

Fig. 3 shows the XRD patterns of the ACFK samples as a function of the KOH/ACF ratio. All samples showed a peak at approximately 24° 2θ and another at approximately 43° 2θ, which was assigned to hexagonal and rhombohedral graphite, respectively [22,23]. The peak at approximately 24° 2θ of ACFK-0 showed higher intensity than those of the other samples, which is characteristic of the highly structured hexagonal graphitic C (002) reflection. In addition, these peaks were shifted increasingly to a low angle.

As shown in Table 1, the interlayered spacing between the adjacent graphite layers ($d_{(002)}$) increased with increasing KOH/ACF ratios and the average stacking height of the carbon planes ($L_{c(002)}$) decreased. The former and latter are related to the disorder in the structure and crystalline size, respectively [24,25]. Therefore, the KOH heat-treatments had a considerable effect on the disorder in the well-arranged alignment of ACF by the KOH heat-treatments. From these two main XRD analysis parameters, the *npg* was also calculated using the formula, $npg = L_c/d_{(002)}$. The *npg* values decreased from 3.08 for the non-treated sample (ACFK-0) to 1.97–2.35 for the KOH heat-treated samples (all samples except for ACFK-0) despite retaining the shape of the fibers after the KOH heat-treatments as shown in Fig. 2.

The decreases in their intensities at C (002) indicated an increase in the irregularity of the layer structures, whereas a widening of the peak range resulted in cracking or collapse of the layer structures [26,27]. This affects the textural properties induced by the KOH heat-treatment.

To obtain information about the elemental content of the ACF surfaces, elemental analysis measurements are carried out, as presented in Table 2. It is well known that carbon fibers are defined as a fiber containing at least 92 and up to 100 wt.% carbon. In particular, the carbon fibers more than 99 wt.% carbon is usually called a graphite fibers. While ACFK samples show a considerable amount of oxygen, which is due to the chemical treatments by concentrated nitric acid. This has probably effectual to the KOH heat-treatments when the carbon surface has acidic character rather than basic one [28]. During the KOH heat-treatments, the gasification also more easily occurs due to the hydroxide radical. It is also confirmed that the carbon content of ACFK samples increased and the oxygen content decreased with increasing the KOH/ACF ratios.

According to Jiménez et al. [23], the activation mechanism could be presented; the reduction of KOH on the carbon surfaces would lead to K, H_2, and K_2CO_3. And a simultaneous possible reaction