



# Effects of surface chemical properties of activated carbon fibers modified by liquid oxidation for CO<sub>2</sub> adsorption



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## ABSTRACT

Activated carbon fibers (ACFs) with controlled pore sizes were prepared by KOH activation to efficiently capture CO<sub>2</sub> molecules. The surfaces of the ACFs were modified by liquid oxidation using hydrofluoric acid to enhance the adsorption of CO<sub>2</sub> by the fibers based on the effects of the oxygen-containing functional groups introduced on the surface. Oxygen-containing functional groups were effectively introduced onto the surfaces of the ACFs based on the fluorine radical effect, and they attached themselves to the pores of the ACFs as the concentration of hydrofluoric acid increased. The oxygen-containing functional groups, such as carboxylic and hydroxyl groups, on the surfaces of the ACFs played an important role in guiding CO<sub>2</sub> into the micropores via the attractive forces experienced by the electrons in the CO<sub>2</sub> molecules.

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## 1. Introduction

The emission of carbon dioxide into the atmosphere from the combustion of fossil fuels is recognized as a major contributor to global warming. There is a growing realization that for at least the next two or three decades, the persistence of the petroleum economy will ensure continuous increases in atmospheric carbon dioxide levels [1]. Hence, there is a renewed urgency to develop feasible methods for the capture and long-term sequestration of carbon dioxide in geologic or oceanic reservoirs. Approximately 30% of the gaseous CO<sub>2</sub> emitted into the atmosphere is derived from fossil fuel power plants [2]. As large-scale point sources, the flue gases generated by these power plants are attractive candidates for the engineered capture and sequestration of CO<sub>2</sub>.

The current or proposed methods for capturing CO<sub>2</sub> from flue gas include absorption, adsorption, cryogenic distillation, and membrane separation. Because adsorption is typically used as a final polishing step in a hybrid CO<sub>2</sub> capture system [3,4], the efficient capture of CO<sub>2</sub> using adsorption requires solid adsorbents with

high CO<sub>2</sub> selectivity and capacity. Studies are currently underway to identify and develop such sorbents, such as activated carbon materials [5–7].

Among the various candidates, activated carbon materials are considered to be promising for CO<sub>2</sub> gas storage media because they can provide excellent properties, such as high surface areas and pore volumes, with light weight. Additionally, the interactions between surface carbon and adsorbates affect the adsorption capacity. The surface chemistry of porous carbon materials can affect the adsorption properties of the materials [8]. Due to the weak Lewis acid role of CO<sub>2</sub>, the introduction of Lewis bases onto porous carbon surfaces may enhance the CO<sub>2</sub> capture performance of these porous materials. Their performance is determined by both their pore structure and surface chemistry. The surface chemistry of carbon materials, particularly surface oxygen complexes, is a very important factor that affects their applications as adsorbent supports for CO<sub>2</sub> capture [9,10].

The surface oxygen complexes of porous carbon materials effectively provide electron-rich properties, which can enhance the interaction between the surface of carbon adsorbents and CO<sub>2</sub> due to the introduction of various polar groups, such as hydroxyl (–OH) and carboxyl (–COOH) groups [11]. Tenney et al. noted that hydroxyl and carboxyl groups are helpful for CO<sub>2</sub> adsorption according to grand canonical Monte Carlo (GCMC) simulations of activated carbon and coal [12]. Therefore, modifying the surfaces

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of porous carbons through various oxygen treatments is expected to enhance the CO<sub>2</sub> adsorption capacity and selectivity.

To characterize surface oxygen complexes, several methods, such as X-ray photoelectron spectroscopy (XPS) and temperature-programmed desorption (TPD), have been used. TPD is a commonly used technique because it provides good information regarding the surface properties of a sample. During TPD, surface oxygen complexes decompose upon the release of CO and/or CO<sub>2</sub> by heating at different temperatures.

In the present work, TPD analysis was used to obtain a fundamental understanding of the role of the surface oxygen complexes on activated carbon fibers during adsorption processes. The required trends are that (a) a CO<sub>2</sub> peak results from carboxylic acids at low temperatures or from lactones at high temperatures; (b) carboxylic anhydrides simultaneously generate a peak for CO and a peak for CO<sub>2</sub>; and (c) hydroxyls, ethers and carbonyls generate a CO peak [11,12]. Therefore, TPD analysis can be helpful in understanding the effects of the surface chemistry of activated carbon fibers containing hydroxyl and carboxylic groups on CO<sub>2</sub> adsorption properties. The surface of poly-acrylonitrile (PAN)-based carbon fibers was activated by KOH and modified by liquid oxidation with hydrofluoric acid in various ratios for use as a CO<sub>2</sub> adsorption material. The effects of the treatments on the surface morphology and the adsorption properties of the activated carbon fibers were also investigated. A mechanism is proposed for the improved CO<sub>2</sub> adsorption efficiency of the activated carbon fibers after the liquid-oxidation treatment.

## 2. Experimental

### 2.1. Materials

In this study, poly-acrylonitrile (PAN) fibers (Kolon Industries, Republic of Korea) were cut to a length of 20 cm (approximately 10 g). In order to develop a porous structure, potassium hydroxide (KOH, bead, 98%, Samchun Co.) was used as a chemical activation agent for the activation process. Hydrofluoric acid (48.0–51.0%, J.T. Baker) was used to treat the surfaces of the carbon fibers to introduce oxygen complexes [18].

### 2.2. Preparation of activated carbon fibers

Before carbonizing the PAN fibers, a stabilization (oxidation) step was performed to convert the polymer from a thermoplastic polymer to a thermosetting polymer because thermoplastic materials may soften and melt at high temperatures [13,14]. The stabilization step was performed at 225 °C for 8 h in air. The stabilized PAN fibers were then heat-treated in a nitrogen atmosphere at 1000 °C under the following conditions: a heating rate of 10 °C/min, a holding time of 1 h and a nitrogen feeding rate of 100 mL/h.

In addition, the optimum activation conditions (such as the optimum reaction time, target temperature, temperature increase rate, gas flow rate and amount of activation agent) were determined based on our previous results. A 6 M KOH solution was prepared as the chemical activation agent based on our previous work [13]. The carbon fiber (CF) was placed in an alumina boat within a steel pipe; a KOH solution was added at a ratio of 15 mL/g (KOH solution/CF sample), followed by chemical activation at 750 °C for 3 h in a nitrogen atmosphere. The heating rate was 5 °C/min, and the argon gas feed rate was 100 mL/min. After chemical activation, the resulting samples were washed several times with distilled water to remove residual potassium and then dried overnight at 120 °C [15,16]. These activated samples were denoted activated carbon fibers (ACFs).

### 2.3. Chemical treatment of activated carbon fibers

Two-hundred milliliters of various concentrations of hydrofluoric acid (1, 2, and 4 mol/L) was mixed with 1 g of the raw ACFs (R-ACF). These mixtures were then mixed using a mechanical shaker for 24 h at 50 °C. The treated ACFs were washed with distilled water until a neutral pH was achieved and then dried for 24 h at 50 °C. The untreated ACFs were denoted R-ACF. The oxidized ACF samples are hereinafter referred to as 1M-ACF, 2M-ACF, and 4M-ACF, depending on the concentrations of hydrofluoric acid used, which were 1, 2, and 4 mol/L, respectively.

### 2.4. Physicochemical characterization

The pore structures of the as-prepared samples were assessed by N<sub>2</sub> adsorption at –196 °C using an ASAP2020 (Micromeritics, USA). The specific surface areas of the samples were evaluated using the Brunauer–Emmett–Teller (BET) equations. The pore-size distributions of the samples were determined using the Horvath–Kawazoe (H–K) and Barrett–Joyner–Halenda (BJH) methods.

X-ray photoelectron spectra (XPS) of the samples were obtained using a MultiLab 2000 spectrometer (Thermo Electron Corporation, England) to investigate the elements present in the samples. Al K $\alpha$  (1485.6 eV) radiation was used as the X-ray source, and the XPS instrument was operated using a 14.9-keV anode voltage, a 4.6-A filament current and a 20-mA emission current. All samples were treated at 10<sup>–9</sup> mbar to remove impurities. The survey spectra were obtained using a 50-eV pass energy and a 0.5-eV step size.

Temperature-programmed desorption (TPD) experiments were conducted using an Autochem II 2920 (Micromeritics, USA). The typical procedure was as follows. A sample (200 mg) was placed over quartz wool in a quartz U-tube (Flow-ThruTM, 10 mm i.d.). The sample was heated to 100 °C under a stream of helium and was maintained at this temperature for 3 h. Then, the sample was further heated to 900 °C at a ramp rate of 10 °C/min. The concentrations of CO and CO<sub>2</sub> were determined by the intensities of *m/z* at 28 and 44, respectively. After the analysis, a multiple Gaussian function was used to fit each of the TPD spectra, taking the position of the peak center as the initial estimate. The numerical calculations were based on a non-linear routine that minimized the square of the deviations, and the Simplex method was used to perform the iterations. The use of Gaussian functions is justified by the shapes of the TPD peaks, which are a result of a continuous random distribution of binding energies of the surface groups [17].

Additionally, we used CO<sub>2</sub>-TPD to investigate the adsorption characteristics of CO<sub>2</sub>. This study was performed using the same analyzer. The sample was loaded with 200 mg of the synthesized material and then heated in flowing helium at 150 °C for 3 h. After it was cooled to 25 °C, CO<sub>2</sub> (diluted in helium gas) at a flow rate of 30 mL/min was introduced to the sample for CO<sub>2</sub> adsorption for 60 min. The TPD experiment was then performed by purging with helium at a rate of 30 mL/min from 25 to 150 °C. The results obtained using these samples indicated that the TPD experiments performed under the abovementioned optimized conditions were reproducible and that diffusion limitations could be ruled out.

## 3. Results and discussion

### 3.1. Surface chemical properties of prepared ACFs

XPS elemental analysis was performed to compare the chemical compositions at the surfaces of the untreated ACFs and liquid-oxidized ACFs. Table 1 lists the atomic percentages of C, O and F for the liquid-oxidized ACFs synthesized in this study. According to the XPS elemental analysis, the O and F contents in the liquid-oxidized

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