KOH-activated graphite nanofibers as CO$_2$ adsorbents

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Abstract

Porous carbons have attracted much attention for their novel application in gas storage. In this study, porous graphite nano-fiber (PGNFs)-based graphite nano fibers (GNFs) were prepared by KOH activation to act as adsorbents. The GNFs were activated with KOH by changing the GNF/KOH weight ratio from 0 through 5 at 900°C. The effects of the GNF/KOH weight ratios on the pore structures were also addressed with scanning electron microscope and N$_2$ adsorption/desorption measurements. We found that the activated GNFs exhibited a gradual increase of CO$_2$ adsorption capacity at CK-3 and then decreased to CK-5, as determined by CO$_2$ adsorption isotherms. CK-3 had the narrowest micropore size distribution (0.6–0.78 nm) among the treated GNFs. Therefore, KOH activation was not only a significant method for developing a suitable pore-size distribution for gas adsorption, but also increased CO$_2$ adsorption capacity as well. The study indicated that the sample prepared with a weight ratio of 3 showed the best CO$_2$ adsorption capacity (70.8 mg/g) as determined by CO$_2$ adsorption isotherms at 298 K and 1 bar.

Key words: activated graphite nanofibers, KOH treatment, CO$_2$ adsorption

The rapid increase of the greenhouse gas carbon dioxide (CO$_2$) in the atmosphere is generally thought to be a major factor in climate change. These changes are increasingly viewed as a threat to both the global economy and the natural environment [1–4]. This increase in CO$_2$ is mainly attributed to human activities [5–10]. However, methane (bases: CH$_4$ 50%–70%, CO$_2$ 30%–40%) is one of reproducible biomass energy, which can obtain available energy sources, but also generate abundant greenhouse gas that goes against the purity of CH$_4$[10]. It is essential to find an ideal material to work out the austere problem. Usually, CO$_2$ capture and storage is an efficient green technology used to reduce emissions by transporting and storing CO$_2$ in deep geologic formations. The capture methods can be classified as post-combustion, pre-combustion, and air separation followed by oxyfuel combustion [7]. Among the currently available technologies, post-combustion is the most easily applied technology. It involves use of absorption, adsorption, cryogenic distillation, membranes, and gas hydrates.

Up to now, high-performance adsorbents have been widely used for CO$_2$ capture. Conventional solid adsorbents include zeolites [11], activated carbon [12], mesoporous silica [13], metal oxide-based adsorbents (e.g., MgO and CaO) [14], and metal-organic frameworks (MOFs) [15]. Nevertheless, in each case, there are defects in the adsorption process. Zeolites and mesoporous silica have the drawback of poor CO$_2$ capture performance. With zeolites, adsorption of moisture could affect the stability of the zeolite frameworks, and demands high regeneration temperature (~573 K). This results in huge energy consumption for CO$_2$ desorption. Meanwhile, although the adsorption capacity for CO$_2$ of activated carbon is high due to pore sizes ranging from micropores to macropores, its selectivity for gases is low. Metal oxide-based adsorbents in the form of dry chemical absorbents, exhibit very high energy consumption in the process of adsorption/desorption (~673 K), and high cost for...
activated carbon with extremely high surface area and narrow micropore distribution, along with a porous structure in which micropores are predominant.

In previous work, the effect of activation temperature was investigated, but the influence of the ratio of the carbon/activation agent, was not fully settled. Therefore, we investigated KOH-activation of carbon by chemical activation to enhance CO₂ adsorption capacity. KOH-activated GNFs were treated with KOH at GNFs/KOH weight ratios ranging from 0 to 5. The CO₂ adsorption capacity of GNFs was determined using CO₂ adsorption isotherms at 298 K and 1 bar.

The GNFs (straight type, length: 25–30 µm; Nanomirae Co., Ltd., Seoul, Korea) were activated with KOH at GNFs/KOH weight ratios ranging from 0 to 5, at 900°C. For ease of discussion, the GNF sorbent variants will be referred to as CK-1, CK-2, CK-3, CK-4, and CK-5. To prepare the KOH-activated GNFs, the impregnation process was initiated by mixing 1 g of GNFs with 0–5 g of KOH, in 10 g of water. The mixture was stirred for 4 h at 60°C and then dried for 24 h at 100°C. The treated carbon was placed into a quartz tube reactor, heated to 900°C at a rate of 5°C/min in flowing N₂ (200 mL/min), and kept at this temperature for 2 h before cooling to room temperature. Then the activated GNFs were obtained using 5 wt% HCl and hot distilled water. This solution was filtered and then dried at 100°C.

A scanning electron microscope (SEM; Hitachi S-4200 Ltd., Tokyo, Japan) was used to examine the pristine samples, and the morphological changes due to activation of the treated samples. Nitrogen sorption isotherms were determined to characterize the textural properties of the carbon materials at 77 K. The specific surface area and total pore volume were determined using the Brunauer-Emmett-Teller method based on adsorption determined with a surface area analyzer (BEL Corp., Toyonaka, Japan). The micropore and mesopore volume were calculated using the Horvath-Kawazoe and Barrett-Joyner-Halenda

Fig. 1. Scanning electron microscope images of the nanoporous graphite nanofibers (GNFs) as a function of GNF/KOH ratio.
KOH-activated porous GNFs adsorbents

occurrence of multilayer adsorption. This implies that both the treated and untreated GNFs have a broad pore-size distribution [23,24]. Comparing the pristine and treated GNFs, we conclude that KOH activation performed with GNF/KOH weight ratios from 1 to 5 contributes to the development of porosity.

The specific surface area, total pore volume, mesopore volume, micropore volume, and micropore fraction of the pristine and treated samples are summarized in Table 1. After KOH activation, the specific surface area, total pore volume, and micropore volume of GNFs increased for weight ratios from 1 to 4 but decreased for sample CK-5. Metallic potassium as a reaction product will become metal vapor above 760°C, and the vaporized potassium can be removed from inside the graphite layers, which also leads to the formation of micropores [25]. Our results show that KOH activation of GNFs has an important effect on the increase of micropore volume. Among all the samples, the largest specific surface area and micropore volume were observed for sample CK-4.

Fig. 3 represents the effect of carbon/agent ratio for pore size distributions of prepared activated carbons. Micropore size distributions and mesopore size distributions were calculated using the Horvath-Kawazoe method and Barrett-Joyner-Halenda method. These results show that they all possess a very narrow pore-size distribution, mainly concentrated in the range 1.4–2.0 nm. However, for all the activated GNFs, there is a broad peak with pore size 12.5–87.5 nm, which may be due to the collapse of the carbon framework at a high GNF/KOH ratio, resulting in the presence of large pores. Furthermore, as shown in Fig. 3b, it is interesting that the mesopore distribution of CK-4 is much broader than the others. This may be the reason for its CO₂ adsorption capacity being a little less than for CK-3, though CK-4 had the largest micropore volume. Based on the above discussion, the increase of the GNF/KOH ratio can promote the development of micropores [26-28].

In previous work with the carbon obtained after KOH activation, the activation mechanisms of different carbon sources, and effects of activation conditions, were investigated. In this study, the main activation mechanism of KOH-GNFs was

![Graph](image)

**Table 1. Pore structure parameters for the nanoporous GNFs from the N₂ adsorption isotherms as a function of the GNF/KOH ratio**

<table>
<thead>
<tr>
<th>Sample</th>
<th>(S_{BET})² (m²/g)</th>
<th>(V_{Micro}^b) (cm³/g)</th>
<th>(V_{Meso}^c) (cm³/g)</th>
<th>(V_{Total}^d) (cm³/g)</th>
<th>(F_{Micro}^e) (%)</th>
<th>(D_f^f) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GNFs</td>
<td>126</td>
<td>0.024</td>
<td>0.166</td>
<td>0.190</td>
<td>12.6</td>
<td>6.0</td>
</tr>
<tr>
<td>CK-1</td>
<td>446</td>
<td>0.114</td>
<td>0.368</td>
<td>0.482</td>
<td>23.7</td>
<td>4.3</td>
</tr>
<tr>
<td>CK-2</td>
<td>690</td>
<td>0.216</td>
<td>0.425</td>
<td>0.641</td>
<td>33.7</td>
<td>3.7</td>
</tr>
<tr>
<td>CK-3</td>
<td>919</td>
<td>0.226</td>
<td>0.831</td>
<td>1.057</td>
<td>21.4</td>
<td>4.6</td>
</tr>
<tr>
<td>CK-4</td>
<td>966</td>
<td>0.248</td>
<td>0.916</td>
<td>1.164</td>
<td>21.3</td>
<td>4.8</td>
</tr>
<tr>
<td>CK-5</td>
<td>760</td>
<td>0.179</td>
<td>1.158</td>
<td>1.337</td>
<td>13.4</td>
<td>7.0</td>
</tr>
</tbody>
</table>

²Specific surface area: Brunauer-Emmett-Teller equation (\(P/P_0 = 0.05-0.1\)).
³Micropore volume: Dubinin-Radushkevich equation.
⁴Mesopore volume: Barrett-Joyner-Halenda equations.
⁵Total pore volume: \(V_{Total} = V_{Total}^d \times 0.995\) × 0.001547.
⁶Fraction of micropore.
⁷Average pore diameter: \(2 \times \frac{S_{BET}}{V_{Total}}\).
have a better CO$_2$ adsorption capacity than the pristine GNFs. This shows that KOH activation increases the adsorption capacity of GNFs towards CO$_2$. According to the CO$_2$ adsorption isotherms, all the carbons showed high CO$_2$ adsorption capacity in the order CK-3 > CK-4 > CK-5 > CK-2 > CK-1 > GNFs, which can be attributed to their high surface area and narrow micropore size distribution. Because the surface provides the adsorption sites and the pore volume is the volume for trapping CO$_2$, the large number of adsorption sites and high trapping volume lead to high CO$_2$ adsorption [10]. Furthermore, sample CK-3 exhibited the best CO$_2$ adsorption capacity (70.8 mg/g). This result shows that the adsorption capacity of the treated GNFs was higher than the value reported by Jin et al. [30] (up to 52 mg/g using porous carbon nanotubes as a CO$_2$ adsorbent) under similar conditions.

The prepared graphite nano fibers activated with KOH at several different weight ratios (GNF/KOH) at 900°C were examined using SEM, N$_2$/77 K full isotherms, and CO$_2$ isothermal adsorption to characterize the morphology, textural properties, and CO$_2$ adsorption capacity, respectively. From the results, it was found that the GNF/KOH ratio had a major influence on the CO$_2$ adsorption capacity and textural properties of the GNFs. The KOH-activated GNFs were microporous and KOH activation increased their micro-porosity. The treated samples had improved CO$_2$ adsorption capacity (up to 70.8 mg/g) as compared to non-activated GNFs.

**Conflict of Interest**

No potential conflict of interest relevant to this article was reported.

**Acknowledgements**

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