# Chemical Treatment of Activated Carbon Fibers for Improvement of Hydrogen Storage Capacity

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**Abstract**

In order to investigate the relation with surface functional groups and hydrogen adsorption properties, the surface of activated carbon fibers were chemically treated with nitric acid, urea and heat treatment. This investigation has involved characteristics of porous structure and surface functional groups of chemically treated activated carbon fibers. And, the change of hydrogen adsorption capacity depended on functional groups and surface structure was studied. Pore texture of activated carbon fibers used in this study was investigated nitrogen adsorption method at 77 K. Using BET and H-K method, specific surface area and pore size distribution of non-treated and chemically treated activated carbon fibers were calculated. Surface functional groups were characterized Boehm method and X-ray photoelectron spectroscopy. Hydrogen adsorption of treated and non treated activated carbon fibers carried out using volumetric method. We calculated that adsorbent-adsorbate and adsorbate-absorbate interaction from hydrogen adsorption isotherm at 77 K by virial equation. And, the best fittable adsorption model was found to understand adsorption mechanism using non-linear curve fitting.
Keyword: Gas storage, Activated carbon, Chemical modified carbons.

## Introduction

Hydrogen is a possible alternative for fossil fuels. To use hydrogen energy to various applications, development of hydrogen storage technology is an indispensable. Many kind of storage method of hydrogen can meet DOE's target because of their scientific, technological and economical problems. The U.S. DOE announced more than 6.5wt% of hydrogen storage capacity is required for automobile. Some believe that these problems might be solved by adsorption on adsorbent. Activated carbon fibers (ACF) have more developed micropore structure than granular/powder activated carbons. The advantages of ACF for gas adsorption are smaller fiber diameter which can reduce diffusion rate and rapid adsorption and desorption than granular/powder activated carbons. Moreover, ACF can be formed in various forms of cloth, felt, etc. therefore activated carbon fibers are more suitable gas storage materials than granular/powder activated carbons. In general, gas adsorption capacity on porous carbon materials depends on surface area and pore structures of adsorbents. Also, surface carbon – gas molecules interaction have influence to gas adsorption capacity. Surface modification is able to change this interaction. In this research, modification with nitric acid was carried out onto activated carbon fibers and the changes of surface properties and pore structure before and after chemical treatment were characterized. And then, we calculated that interaction of adsorbent-adsorbate and adsorbate-adsorbate using virial equation obtained from hydrogen adsorption isotherms of activated carbon fibers at liquid nitrogen temperature.

## Experimentals

### *Materials*

Commercially available pitch based activated carbon fibers were used in this study. These carbon materials were purchased by Osaka gas Co. in Japan. To removal impurities of surface, activated carbon fibers were washed with pure water and dried at 383 K overnight. The as-received activated carbon fibers named R-A10.

***Treatment procedures***

Activated carbon fibers were chemically treated by oxidation using nitric acid to introduce oxygen functional groups on the surface of carbon fibers. 2 g as-received activated carbon fibers and 200 ml nitric acid (1 M) were introduced into round-bottom flask and heated to 373 K with heating mantle for 1 h. After acid treatment, activated carbon fibers were washed by distillated water and dried in oven at 383 K for 24 h and stored in a desicator for later use. acid treated activated carbon fibers named N-A10.

***Characteristics of Pore texture***

The nitrogen adsorption isotherms of activated carbon fibers were measured on ASAP 2020 (Micromeritics Ins. Corp.) at liquid nitrogen temperature. All samples were degassed at 423 K for 3 h before analysis. The specific surface area and pore structure were obtained Langmuir equation and Horvath-Kawazoe method.

***Hydrogen adsorption***

Hydrogen adsorption isotherms were obtained from volumetric method using ASAP 2020 (Micromeritics Ins. Corp.) at 77 K. All samples were out-gased at 473 K for 6 h and hydrogen adsorption was performed at 77 K in pressure range of 0.01~120 kPa. Using virial coefficients obtained from hydrogen adsorption isotherms, interactions between surface carbon and hydrogen molecules were calculated, respectively.

## Results and discussion

***Pore texture characteristics***

Fig. 1 shows that nitrogen adsorption isotherms at 77 K. Both of isotherms of R-A10 and N-A10 represent Langmuir type. Both isotherms of R-A10 and N-A10 are Type I (Langmuir type) in IUPAC classification. In the case of physical adsorption, Langmuir isotherm was indicated that the pores are microporous. In acid treatment, the pore structures were not nearly changed, in spite of the amounts of adsorption were decreased. The pore textures of activated carbon fibers used in this study are listed in Table 2. The specific surface area obtained by Langmuir equation and micropore volume calculated by H-K method, were decreased with nitric acid modification.

**Table 1**. Pore texture parameters of activated caebon fibers.

| Samples | [a]$S_{Langmuir}$ | [b]$V_{total}$ | [c]$V_{micropore}$ | [d]$W_p$ |
|---|---|---|---|---|
| R-A10 | 1231 | 0.437 | 0.432 | 0.578 |
| N-A10 | 1040 | 0.368 | 0.361 | 0.562 |

a: Langmuir specific surface area
b: Total pore volume at $P/P_o$=0.98
c: Micropore volume by H-K method
d: Median pore width by H-K method

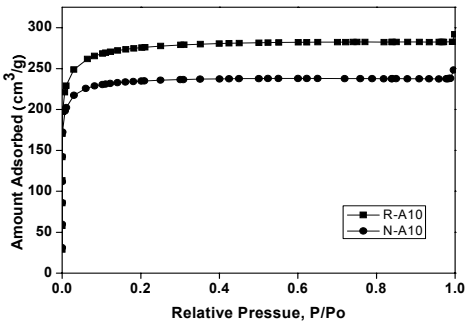


**Figure 1**. Nitrogen adsorption isotherms of activated carbon fibers used in this study.

***Hydrogen adsorption***

Fig. 2 shows the hydrogen adsorption isotherms of R-A10 and N-A10 at 77 K over the hydrogen pressure range 0-120 kPa. The amount of hydrogen adsorbed on N-ACF, 1.37wt% at 120 kPa, was smaller than the amount of as-received. The amount of hydrogen adsorbed on N-ACFs was 1.56wt%.

The Langmuir isotherms can be expressed in the following form:

$$p/n = 1/n_m b + p/n_m \quad (1)$$

where $p$ is the pressure, $n$ is the amount of adsorption, nm is the monolayer capacity and $b$ is the coefficient af adsorption specific to the adsorbate/adsorbent system. Monolayer capacities of hydrogen adsorption on activated carbon fibers are listed in Table 2. $H_2(n_m)$ of R-A10 and N-A10 are 8.89 mmol/g and 7.80 mmol/g, respectively.

The interactions of adsorbate-adsorbent and adsorbate-adsorbate are changed with surface modification. In order to determine on hydrogen molecules and carbon surface interaction and both hydrogen molecules interaction, virial equation was used in this study. The virial equation can be expressed in this form:

$$ln(n/p) = A_0 + A_1 n + A_2 n^2 + \ldots \quad (2)$$

where $n$ is the adsorption amount at pressure $p$ and $A_0$, $A_1$ and $A_2$ are virial coefficients. The first virial coefficient is related Henry's law constant. Henry's law constant, $K_0$ is followed as[5];

$$K_0 = exp(A_0) \quad (3)$$

Henry's law constant is dependent on the interaction between adsorbed molecules and surface of adsorbent. The second virial coefficient $A_1$ is the function of interaction between pairs of adsorbate molecules. Fig. 3 shows virial graphs of R-A10 and N-A10. The first virial constants of R-A10 and N-A10 calculated by virial graphs are -13.151 and -13.249, respectively. This results suggest that the interaction of adsorbate-adsorbent decreased with acid treatment. The drop of amount of hydrogen adsorbed on N-A10 is resulted from the decrease of the interaction of adsorbate-adsorbent.

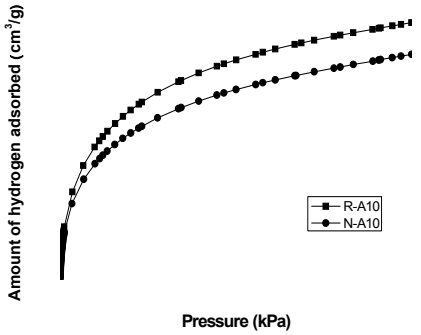


Figure 2. Hydrogen adsorption isotherms of activated carbon fibers used in this study.

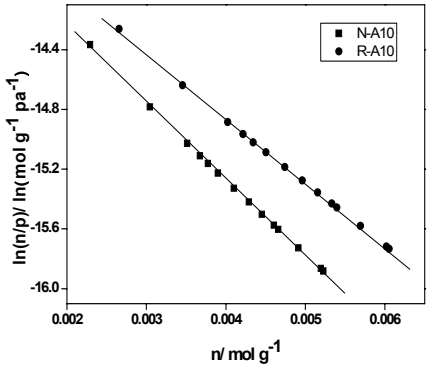


**Figure 3**. Virial graphs for the adsorption of hydrogen on activated carbon fibers at 77 K.

## Conclusion

In order to investigate hydrogen adsorption on activated carbon fibers and chemically treated activated carbon fibers, the surface of activated carbon fibers modified with 1 M nitric acid for 1 h. After chemical treatment, specific surface area and porevolume were decreased. Monolayer capacities of hydrogen adsorption on R-A10 and N-A10 are 8.89 mmol/g and 7.80 mmol/g, respectively. Using virial equation, the interaction of adsorbate-adsorbent was measured. The first virial constants of R-A10 and N-A10 calculated by virial graphs are -13.151 and -13.249, respectively The drop of amount of hydrogen adsorbed on N-A10 is resulted from the decrease of the interaction of adsorbate-adsorbent.

## Acknowledgment

This research was performed for the hydrogen Energy R & D Center, one of the 21st Century Frontier R & D program, funded by the Ministry of Science and Technology of Korea.

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