Influence of Plasma Treatment on Hydrogen Chloride Removal of Activated Carbon Fibers

Soo-Jin Park♠, Byung-Joo Kim and Seung-Kon Ryu*

Advanced Materials Division, Korea Research Institute of Chemical Technology, P.O. Box 107, Yusong, Daejeon 305-600, Korea
*Dept. of Chemical Engineering, Chungnam National University, Daejeon 305-764, Korea
♠e-mail: *psjin@krict.re.kr*

Abstract

The atmospheric pressure plasma treatments (Ar/O_2 and Ar/N_2) of activated carbon fibers (ACFs) were carried out to introduce hydrophilic functional groups on carbon surfaces in order to enhance the hydrogen chloride gas (HCl) adsorption. Surface properties of the ACFs were determined by XPS and SEM. N_2/77 K adsorption isotherms were investigated by BET and D-R (Dubinin-Radushkevich) plot methods. The HCl removal efficiency was confirmed by HCl detecting tubes (range: 1~40 or 40~1000 ppm). As experimental results, it was found that all plasma-treated ACFs showed the decrease in the pore volume, but the HCl removal efficiency showed higher level than that of the untreated ACFs. This result indicated that the plasma treatments led to the conformation of hydrophilic functional groups on the carbon surfaces, resulting in the increase of the interaction between the ACFs and HCl gas.

Keywords : *Activated carbon fibers, Plasma treatment, Hydrophilic functional groups, Hydrogen chloride*

1. Introduction

Activated carbon fibers (ACFs) are excellent adsorbents and thus are widely used for the removal of organic pollutants from wastewater and for gas purification due to its large specific surface area and porosity [1-3].

The adsorption process, usually based on ACFs, is a surface phenomenon in which adsorbate molecules are accumulated on the pores of ACFs. These adsorption properties of ACFs are essentially attributed to their pore structures, large specific surface area, internal surface accessibility, and potential level [2-5].

It is well known that the adsorption properties of ACFs are also significantly affected by the presence of surface functional groups, such as oxygen, nitrogen, chlorine, combined sulfur, and other elements. These surface functional groups usually show hydrophilic in nature. It is normally accepted that hydrophilic surfaces can easily adsorb hydrophilic adsorbate than hydrophobic one. In detail, the hydrophilic surface functional groups can be distinguished by acid or base nature based on its conformation. It is generally accepted that oxygen-containing groups (-OH and -COOH) show the acidic nature, and large nitrogen-containing groups ($-NH_3$, $-NH_2$, and $=NH$) show the basic nature. Basic adsorbent has strong interaction with acidic adsorbate due to the Lewis acid-base interaction [3].

It has been well known that the hydrophilic gases, such as HCl, SO_x and NO_x, are major components of air pollution. Most of all, HCl gas has the strong acidic nature and the highest risk of being exposed to human body [1-2, 6-7].

In this work, the atmospheric pressure plasma treatments with various gases were used for the surface modification to control surface hydrophilicity of the ACFs, resulting in the improvement of the HCl adsorption. Surface characteristics and their relationships with HCl removal of the ACFs were also studied.

2. Experimental

2.1. Materials and sample preparation

The starting materials were commercial ACFs, AW2001 (weight of 45 g/m^2 and specific surface area of 2121 m^2/g), manufactured by Taiwan Carbon Co. that previously were demineralized by distilled water. The plasma treatment of the ACFs was carried out under atmospheric pressure with various gases (Ar/O_2 and Ar/N_2). The radiofrequency-generated plasma was operated at 300 W and 13.56 MHz, respectively [9]. The flow rate of the mixed gas was 5 l/min, and the plasma treatment time and the distance between electrodes were 30 sec and 7 mm, respectively. The source gases for plasma treatment were Ar/O_2 and Ar/N_2 (Ar:O_2 or N_2=100:1), namely, as-received, P-O_2, and P-N_2.

2.2. Surface properties

The surfaces composition and detailed surface functionalities

of the ACFs before and after atmospheric pressure plasma treatment were investigated using a VG Scientific LAB MK-II X-ray photoelectron spectrometer (XPS). The spectra were collected using a MgKα X-ray source (1253.6 eV). The pressure inside the chamber was held below 5×10^{-8} torr during analyzing. Both survey XPS spectra were recorded at a 45° take-off angle. The C_{1s} electron binding energy was referenced at 286.4 eV, and the curve-fitting procedure was carried out by using a nonlinear least square curve-fitting program with a Gaussian-Lorentzian production function [10].

2.3. Textural properties

Nitrogen adsorption isotherms at 77 K were measured using ASAP 2010 (Micromeritics). Prior to each analysis, the samples were degassed at 573 K for 9 hours to obtain a residual pressure of less than 10^{-5} torr. The amount of nitrogen adsorbed on the atmospheric pressure plasma-treated ACFs was used to calculate specific surface area by means of the BET equation [11]. Total pore volume was estimated to be the liquid volume of nitrogen at a relative pressure of about 0.995 [12-13]. Micropore volume was calculated using the Dubinin-Radushkevich (D-R) equation [13]. In addition, a scanning electron microscope (SEM, JEOL JSM 840A) was used to investigate the surface morphologies of the ACFs studied.

2.4. Hydrogen chloride removal

For the present experiment, two types of experimental technique were used for the detection of HCl removal behaviors. In case of low HCl concentration around 0~40 ppm at the outlet of reactor, a gas detecting tube (GASTEC: No. 14 L, range: 1~40 ppm) was used to measure HCl removal efficiency. All samples and the reactor were purged using N_2 gas (99.9999%) of high purity at 295~298 K for 1 hours to remove residual moisture. About 0.1 g of the sample was packed with the cylindrical quartz tube and then HCl gas (concentration 1013 ppm) was injected. Gas flow rate was maintained at 10 ml/min by a mass flow controller (GMC 1000, MKS). HCl removal efficiency was determined from the concentration of HCl at the outlet reactor. Prior to each analysis, HCl adsorption curve was gained by using the 300, 600, and 1000 ppm HCl standard gas.

3. Results and Discussion

3.1. Surface properties

The surface atomic compositions obtained by XPS analysis are given in Table 1. It can be seen that the ACFs mainly consists of carbon, oxygen, and nitrogen. The carbon and oxygen content of the as-received sample are 90.4 and 7.8 at%, respectively. In case of P-O_2, the carbon content is some decreased (83.5 at%), but oxygen content in the ACFs

Table 1. Chemical Composition of the ACFs before (as-received) and after (P-O_2 and P-N_2) Plasma Treatments

	C_{1s} (at.%)	O_{1s} (at.%)	N_{1s} (at.%)	O_{1s}/C_{1s}	N_{1s}/C_{1s}
As-received	90.4	7.8	1.7	0.086	0.019
P-O_2	83.5	14.8	1.6	0.177	0.019
P-N_2	87.9	9.1	2.9	0.116	0.027

is significantly increased (14.8 at%). It is assuming that Ar plasma reacts with edged carbon or hydrogen atoms and conforms some active sites on carbon surfaces, and then oxygen molecules from source gases are reacted with these sites in the plasma chamber. In cases of P-N_2, the oxygen content are slightly increased from 7.8 to 9.1 at%, and then the nitrogen content are changed from 1.7 to 2.9 at% after plasma treatment. These results indicate that mixed gases plasma treatments are an efficient method to produce target functional groups due to the direct reaction of source gases with active sites by plasma treatments [14-15].

For the detailed studies of surface functional groups after plasma treatments, subpeaks of C_{1s} are studied. Fig. 1 shows the relative ratios of each component in C_{1s} subpeaks of XPS spectra before (as-received) and after (P-O_2 and P-N_2) plasma treatments. The C_{1s} subpeaks for the plasma-treated ACFs reveal the presence of seven peaks corresponding to O-C=O (a: B.E.=289.0), C=O or C-N (a: B.E.=288.1), C-O (a: B.E.=286.5), C-N (a: B.E.=285.7), C=C (a: B.E.=285.0), C-C (or C-H) (a: B.E.=284.7), and C_6H_5OH (a: B.E.=284.4) [10]. In case of the P-O_2 sample, C_6H_5OH and O-C=O peaks are largely increased. However C-C or C-H peak is predominantly diminished after the treatment. This result indicates that the reaction of Ar/O_2 plasma leads to the destruction of C-C and edged C-H groups on carbon surfaces and then develops new oxygen-containing functional groups. It is also found that the C-N peak of P-N_2 sample is
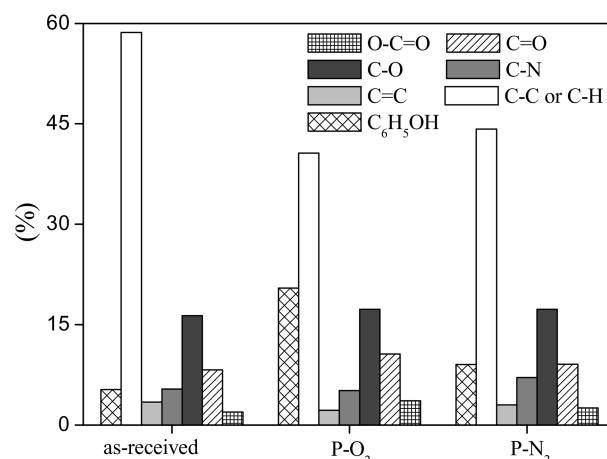

Fig. 1. Specific ratios of the areas of carbon sub-peaks in C_{1s} XPS spectra.

As-received

P-O$_2$

P-N$_2$
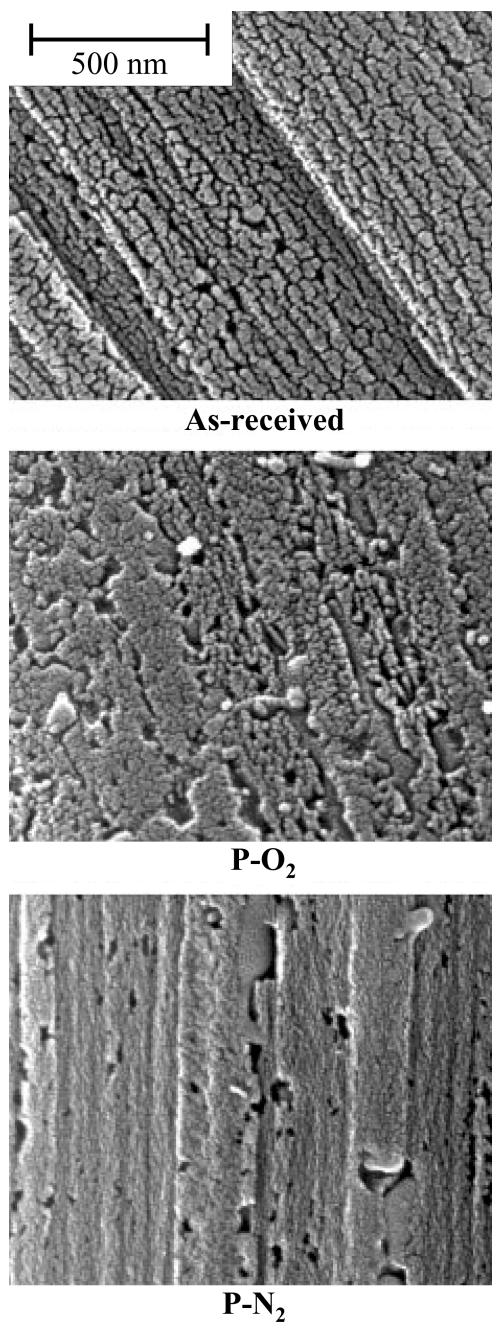
Fig. 2. SEM photographs of the the ACFs before (as-received) and after (P-O$_2$ and P-N$_2$) plasma treatments.

principally increased after Ar/N$_2$ plasma. This result indicates that the increase of C-N peak is attributed to the nitrogen radical reaction with carbon surface in the plasma chamber.

According to the reports [3], carbon surfaces manufactured at high temperature have basic natures, so it can react with acidic gas more actively. In Fig. 1, the decrease rate of C-C or C-H peak is P-O$_2$ > P-N$_2$. Ar gas is non-active gas, and O$_2$ and N$_2$ can be active gases when it conforms radicals. The
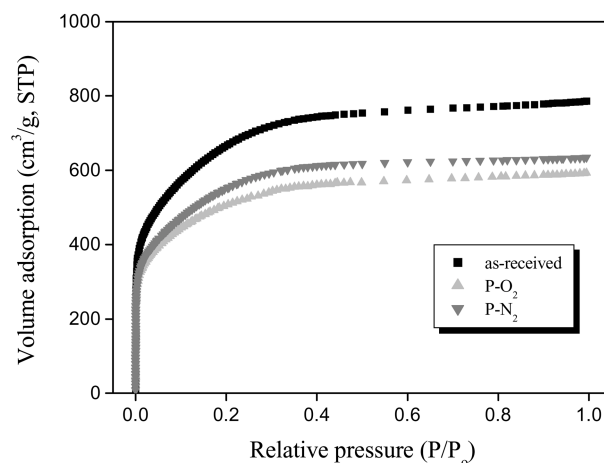
Fig. 3. Adsorption isotherms of N$_2$ at 77 K on the ACFs before (as-received) and after (P-O$_2$ and P-N$_2$) plasma treatments.

conformation of oxygen radical during Ar/O$_2$ plasma can role as an acidic factor, when nitrogen radical shows a basic factor during Ar/N$_2$ plasma. As results, Ar/O$_2$ plasma can destruct carbon surface more largely than Ar/N$_2$ plasma because the destruction by Lewis acid-base reaction can appear more actively due to the basic carbon surfaces.

To study the changes of surface morphologies as-received, P-O$_2$, and P-N$_2$, SEM images are used in the high resolution of $\times 50000$ as shown in Figure 2. It is observed that many macropores appear after the plasma treatment by the destruction of the carbon surfaces, and it can lead the decrease of the specific surface area and total pore volume.
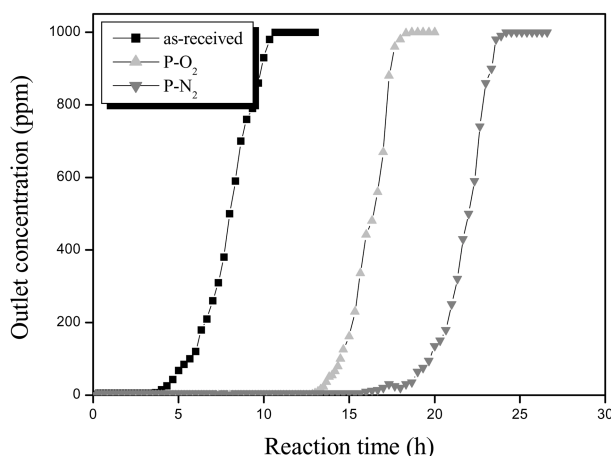
3.2. Textural properties

An understanding of the porosity and specific surface area of an adsorbent can be achieved by the construction of an adsorption isotherm of N$_2$. The adsorption isotherm of the adsorbent is measured in the range 10^{-6}-10^0 torr at 77 K.

Figure 3 shows the N$_2$ isotherm curves for the untreated and the plasma-treated ACFs, and textural properties from the BET equation and D-R plot are listed in Table 2. Their shapes, as seen in Figure 3, indicate that the pore structure are approximately Type I according to the IUPAC classification. It is evident that most of pore volume of samples is filled below the relative pressure (P/P$_0$) about of 0.1,

Table 2. Textural Properties of Plasma-treated ACFs before (as-received) and after (P-O$_2$ and P-N$_2$) Plasma Treatments

	Specific surface area (m^2/g)	Micropore volume (cm^3/g)	Mesopore volume (cm^3/g)	Total pore volume (cm^3/g)
As-received	2121	0.82	0.39	1.22
P-O$_2$	1615	0.64	0.25	0.89
P-N$_2$	1658	0.66	0.27	0.93

Fig. 4. Breakthrough curves of the as-received and plasma-treated ACFs for HCl removal (Input HCl concentration = 1013 ppm, feeding rate = 10 ml/min, and temperature = 25 ^{o}C).

indicating that these samples are highly microporous. After a sharp increase up to the relative pressure of 0.1, the isotherm curves show very small increases in the further adsorption [16].

The detailed information of the textural properties of the samples was listed in Table 2. The specific surface area and total pore volume are slightly decreased with each plasma treatment, and It is found that the decrease in the specific surface area is appeared at P-O_2 in large due to the acid-base reaction, matched with Figure 1.

3.3. Hydrogen chloride removal

Figure 4 shows the HCl removal results of the as-received, P-O_2, and P-N_2. As seen in Figure 4, the removal efficiency of P-O_2 and P-N_2 are strongly increased [17] compared with that of the as-received sample. It is indicated that the atmospheric pressure plasma with O_2 and N_2 gases increases the hydrophilicity of ACFs studied, resulting in the increase of hydrophilic HCl gas removal.

It is also found that the removal efficiency of P-N_2 has higher level than that of P-O_2 by *ca.* 20%. As seen in Figure 3 and Table 2, the differences of textural properties including specific surface area and total pore volume of P-N_2 are negligible compared to P-O_2. There are no significant difference in the textural properties between P-O_2 and P-N_2. This result means that some factors largely influence on the HCl removal efficiency than the textural properties. In Figure 1 and Table 1, acid and base nature of oxygen and nitrogen containing groups are investigated. It is reasonable that the surfaces of P-N_2 have basic nature due to the Ar/N_2 plasma treatment resulting in large nitrogen-containing functional groups, such as NH_4, -NH_2, and =NH. This basic nature of P-N_2 can lead the increase of the removal efficiency of acidic gas, such as HCl. It is concluded that the plasma treatment with active gases like O_2 and N_2 leads to the increase of HCl

removal efficiency. This result shows that the HCl removal system on the ACFs is predominantly ruled by acid-base interactions even though the difference in textural properties of the ACFs is negligible.

4. Conclusions

The atmospheric pressure plasma treatment with various gases on ACFs was carried out to enhance the surface functionality of the ACFs. It was found that the oxygen and nitrogen contents on the ACFs were increased in P-O_2 and P-N_2, respectively. However, the decrease of specific surface area was also shown. HCl removal efficiency of the modified ACFs showed higher than that of as-received sample, and the removal efficiency of P-N_2 showed higher value than that of P-O_2 even though the textural properties of the two were not significantly different. It meant that the acid-base interaction between newly conformed large nitrogen containing functional groups of P-N_2 and acidic HCl gas was a decisive factor in this system.

Acknowledgment

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