REMOVAL OF FORMALDEHYDE WITH ACTIVATED CARBON NANOFIBER DELIVERED FROM ELECTROSPUN PAN-CF

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The adsorption behavior of formaldehyde has been examined using PAN based activated carbon nanofibers (PACNF). PACNF was prepared through the processes of oxidation stabilization and successive steam activation of electrospun polyacrylonitrile nanofiber (Diameter: avg.800nm, Nanotechnics, South Korea). Among simple heat treated PAN nanofibers in the temperature range of 500~800^{o}C, PAN carbon nanofiber heat treated at 600^{o}C for 1h showed the largest adsorption of formaldehyde. The steam activation of PAN nanofiber can further enhance the adsorption capability around twice compared to that of simple heat treated PAN nanofiber. Optimization and detailed analyses of produced activated carbon nanofibers are now in proceeding. The formaldehyde adsorption behavior onto the PACNF is conducted by dry based method with relative low concentration (20 ppm). The coexistence of nitrogen and oxygen functional groups is considered to play an important role for improving adsorption capability of formaldehyde. The PACNF activated at 600℃, which has the most abundant nitrogen functional groups, has the largest breakthrough time.

Introduction

Carbon materials have been used in powerful adsorbent for diverse toxic and harmful compounds to human body such as nitrogen oxide, formaldehyde, benzene [Quinlivan P A et al., Predicting adsorption isotherms for Environ Sci Technol. 2005, Lillo-Rodenas MA et al., Carbon 2006]. Among the carbonaceous adsorbents, activated carbon fiber (ACF) is considered to be one of the promising adsorbent due to their homogeneous and abundant micropores and large surface areas [Mangun CL et al. Chem Mater 2001].

Carbonyl chemicals, such as formaldehyde, acetaldehyde, and propionaldehyde, are listed in air toxics at the Clean Air Act Amendments of 1990 [USEPA 1991]. Formaldehyde which is the most abundant airborne carbonyl chemical has been classified as carcinogenic to humans in June 2004 based on sufficient evidence from epidemiological studies [Cogliano VJ et al., Environmental Health Perspective. 2005]. Moreover, the carbonyl chemicals can be a main cause of recent increased childhood asthma and atopic hypersensitivity, as well as the series of symptoms such as headache, nausea, coryza, pharyngitis, emphysema, lung cancer, and even death [Rong HQ et al., Carbon 2002]. In addition, the pollution of indoor air by formaldehyde steadily increased, because interior decoration which is main cause of formaldehyde such as paint, polymer binder of furniture and artificial fibers increased. Therefore, it is required to develop effective method for formaldehyde removal.

It is well known that adsorption behavior of adsorbent is strongly affected by the surface chemistry, surface area and porosity of adsorbent [Rong HQ et al., J Coll Interf Sci 2003]. The adsorption capability can be improved by controlling the pore structure and surface functionality of activated carbon. Especially, the substitution of adsorbent with some hetero-atoms can significantly enhance such performances for the polar organic molecules. The present authors already reported the homogeneous small micropore and nitrogen based surface functionality could improve the formaldehyde adsorption from comparing the adsorption behaviors of pitch-based ACFs (OG series, Osaka Gas, Japan, Containing non-nitrogen functional groups), and PAN-based ACFs (FE series, Toho TENAX, Japan, Containing 2-5 wt% of nitrogen functional groups) [Yan Song et al., Proceedings of International Symposium on Carbon, England, Aberdeen, 2006].

In this study, the present author developed novel activated carbon nanofiber which contains over 10wt% of nitrogen functional groups through the mild steam activation of PAN electrospun nanofiber (PCNF). The formaldehyde adsorption behaviors were studied using novel PAN based activated carbon nanofiber (PACNF).

Experimental

PAN electrospun nanofiber (PCNF) was supplied from Nanotechnics, and used as a precursor for carbonized or activated carbon nanofiber without further treatment. PCNF was stabilized at 270℃ for 30 min under the air stream and successively carbonized at 600~800℃ or activated at 500~700℃ for certain time under inert or 90% of steam and nitrogen mixture atmospheres, respectively.

A fixed-bed unit with a column of 40 mm in length and 8 mm in diameter was constructed and 0.1 g of ACFs was loaded to obtain the equilibrium data of adsorption at 30 ^{o}C. The 20 ppm formaldehyde-containing standard gas diluted by pure nitrogen (Asahi Gas Co., Japan) was fed to system with the flow rate of 100 ml/min. The outlet concentration of formaldehyde was detected by Model 4160 formaldehyde analysis instrument (JMS Company, U.S.A.). The breakthrough time is defined as the time at which the output concentration (C) reaches 1 % of the inlet concentration (C_0) [22]. The adsorption amount of formaldehyde is calculated according to the following equation (equation [1]):

$$W=P\times V/(R\times T)/m, \qquad [1]$$

where W is the adsorbed amount of formaldehyde per unit gram of ACF, P is atmospheric pressure (1 atm), V is volume of adsorbed formaldehyde calculated from the integrated area over breakthrough curve$\times 10^{-6}\times 0.1$ L/min, R is universal gas constant (0.08204 atm $\times$ mol^{-1} $\times$ K^{-1}), and T is room temperature (298.15 K).

Nitrogen adsorption/desorption isotherms of PCNF and PACNF were measured at 77 K using Belsorp (Nippon-bell, Japan). Samples were out-gassed at 200 ^{o}C in vacuum ($p<10^{-8}$ bar). The surface area was calculated by the Non-localized density function (NLDFT) method.

Element analysis of carbon, hydrogen, nitrogen and oxygen (by difference) of PCNF, stabilized PCNF and PACNF was carried out using Perkin-Elmer CHN Elemental Analyzer, Model 2400. Morphologies of PCNF, stabilized PCNF and PACNF were observed with HR-SEM (JSM-6700F, Jeol, Japan).

Results and Discussion

Some physical properties and morphology of PACNF

Table 1 summarized the results of BET and elemental analysis of FE100 (PAN based activated carbon fiber) and PACNF. PACNF showed the 18wt % of nitrogen contents even after the steam activation. The atomic ratio of N/O is 3 times larger than FE100.

Figure 1 showed Nitrogen adsorption and desorption isotherms and pore sized distribution of PACNF. PANCF showed very homogeneous micropores less than 0.8 nm with the surface area of 348 m^2/g.

Figure 2 showed SEM images of as-received PCNF, stabilized PCNF and PACNF. Scale-like layers were observed in as-received PCNF which should be assumed to be covered layers of PAN polymer in the quenching process. Such scale-like layers were removed through the stabilization process. The resultant PACNF has very lamella surface with average diameter of 800 nm.

Table 1. BET and elemental analysis of FE100 and PACNF

Sample	BET (m^2/g)	Elemental analysis (wt %) C	H	N	O	ash	N/O
FE100	450	70.9	2.0	8.4	17.3	1.4	0.56
600^{o}C90%	348	68.1	1.2	18.0	11.4	1.3	1.80

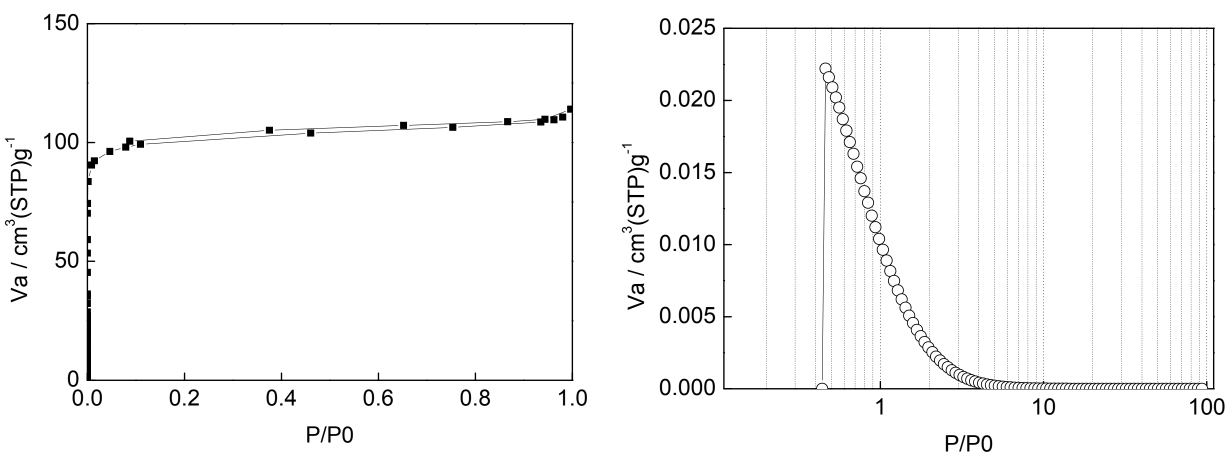

Figure 1. BET isotherms and pore sized distribution of PACNF.

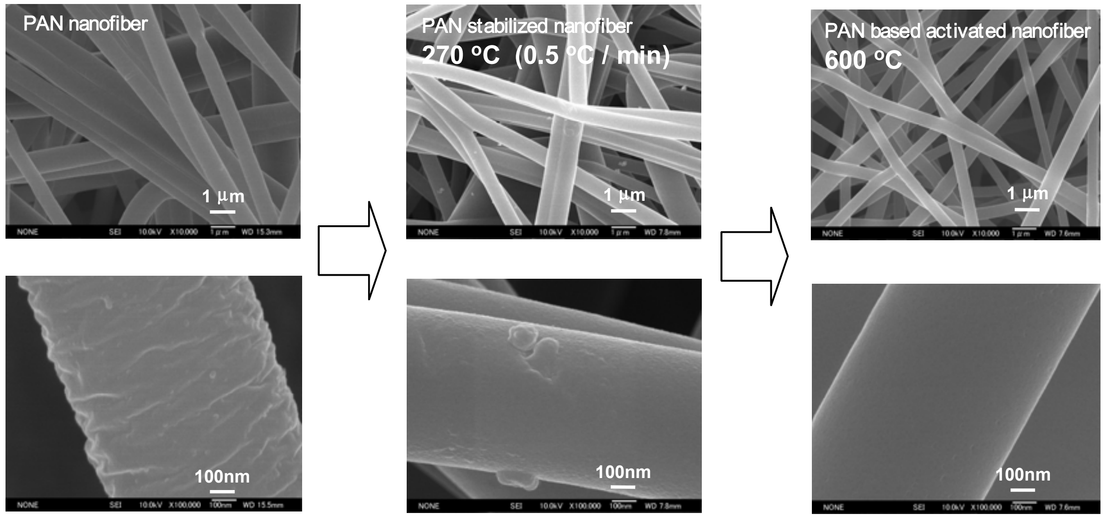

Figure 2. SEM images of PCNF, stabilized PCNF and PACNF.

Formaldehyde adsorption behaviors of carbonized PCNF and PACNF

Figure 3 represents the formaldehyde adsorption behaviors of the stabilized and carbonized PAN nanofibers. The stabilized PCNF did not show formaldehyde adsorption and the carbonized PCNFs had relatively large breakthrough times, implying that large amounts of formaldehyde could be adsorbed on carbonized PCNFs. In addition, the carbonized PCNF at 600℃ showed the largest adsorption capacity of formaldehyde. From such a fact, the carbonized PCNFs have some microporosity through the mild carbonization less than 800℃ and adequate carbonization temperature of 600℃ can make the maximum microporosity only by simple heat treatment. Detailed analyses of the carbonized PCNFs are now in proceeding.

Figure 4 illustrates the formaldehyde adsorption behavior of PACNFs. PACNF activated at 600℃ has the largest formaldehyde adsorption capacity, which means that the mild activation condition is better for making homogeneous micropore and remaining more nitrogen contents. The detailed examination of the relationship between the nitrogen contents and adsorption capacity of PACNFs are proceeding

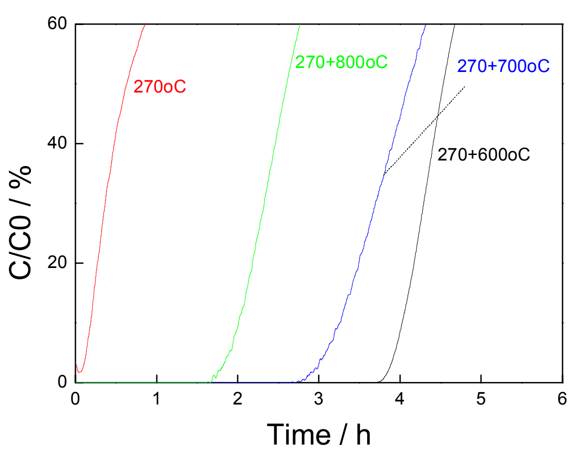

Figure 3. The formaldehyde adsorption behaviors of the stabilized PCNF and carbonized PCNFs

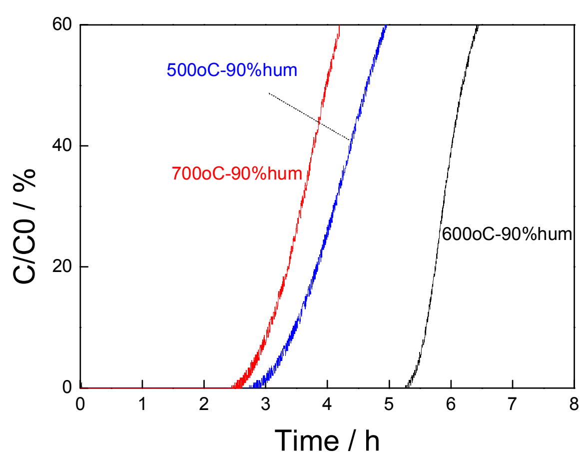

Figure 4. The formaldehyde adsorption behaviors of PACNFs.

Conclusion

Formaldehyde adsorption behavior of PAN electrospun nanofiber derived carbonized and activated nanofibers were investigated at relatively low concentration (20 ppm) under dry based environment. Homogenous microporosity and enormous amounts of nitrogen based functional groups of PACNF are important factors for the adsorption performance of formaldehyde. Among the various activation conditions, the mild activation at 600℃ can afford the best adsorption capacity of formaldehyde because the mild activation can remain more abundant nitrogen-containing groups such as pyrrolic or pyridonic nitrogen, pyridinic nitrogen and quaternary nitrogen-containing groups. Based on the micro-ATR FTIR analysis of PACNFs, it is now in proceeding to examine the role of special nitrogen functional groups such as pyridinic N oxide and oxadiazole to contribute to the adsorption enhancement of formaldehyde.

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