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Nitrogen Adsorption on Fluorinated Activated Carbon Fiber

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Abstract. Nitrogen adsorption isotherms for fluorinated activated carbon fiber (F-ACF) and fluorinated carbon black (F-CB) were measured at 77 K. Surface structures of F-ACF and F-CB were examined by α_s-plot analysis using the adsorption data on the nonporous carbon black (CB) and F-CB. The surface energy of F-ACF was lower than that of ACF. The micropore structure of ACF was preserved even after fluorination, although the limiting adsorption amount and the micropore width decreased with fluorination.

Keywords: micropore analysis, nitrogen adsorption, activated carbon fiber surface fluorination

Introduction

Nitrogen adsorption on activated carbons at 77 K has been actively studied in order to elucidate the micropore filling mechanism on graphitic slit pores (Carrott, et al., 1987; McEnaney, 1988; Kaneko and Ishii, 1992). Recently, molecular simulation studies clearly showed the importance of the enhanced molecule-surface interaction and the intermolecular interaction in micropore filling (Nicholson and Parsonage, 1982; Seaton et al., 1989; Lastoskie et al., 1993). As a nitrogen molecule interacts strongly with the graphitic surface due to the large quadrupole moment of nitrogen, we have a fundamental question as to how nitrogen molecules are adsorbed on micropores with low energy surfaces. A fluorinated surface is a representative low energy surface (Dormant and Adamson, 1968), and also it is well-known that activated carbon fibers (ACFs) have considerable homogeneous slit-shaped micropores (Kaneko et al., 1992; Setoyama et al., 1993; Suzuki and Kaneko, 1993), consisting of micrographitic units (crystalite of graphite). Touhara et al. (1985) fluorinated the ACF (F-ACF) and showed that the F-ACF has some characteristic electrochemical properties. Li et al. (1995) reported that F-ACF shows a perfect hydrophobicity. In this article, nitrogen adsorption by the low energy micropore at 77 K and the micropore structure of F-ACF are described.

Experimental

Cellulose-based ACF (Toyobo KF1500) and ungraphitized carbon black (CB; Mitsubishi-Kasei carbon black) were fluorinated. The gaseous fluorine at 760 mmHg was introduced into a reaction cell after the evacuation at 383 K for 2 days. The fluorination was continued during 24 hrs at 373 K for ACF and during 100 hrs at 303 K for CB. The extent of fluorination was determined from the weight change by use of gravimetric measurement; the compositions of F-ACF and the fluorinated carbon black (F-CB) were $C_{1.4}F$ and $C_{7.7}F$, respectively.

Adsorption isotherms of nitrogen at 77 K were determined by use of a computer-aided gravimetric adsorption apparatus (Kakei et al., 1990). The samples were evacuated for 2 hrs in a high vacuum at 383 K prior to the adsorption measurement.

Results and Discussion

Effect of Surface Fluorination

The adsorption isotherm of nitrogen on F-CB is shown in Fig. 1(a). It is typical type II by the IUPAC classification (Sing et al., 1985), suggesting the nonporosity of F-CB. The specific surface area of F-CB from the BET analysis was 66.6 m^2/g and the c value was 132. The surface area of F-CB was slightly smaller than that of CB (69 m^2/g).

The α_s-plot of F-CB using reference data of CB is shown in Fig. 1(b) (Kaneko et al., 1992). Although the α_s-plot has a good linearity above $\alpha_s = 0.6$, a downward deviation from the linearity is clearly observed below $\alpha_s = 0.6$. The completion of the nitrogen monolayer finishes at $\alpha_s = 0.6$, in the case of CB deduced from the BET analysis. The observed downward deviation of the α_s-plot of F-CB should be ascribed to the fact that F-CB has lower energy surfaces than CB. Thus, we presume that F-CB has a low energy surface like the polytetrafluoroethylene surface (Dormant and Adamson, 1968). Furthermore, the high energy site (surface functional groups located at the edge of micrographites) should be removed upon fluorination, also leading to a lower energy surface. The good linearity of the α_s-plot above $\alpha_s = 0.6$ stems from the intermolecular interaction of nitrogen molecules, and dominates the adsorption process above $\alpha_s = 0.6$ on F-CB, agreeing with that on CB at the multilayer adsorption region.

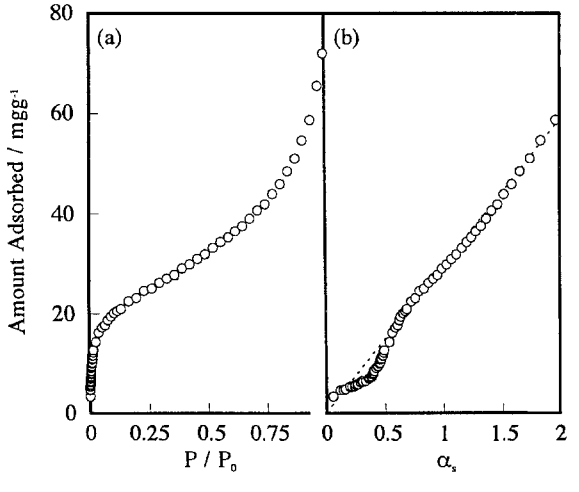

Figure 1. The adsorption isotherm and α_s-plot of nitrogen on fluorinated carbon black (F-CB); (a) adsorption isotherm, (b) α_s-plot.

Microporosity of F-ACF

The nitrogen adsorption isotherms on F-ACF and ACF are shown in Fig. 2(a). The isotherms of F-ACF and ACF are representative of type I, which indicates the presence of uniform micropores (Sing et al., 1985). The fundamental micropore structure of ACF is still preserved on F-ACF. The amount of nitrogen adsorbed on F-ACF is significantly reduced by the fluorination. As the formation of C—F bond should affect the basic structure of micrographite, the micropore structures of ACF should vary with the fluorination.

α_s-plots for both samples are shown in Fig. 2(b). The nitrogen adsorption isotherm on F-CB was used as the reference data for the construction of the α_s-plot of the nitrogen adsorption isotherm on F-ACF, because the surface energy of F-CB was lower than that of CB. The α_s-plot of ACF was obtained using the reference data of CB (Kaneko et al., 1992). The α_s-plot of F-ACF has a typical shape of activated carbons having narrow micropores. That is, this α_s-plot has a marked filling swing in the α_s region of 0.3 to 0.7; the upward deviation from the linear dashed line is ascribed to the enhanced adsorption potentials due to the overlapping of the molecule-surface interaction from the opposite walls of the slit-shaped micropore (Kaneko and Ishii, 1992). The micropore parameters for F-ACF and ACF determined from the α_s analysis are tabulated in Table 1. The micropore volumes were obtained by use

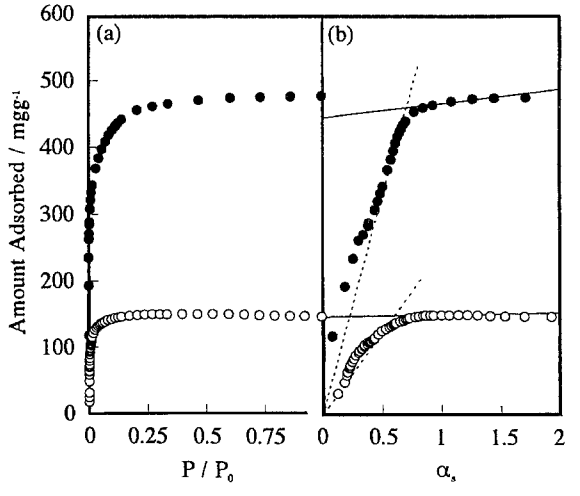

Figure 2. Adsorption isotherms and α_s-plots of nitrogen on fluorinated activated carbon fiber (F-ACF) and activated carbon fiber (ACF). Open symbols: F-ACF, Solid symbols: ACF; (a) adsorption isotherm, (b) α_s-plot.

Table 1. Micropore parameters.

	α_s-analysis		DR analysis		
	a_{tot} m^2g^{-1}	$W_{0,\alpha}$ mlg^{-1}	V_0 mlg^{-1}	E_0 $kJmol^{-1}$	$2\chi_0$ nm
F-ACF	532	0.19	0.196	15.0	1.33
ACF	1147	0.58	0.51	18.1	1.10

Here, a_{tot} and $W_{0,\alpha}$ are the total specific surface area and the micropore volume determined from the α_s-analysis, respectively.

of the density of liquid nitrogen (0.808 g/ml), although nitrogen adsorbed on the micropores may be slightly different from the bulk liquid state. The specific surface area (a_{tot}) and the micropore volume (W_0) are remarkably decreased by fluorination. However, it must be noted that the chemical composition of F-ACF is not the same as ACF. We must take into account the atomic weight difference between carbon and fluorine atoms upon comparison of adsorption data. Hence we will express the amounts of adsorption in terms of the number of adsorbed nitrogen molecules per carbon atom of both samples for comparison. The calculated number of adsorbed nitrogen molecules per carbon atom (Wc), that is, a kind of coverage, were 0.193 and 0.142 for ACF and F-ACF, respectively. The fluorination, therefore, reduces the coverage by 20%. Consequently, the net reduction in the micropore volume due to the fluorination is not so serious compared with the micropore volume expressed by ml/g in Table 1.

The effect of fluorination is more important on the micropore width. We can estimate the average micropore width, assuming that the geometry of the micropores of F-ACF is still slit-shaped. The average micropore width (w) is given as follows (Stoeckli, 1990);

$$w = 1000(2W_0/a_p) \tag{1}$$

W_0 is the micropore volume (ml/g) from α_s analysis, a_p is the specific surface area of micropore walls, which can be determined by $a_{tot} - a_{ext}$. Here a_{tot} and a_{ext} are the total surface area and the external surface area, respectively. We can evaluate a_{tot} and a_{ext} separately from the α_s analysis. The external surface area is small in this case. We determined the a_p value from the slope of the dotted line in Fig. 2. The w values of F-ACF and ACF were calculated as 0.77 and 1.01 nm, respectively. A significant decrease of the micropore width was observed due to the fluorination. The reduction of micropore width is 24%, which corresponds to the reduction of Wc. Accordingly, the decrease of the net adsorption in micropores should come only from the shrinkage of micropores.

The C—F bond length is 0.14 nm and the radius of an ionic fluorine is 0.13 nm. Because fluorine atom has the largest electronegativity and also the previous study showed that the nature of C—F bond in F-ACF is considered as semi-ionic bond in this fluorination condition (Touhara et al., 1985). It is suitable to use the ionic radius rather than the atomic radius (0.07 nm). The micropore wall of ACF mainly consists of trilayered micrographites according to the preceding X-ray diffraction examination (Suzuki and Kaneko, 1993). If both external sides of trilayered micrographite are fluorinated, the micropore width must decrease by 0.20 nm, according to Eq. (2). Here the radius of the surface carbon atom in micrographites is presumed to be a half of the layer distance of perfect graphite crystal (0.34 nm).

$$\begin{aligned}\text{The pore width change} &= 2\,[\text{C—F bond length}] \\ &\quad + 2\,[\text{radius of a F atom}] \\ &\quad - [\text{layer distance of graphite}]\end{aligned} \tag{2}$$

The observed decrease in the pore width (w) is 0.24 (1.01–0.77) nm, agreeing with the calculated value. However, we must take into account the possibility of a serious change in the carbon skeleton structure of the micrographites with fluorination, because the fluorination changes the valence state of a carbon bonding from sp^2 to sp^3. The preceding XPS examination of F-ACF suggested that F-ACF has the chair form of the cyclohexane unit structure (Touhara et al., 1985).

The schematic models of graphite fluoride [$(CF)_n$ and $(C_2F)_n$] and F-ACF are shown in Fig. 3. If F-ACF has a medium structure between $(CF)_n$ and $(C_2F)_n$, considered from the chemical composition of F-ACF ($C_{1.4}F$), the middle layer of trilayered micrographites should also be fluorinated, as are the external layers. In this case, the unit structure of the micrographitic layer of F-ACF will drastically change from that of ACF, that is, a marked swelling should occur in micrographite units. However, the middle layer of trilayered micrographites will not be seriously fluorinated, because the reduction of w discussed above is too small to apply this assumption, and also the geminal C—F bond ($>CF_2$) is formed at the edge of the micrographite, as

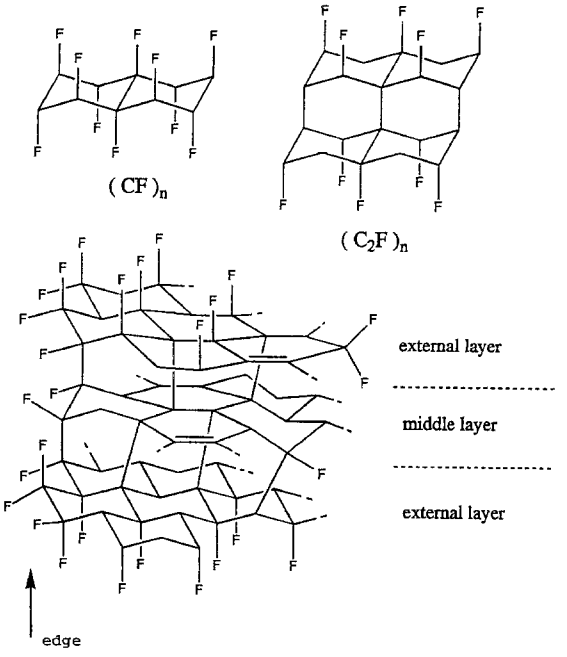

Figure 3. Schematic structure models of graphite fluoride $(CF)_n$ and $(C_2F)_n$, and F-ACF, redrawn but based on reference by Touhara et al. (1985).

shown in Fig. 3. The contribution of the edge carbons in micrographites is much greater than that of perfect graphites. Consequently, the basic unit structures of micrographites are almost preserved and the reduction of w mainly comes from the addition of the C—F bond discussed above.

Evidence of Low Surface Energy of F-ACF

Adsorption isotherms of vapors on microporous carbons are well described by the Dubinin-Radushkevich (DR) equation.

$$\ln W = \ln W_0 - (RT/\beta E_0)^2 \ln^2(P_0/P) \qquad (3)$$

Here, W_0 is the micropore volume and E_0 is the characteristic adsorption energy which is related to the micropore structure. R and T are a universal gas constant and adsorption temperature, respectively. β is an affinity coefficient which depends on the strength of surface-molecule interaction. In activated carbons, β is 0.33 for nitrogen (Dubinin, 1966), using $\beta = 1$ for benzene as a standard adsorptive. Recent theoretical study by Chen and Yang (1994) gave the relationship between βE_0 and the mean potential energy of adsorbate-surface

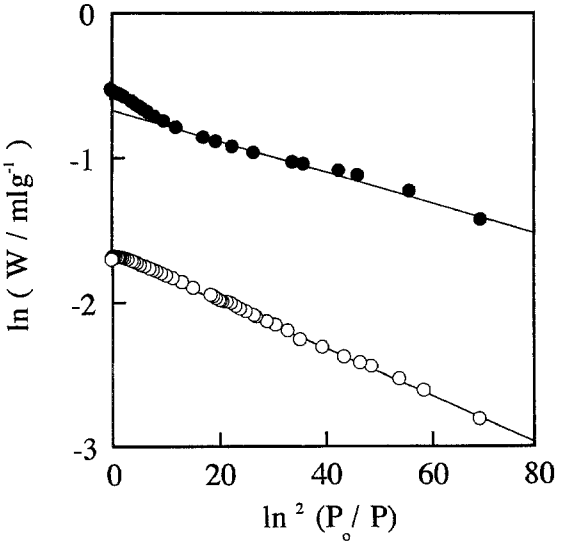

Figure 4. DR plots for F-ACF and ACF. The definition of symbols is same as Fig. 2.

interaction (Φ), which is correlated with the pore width and its geometry. This relation gave a basis for the well-known Dubinin-Stoeckli empirical relation.

The DR plots for F-ACF and ACF are shown in Fig. 4. The DR plot of F-ACF shows a good linearity, suggesting that the micropores of F-ACF are homogeneous. The pristine ACF has slightly heterogeneous micropores, because the DR plot consists of two linear sections, having a bimodal micropore size distribution (Jaroniec et al., 1991). W_0, E_0, and the average pore width $2\chi_0$ from the DR plot are summarized in Table 1. Here, $2\chi_0$ was obtained from the empirical Dubinin-Stoeckli relation with $\chi_0 E_0 = 10$ kJ nm/mol (Dubinin et al., 1991). The $2\chi_0$ value agrees well with w for ACF, while $2\chi_0$ is about twice of the value of w for F-ACF. This disagreement stems from the reduction of the interaction between adsorbed nitrogen and the microporous surface with the fluorination. In this case, the β of nitrogen for F-ACF should have a different value from 0.33 for activated carbons.

If we presume that the estimated w is correct, β of nitrogen for F-ACF should be 0.19, following the Dubinin-Stoeckli relation. Thus it is concluded that the interaction between nitrogen and the micropore surface of F-ACF decreases by 40% on F-ACF. β is approximately proportional to the dispersion interaction between an adsorbate and an adsorbent. Thus the difference of β for ACF and F-ACF depends mainly on the polarizability and ionization potential of the surface

atom or group, as described as follow,

$$\beta_{\mathrm{FACF}} = \beta \frac{\alpha_{\mathrm{CF}} I_{\mathrm{F}} (I_{\mathrm{N}} + I_{\mathrm{C}})}{\alpha_{\mathrm{C}} I_{\mathrm{C}} (I_{\mathrm{N}} + I_{\mathrm{F}})} \tag{4}$$

The group polarizability ($\alpha/4\pi\epsilon_0$) of C—F bond (α_{CF}) is estimated to be 1.0×10^{-30} m^3, while that of carbon (α_C) for an aromatic system is 1.07×10^{-30} m^3. The atomic ionization potential for fluorine (I_{F}), carbon (I_{C}), and nitrogen (I_{N}) are 17.42, 11.26, and 14.53 eV, respectively. Consequently, the change of β value with the surface fluorination is 17% increase from β for ACF, that is $\beta_{\mathrm{FACF}} = 0.39$. However, it must be taken into account that the density of atoms per unit area (ρ_a) exposed on the surface is different for F-ACF and ACF, because the ρ_a is an additional factor for the surface-molecule interaction summed over a semi-infinite plane of surface (Everett and Powl, 1976). The ρ_a for ACF is about two times greater than that for F-ACF if the surface structure of F-ACF is described by the model in Fig. 3; the decrease of the surface-molecule interaction energy is evaluated to be half of β_{FACF} obtained. The β for nitrogen in F-ACF is calculated as 0.19 in this case. These estimated quantities are close to the observed ones. Thus the low β value assures the low energy microporous surface of fluorinated ACF.

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