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Change in the chemical structures of carbon black and active carbon caused by CF_4 plasma irradiation

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Carbon black and active carbon were fluorinated by exposure to CF_4 plasma. Their surface chemical structures were studied by means of elemental analysis, X-ray photoelectron spectroscopy, and inverse gas chromatography as a function of treatment time. Fluorine is mainly introduced onto the carbon black and active carbon surfaces during the CF_4 plasma treatment. The amount and type of carbon–fluorine (C–F) functionality formed on the surfaces of the carbon materials depends on the C–C framework structure as well as the plasma treatment time. C1s chemical shifts caused by C–F bonds on the fluorinated active carbon and carbon black surfaces are slightly different from those reported on the various types of fluorinated organic polymers, and have a somewhat ionic character. For the fluorinated active carbon the C–F bond is relatively stable, whereas for the fluorinated carbon black the C–F bond is unstable and has a significant ionic character. In addition, CO_2 gas adsorption characteristics on the fluorinated active carbon can be controlled by the surface C–F functionality.

1. Introduction

Several publications [1–5] have recently reported the plasma fluorination of various polymeric surfaces and their surface chemistries. The fluorinated surfaces have been proven to have the lowest surface energies due to a layer with strong carbon–fluorine (C–F) covalent bonds, and therefore show the least wettability of any class of materials. When a carbon material is fluorinated at a high temperature, a strong C–F covalent bond is formed [6]. On the other hand, it has recently been found that a type of C–F bond different from the C–F covalent bond is formed on a graphite material through fluorination [7, 8].

Nakajima & Watanabe [6] have reported that graphite fluoride having the C–F covalent bonds is a stable compound in ambient environments and at high temperatures. This stability for critical applications such as lubricants, batteries, and composites with polymers and metals is an important factor. In addition, carbon materials possess other unique properties: excellent heat and electrical conductivity, lubricating properties, and electrochemical catalysis. However, there are few publications on the surface chemistry of fluorinated carbon materials, especially less graphitized carbon materials.

Plasma fluorination has the distinct advantage of affecting only very thin surface layers in a controllable fashion. This paper reports the fluorination of active carbon and carbon black with CF_4 plasma. The principle objectives of this work are to study the effects of fluorination on carbon materials.

2. Experimental procedure

Carbon materials selected for CF_4 plasma treatment were carbon black (Asahi Carbon N220) and active carbon (Shimadzu A-4) for gas chromatography. The carbon black and active carbon have Brunauer–Emmett–Teller (BET) surface areas of 117 and 1470 $m^2 g^{-1}$ respectively. An average grain diameter of the carbon black is 20 nm and the grain size of the active carbon is 60–80 mesh. Commercially available CF_4 gas was used without further purification as a plasma treatment gas.

CF_4 plasma treatment was carried out with a BP-1 basic plasma kit (Samco, 33 Tanakamiy-cho, Takeda, Fushimi-ku, Kyoto 612 Japan) having a parallel plate plasma reactor powered at 13.6 MHz. The reactor contains electrodes separated by ~ 2.5 cm. A microleak attached to the reaction vessel (bell-jar type) containing the carbon black or the active carbon was connected to a vacuum pump and the vessel was first evacuated below 0.015 torr. A constant pressure of the treatment gas of about 0.75 torr was kept during the treatment by combination of the continuous evacuation and the CF_4 gas inlet through another microleak. The flow rates of the CF_4 gas for the carbon black and active carbon were about 100 and

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160 ml min^{-1}, respectively. The input power of plasma discharge was maintained constant, and equal to 50 W. Exposure times were varied between 1 and 240 min. The active carbon powder sample was vibrated mechanically to be treated homogeneously by CF_4 plasma. On the other hand, the carbon black powder was treated without being vibrated mechanically, condensing during the plasma treatment when vibrated.

All analyses in this study were carried out after exposure of the samples to air. Elemental analysis was performed for element fluorine. The change in weight caused by the plasma treatment was measured with a microbalance. The surface chemistry was studied by X-ray photoelectron spectroscopy (XPS or ESCA). XPS spectra were collected with an Escalab MK II (Escalab (VG), The Birches Industrial Estate, Imderhorne Lane, East Grinstead, West Sussex, RH19 IUB, England) instrument (VG) using a $\mathrm{Mg}K_\alpha$ X-ray anode operating at a power of 300 W and 15 keV. The pressure during the runs remained at about 5×10^{-9} torr. Curve fitting with mixed Gaussian/Lorentzian functions for the carbon 1s electron (C1s) peak was carried out on data following background subtraction. Binding energies were calibrated using the lowest energy component of the C1s peak of each sample, which was assumed to be located at 285.0 eV as an internal reference. Relative sensitivity factors determined from the standard reagents, 9-anthracenecarboxylic acid and 2,6-difluorobenzamide, were used to estimate atomic ratios from peak area ratios. When the intensity of the carbon 1s peak is assumed as unity, relative sensitivity factors for F1s and O1s are 2.98 and 2.19, respectively.

The thermal stability of the fluorinated active carbon was also investigated by measuring the fluorine content of the fluorinated active carbon after heat treatment. The fluorine content was determined from elemental analysis. The heat treatment was carried out in the range of 100–300 °C for 1 h *in vacuo*.

In addition, the surface properties of fluorinated active carbons were studied by inverse gas chromatography (IGC). The gas adsorption technique with town gas was carried out by using a 163 gas chromatograph (Hitachi, 5–1, 1-chome, Marunouchi, Chiyoda-ku, Tokyo 104 Japan) equipped with a thermal conductivity detector. The untreated and fluorinated active carbons were packed into stainless steel columns of 2 m length and 2 mm internal diameter. Prior to each measurement, the GC columns were conditioned for 24 h at 150 °C under helium gas flow. The retention data were recorded and analysed by means of an 834-30 Chromato-processor (Hitachi), helium being the carrier gas with a flow rate of 20 ml min^{-1}. The amounts of O_2, N_2, and town gas injected were 0.05, 0.05, and 0.2 ml, respectively. Column, detector and injector temperatures were maintained at 28 and 100 °C, and room temperature, respectively. The gas components detected were monitored by measuring changes in retention time (t_R). The t_R was determined with respect to the zero retention reference time obtained with a H_2 gas probe assumed as a non- or slightly adsorbing probe.

TABLE I Variation in weight and fluorine content for active carbon and carbon black treated with CF_4 plasma (input power, 50 W)

Sample	Treatment time (min)	D_W (wt %)	F (wt %)	F_{add} (wt %)	X'_{add} (wt %)
CB-1	0	0.00	0.00	0.00	0.00
CB-2	10	2.44	2.19	2.24	0.20
CB-3	30	4.53	5.05	5.28	− 0.75
CB-4	60	7.51	4.55	4.89	2.62
CB-5	120	9.01	7.53	8.21	0.80
CB-6	180	11.50	11.39	12.70	− 1.20
CB-7	240	10.30	9.81	10.82	− 0.52
AC-1	0	0.00	0.00	0.00	0.00
AC-2	1	0.57	0.20	0.20	0.37
AC-3	10	1.89	1.71	1.74	0.15
AC-4	60	6.37	5.17	5.50	0.87
AC-5	120	15.06	11.65	13.40	1.66
AC-6	240	15.56	12.63	14.60	0.96

3. Results and discussion

3.1. Variation in weight and fluorine content

Table I shows variations in weight and fluorine content for active carbon and carbon black treated with CF_4 plasma. F in Table I is the wt % of fluorine determined by elemental analysis; D_w is the gain in total weight of the plasma-treated sample in comparison with the total weight of the untreated sample; F_{add} is the wt % of fluorine introduced by the treatment in comparison with the total weight of the untreated sample and expressed as follows:

$$F_{\mathrm{add}} = F(1 + D_W/100)$$

It is reasonable to presume that the variation in weight caused by the plasma treatment contains the introduction of fluorine and carbon fluoride as well as the elimination of carbon constituting the carbon materials. This assumption leads to a definition of X'_{add} expressed as follows:

$$\begin{aligned} X'_{\mathrm{add}} &= X_{\mathrm{add}} - X_{\mathrm{et}} \\ &= F_{\mathrm{add}} - D_W \end{aligned}$$

where X_{add} is the wt % of elements, other than fluorine, introduced by the plasma treatment in comparison with the total weight of the untreated sample, and X_{et} is the wt % of elements etched by the treatment in comparison with the total weight of the untreated sample. Moreover, when the carbon material sample treated with the CF_4 plasma is taken out of the plasma reaction vessel, the reaction of the surface of the sample with oxygen in air and the adsorption of water on the surface of the sample can be considered to proceed. The reaction and adsorption are almost negligible for the carbon black, as the XPS O:C ratio of the untreated carbon black is less than 0.05. The measurements are not consistently increased by the plasma treatment under all conditions, as shown in Table I. On the other hand, the O1s peak in XPS wide-scan spectra for the active carbon was not observed in the treatment time 1–60 min. Therefore it is found that X_{add} described above does not contain oxygen in this region.

D_W, F_{add}, and X'_{add} in Table I are plotted as a function of treatment time, as shown in Fig. 1. For both the carbon black and the active carbon, D_W and F_{add} increase with treatment time. The value of D_W is almost in agreement with that of F_{add} in the range of 1–240 min for both the carbon black and the active carbon. This suggests that the CF_4 plasma treatment results in the introduction of mainly F, rather than oxides and carbon fluorides, to the surfaces of their carbon materials. Therefore it can be assumed that the introduction of oxygen for the active carbon is negligible even in the treatment time 120–240 min. Moreover, X'_{add} is kept at an almost constant value near 0%. This indicates that the surfaces of the carbon materials are etched little by the CF_4 plasma treatments under the conditions of this study.

It can be concluded that the introduction of elements except for fluorine and the etching effects during the CF_4 plasma treatment are negligibly small compared with the introduction of fluorine. Thus CF_4 plasma treatment grafts mainly F radicals directly to the carbons on the carbon material surfaces without destroying the surface carbon–carbon (C–C) skeleton structures.

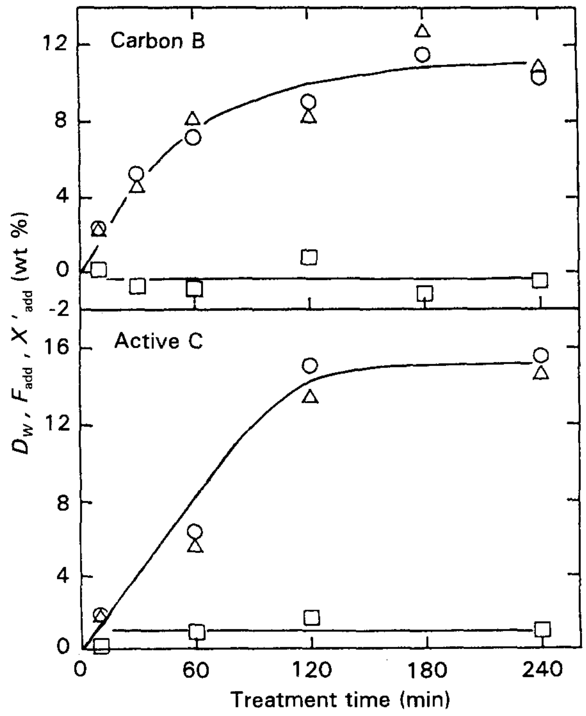

Figure 1 D_W (○), F_{add} (△), and X'_{add} (□) plotted as a function of treatment time.

3.2. XPS studies

Fig. 2 and Table II show the curve-fitted C1s XPS spectra and the relative peak areas of the carbon materials, which represent changes caused by various CF_4 plasma treatment times. The spectra can be fitted to five peaks. The main peak at lowest binding energy is the C–C peak at 285.0 eV. The remaining four peaks for the fluorinated carbon blacks and active carbons are assumed to correspond to carbon fluoride functionalities: –CCF, –CF, $-CF_2$, and $-CF_3$ groups, which are described as fluoride 1 to fluoride 4, to higher binding energy from the C–C peak. C1s XPS chemical shifts for the untreated carbon black and active carbon surfaces are also recognized. The shifts are considered to be mainly due to surface oxides.

It can be seen that the amount of fluoride 1 does not vary much with plasma treatment for both the carbon black and the active carbon. Fluoride 2 peak area percentage for the carbon black increases by about 130% after the plasma treatment from 10 to 240 min, and does not decrease during the treatment time. For the active carbon, it increases by about 60% after the treatment from 1 to 10 min, and decreases by about 30% after the treatment from 10 to 60 min. It is found that the short treatment time (less than 10 min) for the active carbon causes as much change to the surfaces as the long treatment time (240 min) for the carbon black. The decrease in fluoride 2 for the active carbon described above can be related to an increase in fluoride 3 and 4 peaks. Thus a part of fluoride 2 for the active carbon is expected to convert to fluoride 3 and 4 at longer CF_4 plasma treatment time, or 60 min. In the case of the carbon black, the increases in fluoride 3 and 4 are little observed even by prolonged CF_4 plasma treatment. Only fluoride 2 is introduced to the carbon black.

Total fluoride area ratio (%) of carbon fluorine (C–F) functionalities (fluoride 1 + fluoride 2 + fluoride 3 + fluoride 4) in comparison with the C–C peak area obtained from the curve-fitted C1s peak, and the

TABLE II C1s peaks and relative peak areas for active carbon and carbon black surfaces treated with CF_4 plasma (input power, 50 W)

Sample	C1s peaks in different carbon chemical states											
	Main C–C peak		Fluoride 1		Fluoride 2		Fluoride 3		Fluoride 4			
	BE (eV)	Area (%)	BE (eV)	Area (%)	BE (eV)	Area (%)	BE (eV)	Area %	BE (eV)	Area (%)	TF:C (%)	F:C (%)
CB-1	285.0	67	286.5	16	288.2	7	290.2	5	292.0	4	0	0
CB-2	285.0	65	286.8	16	288.7	9	290.6	6	292.8	4	9	15
CB-3	285.0	56	286.7	17	288.7	15	290.7	7	292.8	5	15	32
CB-4	285.0	55	286.8	17	288.9	17	290.9	7	293.0	4	17	39
CB-5	285.0	55	286.8	17	288.9	17	290.9	7	293.0	4	17	37
CB-7	285.0	50	286.8	18	288.9	21	290.9	8	293.1	3	21	47
AC-1	285.0	69	286.3	17	288.3	6	290.4	5	292.2	3	0	0
AC-2	285.0	59	286.6	17	288.4	14	290.3	6	292.5	3	35	25
AC-3	285.0	46	287.0	17	288.6	22	291.0	9	293.2	6	58	60
AC-4	285.0	5	288.2	16	289.7	16	292.3	50	295.2	12	152	120

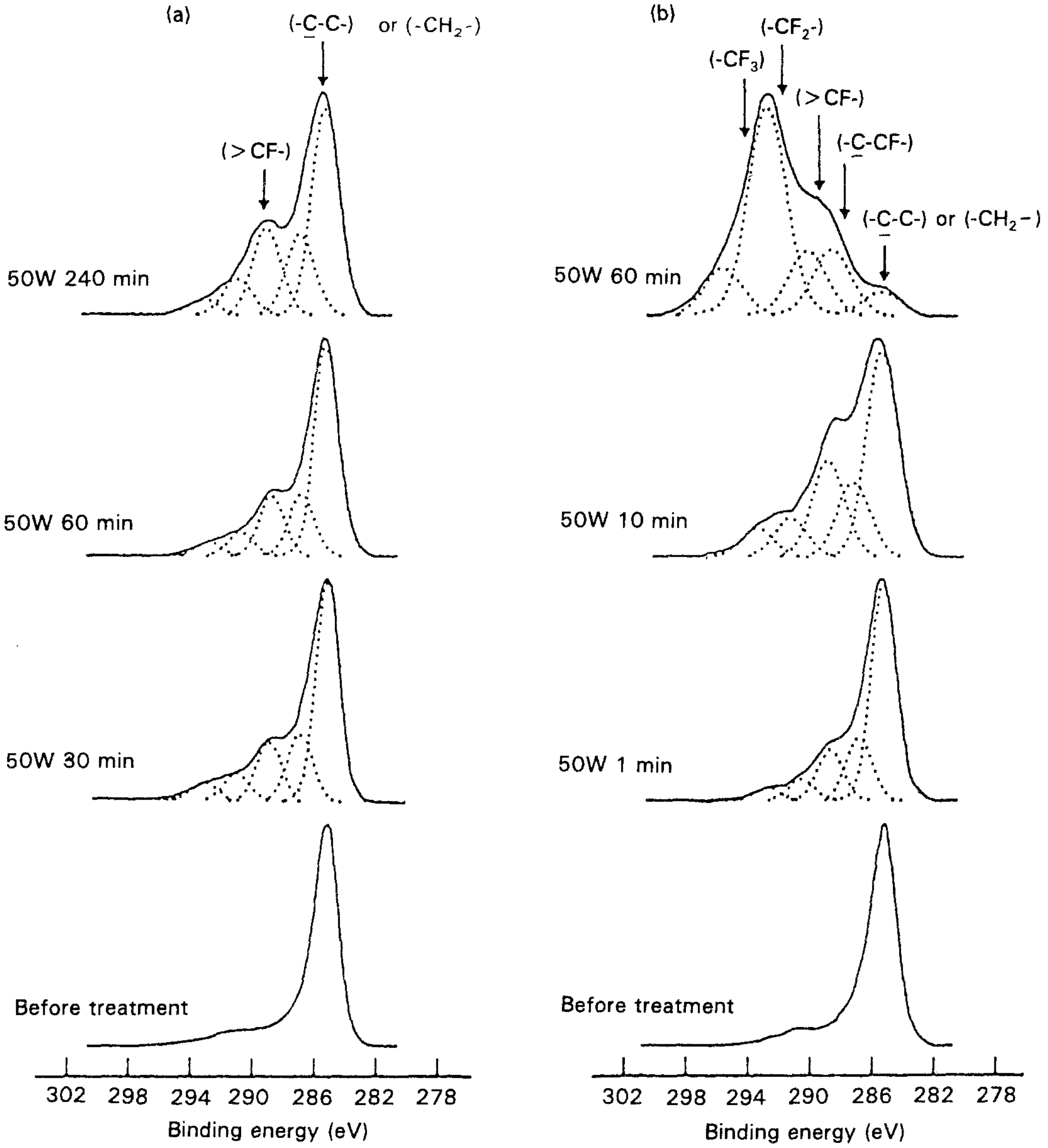

Figure 2 Curve-fitted C1s XPS spectra: (a) carbon black; (b) active carbon.

F:C atomic ratio (%) calculated by using the relative sensitivity factor, are shown in Table II. The total fluoride area ratio and F:C atomic ratio are designated as TF:C and F:C, respectively. In the case of the active carbon, the value of TF:C nearly agrees with that of F:C for each treatment time. This agreement clearly demonstrates that fluorines introduced by the plasma treatment are covalently bonded to active carbons on the active carbon surface. On the other hand, for carbon black the value of TF:C is approximately twice as much as that of F:C for each treatment time. This indicates that the nature of bond for the carbon black is different from that of the C–F bond character for the active carbon. Moreover, when the carbon black fluorinated by CF_4 plasma treatment is stored in a glass sample bottle, the bottle is corroded and becomes white in colour. For the fluorinated active carbons, no similar corrosion is observed. These phenomena relating to the corrosion of glassware and the results of XPS suggest that the fluorinated carbon black surface structure contains fluorides weakly or non-covalently bonded to carbons, rather than those strongly bonded to carbons.

It can be concluded that the kind of fluoride formed on the carbon black surface is different from that on the active carbon surface. The formation of the non-covalent bonds would be affected by the carbon skeleton structures of the carbon material surfaces. Thus it is presumed that the formation is attributed to the interaction between micro-graphite basal planes and fluorines, probably an ionic interaction.

The chemical shift of each fluoride obtained by curve fitting of C1s peaks for all samples except for 60-min-treated active carbon is relatively small in comparison with that reported on fluorinated organic polymers [1–4]. The surfaces of carbon black and active carbon contain crystallites consisting of micro-graphite basal planes, whereas the polymers mentioned above contain condensed rings (with only a few rings). The differences in these carbon skeleton structures appear to affect the values of the chemical shifts. Thus one fluorine atom is considered to bond covalently with only one carbon atom for the organic polymers, whereas it probably interacts somewhat ionically with neighbouring plural-edge carbon atoms on the surfaces, rather than covalently with only one edge carbon for the carbon black and the active carbon. In addition, an extremely low ratio of main C–C peak area for the 60-min-treated active carbon suggests that the surface C–C skeleton structure is destroyed by the plasma treatment and approaches the structure of an organic polymer. Relatively large chemical shifts for the 60-min-treated active carbon also support this suggestion.

A detailed evaluation by XPS of the type and amount of fluoride introduced by CF_4 plasma treatment may be feasible to characterize the surface structures of carbon materials as well as various organic polymers.

The fluorine contents of the active carbon after heat treatment are shown in Fig. 3. A slight decrease in fluorine content is observed at 300 °C. It can be seen that the surface fluorides of the active carbon are relatively stable for the heat treatment at temperatures upto 300 °C. This also suggests that a C–F bond for the active carbon surface has a relatively strong covalent character. Therefore the stability of the active carbon surface fluorides for the heat treatment is consistent with the finding obtained from XPS studies.

3.3. Gas adsorption characteristics on fluorinated carbon materials

Chromatograms for town gas on CF_4 plasma fluorinated active carbons are shown in Fig. 4. It is found that the town gas can be separated to each gas component: O_2, N_2, CO, CH_4, and CO_2. The separation of O_2 and N_2 can be recognized in all samples. The t_R of N_2 (molecular size 0.378 nm) is shorter than that of O_2 (molecular size 0.364 nm). This indicates that the separation is mainly due to probe-surface chemical interactions rather than a molecular size effect. Thus the chemical interactions between O_2 and the surfaces are slightly stronger than those between N_2 and the surfaces.

The t_R/t_{RO} ratio for the each gas component plotted as a function of D_w on fluorinated active carbons is shown in Fig. 5. The t_{RO} means the t_R of the untreated active carbon. It can be seen that the t_Rs of the fluorinated active carbons decrease with fluorination in the all gas components, as the t_R/t_{RO} ratios are less than one. The degree of the reduction is almost the same among the all gas components except for CO_2. The t_R/t_{RO} ratios for the all gases except for CO_2 gas significantly decrease with *DW* at relatively high *DW*. This indicates that only the access manner of CO_2 is different from that of the other gases: O_2, N_2, CH_4 and CO.

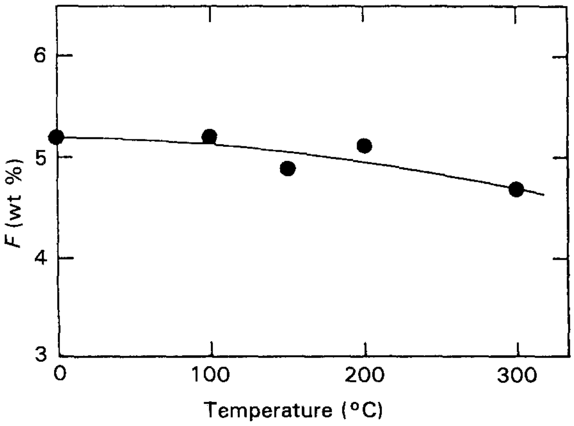

Figure 3 Fluorine contents on the fluorinated active carbons plotted as a function of heat-treatment temperature.

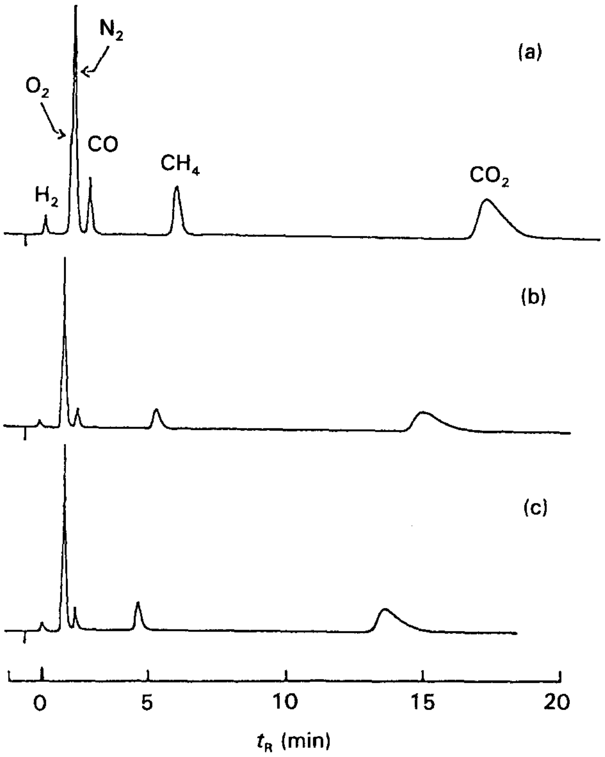

Figure 4 Chromatograms for the town gas on the fluorinated active carbons. (a) Before treatment; (b) CF_4, 1 W, 5 min; (c) CF_4, 50 W, 60 min.

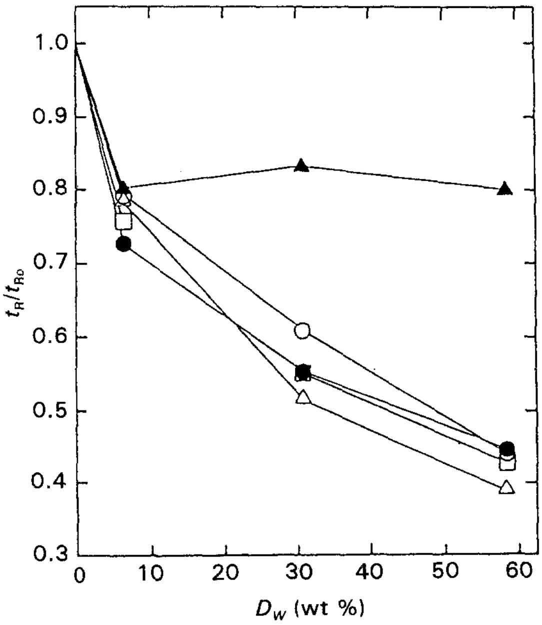

Figure 5 t_R/t_{RO} plotted as a function of *DW* on the fluorinated active carbons. ○, O_2; △, N_2; □, CO; ●, CH_4; ▲, CO_2.

Considering results obtained from XPS studies for the fluorinated active carbon, fluoride 1 exists predominantly around a *DW* of 5%, and fluorides 2 and 3 primarily in the *DW* region of about 30 to 60%.

Therefore the interaction between the gases and the surface functionalities can be stated as follows. The adsorption of CO_2 gas on the active carbon surface is significantly hindered by a –CF functionality, whereas it is hindered little by $-CF_2$ or $-CF_3$ functionalities. On the other hand, the adsorption characteristics of O_2, N_2, CH_4, and CO gases depend little on the type of C–F functionality and their adsorptions are significantly hindered by the all C–F functionalities.

Furthermore, we have made some experimental runs for the desorption characteristics of air ($N_2 + O_2$) on the fluorinated active carbon above. No clear tendencies are recognized with the experiments so far tested.

Finally, a gas adsorption characteristic on carbon materials would be affected by the amount and type of C–F functionality. The amount and type of C–F functionality, as well as a C–F bond character formed on carbon materials, would be dependent on not only the condition of CF_4 plasma treatment, but also on the surface C–C skeleton structure of the carbon materials.

4. Conclusions

The CF_4 radio frequency plasma treatment can introduce mainly fluorine to the active carbon and carbon black surfaces without etching of their surfaces. C1s XPS spectra can be curve-resolved to allow a better understanding of a surface C–F bond character formed on the carbon materials. C–F bonds on the carbon materials fluorinated by the plasma treatment have a somewhat ionic character, compared with the covalent character characterized on fluorinated polymers. C–F bonds formed on the carbon black also have a significant ionic character, different from that of the C–F bonds on the active carbon. The type of C–F functionality formed on the active carbon with the CF_4 plasma is different from that on the carbon black; a –CF functionality is only introduced to the carbon black surface, whereas –CF, $-CF_2$ and $-CF_3$ functionalities are introduced to the active carbon surface. In addition, the presence of the C–F functionalities on the active carbon surface hinders the adsorption of O_2, N_2, CH_4 and CO. The adsorption characteristic of CO depends on the type of C–F functionality; a –CF functionality significantly affects the adsorption of CO_2 in the same manner as O_2, N_2, CH_4, and CO, whereas $-CF_2$ and $-CF_3$ functionalities have little affect on adsorption.

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