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Some Properties of Fluorine-adsorbed Active Carbon

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Properties of fluorine-adsorbed active carbon (FAAC), expected to be a new fluorinating agent, were investigated by means of TG, X-ray diffraction, and ESCA. The fluorine in FAAC was desorbed by heat treatment in a vacuum at temperatures higher than 200 °C. The X-ray diffraction and ESCA measurements suggest that fluorine is inserted between the carbon layer planes of the active carbon, and combines with carbon atoms weakly in comparison with the C–F covalent bond. The reactivity of FAAC against several organic compounds was studied. 1-Butanol, 1-butanethiol, and cyclohexylamine were oxidized. Butyryl chloride was fluorinated to give butyryl fluoride.

Direct fluorination of carbon at temperatures 350—600 °C gives two types of graphite fluoride, identified as polycarbon monofluoride, $(CF)_n$, and polydicarbon monofluoride, $(C_2F)_n$.[1] Some kinds of carbon adsorb a large amount of fluorine at room temperature.[2,3] Active carbon shows 30—50% weight increase when it is exposed to fluorine atmosphere at room temperature.[2] While graphite fluoride is chemically and thermally stable, this fluorine-adsorbed active carbon (FAAC) can oxidize other halogen ions at room temperature,

$$\mathrm{FAAC} + \mathrm{X}^- \text{ in aq soln} \longrightarrow$$

$$\mathrm{C} + \mathrm{F}^- + \frac{1}{2}\mathrm{X}_2 \quad (\mathrm{X}=\mathrm{Cl, Br, I})$$

where C is the residual active carbon.[2] Thus FAAC is expected to be a new fluorinating reagent.

In this study, FAAC was prepared in a laboratory scale and studied by thermogravimetry (TG), X-ray diffraction, and X-ray photoelectron spectroscopy (ESCA). Fluorination of several organic compounds with FAAC was examined.

Experimental

Commercial granular active carbon (extra pure) and organic compounds (guaranteed grade) were used without further purification. TG study was carried out with a thermobalance specially designed for use in a fluorine atmosphere.[2]

A schematic diagram of the reactor for fluorination is shown in Fig. 1. The reaction vessel (5) is made of stainless steel, and can be used at desired temperatures with an electric furnace or appropriate coolant. The fluorocarbon oil (Daifluoil, Daikin Kogyo Co.) placed on the mercury column in the manometer (4) prevents fluorine from reacting with mercury. The gas reservoir (3) and all tubings were made of copper.

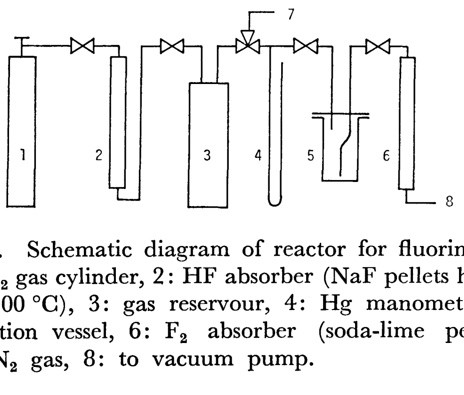

Fig. 1. Schematic diagram of reactor for fluorination. 1: F_2 gas cylinder, 2: HF absorber (NaF pellets heated at 100 °C), 3: gas reservour, 4: Hg manometer, 5: reaction vessel, 6: F_2 absorber (soda-lime pellets), 7: N_2 gas, 8: to vacuum pump.

Results and Discussion

Preparation of Fluorine-adsorbed Active Carbon. FAAC was prepared in the following manner using the apparatus shown in Fig. 1. About 100 g of granular active carbon[4] was placed in the reaction vessel, and heated at *ca.* 150 °C for 2 h in a vacuum to remove water. The vessel was filled with purified nitrogen gas after the active carbon had cooled down to room temperature. Fluorine (0.5 atm) and nitrogen (0.5 atm) were mixed in the gas reservoir. Diluted fluorine was then streamed slowly through the vessel at a flow rate of *ca.* 30 ml/min. The FAAC containing 15—20% fluorine by weight (calculated from the weight increase) was prepared by streaming the gas for 20—30 h. The sample thus obtained had to be washed with nitrogen gas before it was taken out from the reaction vessel. FAAC containing over 20% fluorine would be prepared with further fluorination.

Excessive flow rate of the diluted fluorine sometimes caused explosion in the reaction vessel, or auto-catalytic thermal decomposition of the sample accompanied by a large amount of heat evolution. In the latter case, the sample completely lost the adsorbed fluorine. The reaction vessel should be evacuated as soon as the thermal decomposition takes place, because the inner pressure increases rapidly.

Desorption of Fluorine by Heating. The fluorine adsorbed by FAAC was scarcely desorbed at room temperature even *in vacuo*. This indicates that the fluorine is chemically adsorbed by the active carbon.[2,3] TG was applied in order to study the desorption of

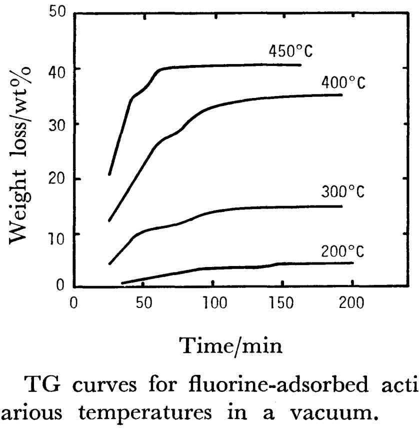

Fig. 2. TG curves for fluorine-adsorbed active carbon at various temperatures in a vacuum.

the fluorine by heating *in vacuo* (Fig. 2). The higher the temperature, the more desorption being observed. The final weight loss at 450 °C corresponds to the desorption of 95% fluorine in FAAC, when no thermal decomposition took place. Various kinds of fluorocarbon were formed in the thermal decomposition of graphite fluoride.[5,6)]

Each TG curve was a straight line at first, and then showed slight decrease in the desorption rate, indicating that fluorine is adsorbed heterogeneously. Supposing that the initial desorption rate follows the first order kinetic, the apparent activation energy was calculated to be 28 kJ/mol from the Arrhenius plot of the rate constants. Takenaka[7)] found the activation energy for the adsorption of fluorine on graphite to be *ca.* 17kJ/mol. These values are smaller than that for the adsorption of oxygen on graphite.[8)] Fluorine might not be combined with carbon covalently like oxides on graphite, but adsorbed weakly on carbon atoms. This was confirmed by ESCA spectra.

Structural Change of Active Carbon by Fluorine Adsorption. The structural change of active carbon was studied by means of X-ray powder diffractometry (Fig. 3). Active carbon has poor regularity as regards carbon layer stacking. Its structure is called turbostratic.[9)] A diffused diffraction between 20 and 30° in 2θ corresponds to three to four layers stacked with the same distance of 3.5—3.7 Å (Fig. 3-a). The broad peak disappeared completely when carbon adsorbed fluorine, as shown in Fig. 3-b. However, the regularity of layer packing was recovered by heat treatment at high temperatures such as 300 or 400 °C *in vacuo* because of the desorption of fluorine (Fig. 3-c, d). In the case of graphite, the adsorbed fluorine strained the graphite structure in a direction vertical to the carbon layers, and the stress given to the crystal lattice of graphite was an elastic deformation.[5)] The results indicate that the fluorine is not only adsorbed on the surface of the active carbon, but also inserted between carbon layer planes.

ESCA Measurement. In order to elucidate the bonding state of fluorine, FAAC was analyzed by ESCA. In Fig. 4 are shown the spectra for C_{1s} photoelectron of (a) original active carbon, (b) FAAC containing 30% fluorine by weight, and (c) FAAC which is heated at 450 °C for 3 h in a vacuum. The main peak at 284.6 eV corresponds to carbon atoms having no interaction with fluorine.

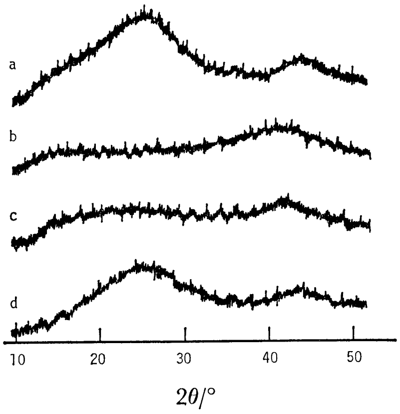

Fig. 3. Variation of X-ray diffraction patterns of fluorine-adsorbed active carbon (FAAC).
a: Original active carbon, b: FAAC, c and d: FAAC after the heat-treatment in a vacuum at 300 and 400 °C, respectively.

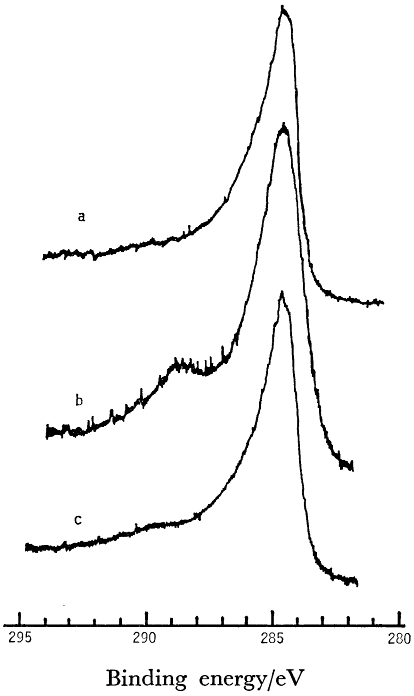

Fig. 4. Variation of ESCA spectra for C_{1s} photoelectron of fluorine-adsorbed active carbon (FAAC).
a: Original active carbon, b: FAAC, c: FAAC after the heat-treatment at 450 °C in a vacuum.

A new peak appeared at 288.7 eV in the spectrum of FAAC (Fig. 4-b). Since the C–F covalent bond in graphite fluoride has a peak at 290.4 eV,[1)] the new peak is due to the interaction between C and F which is weaker than their covalent bond. By heat-treatment, fluorine was desorbed almost completely and a small hump appeared at *ca.* 290 eV, indicating the formation of C–F covalent bond (Fig. 4-c).

A weaker C–F bond was also observed in ESCA spectra of carbon black[3)] and natural graphite[15)] fluorinated at room temperature. These fluorinated samples have similar oxidizability as FAAC. It is not clear, however, whether the adsorbed fluorine is atom or molecule.

Let us discuss the structure of FAAC and the mechanism of the fluorination of active carbon on the basis of the above results. The composition of FAAC containing 30 wt% of fluorine can be expressed as $C_{3.7}F$. The situation thus differs from the simple adsorption of fluorine on active carbon. FAAC loses the characteristic structure of active carbon. Thus, it is concluded that FAAC is an amorphous solid with no crystallinity, holding fluorine with relatively weak bonding on its layered structure like graphite intercalation compounds. FAAC is similar to the intercalation compound since it permits the reversible insertion and withdrawal of fluorine.

Fluorination of active carbon may be influenced by its structural features rather than surface properties,

TABLE 1. REACTION OF SEVERAL ORGANIC COMPOUNDS WITH FLUORINE-ADSORBED ACTIVE CARBON

Run	Substrate	Reaction conditions			Products (Yield/%)
		Solvent	Temp/°C	Time/h	
Oxidation					
1	*n*-BuOH	CCl_4	78	24	$CH_3(CH_2)_2CHO$ (33)
2	*n*-BuSH	CCl_4	78	5.5	Bu-S=S-Bu (10)
3	*cyclo*-$C_6H_{11}NH_2$	—[a]	80	18	*cyclo*-$C_6H_{11}NH_3F$ (20) and oily material
Fluorination					
4	$CCl_2=CCl_2$	—[b]	250	12	fluorochlorocarbons (50)[c]
5	$CCl_2=CCl_2$	—[a]	80	21	no reaction
6	$CH_3(CH_2)_2COCl$	CCl_4	75	21	$CH_3(CH_2)_2COF$ (29)[d]
7	$CH_3(CH_2)_2COCl$	CH_3CN	75	21	$CH_3(CH_2)_2COF$ (62)[d]
8	$CH_3(CH_2)_2COCl$	CH_3CN	75	120	$CH_3(CH_2)_2COF$ (90)[d]
No reaction					
9	C_6H_6	—[a]	80	90	
10	*n*-Bu-X (X=Cl, Br)	CCl_4	78	45	
11	C_6H_5-Br	—[a]	100	24	

a) Solvent was the substrate itself. b) Gas phase reaction in a steel reactor ($3\phi \times 30$ cm) heated by an electric furnace. c) Total yield of CF_4, CF_3Cl, CF_2Cl_2, and $CFCl_3$. They were identified by using IR. d) Calculated from the absorption intensity of the C=O band due to COF group.

since the amount of fluorine taken in far exceeds what is expected for the adsorption. The active carbon having looser structure would hold more fluorine than that having rigid structure.

Reactions of Several Organic Compounds with FAAC. *n*-BuOH and *n*-BuSH were oxidized to their corresponding aldehyde and disulfide, respectively (Table 1). The oxidation of cyclohexylamine gave the adduct with hydrogen fluoride and oily material which could not be identified. When the amine was dropped directly to FAAC at room temperature, it burned violently with a red flame and white smoke. Thus, FAAC can oxidize the compound which easily supplies proton.

Hydrocarbons and alkyl halides were inert to FAAC below 100 °C (Runs 5, 9, 10, and 11), and can be used as an inert solvent. However, at a high temperature such as 250 °C, tetrachloroethylene was fluorinated violently with the rupture of C=C double bond, giving various fluorochlorocarbons.

$$CCl_2=CCl_2 \longrightarrow CF_4,\ CF_3Cl,\ CF_2Cl_2,\ CFCl_3$$

The carbon-chlorine bonds were also ruptured, $NiCl_2$ being formed on a nickel sample holder in the reactor. Carbon tetrachloride also gave a small amount of fluorochlorocarbons at this high temperature.

It is interesting to know whether FAAC can be used for selective fluorination. As an example, the chlorine in butyryl chloride was substituted by fluorine with FAAC. The reactions in CCl_4 and in CH_3CN were compared with each other. The yield of butyryl fluoride in CH_3CN was about twice that in CCl_4 under the same conditions. Aprotic polar solvent seems to be preferable for the fluorination of acyl chloride. Attempt to use dimethyl sulfoxide as solvent was unsuccessful because DMSO reacted with the acyl chloride.

Such solvent effects can be explained in terms of the surface polarity of active carbon. Its polarity is nearly zero, and it adsorbs nonpolar molecules preferentially.[10] In CH_3CN, the acyl chloride may be attracted by the surface of FAAC on account of its longer alkyl chain than the solvent. On the other hand, in CCl_4, FAAC may be surrounded by the inert solvent, and the reaction rate will slow down.

Even in CH_3CN, however, the reaction rate is regarded to be small (90% yield after 120 h). This may be due to the slow diffusion of active fluorine from the inner part to the surface of FAAC. Thus, fluorination with FAAC is considered to occur on its surface or near it. The polarities of reactant and solvent should be taken into accout. Stirring of the reaction system is indispensable, and crushing of FAAC in dry atmosphere is effective for better yield.

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