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Thermal decomposition of 1st stage fluorine–graphite intercalation compounds

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Abstract

A study was made on the thermal decomposition products of fluorine–graphite intercalation compounds (C_xF) with a 1st stage structure. Residual carbon obtained by the decomposition of $C_{2.5}F$ at 500°C possesses graphite structure with a low crystallinity, the distance between carbon sheets being larger than that of the host graphite by 14 pm. Reactive fluorocarbon gases are evolved by the decomposition, and successively react to give the deposits of carbon and fluorocarbons on the reactor wall as well as the gaseous perfluoroalkanes.

Keywords: Fluorine–graphite intercalation compound; Thermal decomposition; Gaseous product

1. Introduction

Fluorine directly reacts with graphite above 350°C to give $(CF)_n$, $(C_2F)_n$ or the mixture of these, depending on the crystallinity of original graphite and reaction temperature [1]. Carbon sheets in these compounds are buckled by sp^3 hybridization of the carbon atoms, fluorine atoms being covalently bound to them. Thermal decomposition of $(CF)_n$ starts at 320–610°C, depending on the crystallinity [2,3]. Thermal decomposition of $(CF)_n$ in vacuum is expressed by the following equation:

$$2(CF)_n \rightarrow nC^* + XCF_2 + YC_2F_4 \qquad (1.1)$$

where $X + 2Y = n$ and C^* is amorphous carbon [4]. Deposition of polymeric fluorocarbon and carbon on the reactor wall occurs as well as the evolution of perfluoroalkanes by the subsequent reactions of CF_2 and/or C_2F_4 [4,5], although these deposition products have not been characterized in detail.

Fluorine does not react with graphite by itself at ambient temperature, however, reacts in the presence of fluoroacid catalysts such as HF [6–8], AsF_5, IF_5 and OsF_6 [9] to give fluorine–graphite intercalation compounds (graphite fluorides; C_xF) in which carbon sheets are maintained their planarity. The bond nature between fluorine and carbon in graphite fluorides changes with fluorine content [7,10]. Those with high fluorine contents ($2 \leq x \leq 5$) generally have 1st stage structures and semi-ionic bonds between carbon and fluorine atoms. On the other hand, compounds with lower fluorine contents ($x > 5$) possess higher stage structures and bonding between carbon sheets and fluorine is essentially ionic.

Studies on the thermal decomposition of C_xF would provide us more detailed information about the chemical bond between carbon and fluorine atoms in the compounds. Nakajima et al. reported thermal analyses of fluorine-intercalated carbon fibers with 3rd stage structures [11]. Thermal decomposition of the compounds starts at 100–150°C, depending on the crystallinity of the host materials. Gupta et al. investigated the thermal stability of fluorine-intercalated carbon fibers having 1st and 2nd stage structures [12]. Two steps were observed in the decomposition of the compounds by means of differential scanning calorimetry (DSC) in nitrogen atmosphere, the first, endothermic at 200–300°C, and the second, exothermic at above 300°C. The 1st stage compound changes to that of higher stages, and finally to graphite. In these studies, a decomposition mechanism was proposed in which fluorine atoms once released from the graphite galleries react again with the residual graphite to form fluorocarbon gases. Analyses of the gaseous products are necessary in order to prove such a reaction mechanism.

We have reported on the thermal decomposition products of C_xF with a 1st stage structure including gaseous products and deposits on the reactor wall [13]. In the present study,

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discussion was made on the total decomposition process of C_xF including subsequent reactions of the gaseous products based on the results obtained from some spectroscopic observations.

2. Results and discussion

Graphite fluorides prepared for the present study contain trace of HF (less than 10 wt.%), their compositions being represented by the formula $C_xF(HF)_\delta$ where $2.40 \leq x \leq 2.61$ and $\delta \leq 0.20$. They are all 1st stage compounds, and their thermal behaviors are essentially the same in this composition range. They will be expressed by '$C_{2.5}F$' in the following discussion.

2.1. Residual materials

The weight losses of $C_{2.5}F$ by the heat treatments in vacuum at fixed temperatures for 20 h are shown in Fig. 1. The decomposition of $C_{2.5}F$ proceeds slowly below 450°C, and drastically above 450°C to result in a weight loss of 47%.

XRD patterns of $C_{2.5}F$ and the residual materials after the heating are shown in Fig. 2. $C_{2.5}F$ as prepared (A) possesses a 1st stage structure with $I_c = 6.30 \times 10^2$ pm and $a = 2.47 \times 10^2$ pm based on a hexagonal lattice. I_c value was decreased to 5.84×10^2 pm by the heating at 250°C in vacuum for a day (B), while the 1st stage structure was preserved without changing the a-lattice parameter. It is considered that both the release of HF molecules [14] and the rearrangement of fluorine atoms in the graphite galleries cause the decrease of the I_c value. Only the broad peaks ascribed to hexagonal graphite are found in the pattern C for the sample kept at 500°C in vacuum for 2 days, although this material still contains 11.0 wt.% of fluorine. The distance between carbon sheets in this material is 3.52×10^2 pm, being larger than that in the original graphite (3.38×10^2 pm). Peaks of $10l$ diffractions observed at 42–44° are too broad to determine the a-lattice parameter. C 1s XPS spectra of the three samples are shown in Fig. 3. Two peaks ascribed to carbon with and without bonding with fluorine atoms are found at 288.1–4 and 285.3–6 eV, respectively, in the spectra A and B. The ratio of the area of the former to that of the latter decreased by the heat treatment at 250°C, suggesting that the surface of $C_{2.5}F$ partially decomposed. In the final state of the decomposition, only the peak of carbon in the graphite was observed at 284.3 eV for the sample C.

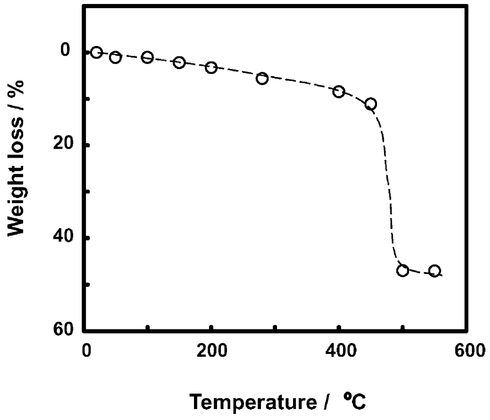

Fig. 1. Dependence of weight loss of the samples on temperature at which $C_{2.5}F$ was kept for 20 h.

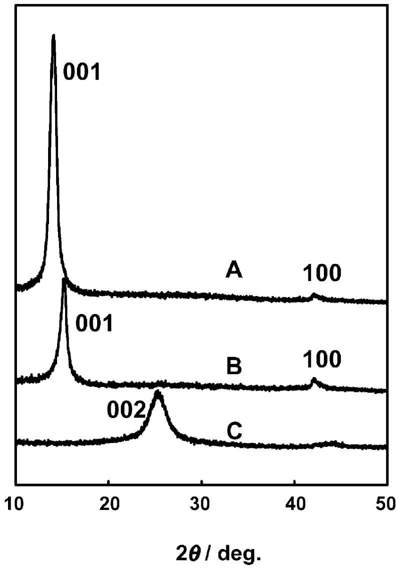

Fig. 2. XRD patterns of graphite fluorides. (A) $C_{2.5}F$ as prepared. After kept in vacuum at (B) 250°C for 1 day, (C) 500°C for 2 days.

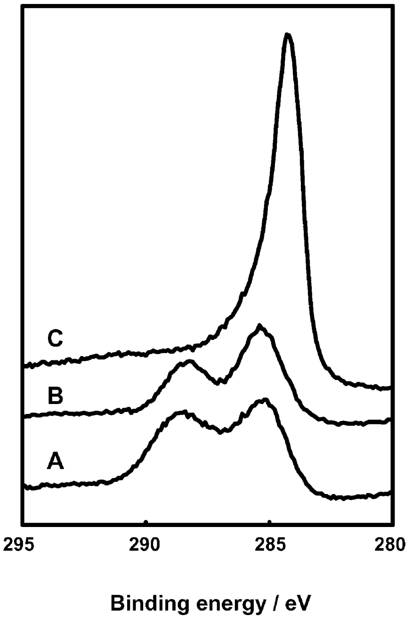

Fig. 3. C 1s XPS spectra of graphite fluorides. (A) $C_{2.5}F$ as prepared. After kept in vacuum at (B) 250°C for 1 day, (C) 500°C for 2 days.

The losses of carbon and fluorine atoms by the decomposition of $C_{2.5}F$ (n_C and n_F/mol per 1 mol $C_{2.5}F$) were estimated by gravimetry and elemental analysis of the residual materials based on the following equations:

$$n_F = \frac{1}{19} \times \left(w_F - \frac{100 - \Delta w}{100} \times w'_F \right) \times \frac{M_0}{100} \tag{2.1}$$

$$n_C = \frac{1}{12.01} \times \left(w_C - \frac{100 - \Delta w}{100} \times w'_C \right) \times \frac{M_0}{100} \tag{2.2}$$

where $w_F^{(')}$ is the fluorine content before (after) the heat treatment (wt.%); $w_C^{(')}$ the carbon content before (after) the heat treatment (wt.%); Δw the weight loss by the heat treatment (%), and M_0 is the formula weight of graphite fluoride ($C_xF(HF)_\delta$) before the heat treatment.

The relation between n_C and n_F is shown in Fig. 4. The slope of the curve ($\Delta n_F/\Delta n_C$) represents the F/C atomic ratio of the evolved gaseous species from the sample which decreases as the decomposition proceeds. The value lower than two at the end of the decomposition suggests that the primary gases at this stage contain unsaturated molecules or intermediates of fluorocarbon with the F/C atomic ratios of two or less. At the beginning of the decomposition ($n_C < 0.15$), most of the intermediate species would immediately react with the remaining graphite fluoride to give gaseous perfluoroalkanes, mainly CF_4. This reaction becomes less likely to occur as the decomposition proceeds, and the reactions of the primary gases by themselves mainly occur on the reactor wall, which will be discussed in the Section 2.3.

2.2. Gaseous products

Gaseous products formed by the decomposition of $C_{2.5}F$ were analyzed by IR spectroscopy. The spectra of the gases evolved from $C_{2.5}F$ below 300°C are shown in Fig. 5. Only the absorption band of HF at 3700–4200 cm^{-1} is observed besides a peak at 1028 cm^{-1} ascribed to contaminating SiF_4 in the spectra A and B. HF contained in $C_{2.5}F$ was almost thoroughly eliminated by evacuation at 200°C for 1 day, and not evolved any more by the subsequent heating at 300°C (spectrum C). It is concluded that small weight loss by the heat treatment below 300°C is mainly caused by the release of HF molecules on the surface and in the graphite galleries of $C_{2.5}F$. On the other hand, weight loss observed above 300°C is due to the evolution of fluorocarbon gases. The spectra of the gases obtained while $C_{2.5}F$ was kept at and above 400°C are shown in Fig. 6(a). Only the peaks ascribed

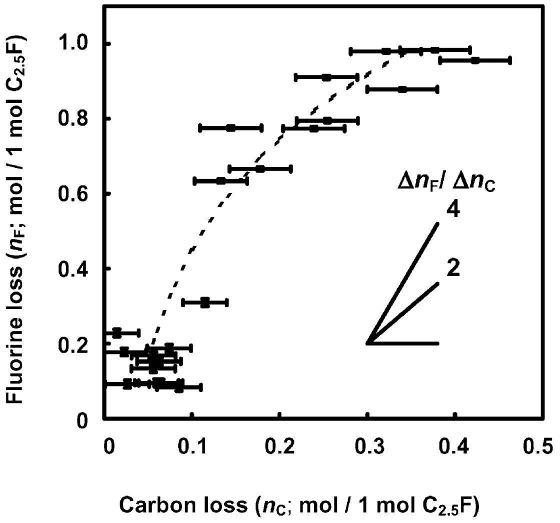

Fig. 4. Relation between the amounts of carbon and fluorine released as the gaseous species by the decomposition of $C_{2.5}F$ at above 400°C.

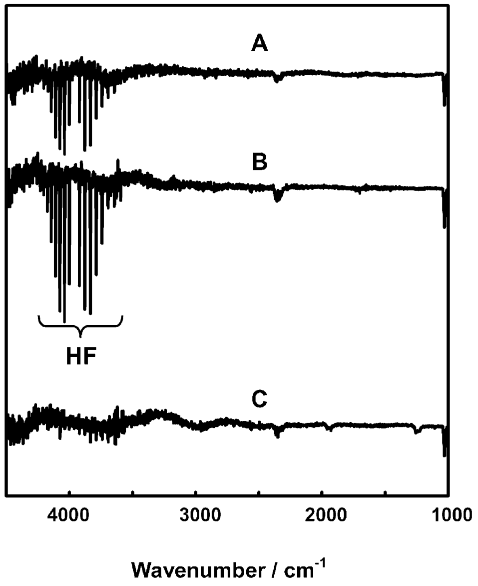

Fig. 5. IR spectra of the gases obtained while $C_{2.5}F$ was kept at (A) 100°C, (B) 200°C, (C) 300°C.

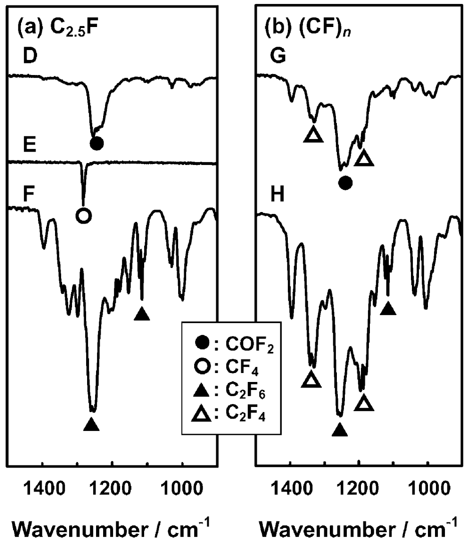

Fig. 6. IR spectra of the gaseous products by the thermal decomposition of $C_{2.5}F$ (a) and $(CF)_n$ (b). Gases were obtained while $C_{2.5}F$ was kept at (D) 400°C, (E) (not trapped) and (F) (trapped): 500°C. Gases were trapped while $(CF)_n$ was kept at (G) 400°C, (H) 500°C.

to COF_2 are found in the spectrum D. The oxygen sources for the formation of COF_2 seem to be the metal oxides on the reactor wall. The pressure in the line was increased by about 1 Pa while $C_{2.5}F$ was kept at 500°C, indicating that some of the evolved gases were not condensable in the U-tube. This gas is identified to be CF_4 from the peak at 1281 cm^{-1} in the spectrum E. On the other hand, C_2F_6 was the dominant species in the gases trapped in the U-tube at liquid nitrogen temperature (spectrum F). Although some peaks found at 1000–1400 cm^{-1} in this spectrum are not ascribed unambiguously, they are supposed to be those of minor fluorocarbons.

Formation of COF_2 suggests that some reactive fluorocarbon gases are evolved by the decomposition of $C_{2.5}F$ at above 300°C. Such intermediates would not be directly detectable by the method performed in the present study, and likely to react immediately to form more stable products such as COF_2 and perfluoroalkanes. By the decomposition of $(CF)_n$ in which every carbon atom is bound to a fluorine atom, $-CF_2CF_2-$ group is easily formed to be evolved as CF_2 and C_2F_4 [4]. C_2F_4 is detected as one of the dominant gaseous products as well as COF_2 and C_2F_6 that seem to be formed by the subsequent reactions of CF_2 or C_2F_4 [4], as shown in Fig. 6(b). On the other hand, only about 40% of carbon atoms in $C_{2.5}F$ are bound with fluorine atoms, therefore $-CF_2CF_2-$ group is less likely to be formed in the decomposition process of $C_{2.5}F$ than in the case of $(CF)_n$. Actually, detectable amount of C_2F_4 is not obtained by the decomposition of $C_{2.5}F$ although it is easily condensable at liquid nitrogen temperature. These suggest that C_2F_4 and other fluorocarbons with higher molecular weights are not the dominant species directly evolved by the decomposition of $C_{2.5}F$. Monomeric CF_2 is the conceivable candidate for the intermediate species. The evolution of atomic fluorine proposed previously [11,12] in the first step of the decomposition is not supported by the results obtained in the present study. It seems more reasonable that fluorocarbon species to be evolved from graphite fluorides are formed by the rearrangement of fluorine atoms only in the graphite galleries followed by the C–C bond cleavage of the graphite layer. Further study mainly on the structures of the residual materials is necessary to prove this mechanism.

2.3. Deposits on the reactor wall

Products formed on the reactor wall by the decomposition of $C_{2.5}F$ at 500°C were recovered, and analyzed by means of XPS and Raman spectroscopy. The surface of nickel plate A (kept at 500°C in the reactor during the decomposition) was covered with a glossy blue-black film while that of plate B (kept at 25°C) seemed unchanged in appearance. C 1s and F 1s XPS spectra of the surfaces of the plates are shown in Fig. 7(a) and (b), respectively. Fluorine was not detected and only a peak of carbon was observed at 284.7 eV in C 1s spectrum on the surface of plate A. This peak is much stronger than that of contaminating carbon atoms observed on the surface of original nickel plate. On the other hand, a strong peak of fluorine covalently bound to carbon was observed at 688.9 eV in F 1s spectrum of plate B. Peaks of carbon in CF, CF_2 and CF_3 groups were found at 289.6, 291.6 and 293.4 eV in C 1s spectrum of the plate, in addition to a peak of carbon unbound to fluorine at 284.7 eV. Raman spectra of the surfaces of the plates are shown in Fig. 8. Some peaks overlapping with each other at 1300–1600 cm^{-1} in the spectrum of the surface of plate A are ascribed to the deposited carbons. On the other hand, a weak peak was observed at around 1100 cm^{-1} for plate B, suggesting the existence of C–F bonds in the deposit. It is concluded that plate A is covered with carbon film while the

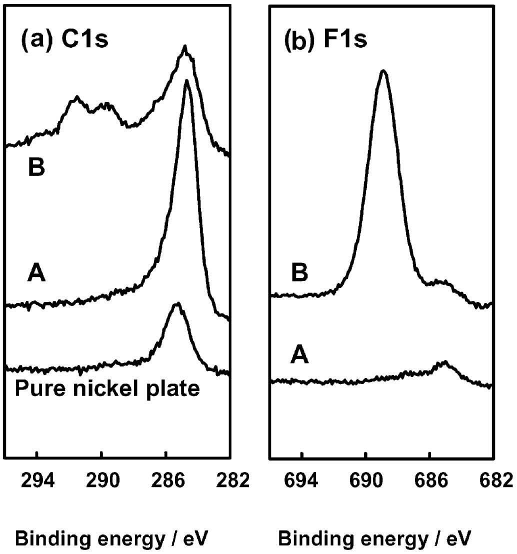

Fig. 7. F 1s and C 1s XPS spectra of the deposits formed on the nickel substrates kept at (A) 500°C, (B) 25°C during the decomposition of $C_{2.5}F$.

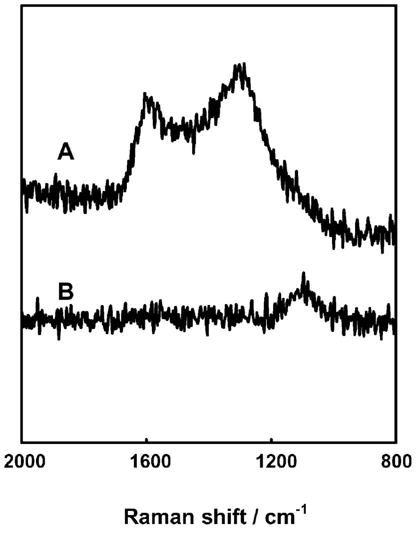

Fig. 8. Raman spectra of the deposits formed on the nickel substrates kept at (A) 500°C, (B) 25°C during the decomposition of $C_{2.5}F$.

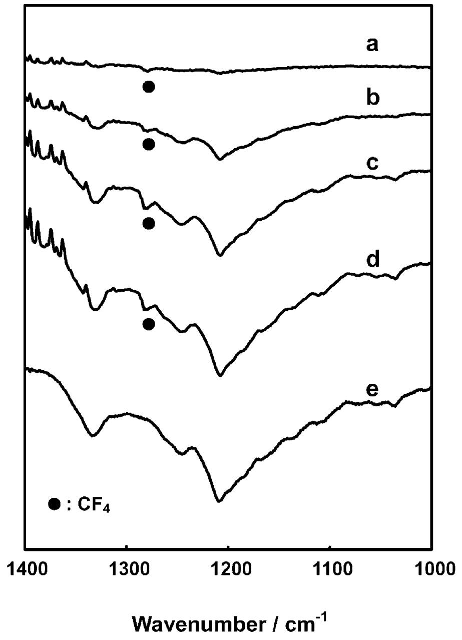

Fig. 9. IR spectra obtained during the decomposition of $C_{2.5}F$ at 500°C in the IR reactor cell. (a) Beginning of the decomposition. After the heating times of (b) an hour, (c) 2 h, (d) 4 h, (e) after the decomposition completed.

deposit on plate B contains fluorine atoms covalently bound to carbon atoms.

IR spectra obtained while $C_{2.5}F$ was kept at 500°C in the IR reactor cell are shown in Fig. 9. Some weak peaks were observed at 1100–1400 cm^{-1}, in addition to that at 1281 cm^{-1} ascribed to gaseous CF_4 (spectrum a). Absorbance at around 1210, 1250 and 1335 cm^{-1} increases with heating time (spectra b–d). These peaks are still observed without decreasing their intensities even after the decomposition of $C_{2.5}F$ is completed under vacuum, while the peak of CF_4 disappeared (spectrum e). These peaks are ascribed to the deposits growing on the windows of the cell as the decomposition proceeds. The C–F covalent bonds in fluorocarbons generally have IR vibration bands in the range of 900–1300 cm^{-1} [15]. It has been reported that polytetrafluoroethylene (PTFE) has three strong IR vibrational modes at around 1155, 1210 and 1240–1254 cm^{-1} [16]. Similar spectra to that of PTFE's have been observed by IR reflection absorption spectroscopy for fluorocarbon polymer films formed on silicon substrates by the reactions of gaseous CF_2 [17]. The peaks found in the spectra a–e also suggest the existence of fluorocarbon groups such as CF_2 in the deposits on the windows of the IR reactor cell.

It is considered that precursors of the deposits discussed above are the gaseous species evolved by the decomposition of $C_{2.5}F$, probably CF_2 as discussed in the Section 2.2. Polymerization of the gases occurs to give the fluorocarbon films on the reactor wall at low temperatures, as well as on the nickel plate B and the windows of the IR reactor cell. On the other hand, the deposition of carbon observed on the plate A suggests the disproportionation of the gases on the reactor wall at high temperatures by which both the gases such as perfluoroalkanes and the solids of carbon are simultaneously formed.

3. Conclusions

Thermal behavior was studied on $C_{2.5}F$ with a 1st stage structure in vacuum. HF molecules remaining in $C_{2.5}F$ are released below 300°C to result in the decrease of I_c. Thermal decomposition of $C_{2.5}F$ drastically proceeds above 450°C. The distance between carbon sheets in the residual material after the decomposition is larger than that in the original graphite by 14 pm. Reactive fluorocarbon gases, main component of which is considered to be CF_2, are evolved by the decomposition of $C_{2.5}F$. Some of the gases immediately react with the remaining graphite fluoride to give CF_4 gas. Disproportionation of the primary gases occurs at high temperatures to form gaseous perfluoroalkanes and solids of carbon, while polymerization of the primary gases at low temperature gives the deposits of fluorocarbon on the reactor wall.

4. Experimental

4.1. Preparation of $C_{2.5}F$

$C_{2.5}F$ was prepared by the reaction of SP-1 graphite powder (Union Carbide, average particle diameter 1×10^2 μm, purity 99.4%) and fluorine gas (Daikin Industries, purity 99.7%) in the presence of liquid AHF (Daikin Industries, purity 98%) at ambient temperature, in the same manner as previously reported [7]. HF and excess fluorine gas were removed by pumping through a chemical trap after the reaction.

4.2. Heat treatments of $C_{2.5}F$

A Monel metal tube was used for a reactor. Prior to the experiments, the inner wall of the tube was fluorinated with 5×10^4 Pa of fluorine gas at 300°C for 1 day. A nickel boat charged with 50–100 mg of $C_{2.5}F$ was placed in the reactor connected to the vacuum line consisted of SUS-316 tubes and joints, as schematically shown in Fig. 10. Samples were kept evacuated at fixed temperatures between 50 and 550°C by an electric furnace. The gaseous products collected in an FEP U-tube cooled by liquid nitrogen were introduced into an IR gas cell with AgCl windows. $(CF)_n$ (Daikin Industries, C/F = 1.05) was also heated in the same manner described above in order to collect the gaseous products by the decomposition.

Products formed on the reactor wall by the decomposition of $C_{2.5}F$ were recovered as follows; pure nickel plates (A and B) were placed in the reactor as substrates so that the products deposit on them. Plate A was placed by the side

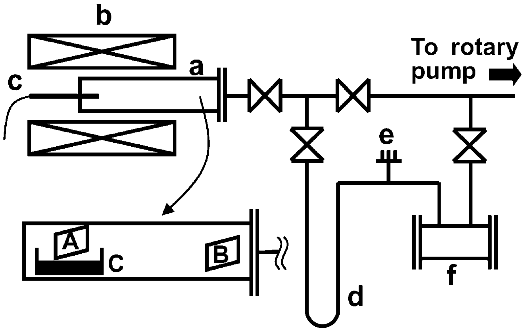

Fig. 10. Schematic diagram of apparatus for the heat treatments of $C_{2.5}F$. (a) Monel tube, (b) electric furnace, (c) thermocouple, (d) U-tube, (e) Pirani gauge, (f) IR gas cell, (A and B) nickel substrates, (C) $C_{2.5}F$ on a nickel boat.

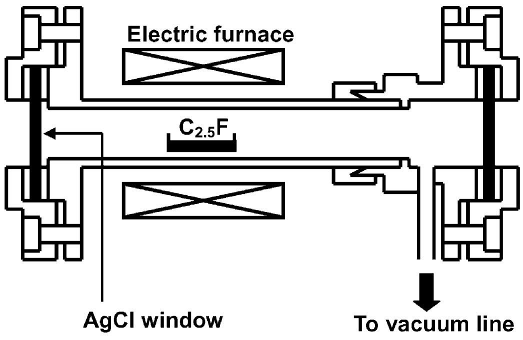

Fig. 11. Schematic diagram of the IR reactor cell.

of $C_{2.5}F$ and heated at 500°C together for 2 days, while plate B was placed near the joint to the line at ambient temperature. An IR reactor cell consisted of a SUS-316 body and AgCl windows was used in order to obtain IR spectra of the deposits (Fig. 11). Prior to the experiments, the inner wall of the cell was fluorinated with 5×10^4 Pa of fluorine gas at ambient temperature for 1 day. About 50 mg of $C_{2.5}F$ on a nickel boat was placed in the cell. The body of the cell was heated at 500°C by an electric furnace, with both edges of the cell being cooled by air to be kept below 200°C. The inside of the cell was continuously evacuated by a rotary pump during the experiment.

4.3. Analyses of the decomposition products

X-ray diffraction (XRD) patterns of graphite fluorides were obtained by a diffractometer using Ni-filtered Cu Kα radiation (JEOL, JDX-8030). The weight change was examined by gravimetry in an argon-purged glove box for each sample after the heat treatment. Elemental analysis of hydrogen, carbon and fluorine were performed at the Laboratory for Organic Elemental Microanalysis of Kyoto University. IR spectra of the gaseous products were obtained by BIO-RAD FTS-155. Raman spectra were obtained by a BIO-RAD FTS-175C spectrometer using Nd:YAG laser (900 mW). The X-ray photoelectron spectroscopy (XPS) measurement was performed by Shimadzu ESCA-3200-01.

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