

Reaction of layered carbon fluorides C_xF ($x = 2.5\text{--}3.6$) and hydrogen

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Abstract

The layered carbon fluorides C_xF ($x = 2.5, 2.8, 3.6$), generally classified as fluorine-graphite intercalation compounds, were heat-treated in hydrogen gas. These fluorides are more reactive with hydrogen compared to $(CF)_n$ and $(C_2F)_n$. Reduction of C_xF to graphite-like carbon starts at about 573 K, and proceeds gradually along with the elevation of temperature. Fluorine atoms in C_xF are eliminated as HF in the reduction process without being substituted by hydrogen atoms. Systematic difference was not found in the average crystallite sizes of the carbon material prepared from C_xF by the reduction with hydrogen and that by the pyrolysis in vacuum. On the other hand, interlayer distance and fluorine content of the former are smaller than those of the latter. In the case that the C_xF precursor maintains a large particle size, the reduced carbon as well as the pyrolytically prepared carbon possesses a foam-like shape due to the exfoliation during the heat treatment.

Keywords: A. Chemically modified carbons, exfoliated graphite; B. intercalation; C. Scanning electron microscopy; D. Microstructure

1. Introduction

The layered carbon–fluorine binary compounds have some varieties as shown in Fig. 1. Poly(carbon monofluoride) $((CF)_n$, Fig. 1a) possesses perfluorinated carbon sheets based on the trans-linked cyclohexane chairs [1], which is prepared by the fluorination of graphite at 723 to 873 K. Poly(dicarbon monofluoride) $((C_2F)_n$, Fig. 1b) is formed only by direct fluorination of crystalline graphite at around 673 K. Only one side of each carbon sheet in this compound is fluorinated, and the adjacent sheets are connected by C–C bonds on the sides not fluorinated to form a diamond-like structure [1]. C_xF (Fig. 1c), which is usually classified as “fluorine–graphite intercalation compound” (fluorine–GIC), is also a layered carbon fluoride prepared by room-temperature fluorination of graphite in the presence of fluoroacid molecules such as HF. Each fluorine atom in this compound is attached to the sp^3 hybridized carbon atom like the former two types of layered carbon fluorides, but sp^2 carbon atoms remain in the sheet to form C=C double bonds [2].

The C–F bond nature in C_xF is essentially covalent [2,3], but the bond length (about 0.140 nm [2]) is a little longer than those in $(CF)_n$ and $(C_2F)_n$ (0.136 nm [1]). The difference in the C–F bond order should affect the thermal and chemical stabilities of

these fluorides. Actually, it has been found that the bulk of stage-1 C_xF prepared from crystalline graphite decomposes to fluorocarbon gases and reduced carbon at 773 K in vacuum [4–8], while $(CF)_n$ and $(C_2F)_n$ obtained from similar graphite materials are thermally stable at the temperature up to 873 K [9–12]. The average crystallite size along the c -axis of the pyrolytically prepared carbon (L_c ; 4–5 nm [8,13–15]) is almost independent of the type of the precursor fluorides, but the graphite-like stacking order of graphene sheets is maintained only in the materials derived from C_xF [8].

Chemical reactivity of layered carbon fluorides is quite limited by the covalent character of the C–F bonds, and only a few reactions involving these compounds have been reported besides the refluorination of C_xF using elemental fluorine [16,17]. Giraudet et al. have reported that both stage-1 C_xF and $(CF)_n$ are reduced to carbon by KOH at 373 K [18], and the reduction of $(CF)_n$ and $(C_2F)_n$ have also been attained by Watanabe et al. using hydrogen gas above 673 K [19,20]. However, the reactivity of C_xF against hydrogen has never been systematically investigated so far.

In the present study, the reactions of stage-1 C_xF having different C/F atomic ratios ($x = 2.5, 2.8, 3.6$) and hydrogen gas were examined for further understanding of their chemical reactivity, and compared to the reduction processes of $(CF)_n$ and $(C_2F)_n$. The differences in the reaction mechanisms between reduction with hydrogen and

pyrolysis in vacuum are discussed, based on the crystallinity and morphology of the carbon materials derived from these layered carbon fluorides.

2. Experimental

2.1, *Sample preparation*

Graphite powder (Union Carbide, SP-1 grade, purity 99.4 %, average particle diameter 0.1 mm) and elemental fluorine (Daikin Industries, purity 99.7 %) were used for the syntheses of the layered carbon fluorides. Three samples of stage-1 C_xF with different C/F atomic ratios ($x = 2.5, 2.8, 3.6$) were obtained by the room-temperature reactions of graphite powder with elemental fluorine of about 0.2 MPa in the presence of HF (Daikin Industries, purity 98 %). HF was supplied as liquid for the preparation of $C_{2.5}F$, or as saturated vapor for $C_{2.8}F$ and $C_{3.6}F$. After the fluorination, co-intercalated HF molecules in these C_xF samples were eliminated by continuous evacuation at 523 K. Details of these preparative methods are described elsewhere [2,21]. In order to obtain well-crystallized $(CF)_n$ at relatively low temperature, the carbon material prepared by the pyrolysis of stage-1 $C_{2.5}F$ at 873 K in vacuum was used as a precursor. Re-fluorination of this carbon host by fluorine gas of about 0.1 MPa was performed at 773 K in the same manner as has been described elsewhere [22]. $(C_2F)_n$ was obtained by direct fluorination of SP-1 graphite with elemental fluorine of about 0.1 MPa at 673 K

in a nickel reaction tube.

Apparatus for the reactions of the layered carbon fluorides and hydrogen gas is schematically illustrated in Fig. 2. Each fluoride sample (50–100 mg) charged in a nickel boat was placed in the reactor tube (SUS316 stainless steel) connected to the vacuum line. Inside of the reactor was once evacuated, and then hydrogen gas of 0.10 MPa (Air Liquide Japan, purity >99.9999 %) was introduced into it at room temperature. The reactor was kept at a fixed temperature by an electric furnace overnight, and then cooled down to room temperature. The PFA (perfluoro-alkoxyalkane) U-tube connected to the reactor was cooled by liquid nitrogen in order to collect the condensable gases. The gases remaining in the reactor after the sampling for infrared (IR) analyses (see Section 2.2) were evacuated through the vacuum line.

Pyrolysis of the layered carbon fluoride charged in a nickel boat was performed in a SUS316 reactor under continuous evacuation.

2.2. Analysis

Elemental analyses of hydrogen, carbon and fluorine were performed at the

Center for Organic Elemental Microanalysis of Kyoto University. IR spectra of the gases evolved by the reaction of the layered carbon fluorides and hydrogen were obtained by BIO-RAD FTS-155. Both the gases condensed in the U-tube and that remaining in the reactor were introduced into the IR gas cell having a SUS-316 body and a pair of AgCl single crystal windows (See Fig. 2). IR analyses of powder samples were performed by sandwiching them between a pair of AgCl single crystal windows. X-ray diffraction (XRD) patterns were obtained by a diffractometer (Rigaku, MultiFlex) with $\text{CuK}\alpha$ radiation. The average crystallite size (L) was estimated using Scherrer's equation (1);

$$L = \frac{K\lambda}{B \cos \theta} \quad (1)$$

where K , λ , B , θ denote the Scherrer constant, the wavelength of $\text{CuK}\alpha$ beam, the corrected half width of a diffraction peak and the Bragg angle, respectively. The K value of 1.0 was used for (002) and (110) reflections from graphitic carbon while that of 1.84 was used for the (10) reflection from the two-dimensional lattices stacked randomly [23]. The X-ray photoelectron spectroscopy (XPS) was performed by means of Shimadzu ESCA-3200-01 with $\text{MgK}\alpha$ radiation for the samples fixed on indium sheets

(Nilaco, purity 99.99 %). Scanning electron microscopy (SEM) images were obtained using Hitachi S-2600H with a low acceleration voltage of 5 kV.

3. Results and discussion

3.1. Reaction of stage-1 $C_{2.5}F$ and hydrogen

Figure 3 shows the weight losses of stage-1 $C_{2.5}F$ by the reaction with hydrogen gas in comparison with those by the heat treatment overnight in vacuum [7] at fixed temperatures. The pyrolysis in vacuum of $C_{2.5}F$ proceeds slowly below 623 K, and drastically above 773 K [7]. On the other hand, $C_{2.5}F$ is reduced by hydrogen at lower temperatures than pyrolysis in vacuum. The reduction begins at about 573 K, and proceeds gradually along with the elevation of the temperature. The weight reduction temperature of 573 K is a little lower than those of $(CF)_n$ and $(C_2F)_n$ [19,20]. Above 773 K, the weight loss of the samples reduced by hydrogen is about 39 wt. % that almost coincides with the value of fluorine content of the pristine $C_{2.5}F$ (38 wt. %) and lower than the weight loss by pyrolysis in vacuum (47 wt. %). Hydrogen was not detected in the reduced carbon materials derived from $C_{2.5}F$ by elemental analysis, suggesting that the substitution of fluorine and hydrogen atoms does not occur during the reduction.

The IR spectra of the gaseous products evolved by the reaction of $C_{2.5}F$ with hydrogen are shown in Fig. 4. The absorption band of HF is found at 3700–4200 cm^{-1} in

all the spectra of the trapped gases (A', B' and C'). Additionally, small amount of fluorocarbon species (C_2F_6 , CF_4 , etc.) are evolved at 673 and 773 K, giving some peaks at 1000–1400 cm^{-1} in the spectra of the gases trapped (B', C') and untrapped (B, C) at liq. N_2 temperature. These fluorocarbon gases are also evolved by the heat treatment of $C_{2.5}F$ in vacuum at 673 and 773 K [7]. Both the reduction and pyrolysis of $C_{2.5}F$ seem to occur at the same time above 673 K in hydrogen gas, while the contribution of the latter to the decomposition is much smaller than that of the former as suggested by the weight loss described above. HF is concluded to be preferentially evolved during the heat treatment of $C_{2.5}F$ in hydrogen gas.

The XRD patterns of stage-1 $C_{2.5}F$ before and after the reduction with hydrogen are shown in Fig. 5. A broad peak ascribed to the (002) diffraction line of the carbon phase appears at around 25° (C), and becomes stronger as the reduction proceeds, shifting to a higher angle (D, E). On the other hand, the (001) diffraction peak from the remaining C_xF domains is attenuated as the reduction proceeds, shifting to a little higher angle (B, C). Such a peak shift is not observed for the thermal decomposition of stage-1 $C_{2.5}F$ in vacuum [8]. The fluorine content of the remaining C_xF domains is gradually decreased by the elimination of fluorine atoms as HF during the reduction with hydrogen, resulting in the decrease of interlayer distance.

The C1s XPS spectra of stage-1 C_{2.5}F before and after the reduction with hydrogen are shown in Fig. 6. Two peaks found at around 288 eV and 285 eV in the spectrum of the original C_{2.5}F (A) are ascribed to carbon atoms bound and unbound to fluorine atoms, respectively [24,25]. The former peak attenuates after the reduction at 623 K (B), and almost disappears after the reduction at and above 673 K (C and D, respectively). The peak ascribed to carbon atoms unbound to fluorine atoms shifts to lower binding energy of around 284 eV after the reduction, corresponding to the increase of graphitic carbon domains (B, C, D).

IR spectra shown in Fig. 7 also verify the elimination of fluorine atoms from C_{2.5}F by the reduction with hydrogen. Three strong absorption bands are found at around 1565, 1220 and 1100 cm⁻¹ in the spectrum of original C_{2.5}F (A). The former two bands are assigned to vibrational modes of carbon sheets in the HF-free C_xF compound [21], while the latter is ascribed to the stretching mode of C–F bonds [21,26,27]. These peaks are attenuated without changing their positions as the C_xF domains in the sample are decreased by the reduction at 573 K (B). The reduced carbon obtained at 673 K gives no absorption peak in the spectrum (C).

3.2. Crystallinity and morphology of the reduced carbon materials from C_xF

The spectroscopic and XRD analyses for the reduced carbon materials prepared from $C_{2.8}F$ and $C_{3.6}F$ indicate that the structural changes occurring in these compounds during the reaction with hydrogen are essentially the same with those for $C_{2.5}F$ described in Section 3.1. The interlayer distances (d_{002}), L_c , L_a (the average crystallite size along the a -axis) and fluorine contents of the carbon materials prepared from the layered carbon fluorides are listed in Table 1. Regardless of the precursor fluorides and reaction conditions, the averaged crystallite sizes of the residual carbon materials are not systematically changed. On the other hand, the samples reduced with hydrogen possess the d_{002} values in the range of 0.342–0.346 nm that are a little smaller than those for the pyrolytically prepared carbon materials. The fluorine contents of the samples reduced with hydrogen are smaller than those thermally decomposed in vacuum in spite of much lower reaction temperatures.

Although the crystallinity of the carbon materials derived from C_xF is not significantly changed as described above, SEM analysis shows that these materials exhibit a variety in their morphology. Figure 8 shows the images of $C_{2.8}F$ before and after the heat treatments in comparison with the particle shape and size of the original

graphite. The original shape and particle size (about 0.1 mm) of graphite (A-0) are almost unchanged by the room-temperature fluorination in the gaseous mixture of fluorine and HF to prepare the $C_{2.8}F$ sample (A-1). Each particle in this $C_{2.8}F$ sample is remarkably exfoliated during the pyrolysis at 873 K in vacuum, giving a spongy, foam-like carbon material (A-2). About a half of the particles in the $C_{2.8}F$ sample are also exfoliated during the reduction with hydrogen (A-3), but the degree of exfoliation is smaller than that of A-2. It is known that the exfoliation of graphite sheets is generally caused by the vaporization of the intercalated species which increases the internal pressure [28,29]. From the difference in the degree of exfoliation between A-2 and A-3, evolution of fluorocarbon gases during pyrolysis in vacuum at 873 K is considered to occur more rapidly than that of HF during the reduction with hydrogen at 673 K. The reduction by hydrogen occurs from the surface of the $C_{2.8}F$ particles, and proceeds slowly under the control of the hydrogen diffusion in the gallery.

The SEM images of $C_{2.5}F$ before and after the heat treatments are shown in Fig. 9. Fluorination of graphite in liquid HF to obtain $C_{2.5}F$ proceeds more drastically than the reaction in gaseous HF to prepare $C_{2.8}F$, resulting in the pulverization of the particles (B-1). Small particles of $C_{2.5}F$ thus obtained are no longer exfoliated either by the pyrolysis at 873 K in vacuum (B-2) or by the reduction with hydrogen at 673 K (B-3). It

is suggested that the evolved gases such as fluorocarbon species and HF inside these small particles are easily discharged before the internal pressure becomes high enough for exfoliation.

4. Conclusion

The layered carbon fluorides C_xF ($x = 2.5, 2.8, 3.6$) were heat-treated in hydrogen gas of 0.1 MPa at fixed temperatures between 473 and 773 K. These fluorides are a little more reactive with hydrogen than $(CF)_n$ and $(C_2F)_n$. Reduction of C_xF to graphite-like carbon starts at about 573 K, and proceeds gradually along with the elevation of temperature. Fluorine atoms in C_xF are not substituted by hydrogen atoms but eliminated as HF gas in the reduction process. Systematic difference was not found in the average crystallite sizes of the carbon materials prepared from C_xF by reduction with hydrogen and that by the pyrolysis in vacuum. On the other hand, interlayer distance and fluorine content of the former material are smaller than those of the latter.

The particle shape of original graphite host is almost maintained in $C_{2.8}F$. The exfoliated carbon materials are prepared from this compound both by the reduction with hydrogen and by the pyrolysis in vacuum. Such exfoliation does not occur during the heat treatment of the pulverized particles of $C_{2.5}F$ from which the evolved gases such as HF and fluorocarbon species are easily discharged.

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Figure captions

Fig. 1. Structures of monolayers in the layered carbon fluorides [1,2]; $(CF)_n$ (a), $(C_2F)_n$ (b) and stage-1 C_xF (c).

Fig. 2. Apparatus for the reactions of the layered carbon fluorides and hydrogen gas.

Fig. 3. Temperature dependences of weight loss observed for stage-1 $C_{2.5}F$ in hydrogen gas (closed circle) and in vacuum (open circle [7]).

Fig. 4. (a) IR spectra of the gases evolved during the reduction of stage-1 $C_{2.5}F$ with hydrogen at 623 (A), 673 (B) and 773 K (C) and untrapped at liq. N_2 temperature. (b) IR spectra of the gases evolved during the reduction of stage-1 $C_{2.5}F$ with hydrogen at 623 (A'), 673 (B') and 773 K (C') and trapped at liq. N_2 temperature.

Fig. 5. XRD patterns of stage-1 $C_{2.5}F$ as prepared (A), after reduced with hydrogen at 573 (B), 623 (C), 673 (D) and 773 K (E).

Fig. 6. C1s XPS spectra of stage-1 $C_{2.5}F$ as prepared (A), after reduced with hydrogen at 623 (B), 673 (C) and 773 K (D).

Fig. 7. IR spectra of stage-1 $C_{2.5}F$ as prepared (A), after reduced with hydrogen at 573 K (B) and 673 K (C).

Fig. 8. SEM images of original SP-1 graphite (A-0), stage-1 $C_{2.8}F$ as prepared (A-1), after pyrolysis in vacuum at 873 K (A-2) and after reduction with hydrogen at 673 K (A-3).

Fig. 9. SEM images of stage-1 $C_{2.5}F$ as prepared (B-1), after pyrolysis in vacuum at 873 K (B-2) and after reduction with hydrogen at 673 K (B-3).

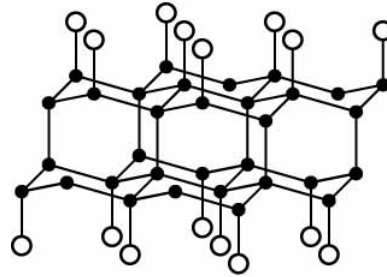
Table 1

Interlayer distances (d_{002}), average crystallite sizes along the c - and a -axes (L_c and L_a , respectively) and fluorine contents of the carbon materials prepared from layered carbon fluorides

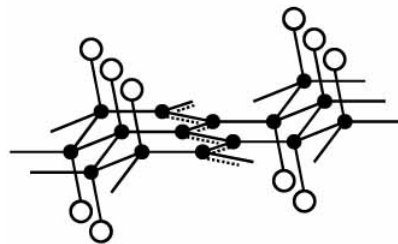
Precursor (d_{001} / nm)	Heat treatment		d_{002} (nm)	L_c (nm)	L_a (nm)	Fluorine (wt. %)
	Atmosphere	Temp. (K)				
C _{2.5} F (0.574)	Vacuum	873	0.346	5.4	59	11.9
	H ₂	673	0.343	5.1	36	9.7
C _{2.8} F (0.559)	Vacuum	873	0.349	5.5	33	16.7
	H ₂	673	0.342	4.2	44	6.3
C _{3.6} F (0.520)	Vacuum	873	0.346	6.0	34	12.6
	H ₂	673	0.342	4.1	67	6.8
(CF) _n (0.641)	H ₂	723	0.346	3.8	21	3.4
(C ₂ F) _n (0.872)	H ₂	673	0.346	5.6	31	4.2
SP-1 graphite	—	—	0.335	> 100	> 100	0



(a) $(CF)_n$



(b) $(C_2F)_n$



(c) Stage-1 C_xF

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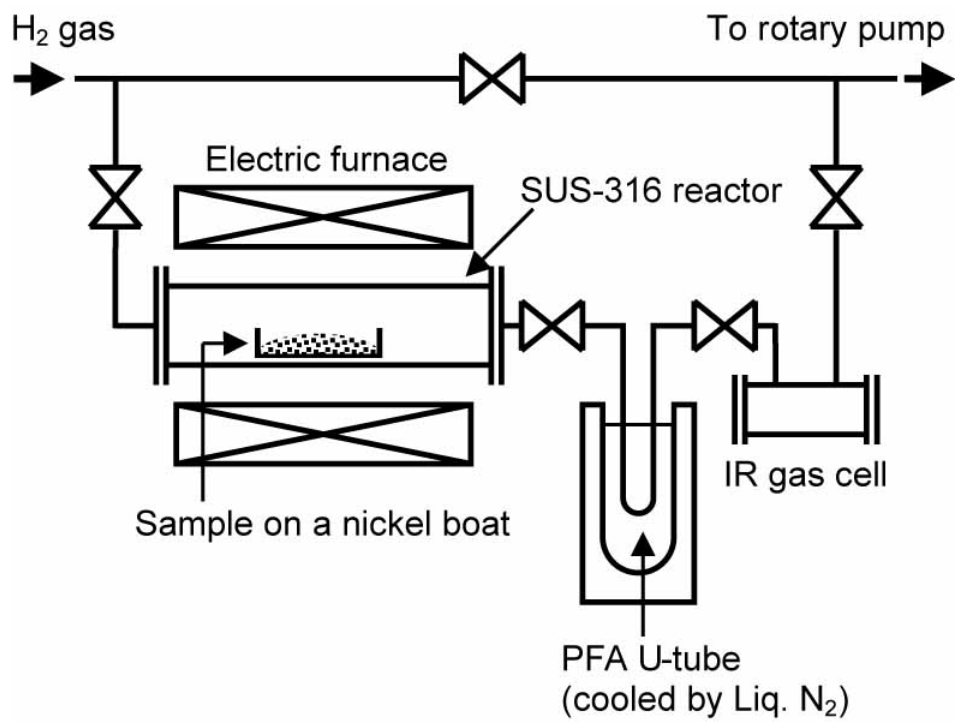


Fig. 2. Apparatus for the reactions of the layered carbon fluorides and hydrogen gas.

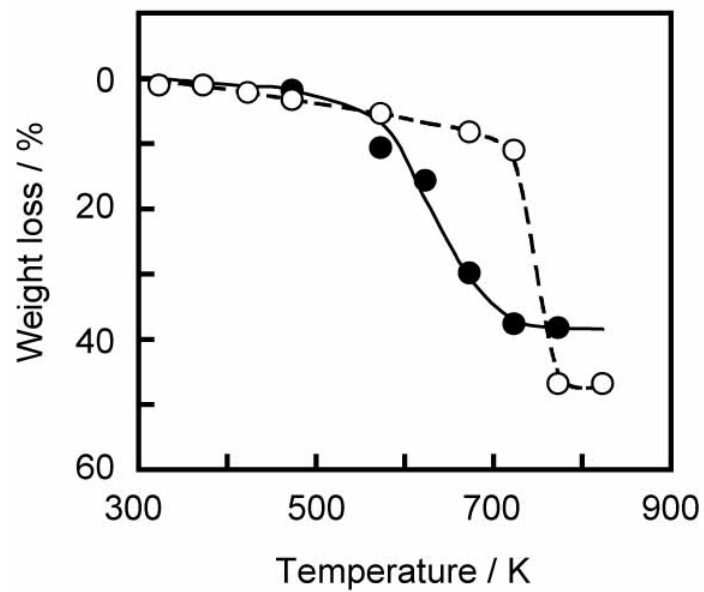


Fig. 3. Temperature dependences of weight loss observed for stage-1 $C_{2.5}F$ in hydrogen gas (closed circle) and in vacuum (open circle [7]).

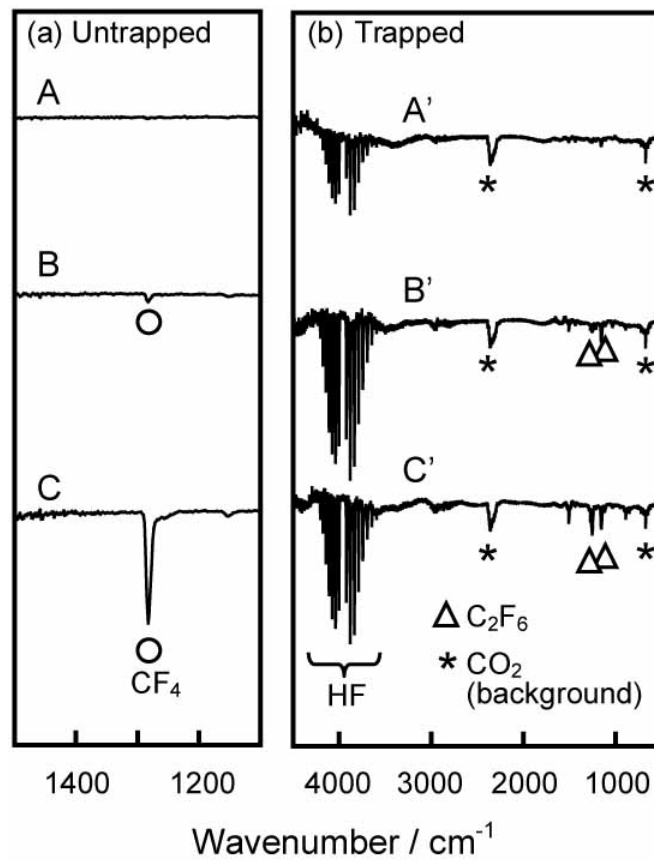


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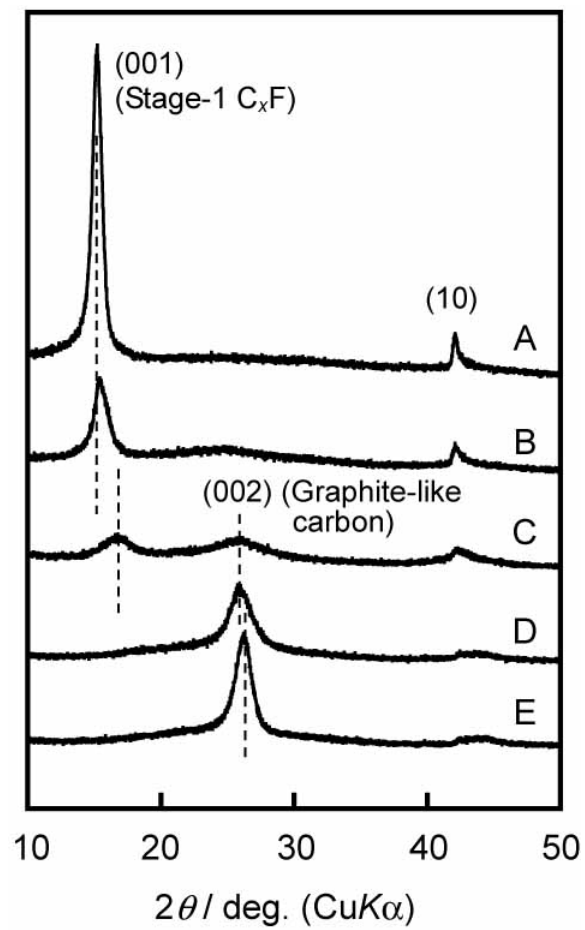


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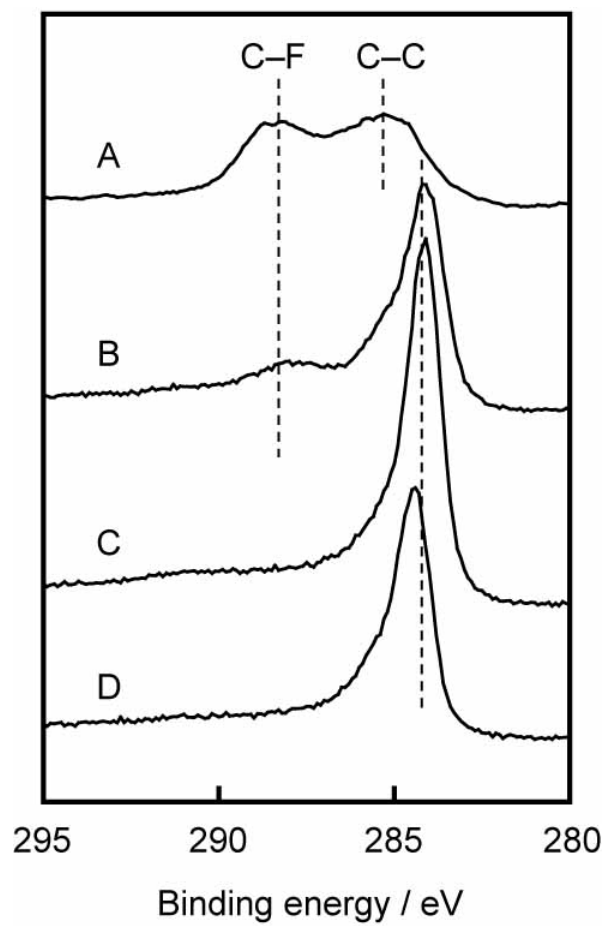


Fig. 6. C1s XPS spectra of stage-1 $C_{2.5}F$ as prepared (A), after reduced with hydrogen at 623 (B), 673 (C) and 773 K (D).

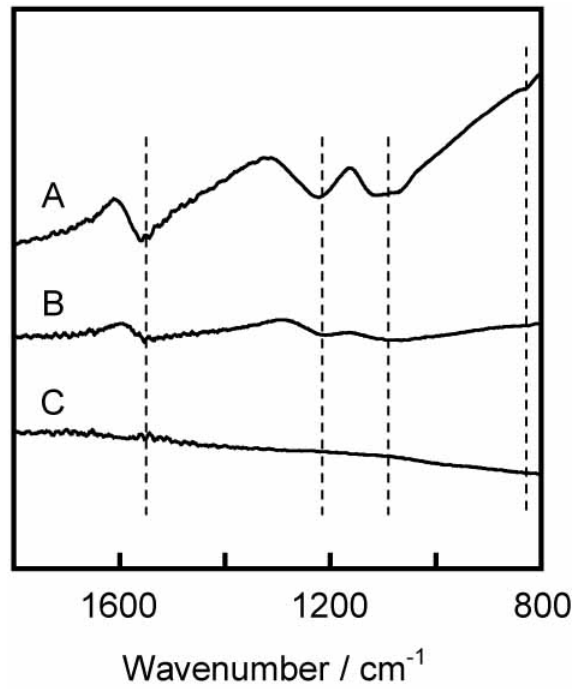


Fig. 7. IR spectra of stage-1 $C_{2.5}F$ as prepared (A), after reduced with hydrogen at 573 K (B) and 673 K (C).

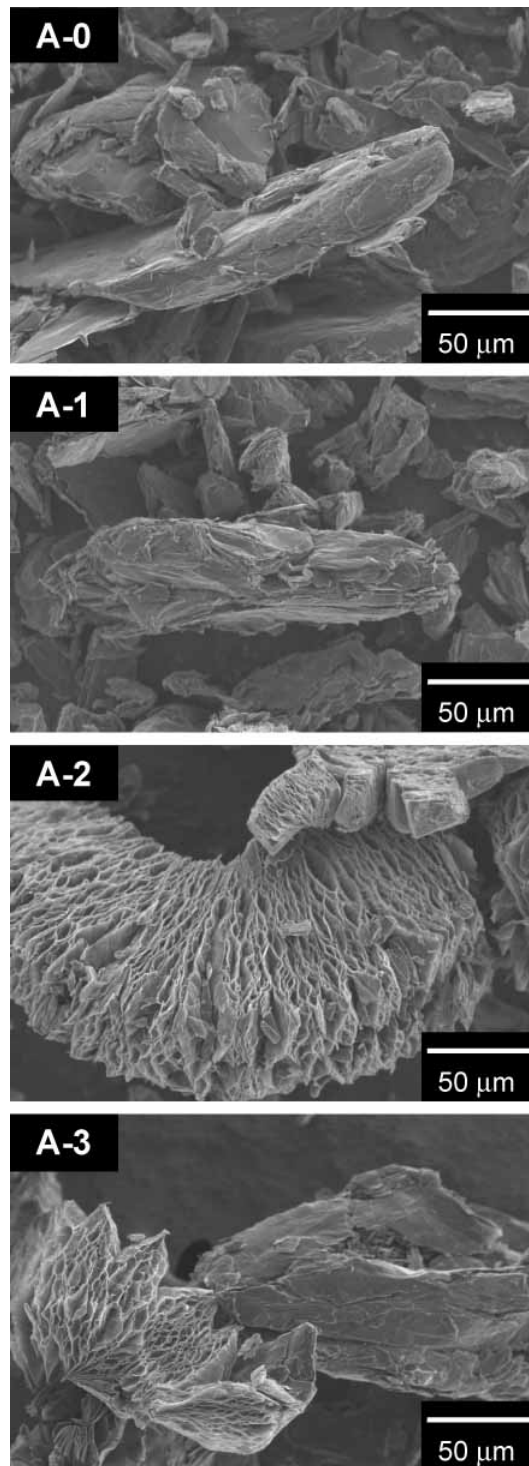


Fig. 8. SEM images of SP-1 graphite (A-0), stage-1 $C_{2.8}F$ as prepared (A-1), after pyrolysis in vacuum at 873 K (A-2) and after reduction with hydrogen at 673 K (A-3).

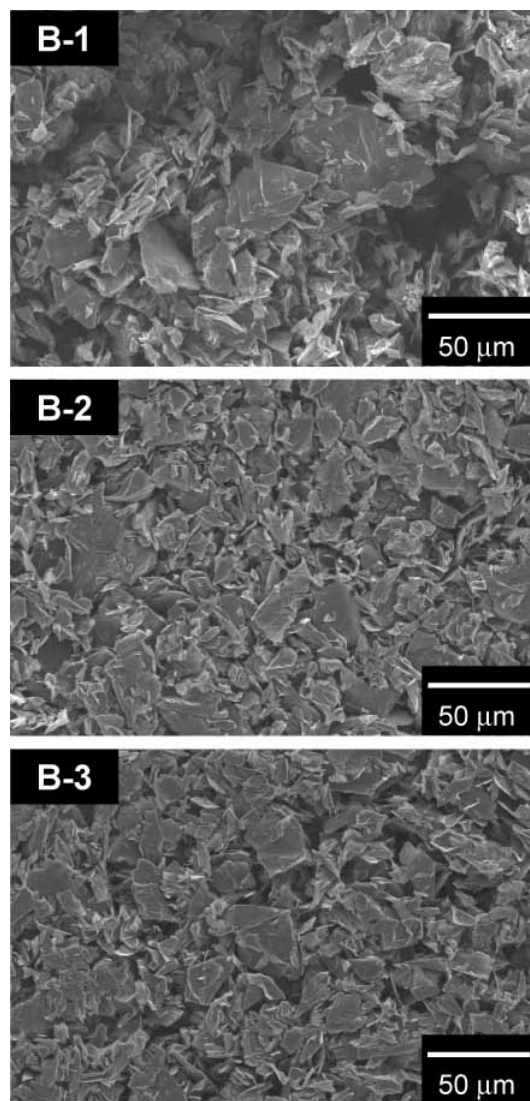


Fig. 9. SEM images of stage-1 $C_{25}F$ as prepared (B-1), after pyrolysis in vacuum at 873 K (B-2) and after reduction with hydrogen at 673 K (B-3).