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Preparation of Poly(dicarbon monofluoride) from Petroleum Coke

Nobuatsu Watanabe,* Yoshinori Ashida, and Tsuyoshi Nakajima
Department of Industrial Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606

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Graphite fluoride containing more than 60% poly(dicarbon monofluoride) $(C_2F)_n$ was prepared from petroleum coke heat-treated at 2700 °C at a temperature between 337 and 460 °C. The interlayer spacings and F/C ratios of these graphite fluorides were in the ranges of 0.82—0.74 nm and 0.58—0.68, respectively. The $(C_2F)_n$ content in graphite fluoride also increased with increasing fluorine pressure.

During the studies on the chemical composition and crystal structure of graphite fluoride,[1] a new compound, poly(dicarbon monofluoride) represented by the formula $(C_2F)_n$ has been found. The $(C_2F)_n$ is formed at a low temperature between 350 and 400 °C from a carbon material with high crystallinity such as natural graphite. Various kinds of artificial carbon materials are generally used in the industrial field. In most cases, these carbons are amorphous, having much smaller crystallites than natural graphite; however, the growing of small crystallites is attained by heat treatment at 2600—2800 °C. In this study, the preparation of $(C_2F)_n$ is attempted from petroleum coke heat-treated at high temperatures.

Experimental

The starting carbon material was petroleum coke (GL coke) of less than 46 μm, heated-treated at temperatures between 1500 and 2700 °C in a graphitization furnace. Structural parameters of these carbon materials are listed in Table 1. With increasing heat treatment temperature, the parameter indicating the interlayer spacing, $C_0(004)$ decreased from 0.690 to 0.672 nm while those indicating the crystallite size, L_c and L_a, increased very much. Half of C_0 (004) length is the distance between two carbon network layers. Fluorination of petroleum coke was made at temperatures of 330—590 °C using an automatic thermobalance specially designed for fluorine atmosphere.[2] Fluorination reaction was continued until no weight increase was observed, and the products were analyzed by elemental analysis and X-ray diffractometry.

Results and Discussion

Figure 1 is an example of the change in (001) X-ray diffraction patterns of graphite fluoride prepared from petroleum coke heat-treated at 2700 °C. The peak position shifted from 14.5° to 10.8° in 2θ (by Cu $K\alpha$) with decreasing reaction temperature. It is known that $(C_2F)_n$ is preferentially formed at temperatures of 350—400 °C from a carbon material having a large crystallite size like natural graphite and its (001) diffraction line appears at 10—11° in 2θ, whereas that for $(CF)_n$ is situated around 14—15°.[1] Figure 1 indicates that $(C_2F)_n$ is formed mainly below 400 °C, however, the peak profile of the product prepared at 337 °C is broader than that of the product prepared at 590 °C, probably because of the simultaneous formation of a small amount of $(CF)_n$. But only a slight change of the peak positions was observed for graphite fluoride prepared from the sample heat-treated at 1500 °C. Even in the reaction at low temperatures such as 330 °C, a product with the peak position much higher than 10° in 2θ was prepared, as shown in Fig. 2. This result shows no formation of $(C_2F)_n$ from this petroleum coke under any

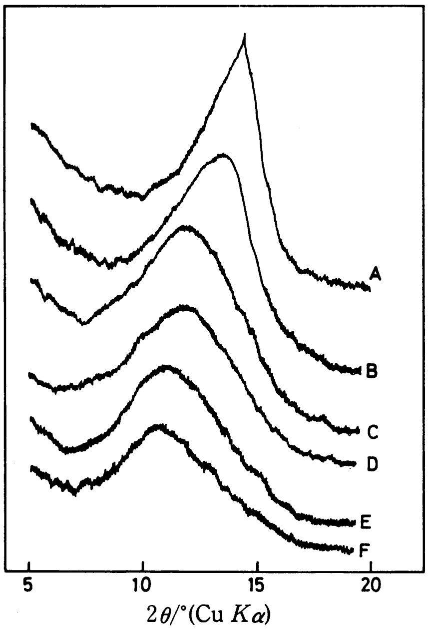

Fig. 1. (001) X-Ray diffraction patterns of graphite fluoride prepared from petroleum coke (PC 2700 °C). Reaction temperature: A: 590 °C, B: 550 °C, C: 467 °C; D: 426 °C; E: 370 °C, F: 337 °C.

Table 1. Structural parameters of heat-treated petroleum cokes (PC) used as starting materials

Materials	$C_0(004)$/nm	$L_c(002)$/nm	$L_c(004)$/nm	$L_c(112)$/nm	$L_a(110)$/nm
PC 2700°C[a)]	0.6722	>100	52	5.5	>100
PC 2300°C	0.6732	79	33	3.3	>100
PC 2100°C	0.6756	56	25	1.6	100
PC 1860°C	0.6770	39	22	1.2	74
PC 1500°C	0.6848	13	7	—	4.8
Original	0.6900	3.6	1.9	—	2.8

a) Heat treatment temperature.

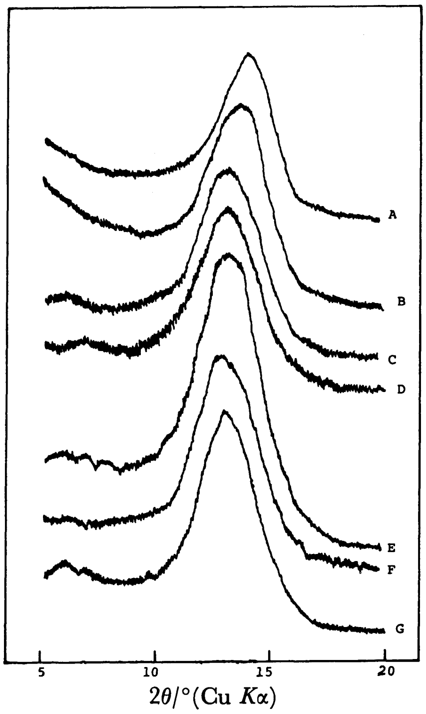

Fig. 2. X-Ray diffraction patterns of graphite fluoride prepared from petroleum coke (PC 1500 °C). Reaction temperature: A: 590 °C, B: 550 °C, C: 460 °C, D: 410 °C, E: 370 °C, F: 350 °C, G: 330 °C.

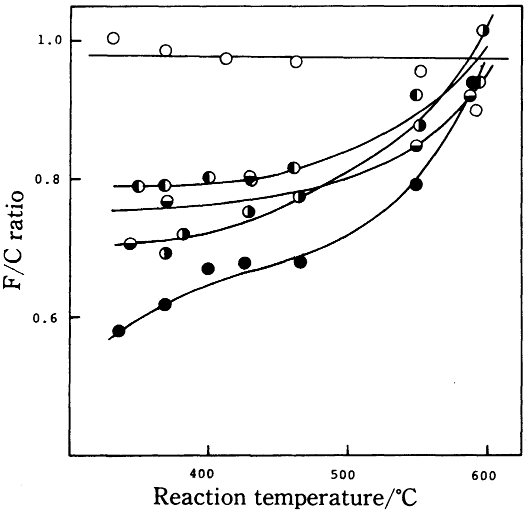

Fig 3. Dependence of F/C ratio of graphite fluoride on reaction temperature.
●: PC 2700 °C, ◑: PC 2300 °C, ◒: PC 2100 °C, ◐: PC 1860 °C, ○: PC 1500 °C.

conditions.

As already reported,[1] since $(CF)_n$ is formed even at low temperatures between 400 and 350 °C from a carbon material with low crystallinity or at a disordered place such as surface of a carbon particle, it is very difficult to obtain pure $(C_2F)_n$ from the artificial carbon materials. The $(C_2F)_n$ content in a product is estimated from the F/C ratio of the product by assuming only $(CF)_n$ as an impurity. By representing the amounts of $(C_2F)_n$ and $(CF)_n$ as X and $1\text{-}X$, respectively, F/C ratio is related with X by the equation $F/C = 1 - 0.5X$. However, as graphite fluoride has CF_2 and CF_3 groups on the surface, the actual content is expected to become slightly higher than the value calculated by the above equation. From Fig. 3, graphite fluoride containing $(C_2F)_n$ by more than 60% is obtained from petroleum coke heat-treated at 2700 °C, that is: at 337—380 °C, $(C_2F)_n$: 70—80% and at 380—460 °C, $(C_2F)_n$: 60—70%. The sample heat-treated at 2300 °C gives graphite fluoride with $(C_2F)_n$ content of about 50% at 350—430 °C. Graphite fluorides prepared from petroleum coke heat-treated at 2100 and 1860 °C contain only about 40—50% $(C_2F)_n$ and only $(CF)_n$ is prepared at any temperature from

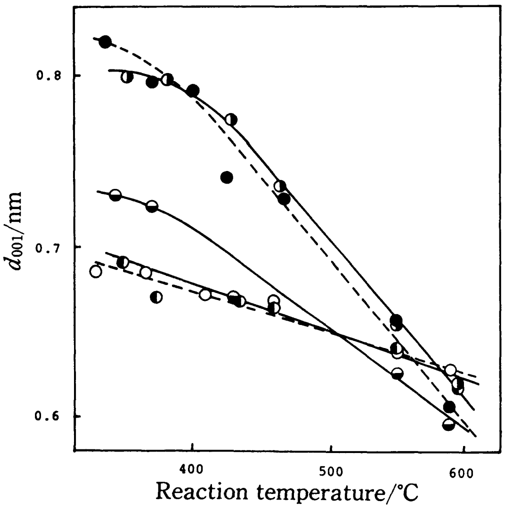

Fig. 4. Change in the interlayer spacings of graphite fluoride as a function of reaction temperature.
●: PC 2700 °C, ◑: PC 2300 °C, ◒: PC 2100 °C, ◐: PC 1860 °C, ○: PC 1500 °C.

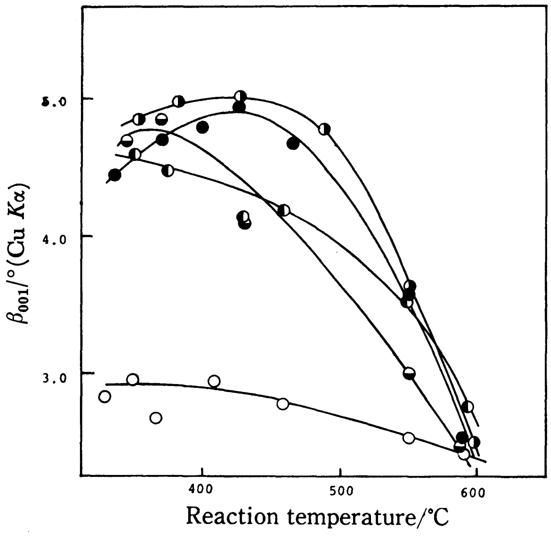

Fig. 5. Change in the half widths of (001) line of graphite fluoride as a function of reaction temperature.
●: PC 2700 °C, ◑: PC 2300 °C, ◒: PC 2100 °C, ◐: PC 1860 °C, ○: PC 1500 °C.

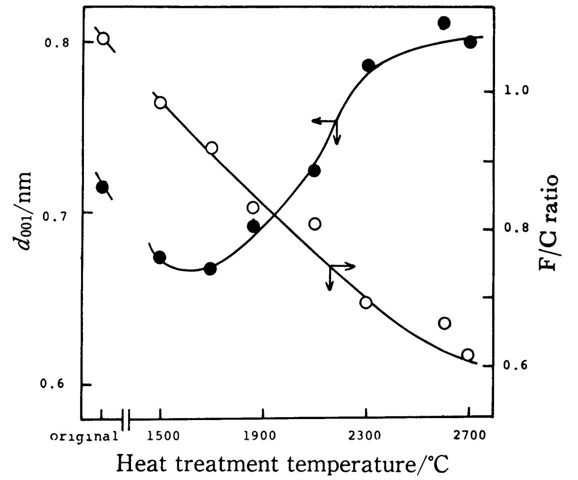

Fig. 6. Variation of the interlayer spacings and F/C of graphite fluoride as a function of heat treatment temperature.
Reaction conditions : 370 °C, F_2, 267 × 10^2 Pa.

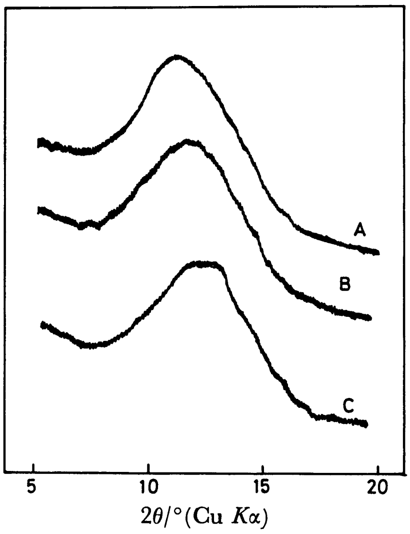

Fig. 7. Effect of fluorine pressure on (001) X-ray diffraction patterns of graphite fluoride prepared from petroleum coke (PC 2700 °C) at 430 °C.
A: 533 × 10^2 Pa, B: 267 × 10^2 Pa, C: 133 × 10^2 Pa.

petroleum coke heat-treated at 1500 °C. It is found by comparison of Fig. 3 with Table 1 that in order to obtain graphite fluoride with a $(C_2F)_n$ content of more than 60%, it is necessary to use petroleum coke with crystallite sizes, $L_c(002)$ and $L_a(110)$, of more than 100 nm.

The interlayer spacings d_{001} of graphite fluoride are *ca.* 0.9 nm for $(C_2F)_n$ and 0.6 nm for $(CF)_n$.[1] Figure 4 shows an increase of d_{001} values with increasing content of $(C_2F)_n$ in graphite fluoride as a function of reaction temperature. The d_{001} of graphite fluoride prepared below 400 °C is about 0.8 nm; this is smaller by 0.1 nm than the reported value 0.9 nm.[1] It is due to the overlapping of two diffraction peaks corresponding to $(C_2F)_n$ and $(CF)_n$. Such a tendency of d_{001} with decreasing temperature is also observed for graphite fluoride prepared from the sample treated at 1500 °C; however, in this case it would be attributable to the lower crystallinity of the prepared $(CF)_n$. Figure 5 shows more clearly the overlapping of two diffraction lines originating from $(C_2F)_n$ and $(CF)_n$. With increasing heat treatment temperature of petroleum coke, the half width of (001) diffraction line changes along more symmetric hyperbola as a function of temperature in accordance with increasing content of $(C_2F)_n$ in graphite fluoride. The hyperbola with a broad width has a maximum point at 430 °C, while in the case of graphite fluorides prepared from natural graphite, the maximum point of hyperbola with a narrow width is situated at 490 °C.[1] This indicates that $(C_2F)_n$ is preferencially formed from a carbon material with higher crystallinity. It is more distinctly shown in Fig. 6, which gives the change in the interlayer spacings d_{001} and F/C ratios of graphite fluoride as a function of crystallinity of a starting carbon material.

The dependence of $(C_2F)_n$ formation on fluorine pressure is given in Fig. 7, in which the peak position of (001) diffraction line shifts to lower angles with increasing fluorine pressure. That is, the interlayer spacing d_{001} increased from 0.72 to 0.80 nm and F/C ratio decreased from 0.67 to 0.64 with increase in the fluorine pressure from 133 × 10^2 to 533 × 10^2 Pa. These data mean that $(C_2F)_n$ is more easily formed under higher fluorine pressure. This is consistent with the previous result obtained for graphite fluoride prepared from natural graphite.[1]

References

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