Ternary Intercalation Compound of Graphite with Aluminum Fluoride and Fluorine

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Dedicated to Prof. Dr. Drs. h. c. Oskar Glemser on the occasion of his 70th birthday

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Graphite Intercalation Compound, Graphite Fluoride

A ternary intercalation compound of graphite with AlF_3 and F_2 , $\text{C}_x\text{F}(\text{AlF}_3)_y$ was prepared under fluorine atmosphere at temperatures of 20–400 °C. The typical 1st stage compound has a composition of $\text{C}_6\text{F}(\text{AlF}_3)_{0.15}$ with a repeat distance of 940 pm. Rapid progress in the reaction led to the formation of graphite fluoride, $(\text{C}_2\text{F})_n$. ESCA spectra indicate that the chemical bond between host graphite and intercalated fluorine has nearly covalent nature similar to that for $(\text{C}_2\text{F})_n$.

A growing interest has been taken in graphite intercalation compounds of fluorides since it was found that some of them have a unique property of a high electrical conductivity. Most of them are, however, hygroscopic and unstable, which makes it difficult to apply them to a wide variety of practical fields. The intercalation of fluorides into graphite hitherto has been restricted to such fluorides as have low melting and boiling points [1]. They are gas or liquid at room temperature. In general it is necessary that an intercalant fluoride has a high vapor pressure at a relatively low temperature. For this reason it was unsuccessful to prepare graphite intercalation compounds of fluorides with high melting and boiling points or an attempt to prepare such compounds has not yet been made. In this paper we report the preparation of a graphite intercalation compound of AlF_3 . As mentioned above, this compound was not formed in an AlF_3 -graphite two components system because AlF_3 has no sufficient vapor pressure even at a high temperature. The preparation was possible only under fluorine atmosphere in the range of room temperature to 400 °C. With respect to the reaction temperature there is another restriction that natural graphite reacts directly with elemental fluorine at temperatures higher than 350–400 °C to give graphite fluoride $(\text{C}_2\text{F})_n$ or $(\text{CF})_n$, which is also a kind of graphite intercalation compound having a covalent bond between carbon and fluorine [2].

Experimental

Flaky natural graphite from Madagascar (grain size over 840 μm or 297–840 μm) was used. The purity was 99.4% after purification with hydrogen fluoride solution. Commercial aluminium fluoride and aluminium powder were used without further purification. The reaction was carried out in a nickel reaction tube or using a thermobalance specially designed for fluorine atmosphere [3]. A trace amount of hydrogen fluoride contained in fluorine gas was removed by sodium fluoride pellets heated at 100 °C. Unreacted fluorine gas was made to react with soda lime. Graphite intercalation compounds prepared were analyzed by means of X-ray diffractometry, elemental analysis, photoelectron spectroscopy (ESCA) and differential thermal analysis (DTA). ESCA measurement was made by a Du Pont 650 B Electron Spectrometer with $\text{Mg-K}\alpha$ radiation. DTA was carried out under air, using $\alpha\text{-Al}_2\text{O}_3$ as a reference. Elemental analysis for C and F was performed at the Laboratory for Organic Elemental Microanalysis, Faculty of Pharmaceutical Science, Kyoto University and Al was analyzed by the atomic absorption method.

Preparation of $\text{C}_x\text{F}(\text{AlF}_3)_y$

A nickel vessel containing a mixture of flaky graphite (ca. 0.5 g) and AlF_3 (ca. 1.0 g) was placed in the reaction tube and the system was evacuated by a rotary pump at 20–100 °C. Fluorine gas was then introduced into the tube to 1 atm. After 0–1 h, the temperature of the reaction tube was raised up to 310–400 °C at a heating rate of ca. 4 °C/min. The temperature was maintained for 24–45 h. Best results were obtained when fluorine gas was made to flow during the temperature raise. After the reaction, the reaction tube was cooled to room temperature and fluorine gas was substituted for nitrogen. The product and excess AlF_3 were separated by a sieve of 297 μm or a pincette.

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Preparation of (C₂F)_n

Flaky natural graphite was put on AlF₃ or Al powder in a reaction vessel, which was then placed in the reaction tube. After evacuation, fluorine gas was introduced into the reaction tube to 1 atm at room temperature. In this case reaction was facilitated with two different methods. One is that after standing for 5–6 h at room temperature, the reaction tube was heated up to 400 °C at the rate of 4.2 °C/min. Another is that after fluorine gas was introduced, the heating was carried out up to 400 °C at the rate of 30 °C/min. The reaction was then continued for 5 h at 400 °C. The product was obtained by the same method as described previously.

Reaction of AlF₃ with F₂

AlF₃ (62.9 mg) was put in the reaction vessel of a specially designed thermobalance, and the system was evacuated. Fluorine gas was then introduced into the reaction tube to 1 atm at room temperature. After 4 h the tube was heated up to 35 and 85 °C, and then fluorine pressure was reduced to 0.5 atm and 0.1 atm. Through this process the weight

change was monitored with an automatic transducer.

Results and Discussion*C_xF(AlF₃)_y*

A reaction carried out at temperatures of 20 to 100 °C gave only a mixed stage or sometimes 2nd stage compound. A 1st stage compound was obtained when the reaction temperature was raised from 20–100 °C up to 310–400 °C after introduction of fluorine gas into the mixture of graphite and AlF₃. No intercalation compound was formed when fluorine gas was introduced into the reaction system at temperatures higher than 200 °C. It was found that the introduction of fluorine gas should be made below around 100 °C to obtain a graphite intercalation compound. On the other hand, rapid increase in the reaction rate led to the decomposition of an intercalation compound and the subsequent

Table I. Analytical data for C_xF(AlF₃)_y and graphite fluoride.

No.	Compound	Elemental analysis	X-ray diffraction data (Cu-Kα)					I _c [pm]	
			Int.	2θ[°]	d[pm]	h	k		l
1	C ₈ F(AlF ₃) _{0.15} slightly bluish black	C: 75.4 F: 21.5 (Al): 3.1	m	9.38	942	0	0	1	944* ±4
			m, br	16.44	539	unknown			
			s	18.70	474	0	0	2	
			vs	28.44	314	0	0	3	
			vw, br	48.42	188	0	0	5	
			vw, br	58.90	157	0	0	6	
2	C ₆ F(AlF ₃) _{0.15} blue-black	C: 69.3 F: 26.7 (Al): 4.0	w, br	9.72	909	0	0	1	940* ±6
			m	18.98	467	0	0	2	
			vs	28.32	315	0	0	3	
			vw, br	48.7	187	0	0	5	
			vw	59.26	156	0	0	6	
3	C ₁₇ F(AlF ₃) _{0.45} black, slightly exfoliated	C: 78.4 F: 16.9 (Al): 4.7	w, br	9.60	920	0	0	1	950* ±14
			m	18.94	468	0	0	2	
			s	27.80	321	0	0	3	
			vw, br	47.4	192	0	0	5	
			vw, br	58.0	159	0	0	6	
4	intermediate product black, exfoliated	C: 73.4 F: 26.8	vw, br	11.16	792	0	0	1	for graphite fluoride
			vs	27.40	325				
			vw, br	56.10	164				
5	graphite fluoride gray, exfoliated	C: 47.4 F: 50.7 (C ₂ F) _n : 65%**	s, br	11.42	774	0	0	1	
			w, br	41.52	217	1	0	0	
6	graphite fluoride gray, exfoliated	C: 49.5 F: 50.7 (C ₂ F) _n : 71%**	s, br	11.10	789	0	0	1	
			w, br	42.12	214	1	0	0	

* Repeat distance for C_xF(AlF₃)_y was calculated from (00l) diffraction lines except broad (001) lines.

** The content of (C₂F)_n was calculated on the assumption that the product contains only (CF)_n as an impurity. By representing the amounts of (C₂F)_n and (CF)_n as *x* and 1 — *x* respectively, F/C ratio is related with *x* by the following equation: F/C = 1 — (1/2) · *x*.

Fig. 1. Change in X-ray diffraction patterns of the products.

formation of graphite fluoride with a covalent bond between carbon and fluorine.

Table I shows the results of elemental and X-ray analyses of the intercalation compound and graphite fluoride. Typical X-ray diffraction patterns of these compounds are given in Fig. 1. Intercalation compound 2 was blue-black in color, whereas compound 1 into which the intercalant was not fully inserted was slightly bluish black. Compound 3 is one which was already slightly decomposed by loss of some fluorine molecules. These compounds were so stable that their exposure to air for 1 day or immersion in water overnight could affect no change in their X-ray diffraction patterns. However, they released a trace amount of fluorine during their storage in a glass ampul for more than 2 weeks. As a result the glass ampul was slightly corroded. The peak position of the (00 l) diffraction line was shifted to lower angle by *ca.* 30 pm and the half width was also broadened. Fig. 2 is the DTA curve for compound 1, which began to decompose at 52 °C, giving an exfoliated residue through two exothermic peaks.

For a typical intercalation compound 2 a composition of $C_6F(AlF_3)_{0.15}$, was determined from a sample kept in a glass ampul for more than 3 months. Atomic absorption spectra for Al gave smaller scattered values than expected, probably because

Fig. 2. DTA curve for $C_6F(AlF_3)_{0.15}$ in air. Heating rate: 20 °C/min.

AlF_3 was not completely dissolved into aqueous solution, remaining between graphite layers. The analytical value for Al was therefore determined by subtracting those for C and F from 100%. The intercalant has more than 3 fluorine molecules to one AlF_3 , which suggested us to use this intercalated fluorine as an oxidizing agent. When compound 1 was immersed in KI solution for several days, the color of the solution changed to yellow.

In an X-ray diffraction study of these intercalation compounds, broad diffraction lines were often observed. The intercalant might take slightly disordered orientation because of the low vapor pressure and mobility of the $(AlF_3)_m \cdot (F_2)_n$ complex. The repeat distance, I_c , was calculated from (00 l) diffraction lines to be 940–950 pm, which is by *ca.* 100 pm larger than in other 1st stage compounds of fluorides [1]. As shown in ESCA spectra, the chemical bond between intercalated fluorine and carbon of the graphite layer is similar to that in graphite fluoride $(C_2F)_n$. This means that intercalated fluorine is situated in contact with carbon of graphite. Provided that intercalated AlF_3 is sandwiched between two sheets composed of fluorine atoms, the dimension of the intercalant becomes *ca.* 600 pm, which is well consistent with the observed value of 605 pm (= 940–335 pm). If the intercalation compound prepared would be a second stage one, only a narrow interlayer gap of 270 pm would remain to accommodate the aluminum fluoride. It is therefore reasonable that $C_xF(AlF_3)_y$ in Table I is regarded as a first stage compound.

Graphite fluoride $(C_2F)_n$

Graphite fluoride, $(C_2F)_n$ prepared in this study has the same appearance in shape as exfoliated graphite (see Fig. 3). Exfoliation of graphite is caused by release of intercalant with increase in

Fig. 3. Photomicrograph of exfoliated $(C_2F)_n$.

temperature. It is considered that graphite fluoride is formed through the decomposition of the intercalation compound and subsequent fluorination of exfoliated residue.

This reaction process is also understandable from Fig. 1 and Table I. $\text{C}_{17}\text{F}(\text{AlF}_3)_{0.45}$ is a slightly decomposed intercalation compound losing *ca.* 2 fluorine molecules. The intermediate product 4 shows two kinds of diffraction lines attributed to graphite fluoride and an intercalation compound with a rather wide repeat distance.

In order to prepare $(C_2F)_n$ by this process, rapid progress in the reaction is necessary. It was accomplished either by insertion of many intercalants into graphite at room temperature or by rapid increase in temperature. Even under mild conditions for the intercalation reaction, prolongation of reaction time *i.e.* a reaction over several days leads to the formation of graphite fluoride. Recently we investigated the fluorination of exfoliated graphite with elemental fluorine and obtained as a result that graphite fluoride, $(C_2F)_n$ was prepared with high reaction rate as compared to the reaction rate of natural graphite [4]. According to the above method, $(C_2F)_n$ is prepared by a more simple process and higher reaction rate.

ESCA spectra

ESCA is one of the most useful means to give us valuable information concerning a chemical bond between host graphite and intercalant. Graphite fluoride, $(C_2F)_n$ has two carbon 1s peaks at 289.0 eV and 287.0 eV relative to contamination carbon 1s peak located at 284.0 eV. The C_{1s} peak at 289.0 eV is derived from C-F bonds and that appearing at 287.0 eV corresponds to C-C bonds adjacent to C-F bonds [2]. Since $(CF)_n$ type graphite fluoride has only C-F covalent bonds, the ESCA spectrum has also only one C_{1s} peak at 289.0 eV.

Fig. 4. ESCA spectra for $\text{C}_x\text{F}(\text{AlF}_3)_y$ and graphite fluoride.

The 2nd stage compound ($I_c = 1270$ pm) prepared at room temperature showed a strong peak at 284.0 eV and a broad shoulder in the range of 286 eV to 291 eV. The latter suggests the presence of fluorine atoms chemically adsorbed and covalently bonded to carbon atoms of host graphite. The F_{1s} spectrum also gave a rather broad peak at 687.6 eV. C_{1s} peaks for $\text{C}_6\text{F}(\text{AlF}_3)_{0.15}$ were situated at the same positions as those for graphite fluoride mainly composed of $(C_2F)_n$, which indicates that the chemical bond between host graphite and intercalated fluorine has nearly covalent nature similar to that for $(C_2F)_n$. Higher mixed stage compounds

were very often formed in reactions made below 100 °C. It was necessary to raise the reaction temperatures up to 310–400 °C in order to prepare a lower stage compound even if it was a mixed stage one. From the results of ESCA measurements, it is supposed that the intercalant molecules inserted into graphite under fluorine atmosphere are partly released when atmospheric fluorine gas is removed from the reaction system. Accordingly the increase in reaction temperature would be required to bring the intercalants in an ordered structure and to strengthen the chemical interaction of intercalated fluorine with the host graphite.

Intercalation mechanism of AlF_3 and F_2

The intercalation compound $\text{C}_x\text{F}(\text{AlF}_3)_y$ was prepared in the range of room temperature to 400 °C where AlF_3 itself has no considerable vapor pressure. In fact no intercalation compound was formed in

the AlF_3 -graphite system. The reaction of AlF_3 with F_2 was performed on a thermobalance and the weight change was monitored. As soon as fluorine gas was introduced into the reaction tube at room temperature, the weight began to decrease, being lighter by 2.8 mg than the original weight in 10 min after the introduction of fluorine gas to 1 atm had finished. The weight decreased still continuously and reached a constant value, when the decrease in weight was 4.4 mg.

The increase in temperature up to 85 °C resulted in no change in weight of AlF_3 . However, the weight was recovered again when the fluorine pressure was reduced to 0.1–0 atm. From this result, it was considered that the gaseous species of $(\text{AlF}_3)_m \cdot (\text{F}_2)_n$ was formed by the reaction of AlF_3 with fluorine gas.

Gaseous species $(\text{AlF}_3)_m \cdot (\text{F}_2)_n$ would be intercalated into graphite.

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