Study on NF3 synthesis using CIF3 as a mediator

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Study on NF_3 synthesis using ClF_3 as a mediator

（ClF_3をメディエーターとして用いるNF_3合成法に関する研究）

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Chapter 1

General Introduction

1-1. Background

1-1-1. Nitrogen trifluoride (NF_3)

The target product in this study is NF_3, which represents an attempt to achieve a new manufacturing process. First, a brief introduction of NF_3 is presented.

Characteristics of nitrogen trifluoride (NF_3)

Table 1-1 presents physical characteristics of NF_3 [1]. Although NF_3 is a stable gas at room temperature, it acts as a powerful oxidizing agent and fluorinating agent at high temperatures or a high plasma vias condition [2–4]. Its reactivity is equivalent to that of oxygen at around 500 K. Over 500 K, decomposition of NF_3 into NF_2 and free fluorine radical increases gradually. The free fluorine radical can react with most organic chemicals and some metal materials, liberating heat energy and causing further dissociation of NF_3. Over 700 K, the reactivity of NF_3 resembles that of fluorine. Thermal dissociation of NF_3 has been examined specifically by several researchers [5–8] and has been found to peak at temperatures of 1073–1273 K. Therefore, NF_3 has already been used as an oxidizing agent for rocket fuels and as a stable fluorinative agent for use in chemical and pharmaceutical industries [9–16].

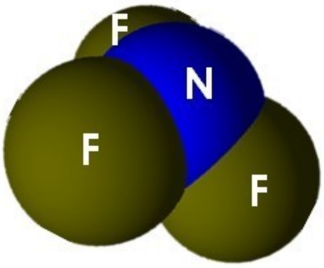

Figure 1-1. Molecular model of nitrogen trifluoride (NF_3).

Table 1-1. Physical properties of nitrogen trifluoride (NF_3) [1]

Properties	value
Boiling Point (K)	143.9
Melting Point (K)	66.2
Liquid Density (kg/dm^3)	1.533
Heat of Vaporization (kJ/mol)	11.59
Triple Point (K/0.263 Pa)	66.2
Heat of Fusion (kJ/mol)	398
Solid Transition Point (K)	56.5
Heat of Transition (kJ/mol)	1.513
Critical Temperature (K)	243.75
Critical Pressure (kPa)	4530
Critical Volume (cm^3)	123.8
Heat of Formation (kJ/mol)	-131.5
Heat Capacity (J/K・mol)	53.59 (gas, 298.15 K)
Water Solubility (mol NF_3/mol H_2O)	1.4×10^{-5}
Dipole Moment (Debye)	0.234
Bonding Energy	
NF_2-F (kJ/mol)	238.91
NF-F (kJ/mol)	297.06
N-F (kJ/mol)	297.06
Vapor Pressure Equation (kPa)	$\log P = 5.90445-501.913/(T-15.37)$

Since the 1980s, the semiconductor industry has expanded dramatically. A few researchers have aimed at developing the application of NF_3 as a laser gas [17–19], as an etchant (etching gas) for a dry etching process [20–23], and as a cleaning gas for apparatus cleaning used in the chemical vapor deposition (CVD) technology [24]. The merits of NF_3 as an etchant over traditional carbon-based etchants such as carbon tetrafluoride (CF_4) and hexafluoroethane (C_2F_6) or sulfur-based etchants such as sulfur hexafluoride (SF_6) are high selectivity for silicon nitride over silicon oxide etching and polysilicon over thermal silicon oxide, and the production of all volatile reaction products, resulting in etching without carbon or sulfur contamination.

Furthermore, the radical lifetime of NF_3 is longer than that of other gases such as CF_4 and SF_6. The reason for this long lifetime is apparently that nitrogen contained in the molecule of NF_3 has an effect of continuing plasma life. Furthermore, NF_3 is used for enhanced plasma or thermal cleaning of CVD chambers. Residual coating such as silicon is deposited on the internal surfaces of CVD chambers during deposition on the wafer. Plasma using NF_3 can remove these deposition materials as volatile fluoride such as silicon tetrafluoride (SiF_4) at the process temperature, eliminating the need to remove the internal CVD chamber components to be cleaned by HF acid wet tank immersion originally. At present, large amounts of NF_3 are consumed by the electronic industry worldwide as a dry etchant and as a cleaning gas for the CVD chamber, as shown in Figure 1-2 [25].

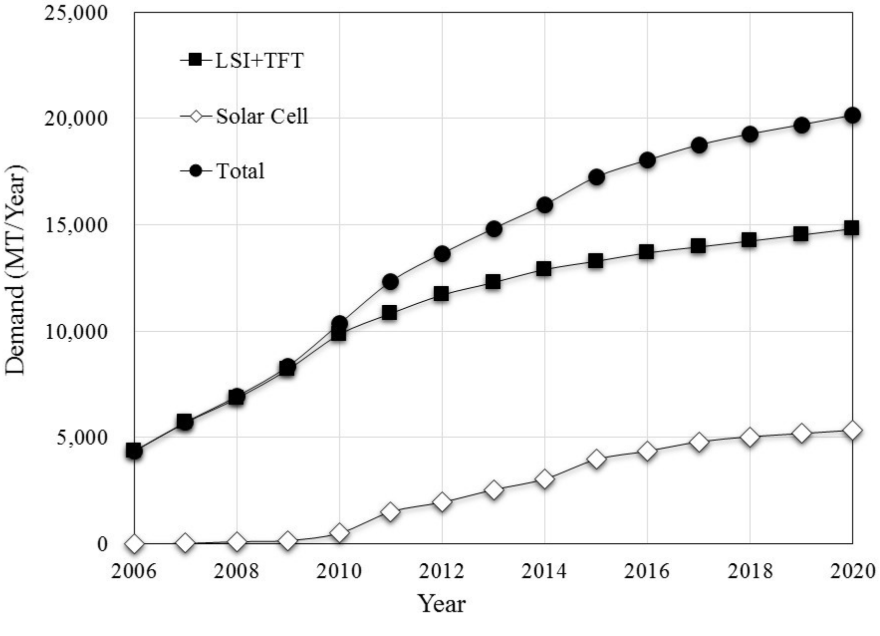

Figure 1-2. World usage of NF_3: ●, total usage; ■, LSI+TFT; ◇, solar cell.

Manufacturing process of nitrogen trifluoride (NF_3)

In actuality, NF_3 can be synthesized in several ways, but three major processes have been found to be economically feasible for large-scale production [26].

One is electrolysis of molten ammonium acid fluoride, shown as reactions (1) and (2): reaction formula (1) corresponds to the anode reaction; reaction formula (2) is the cathode reaction. Consequently, NF_3 is generated on the anode surface. This synthesis can generate NF_3 at once by electrolysis without electrolytic cells for producing fluorine gas. However, for this process, it is common industrially to use a nickel electrode for the anode. When using a nickel anode, 1–5% of the electric power is used for dissolution of nickel. It is therefore necessary to replace the electrode periodically and to remove the nickel fluoride sludge from the NH_4F/nHF molten salt [1]. For this reason, attempts have been undertaken to use carbon electrodes instead of nickel anodes [1].

A second method is direct fluorination using NH_4F/nHF and F_2 as the reaction (3). This synthesis presents a possibility of explosion related to mixture with NH_3 and NF_3 [27]. Actually, HF is added to NH_3 for dilution and explosion prevention. However, because of the lack of solubility of fluorine for NH_4F/nHF, the reaction rate is low [28]. Therefore, to raise the yield, it is often possible to use the reaction with high temperatures and high pressures.

A third method is direct fluorination using $(NH_4)_3AlF_6$ and F_2 as reaction (4). This process enables mild reaction using low reactivity $(NH_4)_3AlF_6$. From the viewpoints of safety and selectivity of the reaction, Central Glass Co. Ltd. has selected the third process: fluorination of ammonium cryolite with F_2, as written in reaction scheme (4) [29]. This process is, at present, a unique gas–solid reaction using a large-scale NF_3 manufacturing process.

$NH_4F/nHF \rightarrow NF_3 + 6H^+ + 6e\text{-}$ (1)

$2H\text{+ } 2e^- \rightarrow 3H_2$ (2)

$NH_4F/nHF + 3F_2 \rightarrow NF_3 + (4+n)HF$ (3)

$(NH_4)_3AlF_6 + 6F_2 \rightarrow 2NF_3 + NH_4AlF_4 + 8HF$ (4)

This process can manufacture NF_3 smoothly even when the F_2 concentration is very low. Moreover, it can be conducted in a monel reactor for gas–solid reactions to give NF_3 in high yield (95% based on F_2). Dry ammonium cryolite powder is charged into a reaction vessel of the compartment tray or plate tower type made of nickel or monel, after which it is heated to the appropriate temperature (above 353 K) before F_2 is introduced at one end of the reaction vessel [26].

The F_2 flow rate is increased gradually while the reaction temperature is controlled carefully to around 423 K. Little need exists for intentional dilution of F_2 because F_2 introduced into the reactor is soon diluted to a desirable level by gaseous reaction products such as NF_3 and HF, even when pure F_2 is used, providing that the feed rate of F_2 is adequate. The gas–solid reaction readily proceeds. The produced NF_3 comes out from the other end of the reactor together with a considerable amount of HF and small amounts of F_2, N_2O, and N_2 [26]. Nevertheless, compared to other processes, $(NH_4)_3AlF_6$ must be manufactured separately. For that reason, manufacturing processes are long and production costs are higher than those of the other two processes.

Table 1-2 presents contents summarizing the three manufacturing methods above. Benefits and shortcomings exist for each process, as written in Table 1-2.

Table 1-2. Comparison of industrialized manufacturing process

	Direct F_2 reaction method	Electrolysis method	Ammonium cryolite method
Chemical reaction formula	$NH_4F/2HF + 3F_2 \rightarrow NF_3 + 6HF$	$NH_4F/2HF \rightarrow NF_3 + 3H_2$	$(NH_4)_3AlF_6 + 6F_2$ $\rightarrow 2NF_3 + 8HF + NH_4AlF_4$
Heat of reaction Kcal/mol-NF_3	-196	-300	-180
Advantage	・Continuous synthesis	・Continuous synthesis ・One step synthesis (Without F_2 electric cell)	・High yield ・Safe reaction (Mild reaction)
Disadvantage	・Low reactivity ・Large heat of reaction ・High pressure reaction (3atm) ・F_2 electric cell	・Dissolution of Ni electrode ・High electricity cost for electric loss ・Many Electronic Cells	・F_2 electric cell ・Raw materials cost ・Solid raw materials ・Batch process
Manufacturing Company	・Kanto Denka (Japan) ・SK Material (Korea) ・Air Products (USA)	・Mitsui Chemical (Japan) ・PERIC (China)	・Central Glass (Japan)

1-1-2. Chlorine trifluoride (ClF_3)

Next, a brief introduction of ClF_3 is presented. It is used as a mediator in this NF_3 novel synthesis study.

Properties and reactivity of chlorine trifluoride (ClF_3)

Chlorine trifluoride (ClF_3) was first synthesized as so-called inter-halogen in the 1930s as a reactive compound in halogen fluorides. Research and commercial interest in ClF_3 began in the 1950s with investigation of its use as an oxidant for rocket fuel. During that time period, other applications were developed in the nuclear industry. One such application, which shall be emphasized here, was the extraction of uranium from irradiated fuels. A more recent and rapidly expanding use of ClF_3 is plasma-less in situ cleaning of tools used in semiconductor production processes. In fact, NF_3 is used with a cleaning method using plasma, whereas ClF_3 can be cleaned without using plasma. Therefore, it is suitable for cleaning devices without a plasma-generating device.

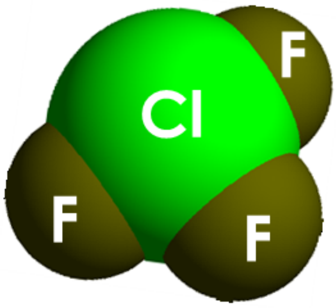

Figure 1-3. Molecular model of chlorine trifluoride (ClF_3).

Physical properties of chlorine trifluoride (ClF_3)

ClF_3 is a colorless gas with an irritating odor similar to chlorine. Actually, it has an extremely low odor threshold, reportedly around 0.02 ppm. Although ClF_3 is nonflammable and thermally stable, it will begin to dissociate at 523 K. The extent of dissociation at this temperature is reported as approximately 1.7%. At temperatures higher than 873 K, the dissociation is almost complete. Table 1-3 shows some common physical properties of ClF_3.

Table 1-3. Physical properties of chlorine trifluoride (ClF_3)

Properties	value	reference
Boiling Point (K)	284.75	[30]
Melting Point (K)	196.68	[30]
Transition Point (K)	190.34	[30]
Vapor Pressure (kPa)	60.1 (273 K), 141.9 (293 K), 297 (313 K)	[30,31]
Liquid Density (kg/dm^3)	1.8555 (283 K), 1.8249 (293 K)	[32]
Solid Density (kg/dm^3)	2.53 (153 K)	[33]
Critical Temperature (K)	447 K	[30]
Critical Pressure (kPa)	5776	[30]
Heat of Vaporization (kJ/mol)	27.53	[30]
Heat of Fusion (kJ/mol)	1.51	[30]
Specific Heat (J/K・mol)	65.2 (gas)	[34]
Viscosity (kg/m・s)	0.435 (293 K)	[35]
Surface Tension (mN/m)	26.7 (273 K)	[35]
Specific Conductivity (ohm^{-1}cm^{-1})	4.9×10^{-9} (298 K)	[36]
Dielectric Constant	4.754 (273 K)	[37]
Heat Capacity (J/K・mol)	63.848 (gas, 298.15 K)	[38]
Enthalpy of Formation (kJ/mol)	-158.866 (gas, 298.15 K)	[38]
Entropy of Formation (J/K・mol)	281.495 (gas, 298.15 K)	[38]
Free Energy of Formation (kJ/mol)	-118.901 (gas, 298.15 K)	[38]

Chemical properties of chlorine trifluoride (ClF_3) [39]

ClF_3, a liquefied gas at room temperature, is a strong oxidizing and fluorinating agent. Under the proper conditions, it reacts with all organic materials, with all metals and with all non-metals except helium, argon, and nitrogen. Especially, high concentrations of ClF_3 react violently and sometimes explosively with many organic and inorganic materials at room temperature. Moreover, ClF_3 interacts violently with water unless precautions are taken to moderate the process, such as using low temperatures and dilution.

Metals such as nickel, copper, and aluminum create an adherent fluoride film of low permeability that prevents further reaction. However, this protective capacity is lost at elevated temperatures. Metals such as molybdenum, tungsten, and titanium form volatile metal fluorides. Such representative non-metals as boron, silicon, phosphorus, sulfur, arsenic, antimony, selenium, and tellurium react at room temperature or with slight warming to produce the corresponding fluorides. These reactions are generally vigorous, accompanied by heat and light [40].

In general, oxides convert to fluorides and oxyfluorides, although no reaction has been reported with ZnO, HgO, SiO_2, ZrO_2, ThO_2, or Fe_2O_3. At elevated temperatures or in the presence of trace amounts of water, these oxides should also react. Under the conditions used for this study, no reaction is observed with NaCl, K_2SO_4, KNO_3, $HgSO_4$, or $HgCl_2$ [41]. Solvolysis reactions of alkali metal fluorides in ClF_3 at 373 K result in the formation of the respective alkali metal tetrafluorochlorates: $KClF_4$, $RbClF_4$, and $CsClF_4$. Tetrafluorochlorates of lithium and sodium are not obtained [42].

Many hydrogen-containing compounds, both organic and inorganic, inflame or explode when mixed with ClF_3. Some of the reactions might be moderated by diluting ClF_3 with an inert gas, by dissolving the reagent in an inert solvent such as carbon tetrachloride or a fluorocarbon, or by lowering the temperature. Some researchers have produced ClF_3 for the fluorination of organic compounds, although the reactions are commonly difficult to control. Ellis and Musgrave investigated the reaction between ClF_3 and benzene derivatives in carbon tetrachloride (CCl_4) solution. Their results show that both addition and substitution products are formed [43,44]. Mury [45] and Brower [46] respectively reported the fluorinations of tetrachlorobutadiene and alkanes.

In the vapor phase, ClF_3 might decompose to ClF, Cl_2, ClOF, ClO_2F, ClO_3F, ClO_2, or HF, depending on the relative concentrations of water and chorine trifluoride [47,48].

1-1-3. Chlorodifluoroamine (NF_2Cl) and dichlorofluoroamine ($NFCl_2$)

Chlorodifluoroamine (NF_2Cl) is prepared by the action of chlorine trifluoride on ammonium fluoride [49] or by the action of fluorine on a mixture of sodium azide and sodium chloride [50]. Results have been presented from the thermal decomposition of the adduct formed between difluoroamine and boron trichloride [51] or the interaction of chlorine and tetrafluorohydrazine under ultraviolet radiation [52].

Dichlorofluoroamine ($NFCl_2$) is prepared on sodium azide by the action of chlorine monofluoride [53]. Although the physical property information of the two compounds is not so detailed, the existing information is presented in Table 1-4.

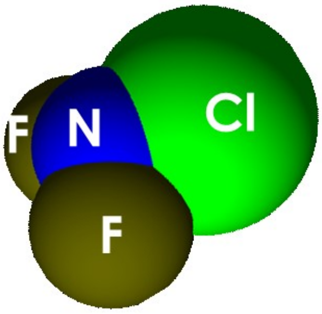

Figure 1-4. Molecular model of chlorodifluoroamine (NF_2Cl).

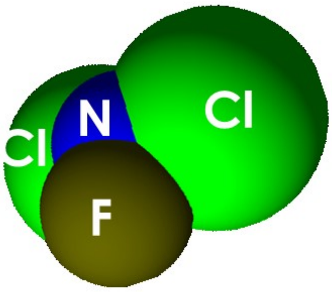

Figure 1-5. Molecular model of dichlorofluoroamine ($NFCl_2$).

The infrared spectrum of NF_2Cl has been elucidated in detail, showing agreement with a pyramidal molecule [54]. The principal infrared bands of $NFCl_2$ have been reported [53]. Mass spectral data are available [51,53]. Gaseous NF_2Cl is stable at room temperature in Pyrex vessels [51]. It reacts with mercury to give tetrafluorohydrazine (N_2F_4) [51]. Actually, $NFCl_2$ absorbs in ultraviolet at 2700 Å and decomposes on irradiation to *cis*-difluorodiazine [53].

$NFCl_2$ is potentially easy to decompose.

Table 1-4. Physical properties of chlorodifluoroamine (NF_2Cl) and dichlorofluoroamine ($NFCl_2$)

Properties	NF_2Cl		$NFCl_2$	
Boiling Point (K)	206	[51]	-	
Melting Point (K)	Between 77-90	[51]	270-271	[53]
Heat of Vaporization (cal/mol)	4,350	[51]	-	
Vapor Pressure Equation (kPa)	$\log P = 7.478\text{-}950/T$	[51]	-	

1-2. Outline of the work

As described in earlier pages, nitrogen trifluoride (NF_3) is a gas for which demand is rapidly expanding for use as a material gas in the semiconductor industry. Regarding NF_3 manufacturing, three commercialized processes are known. This study verified the possibility of a process with higher yield corresponding to more commercialization for methods other than these three methods.

The method verified this time uses chlorine trifluoride (ClF_3) as a mediator. Figure 1-6 portrays the target NF_3 synthesis scheme. The point of this work is to confirm that 1) NF_2Cl and $NFCl_2$ can be synthesized with high selectivity from the reaction between $NH_4F/n HF$ and ClF_3 and that 2) NF_3 can be synthesized from NF_2Cl and $NFCl_2$ as intermediates in high yield. The efficiency of recovering ClF_3 lies in the ability to ascertain whether it can be reused for the first reaction and to check whether all reactions are possible at low pressures such as atmospheric pressure and with completely high yield.

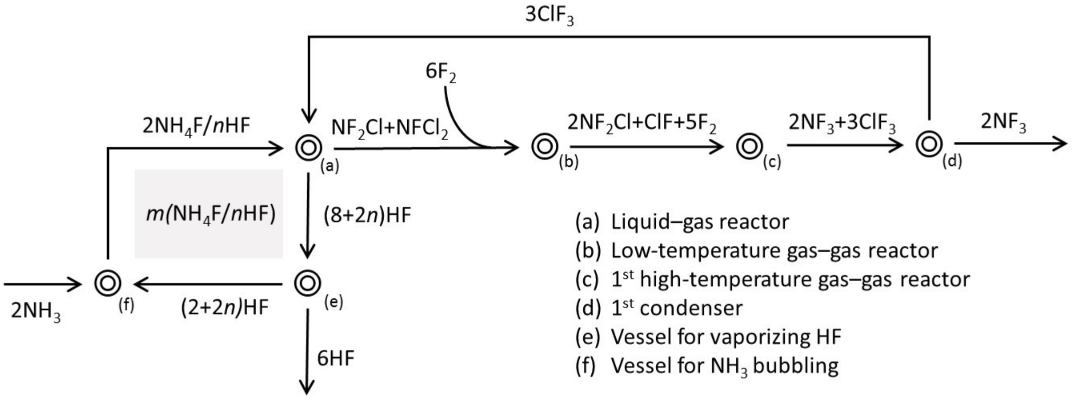

Figure 1-6. Target NF_3 synthesis scheme using ClF_3 as a mediator.

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Chapter 2

Synthesis of NF_2Cl and $NFCl_2$ using $NH_4F/n HF$ and ClF_3

2-1. Introduction

Chlorodifluoroamine (NF_2Cl) and Dichlorofluoroamine ($NFCl_2$) are anticipated for use as new fluorinated agents. Especially, NF_2Cl and $NFCl_2$ present possibilities for use as raw materials for the production of NF_3, which has been used since the 1970s in the electronic industry to clean chemical vapor deposition (CVD) chambers in semiconductor manufacturing equipment. Actually, NF_3, a carbon free molecule, is beneficial because of its long radical life. Currently, almost all semiconductor device manufacturers use NF_3 as the CVD chamber cleaning gas.

Earlier works have reported NF_2Cl synthesis using some methods such as synthesis from a NHF_2 and BCl_3 reaction [1–3], synthesis by NH_4F and ClF_3 [4–6], synthesis by NHF_2 and ClF_3[7], and synthesis by NHF_2 and $COCl_2$ [8]. Petry et al. first reported NF_2Cl synthesis using NHF_2 and BCl_3 [1]. The NHF_2 and BCl_3 reaction produces NF_2Cl without using fluorine gas as a raw material. However, the yield is lower than 50%. Although other proposed reactions have been reported in the literature [3–7], no yield higher than 90% has been reported.

In fact, $NFCl_2$ synthesis has seldom been reported because $NFCl_2$ decomposes easily by disproportionation [1] and reacts explosively with oxidants. Thrasher et al. reported low-temperature synthesis reactions of $NFCl_2$ using N,N-dichloro-1-fluoroformamide [9]. Although this reaction produces 75% yield of $NFCl_2$, the complicated process necessary for an industrial method of N,N-dichloro-1-fluoroformamide synthesis requires the use of N,N-dichloro-1-fluoroformamide, which is not cost effective. Moreover, the necessary liquid nitrogen temperatures entail high costs.

The reports mentioned above have described NF_2Cl or $NFCl_2$ synthesis. Only one report describes NF_2Cl and $NFCl_2$ synthesis [10]. In this reaction, NH_4Cl, NaCl, and fluorine gas were used as raw materials, presenting a convenient and safe means of producing moderate amounts of $NFCl_2$ and NF_2Cl. Nevertheless, it is difficult to increase productivity because of the direct reaction between the solid NH_4Cl and F_2 gas. Moreover, liquid nitrogen temperatures are required, which entails high costs.

One pot synthesis of NF_2Cl and $NFCl_2$ using molten $NH_4F/n\text{HF}$ and gaseous ClF_3 is reported herein. Furthermore, effects on NF_2Cl and $NFCl_2$ selectivity against N_2 related to parameters such as the temperature and the n value of $NH_4F/n\text{HF}$ system are examined.

2-2. Experimental

$NH_4F/n\text{HF}$ melts (n = 2.2, 2.3, 2.4, 2.7, 2.8, 3.0, 3.1, and 4.0) were prepared by feeding gaseous anhydrous HF (Central Glass Co. Ltd.) through $NH_4F/1.0\text{HF}$ (Morita Chemical Industries Co. Ltd.). The n value of $NH_4F/n\text{HF}$ was calculated using the HF feeding weight. Before use, $NH_4F/n\text{HF}$ was dehydrated using F_2 gas until peaks corresponding to the oxygen-containing product on the FT-IR spectrum disappeared. Preparation of these $NH_4F/n\text{HF}$ melts was done with line processing to avoid contamination by moisture. Before starting ClF_3 flow, the reactor was filled with He gas to avoid contamination by air and moisture.

Figure 2-1 portrays the reaction equipment. The gas lines and a reactor were made of SUS304. The reactor volume was 500 mL. They were designed originally to control and monitor reaction pressures and temperatures precisely. ClF_3 (>99.9 wt% purity, Central Glass Co. Ltd.) was used as the raw material. ClF_3 gas was flowed into the reactor using a dip tube without diluted He gas. The ClF_3 flow rates were selected as 20, 50, or 100 standard cc min^{-1}. Total ClF_3 flow amounts were fixed by 4.8 normal liter (0.214 mol), but with changes to several conditions. In the case of

20 standard cc min^{-1}, the continuous ClF_3 gas flow time was 240 min. In the case of 50 standard cc min^{-1}, the continuous ClF_3 gas flow time was 96 min. In the case of 100 standard cc min^{-1}, the continuous ClF_3 gas flow time was 48 min. During the reaction, in other words, during ClF_3 bubbling into $NH_4F/n HF$ melts, the reaction pressure was fixed at 93.3 kPa by controlling the rear valve (9) in Figure 2-1. The reactor mixing speed was fixed at 300 rpm. To obtain the outlet gas flow rate, a vacuum cylinder was connected to the vacuum line at the rear of valve (9) in Figure 2-1. Furthermore, by shutting off the gas flow to the vacuum pump, the increasing speed per unit time in the internal pressure of the cylinder was measured. The outlet gas flow rate was calculated using the cylinder's volume and speed of pressure increase. All analytical apparatus was arranged with in-line analysis to monitor the product composition without decomposition of $NFCl_2$ caused by contamination.

The reaction product was introduced into the 100 mm path length fourier transform infrared spectrophotometer gas cell with a ZnSe window at 1.85 kPa (FT-IR Prestige-21; Shimadzu Corp.). A gas chromatograph – mass spectrometer (GC/MS, GCMS-QP2010; Shimadzu Corp., Column Varian Capillary Column CP-PoraBOND Q, ϕ 0.32 mm, column length 50 m, oven temperature: 393 K) was used to ascertain the N_2 contents. Ultraviolet visible absorption spectroscopy (UV/Vis U-2810; Hitachi Ltd.) was used to ascertain the Cl_2 contents of the outlet gases. Gas cell length of UV/Vis was 0.1 m and 330 nm absorbance wavelength was analyzed for measuring Cl_2 concentration. All outlet gas analyses were conducted after the outlet gas flow rate became stable. Taking the 20 standard cc min^{-1} as an example, outlet gas analysis was performed after 150 min from the start of the flow, after 3.0 normal liter (0.134 mol) of the total flow amount of ClF_3 had been bubbling into the reactor from the dip tube.

The reaction temperature was controlled at 283–318 K. Heat generated during the reaction (exothermic reaction) was removed using a water cooling jacket. Exhaust gases were detoxified using soda lime.

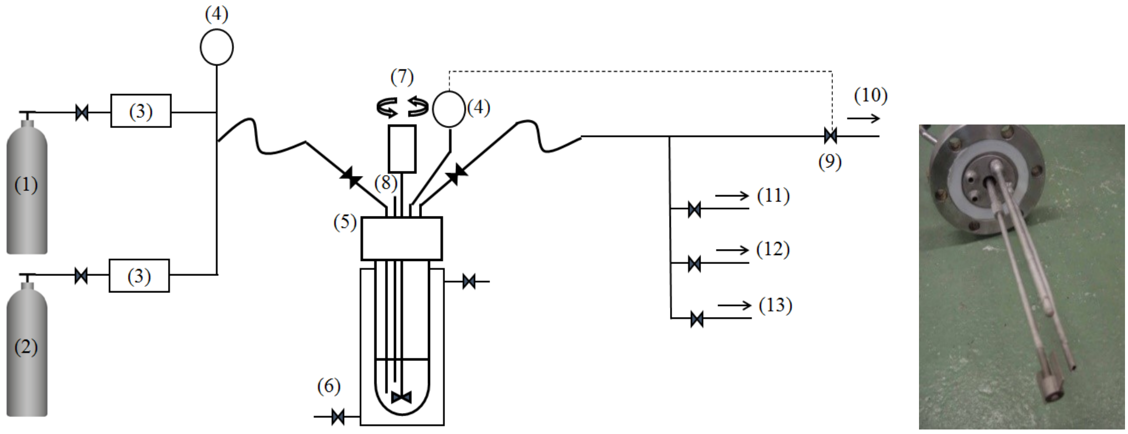

Figure 2-1. Reaction equipment: (1) ClF_3 cylinder, (2) He cylinder, (3) mass flow controller, (4) pressure indicator, (5) 500 mL stainless reactor, (6) temperature controller (jacket), (7) agitator, (8) thermocouple, (9) pressure control valve, (10) vacuum line, (11) online analysis line by FT-IR, (12) online analysis line by GC/MS, and (13) online analysis line to UV/Vis. The photograph above shows the reactor lid.

2-3. Results and discussion

2-3-1. Reaction products

Figure 2-2 shows the outlet gas flow rate from the reactor from $NH_4F/2.3HF$ molten salt obtained from examination under conditions of 20 standard cc min^{-1} ClF_3 flow rate, 293 K reaction temperature, 93.3 kPa reaction pressure, and 300 rpm stirring speed. To obtain the outlet gas flow rate, a full vacuum cylinder was connected to the outlet pipe. The increasing speed per unit time in the internal pressure of the cylinder was measured. The initial outlet gas flow rates were as low as 6.6 standard cc min^{-1} during the initial 3 min, 12.7 standard cc min^{-1} at the lapse of 10 min, and 14.6 standard cc min^{-1} after the lapse of 30 min. Thereafter, the flow rate stabilized at around 14 standard cc min^{-1}. Therefore, to analyze the outlet gas component at the time when the gas flow rate was stabilized, gas analysis was performed after 150 min from the start of the flow, after 3.0 normal liter (0.134 mol) of the total flow amount of ClF_3 had elapsed.

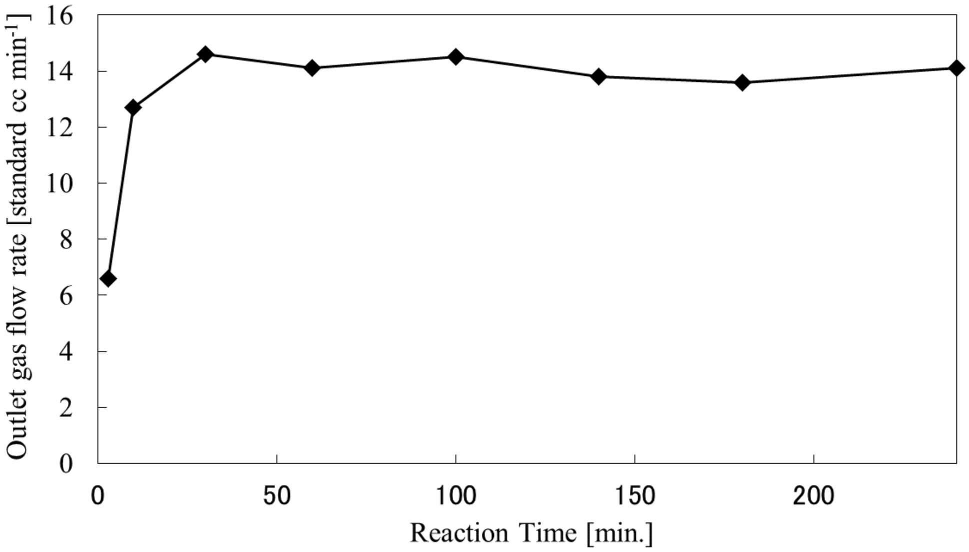

Figure 2-2. Outlet gas flow rate from the reactor. Conditions: molten salt, $NH_4F/2.3HF$; ClF_3 flow rate, 20 standard cc min^{-1}; reaction temperature, 293 K; and reaction pressure, 93.3 kPa.

Figure 2-3 presents the FT-IR spectrum of the outlet gas after 150 min ClF_3 flow. Strong peaks between 800 and 1000 cm^{-1} were observed. Zoomed-in peaks around 800 and 1000 cm^{-1} are portrayed in Figure 2-3 and are explained in the signal profile below. Weak peaks around 4000 cm^{-1} were observed. The spectra were compared to HF data in the NIST library. Peaks around 1600 cm^{-1} and 3800 cm^{-1} correspond to H_2O. Peaks around 2300 cm^{-1} were compared to CO_2 spectra data in the NIST library. These peaks appear as the residue of the background calibration. The signals were detected because H_2O and CO_2 were present not in the product gases but in the environment outside the FT-IR cell.

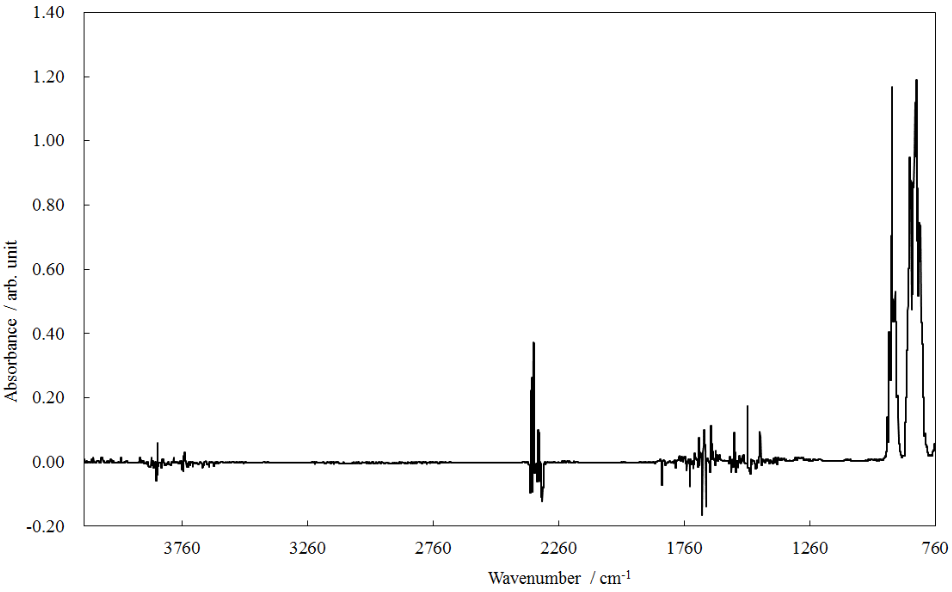

Figure 2-3. FT-IR spectrum of the product in direct reaction (analysis range 760 cm^{-1} – 4150 cm^{-1}): molten salt, $NH_4F/2.3HF$; ClF_3 flow rate, 20 standard cc min^{-1}; reaction temperature, 293 K; reaction pressure, 93.3 kPa.

Figure 2-4 portrays a zoomed-in version of the FT-IR profile for 760–1000 cm^{-1} in Figure 2-3. Left-side peaks comprised a main peak at 930 cm^{-1}, with sub peaks at 918 cm^{-1} and 938 cm^{-1} corresponding to absorption bands of the symmetric N–F stretching modes of NF_2Cl [11,12]. Right-side peaks are NF_2Cl and $NFCl_2$ peaks. Peaks at 854 cm^{-1} and 860 cm^{-1} correspond to absorption bands of asymmetric N–F stretching modes of NF_2Cl [10,11]. Peaks at 821 cm^{-1} and 833 cm^{-1} correspond to absorption bands of asymmetric N–F stretching modes of $NFCl_2$ [11,13]. The absorption peaks of asymmetric N–F stretching modes of $NFCl_2$ were observed below 760 cm^{-1} [13]. The FT-IR results show that NF_2Cl and $NFCl_2$ are the main products.

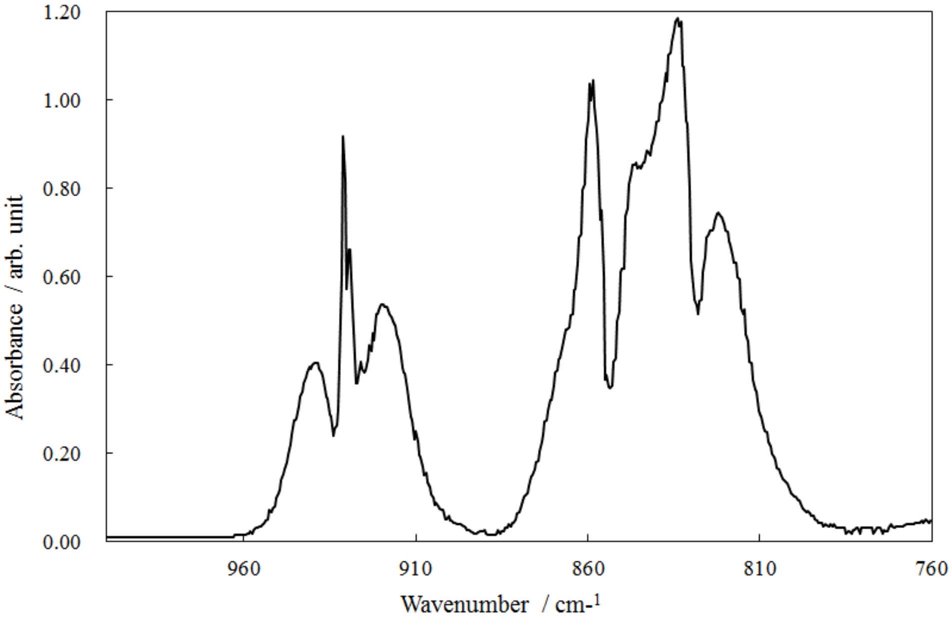

Figure 2-4. FT-IR spectrum of the product in direct reaction: analysis range, 760 cm^{-1} – 1000 cm^{-1}; molten salt, $NH_4F/2.3HF$; ClF_3 flow rate, 20 standard cc min^{-1}; reaction temperature, 293 K; reaction pressure, 93.3 kPa.

The respective NF_2Cl melting and boiling points are 77–90 K and 206 K. The NF_2Cl vapor pressure was described in an earlier report [14]. Except for boiling point data, no physical information of $NFCl_2$ exists in the literature. Reportedly, its boiling point is 270–271 K [2].

Products in the collected outlet gas were separated according to their boiling points using the stainless steel apparatus and poly [tetrafluoroethylene-co-perfluoro (alkylvinylether)] plastic apparatus. $NFCl_2$ is easily decomposed under the effects of humidity. Using a well dried and well F_2 passivated apparatus, $NFCl_2$ in liquid form was separated from the mixture of the products. First, N_2 was removed from the reacted outlet gas at the liquid nitrogen temperature. Secondly, NF_2Cl was removed from the outlet gas at 173 K. Then $NFCl_2$ was transferred to the poly [tetrafluoroethylene-co-perfluoro (alkylvinylether)] plastic tube at 223 K. The $NFCl_2$ vaporized at 223 K, implying that the melting point of $NFCl_2$ is between 173 K and 223 K. As shown in Figure 2-5, the $NFCl_2$ liquid has a light yellow color (RGB value is R167 G174 B89 analyzed using GIMP software). The vapor pressure at 298 K was measured as 0.18 MPa.

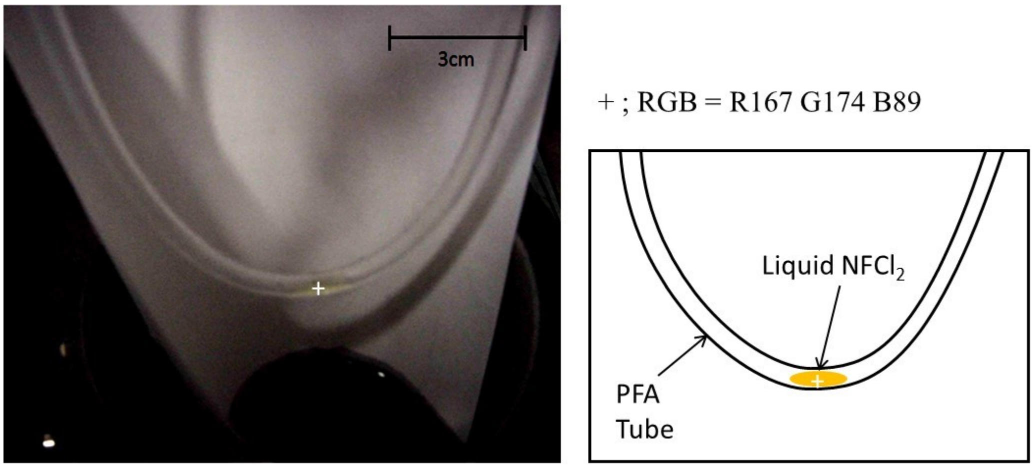

Figure 2-5. Appearance of liquid $NFCl_2$ isolated from outlet mixture gases.

FT-IR spectra of NF_2Cl and $NFCl_2$ were obtained separately using these distilled gases. Figure 2-6 presents the FT-IR spectrum of the NF_2Cl distilled from the product gases. Figure 2-7 portrays the FT-IR spectrum of the $NFCl_2$ distilled from the product gases. Among those peaks shown in Figure 2-4, only the peaks corresponding to NF_2Cl absorption are presented in Figure 2-6. Among the peaks depicted in Figure 2-4, only the peaks corresponding to $NFCl_2$ absorption are portrayed in Figure 2-7.

The difference absorption spectrum, as shown in Figure 2-8, was obtained by subtracting the spectra of NF_2Cl and $NFCl_2$ from that of the outlet gas, as shown in Figure 2-4. Two peaks around 750 cm^{-1} and 790 cm^{-1} are depicted in Figure 2-8. These absorption peaks correspond with the vibrational and rotational constant modes of ClF gas [15, 16].

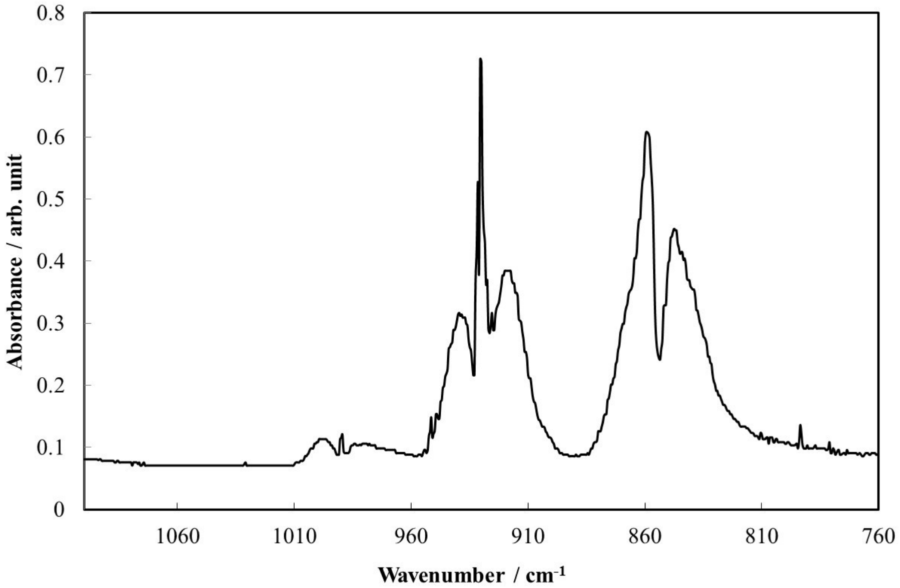

Figure 2-6. FT-IR spectrum of NF_2Cl isolated from the product gas in a direct reaction.

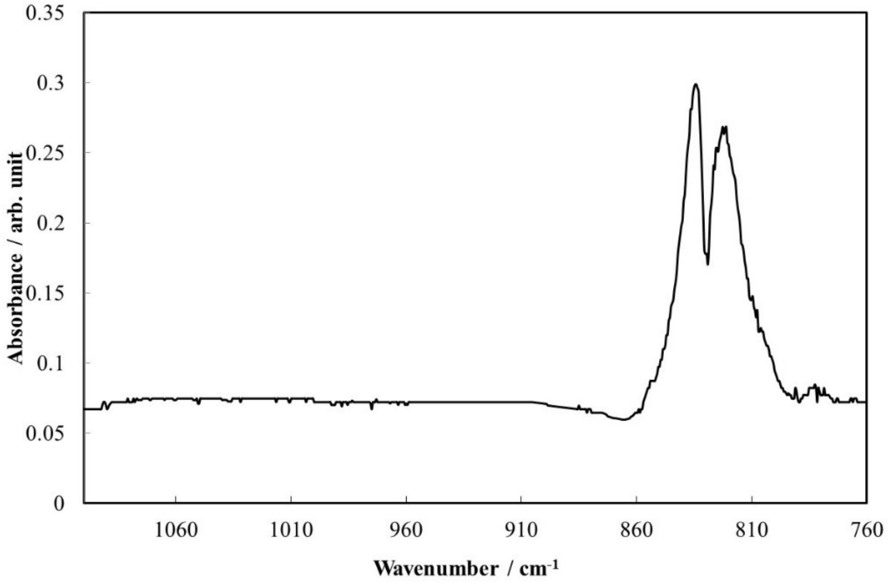

Figure 2-7. FT-IR spectrum of the $NFCl_2$ isolated from the product gas in a direct reaction.

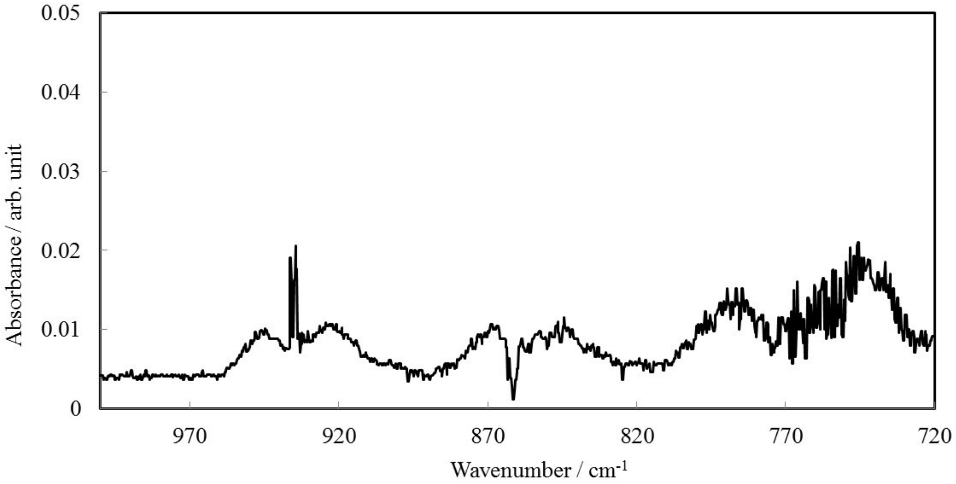

Figure 2-8. Difference absorption spectrum of the outlet gas subtracted the NF_2Cl spectrum and the $NFCl_2$ spectrum.

Table 2-1 presents the compositions of outlet gases and the NF_2Cl+$NFCl_2$ selectivities under various conditions. NF_2Cl, $NFCl_2$, ClF_3, and HF were measured using FT-IR. In addition, ClF was measured using the difference FT-IR method presented above. N_2 was measured using GC/MS. Cl_2 was measured using UV. Each high-purity gas was used for calibration. More than 99% of the gas was introduced into each analyzer while varying the injection amount. A calibration curve was prepared with each gas. Taking NF_2Cl as an example, NF_2Cl synthesized using the distillation process explained above was injected into a 10 cm FT-IR gas cell at 0.147 kPa, 0.560 kPa, 0.0140 kPa, 1.360 kPa, and 1.853 kPa. The intensity of the absorbance peak top at 930 cm^{-1} was measured. Also, the calibration curve of Figure 2-9 was obtained. Using this calibration curve, FT-IR analysis was performed on the outlet gas obtained by synthesis. The injection pressure to FT-IR 10 cm gas cell was 1.83 kPa. The intensity of the peak top at 930 cm^{-1} was obtained to ascertain the partial pressure of NF_2Cl in all outlet gases. The partial pressure was found to be 0.59 kPa from the calibration curve, as shown in Figure 2-9, if absorbance strength of 0.2 was obtained. Therefore, 0.59 kPa of NF_2Cl is present in the measured outlet gas of 1.83 kPa. Finally, the NF_2Cl concentration in the outlet gas was calculated as 32.2 volume %. All gas concentrations shown in Table 2-1 were obtained using the method explained above.

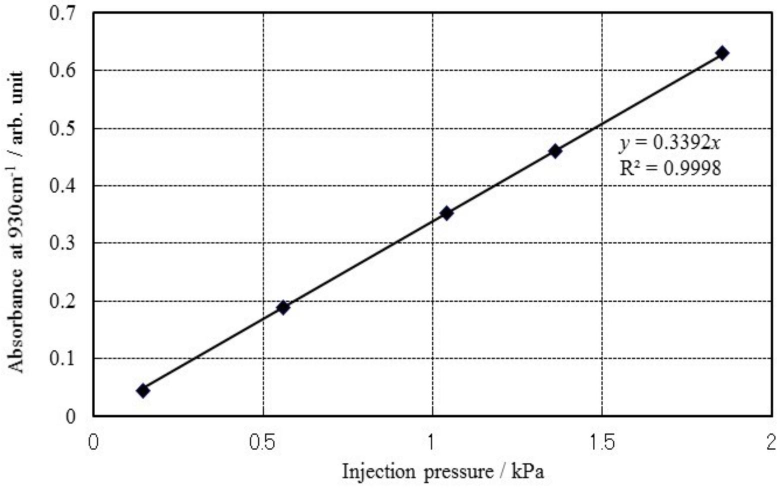

Figure 2-9. Calibration curve of NF_2Cl by FT-IR 10 cm gas cell analysis (930 cm^{-1} peak absorbance).

Table 2-1. Concentrations of outlet gases and NF_2Cl + $NFCl_2$ selectivity by reaction between ClF_3 and NH_4F/nHF systems for each parameter.

Temperature	Gas Flow Amount of ClF_3	n value of NH_4F/n HF	Concentrations of outlet gas (vol%)							Selectivity of NF_2Cl+$NFCl_2$
(K)	(standard cc min^{-1})		N_2	NF_2Cl	$NFCl_2$	Cl_2	ClF	ClF_3	HF	(%)*
283	20	2.2	4.0	51.0	29.0	1.0	12.0	0.0	3.0	91
298	20	2.3	4.1	48.5	30.9	1.0	12.4	0.0	3.1	91
298	50	2.4	4.9	48.5	23.3	5.8	12.6	0.0	4.9	88
298	50	4.0	6.1	39.8	32.7	4.1	5.1	6.1	6.1	86
298	100	3.1	10.2	41.7	18.5	2.8	13.0	8.3	5.6	75
318	20	3.0	12.0	20.0	36.0	1.0	21.0	6.0	4.0	70
318	50	2.8	12.2	30.0	27.8	4.4	15.6	4.4	5.6	70
318	100	2.7	16.4	28.8	21.9	6.8	15.1	4.1	6.8	61

*Nitrogen containing molecule base

Equation (1) shows that NF_2Cl+$NFCl_2$ selectivity was calculated based on the total molar amount of nitrogen atom in the outlet flow gas.

$$NF_2Cl+NFCl_2 \text{ selectivity [\%]} = ([NF_2Cl] + [NFCl_2]) / (2[N_2] + [NF_2Cl] + [NFCl_2]) \quad (1)$$

The reacted gas including 51.0 volume% of NF_2Cl and 29.0 volume% of $NFCl_2$ was obtained at 283 K, 20 standard cc min^{-1} of ClF_3 flow and n=2.2 condition. Only 4.0 volume% of N_2 by-products was found for this condition. Unreacted ClF_3 was not found in this condition. The selectivity of NF_2Cl + $NFCl_2$ at the nitrogen containing molecule base was 91%, as calculated using equation (1). A condition of 298 K, 20 standard cc min^{-1} of ClF_3 flow and n=2.3 also presents nearly the same result as that expressed above. Cl_2 might be generated by the decomposition of $NFCl_2$ ($2NFCl_2 \rightarrow N_2 + 2ClF + Cl_2$) as the side reaction.

At a temperature of 318 K, the selectivity of NF_2Cl + $NFCl_2$ at the nitrogen containing molecule base was less than that at temperatures of 283 K and 298 K. At 318 K, 100 standard cc min^{-1} of ClF_3 flow and under a n=2.7 condition, the selectivity of NF_2Cl + $NFCl_2$ at the nitrogen containing molecule base was calculated as 61% using equation (1).

Unreacted ClF_3 was not found for the low n-value condition between n=2.2 and n=2.4. In all cases, the molten salt temperature increased 1–2 K because of heat from the chemical reaction.

The NF_2Cl and N_2 concentrations in Table 1 are shown against temperature in Figure 2-10. The NF_2Cl concentration decreases with increasing temperature. The N_2 concentration increases concomitantly with decreasing NF_2Cl concentration. Therefore, higher temperatures such as temperatures higher than 320 K decrease the selectivity of the main products of NF_2Cl.

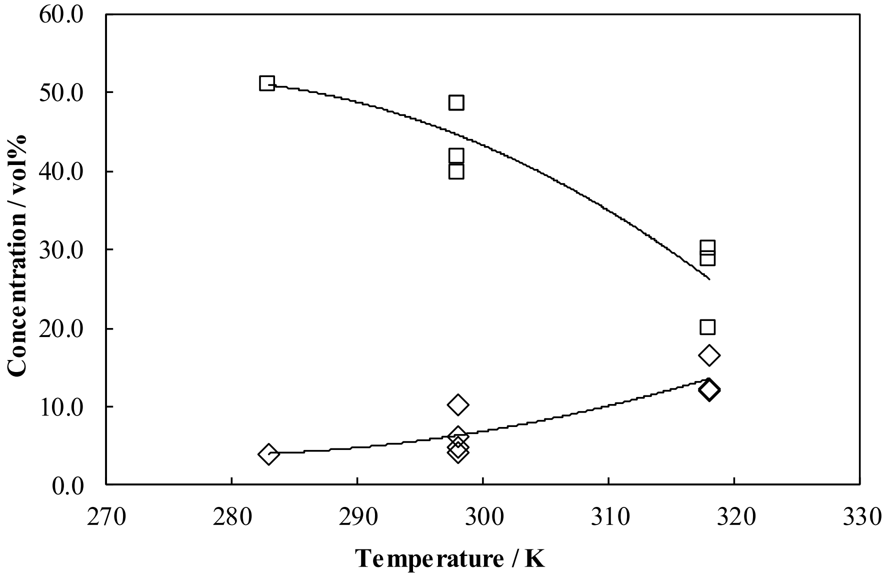

Figure 2-10. NF_2Cl and N_2 concentrations in the reactor outlet gas at various temperatures: (□) NF_2Cl and (◇) N_2.

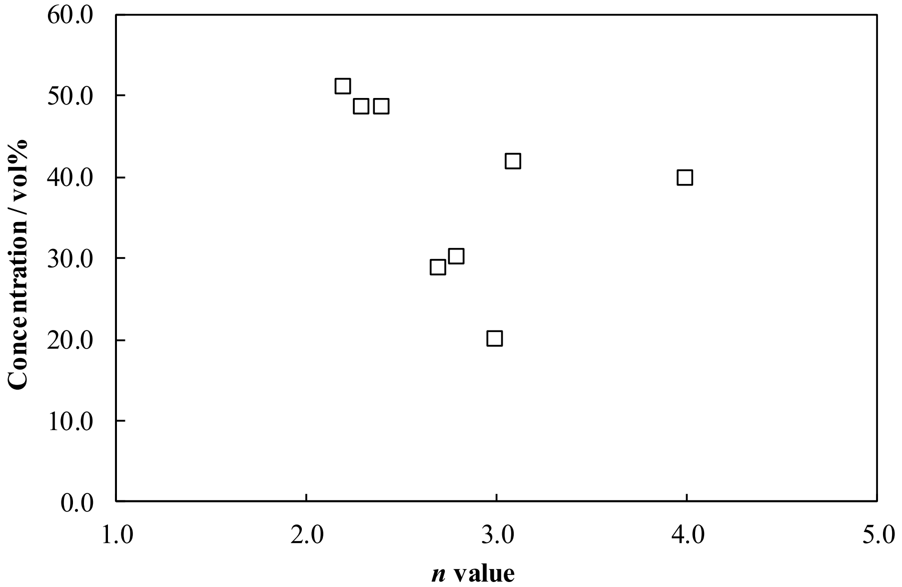

Figure 2-11. NF_2Cl concentrations in reactor outlet gas at various *n* values: (□) NF_2Cl concentration value (%).

Figure 2-11 presents the concentration of NF_2Cl with respect to the n value of NH_4F/nHF. As shown in Figure 2-11, the NF_2Cl concentration decreases when the n-value is 2.7–3.0. This result is apparently related with the melting point of the NH_4F/nHF molten salts. The NH_4F/nHF molten salt requires a specific n-value range to maintain a liquid state under a 298 K condition. The melting points of NH_4F/nHF molten salt were presented in a report of an earlier study [17].

Figure 2-12 shows the n-value range of NH_4F/nHF for the remaining liquid state. Ranges (A) and (B) are liquid states for the NH_4F/nHF system at 298 K.

Figure 2-11 shows that the more the n-value of NH_4F/nHF increases, the lower the concentration of NF_2Cl becomes. Compared to (A) and (B) areas in Figure 2-12, area (A) is suitable for NF_2Cl synthesis. In area (B), the NH_4F concentration decreases in the NH_4F/nHF molten salt system with increasing HF concentration. It engenders passage through the ClF_3 without reaction.

Furthermore, a specific decrease of NF_2Cl concentration occurred for n=2.7–3.0. This result indicates that NH_4F/nHF molten salt reached a partially sherbet state, where some part of the material remains in liquid phase. It also led to passage through ClF_3 without a reaction.

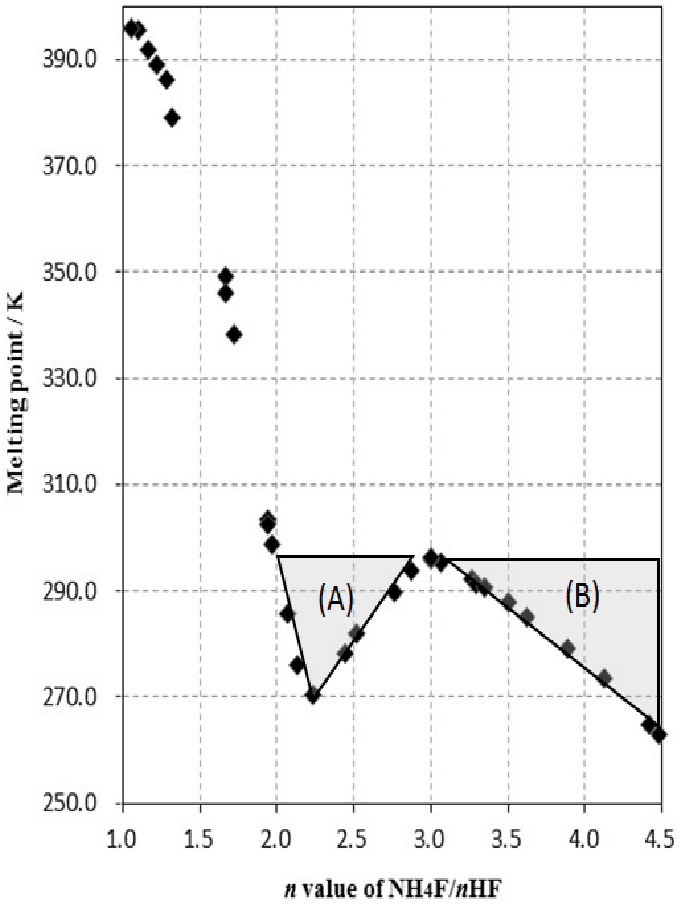

Figure 2-12. Melting points of $NH_4F/n HF$ salt and ranges of the liquid state at 298 K [17].

2-3-2. Reaction mechanism considered with the outlet gas composition

Based on results obtained for the outlet gas data, the total reaction presumably includes one main reaction and one sub-reaction, as presented below.

$$2NH_4F/nHF + 3ClF_3 \rightarrow NF_2Cl + NFCl_2 + (8+2n)HF \tag{2}$$

$$2NH_4F/nHF + 3ClF_3 \rightarrow N_2 + 3ClF + (8+2n)HF \tag{3}$$

In an earlier report, ClF_3 and HF were reported to have some interaction [18, 19]. ClF_3 was presumably retained for a longer time in the NH_4F/nHF molten salts because of this function. It contributes to progress of the reaction. In fact, although the immersion length of the dip tube in the NH_4F/nHF molten salts is less than 0.05 m, ClF_3 did not slip at a bubbling flow rate of 20 standard cc min^{-1}. However, once the NH_4F/nHF molten salt reaches a solid state from a liquid state around n=3.0, the amount of ClF_3 passing through the reactor without interacting with the melt increases.

The NH_4F/nHF melts are known to be formed by NH_4^+ and $(FH)nF^-$ ions in a liquid state [20]. The assumed reaction mechanism is presented as follows. First, $[NH_3ClF_2]^+(FH)nF^-$ is formed by reaction between $[NH_4]^+(FH)nF^-$ and ClF_3 as reaction formula (4). After NF_2Cl is formed by reaction between $[NH_3ClF_2]^+(FH)nF^-$ and ClF_3 as reaction formula (5), $NFCl_2$ is formed as reaction formula (6) by reaction between $[NH_3ClF_2]^+(FH)nF^-$ and ClF, which is formed according to reaction formula (5). Also, the N_2 by-product is formed at an accelerated rate at temperatures higher than 318 K under the reaction temperature conditions. The N_2 is formed as reaction formula (7). Figure 2-13 summarizes these assumed reaction mechanisms.

$$[NH_4]^+(FH)nF^- + ClF_3 \rightarrow [NH_3ClF_2]^+(FH)nF^- + HF \qquad (4)$$

$$[NH_3ClF_2]^+(FH)nF^- + ClF_3 \rightarrow NF_2Cl + ClF + (3+n)HF \qquad (5)$$

$$[NH_3ClF_2]^+(FH)nF^- + ClF \rightarrow NFCl_2 + (3+n)HF \qquad (6)$$

$$2[NH_3ClF_2]^+(FH)nF^- + ClF_3 \rightarrow N_2 + 3ClF + (6+2n)HF \qquad (7)$$

When the reaction proceeds based on formulas (5) and (6), the amount of ClF in Table 2-1 is expected to be greater. As expressed above, ClF_3 and HF reportedly have some interaction [18,19]. Therefore, some possibility exists of having similar interaction between ClF and HF. ClF might remain in the NH_4F/nHF melts.

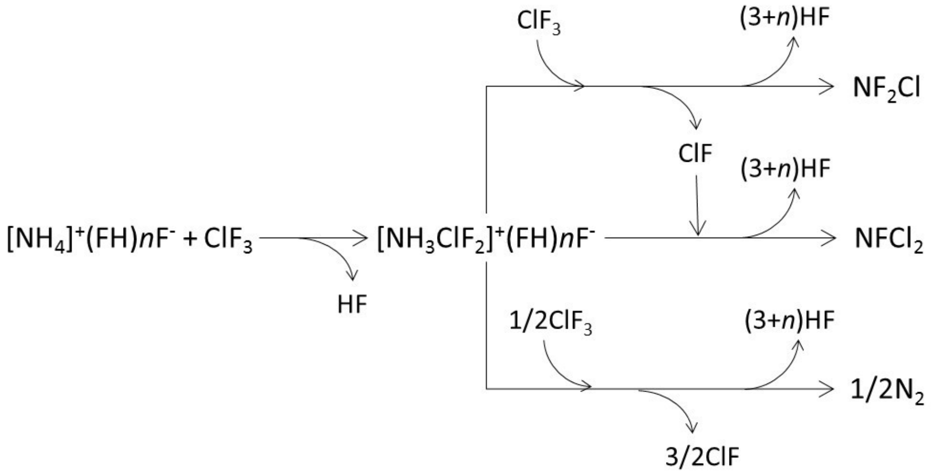

Figure 2-13. Reaction scheme of NF_2Cl and $NFCl_2$ synthesis using NH_4F/nHF.

2-4. Summary

Reactions between NH_4F/nHF of molten salts and gaseous ClF_3 were examined at temperatures of 280–320 K with various n-values (n = 2.2, 2.3, 2.4, 2.7, 2.8, 3.0, 3.1, and 4.0) and three ClF_3 flow ratio (20, 50 and 100 standard cc min^{-1}) conditions. After the reaction, NF_2Cl and $NFCl_2$ gases were obtained, with high selectivity of NF_2Cl and $NFCl_2$. Specifically, the selectivity was higher than 90% as the nitrogen base in specific conditions of temperatures less than 298 K, with n-values around 2.2–2.3 by a direct reaction. Over 90% selectivity of NF_2Cl and $NFCl_2$ is extremely effective for industrial manufacturing. The by-product of N_2 increases at temperatures higher than 318 K. The reaction mechanism of this synthesis is assumed to be NF_2Cl and $NFCl_2$, formed via $[NH_3ClF_2]^+(FH)nF^-$.

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Chapter 3

NF_3 synthesis using ClF_3 as a mediator

3-1. Introduction

Nitrogen trifluoride (NF_3), a stable gas at room temperature, has strong oxidation capability at higher temperatures [1,2]. For that reason, NF_3 has been used as an oxidizing agent for rocket fuels and as a stable fluorine agent [1,3].

Since a few researchers attempted to develop the use of NF_3 as a plasma process gas in the early 1970s [4,5], NF_3 has been used widely to generate plasmas for etching and dry chamber cleaning [1,6]. Logic devices and memory devices require the deposition, via plasma-enhanced chemical vapor deposition (CVD), of various thin-film materials on silicon wafer substrates: polysilicon; typically metals such as tungsten; and dielectrics such as SiO_2 and Si_3N_4. Film material is also deposited on reactor chamber surfaces, from which it must be removed periodically to prevent particulate contamination of processed wafers [6,7]. Currently, almost all semiconductor device manufacturers use NF_3 as the CVD chamber cleaning gas [8,9].

For NF_3, three processes have been reported as technically and economically feasible for large-scale production [6].

One is the electrolysis of molten ammonium acid fluoride, shown as reactions (1) and (2). Reaction formula (1) corresponds to the anode reaction; reaction formula (2) corresponds to the cathode reaction. NF_3 is generated on the anode surface. This synthesis can generate NF_3 by electrolysis without an electrolytic cell for producing fluorine gas. However, for this process, it is commonplace in industry to use a nickel electrode as the anode. When using a nickel anode, 1–5% of the electric power is used to dissolve nickel. It therefore becomes necessary to replace the electrode periodically and to remove the nickel fluoride sludge in the NH_4F/nHF molten salt

[1]. For that reason, attempts have been undertaken to use carbon electrode anodes instead [1].

Second is direct fluorination using NH_4F/nHF and F_2 as reaction (3). This synthesis presents the possibility of explosion of the $NH_3 - NF_3$ mixture [10]. For that reason, HF is added to NH_3 for dilution and for explosion prevention. However, the reaction rate is low because of the lack of solubility of fluorine for NH_4F/nHF [11]. Therefore, to raise the yield, it is often necessary to use a reaction that entails high temperature and high pressure.

A third process is direct fluorination using $(NH_4)_3AlF_6$ and F_2 as reaction (4). This process makes mild reaction possible using low reactivity $(NH_4)_3AlF_6$. However, compared to other processes, $(NH_4)_3AlF_6$ must be manufactured separately, rendering the manufacturing process longer and making production costs higher than either of the other two processes.

$$NH_4F/nHF \rightarrow NF_3 + 6H^+ + 6e- \tag{1}$$

$$2H+ 2e^- \rightarrow 3H_2 \tag{2}$$

$$NH_4F/nHF + 3F_2 \rightarrow NF_3 + (4+n)HF \tag{3}$$

$$(NH_4)_3AlF_6 + 6F_2 \rightarrow 2NF_3 + NH_4AlF_4 + 8HF \tag{4}$$

As described herein, we explain a novel method of NF_3synthesis that differs from the three industrialized processes presented above. Using this method, NH_4F/nHF and ClF_3 are reacted to synthesize NF_2Cl and $NFCl_2$ with high selectivity described in an earlier report [8]. Synthesized NF_3 and ClF_3 are produced by reacting the synthesized NF_2Cl and $NFCl_2$ with F_2. Recycling of synthesized ClF_3 is attempted using the NH_4F/nHF and ClF_3 reaction. Results presented in an earlier report show that NF_2Cl and $NFCl_2$ are obtainable with high selectivity over 90% when NH_4F/nHF and ClF_3 are reacted in $NH_4F/2.2–2.3HF$ in the reaction at a temperature below 298 K [8]. Compared to the reaction of synthesizing NF_3 by the direct reaction of NH_4F/nHF with F_2, the merit of using ClF_3 is the higher solubility in HF solvent [12–14]. Furthermore, in the case of using F_2 instead of ClF_3, the outlet gas flow rate becomes rapidly and constantly an almost equal value to that of the inlet gas flow rate, whereas, in the case of ClF_3, the outlet gas flow rate gently rises and then becomes constant at a value of 70% of the inlet gas flow rate [8]. The ClF_3 is dissolved in NH_4F/nHF, in which it reacts remarkably. Therefore, the synthesis method presented here must be able to achieve a higher yield than the conventional method.

The results of synthesis of NF_3 from NF_2Cl and $NFCl_2$ are reported herein. The possibility of NF_3 synthesis via intermediate products containing chlorine was verified. Furthermore, avoiding the loss of chlorine-containing intermediate chemical species to the greatest degree possible is crucially important for the creation of a high-yield process. Therefore, clarifying the influence of the equilibrium reaction of ClF_3 on synthesis is an important task.

3-2. NF_3 synthesis scheme using ClF_3 as a mediator

3-2-1. Gas phase reaction scheme

The reaction scheme assumed this time is presented in Figure 3-1. Panels (a)–(f) in Figure 3-1 respectively portray the reactors and the condenser. These reactors and a condenser were connected by piping with the flow, as indicated by the arrow in Figure 3-1.

As a first step reaction, NF_2Cl and $NFCl_2$ are synthesized from NH_4F/nHF and ClF_3, as shown in reaction (5) at a liquid–gas reactor in Figure 3-1-(a). It can be reacted by bubbling ClF_3 in a gaseous state to liquid state NH_4F/nHF. After NF_2Cl and $NFCl_2$ generated in this reaction pass through the gas pipe from the reactor outlet, they are transferred to the next reactor. The next reaction is synthesis of NF_2Cl and ClF by the reaction of $NFCl_2$, which is the main component generated in the liquid–gas reactor (a) and F_2 added to the pipeline behind the liquid–gas reactor (a). It is a reaction in the gas phase; $NFCl_2$ is converted to NF_2Cl as shown in reaction (6) in a low-temperature gas–gas reactor in Figure 3-1-(b). Next, in the first high-temperature gas–gas reactor (c), NF_3 is synthesized by reaction between NF_2Cl and F_2, as shown in reaction (7). In addition, ClF_3 is synthesized by reaction of F_2 with ClF produced in the first high-temperature gas–gas reactor (c), as shown in reaction (8). After the generated NF_3 and ClF_3 pass through the gas piping, they are transferred to the condenser as shown in Figure 3-1-(d). After the ClF_3 is liquefied and collected by cooling in this condenser (d), it is used for reaction in the liquid–gas reactor shown in Figure 3-1-(a).

$$2(NH_4F/nHF) + 3ClF_3 \rightarrow NF_2Cl + NFCl_2 + (8+2n)HF \qquad (5)$$

$$NFCl_2 + F_2 \rightarrow NF_2Cl + ClF \qquad (6)$$

$$NF_2Cl + F_2 \rightarrow NF_3 + ClF \qquad (7)$$

$$ClF + F_2 \rightarrow ClF_3 \qquad (8)$$

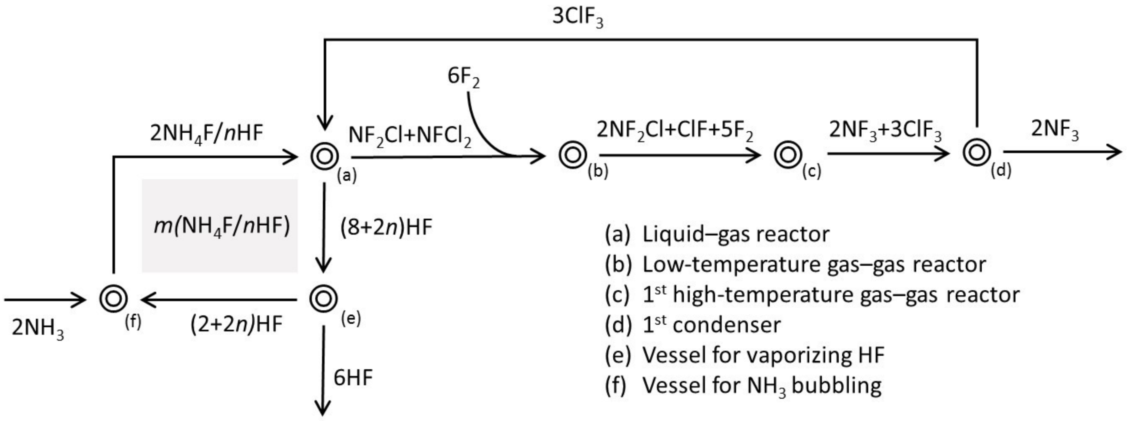


Figure 3-1. NF_3 synthesis target scheme using NF_2Cl, $NFCl_2$ and ClF_3 as a mediator

3-2-2. Liquid phase reaction scheme

Regarding the molten salt circulation scheme, liquid–gas reactor (a), the vessel for vaporizing HF (e), and the vessel for NH_3 bubbling (f) shown in Figure 3-1 are filled by

NH_4F/nHF. Liquid pumps circulate the molten salt.

Most of the by-product HF produced in reaction formula (5) is dissolved in the NH_4F/nHF molten salt. Therefore, the n value of NH_4F/nHF increases as shown in the reaction formula (9). Therefore, removing HF from NH_4F/nHF is necessary. Removal was conducted by taking vaporizing method and bringing HF together with Ar gas by bubbling Ar gas at vessel for vaporizing HF (e) in Figure 3-1, as shown in reaction formula (10). In addition, NH_3 consumed in reaction formula (9) must be supplied. NH_3 gas was injected by bubbling directly to the vessel for NH_3 bubbling in Figure 3-1-(f), as shown in reaction (11).

$$m(NH_4F/nHF) + 3ClF_3 \rightarrow NF_2Cl + NFCl_2 + (m-2)NH_4F/(mn+8)HF \quad (9)$$

$$(m-2)NH_4F/(mn+8)HF + Ar \rightarrow (m-2)NH_4F/(mn+2)HF + Ar + 6HF \quad (10)$$

$$(m-2)NH_4F/(mn+2)HF + 2NH_3 \rightarrow m(NH_4F/nHF) \quad (11)$$

3-3. Experimental

3-3-1. Equipment, raw materials, and analysis

Figure 3-2 portrays a schematic diagram of this series of continuous processes. Regarding the circulation route of molten salt, (a) → (e) → (f) → (a) was circulated using a liquid pump (blue line, Figure 3-2). A diaphragm-type pump (Type E-1000; Kyoritsukiko Co., Ltd.) was used as a liquid pump.The gas flow path was (a) → (b) → (c) → (d) → (g) → (h). The ClF_3 gas collected by the condensers of (d) and (h) was charged to the reactor (a) again for recycling.

Metal tube variable-area flowmeters (NMX Series; Tokyo Keiso Co., Ltd.) were used for gas flow rate measurements. Mass flow controllers (SEC-E400; Horiba Stec Co. Ltd.) were used for the flow rate adjustment of ClF_3, F_2, NH_3, and Ar gases. Metal tube variable-area flowmeters (MX-400 Series; Tokyo Keiso Co., Ltd.) were used as liquid flowmeters for checking the amount of circulating molten salt.

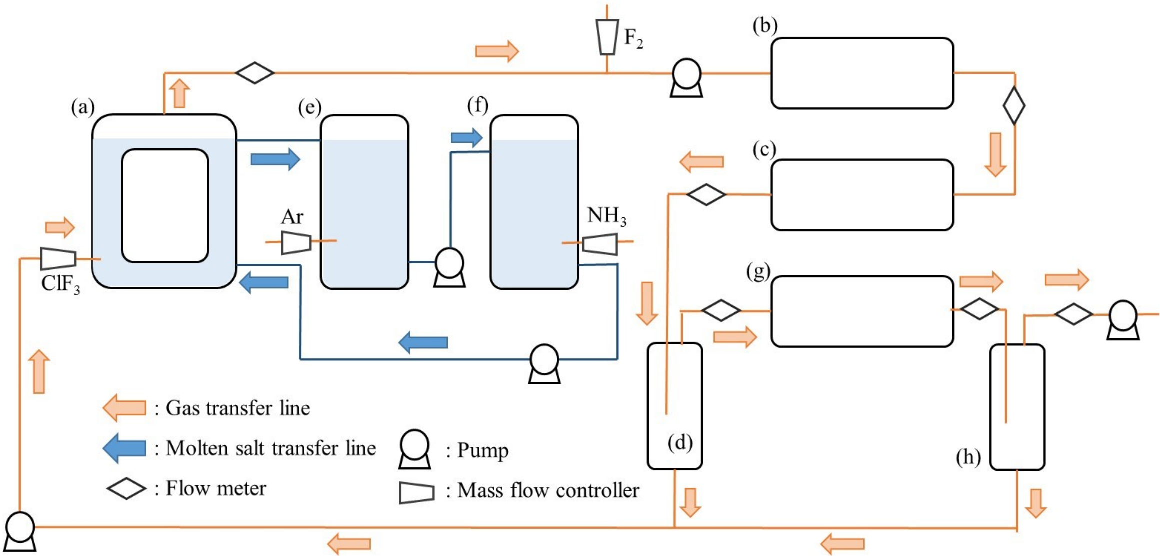
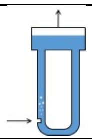
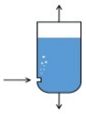
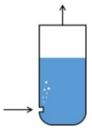
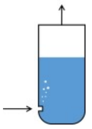
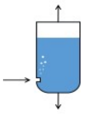


Figure 3-2. Schematic diagram of the reaction system.

Table 3-1 presents shapes, dimensions, and materials of the respective reactors used for the experiment. The liquid–gas reactor (a), a toroidal type used for mixing the molten salt without a stirrer, used the gas buoyancy for purging [15,16]. As the gas–gas reactors used at (b), (c), and (g), cylindrical nickel reactors were used and were selected as piston flow type. As condensers (d) and (h), stainless steel cylindrical condensers were used. For reactor (a) and vessels (e) and (f) filled with NH_4F/nHF, PFA-coated material was used.

Table 3-1. Reactor shapes, dimensions, and wetted surface materials

No.	Item Name	Shape		Dimensions	Volume	Wetted surface material
(a)	Liquid—gas reactor	Toroidal		Tube φ = 70 mm Height = 2500 mm	Filling NH_4F/nHF liquid: 0.035 m^3	PFA coated
(b)	Low temperature gas—gas reactor	Cylindrical (Gas piston flow)		Tube φ=210 mm Length =1500 mm	Heating zone: 0.035 m^3	Nickel
(c)	1st high temperature gas—gas reactor	Cylindrical (Gas piston flow)		Tube φ=210 mm Length =1500 mm	Heating zone: 0.047 m^3	Nickel
(d)	1st condenser	Cylindrical		Tube φ = 260 mm Height = 800 mm	0.039 m^3	Stainless steel (SUS304)
(e)	Vessel for vaporizing HF	Cylindrical		Tube φ = 310 mm Height = 1000 mm	0.070 m^3 Filling NH_4F/nHF liquid: 0.035 m^3	PFA coated
(f)	Vessel for NH_3 bubbling	Cylindrical		Tube φ = 110 mm Height = 2000 mm	0.019 m^3 Filling NH_4F/nHF liquid: 0.015 m^3	PFA coated
(g)	2nd high temperature gas—gas reactor	Cylindrical		Tube φ=210 mm Length =700 mm	Heating zone: 0.020 m^3	Nickel
(h)	2nd condenser	Cylindrical		Tube φ = 130 mm Height = 400 mm	0.005 m^3	Stainless steel (SUS304)

The raw material gases were ClF_3 (>99.9 wt% purity; Central Glass Co., Ltd.), F_2 (>99 vol% purity; Central Glass Co., Ltd.), and NH_3 (>99.999 vol%; Showa Denko K.K.).

We prepared NH_4F/nHF melts by feeding gaseous anhydrous HF (>99.999 wt%; Central Glass Co., Ltd.) through $NH_4F/1.0HF$ (Morita Chemical Industries Co. Ltd.). We calculated the n value of NH_4F/nHF using the HF feeding weight. After feeding HF, the n value of $NH_4F/2.3HF$ was checked using a neutralization titration method.

The reaction product was injected into several analytical devices. A Fourier transform infrared spectrophotometer (FT-IR Prestige-21; Shimadzu Corp.) with 100 mm path length gas cells with ZnSe windows was used to ascertain the NF_2Cl, $NFCl_2$, ClF_3, ClF, and HF concentrations. The injection pressure was maintained at 1.85 kPa. A gas chromatograph – mass spectrometer (GC/MS, GCMS-QP2010; Shimadzu Corp., Column Varian Capillary Column CP-PoraBOND Q) was used to ascertain the N_2 contents. Ultraviolet visible absorption spectroscopy (UV/Vis U-2810; Hitachi Ltd.) was used to ascertain the Cl_2 and F_2 contents of the outlet gases.

3-3-2. Reaction temperature, pressure, and flow rate

Temperature conditions for the respective steps are explained below. The reaction temperature of the liquid–gas reactor (a) is 298 K. The respective reaction temperatures of low-temperature gas–gas reactor (b) and first high-temperature gas–gas reactor (c) are 393 K and 603 K. Furthermore, the second high-temperature gas–gas reactor (g) was operated at 613 K. Condensers (d) and (h) were condensed at 213 K for collecting ClF_3.

For this experiment, 7.64 standard liters per minute (SLM) of F_2 and 2.61 SLM of NH_3 were used as raw materials. In addition, $n = 2.3$ was used as an n value of NH_4F/nHF. In all, 80 kg of NH_4F/nHF was filled as the first filling liquid of the main reactor (a), vessel for vaporizing HF (e), and the vessel for NH_3 bubbling (f). Then 3.91 SLM of collected ClF_3 was flowed to liquid–gas reactor (a). The condensed ClF_3 was used in this experiment, but in view of the insufficient amount, 10 kg of new ClF_3 was charged inside the condenser (d) before testing began.

The m value of NH_4F/nHF in reaction (9) is $m = 964$ because the filling amount of NH_4F/nHF is 80 kg. An earlier report described that, in the condition of the filling amount 0.5 kg (5.5 mol) of NH_4F/nHF and 0.1 SLM of ClF_3, it caused a slip through unreacted ClF_3. However, the conditions of 0.05 SLM of ClF_3 were insufficient to leave unreacted ClF_3. In this experiment, the flow rate ratio of ClF_3 was 3.91 SLM against the filling amount of NH_4F/nHF, which is lower than the slipped condition. Therefore, the test was conducted under a condition in which no unreacted ClF_3 remained. Each experiment was conducted continuously for 100 h or longer.

3-4. Results and discussion

3-4-1. Reaction product of gas phase reaction

An examination was conducted to ascertain whether the scheme of Figure 3-1 works or not. The FT-IR analysis results of the gas phase reaction are presented in Figure 3-3. They show the outlet gas spectrum of Figure 3-1-(a) at spectrum (a), the outlet gas spectrum of Figure 3-1-(b) at spectrum (b), the outlet gas spectrum of Figure 3-1-(c) at spectrum (C), and the outlet gas spectrum of Figure 3-1-(d) at spectrum (D). The FT-IR peaks of NF_3, ClF_3 and HF were assigned using NIST Library data. The peaks of NF_2Cl [17–19], $NFCl_2$ [18,20], and ClF [21,22] were assigned, respectively, relative to peak information from earlier reports of the relevant literature. We used UV/Vis analysis for analyses of F_2 and Cl_2 [23], and used GC-MS for analysis of N_2.

Figure 3-3-(A) portrays the FT-IR spectrum of the outlet gas in Figure 3-1-(a). Results demonstrate that NF_2Cl and $NFCl_2$ can be generated similarly to results obtained under the optimum conditions explained in an earlier report [8].

Figure 3-3-(B) presents the FT-IR spectrum of the outlet gas of Figure 3-1-(b). Passage of outlet gas (a) through the low-temperature gas–gas reactor (b) with fluorine decreases the peak of $NFCl_2$. Because the peak of ClF was generated, The reaction of formula (6) proceeded as expected.

Figure 3-3-(C) portrays the FT-IR spectrum of the outlet gas of Figure 3-1-(c). After passage through the first high-temperature gas–gas reactor, the NF_2Cl and $NFCl_2$ peaks do not appear. It can be confirmed that NF_3 is formed. Moreover, ClF_3 production can be confirmed.

Figure 3-3-(D) depicts the FT-IR spectrum of the outlet gas after cooling and collecting ClF_3 with a condenser in Figure 3-1-(d). 1,1-Dichloro-1-fluoroethane (HCFC-141b) was used as the refrigerant for cooling of condenser (d) to 213 K. Examination of Figure 3-3-(D) reveals that the ClF_3 peaks decrease. The main peaks are NF_3. However, results demonstrated that the peaks of ClF_3 and ClF remains even though the peaks are small.

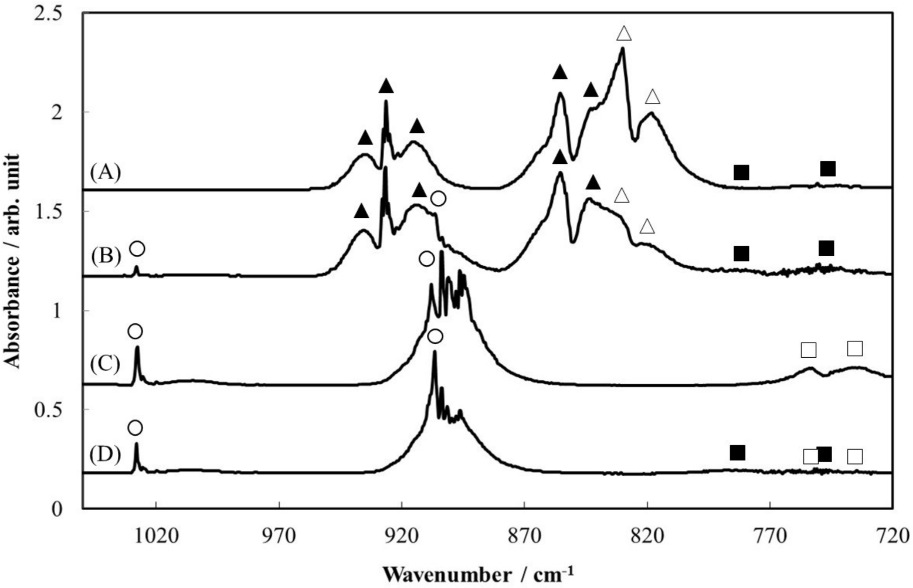


Figure 3-3. FT-IR spectra of outlet gases from each reactor: (A) outlet gas from (a) liquid–gas reactor; (B) outlet gas from (b) low-temperature gas–gas reactor; (C) outlet gas from (c) first high-temperature gas–gas reactor; (D) outlet gas from (d) first condenser (○, NF_3; ▲, NF_2Cl; Δ, $NFCl_2$; ■, ClF; □, ClF_3).

Next, the concentrations of the gas species contained in the outlet gases were found. Then NF_2Cl, $NFCl_2$, ClF_3, and HF were measured using FT-IR. Additionally, ClF was measured using the difference FT-IR method [8]. N_2 was measured using GC/MS. We measured Cl_2 and F_2

using UV/Vis analysis. All calibration curves were prepared for the respective gas species, as described in an earlier report [8].

Table 3-2 presents gas component concentrations of the respective outlet gases in Figure 3-3. Flow amounts of gases in Figure 3-3 were obtained using two parameters: the concentration of each outlet gas in Table 3-2 and the total outlet gas flow rate. To obtain the outlet gas flow rate, we used metal tube, variable-area flowmeters located in the respective outlet gas lines of the reactors.

Table 3-2. Outlet gas concentrations of (a)–(d) in Figure 3-1 (Run 1)

Sampling point	Outlet gas component concentrations (vol%)								
	NF_3	NF_2Cl	$NFCl_2$	N_2	F_2	ClF_3	ClF	Cl_2	HF
(a)	0.0	41.9	37.7	4.3	0.0	0.0	10.8	2.1	3.3
(b)	1.2	20.0	1.1	1.2	61.4	0.0	13.7	0.6	0.9
(c)	32.8	0.0	0.0	1.8	10.5	47.5	5.3	0.9	1.4
(d)	60.2	0.0	0.0	3.3	19.2	3.6	9.7	1.6	2.5

Table 3-3 presents component flow rates of outlet gases in Figure 3-3 and the respective component flow rates calculated as expressed above. For this experiment, 3.91 SLM of ClF_3 and 7.64 SLM of F_2 were used as raw materials; 2.39 SLM of NF_3 was obtained as a result. The ClF_3 amounts collected by the condenser (d) in Figure 3-1 were calculated as 3.27 SLM from the difference in flow rates between ClF_3 at the inlet and outlet of the condenser (d).

We detected 0.13 SLM of N_2 gas at the outlet of liquid–gas reactor (a). No increase was observed in (b), (c), or (d). Because N_2 is not generated in reaction (5), this N_2 might be generated as a by-product because of the progress of reactions (13) and (14).

The selectivity of N_2 and NF_3, a key parameter for the efficient production of NF_3, is calculable based on calculation using formula (12) from the outlet gas of (d) in Figure 3-1. In this experiment, selectivity of NF_3 against N_2 based on nitrogen atoms was 90.2%.

$$NF_3 \text{ selectivity } [\%] = (FR_{NF3})/(FR_{NF3} + FR_{N2} \times 2) \tag{12}$$

FR, flow rate (SLM)

$$2(NH_4F/nHF) + 3ClF_3 \rightarrow N_2 + 3ClF + (8+2n)HF \tag{13}$$

$$2NFCl_2 \rightarrow N_2 + 2ClF + Cl_2 \tag{14}$$

Table 3-3. Gas flow rates of outlet gas components in Figure 3-1 (Run 1)

Sampling point	Outlet gas flow rates (SLM*)									
	NF_3	NF_2Cl	$NFCl_2$	N_2	F_2	ClF_3	ClF	Cl_2	HF	Total
(a)	0.00	1.24	1.12	0.13	0.00	0.00	0.32	0.06	0.10	2.96
(b)	0.12	2.12	0.11	0.13	6.51	0.00	1.45	0.06	0.10	10.60
(c)	2.36	0.00	0.00	0.13	0.75	3.41	0.38	0.06	0.10	7.19
(d)	2.39	0.00	0.00	0.13	0.76	0.14	0.38	0.06	0.10	3.97

* Standard liters per minute

Regarding the efficient utilization of fluorine, it is calculable based on theoretical reaction formulas (15) and (16). When viewed on a fluorine basis, ClF_3 obtained in the reaction formula (16) is recycled as a raw material of reaction formula (15). Therefore, the theoretical amount of fluorine necessary for synthesizing 2 moles of NF_3 is 6 moles.

$$2NH_3 + 3ClF_3 \rightarrow NF_2Cl + NFCl_2 + 6HF \tag{15}$$

$$NF_2Cl + NFCl_2 + 6F_2 \rightarrow 2NF_3 + 3ClF_3 \tag{16}$$

For this experiment, 7.64 SLM of F_2 gas was used to generate 2.39 SLM of NF_3 gas. The recovery loss of ClF_3 gas is calculable as 0.64 SLM based on the amount recovered by the first condenser. Therefore, the fluorine atom base yield is definable by equation (17). In this experiment (run 1), the NF_3 yield of the fluorine atom base was 83%.

$$NF_3 \text{ yield [\%]} = (3\times FR_{NF3})/(FR_{F2}+3/2\times FR_{ClF3\text{-loss}}) \tag{17}$$

To account for the low yield, below 90%, three major explanations can be considered. The first possible cause is a by-product reaction of N_2 generated by reaction formula (13) and reaction formula (14) shown above. The second possible explanation is the ClF_3 loss: the amount not collected by the condenser (d). The last cause is the unreacted ClF and F_2 remaining after ClF_3 is generated in the reaction equation (8).

Table 3-3 shows that the amount of N_2 in outlets (b) and (c) is 0.13 SLM and presents clearly that it does not change. It reacts with NF_2Cl or $NFCl_2$ to NF_3 based on the reaction equations (6), (7), and (16). Results show that the side reaction to N_2 does not proceed. Therefore, the occurrence of N_2 is regarded as occurring in the reaction in (a). Improvement of the NF_3 selectivity can be achieved by controlling the n value and temperature during reaction in the main reactor (a), as described in an earlier report [8].

As a method for improving reduction in the N_2 generating ratio, which is the first cause, it is important to control the n value of $NH_4F/n HF$ and temperature during reaction in the liquid–gas reactor (a). An earlier report described details of the relation between the n value, reaction temperature, and N_2 selectivity [8]. Table 3-3 shows that the by-product reaction of N_2 such as the reaction formula (14) was not increased when reacting NF_2Cl or $NFCl_2$ to NF_3. The N_2 amount is not changed at 0.13 SLM. Therefore, the side reaction of by-product N_2 did not occur.

To reduce the loss of the ClF_3, which is the second cause, it is necessary to raise the recovery rate of the condenser (d), but the recovery loss of condenser (d) depends on the cooling temperature. The ClF_3 vapor pressure at 213 K is obtainable from the Antoine equation reported earlier in the literature [24], which is 3.0 kPa. Calculating the partial pressure from the ClF_3 concentration in the outlet gas (d) of Table 3-3 using the information that the reaction pressure is 93.3 kPa results in 3.3 kPa. This value is consistent with the vapor pressure of ClF_3. The amount lost from the outlet of the condenser (d) is reasonable. It is also conceivable to lower the cooling temperature further to improve the recovery rate of ClF_3, but the boiling point of NF_3 is 144 K. Therefore, it is impossible to adopt a method of cooling with liquid nitrogen or some similar material.

Next, a method of reducing the loss of unreacted materials of F_2 and ClF, which is the third possible cause, is described. The formation reaction of ClF_3 in reaction formula (5) is known to be an equilibrium reaction [25,26]. Therefore, the Kp value of $ClF + F_2 = ClF_3$ in the main reactor (c) was calculated. The Kp value is obtainable by equation (18). When the value in this experiment was obtained from the partial pressures of ClF_3, ClF, and F_2 of the outlet gas of the main reactor (c), the Kp value was 86. The partial pressures of the respective gases were calculated by multiplying the total pressure 93.3 kPa by the concentrations of the respective gases.

$$Kp = P_{\mathrm{ClF_3}}/(P_{\mathrm{ClF}} \times P_{\mathrm{F_2}}) \qquad (18)$$

Actually, the Kp value in the equilibrium of reaction (5) can be shown in Figure 3-4 based on data from an earlier report [25]. In this experiment, the reaction temperature of the first high-temperature gas–gas reactor was set to 603 K, which demonstrates that it is roughly in agreement with the value reported in the literature, as shown in Figure 3-4. Therefore, to decrease the unreacted loss of F_2 and ClF and to increase the production rate of ClF_3, it is better to lower the reaction temperature. However, when the reaction temperature is lowered, the reaction rate decreases remarkably [26,27]. In addition, the fluorination reaction rate from NF_2Cl to NF_3 decreases. Therefore, instead of lowering the reaction temperature, it is necessary to consider a method of reducing the unreacted loss of F_2 and ClF by shifting the equilibrium.

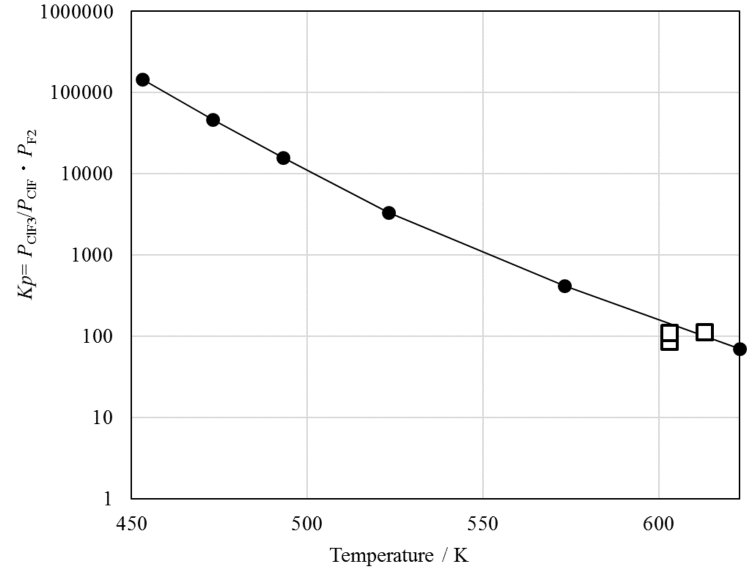


Figure 3-4. *Kp* values for equilibrium ClF + F_2 = ClF_3 [25] and *Kp* results of (c) and (g) reaction in run 1 and run 2 (●, reference; □, results).

Then, as shown in Figure 3-5, after recovering ClF_3 once with a condenser (d), reheating is conducted with the second high-temperature gas–gas reactor (g). There again, ClF_3 is synthesized and recovered by the second condenser (h) there again. It is possible that the equilibrium is shifted by recovering ClF_3 once with condenser (d). After shifting the equilibrium, ClF_3 can be generated again by the second high-temperature gas–gas reactor (g).

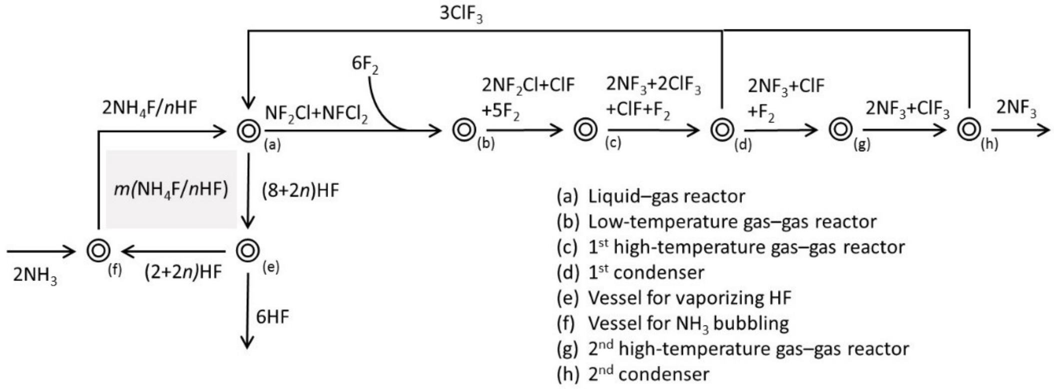


Figure 3-5. NF_3 synthesis target scheme 2 using chlorine compounds as mediators (double condensing method).

Table 3-4 and Table 3-5 show reaction data using the scheme depicted in Figure 3-5. Results of the outlet gases from (a)–(d) are understood to be roughly in agreement with the results obtained in run 1 and shown in Table 3-2 and Table 3-3. The *Kp* value of $ClF + F_2 = ClF_3$ in run 2 was *Kp* = 114 in the first high-temperature gas–gas reactor (c) and 111 in the second high-temperature gas–gas reactor (g). Because the reaction temperatures are 603 K and 613 K, it is apparent from the literature value reported in the literature [25] in Figure 3-4 and the plot data of the results that the results are in agreement with the *Kp* curve. In run 2, the NF_3 yield of fluorine atom base was 91%. Results obtained for the outlet gas (h) also confirmed that the loss of F_2 and ClF was less than that from run 1.

As for synthesizing NF_3, purifying NF_3 to over 99.99 volume % was confirmed as possible using conventional purification processing with distillation, water scrubber, alkali scrubber, and a dehydrating agent such as a molecular sieve after synthesizing NF_3 using this paper's process.

Table 3-4. Outlet gas concentrations in Figure 3-5 (Run 2)

Sampling point	Outlet gas component concentrations (vol%)								
	NF_3	NF_2Cl	$NFCl_2$	N_2	F_2	ClF_3	ClF	Cl_2	HF
(a)	0.0	42.0	39.9	3.7	0.0	0.0	10.2	1.1	3.1
(b)	0.9	20.2	1.7	1.0	61.9	0.0	13.2	0.3	0.9
(c)	34.0	0.0	0.0	1.6	8.1	49.2	5.5	0.4	1.3
(d)	64.5	0.0	0.0	3.0	15.4	3.3	10.4	0.8	2.5
(g)	71.0	0.0	0.0	3.2	7.1	13.4	1.7	0.9	2.7
(h)	79.3	0.0	0.0	3.6	8.0	3.3	1.9	1.0	3.0

Table 3-5. Gas flow rates of respective outlet gas components in Figure 3-5 (Run 2)

Sampling point	Outlet gas flow rates (SLM*)									
	NF_3	NF_2Cl	$NFCl_2$	N_2	F_2	ClF_3	ClF	Cl_2	HF	Total
(a)	0.00	1.23	1.17	0.11	0.00	0.00	0.30	0.03	0.09	2.93
(b)	0.10	2.13	0.18	0.11	6.55	0.00	1.39	0.03	0.09	10.58
(c)	2.41	0.00	0.00	0.11	0.57	3.49	0.39	0.03	0.09	7.09
(d)	2.40	0.00	0.00	0.11	0.57	0.12	0.39	0.03	0.09	3.72
(g)	2.41	0.00	0.00	0.11	0.24	0.45	0.06	0.03	0.09	3.39
(h)	2.41	0.00	0.00	0.11	0.24	0.10	0.06	0.03	0.09	3.04

*Standard liters per minute

3-4-2. NH_4F/nHF molten salt circulation system

Recycling the NH_4F/nHF molten salt requires removal of by-produced HF in reaction formula (5) and the addition of NH_3 consumed by the reaction. The HF generated in the liquid–gas reactor (a) by the reaction partly entrains gas. It is transferred from liquid–gas reactor (a) to a low-temperature gas–gas reactor (b). Results demonstrate that the amount is 0.10 SLM, as shown in Table 3-3.

The vapor pressures of $n = 2, 3, 4$, and 5 of NH_4F/nHF were measured. Figure 3-6 was obtained. It also agrees roughly with results reported earlier in the literature [28]. Reaction temperature of the liquid–gas reactor (a) was 298 K; the n value was $n = 2.3$. As shown in Figure 3-7, the vapor pressure of HF was obtained as 1.8 kPa using a vapor pressure curve which is re-plotted using n-value axis based on the Figure 3-6 data. The reaction pressure was 93.3 kPa (700 Torr). The HF concentrations were 3.3% and 3.1% according to the respective results of run 1 and run 2. Based on these results, the partial pressure of HF was calculated as 2.9 kPa, which is a closely approximate value.

When ClF_3 gas is purged at a flow rate of 3.94 SLM into the liquid–gas reactor (a), HF generated as a by-product is calculated from reaction formula (5) as 10.51 SLM. Assuming that all the 10.51 SLM of HF generated in the reaction is contained in the outlet gas, the concentration is 78%. However, the concentration result for HF contained in the outlet gas was about 3%, which means that 10.41 SLM is accumulated in the molten salt. One can infer that the n value of NH_4F/nHF in the reactor (a) is increased.

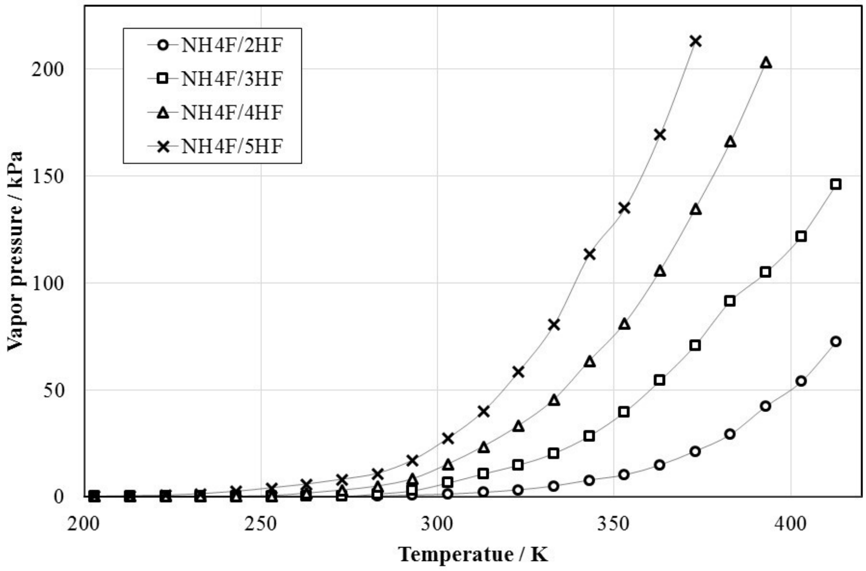


Figure 3-6. HF vapor pressure of NH_4F/nHF: $n = 2, 3, 4, 5$

($n = 2$, ○; $n = 3$, □; $n = 4$, △； $n = 5$, ×)

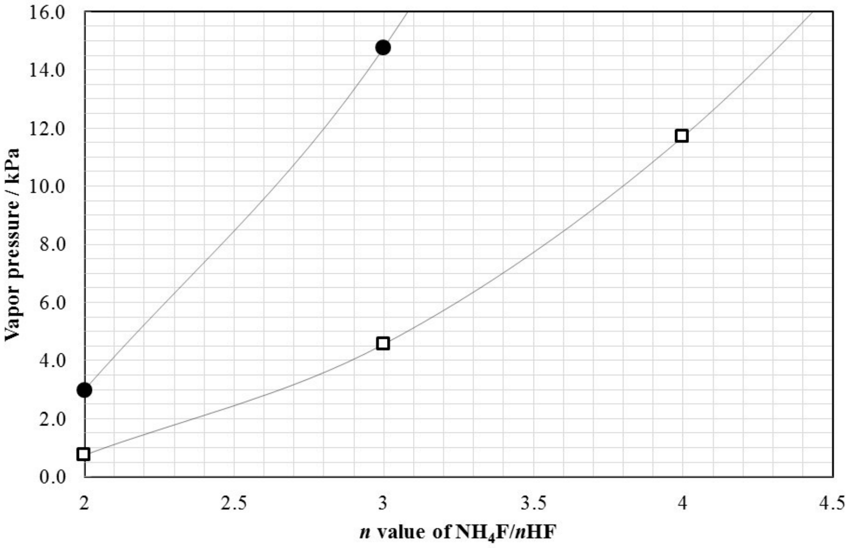


Figure 3-7. HF vapor pressure of NH_4F/nHF at 298 K (□) and 323 K (●).

Regarding the increased *n* value, it is adjusted with the vessel for vaporizing HF (e). In this experiment, a method of adjusting the *n* value was adopted by which Ar gas is bubbled into the molten salt and where HF is removed by accompanying Ar gas with the vapor pressure of HF. When the vessel for vaporizing HF (e) controlled the temperature at 323 K, the partial pressure of HF was 6.4 kPa (Figure 3-7). It was possible to remove HF from the molten salt as entrained steam by 10.4 SLM in terms of the exit of the vessel for vaporizing HF (e) by bubbling Ar gas at a flow rate of 140 SLM. Even when the reaction was continued for more than 100 h in this system, deviation of the *n* value was within 0.1.

The consumed NH_3 was supplied into the vessel for NH_3 bubbling (f). Regarding NH_3, the *n* value can be kept constant by adding the stoichiometric amount shown by reaction formula (1). In this test, NH_3 was supplied with 2.61 SLM, but results show that the *n* value remained at 2.3 even after 100 h.

3-5. Summary

For this method of synthesizing NF_3 using $NH_4F/n HF$, NH_3, and F_2 as raw materials, NF_2Cl, $NFCl_2$, and ClF_3 were used as intermediates. Especially, ClF_3 functions well as a mediator for recycling chlorine atoms. ClF_3 can be reused as intended. Results established a series of schemes. All reactions were able to proceed at low pressure: 93.3 kPa. Results demonstrated that NF_3 can be synthesized with a fluorine yield higher than 90% using ClF_3 as a mediator and using the ClF_3 condensing method two times. After once condensing the synthesized ClF_3, repeated reaction and recondensing of ClF_3 proved to be effective for yield improvement.

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Chapter 4

General Conclusions

The author has conducted a study of the NF_3 synthesis using ClF_3 as a mediator and established a new process for NF_3 manufacturing, which is commercially competitive.

The main results of this work are summarized as presented below.

In Chapter 2, the reaction for synthesizing NF_2Cl and $NFCl_2$ from the reaction of $NH_4F/n HF$ and ClF_3, which is the most important reaction in this process, was described as a preliminary reaction for synthesizing NF_3. Reactions between $NH_4F/n HF$ and gaseous ClF_3 were examined at temperatures of 280–320 K under various n-values ($n = 2.2$, 2.3, 2.4, 2.7, 2.8, 3.0, 3.1, and 4.0) at which $NH_4F/n HF$ was a molten salt, with three ClF_3 gas flow rates (20, 50 and 100 standard cc min^{-1}). From a direct reaction, NF_2Cl and $NFCl_2$ gases were obtained as products. Therefore, conditions able to achieve high selectivity from the viewpoint of reaction temperature, n value, and raw material flow rate were examined. With high NF_2Cl and $NFCl_2$ selectivity for N_2, such as higher than 90% selectivity for the nitrogen containing molecule base at temperatures below 298 K, an n value of around 2.2–2.3 was obtained. The selectivity of NF_2Cl and $NFCl_2$ decreased to less than 70% at temperatures higher than 318 K because of increased amounts of N_2 by-product. High selectivities of NF_2Cl and $NFCl_2$ were obtainable with the reaction mechanism in which $[NH_3ClF_2]^+(FH)_nF^-$ is formed as an intermediate.

In chapter 3, several schemes related to the NF_3 synthesis method using ClF_3 as a mediator were verified. For this method of synthesizing NF_3 using $NH_4F/n HF$, NH_3, and F_2 as raw materials, NF_2Cl, $NFCl_2$, and ClF_3 were used as intermediates. Especially, ClF_3 works as a mediator for recycling the chlorine atoms. ClF_3 can be reused as intended. Results demonstrated that NF_3 can be synthesized with yield of more than 90% - fluorine molecule base. Then ClF_3 produced as a by-product can be recycled for reaction with $NH_4F/n HF$. Improving the yield necessitates improvement of the ClF_3 recovery rate, but using characteristics of $ClF + F_2 = ClF_3$ as an equilibrium reaction can be overcome using a two-step reaction. $NH_4F/n HF$ can be recycled continuously by controlling the n value in $NH_4F/n HF$ through NH_3 addition and HF extraction. Using ClF_3 as a mediator and NH_3 and F_2 as raw materials, NF_3 synthesis was achieved at atmospheric pressure. Results demonstrate that a series of schemes was established. All reactions were able to react at 93.3 kPa at low pressure. Results demonstrated that NF_3 can be synthesized with a fluorine yield higher than 90% using ClF_3 as a mediator and using the ClF_3 condensing method two times. Condensing the synthesized ClF_3 once, reacting it again, and recondensing ClF_3 proved effective to improve the yield.

Based on the discussion presented above, three methods have long been used commercially as NF_3 manufacturing methods, but we were able to find a fourth method offering the potential for commercialization of NF_3 manufacturing. Table 4-1 presents a comparison of NF_3 manufacturing processes and the new method. Although the ClF_3 mediator method developed in this study has a few weak points such as large amounts of equipment and make up Cl_2, it possesses many merits including high yield, low pressure reaction, and continuous synthesis. It therefore has greater potential than other processes for being more competitive and suitable for large-scale manufacturing.

Table 4-1. Comparison of industrialized manufacturing process

	Direct F_2 reaction method	Electrolysis method	Ammonium cryolite method	ClF_3 mediator method
Chemical reaction formula	$NH_4F/2HF + 3F_2 \rightarrow NF_3 + 6HF$	$NH_4F/2HF \rightarrow NF_3 + 3H_2$	$(NH_4)_3AlF_6 + 6F_2$ $\rightarrow 2NF_3 + 8HF + NH_4AlF_4$	1] $2NH_4F/2HF + 3ClF_3 \rightarrow$ $NF_2Cl + NFCl_2 + 10HF$ 2] $NF_2Cl + 2F_2 \rightarrow NF_3 + ClF_3$ $NFCl_2 + 4F_2 \rightarrow NF_3 + ClF_3$
Heat of reaction Kcal/mol-NF_3	-196	-300	-180	1] -98 2] -73
Advantage	・Continuous synthesis	・Continuous synthesis ・One step synthesis (Without F_2 electric cell)	・High yield ・Safe reaction (Mild reaction)	・High yield ・Low pressure reaction ・Continuous synthesis ・Suitable for mass production
Disadvantage	・Low reactivity ・Large heat of reaction ・High pressure reaction (3atm) ・F_2 electric cell	・Dissolution of Ni electrode ・High electricity cost for electric loss ・Many Electronic Cells	・F_2 electric cell ・Raw materials cost ・Solid raw materials ・Batch process	・F_2 electric cell ・Number of equipement ・Make up Cl_2
Manufacturing Company	・Kanto Denka (Japan) ・SK Material (Korea) ・Air Products (USA)	・Mitsui Chemical (Japan) ・PERIC (China)	・Central Glass (Japan)	

Publication List

Chapter 2

Synthesis of NF_2Cl and $NFCl_2$ using NH_4F/nHF and ClF_3

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Chapter 3

NF_3 synthesis using ClF_3 as a mediator

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