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Study on a novel catalytic reaction and its mechanism for CF_3I synthesis

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Abstract

A novel vapor phase production process for CF_3I was successfully developed for the reaction between CHF_3 with I_2 in the presence of a unique catalyst. The most effective catalyst system for this reaction was found to be alkali metal salts which were supported on an activated carbon carrier. A consideration of the reaction mechanism suggests that the reaction proceeds via CF_2 carbenes formed on the catalyst surface as intermediates, followed by carbene disproportionation to CF_3 radicals, followed by reaction with I_2 to give CF_3I.

Keywords: Novel catalytic reaction; CF_3I synthesis; Carbene

1. Introduction

Although both Halon 1301 (CF_3Br) and Halon 1211 (CF_2BrCl) are effective fire extinguishing agents, their production was stopped in 1994 based on the Montreal Protocol, due to their ozone-depleting potential. After production was stopped, CF_3I became the preferred Halon alternative for use as a fire extinguisher [1–4], because of its short lifetime in the atmosphere. Presently, it is expected not only for use as a fire extinguisher, but also for various other applications, such as an echant gas [5,6], trifluoromethylating agent [7,8] or raw materials for fluorochemicals [9], etc.

There are several reports in literature regarding the preparation methods for CF_3I, for example, the thermal decarboxilative iodination of the metal salts of trifluoroacetic acid and iodine (Scheme 1) [10,11]. Recently, another method involving the electrochemical reaction of CF_3Br with zinc followed by addition of chloroiodine (Scheme 2) has been reported [12]. However, these methods do not seem likely candidates for large scale production of CF_3I due to low yield, problems with the disposal of by-product ZnBrCl, and the unfortunate fact that they are batch processes.

On the other hand, of the authors have developed a continuous vapor phase process for the manufacture of CF_3I, and have successfully developed novel catalytic production methods by reacting CHF_3 with I_2 in the presence of a unique catalyst system (Scheme 3) [13,14].

In this paper, the authors will provide details of CF_3I technology and the results of research on the mechanism of this unusual reaction.

2. Experimental

2.1. Preparation of the catalyst

Carrier of the catalyst was added to the aqueous metal salts solution and impregnated at room temperature for 1 h, and remaining water was re-

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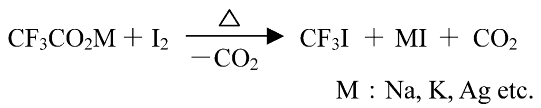
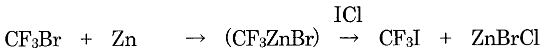


$$CF_3CO_2M + I_2 \xrightarrow[-CO_2]{\triangle} CF_3I + MI + CO_2$$

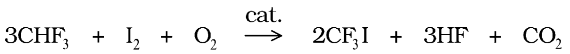
M : Na, K, Ag etc.

Scheme 1.



$$CF_3Br + Zn \rightarrow (CF_3ZnBr) \xrightarrow{ICl} CF_3I + ZnBrCl$$

Scheme 2.



$$3CHF_3 + I_2 + O_2 \xrightarrow{cat.} 2CF_3I + 3HF + CO_2$$

Scheme 3.

moved by heating (80 °C/2.7 kPa, 1 h). Then the catalyst was dried at 90–110 °C for 6 h under atmospheric conditions. The pre-dried catalyst was then calcined at 400–550 °C for 2 h under nitrogen flow conditions.

2.2. Reaction and analytical methods

Hundred milliliters of the catalyst was loaded into a fixed bed reactor (Hastelloy C, diameter 20 mm) and the reactor was heated to reaction temperature under nitrogen flow conditions, then the nitrogen was changed to a mixture of gaseous raw materials (CHF_3, I_2 and/or O_2). Flow rate of the gaseous materials (CHF_3 and O_2) was controlled by mass flow controller, and I_2 was provided by bubbling CHF_3 into molten I_2.

Unreacted I_2 was recovered in a solid state from the gaseous reaction mixture by cooling. After removal of unreacted I_2, the product gases were passed through a 10%. KOH solution and dried with $CaCl_2$. The dried gases were then introduced into a cylinder and trapped at −78 °C, and the products were then analyzed by both GC and GC-Mass analysis.

3. Results and discussion

3.1. Screening of the catalytic activities

Many kinds of catalysts were tested in this reaction. The tested catalysts were made from various alkali metal salts or alkaline earth metal salts with activated carbon as a carrier. In this study, alkali metal salts showed a higher catalytic activity than the alkaline earth metal salts. Table 1 shows a comparison between the alkali metal salts that were used. The order of activity of the alkali metal catalysts was Rb, Cs > K > Na and the order of selectivity was K > Rb, Cs > Na (Table 1). Based on exhaustive studies, it was found that the most suitable catalyst for this reaction is the synergistic combination of K^+ with high selectivity and Rb^+ or Cs^+ with high activity (Table 2). While the anions, counter-ion to the metal cations, have no significant effect on the reaction mechanism or rate. After the reaction, the counter-ions (anions) in all catalysts were changed to fluoride ion with hydrogen fluoride, which was generated as a by-product.

Numerous kinds of catalyst carriers were evaluated in bench trials including SiO_2, Al_2O_3, SiO_2–Al_2O_3, TiO_2, ZrO_2, AC, graphite, ACF and others (Table 3).

Finally, it was observed that only carbonaceous carriers had catalytic activity and that such activity was directly related to the surface area of the carrier (Table 4). Other carriers displayed no catalytic activity or decomposed under reaction conditions.

Table 1
Effects of alkali metal and alkaline earth metal salt catalysts on the reaction of CHF_3 with I_2[a]

Component	CHF_3 conversion (%)	CF_3I selectivity (%)
$NaNO_3$	16	0
KNO_3	68	53
$RbNO_3$	83	38
$CsNO_3$	84	22.5
KCl	63	62
KF	73	47
KOH	65	54
KOAc	62	54

[a] Reaction temperature: 550 °C; I_2/CHF_3 (mol ratio): 2.0; SV: 30 h^{-1}.

Table 2
Synergistic effect of alkaline earth metal (Rb) with alkali metal (K)[a]

Rb/(K + Rb) (mol ratio)	0	0.3	1
CHF_3 conversion (%)	48	58	67
CF_3I selectivity (%)	28	28	20
CF_3I yield (%)	13	16	13

[a] Reaction temperature: 550 °C; I_2/CHF_3 (mol ratio): 0.2; SV: 60 h^{-1}.

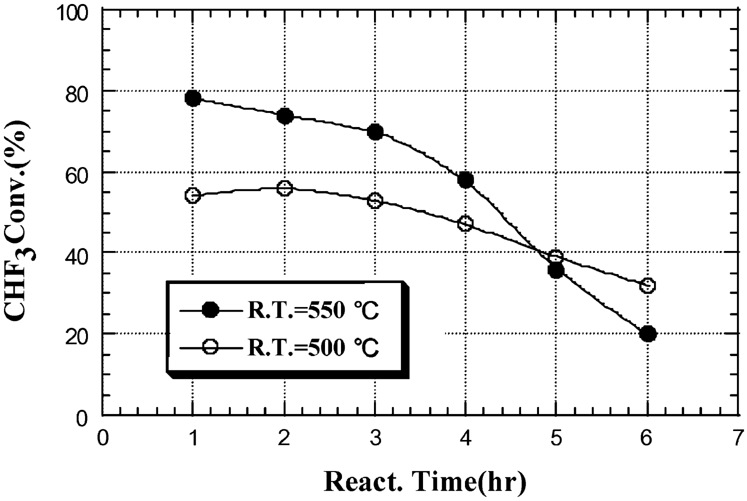


Fig. 1. Effects of reaction temperature on the conversion of CHF_3. Catalyst: KF-$RbNO_3$/AC; CHF_3 = 100 cm^3/min; I_2/CHF_3 (mol ratio) = 0.5; SV = 180 h^{-1}.

Table 3
Effects of catalyst carrier (support) materials[a]

Carrier	Surface area (m^2/g)	CHF_3 conversion (%)
SiO_2	80	1
TiO_2	50–100	5
Al_2O_3	160	1
SiO_2–Al_2O_3	480	5
ZrO_2	95	1
AC	1000–1200	73
Graphite	50	10
ACF	510	15

[a] Reaction temperature: 550 °C; I_2/CHF_3 (mol ratio): 0.5; SV: 60 h^{-1}; catalysts component: KF 9.9 wt.%.

3.2. Life test of the catalyst

Through the life test of the catalyst, it was found that catalytic activity decreases within a few hours (Fig. 1), when tested under accelerated reaction conditions, therefore additional research is needed to overcome this deficiency.

Table 4
The relationship between specific surface area of the catalyst and the catalytic activity[a]

Carrier[b]	Surface area (m^2/g)	CHF_3 conversion (%)	CF_3I selectivity (%)
A	1000–1200	34.9	65.1
B	510	15.1	60.8

[a] Catalyst component: KNO_3–$CSNO_3$/carrier; reaction temperature: 550 °C; I_2/CHF_3 (mol ratio): 0.3; SV: 650 h^{-1}.

[b] Carrier A: SHIRASAGI C2; carrier B: MOLSIEVON (TAKEDA CHEMICAL INDUSTRIES, LTD.).

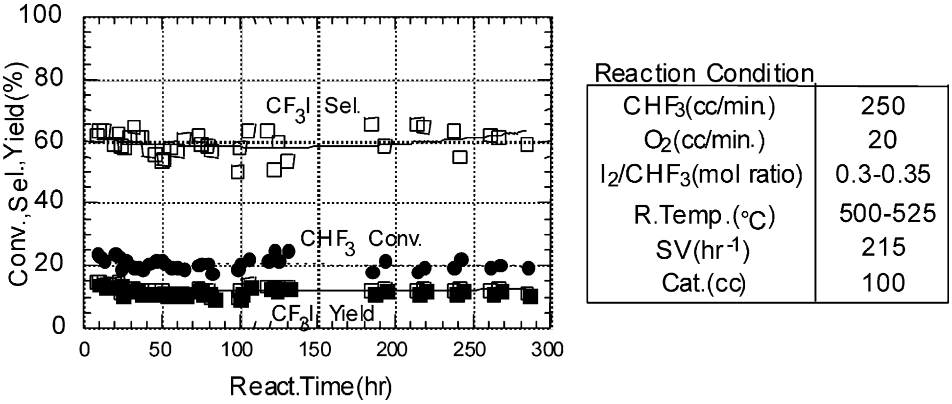
Table 5
Specific surface area of the fresh and used catalyst

	BET surface area (m^2/g)
Fresh	1000
Used	
Without O_2	500
With O_2	800

To find the cause, more comprehensive experimentation has been done. After the catalytic reactions, the specific surface area of the deactivated catalyst was analyzed by BET (Table 5). From the analytical results, it was observed that the surface area of the used catalyst decreased in comparison with the fresh catalyst.

Furthermore, in addition to the catalyst, a large quantity of carbonaceous powder was obtained when the used catalyst was recovered from the reactor. As a result, it was clear that the cause of deactivation was of the deposition of carbonaceous materials (coke) on the catalyst.

The addition of O_2 to the reaction system prevented catalyst deactivation by burning off the coke. Table 5 shows a comparison of the specific surface area on the used catalyst after reaction with and without O_2. However, excessive amount of O_2 caused the oxidation of the catalyst carrier (activated carbon) itself,



Reaction Condition

CHF_3(cc/min)	250
O_2(cc/min.)	20
I_2/CHF_3(mol ratio)	0.3-0.35
R.Temp.(°C)	500-525
SV(hr^{-1})	215
Cat.(cc)	100

Fig. 2. Catalytic life test.

therefore it was necessary to determine the optimum amount of O_2 for burning off the coke alone.

After testing under the various reaction conditions, the lifetime of the catalyst was significantly improved under some specific conditions, such as CHF_3, I_2 and O_2 ratio (Fig. 2). This extensive testing resulted in the development of a viable commercial catalytic process for the production CF_3I from CHF_3 and I_2.

3.3. The reaction mechanism

The following products were detected by both GC and GC-Mass analyses (Table 6). The main products were CF_3I, CF_4, C_2F_5I and smaller amounts of perfluoroalkane derivatives like C_3F_8. The product distribution suggests that the reaction mechanism proceeds through a CF_2 carbene intermediate. On the other hand, analytical result of HF concentration in the 10% KOH solution was strongly suggestive of the reaction scheme described in Scheme 4. It clearly shows that a disproportionate process is involved in this reaction.

Table 6
Product distribution for the catalytic reaction of CHF_3 with I_2

	GC (area %)
CF_4	13
CHF_3	36
CF_3I	42
CF_3CF_2I	2
Others[a]	7

[a] Perfluoroalkane compounds ($CF_3CF_2CF_3$, etc.).

$$3\,CHF_3 \quad + \quad I_2 \xrightarrow{\text{cat.}} 2\,CF_3I \quad + \quad 3\,HF \quad + \quad C$$

Scheme 4.

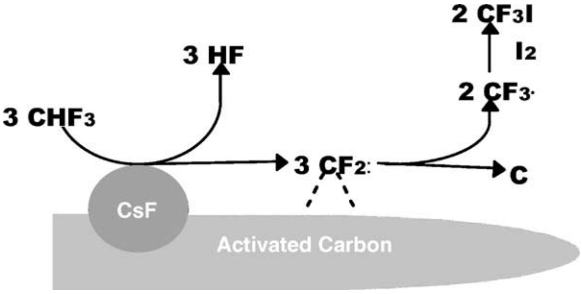


Fig. 3. Proposed reaction mechanism.

$$CHF_2Cl \quad + \quad I_2 \xrightarrow[500℃]{CsF/AC} CF_3Cl \quad + \quad \underset{n=1,2,3}{Cl(CF_2)nCl}$$

Scheme 5.

Also it was suggested that this reaction proceeds by the following mechanism shown in Fig. 3. Namely, the first step causes HF to be eliminated from CHF_3 and CF_2 carbene is formed over the catalyst. Then CF_2 carbenes are disproportionation to CF_3 radicals, and the CF_3 radicals reacted with I_2 to produce CF_3I.

To examine the reaction mechanisms, CHF_2Cl (CFC-22) was used as a raw material for this catalytic reaction process, which seemed to be a more effective CF_2 carbene source than CHF_3. After the reaction, the products were analyzed by GC. From the analytical results, it was confirmed that the composition of the reaction products are CF_3Cl and $Cl(CF_2)nCl$ as the main products (Scheme 5), and CHF_3 and CF_3I as the minor products.

This result suggests that first the CF_2 carbenes were generated, and then underwent disproportionation on the surface of the catalyst to produce CF_3 radicals. Furthermore, in this case, CF_3I was not the main product. Chlorinated compounds were obtained as the main products in spite of the presence of I_2 molecules. This can be easily explained as thermodynamically stable products being produced by the reaction between CF_3 radicals and halogens. Therefore, it is clear that chlorinated compounds are not suitable as raw materials for the production of CF_3I using this catalytic process.

As described above, carbonaceous carriers such as activated carbon are effective in this catalytic reaction process. In order to study the role of these carbonaceous carriers, the behavior of CF_2 carbene on the activated carbon was investigated: ICF_2CF_2I, which has the characteristic of easy thermal decomposition to CF_2 carbene, and I_2 was passed over the activated carbon at 550 °C. Several compounds containing the CF_3 group were formed by the thermal decomposition of ICF_2CF_2I as shown in Scheme 6. Accordingly, it became clear that the disproportionation of CF_2 carbene proceeds on the activated carbon carrier regardless of the type of catalyst.

These results suggest that the alkali metal salts or alkaline earth metal salts catalyze the dehydrofluorination of CHF_3 to CF_2 and the activated carbon catalyzes the disproportionation of CF_2 carbene.

$$ICF_2CF_2I \xrightarrow[500℃]{AC} CF_3(CF_2)nI + CF_3(CF_2)nCF_3$$

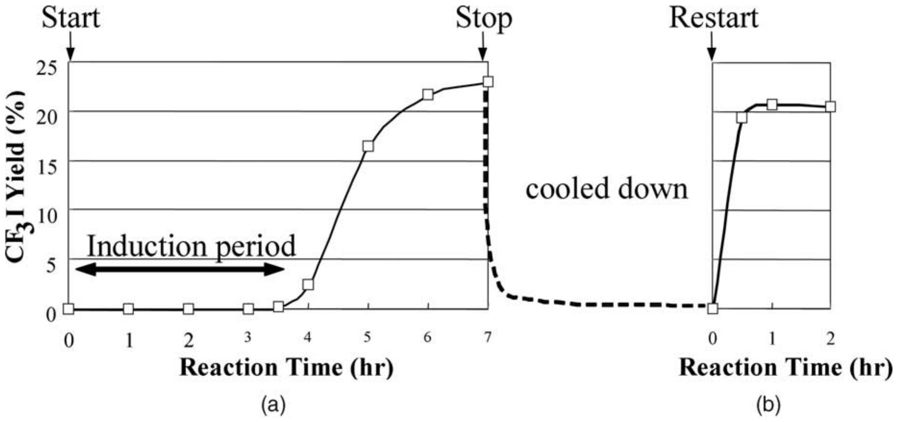
Scheme 6.

In this process, the catalytic reaction seems to proceed by the peculiar behavior of CF_2 carbene on the activated carbon. To confirm this behavior of the CF_2 carbene, the catalytic reactions were then examined under various reaction conditions as shown in Fig. 4. It was evident that an induction period is necessary during the first start up for production of CF_3I, but this induction period disappeared from the second start up on the same catalyst.

This unusual phenomena is thought to be due to the behavior of generated CF_2 carbene as follows: the time required for the generated CF_2 carbene to cover the surface of the catalyst was observed as the induction period of the initial start up. After that, the induction period was not observed since the surface of the catalyst had already been covered by CF_2 carbene.

It is assumed that the CF_2 carbene on the surface of the catalyst did not exist as a free carbene but in some stabilized state.

To confirm this consideration, the catalyst was prepared as follows and investigated. Activated carbon as the carrier was covered in advance with CF_2 carbene by thermal treatment with ICF_2CF_2I, and then the cat-



(a) (b)

Fig. 4. Influence of the start up reaction of CHF_3 with I_2: (a) start up of the reaction over fresh CsF/AC catalysts; (b) restart up of the reaction. Catalysts: 50 ml; reaction temperature: 550 °C; SV: $90\,h^{-1}$.

alyst components were supported on the treated carrier by the usual procedure. As shown in the results, no induction period was observed for this catalyst, which is in good agreement with the above suggestion. Moreover, it became clear that CF_2 carbene on the activated carbon is surprisingly stable enough under the preparation conditions of catalysts, namely the carbene is stable in aqueous solution.

Continuous investigations to identify the composition and properties of these peculiar CF_2 carbenes on the activated carbon have also been studied by our group.

4. Conclusions

TOSOH F-TECH INC. has developed a new and patented technology for the manufacture of CF_3I, relying on the utilization of a novel catalytic system that produces CF_3I via a reaction between CHF_3 and I_2.

Furthermore, a consideration of the reaction mechanisms suggests that the catalytic reaction proceeds via the disproportionation process of generated CF_2 carbene on the surface of the catalyst. The results of some investigations showed that the CF_2 carbene on the catalyst exists in some stabilized state.

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