Short communication

Preparation of trifluoroiodomethane via vapor-phase catalytic reaction between hexafluoropropylene oxide and iodine

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ABSTRACT

Based on our previous investigation on the reaction mechanism to produce difluorocarbene and subsequent CF_3I starting with CHF_3 and I_2, a new route for preparing CF_3I at a relative low temperature, 200 °C, has been developed via a vapor-phase catalytic reaction between hexafluoropropylene oxide with I_2 in the presence of KF supported on activate charcoal as a catalyst. The influence of reaction temperature and reaction time on the amount of CF_3I was investigated. In the reaction process, coke-formation was suggested on the surface of catalysts by means of BET, XPS and TG-DTA analysis. The process for the formation of CF_3I and by-products is also discussed.

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1. Introduction

Trifluoroiodomethane (CF_3I) has drawn growing attention as a promising replacement for halon and other halohydrocarbons in the application of fire extinguishing agent, freezing medium and etching gas since its short atmospheric lifetime and low global warming potential (GWP). In our previous report, we summarized the properties and synthetic methods of CF_3I [1]. Among the synthetic routes, the continuous vapor-phase catalytic process via the reaction between CHF_3 and I_2 in the presence of O_2 at 550 °C makes the CF_3I industrialization possible [2]. With the help of experiments, the mechanism for the formation of CF_3I was attributed to that CF_2 carbene produced in the pyrolysis process of CHF_3 is transferred into CF_3 radical, which converts to CF_3I in the presence of catalyst, I_2 and O_2 [1]. According to the report, a quite high temperature is required for the formation of CF_2 carbene in the pyolysis process. However, high temperature in the presence of O_2 would cause not only the destruction of the supporter of catalyst, activated carbon (AC), but also the coke-formation on the surface of catalyst and deactivation of the catalyst [3].

In order to decrease the reaction temperature, structurally strained fluorocarbons containing three-membered ring instead of CHF_2Cl and CHF_3 were selected as thermal sources of CF_2 carbene under milder conditions. Perfluorocyclopropane and hexafluoropropylene oxide (HFPO) have been used as difluorocarbene

sources employing at below 200 °C. Especially, HFPO is useful because of its commercial availability [4].

Based on our former research on mechanism for the formation of CF_3I, a new route for preparing CF_3I at a relatively low temperature around 200 °C, was developed via a vapor-phase catalytic reaction between HFPO with I_2 in the presence of KF catalyst on AC (KF/AC). We reported here the detailed study on characterization of the catalysts to demonstrate the disproportionation of CF_2 carbene.

2. Experimental

2.1. Materials

AC was obtained from Shanxi Taiyuan Activated Carbon Factory. HFPO was provided by Shandong Dongyue Chemical Co., Ltd., China. I_2 was purchased from Nanjing Yicheng Chemical Co., Ltd., China.

2.2. Instrument and apparatus

Products were analyzed by means of Shimadzu GC-17A. The capillary column was a CP-Pora PLOT Q with 0.32 mm diameter and 30 m length from J&W Scientific Inc. The column was programmed as follows: the initial temperature was set at 60 °C for 6 min; then the temperature was increased at the rate of 40 °C/min, and finally reached to 200 °C and held for 11 min. The instrumental parameters were set up as follows: injection port temperature, 200 °C; TCD detector, 200 °C; the carrier gas rate,

Table 1
Relative response coefficients (kI/k_{std}) determined by GC-TCD.

	kI/k_{std}
CHF_3	1
CF_3CHF_2	0.90
HFPO	0.74
$CF_3CF=CF_2$	0.72
CF_3I	0.69
CF_3CF_2I	0.73

std = CHF_3.

4.1 ml He/min. The products were identified by comparison of their GC retention times and mass spectra with authentic samples. Quantitative analysis of the product standard ratios was obtained by comparison with mixtures prepared for calibration purposes. The relative response coefficients of each compound are given in Table 1.

MS (EI, 70 eV) spectra were measured using the Shimadzu GCMS-QP2010 system equipped with GC-17A. The column was CP-Pora PLOT Q with 0.32 mm diameter and 30 m length from J&W Scientific Inc. The column was programmed as above-mentioned GC conditions. Injection port temperature, 200 °C; the carrier gas rate, 4.1 ml He/min.

The BET surface area of AC was measured by means of low temperature adsorption of nitrogen using a micromeritics ASAP 2010. Samples were degassed under vacuum ($P < 10^{-5}$ torr) at 573 K for 3 h before measurement.

Thermogravimetry and Differential Thermal Analysis (TG-DTA) was conducted on NTEZSCH STA 449C instrument. The experiments were performed under the conditions of 25–350 °C at a heat rate of 10 °C/min with air at flow rate of 100 ml/min. About 20 mg of sample was placed inside of an uncovered Pt pan. Samples of used AC were pretreated by heating at 500 K under vacuum to remove iodine that accumulated on the surface.

The XPS instrument was a Thermo VG ESCALAB 250 which uses a mono-chromatic Al Kα (1486.6 eV) X-ray source with a plot size of 500 μm.

2.3. Reaction procedure

2.3.1. Preparation of catalyst

Twenty grams of AC was added into a KF solution which was prepared by dissolving 5 g of KF into 100 ml of de-ionized water and the mixture was kept at room temperature for 1 h. The catalyst was dried at around 100 °C for 3 h under atmospheric conditions and then at around 200 °C for 2 h under nitrogen flow condition.

2.3.2. Synthesis of CF_3I

About 2 ml of the above mentioned catalyst and 2 g of I_2 were placed in a stainless steel reactor with 80 ml volume. The reactor was cooled to −196 °C, then 10 mmol of HFPO was introduced into the reactor. The reactor was placed in an oil bath and the reaction mixture was stirred by a magnetic stirrer. The reactor was heated at 210 °C for 2 h. The products passed through a KOH solution. Then the washed products were collected in a gas bag and analyzed by GC and GC–MS. The data of MS are listed as follows:

1. CHF_3, m/z: 69, F_3C^+; 51, $^+CHF_2$; 31, FC^+.
2. CF_3CHF_2, m/z: 119, $^+CF_3CF_2$; 101, $^+CF_2CHF_2$; 69, F_3C^+; 51, $^+CHF_2$.
3. HFPO, m/z: 119, $^+CF_3CF_2$; 100, $^+CF_3CF$; 69, F_3C^+; 50, F_2C^+
4. $CF_3CF=CF_2$, m/z: 150, M^+; 131, $^+CF_2CF=CF_2$; 100, $^+CF_2=CF_2$; 69, F_3C^+; 31, FC^+.
5. CF_3I, m/z: 196, M^+; 127, I^+; 69, F_3C^+.
6. CF_3CF_2I, m/z: 246, M^+; 127, I^+; 119, $^+C_2F_5$; 100, $^+C_2F_4$; 69, F_3C^+; 50, F_2C^+.

3. Results and discussion

CF_3I was produced in 59% relative volume of the gaseous products obtained by the reaction between HFPO and iodine in the presence of KF/AC catalyst at 210 °C for 2 h, accompanying with CHF_3, CF_3CHF_2, $CF_3CF=CF_2$, CF_3CF_2I as by-products. The conversion of HFPO reached 99%, as shown in Table 1. When the reaction temperature was 170 °C, HFPO remained in 58% in the mixture of gaseous products, and CF_3I was formed only in 5.4%. When the reaction temperature was 120 °C, reaction did not occur and only raw material of HFPO was detected in gas product (Table 2).

Effect of the reaction time at 210 °C was also examined. The results are shown in Fig. 1. The concentration of HFPO decreased with the increase in reaction time and closed to zero when reaction time reached to 100 min. At the same time, the ratio of CF_3I formed gradually increased. When the reaction time was over 100 min, the concentration of CF_3I reached over 50%.

The BET surface area and pore volume of the fresh and used catalysts were measured. As shown in Table 3, the fresh KF/AC catalyst had a large surface area of 879 m^2/g and a pore volume of 0.40 cm^3/g. Depending on longer reaction time, the surface area of catalysts decreased. When the reaction was conducted at 210 °C for 2 h, the surface area of the catalyst was reduced to 72 m^2/g and pore volume was to 0.04 cm^3/g, respectively, possibly caused by coke-formation during the reaction. When the reaction temperature was lowered to 170 °C, the surface area and pore volume of the used catalyst were 377 m^2/g and 0.18 cm^3/g, respectively. In this case, due to the lower conversion of HFPO, the coke-formation was quite small compared with that at 210 °C. As for the catalyst that was used in the reaction at 120 °C, the reduction in surface area and pore volume would be explained by the absorbed compounds containing fluorine on the surface of the catalyst. Therefore, XPS analysis was carried out to characterize the elemental content on the surface of the fresh and used catalysts. As shown in Table 4, it was found that after the reaction, fluorine content increased and potassium content decreased on the surface of catalyst. These results possibly indicated that the KF surface is covered with products derived from generated CF_2 carbene. As for the catalyst that used in the reaction at 210 °C, XPS study also revealed that the carbon content reached 43.5%, which was far higher than that of

Table 2
Effect of reaction temperature on product distribution[a].

Entry	Temperature (°C)	Distribution of products (%)[b]						
		HFPO	CHF_3	CF_3CHF_2	$CF_3CF=CF_2$	CF_3I	CF_3CF_2I	Others
1	120	100	–[c]	–[c]	–[c]	–[c]	–[c]	–[c]
2	170	58.1	20.4	4.0	10.0	5.4	1.7	0.4
3	210	<0.1	24.9	5.3	4.2	59.1	3.2	3.3

[a] Reaction time: 2 h.
[b] Ratio of relative volume of gaseous compound.
[c] Not detected.
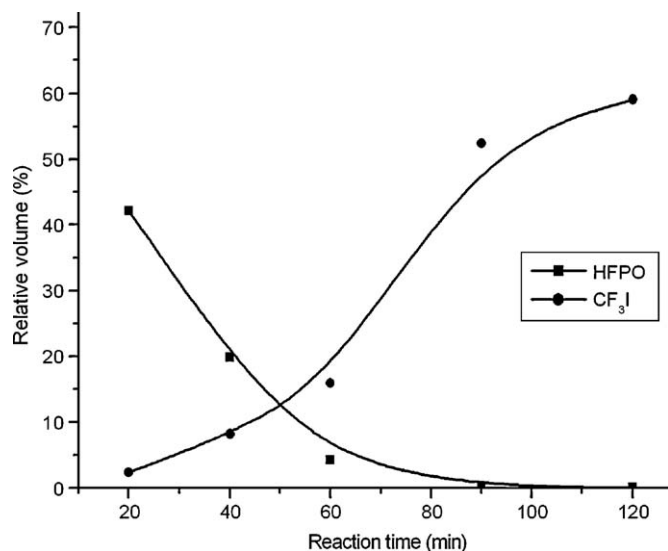
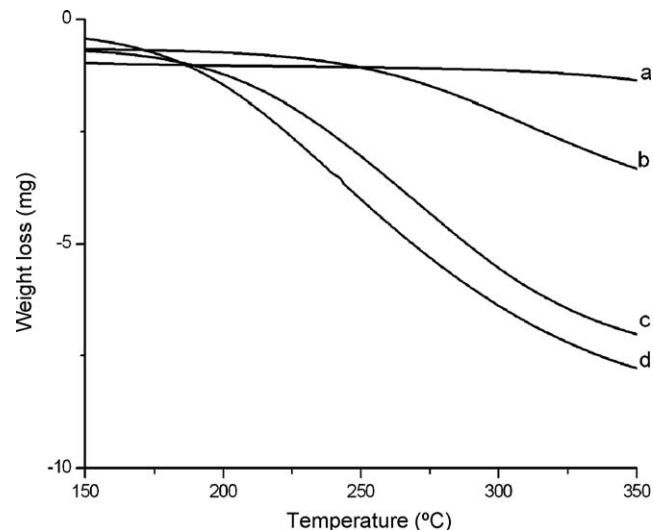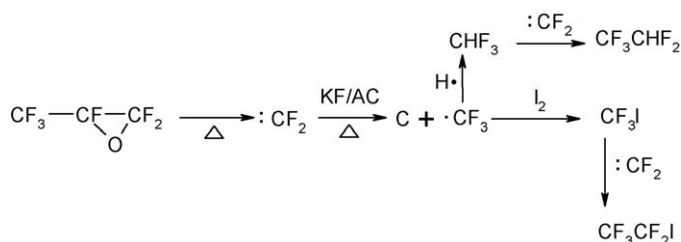Fig. 1. Effect of reaction time on the ratio of HFPO and CF$_3$I at 210 °C.

Fig. 2. TG curves of fresh and used catalysts (a: fresh catalyst, b: catalyst used at 120 °C, c: catalyst used at 170 °C, and d: catalyst used at 210 °C).

the catalysts used in the reaction at 120 and 170 °C. The increase of coke-formation resulted in the increase of carbon content on the surface of used catalyst.

The coke-formation on the used catalysts was characterized by means of TG-DTA technique under air flow (Fig. 2). Magnoux found that coke oxidation and evolution of carbon dioxide generally start at the temperature from 250 to 350 °C [5]. As shown in Fig. 2, line a, within the range of 150–350 °C, the fresh catalyst was relatively stable under air flow and there was no obvious weight loss observed. However, within the same temperature range, the TG curves of the used catalysts showed weight loss due to removal of coke by oxidation. The rates of weight loss for the samples used in the reactions at 210 °C (line d), 170 °C (line c) and 120 °C (line b) were 34%, 29% and 12%, respectively. These results indicated that the amount of coke-formation on the surface of the catalysts increased with the elevation of reaction temperature raising. It revealed that the reaction of HFPO with I$_2$ to prepare CF$_3$I will lead coke-formation and the amount of coke increases with the increase of HFPO conversion.

The compounds containing CF$_3$ group such as CHF$_3$, CF$_3$I, CF$_3$CF$_2$I were formed. These results were in accordance with the

Scheme 1. Suggested process for the formation of CF$_3$I and by-products.

mechanism of CF$_2$ carbene disproportionation to form CF$_3$ radical. We propose the following process for the formation of CF$_3$I and by-products. As shown in Scheme 1, HFPO is decomposed by heating to form the intermediate of CF$_2$ carbene. Then, CF$_2$ carbene is absorbed on the surface of the catalysts and disproportionation reaction takes place to generate CF$_3$ radical. CF$_3$ radical reacts with I$_2$ to form CF$_3$I, whereas with H radical to form CHF$_3$. H radical maybe comes from carboxyls and phenols on the AC surface. Alternatively, CF$_3$ radical reacts with CF$_2$ carbene to form CF$_3$CF$_2$ radical, which generates CF$_3$CF$_2$I and CF$_3$CHF$_2$. In the process of CF$_2$ carbene disproportionation, carbon is formed as coke on the

Table 3
BET surface area and pore volume of the fresh and used catalysts[a].

	Reaction temperature (°C)	BET surface area (m^2/g)	Pore volume (cm^3/g)
Fresh catalyst		879	0.40
Used catalysts	120	591	0.28
	170	377	0.18
	210	72	0.04

[a] Reaction time: 2 h.

Table 4
Element concentration on the surface of the fresh and used catalysts[a].

	Reaction temperature (°C)	Content (at.%)			
		C$_{1s}$	K$_{2p}$	F$_{1s}$	I$_{3d}$
Fresh catalyst		36.9	30.4	32.7	
Used catalysts	120	17.4	21.5	58.7	2.4
	170	17.9	22.8	58.0	1.4
	210	43.5	11.7	46.6	2.2

[a] Reaction time: 2 h.

surface of the catalysts. It caused the reduction of surface area for the used catalysts.

4. Conclusion

A new method for the preparation of CF_3I has been developed via a reaction between HFPO and I_2 in the presence of KF/AC catalyst. The ratio of CF_3I in the gaseous products reached over 50% when the reaction was conducted at 210 °C for 100 min. During the reaction, surface area and pore volume of the catalyst decreased due to coke-formation. Furthermore, the catalyst promotes disproportionation of CF_2 carbene to generate CF_3 radical, which reacts with I_2 to form CF_3I.

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