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Investigation of CF_2 carbene on the surface of activated charcoal in the synthesis of trifluoroiodomethane via vapor-phase catalytic reaction

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ABSTRACT

This paper investigates the synthetic mechanism of trifluoroiodomethane (CF_3I) in the reaction of trifluoromethane and iodine via vapor-phase catalytic reaction. It is suggested that CF_2 carbene is the key intermediate and is formed in the pyrolysis process of CHF_3 at high temperature. However, in pyrolysis of CHF_3 under activated charcoal (AC) existing conditions, no C_2F_4 was detected. H_2 and 2-methyl-2-butene could not trap the CF_2 carbene. When treating the remained compounds on the used AC with H_2, CH_4 is formed on the process. It is proposed that CF_2 carbene combines with AC strongly and transfers into CF_3 radical on heat. In addition, it is found that the AC is not only the catalyst supporter to form CF_3I, but also a co-catalyst to promote the formation of CF_2 carbene and CF_3 radical.

1. Introduction

Trifluoroiodomethane (CF_3I) has a weak C–I bond, which makes it chemically and photochemically active. As a result, CF_3I possesses a short atmospheric lifetime and low global warming potential (GWP) [1]. For example, its lifetime is a few days and GWP is the same grade as CO_2 [2]. On the other hand, CF_3I is efficient in fire suppression and SiO_2 dry etching, and it is miscible with mineral oil and compatible with refrigeration system materials. CF_3I has become the current subject as promising replacements for halon and other halohydrocarbons in the application of fire extinguishing agent, freezing medium and etching gas [3–6].

By now, literatures have reported some methods to prepare CF_3I. A. Banks first prepared CF_3I by the reaction of CI_4 with IF_5 [7]. In addition, CF_3I can be synthesized by thermal decarboxylation of silver trifluoroacetates in the presence of elemental iodine [8], by the reaction of $Hg(CF_3)_2$ and $Hg(CF_3)I$ with elemental iodine [9], by reaction $Bi(CF_3)_3$ and $ZnBr(CF_3)·2L$ (L = DMF, CH_3CN) with iodine monochloride [10,11].

Above-mentioned methods do not seem likely candidates for large-scale production of CF_3I due to the low yield and batch processes. Currently a continuous vapor-phase catalytic process for the manufacture of CF_3I has successfully been developed by reacting CHF_3 or C_2F_5H with I_2 in the presence of a catalyst, which makes the CF_3I industrialization possible [12–14]. Nagasaki et al. have studied the mechanism for CF_3I synthesis on the vapor-phase catalytic reaction, and suggested that the metal salts catalyzed the dehydrofluorination of CHF_3 to produce CF_2 carbene, and the supporter of activated charcoal (AC) catalyzed the disproportionation of CF_2 carbene [15] (Scheme 1).

In our investigation, we successfully obtained CH_2F_2 in the pyrolysis reaction of CHF_3 under hydrogen existing conditions, which may support the synthetic mechanism of CF_3I that the CF_2 carbene is the intermediate during the pyrolysis process of CHF_3, and the formed CF_2 carbene transfers into CF_3 radical in the presence of AC or catalyst, furthermore CF_3 radical reacts with iodine to form CF_3I in the presence of catalyst. Also it was found that CF_3I is formed in the reaction of CHF_3 and I_2 only in the presence of activated charcoal without other catalyst components, which can be attributed to that AC is not only the catalyst of disproportionation of CF_2 carbene and a porous catalyst supporter, but also a co-catalyst to promote the formation of CF_2 carbene.

2. Experimental

2.1. Materials

2-Methyl-2-butene (99.5%), was purchased from Shanghai Sun Chemical Technology Co., Ltd., China. Trifluoroiodomethane were purchased from Zhejiang Xingteng Chemical Co. Inc., China.

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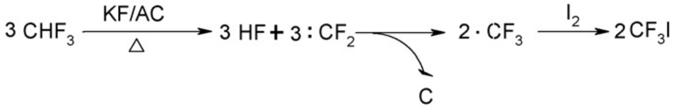


Scheme 1. .

Activated charcoal (AC) was obtained from Shanxi Taiyuan Activited Carbon Factory and KF (99%) was purchased from Sinopharm Chemcial Reagent Co., Ltd., China. HF was obtained from Blue Express, Inc. of China. I_2 was purchased from Nanjing Yicheng Chemical Co., Ltd., China.

2.2. *Instrument and apparatus*

Products were analyzed by means of GC-1002 produced by Beijing analytical instrument factory. The capillary column was a CP-PoraPLOT Q with 0.32 mm i.d. and 30 m 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; FID detector, 250 °C; the carrier gas was N_2 (0.1 MPa).

GC–MS (EI, 70 eV) spectra were measured using the Shimazu GCMS-QP2010 system equipped with GC-2010. The column was CP-PoraPLOT Q with 0.32 mm i.d. 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 cm^3 He/min.

The BET surface area of AC were measured by mean of low temperature adsorption of nitrogen using a micromeritics ASAP 2000. Samples were degassed under vacuum ($P < 10^{-5}$ Torr) at 573K for 3 h before measurement.

2.3. *Preparation of catalysts and reaction procedure*

2.3.1. *Preparation of catalyst*

20 g AC was added into a KF solution which was prepared by dissolving 5 g KF into100 ml de-ionized water, and keep that at room temperature for 1 h. Then the catalyst was dried at around 100 °C for 3 h under atmospheric conditions and at around 250 °C for 2 h under nitrogen flow conditions. Inconel reactor with 12 mm in diameter and 300 mm in length was equipped with an inside Inconel tube for inserting type-K thermocouples with 1 mm diameter. All gas inlets were controlled by the mass flow meters.

2.3.2. *Pyrolysis of CHF_3 in the presence of catalyst*

Heated the catalyst bed to 550 °C under nitrogen flow with the rate of 100 ml/min. Then nitrogen flow was stopped and CHF_3 with 80 ml/min was introduced to reactor, 2.5 h later, the outgases passed through water and a KOH solution to neutralize HF formed. Then the exiting gas was analyzed by GC–MS. The data of MS are listed as follows.

1. CF_4, *m/z*: 69, $^+CF_3$; 50, $^+CF_2$;
2. CF_3CF_3, *m/z*: 119, $^+CF_3CF_2$, 69, $^+CF_3$, 50, $^+CF_2$;
3. CHF_3, *m/z*: 69, $^+CF_3$, 51, $^+CHF_2$, 31, ^+CF;
4. $CF_3CF_2CF_3$, *m/z*: 169, $^+CF_3CF_2CF_2$, 119, $^+CF_3CF_2$, 100, $^+CF_2CF_2$, 69, $^+CF_3$; 50, $^+CF_2$;
5. CF_3CHF_2, *m/z*: 119, $^+CF_3CF_2$, 101, $^+CF_2CHF_2$, 69, $^+CF_3$, 51, $^+CHF_2$;
6. $CF_3CF_2CF_2CF_3$, *m/z*: 219, $^+CF_3CF_2CF_2CF_2$, 169, $^+CF_3CF_2CF_2$, 150, $^+CF_2CF_2CF_2$, 131, $^+CF_2CF_2CF$, 119, $^+CF_3CF_2$, 100, $^+CF_2CF_2$, 69, $^+CF_3$; 50, $^+CF_2$.

Table 1
Pyrolysis of trifluoromethane in the presence of AC[a].

Entry	Regent	Product
1	CHF_3, H_2	CH_4
2	CHF_3, 2-methyl-2-butene	2-Methylbutane, pentadiene, 2-methyl-2-butene and its isomer
3	CHF_3	CF_4, C_2F_6, C_3F_8, C_2HF_5
4	CHF_3, H_2, I_2	CH_4, CH_3CH_3, CH_3I
5[b]	CHF_3, then H_2 after N_2 wash	CH_4
6[c]	CHF_3, then HF after N_2 wash	CHF_3

[a] Reaction temperature is 550 °C.

[b] First CHF_3 passed through the AC in reactor for 2 h at 550 °C, then washes the AC by nitrogen at 550 °C for 1 h, then hydrogen is introduced into the reactor at 550 °C to check the products.

[c] First CHF_3 passed through the AC in reactor for 2 h at 550 °C, then washes the AC by nitrogen at 550 °C for 1 h, then HF is introduced into the reactor at 550 °C to check the products.

2.3.3. *Pyrolysis of CHF_3 in the presence of catalyst and H_2*

The reaction procedure and conditions were same with Section 2.3.2, but CHF_3 flow was replaced by the mixture of CHF_3 with 50 ml/min and H_2 with 50 ml/min. Then the gas was analyzed by GC–MS. Its data of MS are listed as follows.

1. CH_4, *m/z*: 16, ^+M; 15, $^+CH_3$, 14, $^+CH_2$, 13, ^+CH.

2.3.4. *Pyrolysis of CHF_3 in the presence of AC*

18 ml AC was packed into the reactor. The reaction procedure and conditions were same as Section 2.3.2. Then the exit gas was analyzed by GC–MS. The data of MS were same as Section 2.3.2 (see Table 1).

2.3.5. *Reaction of H_2 and the remained compounds on the surface of used AC*

At 550 °C, nitrogen flow with 100 ml/min was passed through the reactor used in Section 2.3.4 to wash the remained CHF_3 for 2 h, then H_2 with 50 ml/min was introduced into the reactor for 1 h. The outgas was passed through water, and a KOH solution to neutralize HF generated. Finally the gas was analyzed by GC–MS. The results were listed as follows.

1. CH_4, *m/z*: 16, ^+M; 15, $^+CH_3$, 14, $^+CH_2$, 13, ^+CH.

2.3.6. *Pyrolysis of CHF_3 in the presence of AC and H_2 flow*

The reaction procedure and conditions were same as Section 2.3.4, but CHF_3 was replaced by a mixture of CHF_3 with 50 ml/min and H_2 with 50 ml/min. The outgas was analyzed by GC–MS to obtain following results.

CH_4, *m/z*: 16, ^+M; 15, $^+CH_3$, 14, $^+CH_2$, 13, ^+CH.

Then reaction temperature was increased to 850 °C and kept at that temperature for 2 h, the out products were analyzed by GC–MS. The results were same as that at 550 °C (see Table 2).

Table 2
Pyrolysis of trifluoromethane on catalyst of KF/AC.

Entry	Regent	Catalyst	Temperature (°C)	Products
7	CHF_3	KF/AC	550	CF_4, C_2F_6, CHF_3, C_3H_8, C_2F_5H
8	CHF_3, H_2	KF/AC	550	CH_4
9	H_2	AC	550	–
10	CHF_3, H_2	Empty	850	CH_4, CH_2F_2, CF_3CH_2F, CHF_2CHF_2
11	CHF_3, H_2	AC	850	CH_4

–: no products detected.

2.3.7. Reaction of HF and the remained compounds on the surface of AC

At 550 °C, nitrogen flow with 100 ml/min was passed through the reactor used in Section 2.3.4 to wash the remained CHF$_3$ for 2 h. Then HF with 50 ml/min was introduced into above reactor for 1 h. The outgas was analyzed by GC–MS to obtain following results.

CHF$_3$, *m*/*z*: 69, $^+$CF$_3$, 51, $^+$CHF$_2$, 31, $^+$CF.

2.3.8. Pyrolysis of CHF$_3$ in the presence of AC and 2-methyl-2-butene vapor flow

The reaction procedure and conditions were same as that in Section 2.3.4. In the process of reaction, 2-methyl-2-butene with 0.2 g/min was vaporized and introduced into the reactor at the temperature of 100 °C. The oily products were washed by water and analyzed by GC–MS, but gem-difluorotrimethylcyclopropane was not detected.

2.3.9. Reaction of H$_2$ and CHF$_3$ in empty reactor

The reaction procedure and conditions were same as that in Section 2.3.2. The mixture of CHF$_3$ with 50 ml/min and H$_2$ with 50 ml/min were introduced into an empty reactor with 850 °C, the outgas was analyzed by GC–MS. The results were listed as follows.

1. CH$_4$, *m*/*z*: 16, $^+$M; 15, $^+$CH$_3$, 14, $^+$CH$_2$, 13, $^+$CH;
2. CHF$_3$, *m*/*z*: 69, $^+$CF$_3$, 51, $^+$CHF$_2$, 31, $^+$CF;
3. CH$_2$F$_2$, *m*/*z*: 52, $^+$M, 51, $^+$CHF$_2$, 33, $^+$CH$_2$F;
4. CF$_3$CH$_2$F, *m*/*z*: 102, $^+$M, 83, $^+$CF$_3$CH$_2$, 69, $^+$CF$_3$, 51, $^+$CHF$_2$, 33 $^+$CH$_2$F;
5. CHF$_2$CHF$_2$, *m*/*z*: 102, $^+$M, 101$^+$CHF$_2$CF$_2$, 83, $^+$CHF$_2$CHF, 63 $^+$CHF$_2$C, 51, $^+$CHF$_2$.

2.3.10. Synthesis of CF$_3$I in the presence of AC and H$_2$

The reactor was packed with AC, and heated to 550 °C under nitrogen. After 2.5 h, then CHF$_3$ with 50 ml/min, vaporized I$_2$ with 10 g/h and H$_2$ with 50 ml/min were passed through the reactor. The products were neutralized by KOH solution, dried and analyzed by GC–MS. The results were listed as follows.

1. CH$_4$, *m*/*z*: 16, $^+$M; 15, $^+$CH$_3$, 14, $^+$CH$_2$, 13, $^+$CH.
2. CH$_3$CH$_3$, *m*/*z*: 30, $^+$M, 28, $^+$CH$_2$CH$_2$, 15, $^+$CH$_3$;
3. CHF$_3$, *m*/*z*: 69, $^+$CF$_3$, 51, $^+$CHF$_2$, 31, $^+$CF;
4. CH$_3$I, *m*/*z*: 142, $^+$M, 127, $^+$I.

2.3.11. Synthesis of CF$_3$I in the presence of catalyst KF/AC and O$_2$

The reactor was packed with AC, and heated to 550 °C under nitrogen. After 2.5 h, then CHF$_3$ with 50 ml/min, vaporized I$_2$ with 10 g/h and O$_2$ with 50 ml/min were passed through the reactor. The products were neutralized by KOH solution, dried and analyzed by GC–MS. The results were listed as follows.

1. CF$_4$, *m*/*z*: 69, $^+$CF$_3$; 50, $^+$CF$_2$;
2. CF$_3$CF$_3$, *m*/*z*: 119, $^+$CF$_3$CF$_2$, 69, $^+$CF$_3$, 50, $^+$CF$_2$;
3. CHF$_3$, *m*/*z*: 69, $^+$CF$_3$, 51, $^+$CHF$_2$, 31, $^+$CF;
4. CF$_3$CF$_2$CF$_3$, *m*/*z*: 169, $^+$CF$_3$CF$_2$CF$_2$, 119, $^+$CF$_3$CF$_2$, 100, $^+$CF$_2$CF$_2$, 69, $^+$CF$_3$; 50, $^+$CF$_2$;
5. CF$_3$CHF$_2$, *m*/*z*: 119, $^+$CF$_3$CF$_2$, 101, $^+$CF$_2$CHF$_2$, 69, $^+$CF$_3$, 51, $^+$CHF$_2$;
6. CF$_3$I, *m*/*z*: 196, $^+$M, 127, $^+$I, 69,
7. CF$_3$CF$_2$I, 246 $^+$M, 127, $^+$I, 119, $^+$C2F5, 100, $^+$C$_2$F$_4$, 69, $^+$CF$_3$; 50, $^+$CF$_2$;

3. Results and discussion

3.1. Pyrolysis of trifluoromethane on activated charcoal

It was reported that pyrolysis of CHF$_3$ at high temperature leads to the formation of tetrafluoroethene (TFE) as the major product, and the mechanism of this process involves the dehydrofluorination of CHF$_3$ to form difluorocarbene, which then dimerizes to form TFE [16–18].

Raphaele et al. obtained CH$_2$F$_2$ by reacting H$_2$ with CHF$_3$ at the temperature of 775 °C, and proposed the mechanism involved CF$_2$ carbene intermediate [16]. Wheaton and Burton used 2-methyl-2-butene, a electron-rich alkenes, to trap CF$_2$ carbene intermediate at the temperature of 120 °C and obtained gem-difluoro-2,2,3-trimethylcyclopropane to confirm the CF$_2$ carbene intermediate [19].

In our laboratory, CH$_2$F$_2$ are obtained successfully when hydrogen is introduced into the pyrolysis process of CHF$_3$ at 850 °C which indicates that CF$_2$ carbene is as the reaction intermediate in the pyrolysis process of CHF$_3$. The results are consistent with the CF$_2$ carbene process depicted [16].

However, in our experimental, when AC or catalyst is charged into reactor, TFE is not detected in the pyrolysis process of CHF$_3$. Also CH$_2$F$_2$ cannot be obtained in the pyrolysis process even though in the presence of hydrogen. Above-mentioned results indicate that the induction period of synthetic mechanism of CF$_3$I is different from the pyrolysis mechanism of CHF$_3$. The result is attributed to the existence of activated charcoal or catalysts in process.

As reported, in the synthetic process of CF$_3$I by vapor-phase catalytic reaction, induction period was suspected that the dehydrofluorination of CHF$_3$ to form CF$_2$ carbene, and the CF$_2$ carbene cover the surface on the catalyst, but no TFE reported in by-products, [15].

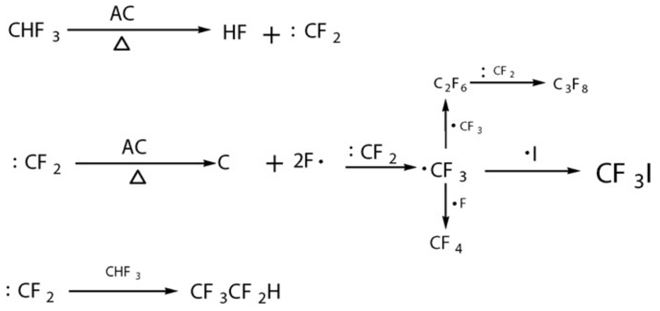
To confirm above-mentioned hypothesis, we try to capture the CF$_2$ carbene intermediate with the help of hydrogen and an electron-rich alkenes to confirm the CF$_2$ carbene mechanism during the pyrolysis process of CHF$_3$ in the presence of AC. Hydrogen and 2-methyl-2-butene are used as trapping reagents in the induction period. The results are shown in Table 1. Based on the experimental 1, we do not get CH$_2$F$_2$ in the products when hydrogen is used to capture CF$_2$ carbene, but a certain amount of CH$_4$ exists in products. The results indicate no free CF$_2$ carbene formed in the process, or the formed CF$_2$ carbene transferred into CH$_2$ carbene in the presence of hydrogen to get CH$_4$.

In the experimental 2 in Table 1, when 2-methyl-2-butene is used as a trapping reagent in pyrolysis of CHF$_3$, also no gem-difluorotrimethylcyclopropane is detected in the process. At least, formed CF$_2$ carbene is not so easy to combine with 2-methyl-2-butene.

The interesting results are from the pyrolysis of CH$_3$F in the presence of AC. If the reaction gas is only CHF$_3$ without hydrogen, the products contain CF$_4$, C$_2$F$_6$, C$_3$F$_8$, and C$_2$HF$_5$ (see experimental 3 in Table 1). The results clearly indicate that CF$_3$ radical exists in the pyrolysis process.

Based on above results, we suppose that the pyrolysis mechanism of CH$_3$F in the presence of AC is as Scheme 2. Firstly pyrolysis of CHF$_3$ at high temperature leads to the dehydrofluorination of unimolecular HF of CH$_3$F to form CF$_2$ carbene. CF$_2$ carbene combines with AC strongly so that it do not dimerize. It might be decomposed into carbon and F radical on the surface of AC. F radical reacted with CF$_2$ carbene to form CF$_3$ radical. As the finally results, CF$_3$ radical becomes into CF$_4$, C$_2$F$_6$, C$_3$F$_8$. In addition, a part of CF$_2$ carbene reacts with CHF$_3$ to form by-product C$_2$HF$_5$. If H$_2$ is introduced into the reaction process, the F radical will react with H$_2$ to form HF so that CF$_4$, C$_2$F$_6$, C$_3$F$_8$ and C$_2$HF$_5$ could not be obtained in the process.

In addition, when pyrolysis outlet gas passes through deionized water, the water became into acidic from experimental 1 to 5 in Table 1, which might be attributed to that the HF formed solved into H$_2$O in pyrolysis process. This is another identification to support CF$_2$ carbene formation in the pyrolysis process of CHF$_3$. As reported in literature, the activation energy of elimination of a HF molecule from CHF$_3$ is much lower than the dissociation



Scheme 2. Proposed mechanism for the formation of CF_4, C_2F_6, C_3F_8 and C_2HF_5.

energies of C–F bond and C–H bond, and HF elimination to form CF_2 carbene may be an important pathway for CHF_3 decomposition and the CF_3 radical formation [20]. In the study on the mechanism of hydrogenation of CCl_2F_2 into CH_2F_2, van de Sandt reported that CF_2 carbene would absorb on the PdC catalyst and it was the most important intermediate to form CH_2F_2, CH_3F, CH_4 [21].

In our experimental, we suppose that CHF_3 cracks into HF and CF_2 carbene, then the CF_2 carbene combines with AC tightly since CF_2 carbene itself do not form CF_2=CF_2, and also the trapping reagents do not capture the CF_2 carbene. Although CF_2 carbene combined with catalyst strongly do not dimerize or react with the trapping reagents, but it will decomposed into carbon and F radical on heat. F radical reacts with CF_2 carbene to form CF_3 radical, then form CF_4, C_2F_6, C_3F_8 gradually in the reaction (see Scheme 2).

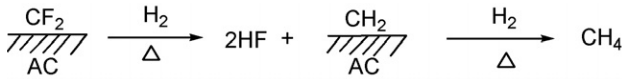
When H_2 joins the reaction, firstly the F radical reacts with H_2 to generate HF so that no CF_3 radical forms, then CF_4, C_2F_6, C_3F_8 and C_2HF_5 could not be detected in the products. Based on the experimental 4 in Table 1, the absence of CF_3I in the products during the reaction of I_2 and CHF_3 in the presence of H_2 further enhances our hypothesis, the primary products are CH_4, CH_3I. In addition, the absence of CH_2F_2 is attributed to that hydrogenation of CF_2 carbene transfers into CH_2 carbene, then becomes into CH_4 as shown in experimental 5.

In the experimental 5 of Table 1, first CHF_3 with 100 ml/min passes through the catalyst for 2 h at 550 °C, then nitrogen with 100 ml/min washes AC surface at 550 °C for 1 h, hydrogen passes through the catalyst to obtain CH_4, which indicates that the CF_2 carbene still remind on AC even though heating at 550 °C under nitrogen flow. The results indicate that the combination between CF_2 carbene and AC is quite strong, this is correspond to that CF_2 carbene itself does not easily dimerize to TFE when AC exists in the reaction. When hydrogen is introduced into AC surface, CF_2 carbene quickly transferred into CH_2 carbene. The mechanism can be schemed as following (Scheme 3).

Instead of the hydrogen passing through by HF on the surface of AC, CHF_3 is detected in the product, which is attributed to that CF_2 carbene in AC reacts with HF. It further confirms our hypothesis that CF_2 carbene is strongly combine with AC in the pyrolysis process of CHF_3 (see experimental 6 in Table 1).

3.2. Pyrolysis of trifluoromethane on catalyst KF/AC

To check the effect of catalyst of KF/AC in pyrolysis reaction of CHF_3, KF/AC is packed into reactor instead of AC. The experimental data are listed in Table 2. The results indicate that the products are same as those of reactions in the presence of AC (see experimental 7 and 8 in Table 2). It is was presumed that AC co-catalyzes the dehydrofluorination of CHF_3 to form CF_2 carbene, then CF_2 carbene combines with AC or catalyst strongly, thus CF_2 carbene does not dimerize into TFE or does not react with H_2 to form CH_2F_2 even at high temperature of 850 °C.



Scheme 3. Proposed mechanism for the formation of CH_4.

Table 3
Synthesis of CF_3I in the presence of catalyst KF/AC[a].

Entry	Regent	GC area%						
		CF_4	CHF_3	C_2F_6	C_3F_8	C_2F_5H	CF_3I	C_2F_5I
12	CHF_3, O_2, I_2	3.9	40.2	0.4	0.2	1.0	50.3	4.0

Reaction temperature: 550 °C.
[a] Catalyst: KF/AC.

CH_4 can be formed through pyrolysis of CHF_3 and H_2 in the presence of KF/AC (see No. 8 in Table 2), but does not generate from the reaction of AC and H_2 (see No. 9 in Table 2). Also CH_2F_2 existed in the products indicates that hydrogen capture CF_2 carbene in the pyrolysis process of CHF_3 (see No. 10 in Table 2), which further proves that CF_2 carbene appears in the pyrolysis process of CHF_3. AC is the co catalyst to promote the formation of CF_2 carbene and CF_3 radical in the synthesis of CF_3I by vapor-phase catalytic reaction.

Also we check the surface area of AC fresh (1161.7 m^2/g) and used AC (1085.0 m^2/g) in the pyrolysis of CHF_3, the result shows that the surface area decreases slightly after the reaction. Might be it can be attributed to that the coke-formation formed in the pyrolysis process of CHF_3.

3.3. Synthesis of trifluoroiodine by vapor-phase catalytic reaction

Based on the hypothesis above on the synthetic mechanism of CF_3I, the pyrolysis of CH_3F in the presence of AC or catalyst KF/AC leads to the dehydrofluorination of CH_3F to form CF_2 carbene, then CF_2 carbene decomposes into carbon and F radical on the surface of AC. F radical reacts with CF_2 carbene to form CF_3 radical. When iodine gas passes through catalyst bed with pyrolysis products, CF_3I is successfully prepared by vapor-phase catalytic reaction, the results is shown in Table 3.

4. Conclusion

A series of experimental indicate that the synthetic mechanism of CF_3I is described as follows. In high temperature, AC promotes the dehydrofluorination of CHF_3 to form CF_2 carbene, then CF_2 carbene combines with AC strongly to form CF_3 radical when F radical generated from decomposition of CF_2 carbene. Therefore, CF_2 carbene does not dimerize to form tetrafluoroethane, but takes place disproportionation reaction to generate CF_3 radical and carbon. As the final result, CF_3I is prepared from the reaction of CF_3 radical reacts and iodine in the presence of AC or catalyst. In the process, AC is not only the catalyst supporter, but also a co-catalyst to promote CF_2 carbene formation and CF_3 radical to produce CF_3I.

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