



The disproportionation of CF₂ carbene in vapor-phase pyrolysis reaction over activated carbon and porous aluminum fluoride

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ARTICLE INFO

Article history:

Received 6 March 2009

Received in revised form 2 June 2009

Accepted 3 June 2009

Available online 10 June 2009

Keywords:

CF₂ carbene

Disproportionation

Pyrolysis reaction

R22

ABSTRACT

During the process of pyrolysis of chlorodifluoromethane, trifluoromethane and hexafluoropropylene oxide in the presence of supportors, like activated carbon (AC) and porous aluminum fluoride (PAF), no tetrafluoroethene (TFE) was detected at early time-on-stream (TOS), and some compounds containing CF₃ group were generated instead of the formation of TFE. The pyrolysis process is much different from that without supportors. It is proposed that the disproportionation reaction of CF₂ carbene may take place on the surface of supportors to produce CF₃ radical and carbon.

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1. Introduction

CF₂ carbene is a very important intermediate for the preparation of other fluorinated molecules, for instance, tetrafluoroethene (TFE) [1], trifluoriodomethane [2] and gem-difluorocyclopropanes [3]. A variety of methods to generate difluorocarbene have been reported, such as by thermolysis of sodium chlorodifluoroacetate [4], chlorodifluoromethane (R22), trifluoromethane (R23) [5], perfluorocyclopropane or hexafluoropropylene oxide (HFPO) [6], and by reaction of dibromodifluoromethane with zinc in tetrahydrofuran [7], etc. CF₂ carbene is more stabilized and less reactive than other halo- and dihalocarbenes [6].

Vapor-phase pyrolyses of R22, R23 and HFPO are convenient methods to prepare TFE. Pyrolysis of HFPO at the temperature up to 150 °C led to formation of TFE and trifluoroacetyl fluoride. The TFE was formed by dimerization of CF₂ carbene intermediate [5]. Pyrolysis of R22 and R23 at high temperature led to the formation of TFE as the major product, and the mechanism of this process involves the dehydrohalogenation to generate CF₂ carbene, which then dimerizes to form TFE [6]. The direct pyrolysis of R22 was an important method to produce TFE commercially. To increase the selectivity and yield of TFE, a lot of research work was carried out in recent years. With increasing reaction temperature and/or residence time, the conversion of R22 increased, however, the yield of TFE decreased due to the increase of by-products [8,9]. Sung et al.

[10,11] studied the pyrolysis of R22 to prepare TFE over Cu-based catalysts that were supported on metal fluorides and activated carbon (AC). With time-on-stream (TOS), the selectivity for TFE grew up and the selectivity for by-product of R23 decreased gradually, in the meantime, catalysts deactivation by coke-formation was observed. Nagasaki et al. [12] investigated the reaction between R23 and I₂ vapor to prepare CF₃I over KF/AC catalyst at 550 °C, and proposed a mechanism that KF catalyzed the dehydrofluorination of R23 to produce CF₂ carbene, then, the supporter of AC catalyzed the disproportionation of CF₂ carbene. If the suggested mechanism is correct, the similar reactions will happen during pyrolysis of R22 and HFPO over catalysts supported on AC, especially at early TOS. Because the AC has a large surface area and large pore volume at the beginning of reaction, a lot of CF₂ carbene will be absorbed on the surface of AC to lead the disproportionation reaction.

In our research, R22, R23 and HFPO were used as CF₂ carbene sources to conduct the pyrolysis experimentation over AC or porous aluminum fluoride (PAF). We found that the disproportionation of CF₂ carbene occurred on the surface of supportors to form CF₃ radical compounds based on the experimental results.

2. Experimental

2.1. Materials

R22 and R23 were purchased from Zhejiang Xingteng Chemical Co. Inc., China. AC was obtained from Shanxi Taiyuan Activated Carbon Factory and HFPO was provided by Shandong Dongyue

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Chemical Co., Ltd., China. PAF was purchased from Xi'an Jinzhu group, China.

2.2. Instrument and apparatus

Products were analyzed by means of Shimadzu GC-2014. 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 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, 4.1 ml He/min. The products were identified by their mass spectra and comparison of GC retention times with authentic samples.

MS (EI, 70 eV) spectra were measured using the Shimadzu 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 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 outgassed under vacuum ($P < 10^{-5}$ Torr) at 573 K for 3 h before measurement.

Energy-dispersive X-ray (EDX) analyses of samples were performed on a Hitachi S4800 field-emission scanning electron microscope (SEM). The accelerating voltage was 1 kV.

2.3. Reaction procedure

2.3.1. Pyrolysis of R22

3 ml AC was packed in an Inconel tubular reactor with 6.35 mm in diameter and 300 mm in length. Heated the reactor to 550 °C under nitrogen flow with the rate of 10 ml/min, then nitrogen flow was stopped and R22 with 10 ml/min was introduced to the reactor, the outgases passed through water and a KOH solution to neutralize HX (X = Cl, F) formed. Then the exiting gas was analyzed by GC-MS. The data of MS are listed as follows:

1. CHF₃, m/z : 69, ⁺CF₃; 51, ⁺CHF₂; 31, ⁺CF.
2. CF₃Cl, m/z : 85, ⁺CF₂Cl; 69, ⁺CF₃; 50, ⁺CF₂; 35, ⁺Cl.
3. CHF₂Cl, m/z : 86, ⁺M; 51, ⁺CHF₂; 31, ⁺CF.
4. CF₂Cl₂, m/z : 101, ⁺CFCl₂; 85 ⁺CF₂Cl; 50, ⁺CF₂.

When AC was replaced by PAF, the data of MS are listed as follows:

1. CF₄, m/z : 69, ⁺CF₃; 50, ⁺CF₂.
2. CHF₃, m/z : 69, ⁺CF₃; 51, ⁺CHF₂; 31, ⁺CF.
3. CF₃Cl, m/z : 85, ⁺CF₂Cl; 69, ⁺CF₃; 50, ⁺CF₂; 35, ⁺Cl.
4. CHF₂Cl, m/z : 86, ⁺M; 51, ⁺CHF₂; 31, ⁺CF.
5. CF₂Cl₂, m/z : 101, ⁺CFCl₂; 85 ⁺CF₂Cl; 50, ⁺CF₂.

Pyrolysis though empty reactor, the data of MS are listed as follows:

1. CF₂=CF₂, m/z : 100, ⁺M; 81, ⁺CF₂CF; 50, ⁺CF₂; 31, ⁺CF₂.
2. CHF₂Cl, m/z : 86, ⁺M; 51, ⁺CHF₂; 31, ⁺CF.

2.3.2. Pyrolysis of R23

The reaction procedure and conditions were same with Section 2.3.1, but R22 flow was replaced by R23 flow. Then the exiting gas was analyzed by GC-MS. Pyrolysis over AC, the data of MS are listed as follows:

1. CF₄, m/z : 69, ⁺CF₃; 50, ⁺CF₂.
2. CF₃CF₃, m/z : 119, ⁺CF₃CF₂; 69, ⁺CF₃; 50, ⁺CF₂.
3. CHF₃, m/z : 69, ⁺CF₃; 51, ⁺CHF₂; 31, ⁺CF.
4. CF₃CF₂CF₃, m/z : 169, ⁺CF₃CF₂CF₂; 119, ⁺CF₃CF₂; 100, ⁺CF₂CF₂; 69, ⁺CF₃; 50, ⁺CF₂.

When AC was replaced by PAF, the data of MS are listed as follows:

1. CF₄, m/z : 69, ⁺CF₃; 50, ⁺CF₂.
2. CF₃CF₃, m/z : 119, ⁺CF₃CF₂; 69, ⁺CF₃; 50, ⁺CF₂.
3. CHF₃, m/z : 69, ⁺CF₃; 51, ⁺CHF₂; 31, ⁺CF.

Pyrolysis though empty reactor, only raw material was detected.

2.3.3. Pyrolysis of HFPO

The reaction procedure and conditions were same with Section 2.3.1, but R22 flow was replaced by HFPO flow. Then the exiting gas was analyzed by GC-MS. Pyrolysis over AC, the data of MS are listed as follows:

1. CF₄, m/z : 69, ⁺CF₃; 50, ⁺CF₂.
2. CF₃CF₃, m/z : 119, ⁺CF₃CF₂; 69, ⁺CF₃; 50, ⁺CF₂.
3. CHF₃, m/z : 69, ⁺CF₃; 51, ⁺CHF₂; 31, ⁺CF.
4. CO₂, m/z : 44, ⁺M; 28 ⁺CO; 12, ⁺C.

When AC was replaced by PAF, the data of MS are listed as follows:

1. CF₄, m/z : 69, ⁺CF₃; 50, ⁺CF₂.
2. CF₃CF₃, m/z : 119, ⁺CF₃CF₂; 69, ⁺CF₃; 50, ⁺CF₂.
3. CHF₃, m/z : 69, ⁺CF₃; 51, ⁺CHF₂; 31, ⁺CF.
4. CF₃CF₂=CF₂, m/z : 150, ⁺M; 131, ⁺CF₂ CF₂=CF₂; 100, ⁺CF₂=CF₂; 69, ⁺CF₃; 31, ⁺CF.
5. CO₂, m/z : 44, ⁺M; 28, ⁺CO; 12, ⁺C.

Pyrolysis though empty reactor, the data of MS are listed as follows:

1. CF₂=CF₂, m/z : 100, ⁺M; 81, ⁺CF₂CF; 50, ⁺CF₂; 31, ⁺CF₂.
2. CF₃CF₂=CF₂, m/z : 150, ⁺M; 131, ⁺CF₂ CF₂=CF₂; 100, ⁺CF₂=CF₂; 69, ⁺CF₃; 31, ⁺CF.
3. CO₂, m/z : 44, ⁺M; 28, ⁺CO; 12, ⁺C.

2.3.4. Pyrolysis of the compounds absorbed on AC and PAF surface

3 ml used AC, which had been used in the pyrolysis reaction of R22, was packed in the reactor. At the temperature of 550 °C, nitrogen flow with 5 ml/min was inlet to the reactor to draw out the pyrolysis products. At the outlet, the outgases passed through water and a KOH solution to neutralize the HF and HCl generated. Then the exiting gas was analyzed by GC-MS. Its data of MS are listed as follows:

1. CF₄, m/z : 69, ⁺CF₃; 50, ⁺CF₂.
2. CHF₃, m/z : 69, ⁺CF₃; 51, ⁺CHF₂; 31, ⁺CF.
3. CF₃Cl, m/z : 85, ⁺CF₂Cl; 69, ⁺CF₃; 50, ⁺CF₂; 35, ⁺Cl.
4. CO₂, m/z : 44, ⁺M; 28, ⁺CO; 12, ⁺C.

The outgases from the AC used in pyrolysis of R23 was analyzed by GC-MS, the data of MS are listed as follows:

1. CF₄, m/z : 69, ⁺CF₃; 50, ⁺CF₂.
2. CHF₃, m/z : 69, ⁺CF₃; 51, ⁺CHF₂; 31, ⁺CF.
3. CO₂, m/z : 44, ⁺M; 28, ⁺CO; 12, ⁺C.

The outgases from the PAF used in pyrolysis of R22 was analyzed by GC-MS, the data of MS are listed as follows:

1. CHF₃, *m/z*: 69, ⁺CF₃; 51, ⁺CHF₂; 31, ⁺CF.
2. CF₃Cl, *m/z*: 85, ⁺CF₂Cl; 69, ⁺CF₃; 50, ⁺CF₂; 35, ⁺Cl.
3. CO₂, *m/z*: 44, ⁺M; 28, ⁺CO; 12, ⁺C.

2.3.5. Hydrogenation of the compounds absorbed on AC and PAF surface

3 ml used AC, which had been used in the pyrolysis reaction of R22, was packed in the reactor. At the temperature of 550 °C, hydrogen flow with 5 ml/min was inlet to the reactor to draw out the pyrolysis products. At the outlet, the outgases passed through water and a KOH solution to neutralize the HF and HCl generated. Then the exiting gas was analyzed by GC–MS. Its data of MS are listed as follows:

CH₄, *m/z*: 16, ⁺M; 15, ⁺CH₃; 14, ⁺CH₂; 13, ⁺CH.

The components from the AC used in pyrolysis of R23 and the PAF used in pyrolysis of R22 are same as the data from R22.

3. Results and discussion

It was reported [10,11] that during pyrolysis of R22 over AC or PAF at the temperature of 700 °C, TFE was formed as the major product, and the conversion of R22 decreased with TOS, whereas the selectivity of TFE increased. To investigate the pyrolysis process at the early TOS, the experimental of pyrolysis R22 over AC was conducted at the temperature of 550 °C so that the deactivation process was prolonged under a relative low pyrolysis temperature. The results of pyrolysis R22 were shown in Fig. 1, at the TOS of 1 h, the products were 6.0% R23, 42.8% CF₃Cl and 17.9% CF₂Cl₂, respectively, according to the GC area of the analytical results. The conversion of R22 decreased gradually during the whole process of pyrolysis reaction. The amount of R22 increased from 31% at TOS of 1 h to 94% at TOS of 5 h and TFE has not detected during the above pyrolysis process. With the progress of the pyrolysis progress, the surface area of AC reduced. The amount of CF₂ carbene that was absorbed on AC surface decreased, and the trace amount of CF₂ carbene that dimerized to form TFE increased. It is in accordance with previous results [10] that the selectivity for TFE increased with TOS and conversion of R22 decreased due to the coke formation.

The experiment of non-catalytic pyrolysis R22 was carried out in an empty tubular reactor at the temperature of 550 °C. Only a small part of R22 was converted, exiting gas contains 93% R22 based on the GC area (see Table 1), and the main product was TFE. However, in the presence of AC or PAF, the conversion of R22

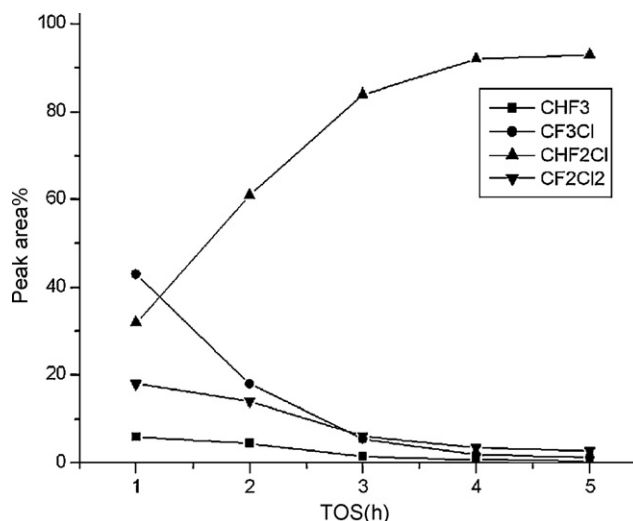


Fig. 1. Pyrolysis of R22 over AC. Space velocity: 200 h⁻¹; reaction temperature: 550 °C.

increased greatly at the same pyrolysis temperature. The amount of R22 reduced to 61.2% and 4.9% over AC and PAF, respectively (see Table 1). The products are 7.6% CHF₃, 15.4% CF₃Cl and 11.8% CF₂Cl₂ in the presence of AC, and 1.2% CF₄, 48.7% CHF₃, 38.7% CF₃Cl and 4.4% CF₂Cl₂ in the presence of PAF. In the reaction process, TFE has not been detected. TFE is an important compound in this paper. It was identified by mass spectra and comparison of their GC retention times with authentic samples (MS spectroscopy of TFE was shown in Fig. 2).

As for the products in pyrolysis of R22 over AC or PAF, it is agreed with the mechanism of CF₂ carbene disproportionation. During pyrolysis of R22 over AC and PAF, the CF₂ carbene was absorbed on the surface of AC or PAF and would take place disproportionation reaction to get CF₃ radical. Then the CF₃ radical reacted with H radical, Cl radical and F radical to form R23, CF₃Cl and CF₄, respectively. CF₂Cl₂ may come from disproportionation of CFCI carbene or the reaction of CF₂ carbene with two Cl radicals.

PAF is one of typical strong Lewis acid with large surface area and bigger volume porous metal fluoride, it has an excellent thermal and chemical stability to a strong corrosive medium like the environment of HF and HCl. It is much easier to coordinate with chlorinated compound like CHF₂Cl, so PAF shows more obvious

Table 1
Pyrolysis of chlorodifluoromethane.

Entry	Catalyst	Products and GC area (%)						
		CF ₂ =CF ₂	CHF ₂ Cl	CF ₄	CHF ₃	CF ₃ Cl	CF ₂ Cl ₂	Others
1	Non-catalyst	4.7	93.1	–	–	–	–	2.2
2	AC	–	61.2	–	7.6	15.4	11.8	4.1
3	PAF	–	4.9	1.2	48.7	38.7	4.4	2.1

–: not detected, space velocity: 200 h⁻¹, reaction temperature: 550 °C and TOS: 2 h. Bold value signifies that the corresponding component does not to be detected in reaction by means of our GC–MS.

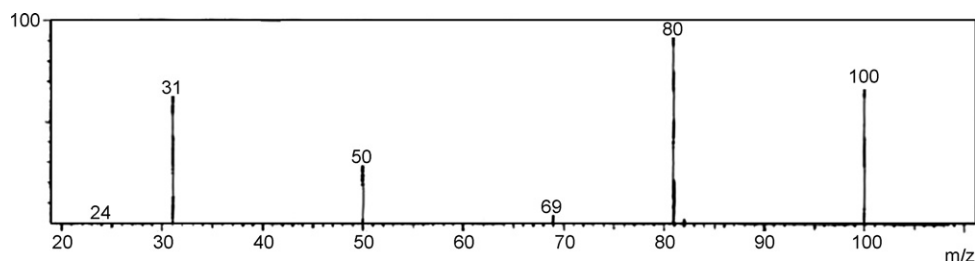


Fig. 2. MS spectroscopy of TFE.

Table 2
Pyrolysis of trifluoromethane.

Entry	Catalyst	Products and GC area (%)				
		CF ₄	CF ₃ CF ₃	CHF ₃	C ₃ F ₈	Others
4	Non-catalyst	–	–	100	–	–
5	AC	1.7	4.1	92.7	1.3	0.2
6	PAF	0.4	0.1	99.5	–	–

–: not detected, space velocity: 200 h⁻¹, reaction temperature: 550 °C and TOS: 2 h.

Table 3
Pyrolysis of hexafluoropropene oxide.

Entry	Catalyst	Products and GC area (%)						
		CF ₄	CF ₃ CF ₃	CF ₂ =CF ₂	CF ₃ CF ₂ =CF ₂	CHF ₃	CO ₂	Others
7	Non-catalyst	–	–	65.6	32.2	–	–	2.2
8	AC	3.8	23.1	–	–	40.9	30.1	2.1
9	PAF	77.9	8.5	–	6.0	3.4	0.2	4.0

–: not detected, space velocity: 200 h⁻¹, reaction temperature: 550 °C and TOS: 2 h.

activity than activated carbon (AC) in the pyrolysis of R22 (see Table 1). However, PAF and AC have almost same activity in the pyrolysis process of hydrofluorocarbon like CHF₃ (see Table 2).

To verify the hypothesis that the CF₂ carbene absorbed on the surface of AC or PAF causes the disproportionation reaction to form the compounds containing CF₃ group, R23 and HFPO as other CF₂ carbene sources were used to conduct the similar experiments under the same condition. The results were shown in Tables 2 and 3.

It was reported that pyrolysis of R23 at the temperature of 775 °C led to the formation of TFE as the major product, and the mechanism of this process involved dehydrofluorination of R23 to form difluorocarbene [13]. Our previous work [14] investigated the CF₂ carbene on the surface of activated charcoal in the synthesis of trifluoroiodomethane. It was proposed that CF₂ carbene combines with AC strongly and transfers into CF₃ radical when heated. In this paper, pyrolysis of R23 in the presence of PAF was conducted. At the temperature of 550 °C, no reaction was observed in pyrolysis of R23 without supporters. In the presence of AC or PAF, R23 decomposed partly. The conversion of R23 was 7.3% and 0.5% over AC and PAF, respectively. When pyrolysis exiting gas passed through de-ionized water, the PH value of the water was about 3. It is attributed to that the pyrolysis reaction of R23 may crack into HF and CF₂ carbene. The CF₂ carbene may be absorbed on the surface AC and PAF. Afterwards, the absorbed CF₂ carbene took place disproportionation reaction and then generated CF₄, C₂F₆ and C₃F₈. C₂F₆ could be regarded as the product of CF₃ radical dimerization, and C₃F₈ may be formed by the reaction of CF₂ carbene with two CF₃ radicals.

During pyrolysis of HFPO at the temperature of 550 °C, TFE and hexafluoropropene was produced (see Table 3). It was suggested that TFE and hexafluoropropene came from dimerization and trimerization of CF₂ carbene, respectively. However, in the presence of AC or PAF, Some compounds containing CF₃ group were detected in the process, such as CF₄, R23 and CF₃CF₃, which was in accordance with our hypothesis that the CF₂ carbene intermediate was absorbed on the surface of AC and PAF, then disproportionation to CF₃ radical. So CF₂ carbene could not trap other CF₂ carbene to form TFE.

Table 4
EDX analysis results of the used AC.

AC sample	Contents (mol%)		
	O	Cl	F
Used in pyrolysis of R22	38.4	–	61.6
Used in pyrolysis of R23	38.8	0.32	60.9
Used in pyrolysis of HFPO	39.5	–	60.5

–: not detected.

Table 4 shows the surface composition of used AC in pyrolysis of R22, R23 and HFPO by means of energy dispersive X-ray fluorescence spectrometer (EDX), the results indicated that all of the AC samples embodied some fluorine species on the surfaces, which may support our hypothesis that CF₂ was absorbed on the surface of AC. The AC used in pyrolysis of R22 has some Cl component, which was from the decomposition of R22 absorbed on the surface of AC.

In order to investigate the species absorbed on the AC or PAF surface during the pyrolysis process, thermal desorption and hydrogenation of those compounds were conducted. The results were shown in Tables 5 and 6.

CF₄, R23 and CO₂ were obtained by the thermal desorption of the compounds absorbed on the surface of AC or PAF (see Table 5). When heated the supporters used in pyrolysis process, the absorbed CF₂ carbene took place disproportionation reaction to form CF₃ radical. Pyrolysis products of CF₄, R23 and CF₃Cl may be formed via CF₃ radical. CF₃ radical reacts with F radical to form CF₄ and reacts with H radical to get R23. H radical maybe come from the cardoayls and phenols on the AC surface and hydroxyl group on the PAF surface. The CO₂ comes from the reaction between carbon and O element that exists in cardoayls and phenols of AC surface and hydroxyl group on the PAF surface. In this process, F radical may

Table 5
Pyrolysis of the compounds absorbed on the used AC and PAF.

Entry	Reagent	Products and GC area (%)			
		CF ₄	CO ₂	CHF ₃	CF ₃ Cl
10	A	1.4	6.2	4.4	88
11	B	14.2	45.3	40.5	–
12	C	–	36.9	33.8	29.3

Temperature: 550 °C, A: compounds absorbed on the surface of AC used in pyrolysis of R22, B: compounds absorbed on the surface of AC used in pyrolysis of R23 and C: compounds absorbed on the surface of PAF used in pyrolysis of R22.

Table 6
Hydrogenation of the compounds absorbed on the used AC and PAF.

Entry	Reagent	Product
13	A	CH ₄
14	B	CH ₄
15	C	CH ₄

Temperature: 550 °C, the flow rate of H₂: 10 ml/min, A: compounds absorbed on the surface of AC used in pyrolysis of R22, B: compounds absorbed on the surface of AC used in pyrolysis of R23 and C: compounds absorbed on the surface of PAF used in pyrolysis of R22.

Table 7
BET surface area of the fresh and used AC.

		BET surface area (m ² /g)
Fresh		1162
Used	Pyrolysis R23	1085
	Pyrolysis R22	377
	Pyrolysis R22 and H ₂	863

react with H element to form HF, which is supported by the fact that when pyrolysis exiting gas passed through de-ionized water, the water became into acidic and PH value is <3 at last in experimental 10–12. As for CF₃Cl, it may be from the reaction between Cl radical and CF₃ radical. Because C–Cl bond is much weaker than C–F bond, so when heat, Cl radical is formed easily from some containing Cl fragments that were absorbed on the surface of AC or PAF during pyrolysis process.

When a flow of hydrogen was fed into the pyrolysis reaction, all of the halohydrocarbon disappeared and only CH₄ as product detected (see Table 6). It may be explained that difluorocarbene transferred into carbene to form CH₄ in the presence of hydrogen or hydrogen reacted with the activated F atom to form HF so that the activated F atom cannot react with CF₂ carbene to form CF₃ radical. Therefore the compounds containing CF₃ radical were not detected in the products, like CF₄, R23 and CF₃Cl.

From the change of surface area of fresh AC and used AC in the pyrolysis process (see Table 7), it indicated that the coke-formation should be produced on the surface of AC. It is attributed to that disproportionation reaction of absorbed CF₂ carbene occurred to produce CF₃ radical and carbon deposit on the surface of AC.

Due to the disproportionation of CF₂ carbene on AC, coke will be generated and makes the surface area decrease. At the temperature of 550 °C, the dehydrofluorination of R23 to form CF₂ carbene carried out slightly, otherwise, under the same condition, the pyrolysis of R22 took place easily. And much CF₂ carbene formed and covered on the surface of AC, then the CF₂ carbene disproportionated into CF₃ radicals and carbon. In pyrolysis of R22, the surface area of used AC was 377 m²/g. It decreased intensively compared with that of fresh AC. However, in pyrolysis of R23, the surface area of used AC decreased slightly compared with that of fresh AC. After pyrolysis of R22 in the presence of H₂, the surface area of AC was 863 m²/g. Compared with surface area of pyrolysis of R22 without H₂, the

coke was lessened distinctly under the same condition. It may be explained that a small part of CF₂ carbene combined with AC was disproportionated into CF₃ radicals and coke, other part of the CF₂ carbene was hydrogenized to form CH₄, which was in accordance with the results of hydrogenization reaction in Table 6. R. Romelaer [5] found that pyrolysis of R22 in the presence of hydrogen, carbon balance increased with increasing H₂ content, which supports our experimental results.

4. Conclusion

The results indicated that in the pyrolysis reaction of R22, R23 and HFPO, TFE could not be generate at early TOS in the presence of AC and PAF. Our proposed pyrolysis mechanism is that absorbed CF₂ carbene on the surface of supporters takes place disproportionation reaction to produce CF₃ radical and carbon. CF₃ radical reacts with other radicals to form a series of compounds containing CF₃ function group in the process. The proposed mechanism about disproportionation of CF₂ carbene can be used to explain some phenomena in pyrolysis reactions, including complicated pyrolytic products, disappearance of TFE and formation of coke. TFE was the major product in pyrolysis of those three without supporters. In addition, above-mentioned mechanism was confirmed with the help of hydrogenation products, and desorption products from the supporter surface.

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