



## Review

Treatment of the potent greenhouse gas, CHF<sub>3</sub>—An overview

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## ABSTRACT

CHF<sub>3</sub> is a potent and synthetic greenhouse gas with global warming potential of 11,700 times higher than that of CO<sub>2</sub>. It is mainly produced as a by-product during the manufacture of HCFC-22. Many methods have been proposed for the treatment of CHF<sub>3</sub>, including thermal oxidation (incineration), catalytic hydrolysis, plasma destruction and conversion to environmentally benign compounds. This review reports the recent research advances in the treatment of CHF<sub>3</sub> waste. It has been found that pyrolysis process, especially in the presence of a catalyst, and reaction of CHF<sub>3</sub> with I<sub>2</sub> or CH<sub>4</sub>, has great potential for the conversion of CHF<sub>3</sub> to valuable and environmentally benign chemicals. In this regard, the review is largely focused on the conversion of CHF<sub>3</sub> to C<sub>2</sub>F<sub>4</sub>, CF<sub>3</sub>I and VDF, as well as the chemistry involved.

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## 1. Introduction

Global production and use of chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs) and halons has decreased significantly as a result of the phase out schedules of the 1987 Montreal Protocol and its subsequent amendments and adjustments [1]. However, chlorodifluoromethane (CHClF<sub>2</sub>, R22 and HCFC-22), a typical HCFC, its feedstock production is permitted to continue indefinitely because it does not involve the release of

HCFCs and HFCs to atmosphere in the same way as disperse use, such as production of poly-tetrafluoroethene (PTFE), poly-vinylidene fluoride (PVDF) from CHClF<sub>2</sub> and synthesis of fluorine containing refrigerants, fire extinguishing agent and foams. During the manufacture of CHClF<sub>2</sub> (HCFC-22), trifluoromethane (CHF<sub>3</sub>, HFC-23, fluoroform, FE-13 and R23) is an unintentional by-product generated and has limited application as a refrigerant or as a raw material for other products. It has a global warming potential 11,700 times (for a 100-year time horizon) higher than carbon dioxide which is the second highest global warming potential among all greenhouse gases and an atmospheric lifetime of 264 years [2]. It is reported that the concentration of CHF<sub>3</sub> is steadily increasing in the atmosphere since at least 1978 at a present rate of increase of 5% per year [3]. More recently, it was

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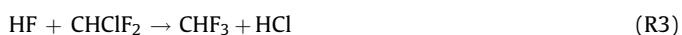
E-mail addresses: [jackhanwf@hotmail.com](mailto:jackhanwf@hotmail.com), [hanwf@zjut.edu.cn](mailto:hanwf@zjut.edu.cn) (W. Han), [cuihua@zjut.edu.cn](mailto:cuihua@zjut.edu.cn) (H. Liu).

reported that the mean rate of global emission of CHF<sub>3</sub> between 2006 and 2008 is 13.5 ± 2 Gg/yr (200 ± 30 × 10<sup>12</sup> gCO<sub>2</sub>-equivalent/yr, or MtCO<sub>2</sub>-eq./yr), 50% higher than the 8.7 ± 1 Gg/yr (130 ± 15 MtCO<sub>2</sub>-eq./yr) for 1990s [4].

Unlike the versatile application of HCFC-22, HFC-23 has limited uses, generally for specific applications in refrigeration or for dry etching in the semiconductor industry and has limited application as a fire inhibition agent. Thus, the development of suitable methods for the treatment of HFC-23 is of great practical significance. However, limited research has focused on the development of treatment process specifically for HFC-23, especially in comparison with the extensive research on technologies for destruction of halons, CFCs and CO<sub>2</sub> emissions. As a result, developing an effective and sustainable technology for CHF<sub>3</sub> abatement has become a worldwide issue. Also, it is an important part for the global carbon emission reduction which is one of the most serious challenges faced by the entire world nowadays.

## 2. Emission source of CHF<sub>3</sub>

Considerable quantities of CHF<sub>3</sub> are majorly produced during the manufacture of HCFC-22 as an unintended and inevitable by-product. HFC-23 emissions were estimated to be 24.3 ktonnes in 2015 for a “business as usual” scenario in which existing capacity continued to operate with an average emission function of 1.9% and the new capacity in developing countries was operated without significant abatement with an emission function equal to the production factor of 4% [5]. HCFC-22 was once widely used as a propellant and refrigerant and it is now being phased out due to its ozone depletion potential. In addition, it is the key intermediate for the production of various materials, such as TFE (tetrafluoroethene), PTFE and other HFCs (hydrofluorocarbons). This application is excluded from the CFCs phase-out scheme for unlimited period. Generally, HCFC-22 is synthesized via the following reactions ((R1)–(R3)) in the presence of antimony pentachloride [6].



Although the formation of CHF<sub>3</sub> can be reduced by optimising the processes, not only is it not possible to completely eliminate HFC-23 production by this means, but the scope for optimisation is inhibited by factors such as the process design and the fact that optimisation to reduce HFC-23 generally results in lower plant capacity which may have significant economic effects. In optimised processes, the likely range of emissions is roughly 1.5–3% of HCFC-22 production [5]. More recently, a similar emission trend was reported [4,7].

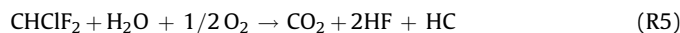
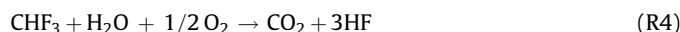
## 3. Thermal destruction

### 3.1. Thermal oxidation

Destruction will be the simplest route for the disposal of these synthetic fluorocarbons. However, extreme conditions are necessary for the conversion these chemicals since they can serve as fire extinguishing agents.

The typical HFC-23 thermal oxidation process generally includes five major operating units; thermal oxidizer, quench, absorption tower, neutralisation tower and exhaust stack. In this technology of thermal oxidation, HFC-23 (containing traces of HCFC-22) is oxidised to CO<sub>2</sub>, HF and HCl as summarised in

reactions ((R4)–(R6)) [8].



Thermal oxidation is well established technology and certified by United Nations Framework Convention on Climate Change (UNFCCC) under Clean Development Mechanism (CDM) for the destruction of HFC-23 [9]. In this process, liquid petroleum gas (LPG), combustion air coming from a combustion air fan and a HFC-23 waste stream are converted in a burner to form hot fumes (temperatures are generally higher than 1473 K in the burner and the residence time is 2 s). The flue gas leaving the thermal oxidizer is cooled in a quench. The majority of acid gases (HF and HCl) are absorbed into solution through this cooling process. Any unabsorbed acid gases along with CO<sub>2</sub>, N<sub>2</sub> (from the air) pass from the quench to the caustic scrubber. The remaining acid gases along with CO<sub>2</sub>, N<sub>2</sub> are fed to an absorption tower. The acid gases can be absorbed by alkali water through this process. The diluted HF solution is recycled to a quench where concentrated HF acid (30–40%) is produced and sent to storage for future use. N<sub>2</sub> passes through the caustic scrubber before being vented into the atmosphere. Fumes coming from the absorption tower are sent to a neutralisation tower where they are washed by caustic soda solution. Acid gases are removed following this washing. The tail gas from the neutralisation tower is transferred into an exhaust stack and finally emitted to the atmosphere.

According to the data of UNFCCC, around 20 projects have been registered under the clean development mechanism (CDM), which will reduce net CO<sub>2</sub> equivalent by about 82.6 million tonnes of CO<sub>2</sub> via HFCs abatement, majorly HFC-23. These projects are summarised in Table 1, together with the distribution of projects, methodologies adopted and volumes of CO<sub>2</sub> emission reductions. These data also can be obtained from the website of UNFCCC. Table 1 is also an indication of the significant demands and potential reduction of carbon emission from the treatment of synthetic greenhouse gases.

One serious shortcoming with these oxidation processes is that the fluorine has to be scrubbed as HF from the exhaust gas stream which then requires disposal, usually as a fluoride salt. Another challenge is the difficulty in finding suitable materials for the reactor which can operate at temperatures as high as 1473 K and in presence of the strongly corrosive HF. Furthermore, the potential formation of other hazardous materials such as dioxin poses another environmental concern during the cooling procedure of reaction flows from 1473 K to ambient temperatures.

### 3.2. Catalytic hydrolysis

It has been reported that the introduction of a catalyst can lead to the decomposition of CHF<sub>3</sub> at relatively low temperatures. For this technology to be viable, the catalytic materials employed by the process must be both highly reactive and be able to function for extended periods of time in a highly corrosive acidic environment. Feaver et al. [10] studied the destruction of CHF<sub>3</sub> at low concentration (3000 ppm) over ZrO<sub>2</sub> and ZrO<sub>2</sub>-SO<sub>4</sub> at 573–773 K and residence time of 0.4 s. It was found that CHF<sub>3</sub> was converted into CO<sub>2</sub> following the addition of 2.5% water to the feed stream through a catalysed hydrolysis reaction. In the absence of water, ZrO<sub>2</sub>-SO<sub>4</sub> was found to be virtually inactive, suggesting that decomposition of CHF<sub>3</sub> follows the route of hydrolysis rather than oxidation. Although sulphate groups in the catalyst are well known acidic sites, it was suggested that the promotion effect of these sulphate groups is the enhancement of water adsorption for

**Table 1**

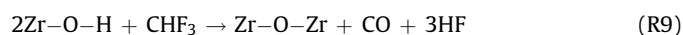
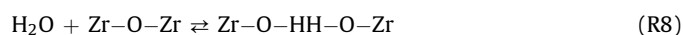
Projects of thermal oxidation of synthetic greenhouse gases registered under CDM program of UNFCCC (available at <http://cdm.unfccc.int/Projects/index.html>, data accessed January 8, 2010).

Registered	Title	Host parties	Methodology <sup>a</sup>	Reductions <sup>b</sup>
08 March 05	Project for GHG emission reduction by thermal oxidation of HFC23 in Gujarat, India	India	AM0001 ver. 2	3000000
24 March 05	HFC Decomposition Project in Ulsan	Republic of Korea	AM0001 ver. 2	1400000
24 December 05	GHG emission reduction by thermal oxidation of HFC23 at refrigerant (HCFC-22) manufacturing facility of SRF Ltd	India	AM0001 ver. 3	3833566
03 March 06	HFC23 Decomposition Project of Zhejiang Juhua Co., Ltd, P.R. China	China	AM0001 ver. 3	5789682
13 March 06	Shandong Dongyue HFC23 Decomposition Project	China	AM0001 ver. 3	10110117
04 June 06	Project for GHG Emission Reduction by Thermal Oxidation of HFC23 in Jiangsu Meilan Chemical Co., Ltd., Jiangsu Province, China	China	AM0001 ver. 3	8411432
14 June 06	Quimobásicos HFC Recovery and Decomposition Project	Mexico	AM0001 ver. 3	2155363
08 August 06	Project for HFC23 Decomposition at Changshu 3F Zhonghao New Chemical Materials Co. Ltd, Changshu, Jiangsu Province, China	China	AM0001 ver. 3	10437249
27 October 06	Project for HFC23 Decomposition at Limin Chemical Co., Ltd. Linhai, Zhejiang Province, China	China	AM0001 ver. 4	4783753
27 October 06	Project for HFC23 Decomposition at Zhejiang Dongyang Chemical Co., Ltd., China	China	AM0001 ver. 4	3656598
16 February 07	Destruction of HFC-23 at refrigerant (HCFC-22) manufacturing facility of Chemplast Sanmar, Ltd.	India	AM0001 ver. 3	539163
10 March 07	Frio Industrias Argentinas S.A ("FIASA") Hydro-fluorocarbon 23 ("HFC23") Capture, Storage and Decomposition Project	Argentina	AM0001 ver. 4	1434143
30 March 07	GHG emission reduction by thermal oxidation of HFC23 at Navin Fluorine International Limited (NFIL), Surat, Gujarat, India	India	AM0001 ver. 4	2802150
05 April 07	No.2 HFC-23 Decomposition Project of Zhejiang Juhua Co., Ltd, P.R. China	China	AM0001 ver. 4	4809631
01 May 07	HFC23 Decomposition Project at Zhonghao Chenguang Research Institute of Chemical Industry, Zigong, SiChuan Province, China	China	AM0001 ver. 4	2065533
14 September 07	China Fluoro HFC23 abatement project in China	China	AM0001 ver. 5	4248092
15 February 08	Changshu Haike HFC23 Decomposition Project	China	AM0001 ver. 5	3473385
14 November 08	GHG emission reduction by thermal oxidation of HFC23 at refrigerant (HCFC-22) manufacturing facility of HFL Ltd.	India	AM0001 ver. 5	442310
20 April 09	Yingpeng HFC23 Decomposition Project	China	AM0001 ver. 5	7865277
28 May 09	SF <sub>6</sub> Switch at Ortal Diecasting 1993 Ltd.	Israel	AM0065 ver. 1	11025
Withdrawn	Quimobásicos HFC Recovery and Destruction Project (plant 2)	Mexico	AM0001 ver. 5	783182
08 November 09	Avoidance of HFC-134a emissions in rigid Poly Urethane Foam (PUF) manufacturing by Acme TelePower Limited (ATPL)	India	AMS-III.N. ver. 2	24540
03 February 11	Avoidance of HFC-134a emissions in rigid poly urethane foam (PUF)	India	AMS-III.N. ver. 3	15282

<sup>a</sup> AM-large scale, ACM-consolidation methodologies and AMS-small scale.

<sup>b</sup> Estimated emission reductions in metric tonnes of CO<sub>2</sub> equivalent per annum (as stated by the project participants).

catalyst. In the presence of water, the catalyst was proposed to undertake the following reactions.



Therefore, according to this mechanism, hydroxyl groups on the catalysts play an important role in the destruction of CHF<sub>3</sub>. Similarly, hydrolytic decomposition of CF<sub>4</sub> over AlPO<sub>4</sub>-Al<sub>2</sub>O<sub>3</sub> was found to be only influenced by the concentration of water and no effect of O<sub>2</sub> was observed [11]. During this reaction, γ-alumina showed the highest activity while AlPO<sub>4</sub>-Al<sub>2</sub>O<sub>3</sub> exhibited higher stability which implies that phosphate in the catalyst acts as a structure promoter to prevent the fluorination and phase change of γ-alumina. Probably similar with the proposal of Feaver et al. [10], hydroxyl groups on the alumina surface also play an important role in the hydrolytic destruction of CF<sub>4</sub>. Onoda reported that nickel pyrophosphate (Ni-Mg P2) catalysts had suitable catalytic activity for the decomposition of CHF<sub>3</sub> at 773 K over an extended time-on-stream [12]. Selectivity of almost 100% to CO<sub>2</sub> was achieved under the conditions investigated. Although the conversion levels of CHF<sub>3</sub> was relatively lower than that of AlPO<sub>4</sub> catalyst, it was more stable as the activity of AlPO<sub>4</sub> dropped sharply in 5 h. Based on this, Onoda suggested a different mechanism from Feaver for the decomposition of CHF<sub>3</sub>, as presented in Fig. 1. Because AlPO<sub>4</sub> has strong acidic sites, CHF<sub>3</sub> is strongly adsorbed on the surface of catalyst. Therefore, coupling reaction and deep decomposition occur. As a result, carbon deposition and polymer accumulated on the surface lead to the rapid deactivation of catalyst. On the other

hand, as the acidic sites of Ni-Mg P2 are relatively weak, most of adsorbed CHF<sub>3</sub> was converted to CO<sub>2</sub> and HF in the presence of H<sub>2</sub>O and O<sub>2</sub> and carbon or polymer deposition was less obvious than AlPO<sub>4</sub>. The hydrolysis of CCl<sub>2</sub>F<sub>2</sub> in the presence of water vapour and air was also studied over mesoporous metal phosphates [13]. The results are consistent with the mechanism proposed by Onoda et al. that the acid sites on the catalyst play a major role in converting CCl<sub>2</sub>F<sub>2</sub> into CO<sub>2</sub> via interaction with the adsorbed fluorocarbons [12].

With CHClF<sub>2</sub> as a target waste, Zhang et al. obtained more than 90% of CHClF<sub>2</sub> conversion and 95% selectivity to CO<sub>2</sub> at 613 K over platinum promoted non-sulphated TiO<sub>2</sub>-ZrO<sub>2</sub> catalyst [14]. Pt is believed to play a major role for the high selectivity to CO<sub>2</sub> rather than CO. Metallic platinum was formed by the reduction of the platinum precursor, with carbon monoxide produced during the hydrolysis of chlorodifluoromethane over the acidic mixed oxide and promoted the oxidation of CO.

In summary, catalytic hydrolysis is suitable for the disposal of CFCs, HCFCs, HFCs and even PFCs when their concentrations are very low (usually lower than 5000 ppm). For high concentration wastes or pure fluorocarbons, without dilution, the efficiency and stability of catalysts are vulnerable. In addition, in order to avoid the formation of CO, a noble metal, such as Au [15], Pt [10,14], Pd [16] and Ti [13] or other metals like Ni [12] and Ga [17] is essential for a catalyst to convert CO into CO<sub>2</sub> during hydrolysis. This requirement makes the catalysts very expensive and subsequently less competitive. If a noble metal is not introduced, the reaction temperature required must be increased to 973 K or even higher [11].

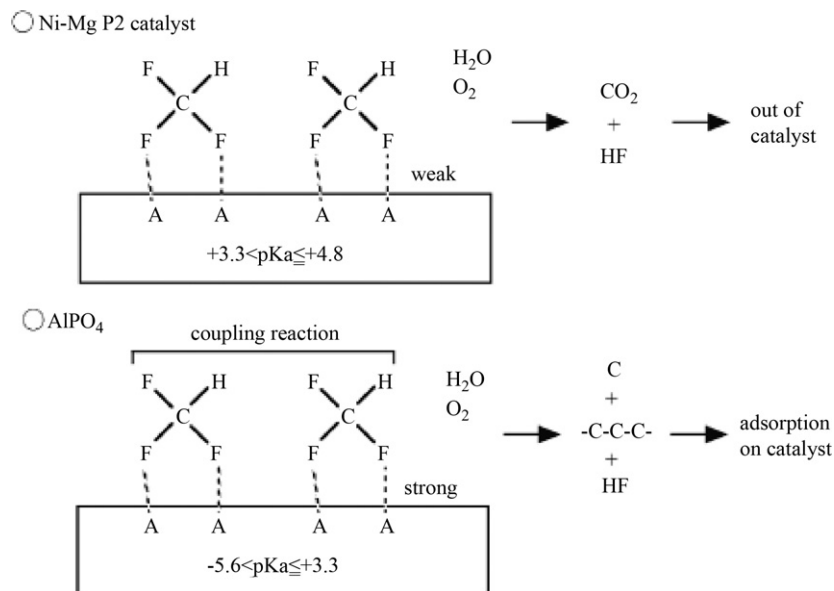


Fig. 1. Models of decomposition reaction of CHF<sub>3</sub> over Ni-Mg P2 catalyst and AlPO<sub>4</sub> [12].

During hydrolysis treatment, HCl and HF are inevitable reaction products which pose severe challenges to any catalyst included in the process. HF is known to react with most known materials, and thus there are very few choices of materials for the preparation of catalysts. For example, the gold on sulphated TiO<sub>2</sub>-ZrO<sub>2</sub> catalyst prepared by deposition with sodium hydroxide was active for the oxidation of carbon monoxide at room temperature during the decomposition of chlorodifluoromethane in the presence of water vapour. The gold nanoparticles were deactivated for CO oxidation by HF and HCl formed during the hydrolysis of HCFC-22 [15]. A SO<sub>4</sub>-ZrO<sub>2</sub> catalyst rapidly deactivated in dry air conditions and the deactivation is attributed to the fluorination of the zirconium, which results in the loss of oxygen and sulphur from the catalyst and a significant decrease in surface area of the catalyst. The

addition of 2.5% water to the feed stream greatly improves the catalyst's stability; however, some deactivation was still observed. Deactivation in humid air was attributed to a gradual accumulation of fluorine on the catalyst, which results in a loss of sulphate and oxygen from the zirconia, and a decrease in the surface area of the catalyst [10].

### 3.3. Plasma destruction

Plasma is the only commercially available technology for the destruction of fluorocarbons based on pyrolysis of the material in a plasma arc at very high temperatures, typically between 10,000 and 30,000 K [18–27]. The PLASCON process technology, developed by Australian Commonwealth Scientific and Research

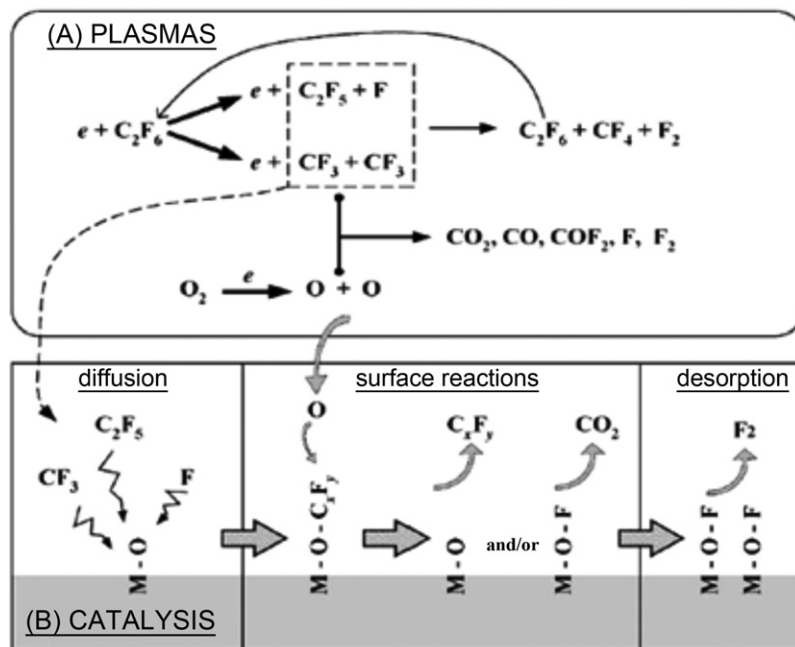


Fig. 2. Proposed pathways of C<sub>2</sub>F<sub>6</sub> abatement by CPC (combined plasma catalysis). The top one shows the major pathways of processing C<sub>2</sub>F<sub>6</sub> by plasmas (A); while the bottom one by catalysis (B) [31].

Organization (CSIRO) and SRL Plasma Ltd [28], was adapted for the destruction of CFCs and halons in 1992, and the commercial PLASCON system was installed in 1997 by SRL Plasma to destroy ODSs and for CHF<sub>3</sub> in 2007. Under the conditions of the PLASCON process, halons and CFCs are decomposed into corrosive halogen acids (HF, HCl and HBr) and free halogen molecules (F<sub>2</sub>, Cl<sub>2</sub> and Br<sub>2</sub>), which, at high temperatures, pose significant handling problems. Wofford [29,30] reported that surface plasma also can be used for the abatement of CHF<sub>3</sub> with effective (up to 99.9%) destruction and removal efficiencies. However, an extremely poisonous product, COF<sub>2</sub>, was detected in the effluent gas.

In attempt to reduce the emission of F<sub>2</sub>, CO, COF<sub>2</sub> and CF<sub>4</sub> during the abatement of C<sub>2</sub>F<sub>6</sub>, Chang et al. combined plasma with the a catalyst [31].

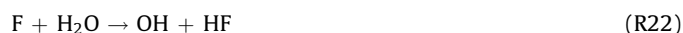
As Fig. 2 shows, the major products formed in plasma process are CO<sub>2</sub>, COF<sub>2</sub> and trace amounts of CO. Minor quantities of CF<sub>4</sub> is also formed during C<sub>2</sub>F<sub>6</sub> abatement. These unwanted chemicals must be further treated. In contrast, the major products in CPC (combined plasma catalysis) process are CO<sub>2</sub> and trace amounts of CO, which are less harmful to human health and to the environment. On the active surfaces of CuO/ZnO/MgO/Al<sub>2</sub>O<sub>3</sub> catalyst, CF<sub>3</sub> and C<sub>2</sub>F<sub>5</sub> radicals are generally dissociatively adsorbed, producing a carbon atom and three fluorine atoms that bond to the active site. In addition, CF<sub>3</sub> radicals can be oxidised by oxygen atoms (and, possibly, O<sub>2</sub> molecules) on the catalyst surface. In a bath of H<sub>2</sub>, rather than O<sub>2</sub>, formation of CO and COF<sub>2</sub> also can be avoided [32].

It has been reported that using steam instead of oxygen as the oxidising gas can minimise the production of other fluorochemicals and give superior destruction performance [22].

In an oxygen bath, the plasma process for the abatement of CF<sub>4</sub> will include the following reactions.



If steam is used as oxidising gas, more HF and less F<sub>2</sub>, COF<sub>2</sub> will be formed, as illustrated by reactions (R16)–(R22).



To control the emission of halides into the environment, the effect of H<sub>2</sub> and alkaline addition on the plasma decomposition of CF<sub>4</sub>, CHF<sub>3</sub>, C<sub>2</sub>HCl<sub>3</sub>, and CHClF<sub>2</sub> was conducted in a wire-in-tube corona reactor [33]. With the addition of H<sub>2</sub> in N<sub>2</sub> plasma gas, the decomposition rate of CF<sub>4</sub>, C<sub>2</sub>HCl<sub>3</sub>, and CHClF<sub>2</sub> increased. In contrast, the decomposition rate of CHF<sub>3</sub> in a hydrogen-rich atmosphere was lower than that in an N<sub>2</sub> atmosphere. The yields of

HF and/or HCl formed during halide decomposition clearly increase with the presence of H<sub>2</sub> in the N<sub>2</sub> gas. Furthermore, in order to prevent the production of unwanted products during decomposition, a combination of plasma decomposition and in situ alkaline absorption was devised by coating a layer of Ca(OH)<sub>2</sub> onto the surface of the grounding electrode. It was found that the Ca(OH)<sub>2</sub> sorbent played an effective role as a scavenger, participating in halide decomposition by capturing reaction products such as HCl and HF, therefore resulting in increased fluorochemical decomposition.

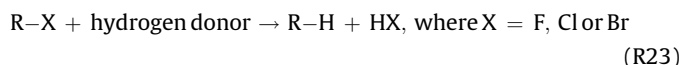
In summary, the formation of unwanted fluorocarbons and other hazardous by-products are significant challenges for the destruction of fluorochemicals by plasma, although plasma can decompose these stable chemicals at very high temperatures. Furthermore, the operating cost of these processes are similar with that of the operation of conventional thermal incinerations, which may restrict the wide application of thermal plasma technology for the destruction of fluorochemicals.

#### 4. Conversion to environmentally benign compounds

CHF<sub>3</sub> is stable even under combustion conditions (it can function as fire extinguishing agent), and thermal destruction or oxidation is not energetically favourable routes for the treatment process, while plasma process is very costly. Furthermore, CHF<sub>3</sub> and other fluorochemicals possess valuable C–F bonds, which make them attractive chemical feedstock for production of useful and environmentally benign chemicals. In addition, these chemicals were originally produced at high cost and are available as relatively pure chemicals, so it is desirable to transform them into useful and environmentally benign products.

##### 4.1. Catalytic hydrogenolysis

Hydrodehalogenation is a conversion method, which can be presented by the following equation:



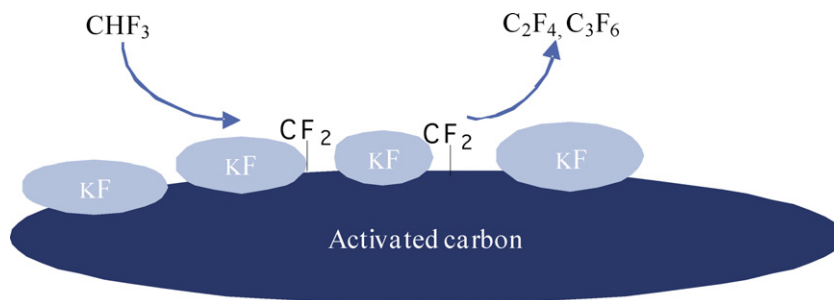
The resulting products from the reaction are usually a mixture of hydrofluorocarbons (HFCs), hydrocarbons and mineral acids. Generally, the catalysts developed for this process reduce the reaction temperature and improve the conversion and selectivity to specific products; otherwise, higher temperatures are necessary and the product profiles are complex [34]. According to the available literature, the most intensively investigated fluorocarbons are CCl<sub>2</sub>F<sub>2</sub> (CFC-12) and CHClF<sub>2</sub> (HCFC-22), which are both converted to CH<sub>2</sub>F<sub>2</sub> (HFC-32) catalysed by palladium [35–44], ruthenium [45] and nickel [46]. A detailed review has been published covering the role of catalysts on the conversion of CFCs, HCFCs and halons [47].

As reported by all the investigations, the major product of this process is CH<sub>2</sub>F<sub>2</sub>. Other products include CH<sub>4</sub>, CHClF<sub>2</sub>, CH<sub>3</sub>Cl and CH<sub>3</sub>F. CH<sub>2</sub>F<sub>2</sub> was initially thought to be an alternative to the CFC refrigerants with zero ozone depleting potential (ODP). However, CH<sub>2</sub>F<sub>2</sub> (known as HFC-32) is still a greenhouse gas with global warming potential (GWP) 670 times higher than that of CO<sub>2</sub> and its use is strictly controlled by the Kyoto Protocol and its subsequent amendments. This route is even less attractive than before as its major products and other by-products cannot be claimed as environmentally friendly or benign chemicals.

For HFCs, especially for simple fluorocarbons, such as CHF<sub>3</sub>, CF<sub>4</sub> and CH<sub>2</sub>F<sub>2</sub>, there is very little literature found about their hydrogenolysis. The exception is a study by Coq who compared the reactions of CHF<sub>3</sub> and CH<sub>2</sub>F<sub>2</sub> with CCl<sub>2</sub>F<sub>2</sub> and other CFCs [34,48].

**Table 2**Product distribution for the pyrolysis of CHF<sub>3</sub> over activated carbon supported potassium catalyst and non-catalytic reaction at temperature of 1073 K [61].

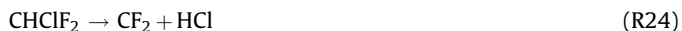
Entry	CHF <sub>3</sub> conversion, %	Selectivity, % <sup>a</sup>					Yield, % <sup>a</sup>		
		TFE	HFP	CF <sub>4</sub>	C <sub>2</sub> F <sub>6</sub>	C <sub>3</sub> F <sub>8</sub>	TFE	HFP	TFE + HFP
Non-catalytic <sup>b</sup>	15.1	55.9	8.03	–	–	–	8.45	1.21	9.66
Catalytic <sup>c</sup>	61.1	33.3	23.6	0.23	4.30	5.05	16.1	14.4	34.7

<sup>a</sup> Based on the conversion of CHF<sub>3</sub>.<sup>b</sup> At residence time of 0.5 s, and pressure of 1 bar.<sup>c</sup> At space velocity of 4300 h<sup>-1</sup> and pressure of 1 bar.**Fig. 3.** Proposed mechanism for the pyrolysis of CHF<sub>3</sub> over activated carbon supported potassium catalyst [61].

Unlike CFCs and HCFCs, HFCs do not contain Cl, and therefore lack relatively weak bond which facilitates decomposition and conversion. Thus, in order to achieve high conversion, elevated temperatures are usually needed during hydrogenolysis, which poses significant challenge to the stability of the catalysts.

#### 4.2. Conversion to C<sub>2</sub>F<sub>4</sub> (TFE), C<sub>3</sub>F<sub>6</sub> (HFP) and CF<sub>3</sub>I

TFE is produced commercially from the non-catalytic gas-phase pyrolysis of chlorodifluoromethane (HCFC-22) at high temperatures (873–1173 K), at atmospheric or subatmospheric pressures [49,50]. The reaction is assumed to occur via the formation and dimerisation of difluorocarbene and high yields (95%) are achieved:



More recently, a catalyst (Cu/MgF<sub>3</sub>-AlF<sub>3</sub>) was developed by Sung et al. which can improve the conversion of CHClF<sub>2</sub> and selectivity to C<sub>2</sub>F<sub>4</sub> with a space velocity of 15,000 h<sup>-1</sup> [51,52]. This process can also be used to treat the CHClF<sub>2</sub>, but only with those wastes containing a high concentration of CHClF<sub>2</sub>. In practice, most of the wastes are mixtures which usually contain other CFCs and HCFCs. Compared with the above process, lower selectivity to C<sub>2</sub>F<sub>4</sub> and wider range of unsaturated chlorinated hydrocarbons will be expected.

The pyrolysis of CHF<sub>3</sub>, although much less studied and requiring considerable higher temperatures (>1023 K), follows essentially the same mechanism route and also represents a potential source of C<sub>2</sub>F<sub>4</sub> [53–55]. The overall rate of CHF<sub>3</sub> decomposition of CHF<sub>3</sub> can be expressed as  $5.2 \times 10^{13} [\text{s}^{-1}] e^{-295[\text{kJ/mol}]/RT}$  indicating it is a first order reaction under moderate pressures [56]. At pressures below 0.29 atm, Modica et al. found that the decomposition reaction could also be interpreted by a second-order mechanism, suggesting that this reaction may be pressure-dependent and lie in the fall-off region near the second-order limit [57,58]. Unlike HCFC-22, CHF<sub>3</sub> waste is generally in high purity and quantity. A significant proportion of CHF<sub>3</sub> waste is produced during the manufacture of HCFC-22 as a by-product (3–4% of HCFC-22) [6]. At present, these

almost pure CHF<sub>3</sub> are destroyed by thermal oxidation [9] or simply emitted into the atmosphere [5].

Moon et al. reported that hexafluoropropylene (C<sub>3</sub>F<sub>6</sub>, HFP) can be synthesized selectively via co-pyrolysis of CHF<sub>3</sub> with C<sub>2</sub>F<sub>4</sub> under the conditions of reaction temperatures of 973–1273 K, residence times of 0.01–14 s [59,60]. HFP is presumably formed through the decomposition of CHF<sub>3</sub> and dimerisation of C<sub>2</sub>F<sub>4</sub>, an intermediate resulted from CHF<sub>3</sub> pyrolysis. Optimising the reaction conditions such as reaction temperature and residence time can enhance the selectivity and yield of HFP significantly. In the presence of K/AC catalyst, with pyrolysis of CHF<sub>3</sub> alone, both the conversion of CHF<sub>3</sub> and selectivity to TFE and HFP are enhanced significantly, as presented in Table 2 [61]. During the catalytic pyrolysis process, it is speculated that the effect of activated carbon is to enhance the localised surface concentration of the key intermediate, CF<sub>2</sub> carbene, which arises following the elimination of HF from absorbed CHF<sub>3</sub>, as illustrated in Fig. 3. The rate of polymerisation of CF<sub>2</sub> on the surface is enhanced, and is higher than that occurring during the gas phase reaction. For the gas phase reaction, it has been suggested that HEP might form through the following reactions [51]:



However, high activation energies were found for all the above reactions and consequently a low HFP yield is observed at moderate temperatures. With the introduction of catalyst, the activation energy for the cleavage of C–F bond is lowered with respect to the gas phase reaction, and as a result, both HFP and other saturated fluorocarbons can be formed more readily and directly. However, further investigation needs to be performed to clarify the surface mechanism.

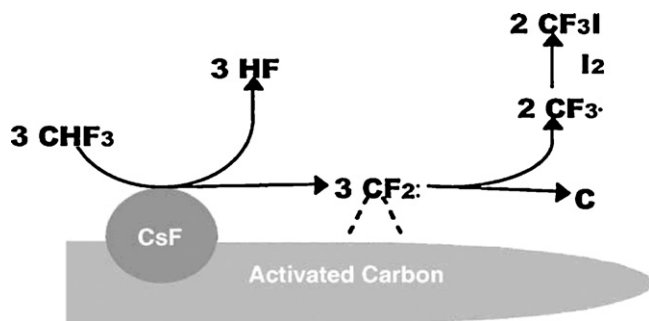


Fig. 4. Proposed reaction scheme between  $\text{CHF}_3$  and  $\text{I}_2$  over alkali/AC catalyst [62].

Following the ban on the manufacture of halons,  $\text{CF}_3\text{I}$  was considered as a preferred alternative to halon 1301 because of its short lifetime in the troposphere. Traditionally,  $\text{CF}_3\text{I}$  is obtained from reactions which involve the Br/Cl/I exchange between  $\text{CBrF}_3$  or  $\text{CF}_3\text{Cl}$  and  $\text{I}_2$ , HI and other iodine sources. Nagasaki et al. was the first to claim that  $\text{CF}_3\text{I}$  can be formed via reaction between  $\text{CHF}_3$ ,  $\text{O}_2$  and  $\text{I}_2$  catalysed by activated carbon supported alkali catalysts at temperatures of 773–823 K and space velocities of 60–650  $\text{h}^{-1}$  [62].

They suggested a mechanism as shown in Fig. 4 that alkali/AC (activated carbon) catalyst can facilitate the decomposition of  $\text{CHF}_3$  and formation of  $\text{CF}_2$  at moderate temperatures (around 773 K). The intermediate of  $\text{CF}_2$  adsorbs so strongly on the carbon surface that dimerisation of  $\text{CF}_2$  does not occur. The role of  $\text{O}_2$  is not fully elucidated. Later, Yang et al. confirmed this reaction with similar reactions and catalysts [63,64]. They concluded that at high temperatures, AC promotes the dehydrofluorination of  $\text{CHF}_3$  to form  $\text{CF}_2$  carbene, then  $\text{CF}_2$  carbene combines with AC strongly to form  $\text{CF}_3$  radical when F radical generated from decomposition of  $\text{CF}_2$  carbene. Therefore,  $\text{CF}_2$  carbene does not dimerize to form tetrafluoroethane, but takes place disproportionation reaction to generate  $\text{CF}_3$  radical and carbon. Finally,  $\text{CF}_3\text{I}$  is prepared from the reaction of  $\text{CF}_3$  radical and iodine in the presence of AC or catalyst. In the process, AC is not only the catalyst support, but also a co-catalyst to promote  $\text{CF}_2$  carbene formation and  $\text{CF}_3$  radical to produce  $\text{CF}_3\text{I}$ .

During the catalytic pyrolysis of  $\text{CHF}_3$ , Han et al. suggested that the oxygen groups on the surface of carbon played a major role on the decomposition of  $\text{CHF}_3$ , probably  $\text{CF}_3$  and  $\text{CF}_2$  as well, as illustrated in Fig. 5 [61]. This speculation was confirmed by experimental results which show that a much lower conversion level of  $\text{CHF}_3$ , rates of formation of  $\text{CF}_4$ ,  $\text{C}_2\text{F}_6$  and  $\text{C}_3\text{F}_8$  were observed when these oxygen groups were removed by pre-treating the activated carbon in  $\text{H}_2$  at high temperatures. It explains why the presence of  $\text{O}_2$  is crucial during the synthesis of  $\text{CF}_3\text{I}$  via the reaction of  $\text{CHF}_3$  with  $\text{I}_2$  over activated carbons [62]. During the

reaction,  $\text{O}_2$  is likely to produce large surface oxygen groups on activated carbon, which then catalyse the formation of  $\text{CF}_3$  and ultimately  $\text{CF}_3\text{I}$ .

Due to the high cost of  $\text{I}_2$ , this process or  $\text{CF}_3\text{I}$  is less competitive than some of HFC refrigerants whose global warming potentials are low and not regulated by Kyoto protocol. For example, Du pont and Honeywell are developing a new refrigerant, HFO-1234yf ( $\text{CF}_3\text{CF}=\text{CH}_2$ ) with high performance and GWP only 4 [65,66].

#### 4.3. Conversion to $\text{CH}_2=\text{CF}_2$ (vinylidene fluoride, VDF)

Mukhopadhyay et al. successfully transformed  $\text{CHF}_3$  into trifluoromethanesulfonic acid (TFMSA) at low temperatures in a liquid-phase reaction in a strong acid such as fuming sulfuric acid as well as in a strong basic solution such as the potassium tert-butylate/dimethylformamide (t-BuOK/DMF) [67]. This route is rather expensive, and is not a feasible way to treat large quantities of  $\text{CHF}_3$ .

$\text{CH}_2=\text{CF}_2$  is a monomer for the synthesis of poly(vinylidene fluoride), PVDF and other fluoroelastomers which are thermoplastics that exhibit very interesting piezo-, pyro- and ferroelectric properties, is inert to various solvents, oils, acids and shows low permeabilities to gases and liquids [50,68]. They find applications in a number of areas: aerospace, appliances, fluid power, the chemical industry, the oil field, semiconductor fabrication, and a variety of industrial uses. In many applications, fluoroelastomers are replacing other elastomers, as performance requirements become more stringent. Fluoroelastomers give improved long-term, maintenance-free service in severe environments and more reliable protection of the environment [69]. A detailed review about the applications of VDF-containing polymers and copolymers is available [70].

Commercial synthesis of VDF monomer involves gaseous pyrolysis reactions at temperatures between 573 and 1273 K [71]. Typical preparation reactions are:



The difficulties and cost for preparation of these starting materials make the production of VDF very expensive. Researcher at the University of Newcastle, Australia discovered that halons can be converted into other more environmentally acceptable and valuable compounds via reaction with  $\text{CH}_4$  [72–75]. In addition to its high hydrogen content on a per-atom molecule basis, methane is relatively a low cost source of hydrogen (in the form of natural gas, which consists primarily of methane). Later, this process was

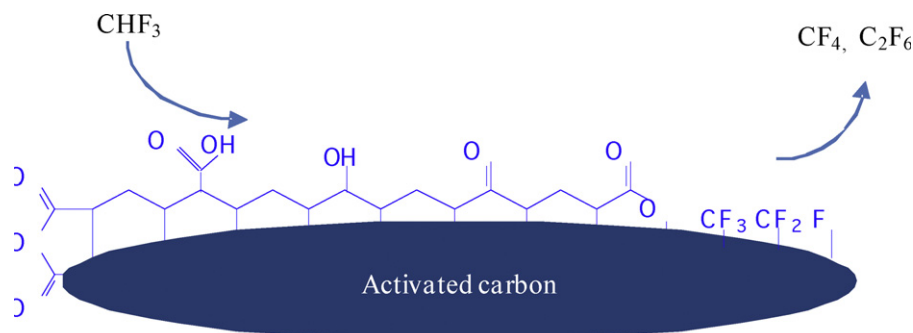


Fig. 5. Proposed mechanism for the pyrolysis of  $\text{CHF}_3$  over activated carbon support [61].

extended to the conversion of CFCs and HCFCs and high yield of  $\text{CH}_2=\text{CF}_2$  was achieved [76–79]. The suggested major reactions involved in this process are summarised as follows. As shown in reaction (R44), VDF is formed via the combination of  $\text{CF}_2$  and  $\text{CH}_3$  radicals.



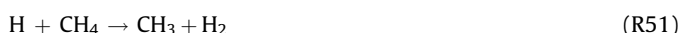
Recently, it was discovered that  $\text{CHF}_3$  can be also converted to vinyl difluoride,  $\text{CH}_2=\text{CF}_2$ , through its reaction with  $\text{CH}_4$  [80]. It was found that during the reaction of  $\text{CHF}_3$  and  $\text{CH}_4$ , the major products are  $\text{C}_2\text{F}_4$ ,  $\text{CH}_2=\text{CF}_2$ , and HF over the temperature range of 973–1173 K and residence time of 0.5 s. The initial step is the gas-phase unimolecular decomposition of  $\text{CHF}_3$ , producing  $\text{CF}_2$  and HF.

The major difference between reaction of halons and CFCs with  $\text{CH}_4$  and reaction of  $\text{CHF}_3$  with  $\text{CH}_4$  is the lack of relatively weak bond of C–Br or C–Cl in  $\text{CHF}_3$ . As demonstrated in reactions ((R36) and (R37)), C–Br or C–Cl bonds readily cleave at elevated temperatures, producing reactive Br or Cl radicals. Then, these radicals function as important sources for the activation of  $\text{CH}_4$  to form  $\text{CH}_3$ . Consequently, high conversion of  $\text{CH}_4$  and high yield of  $\text{CH}_2=\text{CF}_2$  can be obtained through this process. Due to the lack of these sources for the activation of  $\text{CH}_4$ , very low conversion of  $\text{CH}_4$  and yield of  $\text{CH}_2=\text{CF}_2$  was observed, even at 1173 K during the reaction of  $\text{CHF}_3$  with  $\text{CH}_4$ . It is suggested that the initial step involving the decomposition of  $\text{CHF}_3$  with the formation of  $\text{CF}_2$  radical and HF. This reaction dominates the pyrolysis of  $\text{CHF}_3$  and reaction of  $\text{CHF}_3$  with  $\text{CH}_4$ . Trace amounts of  $\text{CH}_4$  decompose on the surface of reactor, producing H radical. It is proposed that  $\text{CH}_4$  is activated by a series of chain reactions ((R45)–(R52)) which are initiated by this small amount of H radicals [56]. However,  $\text{CH}_4$  is stable at temperature as high as 1173 K. Low  $\text{CH}_4$  conversion levels inhibit a high subsequent yield of VDF.

Initiation:

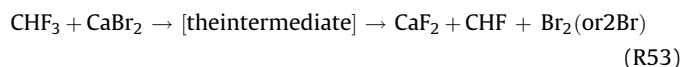


Propagation:



In order to improve the selectivity and yield of  $\text{CH}_2=\text{CF}_2$ , it is critical to find efficient approaches to enhance the activation of

$\text{CH}_4$  and formation of  $\text{CH}_3$ . Recently, activation of  $\text{CH}_4$  has attracted intensive attention from the academic world, especially for gas-to-liquids technologies. However, the results of these studies are generally not applicable in this process as the presence of HF in this reaction system will deactivate most conventional catalysts. Also, for the oxidative activation, the introduction of  $\text{O}_2$  in this system can result in the formation of the highly toxic products, such as  $\text{COF}_2$ . Han et al. tried to use  $\text{CaBr}_2$  aiming at discovering effective reactant to facilitate  $\text{CH}_4$  activation and improving the yield of  $\text{CH}_2=\text{CF}_2$  [81].  $\text{CaBr}_2$  is chosen because it has relatively weak Ca–Br bond and can provide Br radicals at relatively low temperatures. It is expected that the active Br radicals can activate  $\text{CH}_4$  readily, facilitating the formation of  $\text{CH}_3$  radicals and improving the yield of  $\text{CH}_2=\text{CF}_2$ . However, the results showed that  $\text{CaBr}_2$  can react with  $\text{CHF}_3$  forming  $\text{Br}_2$  or Br radicals rather than  $\text{CH}_4$  at elevated temperatures (R53). The active Br species, such as atomic Br and molecular  $\text{Br}_2$ , can readily react with  $\text{CHF}_3$  on the surface or in the gas phase, leading to the formation of  $\text{CBrF}_3$ . In the presence of  $\text{CH}_4$ , both Br and  $\text{CF}_3$  can also react with  $\text{CH}_4$ , generating  $\text{CH}_3$  radicals. Subsequently,  $\text{CH}_3$  reacts with both  $\text{CF}_2$  and  $\text{CF}_3$  to produce  $\text{CH}_2=\text{CF}_2$ . These steps are believed to be the major contributors to the enhanced conversion of  $\text{CH}_4$  and yield to  $\text{CH}_2=\text{CF}_2$ , compared to the gas phase reaction of  $\text{CH}_4$  with  $\text{CHF}_3$ .



This conclusion was confirmed by the study with small amounts of  $\text{BrF}_3$  as the promoter of the gas-phase reaction of  $\text{CHF}_3$  with  $\text{CH}_4$  [82]. In the presence of less than 6000 ppm of  $\text{CBrF}_3$ , the rate of formation of  $\text{CH}_2=\text{CF}_2$  is significantly enhanced, and a much lower rate of formation of the major by-product,  $\text{C}_2\text{F}_4$  is observed. The reaction pathways involved in the reaction of  $\text{CHF}_3$  with  $\text{CH}_4$  in the presence of small amounts of  $\text{CBrF}_3$  are represented in Fig. 6. Further increasing the proportion of  $\text{CBrF}_3$  in the feed resulted in an even higher rate of formation of  $\text{CH}_2=\text{CF}_2$ . In addition, the presence of small amounts of  $\text{CH}_3\text{OH}$  (5% of  $\text{CHF}_3$

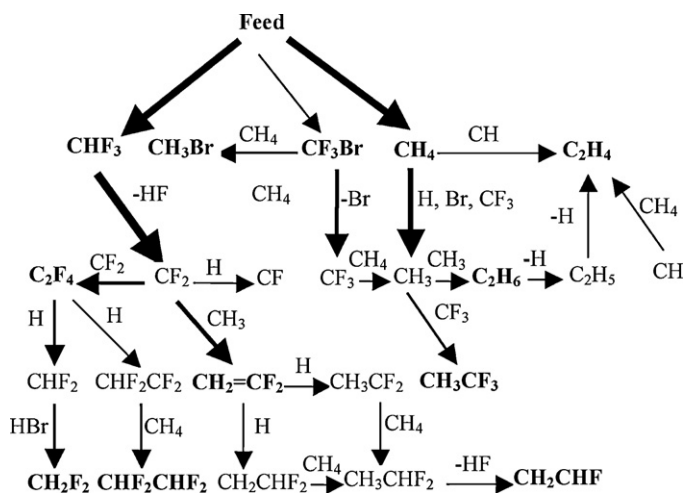


Fig. 6. The reaction pathways leading to formation of carbon containing products during the reaction of  $\text{CHF}_3$  with  $\text{CH}_4$  in the presence of  $\text{CBrF}_3$ . Where species are bold, these compounds have been detected during experiments [82].



concentration) also has a significant influence on both the conversion and selectivity of the reaction [79]. It is generally accepted that the initial step of  $\text{CH}_3\text{OH}$  pyrolysis forms  $\text{CH}_3 + \text{OH}$  (~80%).  $\text{CH}_3$  and  $\text{OH}$  then trigger the formation of other radicals, such as  $\text{CH}_2\text{OH}$ ,  $\text{HCHO}$ ,  $\text{HCO}$ ,  $\text{H}$  and  $\text{CO}$  via a series of chain reactions [83]. By this way,  $\text{CH}_3\text{OH}$  provides  $\text{H}$  and  $\text{CH}_3$  (enhancing the conversion of  $\text{CH}_4$  and rate of formation of  $\text{CH}_2=\text{CF}_2$ ) and other radicals such as  $\text{OH}$  (enhancing the conversion of  $\text{CHF}_3$  and rate of formation of  $\text{CH}_2=\text{CF}_2$ ) to the reaction pool [84].

## 5. Conclusions and future prospects

As  $\text{CHF}_3$  is a potent synthetic greenhouse gas with GWP of 11,700 times higher than that of  $\text{CO}_2$ , the research and development of its treatment are of practical significance. The established incineration processes which are adopted in CDM projects of UNFCCC can destroy  $\text{CHF}_3$  almost completely at high temperatures. One concern of this process is that the fluorine has to be scrubbed as  $\text{HF}$  from the exhaust gas stream which then requires disposal, usually as a fluoride salt. Another challenge is the cost in materials for the reactor which can operate at temperatures as high as 1473 K and in presence of the strongly corrosive  $\text{HF}$ . With the presence of catalyst and steam,  $\text{CHF}_3$  can be decomposed at relatively low temperatures, thus with relatively low energy consumption. However, it usually operates under conditions with low  $\text{CHF}_3$  concentrations and sometimes noble metals such as Pt, Pd are necessary for the selective formation of  $\text{CO}_2$  rather than  $\text{CO}$ . In addition, catalysts suffer deactivation during long time operation. Plasma is able to decompose stable perfluorocarbons effectively, but the formation of unwanted fluorocarbons and other hazardous by-products are significant challenges. Also, its operating cost may be similar with that of incineration.

$\text{CHF}_3$  and other fluorochemicals possess valuable C–F bonds and are available as relatively pure chemicals which make them attractive chemical feedstock for production of useful and environmentally benign chemicals. The possibility of  $\text{CHF}_3$  as the source of  $\text{C}_2\text{F}_4$  (TFE) and  $\text{C}_3\text{F}_6$  (HFP) has been reported in the bench scale. Compared with the commercial production process of TFE via pyrolysis of  $\text{CHClF}_2$  (HCFC-22), although it is stable and less investigated, pyrolysis of  $\text{CHF}_3$  accurately follows the similar mechanism except with relatively low conversion and selectivity to TFE. In the presence of a catalyst, both the conversion level and selectivity to TFE and HFP can be improved significantly. Recently, via reaction with  $\text{I}_2$ , it was found that  $\text{CHF}_3$  can be converted to  $\text{CF}_3\text{I}$  which was considered as a preferred alternative to halon 1301 because of its short lifetime in the troposphere. Due to the high cost of  $\text{I}_2$ , this process or  $\text{CF}_3\text{I}$  is less competitive than some of HFC refrigerants whose global warming potentials are low and not regulated by Kyoto protocol. Therefore, catalyst with high selectivity to  $\text{CF}_3\text{I}$  and stability is the key challenge for this process. Further efforts are necessary to elucidate the chemistry involved and to explore efficient, stable and selective catalysts.

VDF is one of the most widely used fluoroelastomers to produce polymers with unique and interesting properties. It was reported that VDF can be formed via the reaction of  $\text{CHF}_3$  and  $\text{CH}_4$  at elevated temperatures. Because there is no relatively weak bond, such as C–Cl and C–Br, which can provide Br and Cl radical species for the activation of  $\text{CH}_4$ , very low conversion of  $\text{CH}_4$  and yield of VDF was observed, even at 1173 K during the reaction of  $\text{CHF}_3$  with  $\text{CH}_4$ . In the presence of small amounts of promoters, such as  $\text{CaBr}_2$ ,  $\text{CBrF}_3$  and  $\text{CH}_3\text{OH}$ , both the conversion levels of reactants and yield of VDF are enhanced markedly. It is suggested that these compounds generates different types of radicals, including Br, H,  $\text{CF}_3$  and OH, which then initiates a series of chain reactions. According to the mechanistic study,  $\text{CHF}_3$  and  $\text{CH}_4$  are most probably activated via these chain reactions.

In addition, the development of a suitable catalyst which is capable of activating these reactants and selectively synthesizing VDF is of significance and worth of trying.

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