



## Catalytic pyrolysis of CHF<sub>3</sub> over activated carbon and activated carbon supported potassium catalyst

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### ABSTRACT

The catalytic activity of activated carbon (AC) and activated carbon supported potassium for the decomposition of CHF<sub>3</sub> was investigated at temperatures between 873 and 1173 K and at a space velocity of 4300 h<sup>-1</sup>. It is found that activated carbon supported potassium shows high and relatively stable activity during the pyrolysis of CHF<sub>3</sub> under the conditions studied. Compared with the gas phase reaction, the conversion of CHF<sub>3</sub> increases by up to 10 times between 873 and 1123 K, with the major products being C<sub>2</sub>F<sub>4</sub> and C<sub>3</sub>F<sub>6</sub>. Selectivities as high as 55% to C<sub>2</sub>F<sub>4</sub> and 35% to C<sub>3</sub>F<sub>6</sub> are achieved under optimum conditions. The main byproduct HF readily reacts with K<sub>2</sub>O in the catalyst, converting the catalyst from K<sub>2</sub>O/AC into KF/AC. Selectivity to the major products remains relatively constant following this transformation.

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## 1. Introduction

CHF<sub>3</sub> (HFC-23) has limited use, generally for specific applications in refrigeration or for dry etching in the semiconductor industry and has limited applications as a fire inhibition agent. More importantly, it is formed as a byproduct of HCFC-22 (CHClF<sub>2</sub>) production. It has recently been reported that its emission and rate of accumulation into the atmosphere has increased very rapidly [1]. CHF<sub>3</sub> has a large global warming potential (GWP), roughly 11,700 times that of CO<sub>2</sub> and its emission is now being regulated by the Kyoto Protocol. Hence, an effective treatment method for CHF<sub>3</sub> is required to minimize its emission into the receiving environment. Until very recently, the treatment of this gas has received very limited research attention.

Thermal oxidation is an established technology which is sometimes used for the destruction of HFC-23 and its use to destroy CHF<sub>3</sub> has been ratified by the United Nations Framework Convention on Climate Change [2]. This process uses steam, O<sub>2</sub> and natural gas as reactants to destroy the CHF<sub>3</sub> at the temperatures around 1473 K. It is also reported that phosphates and ZrO<sub>2</sub>-SO<sub>4</sub>

are active and stable catalysts for the destruction of HFC-23 in the presence of O<sub>2</sub> and steam at relatively low temperatures [3,4]. A major problem associated with these oxidative processes is that fluorine is removed in the form of HF from the exhaust gas stream and is then recycled or disposed of as a fluoride salt. It would be environmentally more sustainable to use waste HFC-23 as a feed stocks for production of other valuable chemicals, rather than simply destroying it.

In previous work, we reported that CHF<sub>3</sub> can be converted to vinyl difluoride (CH<sub>2</sub>=CF<sub>2</sub>), a highly valuable feedstock, through its reaction with CH<sub>4</sub>, although the conversion of CH<sub>4</sub> and subsequently the yield of the targeted product was low [5]. The gas phase homogeneous pyrolysis of CHF<sub>3</sub> is reported to be a potential route to the production of tetrafluoroethylene (TFE, C<sub>2</sub>F<sub>4</sub>) and hexafluoropropylene (HEP, C<sub>3</sub>F<sub>6</sub>) [6]. TFE and HEP are valuable chemicals and are used as monomers for the manufacture of polytetrafluoroethylene (PTFE), which is usually prepared by the gas phase pyrolysis of CHClF<sub>2</sub> (HCFC-22) [7]. The introduction of a solid catalyst to enhance the yield of C<sub>2</sub>F<sub>4</sub> and C<sub>3</sub>F<sub>6</sub> during the decomposition of either CHF<sub>3</sub> or CHClF<sub>2</sub> is desirable, as this will allow the process to operate at low temperatures. However, catalytic materials employed in these processes suffered severe deactivation in the highly corrosive acid gas (HCl and HF) environment.

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In this contribution, we report a novel catalyst, K<sub>2</sub>O/AC (activated carbon), for the decomposition of CHF<sub>3</sub> into C<sub>2</sub>F<sub>4</sub> (TFE) and C<sub>3</sub>F<sub>6</sub> (HEP). Activated carbon is chosen because it is stable in strongly acid and basic environments. Catalysts supported on various silica and metal oxides are reportedly unstable because of the degradation of supports in the presence of corrosive HF. The catalytic reaction was carried out in a fixed-bed reactor and the effect of temperature on the reaction, as well as catalyst stability, were investigated.

## 2. Experimental

### 2.1. Catalyst preparation

Activated carbon (1.0–1.4 mm) used as catalyst support, originated from coconut shell, was provided by Hainan Activated Carbon Co., China, with BET surface area of 993 m<sup>2</sup> g<sup>-1</sup> and pore volume of 0.51 cm<sup>3</sup> g<sup>-1</sup>. Catalysts were prepared by traditional impregnation methods with KNO<sub>3</sub> (Aldrich, 99%) as precursor. Prior to impregnation, activated carbon was treated in 30% HNO<sub>3</sub> solution at 363 K for 5 h in order to eliminate ash content in the carbon. The nominal K loading was 10 wt%. The decomposition temperature of KNO<sub>3</sub> is approximately 673 K.

### 2.2. Temperature-programmed desorption-mass spectrometry (TPD-MS) experiment of activated carbon

TPD-MS experiment was carried out on AutoChem 2910 (Micromeritics Co.) attached to a QMS 200 (Omnistar) mass spectrometer. A 50 mg of sample was heated to 373 K in the sample tube and held that temperature for 0.5 h in flowing helium gas to remove adsorbed water and other impurities on the surface of the sample. After cooling down to room temperature, the sample was heated to 1273 K at a ramp rate of 10 K min<sup>-1</sup> in He with a flow rate of 40 mL min<sup>-1</sup>. The effluent gas was monitored by a thermal conductivity detector and mass spectrometer detector.

### 2.3. Catalytic experiments

A tubular high purity (99.99%) alumina reactor (i.d. 7.0 mm) was employed for all experiments. Flow rates of CHF<sub>3</sub> (>98%, Core Gas) and diluting gas N<sub>2</sub> (BOC gases, 99.99%) were controlled by mass flow controllers (Brooks) to give a total flow rate of 220 mmol h<sup>-1</sup>, with CHF<sub>3</sub> accounting for 10% of the total volume flow. The catalytic pyrolysis of CHF<sub>3</sub> was carried out at a reaction temperature between 873 and 1173 K, space velocity of 4300 h<sup>-1</sup>, and at atmospheric pressure. HF formed during reaction was trapped by a caustic scrubber (NaOH solution) before the reactor effluent reached an online micro gas chromatograph. Carbon containing products were identified by a GC/MS (Shimadzu QP5000) equipped with an AT-Q column, and quantified with a micro GC (Varian CP-2003) equipped with molecular sieve 5A and PorapLOT Q columns. Relative molar response (RMR) factors of fluorocarbons for TCD detection were experimentally obtained from standard gas mixtures, and quantification of halogenated hydrocarbons was performed with diluted halogenated hydrocarbons in nitrogen. Quantification of other species was estimated from published correlations [8–10].

## 3. Results and discussion

### 3.1. CHF<sub>3</sub> pyrolysis over activated carbon

#### 3.1.1. Decomposition of CHF<sub>3</sub> over activated carbon

Pyrolysis of CHF<sub>3</sub> was conducted over activated carbon at temperature range of 873–1173 K and gas hourly space velocity

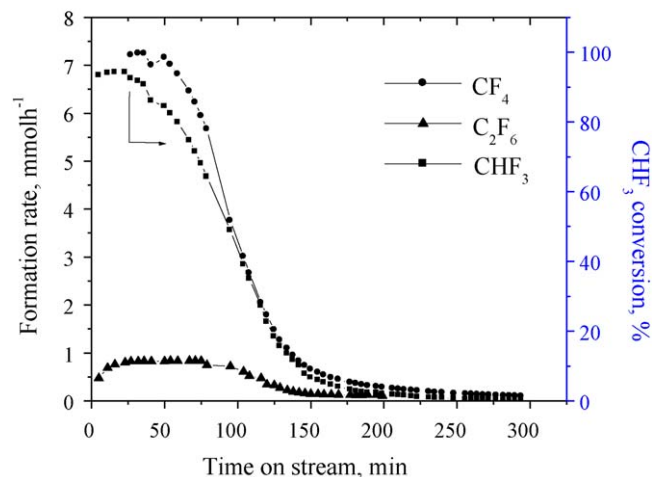


Fig. 1. Conversion of CHF<sub>3</sub>, carbon balance and formation rate of products as a function of time-on-stream over activated carbon at 1073 K and a GHSV of 4300 h<sup>-1</sup>.

(GHSV) of 4300 h<sup>-1</sup> to investigate the effect of support. The support has little influence on the reaction compared to K<sub>2</sub>O/AC (shown in Section 3.2), in particular after several hours on stream. CF<sub>4</sub> is the dominant carbon containing product with C<sub>2</sub>F<sub>6</sub> being a minor product. C<sub>2</sub>F<sub>4</sub> and C<sub>3</sub>F<sub>6</sub> were detected only in trace amounts. Fig. 1 shows a typical run of CHF<sub>3</sub> pyrolysis at temperature of 1073 K. The rate of formation of CF<sub>4</sub> was relatively high in the first hour and dropped rapidly until it reached a stable value.

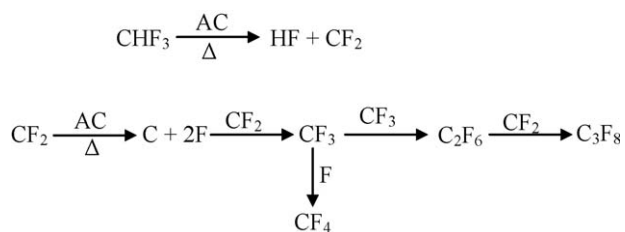
Consensus exists in the literature that the initial step of homogeneous gas phase pyrolysis of CHF<sub>3</sub> is the elimination of HF at temperatures above 1023 K leading to formation of CF<sub>2</sub>, which rapidly dimerises to C<sub>2</sub>F<sub>4</sub> which is the major product of the reaction [10,11].



During decomposition of CHF<sub>3</sub> over activated carbon, however, only trace amounts of C<sub>2</sub>F<sub>4</sub> are detected. This indicates that the decomposition of CHF<sub>3</sub> over activated carbon follows a mechanism which is different from the homogeneous mechanism. Recently, Yang et al. [12–14] studied the pyrolysis of CHF<sub>3</sub> over activated carbon and in their experiments, C<sub>2</sub>F<sub>4</sub> was not detected. They suggest that the reactions leading to formation of CF<sub>4</sub> and C<sub>2</sub>F<sub>6</sub> is likely to be via the steps as illustrated in Scheme 1. However, this seems to contradict the results of their efforts to capture the difluorocarbene intermediate with H<sub>2</sub> and 2-methyl-2-butene, where no CH<sub>2</sub>F<sub>2</sub> or *gem*-difluorotrimethylcyclopropane was captured. Furthermore, when CHClF<sub>2</sub> was introduced instead of CHF<sub>3</sub>, virtually no CF<sub>4</sub> or C<sub>2</sub>F<sub>6</sub> were found in the products [15]. CHClF<sub>2</sub> is believed to form CF<sub>2</sub> radicals more readily via dehydrochlorination compared with the elimination of HF from CHF<sub>3</sub>. Apparently, an increase of CF<sub>2</sub> does not facilitate the formation of CF<sub>4</sub> and C<sub>2</sub>F<sub>6</sub>, and the reaction steps proposed in Scheme 1 likely play only a relatively minor role in the overall reaction.

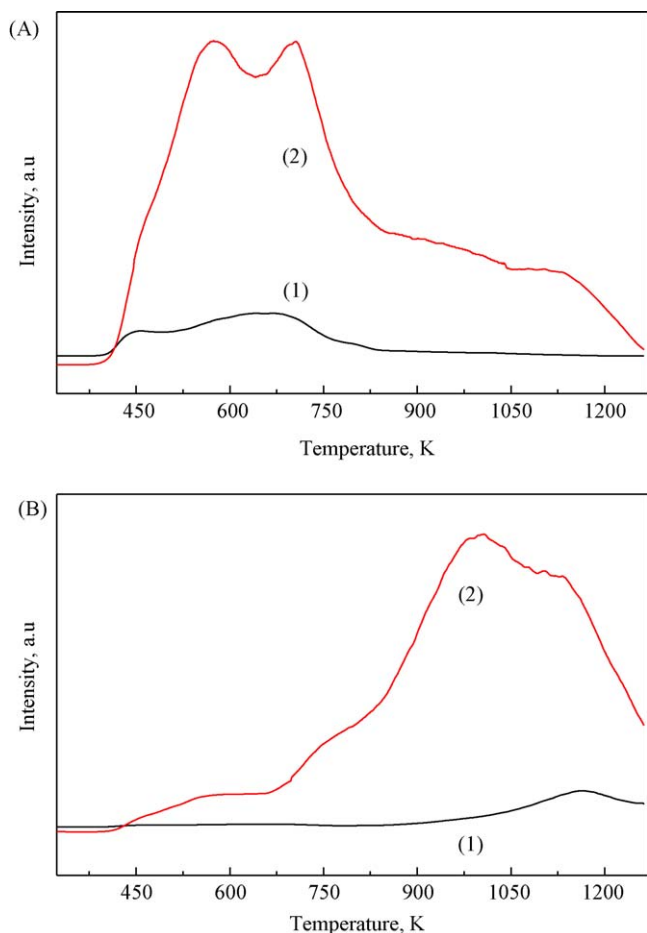
#### 3.1.2. Effect of surface oxygen groups

For the purpose of destruction of chlorofluorocarbons (CFCs), Burdeniuc and Crabtree [15] discovered that the reaction of sodium oxalate (Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>) with CFCs enables the complete conversion of these environmentally hazardous species at temperatures as low as 543 K. It is important to note that the existence of oxygen groups on the surface of activated carbon,



**Scheme 1.** Proposed mechanism for the formation of  $\text{C}_2\text{F}_6$  and  $\text{CF}_4$ .

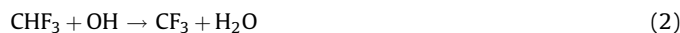
which have the similar structures as that of oxalate, is well known [16–18]. It has been found that large amounts of oxygen-containing species exist on the surface of carbon, and these groups have often been attributed to influence its chemical and catalytic properties [16,18–20]. TPD experiments can provide information to quantify and characterize the nature of these surface oxygen groups. During thermal desorption, these groups decompose primarily as CO and  $\text{CO}_2$ , at different temperatures. Fig. 2 shows the CO and  $\text{CO}_2$  evolution profiles obtained with the activated carbon used in this study. It can be seen that the carbon-based material treated with  $\text{HNO}_3$  contains large amounts of carboxyl ( $-\text{COOH}$ ), carboxylic anhydride ( $-\text{C}_2\text{O}_3-$ ) and lactonic ( $-\text{COO}-$ ) groups evolving as  $\text{CO}_2$  (decomposition temperatures are 473–673 K and above 673 K respectively). Also, numerous phenolic ( $-\text{C}_5\text{H}_5-\text{OH}$ ), quinine and carbonyl ( $-\text{CO}-$ ) groups were detected,



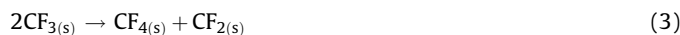
**Fig. 2.** He-TPD-MS spectrums of activated carbon (heating rate:  $10\text{ K min}^{-1}$ ). (A)  $\text{CO}_2$ :  $m/e = 44$  and (B) CO:  $m/e = 28$ . (1) Activated carbon treated in  $\text{H}_2$  at 1073 K for 3 h and (2) activated carbon treated in 30%  $\text{HNO}_3$  solution at 363 K for 5 h.

whose decomposition temperatures were between 873 K and 1173 K in the CO evolution [21–25].

The effect of these surface groups involved in the reaction with  $\text{CHF}_3$  is unclear. However, the attack of a hydroxyl radical on the C–H bonds in  $\text{CHF}_3$  was proposed in a number of studies both experimentally and theoretically [10]

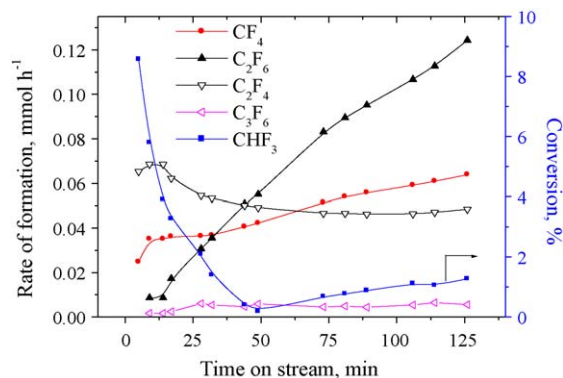


There are numerous OH groups on the surface of carbon as shown in the TPD experiment (Fig. 2). It is likely that reaction (2) occurs on the surface of the activated carbon, as confirmed by the appearance of  $\text{C}_2\text{F}_6$ , which forms as a result of the dimerization of  $\text{CF}_3$ . As shown in Fig. 1, the rate of formation of  $\text{C}_2\text{F}_6$  is rather low compared with that of  $\text{CF}_4$ . Hence, we suggest that  $\text{CF}_3$  and  $\text{CF}_2$  species adsorbed on the surface of carbon, dismutation and/or decomposition of  $\text{CF}_3$  over carbon surface dominate the reaction mechanism rather than dimerization via the following reactions:



To confirm the effect of the surface oxygen groups on pyrolysis of  $\text{CHF}_3$ , activated carbon treated in  $\text{H}_2$  flow at 1073 K for 3 h was examined. As shown in Fig. 2, following  $\text{H}_2$  treatment, only trace amounts of  $\text{CO}_2$  and CO desorption are observed during He-TPD experiments which suggests that most of these oxygen groups can be removed via reaction with  $\text{H}_2$  at 1073 K.

Fig. 3 presents the catalytic performance of the  $\text{H}_2$  treated activated carbon material for the pyrolysis of  $\text{CHF}_3$  as a function of time-on-stream at 1073 K. As expected, in the absence of the surface oxygen groups, the rate of formation of  $\text{CF}_4$  and  $\text{C}_2\text{F}_6$  drops below  $0.10\text{ mmol h}^{-1}$  during the first hour of time-on-stream, almost 70 times lower than the rates shown in Fig. 1. Although the conversion of  $\text{CHF}_3$  follows the similar trend as the reaction over  $\text{HNO}_3$ -treated activated carbon (Fig. 1), its initial conversion level is only 9% and drops to almost zero in less than 1 h. Comparatively, for the reaction over  $\text{HNO}_3$ -treated activated carbon, the initial conversion level is close to 100% and takes roughly 3 h to reach zero. It is noted that the rate of formation of  $\text{C}_2\text{F}_6$  increases with



**Fig. 3.** Conversion of  $\text{CHF}_3$ , rate of formation of products as a function of time-on-stream over activated carbon (treated in  $\text{H}_2$  at 1073 K for 3 h) at 1073 K and a GHSV of  $4300\text{ h}^{-1}$ .

**Table 1**

CHF<sub>3</sub> conversion, rate of formation of products and elemental balance for the catalytic pyrolysis of CHF<sub>3</sub> over HNO<sub>3</sub>-treated activated carbon.

TOS (min)	Conversion (%)	Product profile (mmol h <sup>-1</sup> )				Element balance (%) <sup>c</sup>		
		CF <sub>4</sub>	C <sub>2</sub> F <sub>6</sub>	C <sub>2</sub> F <sub>4</sub>	HF	C	H	F
47	82.1	4.77	0.085	0	9.66	67.9	98.6	99.3
80	61.7	3.64	0.056	0.004	6.31	75.8	94.5	100.1
131	27.5	3.38	0.061	0.009	3.87	78.3	79.6	96.0
178	15.4	2.60	0.072	0.017	2.73	85.0	84.6	97.9
238	0.64	1.48	0.079	0.043	1.43	96.0	87.8	96.9

time-on-stream. We suggest that this trend can be attributed to the gradual diffusion of oxygen groups from the small pores in activated carbon since this material has well developed porosity. It is evident that the oxygen groups on the surface of activated carbon play a major role during the catalytic pyrolysis of CHF<sub>3</sub>. With these results in mind, it becomes clear why the presence of O<sub>2</sub> is crucial during the synthesis of CF<sub>3</sub>I via the reaction of CHF<sub>3</sub> with I<sub>2</sub> over activated carbons [26]. Similar to the effect of HNO<sub>3</sub> treatment, O<sub>2</sub> is also likely to produce large surface oxygen groups, which then catalyze the formation of CF<sub>3</sub> and ultimately CF<sub>3</sub>I.

### 3.1.3. Mass balance of pyrolysis of CHF<sub>3</sub> over activated carbons

Conversion of CHF<sub>3</sub> and elemental balances for the pyrolysis of CHF<sub>3</sub> over HNO<sub>3</sub>-treated activated carbon are illustrated in Table 1. Generally, satisfactory H and F balance levels are achieved; a maximum level of 96% F is recovered. Much lower carbon balances were observed, although they gradually increase with time-on-stream. For instance, at 47 min time-on-stream, the carbon balance is roughly 68%. During the reaction of sodium oxalate with CFCs, Burdeniuc and Crabtree [15] found the stoichiometric formation of carbon from CFCs and F and Cl were detected in the form of mineral acids, namely HF and HCl. Catalyzed by the oxygen groups, we suggest that similar reactions could also take place on the surface of carbon and consequently are responsible for the carbon loss. This explanation is consistent with the observations that the surface area of the used catalyst drops to roughly 50% of the fresh material, presumably due to the deposition of carbonaceous materials (coke) on the catalyst [26].

## 3.2. CHF<sub>3</sub> pyrolysis over activated carbon supported potassium catalyst

### 3.2.1. Comparison of catalytic and gas phase pyrolysis of CHF<sub>3</sub>

Similar to the non-catalytic pyrolysis of CHF<sub>3</sub>, the main reaction products detected over potassium catalyst are C<sub>2</sub>F<sub>4</sub> (TFE) and C<sub>3</sub>F<sub>6</sub> (HFP), as well as trace quantities of CF<sub>4</sub>, C<sub>2</sub>F<sub>6</sub> and C<sub>3</sub>F<sub>8</sub>. Table 2 compares the conversion of CHF<sub>3</sub>, selectivity and yield between catalytic and non-catalytic pyrolysis. Catalytic pyrolysis reactions are carried out at a reaction temperature of 1073 K, space velocity of 4300 h<sup>-1</sup> and at atmospheric pressure. Non-catalytic pyrolysis was conducted under the same temperature and pressure conditions, with a reaction residence time of 0.5 s. As shown in

**Table 2**

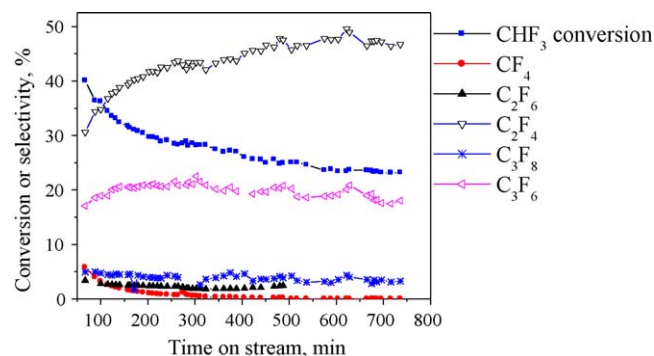
Product distribution for the pyrolysis of CHF<sub>3</sub> over activated carbon supported potassium catalyst and non-catalytic reaction at temperature of 1073 K.

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. 4.** Conversion of CHF<sub>3</sub> and selectivity of products as a function of time-on-stream over K<sub>2-x</sub>O/AC at 1073 K and a GHSV of 4300 h<sup>-1</sup>.

Table 2, the conversion of CHF<sub>3</sub> and selectivity to HFP in the catalytic pyrolysis is significantly higher than that in non-catalytic case, except the selectivity to TFE which by contrast is much lower than the non-catalytic conversion. However, both the yields of TFE and HFP in catalytic pyrolysis are significantly higher compared with the non-catalytic process due to the higher conversion of CHF<sub>3</sub> in the catalytic reaction. In addition to the major products, trace amounts of CF<sub>4</sub>, C<sub>2</sub>F<sub>6</sub> and C<sub>3</sub>F<sub>8</sub> were formed during the reaction over catalyst. During the catalytic pyrolysis process, we speculate that the effect of activated carbon is to enhance the localized surface concentration of the key intermediate, CF<sub>2</sub> carbene, which arises following the elimination of HF from absorbed CHF<sub>3</sub>. The rate of polymerization of CF<sub>2</sub> on the surface is enhanced, and is higher than that occurring during the gas phase reaction. As shown in Table 2, both the selectivity and yield of HFP increase dramatically following the introduction of a catalyst.

### 3.2.2. Catalytic pyrolysis of CHF<sub>3</sub> as a function of TOS

Fig. 4 shows the conversion of CHF<sub>3</sub> and selectivity of products as a function time-on-stream (TOS) over the catalyst at 1073 K and space velocity of 4300 h<sup>-1</sup>. The conversion of CHF<sub>3</sub> decreases during an initial period of catalyst deactivation, gradually reaching steady state. Over the potassium catalyst, we suggest that the initial step in CHF<sub>3</sub> pyrolysis is the elimination of HF [26] as shown in reaction (1). This byproduct readily reacts with K<sub>2</sub>O, which is present on the catalyst, converting the catalyst from K<sub>2</sub>O/AC into KF/AC. Consuming HF by K<sub>2</sub>O, the reaction of HF with K<sub>2</sub>O enhances the rate of decomposition of CHF<sub>3</sub> during the initial time-on-stream. Following the transformation of K<sub>2</sub>O into KF, the conversion level of CHF<sub>3</sub> gradually reduces to a stable state level. Nagasaki et al. investigated similar catalysts to synthesize CF<sub>3</sub>I from CHF<sub>3</sub> and I<sub>2</sub> in the presence of O<sub>2</sub>, and found that using various anions had little effect on the steady-state reaction selectivity or overall rate. Furthermore, they discovered that all the anions present in the catalysts they studied were converted to fluoride, presumably via reaction with hydrogen fluoride [26]. As shown in Fig. 4, the reaction selectivity remains relatively constant once the reaction reaches this pseudo-steady-state. The transfor-



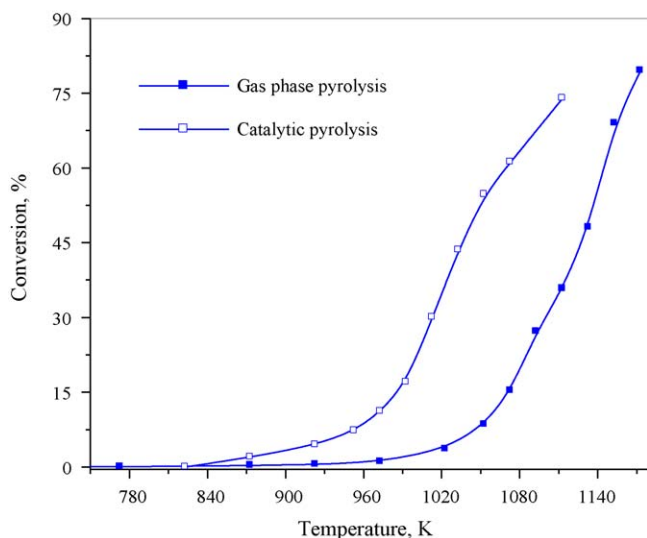


Fig. 5. Conversion of  $\text{CHF}_3$  during the catalytic and non-catalytic pyrolysis as a function of temperature. For the catalytic reaction, GHSV is  $4300 \text{ h}^{-1}$  and residence time is 0.5 s for the non-catalytic case.

mation of catalyst precursor does not affect the selectivity of products except TFE and  $\text{CF}_4$ , where selectivity to TFE increases gradually before it reaches steady state. Conversely, selectivity of  $\text{CF}_4$  drops steadily until it is below detection limits. As discussed, although the catalyst was calcined at 973 K, we presume some oxygen groups remain on the surface of carbon, and therefore, a proportion of  $\text{CF}_2$  species were consumed by these surface oxygen species, forming  $\text{CF}_4$  through disproportionation of  $\text{CF}_2$  carbene before these groups completely disappear.

### 3.2.3. Catalytic pyrolysis of $\text{CHF}_3$ as a function of temperature

The conversion of  $\text{CHF}_3$  and selectivity towards various products as a function of temperature are shown in Figs. 5 and 6. Conversion of  $\text{CHF}_3$  during non-catalytic pyrolysis is also included in Fig. 5 for comparison. As expected, conversion of  $\text{CHF}_3$  increases with temperature in both cases. To achieve a similar conversion level, the non-catalytic reaction requires a temperature approximately 100 K higher than that when a catalyst is introduced. Furthermore, the gas phase decomposition of  $\text{CHF}_3$  commences at 973 K, but in the presence of catalyst, the reaction occurs at temperatures below 873 K. Generally, following the introduction of catalyst,  $\text{CHF}_3$  conversion levels increase by 2–10 times at temperatures between 873 and 1123 K.

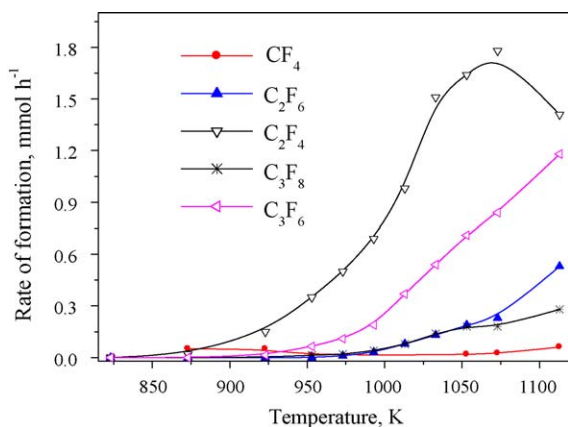


Fig. 6. Selectivity of products during the catalytic pyrolysis as a function of temperature.

As shown in Fig. 6, the rate of formation of products increases steadily with temperature except for TFE. With increasing temperature, the maximum rate of formation of TFE,  $1.8 \text{ mmol h}^{-1}$  is achieved at about 1073 K before it drops gradually. This phenomenon implies that  $\text{CF}_2$  carbenes formed on the surface of catalyst undergo disproportionation in a parallel pathway to dimerization [11,27]. However, unlike pyrolysis over activated carbon, saturated fluorocarbons,  $\text{C}_2\text{F}_6$  and  $\text{C}_3\text{F}_8$  are formed rather than  $\text{CF}_4$ . The carbon balance remains between 98 and 100% at reaction temperatures below 973 K, although with increasing temperature, the carbon balance drops dramatically. This change is consistent with the disproportionation mechanism for  $\text{CF}_2$ . The decreasing carbon balance at high temperatures implies that large amounts of coke are deposited on the catalyst during the reaction. We suggest that reaction (5), (6) and (10) are the primary reactions which are responsible for the formation of coke

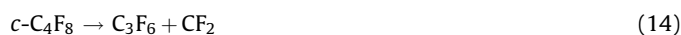
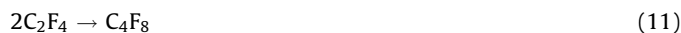


Through these reactions,  $\text{CF}_3$  can readily form and result in formation of gaseous  $\text{C}_2\text{F}_6$  and  $\text{C}_3\text{F}_8$  as well as  $\text{C}_3\text{F}_6$ .



However, the exact surface mechanism is yet unclear. At low temperatures, the high dissociation energy of carbon and fluorine bond inhibits the above reactions in the gas phase (Fig. 5). Clearly, the catalyst plays a major role for the activation of C–F, although, at temperature above 1023 K, gas phase reactions also contribute to the overall product scheme (Fig. 5).

For the gas phase reaction, it has been suggested that HEP might form through the following reactions [6]:



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.

### 3.2.4. Yield of TFE and HFP

Recently, Sung et al. [6] reported 28.7% yield of TFE through pyrolysis of  $\text{CHClF}_2$  over a surface of metal fluorides at 923 K, a GHSV of  $15,000 \text{ h}^{-1}$  and atmospheric pressure. The gas phase reaction of a mixture of  $\text{CHF}_3$  and TFE, resulted in a selectivity of 28.5% to HFP at 1145 K and under optimized conditions [11]. Under similar conditions and as shown in Fig. 7, the yield of HFP reached 20.2% at 1113 K for the catalytic pyrolysis of  $\text{CHF}_3$  alone. At 1073 K, total yield of TFE and HFP is about 35%. However, at higher temperature, the yield of TFE does not increase with temperature, probably due to the polymerization of TFE into higher polymers than HFP.

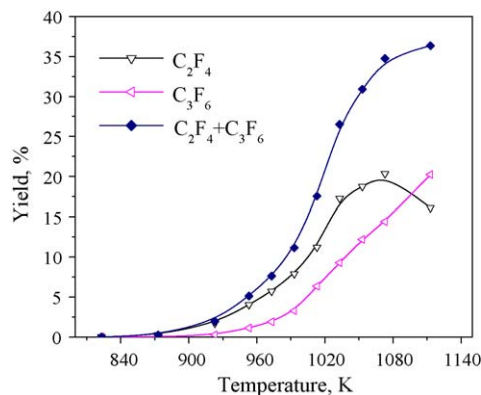


Fig. 7. Yield of TFE and HFP during the catalytic pyrolysis as a function of temperature.

#### 4. Conclusion

Activated carbon shows significant effect on the pyrolysis of CHF<sub>3</sub>, with a high rate of formation of CF<sub>4</sub> and relatively small amounts of C<sub>2</sub>F<sub>6</sub> and C<sub>3</sub>F<sub>8</sub>. We suggest that the oxygen groups on the surface of carbon play a major role for the decomposition of CHF<sub>3</sub>, probably CF<sub>3</sub> and CF<sub>2</sub> as well. This speculation was confirmed by experimental results that show that a much lower conversion level of CHF<sub>3</sub>, rates of formation of CF<sub>4</sub>, C<sub>2</sub>F<sub>6</sub> and C<sub>3</sub>F<sub>8</sub> were observed when these oxygen groups were removed by pre-treating the activated carbon in H<sub>2</sub> at 1073 K for 3 h.

It is found that activated carbon supported potassium catalyst has high catalytic activity for the pyrolysis of CHF<sub>3</sub> into TFE and HFP. Activated carbon as a support material is relatively stable during reaction, except for its surface oxygen groups which can react with CHF<sub>3</sub> and adsorbed reaction intermediates, such as CF<sub>3</sub> and CF<sub>2</sub>. Compared with non-catalytic pyrolysis cleavage of C–F appears to be enhanced by the carbon support which results higher yields of TFE and HFP.

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