

# Investigation into antimony pentafluoride-based catalyst in preparing organo-fluorine compounds

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## Abstract

Antimony pentafluoride ( $\text{SbF}_5$ )/porous metal fluorides (PMF) were prepared by impregnating PMF with  $\text{SbCl}_5$ , and then fluorinating with anhydrous hydrogen fluoride (AHF). It demonstrates excellent activity in vapor-phase catalytic fluorination and overcomes such drawbacks as hygroscopicity, corrosion and toxicity that appear while  $\text{SbF}_5$  was used alone. Furthermore,  $\text{SbF}_5$ /PMF was characterized by means of X-ray diffraction, X-ray photoelectron spectroscopy, BET surface area measurement and SEM. Its catalytic activity was evaluated for vapor-phased fixed-bed catalytic fluorination.

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## 1. Introduction

Being widely used for pharmaceuticals, agrochemicals, liquid crystals and chlorofluorocarbons (CFCs) alternatives due to their unique properties, the organo-fluorine compounds have become very important [1,2]. Efforts have been focused on synthesizing organo-fluorine compounds at low cost. The fluorinated compounds can be prepared through a wide variety of chemistries, such as the fluorination of hydrocarbons using gaseous fluorine diluted with an inert gas, the selective fluorination of substrates absorbed on porous materials by gaseous fluorine, and catalytic fluorination for halogen-exchange by anhydrous hydrogen fluoride (AHF). In the catalytic process for preparation of organo-fluorine compounds, the key reactions involve halogen addition and exchange in the vapor-phase or liquid-phase [3,4]. Until now, one of the most important methods for producing organic fluorine compounds has been the reaction of organic halogen derivatives and AHF with antimony fluorides (Swarts' reaction) [5–7]. In this method, the antimony catalysts play

quite an important role. They exchange halogens for fluorine under much milder conditions than with anhydrous hydrogen fluoride alone [8,9].

Traditionally, Cr-based catalysts have been used in industry for production of CFCs and hydrofluorocarbons (HFCs) [10–13]. However, some chromium compounds have been proven to be carcinogens, and the chromic acid or chromate salts constitute industrial hazards [14]. Thus, to find a replacement for the Cr-based catalyst has come to be an issue. Antimony pentafluoride ( $\text{SbF}_5$ ) has been recognized as a powerful oxidant, a fluorination reagent and a fluorination catalyst for halogen-exchange. It was also considered to be a candidate for replacing the Cr-based catalyst in halogen-exchange. However, it is very difficult to handle  $\text{SbF}_5$  practically, since it fumes strongly in the moist air due to its hygroscopic property [15–17].

In our laboratory, the research has been concentrated on the synthesis and characterization of porous metal fluorides (PMF) with a large surface area. A series of inert metal fluorides, such as porous aluminum fluoride (PAF), porous magnesium fluoride (PMgF), porous calcium fluoride (PCF) and porous chromium fluoride (PCrF), have been prepared and characterized by the BET method, DSC, TG, SEM and X-ray

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diffraction (XRD) [18–20], which exhibit excellent chemical stability in corrosive media and thermo-stability.

In an effort to improve the properties of  $\text{SbF}_5$  and develop its application,  $\text{SbCl}_5$ , the precursor of  $\text{SbF}_5$ , was absorbed to the above-mentioned inert porous metal fluorides, then treated with anhydrous hydrogen fluoride (AHF) in vapor-phase. Eventually,  $\text{SbCl}_5$  in PMF was fluorinated and changed into  $\text{SbF}_5$ .  $\text{SbF}_5$  and PMF were combined much closer through the fluorination process. More importantly, the prepared  $\text{SbF}_5$ /PMF not only keeps the activity of  $\text{SbF}_5$ , but also overcomes the drawbacks of  $\text{SbF}_5$ , such as hygroscopicity, corrosion and toxicity. The said process made the application of  $\text{SbF}_5$  more easy, especially as a fixed-bed catalyst in halogen-exchange reaction [19], and as a fluorinating reagent in organic synthesis [21].

## 2. Experimental

The catalyst support, like PAF and PCrF, was able to be prepared by different methods. For example, D-PAF was prepared by the following procedure: 30 ml of  $\gamma\text{-Al}_2\text{O}_3$  was packed into an Inconel reactor 14 mm in diameter and 300 mm in length, dried with  $\text{N}_2$  (200 ml/min) at 300 °C for 4 h, then activated with a mixture stream of AHF (100 ml/min) and  $\text{N}_2$  (300 ml/min) at 300 °C for 16 h. Then the pure AHF was passed through the reactor for 2 h. The prepared PAF was used as the support of catalyst. H-PAF was prepared by heating  $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$  at 300 °C for 10 h. W-PAF was obtained from the reaction of  $\text{Al}_2\text{O}_3$  with aqueous HF at 90 °C for 3 h. PCrF were prepared by the reaction of porous chromium oxide and AHF at 300 °C according to our reported methods [20,22].

A typical process of preparing  $\text{SbF}_5$ -based catalyst and fluorination of dichloromethane is described as follows: about 25 g of  $\text{SbCl}_5$  was dropped gradually into 40 g PMF under nitrogen atmosphere. Then  $\text{SbCl}_5$ /PMF was charged to the above-mentioned Inconel reactor and dried at 100 °C for 3 h in the presence of nitrogen. AHF diluted by nitrogen was passed through the reactor at 200 °C ( $\text{N}_2$ :AHF = 100:100 ml/min) for 2 h; then pure AHF was passed at the rate of 200 ml/min for 3 h. Finally, the residual AHF in the reactor was purged by  $\text{N}_2$  for 10 h. The prepared catalyst,  $\text{SbF}_5$ /PMF, was stored in plastic or glass bottles.

The apparatus for the preparation and the evaluation of catalyst consists of two mass flow controllers (one is for  $\text{N}_2$  and the other for AHF) and an electrically heated tubular Inconel reactor (14 mm in diameter and 300 mm in length) equipped with an inside Inconel tube for inserting type-K thermocouples with a 1 mm diameter. A thermocouple was loaded into the reactor through a type-Monel CAJON® fitting and penetrated to the whole of the catalyst bed to measure the temperature distribution along the reactor. While running the fluorination of dichloromethane, dichloromethane was fed into the reactor via a vaporizer by a Masterflex (Cole-Parmer Instrument Co.) metering pump. AHF was supplied

to the vaporizer in vapor-phase. The product stream from the reactor was scrubbed with  $\text{H}_2\text{O}$  at 60 °C, then passed through a drier packed with  $\text{CaCl}_2$ , and finally, analyzed by a Shimadzu GC-14 A on-line. The capillary column was a Pora plot Q with 0.32 mm i.d. and 25 m length from J&W Scientific Inc. The column was programmed as follows: the initial temperature was set at 80 °C for 15 min; then the temperature was increased at the rate of 20 °C/min, and finally, to 200 °C and held for 5 min. The instrumental parameters were set up as follows: both injection port and TCD detector, 200 °C; the carrier gas rate, 10  $\text{cm}^3$  He/min. In order to calculate the conversion of  $\text{CH}_2\text{Cl}_2$  and the yield of  $\text{CH}_2\text{FCl}$  and  $\text{CH}_2\text{F}_2$ , their GC relative response factors ( $\text{CH}_2\text{F}_2$ : $\text{CH}_2\text{FCl}$ : $\text{CH}_2\text{Cl}_2$  = 1:1.23:1.67) were used [22]. The products were determined by comparing their NMR patterns with those of authentic samples.

The BET surface area and the pore volume of the catalyst were determined by means of low temperature adsorption of nitrogen using a Micromeritics ASAP 2010 instrument. The sample was degassed under vacuum at 300 °C for 3 h before measurement.

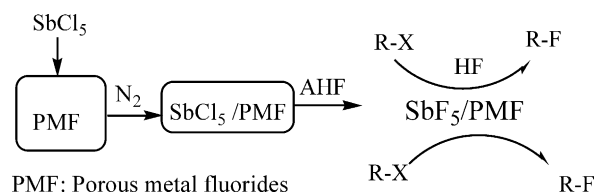
$^1\text{H}$  NMR and  $^{19}\text{F}$  NMR of substrates and products were analyzed by a JNM-EX270 (JEOL, 270 MHz) spectrometer at 25 °C with  $\text{Me}_4\text{Si}$  and  $\text{CFCl}_3$ , respectively, as internal references in  $\text{CDCl}_3$  solvent.

X-ray diffraction was employed to determine the bulk crystalline phase of samples. The pattern of samples was recorded by a Mac Science MPX-18 diffractometer. X-ray diffraction was measured by using  $\text{Cu K}\alpha_1$  (0.1542 nm) radiation and the X-ray tube was operated at 40 kV and 150 mA.

X-ray photoelectron spectroscopy (XPS) spectra of samples were taken by an ESCA 5400 electron spectrometer equipped with an Mg  $\text{K}\alpha$  operated at 300 W. The detector conditions: pass  $E$  35.5 eV, 0.1 eV per step, detecting angle 45°. No special treatments were applied to the samples in the UHV chamber. All binding energies were referenced to the C (1s) peak at 284.6 eV.

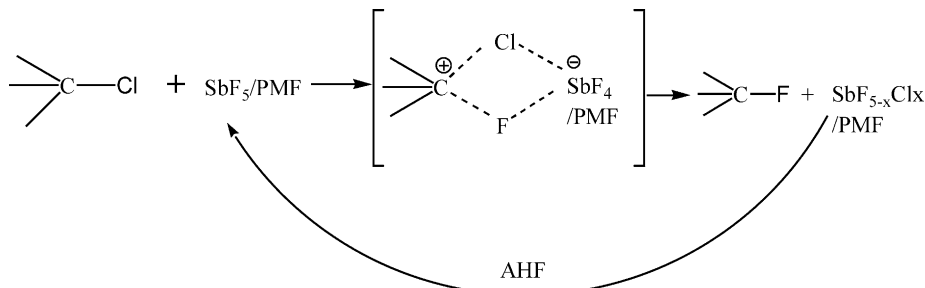
## 3. Results and discussion

The procedure for preparing  $\text{SbF}_5$ /PMF and its application are shown below:



$\text{SbF}_5$ /PMF possesses a multi-functional character. It is an excellent fluorination reagent in halogen-exchange reaction independently. In addition, it can be used as a fixed-bed catalyst in vapor-phase catalytic fluorination. When used for fluorination reaction,  $\text{SbF}_5$ /PMF is a much more convenient reagent than  $\text{SbF}_5$  because of simplification of the handling.

Another great advantage of  $\text{SbF}_5/\text{PMF}$  is the possibility of working in glass apparatus as a fluorination reagent in atmospheric environment. There is no appreciable corrosion on the surface of glass when  $\text{SbF}_5/\text{PAF}$  is stored in a glass bottle. The reaction mechanism in the presence of  $\text{SbF}_5/\text{PMF}$  is classified into catalytic fluorination as shown below.



### 3.1. Characterization of $\text{SbF}_5/\text{PAF}$

$\text{SbF}_5/\text{PAF}$  was investigated in terms of a typical reagent. The surface area and the pore volume of the prepared reagent decreased with the increase in the amount of  $\text{SbF}_5$  absorbed. While the surface area of PAF is  $92.0 \text{ m}^2/\text{g}$  with 20 wt.%  $\text{SbCl}_5$  to PAF, the surface area decreased to  $72.2 \text{ m}^2/\text{g}$ , and with 50 wt.%  $\text{SbCl}_5$  to PAF, it decreased to  $53.0 \text{ m}^2/\text{g}$ . The pore volume of  $\text{SbF}_5/\text{PAF}$  decreased to  $0.31 \text{ ml/g}$  and  $0.21 \text{ ml/g}$  from  $0.35 \text{ ml/g}$ , respectively. It is suggested that the pores of PAF were occupied by  $\text{SbF}_5$  and part of the surface area and the pore volume decreased.

X-ray powder diffraction indicates that the prepared  $\text{SbF}_5/\text{PAF}$  has almost the same crystalline phase with PAF when the amount of  $\text{SbCl}_5$  to PAF is around 20 wt.%. A new crystalline phase appears on the surface of  $\text{SbF}_5/\text{PAF}$  in addition to a typical PAF when the amount of  $\text{SbCl}_5$  to PAF increased to 50 wt.% to PAF (Fig. 1). It might be that the small amount of  $\text{SbF}_5$  was intercalated into the lattice of PAF.

X-ray photoelectron spectroscopy was applied to identify the chemical state of elements in  $\text{SbF}_5/\text{PAF}$ . The F 1s spectra (Fig. 2a) reveal that the binding energy of F in PAF, PAF treated by gaseous fluorine and  $\text{SbF}_5/\text{PAF}$  are 686.5 eV, which indicates the binding energy of F–Al is similar to that of F–Sb. XPS spectra in Fig. 2b show that the binding energy of Al in three kinds of samples are about 76.2 eV, which means that the chemical state of Al in PAF is not significantly affected by chemical environment, even though the PAF has been treated by gaseous fluorine and  $\text{SbCl}_5$  or  $\text{SbF}_5$ . XPS spectra of Sb 3d indicate that the peak at 531.3 eV is a typical character of Sb 3d (Fig. 2c). Combining the characterization results of PAF, PAF treated by gaseous fluorine and  $\text{SbF}_5/\text{PAF}$ , it is not difficult to conclude that the amount of oxygen in  $\text{SbF}_5/\text{PAF}$  can be neglected despite the fact that the position of binding energy of O 1s and Sb 3d is the almost same. Furthermore, XPS analysis indicated that no chlorine exists in  $\text{SbF}_5/\text{PAF}$ , which means all chlorine was replaced by fluorine in the reaction of  $\text{SbCl}_5/\text{PAF}$  with AHF.

### 3.2. Application of $\text{SbF}_5/\text{PMF}$

As a fixed-bed catalyst,  $\text{SbF}_5/\text{PAF}$  was used to prepare HFC-32 from  $\text{CH}_2\text{Cl}_2$ . The reaction was operated continuously for about 48 h from  $270^\circ\text{C}$  to  $360^\circ\text{C}$ . The reaction (at a set temperature) continued for 5 h to be stabilized and to take

the data on-line. The results are shown in Fig. 3 and Table 2, which indicates that  $\text{CH}_2\text{Cl}_2$  is easily transformed to  $\text{CH}_2\text{F}_2$  in the presence of  $\text{SbF}_5/\text{PAF}$ . In the range of reaction temperature higher than  $330^\circ\text{C}$ , the conversion of  $\text{CH}_2\text{Cl}_2$  and the selectivity of  $\text{CH}_2\text{F}_2$  does not change so much, which is attributed to the fact that the reaction is close to equilibrium. In order to decrease the coke formation on catalyst surface and extend the life span of the catalyst, the reaction temperature is strictly controlled below  $300^\circ\text{C}$ .

Three kinds of PAFs with different surface area and pore distribution were prepared and used as the support of  $\text{SbF}_5$ . In the reaction to prepare  $\text{CH}_2\text{F}_2$ , the pore distribution and pore diameter of PAF have a great effect on the activity of catalyst. The larger surface area of  $\text{SbF}_5/\text{PAF}$  results in the higher catalytic activity [19].

In addition, some fluorinated compounds are prepared from corresponding chlorinated compounds in the pres-

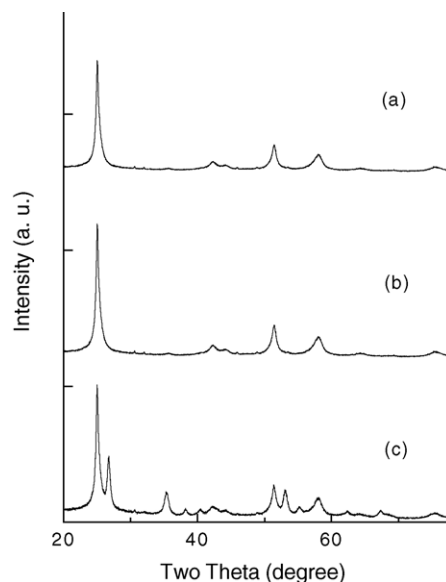


Fig. 1. XRD spectra of PAF and  $\text{SbF}_5/\text{PAF}$ .

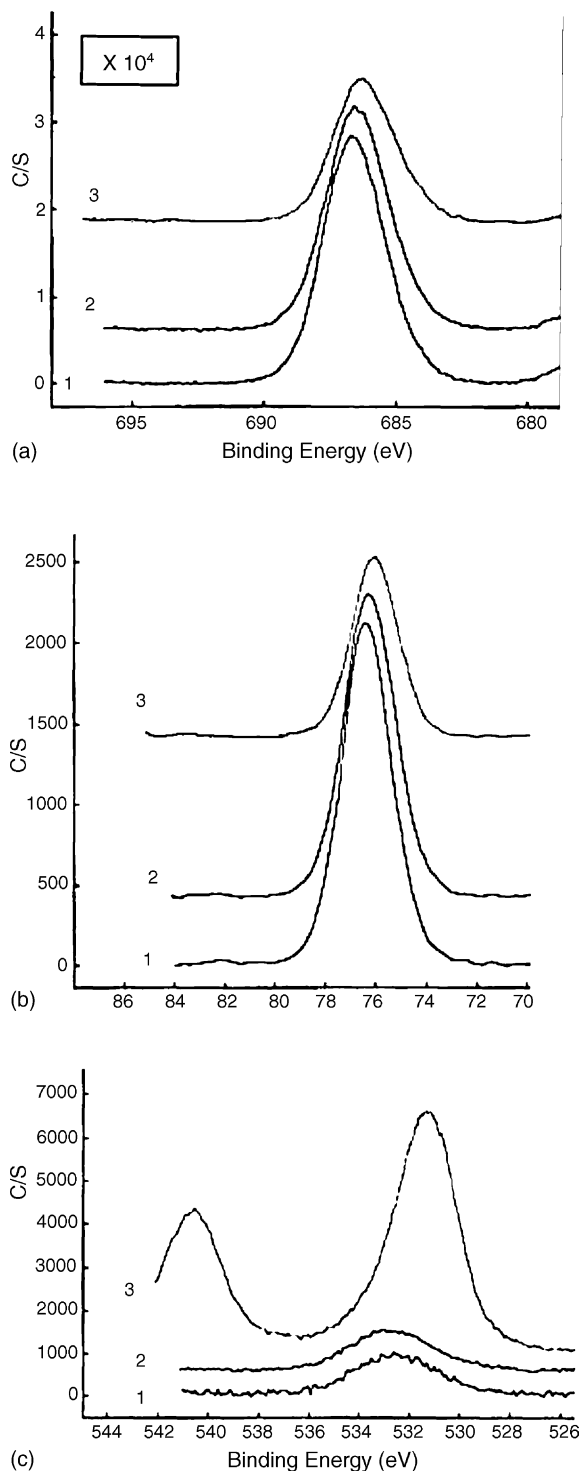


Fig. 2. (a) XPS spectra of F in PAF, PAF treated by  $F_2$  and  $SbF_5/PAF$ . (b) XPS spectra of Al in PAF, PAF treated by  $F_2$  and  $SbF_5/PAF$ . (c) XPS spectra of Sb 3d in PAF, PAF treated by  $F_2$  and  $SbF_5/PAF$ .

ence of  $SbF_5/PAF$  via a vapor-phase fluorination with hydrogen fluoride. The yields of the products were calculated based on the amount of the products after the reaction run 6 h. In the entries 1 and 2 in Table 1, the products were mainly *trans*- $CF_3CH=CHCl$  and *trans*- $CF_3CH=CHF$ ,

Table 1

Fluorination of chlorinated compounds with AHF in the presence of  $SbF_5/PAF^a$

Entry	Substrate	Reaction temperature ( $^{\circ}C$ )	Product	Yield (%)
1	$CCl_3CH_2CHCl_2$	316	$CF_3CH=CHCl$	55.2
			$CF_3CH=CHF$	6.1
2	$CCl_3CH_2CHCl_2$	334	$CF_3CH=CHCl$	75.9
			$CF_3CH=CHF$	8.3
3	$CF_3CH=CHCl$	303	$CF_3CH=CHF$	38.8
			$CF_3CH_2CHF_2$	44.6
4	$CF_3CH=CHCl$	350	$CF_3CH=CHF$	63.2
			$CF_3CH_2CHF_2$	27.8
5	$CH_3OCF_2CF_2Cl$	200	$CH_3OCOCF_2Cl$	67.0
			$CH_3OCOCF_2Cl$	1
6	$CH_3OCF_2CF_2Cl$	300	$CH_3OCOCF_2Cl$	67.0
			$CH_3OCOCF_2Cl$	1

<sup>a</sup> From 1 to 2, HF 300 ml/min,  $CCl_3CH_2CHCl_2$  0.15 ml (liquid)/min, catalyst 10 ml, reaction contact time 1.9 s, reaction run 6 h; from 3 to 4, HF 300 ml/min,  $CF_3CH=CHCl$  (vapor-phase) 50 ml/min, catalyst 10 ml, reaction contact time 1.7 s, reaction run 6 h; from 5 to 6, substrate 2.0 mmol, reaction time 2 h; Sb wt.% 6.5 in the  $SbF_5/PAF$ . The yield of products was determined by  $^1H$  NMR and  $^{19}F$  NMR.

respectively. Only a trace amount of *cis*- $CF_3CH=CHCl$  and *cis*- $CF_3CH=CHF$  were formed. This is ascribed to the fact that the Sb in Lewis super acid ( $SbF_5$ ) withdrew the Cl in  $-CHCl_2$  and promoted the elimination of hydrogen chloride to form intermediate,  $CCl_3CH=CHCl$ , which was then transformed to  $CF_3CH=CHCl$  or  $CF_3CH=CHF$  through the reaction with HF. For entries 3 and 4 in Table 1, the reaction of  $CF_3CH=CHF$  with HF occurred to produce  $CF_3CH_2CHF_2$ , a prime candidate of CFCs alternatives [23]. In entries 5 and 6 in Table 1,  $SbF_5/PAF$  works as a Lewis super acid and coordinate to halogen atom to polarize the  $\alpha$ -carbon more positive in ether. Nucleophilic attack of a trace amount of hydroxide anion to the  $\alpha$ -carbon gives intermediate fluoroalcohol, and the removal of HF from this intermediate forms ester [21].

The effect of the amount of Sb in  $SbF_5/PAF$  on the catalytic activity was investigated as well. In the process of preparing  $CH_2F_2$  from  $CH_2Cl_2$  in the presence of 10 ml  $SbF_5/D-PAF$  catalyst, the reaction was operated for 10 h in the following conditions: AHF 300 ml/min,  $CH_2Cl_2$  0.3 ml/min, reaction contact time 1.6 s, reaction temperature at about  $320^{\circ}C$ . The yields of  $CH_2F_2$  were 37.9%, 49.7% and 61.0% when the

Table 2

Fluorination of  $CH_2Cl_2$  with AHF in the presence of  $SbF_5/PCrF^a$

Reaction temperature ( $^{\circ}C$ )	Products sel. (%)			Yield (%)	
	$CH_2F_2$	$CH_2ClF$	Conversion of $CH_2Cl_2$ (%)	$CH_2F_2$	$CH_2ClF$
245	84.2	15.8	78.7	66.3	13.3
270	84.6	15.4	82.5	69.8	12.7
300	84.4	15.6	84.4	71.2	13.2
330	84.2	15.8	86.2	72.6	13.6
360	83.3	16.7	86.3	71.9	14.4

<sup>a</sup> HF 300 ml/min,  $CH_2Cl_2$  80 ml (vapor-phase)/min, catalyst 10 ml, CT 1.58 s.

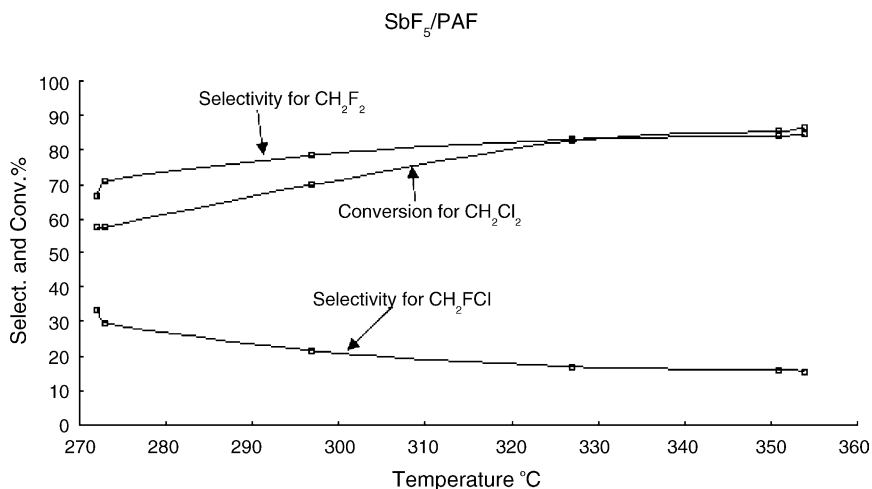


Fig. 3. Fluorination of dichloromethane with AHF in the presence of SbF<sub>5</sub>/PAF.

Sb wt.% were 3.0, 4.9 and 6.5, respectively. The results indicate that the increase of the amount of Sb in SbF<sub>5</sub>/PAF is advantageous to the catalytic activity.

When the prepared SbF<sub>5</sub>/PAF containing about 20% SbF<sub>5</sub> were immersed in water for 24 h, no obvious leaching of antimony occurred from the reagent. Moreover, it was dried in the reactor under nitrogen flow at 200 °C for 3 h and used for the vapor-phase reaction of CH<sub>2</sub>Cl<sub>2</sub> with AHF. The catalyst still kept high activity with about 70% conversion of CH<sub>2</sub>Cl<sub>2</sub> and 80% selectivity of CH<sub>2</sub>F<sub>2</sub>, which indicates that SbF<sub>5</sub>/PAF has an excellent resistance to hydrolysis (Fig. 3). Related literature reports that SbF<sub>5</sub> can be intercalated easily in the lattice of graphite simply by heating a mixture of SbF<sub>5</sub> and graphite at 110 °C for a few days [24]. After intercalation, no antimony salt could be extracted from the intercalate, even with HCl–HNO<sub>3</sub>. In our catalyst, SbF<sub>5</sub> might be intercalated into the lattice of PMF, which is similar to graphite, under vapor-phase fluorination reaction at high temperature. In addition, SbF<sub>5</sub>/PAF exhibits an excellent thermo-stability; it can be used up to 360 °C without serious loss of the catalytic activity although the antimony pentafluoride is relatively volatile, since its boiling point is only 141 °C.

Porous chromium fluoride, one of PMF, was also employed as the support of SbF<sub>5</sub>. The ways to prepare SbF<sub>5</sub>/PCrF and SbF<sub>5</sub>/PAF are quite similar [22]. The obtained SbF<sub>5</sub>/PCrF was applied to vapor-phase fixed-bed catalytic fluorination in preparing CH<sub>2</sub>F<sub>2</sub>. The results (Table 2) indicate that SbF<sub>5</sub>/PCrF is also an excellent catalyst for the fluorination of CH<sub>2</sub>Cl<sub>2</sub>.

In summary, SbCl<sub>5</sub>, as the precursor of SbF<sub>5</sub>, was absorbed to the inert porous metal fluorides, and then treated with AHF in vapor-phase. The approach is facile and economical since SbF<sub>5</sub> is prepared from the reaction of SbCl<sub>5</sub> and HF in a special Al vessel, which is fitted with an Al reflux condenser kept at –45 °C [25]. Furthermore, SbF<sub>5</sub> is too viscous to combine with support homoge-

neously. More importantly, the prepared SbF<sub>5</sub>/PMF not only keeps the activity of SbF<sub>5</sub>, but also overcomes the drawbacks of SbF<sub>5</sub>, such as hygroscopicity, corrosion and toxicity.

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