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Fluorination of chlorofluoroether using catalysts supported by porous aluminum fluoride

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Abstract

Reaction of 1,2-dichloro-1,1,2-trifluoro-2-methoxyethane with anhydrous hydrogen fluoride (AHF) was investigated in the presence of metal fluorides supported on porous aluminum fluoride (PAF). 2-Chloro-1,1,2,2-tetrafluoro-2-methoxyethane, a new compound, was prepared in 85% yield in the presence of CoF_2/PAF. Methyl chlorodifluoroacetate was also obtained and its formation was discussed.

Keywords: Porous aluminum fluoride; 1,2-Dichloro-1,1,2-trifluoro-2-methoxyethane; 2-Chloro-1,1,2,2-tetrafluoro-2-methoxyethane; Methyl chlorodifluoroacetate

1. Introduction

Partially fluorinated ethers have been proposed as possible third generation alternatives to replace CFCs, HCFCs, and PFCs as refrigerants, form blowing agent, and cleaning solvents because of their low environmental effect, inflammability, low toxicity, and similar physical properties to CFCs [1].

As we know, the replacement of chlorine atoms by fluorine atoms occupies a practically important position in the preparation of partially fluorinated ethers. In the literatures, the replacement of chlorines in chlorinated ether by fluorine was studied by fluorination with metal fluorides [2,3], liquid-phase fluorination by Swart's reaction [4,5], direct fluorination with gaseous fluorine [6], and electrochemical fluorination [7].

In our previous work, partially halogen-ethers were fluorinated by gaseous fluorine when substrates were absorbed on porous aluminum fluoride (PAF) [8]. The PAF was also used as a catalyst support to prepare 1,2,2,2-tetrafluoroethane (HFC-134a) by vapor-phase catalytic fluorination [9].

Here, we investigated the preparation of partially fluorinated ethers via exchange of halogens by vapor-phase catalytic fluorination. The reaction of 1,2-dichloro-1,1,2-trifluoro-2-methoxyethane (**1**) with anhydrous hydrogen fluoride (AHF) in the presence of metal fluorides supported on PAF was investigated for the first time. In the reaction, 2-chloro-1,1,2,2-tetrafluoro-2-methoxyethane (**2**), a new compound, was obtained in 85% yield when CoF_2/PAF was used as a catalyst. Compound **2** will be a possible intermediate of 1,1,1,2,2-pentafluoro-2-methoxyethane (HFE-245mc), which is expected as a prime candidate of CFCs alternatives [10]. On the other hand, methyl chlorodifluoroacetate (**3**) was obtained around 50% yield in the presence of PAF or CrF_3/PAF in the reaction.

2. Results and discussion

The reaction of **1** with PAF or with AHF in the presence of metal fluorides supported on PAF was attempted and the results were listed in Table 1. The reaction proceeded as shown in Scheme 1.

From the results, **2** and **3** were formed as main products in the reaction of PAF alone with **1** at 200°C. The results indicated that PAF has not only activity of fluorination, but also activity of esterification (Table 1, No. 1). In order to observe the effect of AHF, we tried to put AHF to reaction. Then the yield of **2** increased to 27%, and **3** increased to 54% at 200°C (Table 1, No. 2). The results indicated the yields of products **2** and **3** were improved and the decomposition products, such as CH_3Cl and CF_2ClCOF, were reduced in the presence of AHF.

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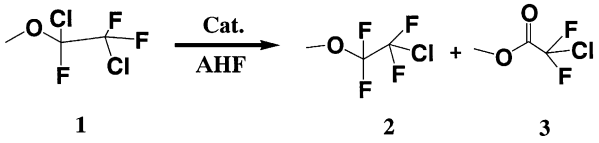
Table 1
Catalyst effect for reaction of **1**[a]

No.	Catalyst	**1** (mmol)	AHF (mmol)	Products (yield %)		Recovery of **1** (%)
				2	**3**	
1	PAF	2.9	–	12	33	0
2	PAF	2.6	6.7	27	54	4
3	CrF_3/PAF[b]	1.0	5.9	46	42	4
4	CoF_2/PAF[c]	1.0	6.0	85	9	2

[a] Reaction temperature, 200°C; reaction time, 1 h; catalyst, 2 g, for each reaction.
[b] Cr, 5 wt.%.
[c] Co, 5 wt.%.



1 **2** **3**

Scheme 1.

Catalysts supported on PAF, CoF_2/PAF and CrF_3/PAF, were studied. Ether **2** was formed in 85% yield when CoF_2/PAF was used in the reaction at 200°C (Table 1, No. 4). On the other hand, ether **2** and ester **3** were obtained in 46 and 42% yield, respectively, when CrF_3/PAF was used at 200°C (Table 1, No. 3). The results indicate the efficacy of the catalysts with respect to the fluorination falls in the sequence: $CoF_2/PAF > CrF_3/PAF > PAF$.

The effect of temperature for the reaction of **1** using CoF_2/PAF and CrF_3/PAF were investigated and the results were listed in Tables 2 and 3, respectively. In each case, the reaction at 200°C gave best results. Starting material was recovered when reaction temperature is <200°C, and charring occurred at 300°C.

Table 2
Effect of temperature for reaction of **1** using catalyst CoF_2/PAF[a]

No.	AHF (mmol)	Reaction temperature (°C)	Products GC area (%)		
			2	**3**	**1**
1	4.3	100	1	4	83
2	5.2	150	40	18	33
3	6.0	200	85	9	2
4	4.6	300	Decomposition		

[a] Starting material **1** is 1 mmol for each reaction; reaction time, 1 h; catalyst amount, 2 g; Co, 5 wt.%.

Table 3
Effect of temperature for reaction of **1** using catalyst CrF_3/PAF[a]

No.	AHF (mmol)	Reaction temperature (°C)	Products GC area (%)		
			2	**3**	**1**
1	7.0	150	23	20	55
2	5.9	200	46	42	4
3	4.0	300	Decomposition		

[a] Starting materials **1** is 1 mmol for each reaction; reaction time, 1 h; catalyst amount, 2 g; Cr, 5 wt.%.

From these results, the reaction mechanism may be inferred as follows: MF_n (M = Al, Co, Cr) acts as a Lewis acid to activate chlorine reactivity. The fluorine atom of MF_n attacks the α-carbon to replace chlorine atom to form **2** and MF_mCl_{n-m} (Scheme 2, route 1). The MF_n was regenerated by the reaction of MF_mCl_{n-m} with AHF. $AlF_m(OH)_{3-m}$ exists on the surface of aluminum fluoride after it was dried at about 350°C [11,12]. The OH group should be on the surface of PAF and catalysts because their treating temperature was about 300°C. The OH group of $AlF_m(OH)_{3-m}$ could attack the α-carbon of **1** to give ester **3** and $AlClF_{m-1}(OH)_{3-m}$ (Scheme 1, route 2). The esterification competes with fluorination, so both **2** and **3** were obtained. In the case of CoF_2/PAF, ether **2** was predominately obtained, which shows that the fluorination with CoF_2 overcome esterification by $AlF_m(OH)_{3-m}$. As the fluorination ability of CrF_3 would be weaker than that of CoF_2, so that the yield of **2** was almost same as that of **3** in the presence of the existing of CrF_3/PAF. In the case of PAF, the fluorination ability would much weaker, so the ester formation was predominant.

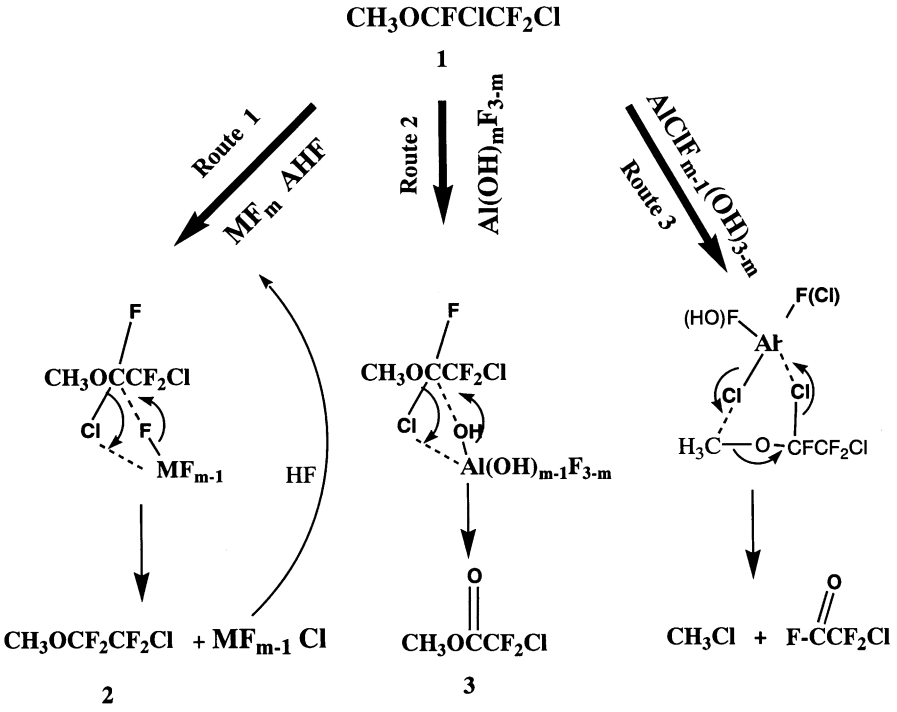
On the other hand, after $AlF_m(OH)_{3-m}$ reacted with **1**, it would generate $AlClF_m(OH)_{2-m}$, and this would catalyze the decomposition of **1** to form CF_2ClCOF and CH_3Cl (Scheme 1, route 3). In the presence of AHF, $AlClF_{m-1}(OH)_{3-m}$ would be converted into $AlF_m(OH)_{3-m}$, so that the addition of AHF to the reaction can reduce the decomposition of **1** and increase the yield of **2** and **3**.

Further fluorination studies of **2** to HFE-245mc are currently being investigated.

3. Experimental

3.1. Chemicals

Surface area and pore volume (V_s) of PAF were 75 m^2/g and 0.3 cm^3/g, respectively [8]. 1,1,2-Trifluoro-2-methoxyethene (**4**) was from Daikin fluorochemical Co. The AHF was obtained from Morita Chem. Ind. Co. Ltd. 1,2-Dichloro-1,1,2-trifluoro-2-methoxyethane (**1**) was prepared by the reaction of **4** with equimolar amount of gaseous chlorine [13].



Scheme 2.

3.2. Instrument

^{1}H NMR and ^{19}F NMR were recorded on JNM-EX270 (JEOL, 270 MH_Z) at 25°C with Me_4Si and $CFCl_3$, respectively, as internal reference in $CDCl_3$ as a solvent.

The FT-IR spectrometer (FT-IR 620, Japan Spectroscopic Co. Ltd.) was used for measuring.

The GC–MS was a Hewlett-packard 5790 series system equipped with a Jet Separator for the 5890A GC. The capillary column was Pora plot Q with 0.32 mm i.d. and 25 m length from J & W Scientific Inc. The operation condition of GC is as follows: column temperature 80°C for 2 min and heated for 20 min at a rate of 10°C/min; detector temperature, 200°C; carrier gas, 1 cc He/min; split ratio, 45:1; sample size, 1.2 μl; pressure, 50 kPa.

Products were handled in glass and metal vacuum line system. Amounts and molecular weight of products were determined by measuring the sample pressure under a certain volume in the vacuum line.

3.3. Preparation of catalyst

Apparatus for preparing catalyst consists of two mass flow controllers (one is for N_2 and another for AHF) and an electrically heated tubular Monel reactor 14 cm in diameter and 30 cm in length equipped with an inside Monel tube for inserting type-K thermocouples with a 1 mm diameter. A thermocouple enters the reactor through a type-Monel CAJON® fitting and penetrates to the whole of the catalyst bed to measure the temperature change of different position of the reactor.

Catalysts were prepared by following way. First, the PAF was dehydrated by heating at 300°C for 10 h and then impregnated to a sufficient amount of salt solution overnight. The amount of salt in the solution was adjusted to give final metal loading from 1–5 wt.%. The saturated support was dried at 120°C for 2 h and 200°C for 2 h. The dried pellets were packed on Monel alloy reactor and fluorinated by N_2:AHF = 1:1 (100:100 ml) at 200°C for 2 h, then pure AHF passes through the reactor at 200°C for 2 h and 300°C for 2 h. Finally, remaining AHF on the catalyst was washed by N_2. The prepared catalyst is used to fluorination procedure.

3.4. Reaction of *1* with AHF in the presence of catalyst

About 2 g of catalyst was placed in a stainless steel reactor with 80 cm^3 volume. The reactor was cooled to −196°C, and 1 mmol of **1** and 3 mmol AHF were introduced into the reactor. The reactor was heated to 200°C and kept at this temperature for 1 h. Remaining AHF was adsorbed by NaF. The products were analyzed by FT-IR, GC–MS, and NMR. The results were listed in Table 1. Compounds **2** and **3** were formed as main products.

Compound **2** is a new compound. The boiling point is 41–42°C at 760 mmHg. The spectra data were listed as follows; IR: 2974 (w), 1460 (w), 1351 (m), 1251 (s), 1181 (vs), 1129 (vs), 1050 (w), 1015 (s), 947 (s).

MS peaks *m/e*: 15 CH_3^+; 81 $CH_3OCF_2^+$; 131 CH_2OCF_2-CF_2H^+; 147 $CH_3OCF_2CFCl^+$; 165 $CH_2OCF_2CF_2Cl^+$.

NMR chemical shifts:

$$\underset{1}{CH_3}-O-\underset{2}{CF_2}-\underset{3}{CF_2}Cl$$

H1(3)δ: 3.73s; F2(2)δ: −73.11m; F3(2)δ: −93.07m.

Compared with spectra data of authentic sample, the structure of **3** was determined [14].

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