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Esterification of 1,2-dichloro-1,1,2-trifluoro-2-methoxyethane with $AlF_m(OH)_{3-m}$

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Abstract—Porous $AlF_m(OH)_{3-m}$ was prepared by heating $AlF_3{\cdot}3H_2O$. Methyl chlorodifluoroacetate was synthesized in 77% yield by the reaction of 1,2-dichloro-1,1,2-trifluoro-2-methoxyethane with $AlF_m(OH)_{3-m}$. The reaction mechanism was inferred in terms of surface property of $AlF_m(OH)_{3-m}$. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

Porous aluminum fluoride (PAF) is an excellent catalyst carrier for Swarts' reaction, for example, it has been used for preparing 1,2,2,2-tetrafluoroethane.[1]

The application of aluminum fluoride has been paid wide attention, especially in acid-catalyzed reactions of hydrocarbons such as cracking, isomerization, polymerization, and disproportionation.[2]

In our previous work, PAF was used to adsorb substrates to control the selectivity of products and avoid burning in fluorination reaction by gaseous fluorine.[3]

The investigation of thermal behavior indicated that $AlF_3{\cdot}3H_2O$ changes its structure depending on the heating temperature. $AlF_3{\cdot}0.5H_2O$, AlF_3, and Al_2O_3were obtained in the temperature ranges from 108°C to 277°C, 277°C to 550°C, and above 380°C, respectively.[4] The characterization of obtained aluminum (III) salts is also known,[5] but there is no report of its application in organic synthesis.

On the other hand, methyl chlorodifluoroacetate (**2**) was prepared by fluorination of methyl trichloroacetate with the mixture of antimony (V)-chloride and antimony (III)-fluoride.[6]

Here $AlF_m(OH)_{3-m}$ (**3**) was prepared by heating $AlF_3{\cdot}3H_2O$,

Table 1. Effect of treatment temperature of $AlF_3{\cdot}3H_2O$ on yield of **2**

No.	Pre-treatment temp. °C	Surface area m^2/g	Vs cc/g	Yield of **2** (%)	Recovery of **1** (%)
1	20	[a]	[a]	5	82
2	100	3	0.0	42	44
3	200	144	0.29	77	0
4	300	70	0.34	75	1
5[b]	400	51	0.32	43	1
6[b]	500	50	0.29	33	0
7[b]	700	8	0.0	12	0.5

1.2 g $AlF_3{\cdot}3H_2O$ treated for 10 h under different temperatures was used in each reaction; starting material **1** ($CH_3OCFClCF_2Cl$) 2.5 mmol for each reaction; reaction temp. 200°C. Reaction time 1 h.

[a] Surface area and Vs cannot be measured.

[b] Decomposition products, CH_3Cl, CH_3F, and $FCOCF_2Cl$, were formed.

Keywords: $AlF_m(OH)_{3-m}$; 1,2-dichloro-1,1,2-trifluoro-2-methoxyethane; methyl chlorodifluoroacetate.

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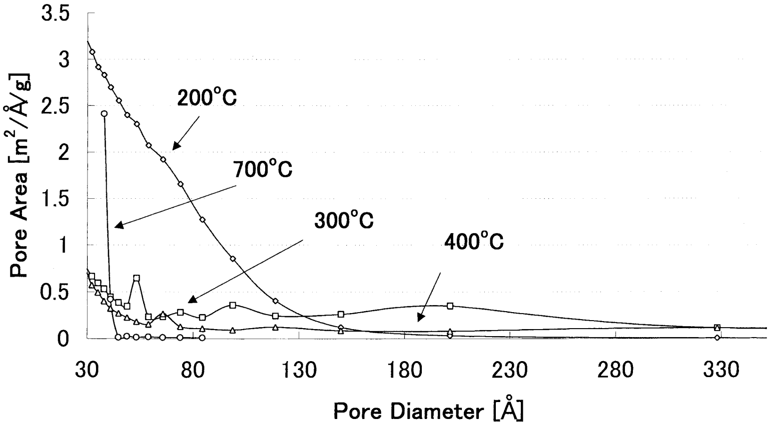


Figure 1. Relationship between treatment temperature of $AlF_3 \cdot 3H_2O$ and distribution of pore area.

and it was used for the first time as a reagent of organic synthesis. A novel synthetic method is described to prepare **2** by the reaction of 1,2-dichloro-1,1,2-trifluoro-2-methoxyethane (**1**) with **3** as a reactant.

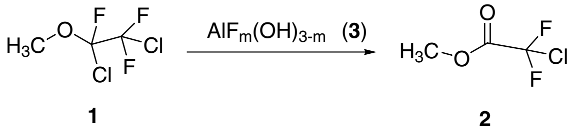
2. Results and discussion

2.1. Characterization of 3

BET surface areas and distribution of pore area of various **3** obtained by heating $AlF_3 \cdot 3H_2O$ under different temperatures are shown in Table 1 and Fig.1. The results indicate **3** exhibited a large surface area (144 m^2/g) when heating temperature was about 200°C. The surface area decreased from 144 m^2/g to 70 m^2/g when heating temperature increased from 200°C to 300°C. In the temperature range between 300°C and 500°C, the surface area of **3** was from 70 m^2/g to 50 m^2/g, and the pore volume was almost the same, which shows the structure of **3** does not change so much in this range of temperature. The surface area and pore volume of **3** at 700°C decreased to 8 m^2/g and 0 cc/g, which is attributed to sintering of **3** at this temperature.

2.2. Effect of treatment temperature of $AlF_3 \cdot 3H_2O$

3 prepared under different temperatures were used in the reaction (Scheme 1). The results are shown in Table 1. When $AlF_3 \cdot 3H_2O$ was treated under 200°C, **2** was obtained in 77% yield. The yield of **2** decreased from 75% to 12% and chlorodifluoroacetyl fluoride, CH_3Cl, and CH_3F were formed when treatment temperature of $AlF_3 \cdot 3H_2O$ was increased from 300°C to 700°C.



Scheme 1.

To investigate the reaction mechanism, XPS of **3** treated under 200°C and 700°C was measured and the results are listed in Table 2. It indicates the difference of chemical states of oxygen, fluorine and aluminum on surface of **3** at different temperatures. In the case of $AlF_3 \cdot 3H_2O$ treated at 200°C, the Binding Energy (BE) of O1s, Al2p and F1s correspond to the chemical state of O, F and Al of $AlF_m(OH)_{3-m}$. In the case of $AlF_3 \cdot 3H_2O$ treated at 700°C, the BE of O1s and F1s, and Al2p indicate there are two coexisting phases on the surface of **3**. They correspond to γ-Al_2O_3 and α-AlF_3.[7]

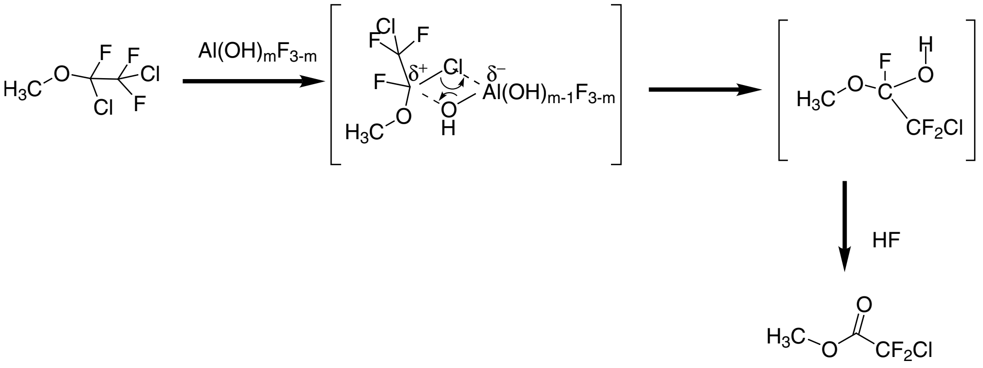
The above results indicate that the reaction of **1** with $AlF_m(OH)_{3-m}$ gives **2** in high yield. The results can be explained by the reaction mechanism as follows (Scheme 2); $AlF_m(OH)_{3-m}$ works as a strong Lewis acid in the reaction. Aluminum atom in $AlF_m(OH)_{3-m}$ coordinates to chlorine atom to polarize the α-carbon more positive. Nucleophilic attack of the hydroxy group of $AlF_m(OH)_{3-m}$ to the α-carbon gives intermediate hemiacetal, and the removal of HF from this hemiacetal to form ester **2**.[8]

On the other hand, in the case of $AlF_3 \cdot 3H_2O$ treated at 700°C, $AlF_m(OH)_{3-m}$ was not observed, however γ-Al_2O_3 and α-AlF_3 exist on the surface by XPS. The reaction of **1** with coexisting γ-Al_2O_3 and α-AlF_3 results in the formation of CH_3Cl, CH_3F and chlorodifluoroacetyl, which suggests that either γ-Al_2O_3 or α-AlF_3 makes **1** decompose. To confirm this, the reaction of **1** with γ-Al_2O_3 or α-AlF_3 was

Table 2. The characterization of surface of $AlF_m(OH)_{3-m}$ by XPS

Binding Energy (eV)	Experimental data Pre-treatment temp. °C 200	700	γ-Al_2O_3	Reference data[7] α-AlF_3	$AlF_{2.3}(OH)_{0.7} \cdot H_2O$
O1s	534.4	531.1	531.9		534.6, 532.6
F1s	686.2	686.8		687.5	687.0
Al2p	76.2	77.1, 74.3	74.4	77.1	75.8

XPS Data obtained with reference samples (Static Charge Reference: C1s =284.8 eV).



Scheme 2. Mechanism

Table 3. Effect of reagent on main product

No.	Reagent	**1** (mmol)	Yield of **2** (%)	Recovery of **1** (%)
1	$AlF_3\cdot 3H_2O$	2.5	5	82
2	α-AlF_3	2.6	5	65
3	γ-Al_2O_3	2.6	13	4[a]
4	KOH	2.6	0	70

Reaction temperature 200°C, reaction time 1 h, reagent 2 g for each reaction.

[a] Main decomposition product CH_3Cl.

attempted and the results are shown in Table 3. When **1** reacted with γ-Al_2O_3 and α-AlF_3, **2** was obtained in 13% yield and 5% yield, respectively, which indicates an hydroxy group on the surface of aluminum salts is necessary for the formation of **2**.

When untreated $AlF_3\cdot 3H_2O$ was used in the reaction, **2** was obtained in only 5% yield, which can be attributed to the fact that $AlF_3\cdot 3H_2O$ does not show Lewis acidity because the vacant orbital of aluminum in AlF_3 is occupied by H_2O.[7,9] When **1** reacted with KOH, 70% of **1** was recovered and **2** was not formed, which indicates that not only an hydroxy group but also a Lewis acid is necessary for the formation of **2**.

3. Conclusion

$AlF_m(OH)_{3-m}$ was prepared by heating $AlF_3\cdot 3H_2O$, and it was used for the first time as a reagent of organic synthesis. Methyl chlorodifluoroacetate is obtained in 77% yield when 1,2-dichloro-1,1,2-trifluoro-2-methoxyethane is reacted with $AlF_m(OH)_{3-m}$ prepared under 200°C.

4. Experimental

4.1. Chemicals

$AlF_3\cdot 3H_2O$ was purchased from Aldrich Chem. Co. 1,1,2-Trifluoro-2-methoxyethene (**4**) was from Daikin Fluorochemical Co. Anhydrous hydrogen fluoride (AHF) was obtained from Morita Chem. Ind. Co. Ltd.

4.2. Instruments

The BET surface area and the distribution of pore diameter of **3** were determined by means of low temperature adsorption of nitrogen using NOVA 1000 (Yuasa Ionics Co.). **3** was degassed under vacuum for 3 h before measurement.

^1H NMR and ^{19}F NMR were recorded on JNM-EX270 (JEOL, 270 MH_Z) at 25°C with $(CH_3)_4Si$ and $CFCl_3$, respectively, as internal reference in $CDCl_3$ as a solvent.

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

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 was 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, $\sim$1cc He/min; split ratio 45:1; sample size 1.2 μl; pressure 50 kPa.

X-Ray photoelectron spectroscopy (XPS) was used to determine the surface composition of **3**. XPS spectra were taken using a PH1-ESCA 5500 Electron Spectrometer equipped with a magnesium anode (Mg $K\alpha$=1254 eV) operated at 150 W. 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. The results were shown in Table 2.

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.

4.3. Preparation of 1

18 mmol of **4** and the same amount of gaseous chlorine were introduced to a 200 ml glass reactor cooled to −196°C. The reactor was allowed to warm up from −196°C to room temperature during 5 minutes. The products (97% yield) were determined by FT-IR, GC-MS and ^1H NMR and ^{19}F NMR. The data of IR, MS and NMR chemical shifts of **1** are listed as follows; IR: 2968 (w), 1456 (w), 1287(m), 1214(s), 1183 (vs), 1107 (s), 1050 (m), 1014 (s), 967 (s),901 (w),832 (m). MS: m/e: 15 $^+CH_3$; 85 $^+CClF_2$; 97 $^+CH_3OCFCl$; 147 $^+CH_3OCFClCF_2$; 151 $^+CFClCF_2Cl$; 163 $^+CH_3OCFClCFCl$.

^1H NMR: δ (ppm) 3.80 (s, 3H); ^{19}F NMR: δ (ppm) −74.56 (t,1F, *J*=6.10); δ (ppm) −69.43 (d,2F, *J*=6.10).

4.4. Reaction of 1 with 3

3 was prepared by the following procedure: around 100 g of $AlF_3\cdot 3H_2O$ was treated under different temperatures between 20°C and 700°C and kept for 10 h at the same temperature (see Table 1). About 1.2 g of **3** was measured and it was placed in an 80 cm^3 stainless steel reactor, then 2.5 mmol of **1** was transferred into the reactor using vacuum line. The reactor was heated to 200°C and kept for 1 h under stirring. The products were transferred to a trap (−196°C) and separated by trap-to-trap distillation (−90°C and −196°C), and their amount and molecular weight were measured. Then main products were analyzed by FT-IR, GC-MS and ^1H NMR and ^{19}F NMR. The results are shown in Table 1. The spectra data of **2** were listed as follows; IR: 2969 (w); 1801(vs); 1449 (m); 1314 s; 1191 (vs); 1132 (vs); 1006 (s); 946 (s). MS peaks m/e: 15 $^+CH_3$; 50 $^+CF_2$; 59 $^+CH_3CO$; 85 $^+CF_2Cl$; 109 $^+CH_3COCF_2$; 125 $^+CH_3COCFCl$; 159 $^+CH_2OCOCF_2Cl$. ^1H NMR: δ (ppm) 3.98 (s,3H); ^{19}F NMR: δ (ppm) −64.29 (s, 2F).

Chlorodifluoroacetyl fluoride was obtained as a main product when $AlF_3\cdot 3H_2O$ was heated to 700°C before the reaction. FT-IR data and ^{19}F NMR data were as follows; IR: 2980 (w); 1888 (vs); 1273 (m); 1193 (s); 1106 (vs); 1028 (w); 969 (s). ^{19}F NMR: δ (ppm) 11.45 (s,1F); F2(2) δ −65.04 (s, 2F).

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