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Metal halide catalysts to synthesize dichloropentafluoropropanes by the reaction of dichlorofluoromethane with tetrafluoroethylene

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ABSTRACT

A series of metal halides were studied as Lewis acid catalysts for the reaction of dichlorofluoromethane with tetrafluoroethylene to form dichloropentafluoropropanes (HCFC-225s) which are being manufactured as an alternative to CFC-113. Zirconium tetrachloride and hafnium tetrachloride had high catalytic activity in the reaction and much better selectivity towards HCFC-225ca and HCFC-225cb than conventional aluminum trichloride. The Cl-F exchange reaction of zirconium tetrachloride or titanium tetrachloride with chlorofluoromethane produced metal chlorofluorides. When chlorofluoromethane-treated $ZrCl_4$ or $TiCl_4$ were used as a catalyst the reaction of dichlorofluoromethane with tetrafluoroethylene proceeded without the induction period that was observed using $ZrCl_4$ or $TiCl_4$ without pretreatment, indicating that the metal chlorides needed an activation time to become chlorofluorides before developing catalytic activity. Trichlorofluoromethane-treated $ZrCl_4$, metal chlorofluoride, was characterized by thermogravimetry (TG), differential thermal analysis (DTA), and X-ray diffraction.

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1. Introduction

In 1974, F.S. Rowland and M. Molina were the first to publish a paper [1] warning that chlorofluorocarbons (CFCs) could be split apart by solar radiation to produce chlorine atoms, which could catalyze the destruction of Earth's protective ozone layer. Following the discovery of the Antarctic ozone hole in late 1985, governments recognized the need for measures to reduce the production and consumption of some CFCs (CFC-11, 12, 113, 114, and 115) and Halons (1211, 1301, 2402). The Montreal Protocol on Substances that Deplete the Ozone Layer was adopted in 1987 and the Protocol was adjusted to accelerate the phase out schedules in London in 1990, Copenhagen in 1992, Vienna in 1995, Montreal in 1997 and Beijing in 1999. In the late 80s, Asahi Glass, formerly one of the major producers of CFCs, began to work on developing alternative CFCs and finally succeeded in manufacturing dichloropentafluoropropane, HCFC-225s (225ca: $CF_3CF_2CHCl_2$, 225cb: $CClF_2CF_2CHClF$), an alternative to CFC-113 (CCl_2FCClF_2) that had been widely used as an industrial solvent [2,3]. CFCs had already been phased out by 1996, and all HCFCs, including HCFC-225s, are subject to additional reductions in production and consumption with a final phase out in developed countries in 2020. In 1949 the first synthesis of HCFC-225 was reported which was by the addition reaction of dichlorofluoromethane ($CHCl_2F$) with tetrafluoroethylene ($CF_2 = CF_2$) in the presence of aluminum trichloride ($AlCl_3$) [4]. Later Paleta et al. [5] identified two isomers of dichloropentafluoropropanes, HCFC-225ca and 225cb, which were given in the same addition reaction. Aluminum chloride, one of the strong Lewis acids, is commonly used as a catalyst in Friedel-Crafts reactions, and aluminum chloride needs to become aluminum chlorofluoride ($AlCl_xF_{3-x}$) to be catalytically active [6]. Recently aluminum chlorofluoride and bromofluoride were thoroughly reviewed [7]. In the review, the authors mentioned the potential interest for zirconium chlorofluoride for catalytic reactions where aluminum chlorofluoride behaves as a too strong Lewis acid, but they could not confirm its catalytic activity. The purpose of this paper is to show that $ZrCl_4$ and $HfCl_4$ can be used as appropriate catalysts for the addition reaction of $CHCl_2F$ with $CF_2{=}CF_2$ to produce HCFC-225s because they have high catalytic activity and even better selectivity towards object products than $AlCl_3$, the conventional catalyst. Furthermore, this paper presents the activation process of catalysts in forming metal chlorofluorides from a reaction of metal chlorides with chlorofluoromethanes.

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2. Experimental

2.1. Reactions of dichlorofluoromethane with tetrafluoroethylene using metal halide catalysts

Before using the catalysts for the reaction, gallium trichloride (3.0 g), tantalum pentachloride (8.5 g), and titanium tetrachloride (17.3 g) were all mixed with $CHCl_2F$ (50 g, boiling point: 8.9 °C) in a 200 ml autoclave (Hastelloy C) and stirred at room temperature for 3, 4, and 12 h, respectively. After removing the liquid, the remaining solids were dried under reduced pressure at about 40 °C. Then the dried solids were used as catalysts. The other catalysts, BCl_3, $HfCl_4$, $ZrCl_4$, and $AlCl_3$ were used without being treated with $CHCl_2F$. In addition to $CHCl_2F$-treated $TiCl_4$, titanium tetrachloride was also used as a catalyst without $CHCl_2F$ treatment.

A 200 ml autoclave (Hastelloy C) containing a catalyst and dichlorofluoromethane (103 g, 1.0 mol) was vacuumed to remove oxygen at −196 °C. The inside temperature was gradually raised, while tetrafluoroethylene was fed intermittently, keeping the reaction temperature and pressure shown in Table 1. After the mixture in the autoclave was continuously stirred for a certain period of time, the inside temperature was lowered to 0 °C and the pressure was reduced to ambient pressure by releasing the inner gases. The identification of the reaction products in the liquid phase was made by gas chromatography (GC) with a flame ionization detector and a DB-1301 capillary column (Agilent J&W GC Columns), ^{19}F NMR, ^{1}H NMR and GC–mass spectroscopy (MS) as shown in our previous paper [15]. The main products were 3,3-dichloro-1,1,1,2,2-pentafluoropropane (225ca, boiling point: 51 °C), 1,3-dichloro-1,1,2,2,3-pentafluoropropane (225cb, boiling point: 56 °C), 1,3,3-trichloro-1,1,2,2-tetrafluoropropane (224ca, boiling point: 92 °C), and chloroform (boiling point: 61 °C). As minor products, 2,2-dichloro-1,1,1,3,3-pentafluoropropane (225aa, boiling point: unknown), 2,3-dichloro-1,1,1,2,3-pentafluoropropane (225ba, diastereomer I, II, boiling points: unknown), and chlorodifluoromethane (boiling point: −41 °C) were detected. One of the HCFC-225ba diastereomers was not separable from HCFC-225aa by gas chromatography. Quantification of reaction products was carried out by gas chromatography. The $CHCl_2F$ conversions and product selectivities in Table 1 were calculated by using GC relative molar response factors as follows: HCFC-225ca (1.00), HCFC-225cb (0.924), HCFC-224ca (1.037), $CHCl_3$ (0.265), $CHCl_2F$ (0.153), and $CHCl_2F_2$ (0.237), HCFC-225aa (1), HCFC-225ba (1), and others (1). The relative molar response factors were determined by experiments using a mixture of pure HCFCs and halomethanes, except for HCFC-225aa, HCFC-225ba and others, which employed a tentative factor, 1.

2.2. Reactions of 3,3-dichloro-1,1,1,2,2-pentafluoropropane (225ca) and 1,3-dichloro-1,1,2,2,3-pentafluoropropane (225cb) with trichlorofluoromethane-treated aluminum trichloride

Trichlorofluoromethane (CCl_3F)-treated $AlCl_3$ was prepared in the following manner. Aluminum trichloride (100 g, 0.75 mol) and CCl_3F (1000 g, 7.3 mol, boiling point: 24 °C) were mixed and stirred slowly in an autoclave at 0 °C for 12 h. Then the liquid was removed and the remaining solid was dried under reduced pressure at about 40 °C.

HCFC-225ca and 225cb (100 g, 0.49 mol) were separately mixed with CCl_3F-treataed $AlCl_3$ (10 g) in an autoclave and stirred slowly at room temperature for 11 h. The main reaction products in the liquid phase were analyzed by gas chromatography and ^{19}F NMR, and minor products were identified by GC–MS. The conversions and product selectivities were calculated by using GC as in Section 2.1.

2.3. Reaction of zirconium tetrachloride with trichlorofluoromethane

The mixture of $ZrCl_4$ (50 g, 0.2 mol) and CCl_3F (500 g, 3.6 mol) were stirred slowly in an autoclave at 0 °C. Ten grams of the mixture in a heterogeneous liquid phase was repeatedly taken out at intervals. After removing the liquid, the solid was dried under reduced pressure at about 40 °C. The fluorine contents in the sample were determined using ion chromatography after extraction by sodium carbonate fusion [16]. In the case of $ZrCl_4$, after treating the solid with CCl_3F for 1 h, the fluorine content was 17.7 wt%, a fluorine content equivalent to $ZrCl_{2.1}F_{1.9}$. Along with this solid, $ZrCl_4$ (Junsei Chemical, 99% reagent grade) and ZrF_4 (Aldrich, 99% reagent grade) were characterized by X-ray diffraction, thermogravimetry (TG), and differential thermal analysis (DTA). X-ray diffraction patterns of the samples were recorded at room temperature on a Rigaku X-ray diffractometer, RINT2500, using Cu Kα radiation (1.5405 Å). For thermal analyses, a differential thermal analysis system, TG-DTA 2010SA (Bruker AXS K.K.), was used.

2.4. Reaction of dichlorofluoromethane with tetrafluoroethylene in 1,1,1-trichloropentafluoropropane

The mixture of 1,1,1-trichloropentafluoropropane (CFC-215cb, 600 g) and a catalyst, CCl_3F-treated $ZrCl_4$ (6.0 g, fluorine content:

Table 1

Reactions of $CHCl_2F$ with $CF_2{=\!=}CF_2$ using metal chloride catalysts

Catalysts	BCl_3	$GaCl_3$[a]	$TaCl_5$[a]	$TiCl_4$[a]	$TiCl_4$	$HfCl_4$	$ZrCl_4$	$AlCl_3$
Reaction conditions								
Catalyst (mol%/$CHCl_2F$)	11.9	1.7	2.4	9.1	9.1	3.1	4.3	7.5
Temperature (°C)	40	25	25	25	25	0	0	0
Pressure (MPa)	1.0	1.0	1.0	1.0	1.0	0.5	0.5	0.5
Time (h)	14	3	6	6	8	2	2	2
$CHCl_2F$ conversion (%)	12	29	60	100	100	100	100	100
Selectivity (%)								
HCFC225ca	Trace	4.7	26.3	32.5	29.0	43.7	44.4	59.5
HCFC225cb	Trace	6.5	27.8	38.2	30.0	44.4	44.0	28.5
HCFC-225aa, ba	–	–	–	<0.05	<0.05	<0.05	<0.05	2.0
HCFC224ca	Trace	11.0	44.4	27.6	27.0	9.3	9.3	6.5
$CHCl_3$	>99	77.0	0.5	1.2	13.2	2.1	1.7	2.9
Others	–	0.9	1.0	0.5	0.8	0.8	0.6	0.5
Total	100	100	100	100	100	100	100	100
225cb/225ca	–	1.38	1.06	1.18	1.04	1.02	0.99	0.48
225s/224ca	–	1.02	1.22	2.56	2.19	9.49	9.49	13.51

[a] Catalysts were treated with $CHCl_2F$ before using for the reaction.

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