

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
5 August 2010 (05.08.2010)

(10) International Publication Number
WO 2010/087465 A1

PCT

(51) International Patent Classification:
C07C 17/00 (2006.01) C07C 21/18 (2006.01)

(21) International Application Number:
PCT/JP2010/051300

(22) International Filing Date:
25 January 2010 (25.01.2010)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/147,576 27 January 2009 (27.01.2009) US

(71) Applicant (for all designated States except US): **DAIKIN INDUSTRIES, LTD.** [JP/JP]; Umeda Center Building, 4-12, Nakazaki-Nishi 2-Chome, Kita-ku, Osaka-shi, Osaka, 5308323 (JP).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **KOMATSU, Yuzo** [JP/JP]; c/o Yodogawa Seisakusho, DAIKIN INDUSTRIES, LTD., 1-1, Nishihitotsuya, Settsu-shi, Osaka, 5660044 (JP). **SUGIYAMA, Akinari** [JP/JP]; c/o Yodogawa Seisakusho, DAIKIN INDUSTRIES, LTD., 1-1, Nishihitotsuya, Settsu-shi, Osaka, 5660044 (JP). **SHIBANUMA, Takashi** [JP/JP]; c/o Yodogawa Seisakusho, DAIKIN INDUSTRIES, LTD., 1-1, Nishihitotsuya, Settsu-shi, Osaka, 5660044 (JP).

(74) Agent: **Saegusa & Partners**; Kitahama TNK Building, 1-7-1, Doshomachi, Chuo-ku, Osaka-shi, Osaka, 5410045 (JP).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) Title: PROCESS FOR PREPARING FLUORINE-CONTAINING OLEFIN

(57) Abstract: The present invention provides a process for preparing a fluorine-containing olefin represented by Formula (2): $R^1CF=CH(R^2)$ wherein R^1 is F, H, $F(CF_2)_n$ (n is an integer ranging from 1 to 10) or $H(CF_2)_m$ (m is an integer ranging from 1 to 10) and R^2 is H, $F(CF_2)_n$ (n is an integer ranging from 1 to 10) or $H(CF_2)_m$ (m is an integer ranging from 1 to 10), the process including a step of reacting a fluorine-containing alcohol represented by Formula (1): $R^1CF_2CH(R^2)OH$, wherein R^1 and R^2 are the same as above, with a reducing gas in the presence of a specific metal oxide. According to the process of the invention, a desired fluorine-containing olefin can be produced with high selectivity in a single reaction step using a fluorine-containing alcohol as a raw material.



WO 2010/087465 A1

-1-

Description

Title of Invention: PROCESS FOR PREPARING FLUORINE-CONTAINING OLEFIN

5 Technical Field

The present invention relates to a process for preparing a fluorine-containing olefin.

Background Art

10 Fluorine-containing olefin compounds are useful as monomer components for polymer materials, and are also widely used industrially as raw materials for producing hydrofluorocarbons (HFC) and the like, which are used for refrigerants, cleaning agents, foaming agents and the like.
15 Particularly, a fluorine-containing propylene compound represented by the chemical formula $\text{CF}_3\text{CF}=\text{CH}_2$ exhibits a low toxicity and low global warming potential. Therefore, this compound is drawing attention as a promising alternative solvent. Accordingly, a method of producing $\text{CF}_3\text{CF}=\text{CH}_2$ with high selectivity
20 in a single reaction step while using inexpensive materials and maintaining industrially advantageous conditions is desired.

Preparing a fluorine-containing olefin by substituting the hydroxy group of a fluorine-containing alcohol with a halogen, followed by dehalogenation of the obtained halogenide in the
25 presence of zinc or a like metal is a known method.

A method that can be used for producing a halogenide is disclosed, for example, in Nonpatent Literature (NPL) 1 listed below. In this method, a fluorine-containing alcohol represented by $\text{R}_f\text{CF}_2\text{CH}_2\text{OH}$, wherein R_f is a fluorine-containing hydrocarbon
30 group, is converted into a p-toluene sulfonic acid ester, and the obtained p-toluene sulfonic acid ester is reacted with a halogenide, such as sodium iodide, thereby producing an iodide represented by $\text{R}_f\text{CF}_2\text{CH}_2\text{I}$. This method is useful as a laboratory method; however, it requires an expensive reagent, such as p-
35 toluene sulfonic acid chloride, in the first reaction step.

-2-

Furthermore, the second reaction step also uses an expensive reagent, such as sodium iodide, and the reaction is carried out at a high temperature using a solvent having a high boiling point, such as diethylene glycol. Therefore, this method requires the disposal of a large amount of waste reaction liquid that has a high boiling point. For these reasons, the method disclosed in Nonpatent Literature 1 is not appropriate for industrial production.

Patent Literature (PTL) 1 listed below discloses another example of a halogenide production process in which a fluorine-containing alcohol represented by $R_fCF_2CH_2OH$ is reacted with a thionyl halide in the presence of an amide compound, thereby synthesizing a halogenide represented by R_fCF_2CHX , wherein X is Cl or Br. Although this reaction is simpler than the aforementioned method, it has some disadvantages. For example, the method uses a toxic compound such as thionyl chloride, and produces a large amount of acid gas. Accordingly, this method is also not appropriate for industrial production.

The halogenide obtained through the above method can be converted into an olefin compound represented by $R_fCF=CH_2$ by subjecting it to a dehalogenation reaction in the presence of zinc. However, when the halogenide represented by $R_fCF_2CH_2X$ is a chloride, the reaction speed is extremely low, and therefore the yield of the fluorine-containing olefin tends to decrease. Moreover, because the dehalogenation reaction generally uses an organic solvent such as methanol, tetrahydrofuran, dimethyl formamide or the like, waste solvent treatment is necessitated and a treatment for discarding zinc halide containing unreacted zinc is required. Further, since the method through the preparation of a halogenide requires reacting the fluorine-containing alcohol in two or more steps, the desirable efficiency is not ensured.

Furthermore, Patent Literature (PTL) 2 listed below discloses a method of reacting a fluorine-containing alcohol, such as $H(CF_2)_4CH_2OH$ or $CF_3CF_2CH_2OH$, with hydrogen, thereby

-3-

producing a fluorine-containing olefin represented by $H(CF_2)_3CF=CH_2$, $CF_3CF=CH_2$ or the like. However, in this method, when $CF_3CF_2CH_2OH$ is used as a raw material, the conversion is 25%, the selectivity is 70%, and a large amount of by-product is produced.

Furthermore, Patent Literature (PTL) 3 listed below discloses a method for producing $CF_3CF=CH_2$ with a conversion of 60% and a selectivity for HFO-1234yf of 58%, by using methane instead of hydrogen used in the method of Patent Literature 2. However, selectivity is low in this method compared with the method using hydrogen, and the method tends to produce a large amount of C_1 or C_2 by-product.

Accordingly, there are many disadvantages to using the existing processes for preparing fluorine-containing olefins for industrial application.

Citation List

Patent Literature

- PTL 1: US Patent No. 3038947
PTL 2: Japanese Unexamined Patent Publication No. H01-207250
PTL 3: US Patent No. 7026520

Non Patent Literature

- NPL 1: J. AM. CHEM. SOC., 1953, 75, 5978

Summary of Invention

Technical Problem

The present invention was made in view of the aforementioned present circumstances of the prior art. An object of the present invention is to provide a relatively simple process for preparing fluorine-containing olefin that can solve the above described disadvantages of the existing methods and be carried out using a simple industrial process. Particularly, the process of the present invention produces a desired fluorine-containing olefin with high selectivity, generates less waste, and can be performed with a simple reaction process.

-4-

Solution to Problem

The inventors of the present invention conducted extensive research to achieve the above mentioned object. They found that a method of reacting a fluorine-containing alcohol with a reducing gas in the presence of a specific metal oxide enables the production of a desired fluorine-containing olefin in a single reaction step while ensuring high selectivity; thus, efficient and inexpensive production of fluorine-containing olefins with less waste production is possible. The inventors completed the present invention based on these findings.

Specifically, the present invention provides the following processes for preparing fluorine-containing olefins.

Item 1. A process for preparing a fluorine-containing olefin represented by Formula (2): $R^1CF=CH(R^2)$ wherein R^1 is F, H, $F(CF_2)_n$ - (n is an integer ranging from 1 to 10) or $H(CF_2)_m$ - (m is an integer ranging from 1 to 10) and R^2 is H, $F(CF_2)_n$ - (n is an integer ranging from 1 to 10) or $H(CF_2)_m$ - (m is an integer ranging from 1 to 10),

the process comprising reacting a fluorine-containing alcohol represented by Formula (1): $R^1CF_2CH(R^2)OH$, wherein R^1 and R^2 are the same as above, with a reducing gas in the presence of at least one metal oxide selected from the group consisting of Periodic Table Group 3 element-containing oxides, Periodic Table Group 4 element-containing oxides, Periodic Table Group 5 element-containing oxides, Periodic Table Group 6 element-containing oxides, Periodic Table Group 11 element-containing oxides, Periodic Table Group 12 element-containing oxides, Periodic Table Group 13 element-containing oxides, Periodic Table Group 14 element-containing oxides, and Periodic Table Group 15 element-containing oxides.

Item 2. The process according to Item 1, wherein the reducing gas is hydrogen.

Item 3. The process according to Item 1 or 2, wherein the metal oxide is at least one member selected from the group consisting of Periodic Table Group 3 element-containing oxides,

Periodic Table Group 4 element-containing oxides, Periodic Table Group 11 element-containing oxides, and Periodic Table Group 13 element-containing oxides.

Item 4. The process according to any one of Items 1 to 3, wherein the metal oxide is an oxide containing at least one element selected from the group consisting of Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Ti, Zr, Hf, Cu, Ag, Au, Ga, and In.

Item 5. The process according to any one of Items 1 to 4, wherein the fluorine-containing alcohol represented by Formula (1) is a fluorine-containing alcohol represented by Formula (1'): $R^1CF_2CH_2OH$, wherein R^1 is F, H, $F(CF_2)_n-$ (n is an integer ranging from 1 to 10) or $H(CF_2)_m-$ (m is an integer ranging from 1 to 10).

Item 6. The process according to any one of Items 1 to 5, wherein the fluorine-containing alcohol represented by Formula (1) is 2,2,3,3,3-pentafluoro-1-propanol.

Item 7. The process according to any one of Items 1 to 6, wherein the reaction is performed in a gas phase under atmospheric pressure or elevated pressure at a temperature range from 200°C to 800°C.

The process for preparing a fluorine-containing olefin according to the present invention is characterized by the reaction of a fluorine-containing alcohol and a reducing gas in the presence of a specific metal oxide. The process for preparing the fluorine-containing olefin according to the present invention is more specifically described below.

▪Fluorine-Containing Alcohol

In the present invention, a fluorine-containing alcohol represented by Formula (1): $R^1CF_2CH(R^2)OH$ is used as a raw material. In Formula (1), R^1 represents F, H, $F(CF_2)_n-$ (n is an integer ranging from 1 to 10), or $H(CF_2)_m-$ (m is an integer ranging from 1 to 10), and R^2 represents H, $F(CF_2)_n-$ (n is an integer ranging from 1 to 10), or $H(CF_2)_m-$ (m is an integer

ranging from 1 to 10).

Examples of these fluorine-containing alcohols include compounds represented by the formula: $F(CF_2)_nCH_2OH$ (n is an integer ranging from 1 to 10), compounds represented by the formula: $H(CF_2)_nCH_2OH$ (n is an integer ranging from 1 to 10), and
5 compounds represented by the formula: $F(CF_2)_nCH(CF_3)OH$ (n is an integer ranging from 1 to 4).

When R^2 is an electron-withdrawing group, the conversion of the raw material tends to decrease. Accordingly,
10 among the above compounds as the fluorine-containing alcohol represented by Formula (1), a fluorine-containing alcohol represented by Formula (1'): $R^1CF_2CH_2OH$, wherein R^1 is F, H, $F(CF_2)_n-$ (n is an integer ranging from 1 to 10), or $H(CF_2)_m-$ (m is an integer ranging from 1 to 10) is preferable.

15 Examples of these fluorine-containing alcohols include 2,2,3,3,3-pentafluoro-1-propanol, 2,2,3,3-tetrafluoro-1-propanol, trifluoroethanol, difluoroethanol, 2,2,3,3,4,4,4-heptafluoro-1-butanol, 2,2,3,3,4,4-hexafluoro-1-butanol, 1H,1H-perfluoro-1-pentanol, 1H,1H,5H-perfluoro-1-pentanol, 1H,1H-perfluoro-1-hexanol,
20 1H,1H-perfluoro-1-heptanol, 1H,1H,7H-perfluoro-1-heptanol, 1H,1H-perfluoro-1-octanol, 1H,1H-perfluoro-1-nonanol, 1H,1H,5H-perfluoro-1-nonanol, and the like.

The above fluorine-containing alcohols represented by Formula (1) are all known compounds that can be easily obtained.

25

▪Metal Oxide

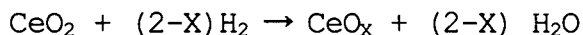
The production process of the present invention uses, as a catalyst, at least one metal oxide selected from the group consisting of Periodic Table Group 3 element-containing oxides, Periodic Table Group 4 element-containing oxides, Periodic Table Group 5 element-containing oxides, Periodic Table Group 6 element-containing oxides, Periodic Table Group 11 element-containing oxides; Periodic Table Group 12 element-containing oxides, Periodic Table Group 13 element-containing oxides,
30 Periodic Table Group 14 element-containing oxides, and Periodic
35

Table Group 15 element-containing oxides.

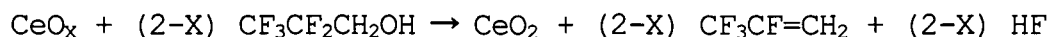
A desired fluorine-containing olefin can be obtained in a single reaction step with high selectivity by reacting the fluorine-containing alcohol represented by Formula (1) and a
5 reducing gas in the presence of at least one of the above metal oxides, under the conditions that are described later in this specification.

The principle of this production method is not completely clear; however, heating at least one of the above
10 metal oxides in the presence of a reducing gas is assumed to have a tendency to cause an oxygen deficiency to the oxide. When the oxygen deficiency is caused, the resulting oxide has a high affinity to oxygen. This metal oxide, which is characterized by its high affinity to oxygen due to its oxygen-deficiency, is
15 assumed to be capable of reacting with a compound having a low electron-donating oxygen atom, such as a fluorine-containing alcohol, taking the oxygen from the fluorine-containing alcohol, thereby developing the reaction to produce a fluorine-containing olefin.

For example, when a cerium oxide is used as the metal
20 oxide and hydrogen is used as the reducing gas, oxygen is taken from the crystal lattice as a result of the reduction caused by hydrogen, thereby forming an oxygen-deficient cerium oxide (CeO_x , wherein x is a positive number less than 2) according to the
25 following reaction formula.



It is assumed that the cerium oxide then reacts with the fluorine-containing alcohol in a hydrogen gas atmosphere according to the following reaction formula, thereby serving as a
30 catalyst.



It is further assumed that, thereafter, the reproduced CeO_2 is reduced to a low valent state again by the hydrogen in the system, thereby completing the catalyst cycle.

35 In contrast, Pd, Rh, Pt, Ni and like metals are not

desirable because, although they are capable of causing an oxygen deficiency, their low oxygen affinity causes a side reaction such as a reduction of C-F bond to C-H bond.

Among the above metal oxides, at least one metal oxide
5 selected from the group consisting of Periodic Table Group 3 element-containing oxides, Periodic Table Group 4 element-containing oxides, Periodic Table Group 12 element-containing oxides, and Periodic Table Group 13 element-containing oxides is preferable in terms of its high affinity to oxygen.

10 The present invention particularly favors an oxide containing at least one element selected from the group consisting of Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Ti, Zr, Hf, Cu, Ag, Au, Ga and In. Examples of these oxides include Sc_2O_3 , Y_2O_3 , La_2O_3 , CeO_2 , Pr_6O_{11} , Nd_2O_3 , Pm_2O_3 ,
15 Sm_2O_3 , Eu_2O_3 , Gd_2O_3 , Tb_4O_7 , Dy_2O_3 , Ho_2O_3 , Er_2O_3 , Tm_2O_3 , Yb_2O_3 , Lu_2O_3 , TiO_2 , Ti_2O_3 , TiO , ZrO_2 , HfO_2 , CuO , Cu_2O , Ag_2O , Au_2O_3 , Ga_2O_3 , and In_2O_3 .

Among these metal oxides, Sc_2O_3 , Y_2O_3 , La_2O_3 , CeO_2 , Nd_2O_3 , Sm_2O_3 , Gd_2O_3 , Dy_2O_3 , Ho_2O_3 , Er_2O_3 , Tm_2O_3 , Yb_2O_3 , ZrO_2 , HfO_2 , CuO , Cu_2O , Ag_2O , Ga_2O_3 , In_2O_3 and the like are particularly preferable.

20 Among these metal oxides, CuO , Cu_2O , CeO_2 , In_2O_3 , Ag_2O , Hf_2O , Sc_2O_3 , Gd_2O_3 and the like are particularly preferable in terms of producing a fluorine-containing olefin with high selectivity.

The above metal oxides may be used solely or in a
25 combination of two or more oxides.

▪Reducing Gas

The reducing gas which can be used in the present invention is not particularly limited insofar as it is in the gas
30 phase at the reaction temperature, and is capable of causing the above metal oxide to induce oxygen deficiency. Examples of these reducing gases include hydrogen, nitrogen monoxide, sulfur dioxide, hydrogen sulfide, ammonia, diborane, phosphine, silane, and arsine. These reducing gases may be used solely or in a
35 combination of two or more gases.

▪Process for Preparing Fluorine-Containing Olefin

In the process for preparing fluorine-containing olefins according to the present invention, a fluorine-containing alcohol is reacted with a reducing gas in the presence of at least one of the aforementioned specific metal oxides.

The reaction method is not particularly limited. For example, the reaction may be performed by supplying gaseous raw materials, i.e., a fluorine-containing alcohol represented by Formula (1) and a reducing gas to a reactor containing at least one of the aforementioned metal oxides. Using this method, it is possible to obtain a fluorine-containing olefin represented by Formula (2): $R^1CF=CH(R^2)$, wherein R^1 and R^2 are the same as above, with high selectivity in a single reaction step.

The form of the reactor used in the process of the present invention is not particularly limited. Examples of the reactors include an adiabatic reactor containing a metal oxide, and a multitubular reactor having a heat transmitting medium to remove heat. The reactor is preferably formed of a material resistant to the corrosive action of hydrogen fluoride, such as HASTALLOY, INCONEL, MONEL or the like.

In the present invention, the ratio of the raw materials, i.e., the ratio of reducing gas to fluorine-containing alcohol represented by Formula (1) is not particularly limited. However, if the proportion of the reducing gas is too low, the amount of the decomposition product of the fluorine-containing alcohol tends to increase, thereby decreasing the selectivity of the fluorine-containing olefin of Formula (2); the selectivity of the fluorine-containing olefin tends to increase as the proportion of reducing gas increases. Generally, the reducing gas is preferably supplied in an amount of not less than about 0.5 equivalent weight, more preferably, about 1 to 20 equivalent weight, per equivalent weight of the fluorine-containing alcohol.

The above raw materials may be directly supplied to the reactor, or they may be diluted by an inert gas such as nitrogen,

helium, argon or the like, before being supplied to the reactor.

Generally, it is preferable to set the reaction temperature inside the reactor to a temperature ranging from about 200°C to about 800°C, and more preferably from about 350°C to about 650°C. If the reaction temperature is too low, the reaction speed tends to decrease, thereby decreasing the conversion. In contrast, if the reaction temperature is too high, the selectivity tends to decrease as a result of decomposition reaction or the like.

The pressure during the reaction is not particularly limited. The reaction of the present invention can be performed either under atmospheric pressure or elevated pressure. More specifically, the reaction can be performed under atmospheric pressure (0.1 MPa); but the reaction may also be performed under an elevated pressure up to about 1.0 MPa.

The reaction time is not particularly limited. However, the contact time represented by W/F_0 , which is the ratio of the supplying amount $W(g)$ of metal oxide catalyst to the total flow rate F_0 (flow rate at 0°C and at 1 atm: cc/sec) of the gas material (i.e. a fluorine-containing alcohol and a reducing gas) supplied to the reaction system, is preferably about 0.1 to 90 g·sec/cc, and more preferably about 1 to 30 g·sec/cc.

In the present invention, as required, a pre-reaction step may be performed by previously bringing the metal oxide that serves as a catalyst into contact with the reducing gas. For example, the metal oxide may be brought into contact with a reducing gas current for 1 to 24 hours at a temperature between 100°C and 800°C. By thus contacting the metal oxide with the reducing gas under a high temperature, a part of the oxygen in the metal oxide is removed as it bonds with the reducing gas. As a result, a part of the metal oxide becomes oxygen deficient, thereby inducing an oxygen-deficient state. This pre-reaction step makes it possible to obtain the target fluorine-containing olefin with sufficient selectivity even at an early stage of the reaction.

-11-

The aforementioned process for preparing fluorine-containing olefin according to the present invention enables production of a fluorine-containing olefin represented by Formula (2): $R^1CF=CH(R^2)$, wherein R^1 and R^2 are the same as above, with
5 high selectivity in a single reaction step using the fluorine-containing alcohol represented by Formula (1): $R^1CF_2CH(R^2)OH$, wherein R^1 and R^2 are the same as above, and a reducing gas, as raw materials. For example, when 2,2,3,3,3-pentafluoro-1-propanol represented by Chemical Formula: CF_3CF_2CHOH is used as a raw
10 material, it is possible to obtain 2,3,3,3-tetrafluoropropene represented by Chemical Formula: $CF_3CF=CH_2$ with high selectivity.

The selectivity for the fluorine-containing olefin and the conversion of the fluorine-containing alcohol can be controlled by selecting the type of metal oxide used, the
15 reaction temperature, the contact time, and the like. Depending on the reaction conditions, the selectivity can be 75% or greater. If the reaction is performed under optimal conditions, it is possible to obtain the target fluorine-containing olefin with a selectivity of 90% or greater.

20

Advantageous Effects of Invention

The process for preparing fluorine-containing olefin according to the present invention enables the production of a desired fluorine-containing olefin with high selectivity in a
25 single reaction step using a fluorine-containing alcohol as a raw material.

Accordingly, the process of the present invention can reduce industrial waste while relatively easily producing fluorine-containing olefins with a single process. Thus, the
30 present invention is significantly useful as an industrial production process for fluorine-containing olefins.

Description of Embodiments

The present invention is more specifically described
35 below with reference to Examples.

Example 1

18 g of CuO in pellet form (with a cylindrical column shape, 3 mm in diameter and 4 mm in height), as a catalyst, was placed into a gas-phase reactor including a cylindrical reaction tube (made of SUS316, 1.0 cm in diameter, 30 cm in length) equipped with an electric furnace. As CF₃CF₂CH₂OH (5FP) (60 mg/min), H₂ (40 mL/min) and N₂ (15 mL/min) (their flow rates were measured under standard conditions) were supplied to the reactor. The temperature of the reaction tube was brought to 469°C.

The reaction product that flowed out of the reaction tube was collected in a cold trap cooled with an ice bath. NMR analysis of the collected liquid showed that the conversion was 21%. Further, NMR and gas chromatography analysis of the product showed that the composition of the product was CF₃CF=CH₂ (96 mol%), CO₂ (3 mol%), CF₂=CF₂ (1 mol%), and that the selectivity of CF₃CF=CH₂ (HFO-1234yf) was 96%. The results are shown in Table 1.

Examples 2 to 9

Using the same vapor-phase reactor as in Example 1, the reaction was performed using the catalyst (metal oxide) and conditions, i.e., reaction temperature, H₂/5FP mole ratio, and contact time (W/F₀), given in Table 1. The results are shown in Table 1.

[Table 1]

	Reaction Conditions				Reaction Results	
	Catalyst	Reaction Temperature (°C)	H ₂ /5FP Mole Ratio	W/F ₀ (g·sec/cc)	CF ₃ CF ₂ CH ₂ OH Conversion (%)	HFO-1234yf Selectivity (%)
Example						
1	CuO	469	4.4	17	21	96
2	CuO	486	8.5	11	22	91
3	CuO	487	2.7	9	4	85
4	CuO	553	4.0	7	16	86
5	CeO ₂	510	6.2	6	32	82
6	CeO ₂	579	6.3	6	56	84
7	In ₂ O ₃	448	6.5	6	10	90
8	In ₂ O ₃	538	6.6	6	22	78
9	In ₂ O ₃	604	6.3	6	63	77

25 Comparative Example 1

-13-

10 g of activated carbon, as a catalyst, was placed into a vapor-phase reactor including a cylindrical reaction tube (made of SUS316, 1.0 cm in diameter, 30 cm in length) equipped with an electric furnace. As $\text{CF}_3\text{CF}_2\text{CH}_2\text{OH}$ (5FP) (201 mg/min), H_2 (120 mL/min) and N_2 (50 mL/min) (their flow rates were measured under standard conditions) were supplied to the reactor. The temperature of the reaction tube was brought to 493°C.

The reaction product that flowed out of the reaction tube was collected in a cold trap cooled with an ice bath. NMR analysis of the collected liquid showed that the conversion was 21%. Further, NMR and gas chromatography analysis of the product showed that the composition of the product was $\text{CF}_3\text{CF}=\text{CH}_2$ (49 mol%), CO_2 (22 mol%), $\text{CF}_3\text{CF}_2\text{H}$ (23 mol%), and that the selectivity of $\text{CF}_3\text{CF}=\text{CH}_2$ (HFO-1234yf) was 49%. The results are shown in Table 2.

15

Comparative Examples 2 and 3

Using the same vapor-phase reactor as in Example 1, the reaction was performed using the catalyst and conditions, i.e., reaction temperature, H_2 /5FP mole ratio, and contact time (W/F_0), given in Table 2. The results are shown in Table 2.

20

[Table 2]

Reaction Conditions					Reaction Results	
	Catalyst	Reaction Temperature (°C)	H_2 /5FP Mole Ratio	W/F_0 (g·sec/cc)	Conversion (%)	Major Product and Selectivity (%)
Comparative Example						
1	Activated Carbon	469	4.0	5	21	HFO1234yf (49) HFC125 (23)
2	3%Pd/C	414	2.8	5	19	HFC125 (62) HFO1234yf (trace)
3	NiO	310	2.4	3	13	CH_4 (72) HFO1234yf (0)

Example 10

12 g of CuO in pellet form (with a cylindrical column shape, 3 mm in diameter and 4 mm in height), as a catalyst, was placed into a vapor-phase reactor including a cylindrical reaction tube (made of SUS316, 1.0 cm in diameter, 30 cm in length) equipped with an electric furnace. As $\text{H}(\text{CF}_2)_4\text{CH}_2\text{OH}$ (160

25

mg/min) and H₂ (90 mL/min) (their flow rates were measured under standard conditions) were supplied to the reactor, the temperature of the reaction tube was brought to 470°C.

The reaction product that flowed out of the reaction tube was collected in a cold trap cooled with an ice bath. NMR analysis of the collected liquid showed that the conversion was 37%. Further, NMR and gas chromatography analysis of the product showed that the selectivity of H(CF₂)₃CF=CH₂ was 96%. The results are shown in Table 3.

10 Examples 11 to 15

Using the same vapor-phase reactor as in Example 10, the reaction was performed using the catalyst (metal oxide) and conditions, i.e., reaction temperature, H₂/H(CF₂)₄CH₂OH mole ratio, and contact time (W/F₀), given in Table 3. The results are shown in Table 3.

[Table 3]

Reaction Conditions					Reaction Results	
	Catalyst	Reaction Temperature (°C)	H ₂ /C ₅ H ₄ F ₈ O Mole Ratio	W/F ₀ (g·sec/cc)	H(CF ₂) ₄ CH ₂ OH Conversion (%)	H(CF ₂) ₃ CF=CH ₂ Selectivity (%)
Example						
10	CuO	470	6.5	6	37	96
11	Cu ₂ O	489	6.4	7	35	94
12	Ag ₂ O	520	6.3	7	43	89
13	HfO ₂	490	6.6	7	39	87
14	Sc ₂ O ₃	472	6.2	6	28	92
15	Gd ₂ O ₃	515	6.3	6	41	90

-15-

Claims

[Claim 1] A process for preparing a fluorine-containing olefin represented by Formula (2): $R^1CF=CH(R^2)$ wherein R^1 is F, H, $F(CF_2)_n-$ (n is an integer ranging from 1 to 10) or $H(CF_2)_m-$ (m is an integer ranging from 1 to 10) and R^2 is H, $F(CF_2)_n-$ (n is an integer ranging from 1 to 10) or $H(CF_2)_m-$ (m is an integer ranging from 1 to 10),

the process comprising reacting a fluorine-containing alcohol represented by Formula (1): $R^1CF_2CH(R^2)OH$, wherein R^1 and R^2 are the same as above, with a reducing gas in the presence of at least one metal oxide selected from the group consisting of Periodic Table Group 3 element-containing oxides, Periodic Table Group 4 element-containing oxides, Periodic Table Group 5 element-containing oxides, Periodic Table Group 6 element-containing oxides, Periodic Table Group 11 element-containing oxides, Periodic Table Group 12 element-containing oxides, Periodic Table Group 13 element-containing oxides, Periodic Table Group 14 element-containing oxides, and Periodic Table Group 15 element-containing oxides.

[Claim 2] The process according to claim 1, wherein the reducing gas is hydrogen.

[Claim 3] The process according to claim 1, wherein the metal oxide is at least one member selected from the group consisting of Periodic Table Group 3 element-containing oxides, Periodic Table Group 4 element-containing oxides, Periodic Table Group 11 element-containing oxides, and Periodic Table Group 13 element-containing oxides.

[Claim 4] The process according to claim 1, wherein the metal oxide is an oxide containing at least one element selected from the group consisting of Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Ti, Zr, Hf, Cu, Ag, Au, Ga, and In.

[Claim 5] The process according to claim 1, wherein the fluorine-containing alcohol represented by Formula (1) is a fluorine-containing alcohol represented by Formula (1'): $R^1CF_2CH_2OH$, wherein R^1 is F, H, $F(CF_2)_n-$ (n is an integer ranging from 1 to 10) or $H(CF_2)_m-$ (m is an integer ranging from 1 to 10).

[Claim 6] The process according to claim 1, wherein the fluorine-containing alcohol represented by Formula (1) is 2,2,3,3,3-pentafluoro-1-propanol.

10

[Claim 7] The process according to claim 1, wherein the reaction is performed in a gas phase under atmospheric pressure or elevated pressure at a temperature range from 200°C to 800°C.

INTERNATIONAL SEARCH REPORT

International application No

PCT/JP2010/051300

A. CLASSIFICATION OF SUBJECT MATTER

INV. C07C17/00 C07C21/18
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 7 026 520 B1 (MUKHOPADHYAY SUDIP [US] ET AL) 11 April 2006 (2006-04-11) cited in the application the whole document -----	1-7



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

6 April 2010

Date of mailing of the international search report

13/04/2010

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Delanghe, Patrick

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/JP2010/051300

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 7026520	B1	11-04-2006	
		CN 101115703 A	30-01-2008
		EP 1828083 A2	05-09-2007
		JP 2009518282 T	07-05-2009
		WO 2006063069 A2	15-06-2006