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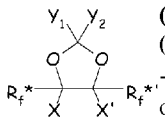
(54) Title: METHOD FOR THE MANUFACTURE OF PERFLUOROVINYLETHERS



(57) Abstract: A method for the hydrodehalogenation of a halofluoroether (HaloFE) having general formula (I-A) or (I-B): (I-A) $R_fO\text{-}CR_f'X\text{-}CR_f''R_f'''X'$ wherein - Rf represents a C_1-C_6 perfluoroalkyl or a C_1-C_6 perfluorooxyalkyl group; - R_f', R_f'' and R_f''', equal or different from each other, independently represent fluorine atoms or C_1-C_5 perfluoroalkyl or C_1-C_5 perfluorooxyalkyl groups; X and X', equal or different from each other, are independently selected from CI, Br or I; (I-B) wherein: - R_f* and R_f*', equal or different from each other, independently represent fluorine atoms or C_1-C_3 perfluoroalkyl or C_1-C_3 perfluorooxyalkyl groups; - Y_1 and Y_2, equal or different from each other, independently represent fluorine atoms or C_1-C_3 perfluoroalkyl groups; X and X' are as above defined; is herein disclosed, the method comprising contacting said halofluoroether (HaloFE) with hydrogen in the presence of a catalyst comprising at least one transition metal of group VI 11 B and at least one alkali metal of group IA.

Method for the manufacture of perfluorovinylethers

Cross-reference to related applications

[0001] This application claims priority to European patent application No. 16181317.5 filed on July 26, 2016, the whole content of this application being incorporated herein by reference for all purposes.

Technical Field

[0002] The present invention relates to a method for the hydrodehalogenation of halofluoroethers to perfluorovinylethers.

Background Art

[0003] Perfluorovinylethers are useful monomers for the manufacture of various fluoropolymers, in particular of thermoprocessable tetrafluoroethylene-based plastics and fluoroelastomers.

[0004] Methods for manufacturing perfluorovinylethers from halofluoroethers are known in the art. Generally known methods involve the dehalogenation of suitable halofluoroether precursors in liquid phase in the presence of transition metals. For instance, **US 2007203368** (SOLVAY SOLEXIS SPA) 30/08/2007 discloses a liquid-phase process for the manufacture of perfluorovinylethers by dehalogenation of certain halofluoroethers in the presence of transition metals as zinc, copper, manganese or metal couples as Zn/Cu, Zn/Sn, Zn/Hg. However, liquid phase processes generally suffer from the disadvantage that significant amounts of metal halides solutions or muds are typically obtained as by-products (e.g. $ZnCl_2$ solutions/muds are produced when a chlorofluoroether is dechlorinated over zinc). The separation of by-products from the target perfluorovinylethers and their handling and disposal are time-consuming, costly and very burdensome from an industrial point of view, as the muds are highly corrosive and possibly have a detrimental environmental impact.

[0005] In order to overcome such problems, gas-phase processes have been developed. For example, **WO 2009/150091** (SOLVAY SOLEXIS SPA)

17/12/2009 discloses a process for the manufacture of a perfluorovinylether by hydrodehalogenation of a halofluoroether, said process comprising contacting the halofluoroether with hydrogen in the presence of a catalyst comprising at least one transition metal of group VIII B at a temperature of at most 340°C.

[0006] **WO 2012/104365** (SOLVAY SPECIALTY POLYMERS ITALY) 9/08/2012 discloses a process for the manufacture of a perfluorovinylether by hydrodehalogenation of a halofluoroether, said process comprising contacting the halofluoroether with hydrogen in the presence of a catalyst comprising palladium and at least one transition metal selected from the group consisting of the metals of group VIIIB, other than palladium, and of group IB. The presence of at least a second transition metal selected from group VIIIB and group IB allows retaining the activity of the catalyst (i.e. its ability to transform the halofluoroether in the desired halofluoroether) for a longer period of time, thus increasing the economic profitability of the process.

[0007] However, the processes disclosed in **WO 2009/150091** and **WO 2012/104365** lead also to the formation of monohalo-fluorovinylethers (i.e. fluorovinylethers comprising one halogen other than fluorine) as side-products which, despite being in a relative low amount, are not desired in subsequent polymerization reactions and are difficult to remove from the desired perfluorovinylether.

[0008] Therefore, the need is still felt to provide a method for the manufacture of highly pure perfluorovinylethers from halofluoroethers, namely perfluorovinylethers that are not contaminated by halofluorovinylethers.

[0009] The use of metals of group IA of the periodic table as catalysts is known in the art. For example, **US 5089454** (SOLVAY AND CIE) 18/02/1992 relates to catalytic compositions for the hydrogenation of chlorofluoroalkenes to fluoroalkenes, said composition comprising a porous carrier impregnated with a metal of group VIII of the Periodic Table of the elements and with one or more compounds selected from the salts of an alkali metal or alkaline-earth metal, in particular from sodium, potassium, caesium, lithium, barium, calcium or rubidium chlorides, fluorides or hydroxides.

[0010] **EP 0434408** (E.I.DU PONT DE NEMOURS AND COMPANY) 26/06/1991 discloses the use of a catalyst comprising CuO, NiO and Cr_2O_3 on CaF_2, promoted on an alkali metal selected from K, Cs and Rb for the hydrodehalogenation of CF_3-CFCl-CF_3 to $CF_3CF=CF_2$, for the hydrodehalogenation of $CFCl_2$-CF_2Cl to $CFCl=CF_2$ and also for the hydrodehalogenation of CF_2ClCF_2Cl to $CF_2=CF_2$.

[0011] **WO 97/44303** (E.I.DU PONT DE NEMOURS AND COMPANY) 27/11/1997 discloses the use of fluorides of metals of Group IA in the reaction of of hexafluoropropylene epoxide (HFPO) with a mixture of carbonyl fluoride (CF) and perfluoroacetyl fluoride (PAF) in a process for the production of perfluoromethyl perfluorovinyl ether (PMVE) and perfluoroethyl perfluorovinyl ether (PEVE).

[0012] The use of cesium oxide supported on metal oxides to catalyze the ozone initiated oxidation of tetrachloro-*o*-benzoquinone is disclosed in **MADDILA, Suresh, et al.** Dechlorination of tetrachloro-o-benzoquinone by ozonation catalyzed by cesium loaded metal oxides. *Applied Catalysis B: 138-139* . 2013, p.149 - 160.

Summary of invention

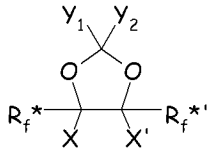
[0013] The Applicant has now surprisingly found out that a catalyst comprising a transition metal of group VIIIB and an alkali metal of group IA is able to promote the hydrodechlorination reaction of halofluoroethers to provide perfluorovinylethers without giving rise to halofluorovinylethers as by-products.

[0014] Accordingly, the present invention relates to a method for hydrodehalogenation of a halofluoroether (HaloFE) having general formula (I-A) or (I-B):

(I-A) $R_fO\text{-}CR_f'X\text{-}CR_f''R_f'''X'$

wherein R_f represents a C_1-C_6 perfluoro(oxy)alkyl group; R_f', R_f'' and R_f''', equal or different from each other, independently represent fluorine atoms or C_1-C_5 perfluoro(oxy)alkyl groups; X and X', equal or different from each other, are independently selected from Cl, Br or I;

(IB)

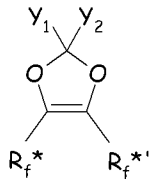


wherein R_f* and R_f*', equal or different from each other, independently represent fluorine atoms or C_1-C_3 perfluoro(oxy)alkyl groups;
Y_1 and Y_2, equal or different from each other, independently represent fluorine atoms or C_1-C_3 perfluoroalkyl groups; X and X' are as above defined;
said method comprising contacting said halofluoroether (HaloFE) with hydrogen in the presence of a catalyst comprising at least one transition metal of group VIIIB and at least one alkali metal of group IA.

[0015] The method of the present invention enables to selectively provide compounds (herein after referred to as "perfluorovinylethers") of formulae (A*) and (B*), respectively:

(A*) $R_fO\text{-}CR_f'=CR_f''R_f'''$

(B*)



wherein R_f, R_f', R_f'', R_f''', Y_1, Y_2, R_f* and R_f*' have same meanings as above defined
without the need to frequently regenerate the catalyst at high temperature with H_2 due to its high stability.

[0016] The method is carried out at temperatures generally not exceeding 340°C; thus, poisoning from HF, sintering or coking phenomena otherwise known as significantly reducing the life of group VIIIB transition metal catalysts can be essentially avoided.

[0017] The term "hydrodehalogenation", as used therein, is intended to denote the selective elimination of two halogen atoms, X, X' in formulae (I-A) an (I-B), selected from Cl, Br or I, from two adjacent fluorine-substituted carbon atoms of said halofluoroether (HaloFE), in the presence of hydrogen, to yield the corresponding perfluorovinylethers, i.e. the corresponding compounds comprising a $-O\text{-}CR_f'=CR_f''R_f'''$ or

a -O-CR_f*=CR_f*'-O- moiety, wherein R_f', R_f'', R_f''', R_f* and R_f*' are as defined above.

[0018] The expression "perfluoro(oxy)alkyl group" is intended to indicate either a perfluoroalkyl group or a perfluorooxyalkyl group, that is a perfluoroalkyl group comprising one or more than one catenary oxygen atom.

[0019] According to a first embodiment of the invention, the halofluoroether (HaloFE) of the invention is a chlorofluoroether (HaloFE-1) having general formula (I-A) as described above, wherein X and X', equal or different from each other, are independently selected from Cl, Br or I, with the proviso that at least one of X and X' in said formula (I-A) is a chlorine atom.

[0020] The halofluoroether (HaloFE) of this first embodiment is preferably a chlorofluoroether (HaloFE-2) having general formula (I-A) as described above, wherein X and X' are equal to each other and are chlorine atoms, that is to say that chlorofluoroether (HaloFE-2) complies with formula (II-A) here below:

(II-A) R_fO-CR_f'Cl-CR_f''R_f'''Cl

wherein:

R_f represents a C_1-C_6 perfluoro(oxy)alkyl group, preferably a C_1-C_4 perfluoroalkyl group, more preferably a C_1-C_3 perfluoroalkyl group;

R_f', R_f'' and R_f''', equal or different from each other, independently represent fluorine atoms or C_1-C_5 perfluoro(oxy)alkyl groups, preferably fluorine atoms or C_1-C_3 perfluoroalkyl groups, more preferably fluorine atoms or C_1-C_2 perfluoroalkyl groups, even more preferably fluorine atoms.

[0021] The chlorofluoroether (HaloFE-2) of the present invention is typically a gaseous compound under process conditions.

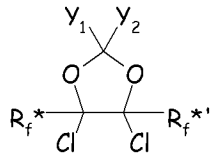
[0022] Representative compounds of chlorofluoroethers (HaloFE-2) described by formula (II-A) useful in the present invention include, but are not limited to, the following compounds: $CF_3OCFClCF_2Cl$, $CF_3CF_2OCFClCF_2Cl$, $CF_3CF_2CF_2OCFClCF_2Cl$, $CF_3OCF_2OCFClCF_2Cl$, $CF_3CF_2OCF_2OCFClCF_2Cl$, $CF_3OCF_2CF_2OCF_2OCFClCF_2Cl$.

[0023] According to a second embodiment of the invention, the halofluoroether (HaloFE) of the invention is a chlorofluorodioxolane (HaloFE-3) having

general formula (I-B) as described above, wherein X and X', equal or different from each other, are independently selected from Cl, Br or I, with the proviso that at least one of X and X' in said formula (I-B) is a chlorine atom.

[0024] The halofluoroether (HaloFE) of this second embodiment is preferably a chlorofluorodioxolane (HaloFE-4) having general formula (I-B) as described above, wherein X and X' are equal to each other and are chlorine atoms, that is to say that chlorofluorodioxolane (HaloFE-4) complies with formula (II-B) here below:

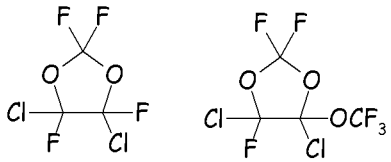
(II-B)



wherein R_f* and R_f*', equal or different from each other, independently represent fluorine atoms or C_1-C_3 perfluoro(oxy)alkyl groups, preferably fluorine atoms or C_1-C_3 perfluorooxyalkyl groups, more preferably fluorine atoms or $-OCF_3$ groups; Y_1 and Y_2, equal or different from each other, independently represent fluorine atoms or C_1-C_3 perfluoroalkyl groups, preferably fluorine atoms.

[0025] The chlorofluorodioxolane (HaloFE-4) of the present invention is typically a gaseous compound under process conditions.

[0026] Representative compounds of chlorofluorodioxolanes (HaloFE-4) described by formula (II-B) useful in the present invention include, but are not limited to, the following compounds:



[0027] The method of the present invention is carried out in the presence of a catalyst comprising at least one transition metal selected from group VIIIB [metal (M1)] and at least one alkali metal of group IA [metal (M2)].

[0028] For the avoidance of doubt, the term "transition metal of group VIIIB" is hereby intended to denote the following metals: Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt. Preferably, the catalyst comprises one metal of group VIIIB [metal

(M1)], preferably one of Rh, Ir, Pd and Pt; more preferably, the metal (M1) is Pd.

[0029] The term “alkali metal of group IA” is intended to denote Li, Na, K, Rb, Cs and Fr; preferably, the alkali metal of group IA [metal (M2)] is K or Cs; more preferably, the alkali metal of group IA is Cs.

[0030] Preferably, the catalyst comprises one transition metal of group VIII B [metal (M1)] and one alkali metal of group IA [metal (M2)]. In one preferred embodiment, the catalyst comprises Pd as metal (M1) and K as metal (M2). In another preferred embodiment, the catalyst comprises Pd as metal (M1) and Cs as metal (M2). Catalysts comprising Pd and Cs are particularly preferred because, in addition to avoiding the formation of halofluorovinylethers, they provide the desired perfluorovinylethers with higher selectivities.

[0031] The molar ratio between metal (M1) and metal (M2) typically ranges from 0.50 to 1.50; preferably, the molar ratio ranges from 0.90 to 1.10.

[0032] The catalyst of the invention is typically a supported catalyst, that is to say that it comprises metals (M1) and (M2) as above described and an inert carrier.

[0033] The inert carrier is generally selected from activated carbon, silica and alumina; preferably, the carrier is activated carbon. Suitable inert carriers generally have a BET surface area of from 800 to 1600 m^2/g, preferably from 1000 to 1600 m^2/g, even more preferably from 1100 to 1500 m^2/g.

[0034] The BET surface area is measured by N_2 adsorption as per the Brunauer, Emmett and Teller method of calculation, according to ISO 9277.

[0035] When supported, the catalyst generally comprises metal (M1), preferably Pd, in an amount of from 0.1 wt% to 2 wt%, preferably from 0.3 wt % to 1.8 wt %, more preferably from 0.5 wt % to 1.5 wt % with respect to the inert carrier.

[0036] The amount of metal (M2), preferably K or Cs, in the supported catalyst is determined, on the basis of the weight of metal (M1), in order to obtain a (M1):(M2) molar ratio falling within the above identified ranges of from 0.50 to 1.50.

[0037] When supported, the catalyst can be advantageously prepared by the incipient wetness impregnation method. In such a method an aqueous solution of a suitable metal precursor is added to the inert carrier and dried. The metal is then typically reduced by treatment with H_2. Suitable precursors of metal (M1) are halides, preferably chlorides, and ammoniacal complexes of such metals. Suitable metal precursors of metal (M2) are organic and inorganic salts of such metals. Organic salts can be selected from carboxylates, alcoholates and acetylacetonates whose alkyl chain usually contains from 1 to 10 carbon atoms. Inorganic salts can be halides, hydroxides or nitrates. Preferably, an inorganic salt of metal (M2) is used, more preferably a chloride.

[0038] In the preparation of the catalyst to be used in the method of the invention, impregnation of the inert carrier with the precursor of the at least one metal (M1) and the at least one metal (M2) can be carried out either sequentially or simultaneously. In a sequential process, the inert carrier is first impregnated with a solution of the precursor of the at least one metal (M1), optionally dried and then impregnated with a solution of the precursor of metal (M2). In a simultaneous process, the inert carrier is impregnated with a solution comprising both the at least one metal (M1) and the precursor of the at least one metal (M2), followed by drying and reduction, if needed.

[0039] Catalysts used in the method of the invention are generally activated before use by pre-reduction under hydrogen at temperatures comprised between 250°C and 450°C, more preferably between 250°C and 400°C, even more preferably between 300°C and 400°C.

[0040] Typically, regeneration of the catalyst is also carried out under hydrogen at temperatures comprised between 300°C and 500°C, more preferably between 350°C and 500°C, even more preferably between 400°C and 500 °C. The term “regeneration” refers to the process of restoring the catalytic activity of the catalyst which has been deactivated by use in the hydrodehalogenation method.

[0041] Very good results can be obtained using catalysts comprising Pd as metal (M1) and K or Cs as metal (M2) supported on carbon, wherein the molar

ratio between (M1) and (M2) ranges from 0.50 to 1.50, preferably from 0.90 to 1.10, in particular in a method for the hydrodechlorination of chlorofluoroethers (HaloFE-2) of formula (II-A) as described above. In both cases, the desired perfluorovinylether was obtained without formation of chlorofluorovinylethers. Catalysts comprising Pd as metal (M1) and Cs as metal (M2) supported on carbon are particularly advantageous in that they allow obtaining the desired perfluorovinylether with selectivities of at least 80%.

[0042] The method of the present invention is preferably carried out at a temperature of at most 340°C.

[0043] The Applicant has found that for obtaining perfluorovinylethers in high yields it is generally advantageous to carry out the method at temperatures not exceeding 340°C, in order to avoid decomposition of the halofluoroether (HaloFE).

[0044] Lower limits of temperatures suitable for achieving efficient conversion of halofluoroethers to perfluorovinylethers are not particularly limited. Temperatures of advantageously at least 170°C, preferably at least 200°C, more preferably at least 210°C, and even more preferably at least 230°C are generally used. Best results can be obtained at temperatures comprised between 230°C and 320°C.

[0045] The method of the present invention is advantageously carried out in gas-phase, that is to say in conditions wherein hydrogen and both the halofluoroether (HaloFE) and the corresponding perfluorovinylether are in gaseous state. It is nevertheless understood that the catalyst is generally used as a solid, so that the reaction takes place between the reactants in the gas phase and the catalyst in the solid state.

[0046] Hydrogen can be fed either as neat reactant or diluted with an inert gas, e.g. nitrogen, helium or argon. Conveniently, the inert gas is nitrogen.

[0047] The method of the invention is carried out in any suitable reactor, including fixed and fluidized bed reactors. The method is generally carried out in continuous using a plug flow reactor comprising a fixed bed of catalyst.

[0048] The reaction pressure is not critical to the method. The method of the invention is typically carried out under atmospheric pressure, even though pressures between 1 and 3 bar can be employed.

[0049] Contact time between the halofluoroether (HaloFE) and the catalyst is not particularly limited and will be chosen by the skilled in the art in relation, notably, with the reaction temperature and other process parameters. Contact time, which, for continuous processes, is defined as the ratio of the catalyst bed volume to the gas flow rate in standard conditions at 0°C and 1 bar, may vary between a few seconds and several hours. Nevertheless, it is understood that this contact time is generally comprised between 2 and 200 seconds, preferably between 5 and 150 seconds, more preferably between 5 and 50 seconds.

[0050] For continuously operated processes, time-on-stream may vary between 5 and 500 hours, preferably between 20 and 200 hours. A time-on-stream of at least 50 hours without a significant decrease of conversion may generally be advantageous. Even more advantageous might be a time-on-stream of at least 50 hours without a significant decrease of both conversion and selectivity. For the purpose of the present application, the expression “time-on-stream” means the period of time in which the catalyst is contacted with the HaloFE to provide the desired perfluorovinylether. It is also understood that the spent catalyst can be advantageously regenerated as above mentioned and recycled in the method of the invention.

[0051] Good conversions are generally obtained in the presence of a hydrogen/halofluoroether (HaloFE) molar ratio comprised between 0.25 and 4, more preferably between 0.50 and 2.0.

[0052] It has been found that conversion typically increases by increasing the hydrogen/halofluoroether (HaloFE) molar ratio up to 4. A hydrogen/halofluoroether (HaloFE) molar ratio greater than 4 could be used but it does not provide any additional increase in conversion and and is usually uneconomical.

[0053] A halogenidric acid is obtained as a by-product from the method of the invention. When the halofluoroether (HaloFE) is selected from a

chlorofluoroether (HaloFE-1), a chlorofluoroether (HaloFE-2), a chlorofluorodioxolane (HaloFE-3) or a chlorofluorodioxolane (HaloFE-4), hydrogen chloride is typically obtained; halogenidric acids can be easily recovered by neutralization in an aqueous alkaline solution or by absorption in water.

[0054] The invention is described in more detail in the following Experimental Section by means of examples whose purpose is merely illustrative and not limitative of the scope of the invention.

[0055] Should the disclosure of any patents, patent applications, and publications which are incorporated herein by reference conflict with the description of the present application to the extent that it may render a term unclear, the present description shall take precedence.

EXPERIMENTAL SECTION

Catalyst preparation

[0056] 80 g of extruded carbon having pellet size of about 1.5 mm and specific surface area SSA (BET method) of about 1500 m2/g [NORIX RX1.5 EXTRA (Norit Nederland B.V.)] was dried under vacuum at 200°C and thus impregnated by wet impregnation method with a water hydrochloric acid solution of the chloride salts of the selected metals as metal precursors in order to obtain a palladium loading of about 1%wt with respect to carbon and a molar ratio equal to 1 in the case of bimetallic catalysts, as reported in detail in Table 1 below. The amounts of chloride salts were calculated in order to obtain the desired percentage of metal in the zero oxidation state.

Table 1

Catalyst	Carbon support (g)	Pd (µg/g carbon support)	Pd (wt %)	Other metal than Pd	Amount of metal (M2) (µg/g carbon support)	Other metal :Pd (mol)
A	20	997	1.06	K	363	1.02
B	20	993	1.03	Cs	1236	1.01
C	20	1008	1.13		-	-
D	20	752	0.8	Ru	3018	4.21

[0057] The catalyst was subsequently dried at 120°C in a nitrogen flow for 6 hours and then reduced with hydrogen (H_2) at 330°C for one hour.

Example 1 - Hydrodechlorination of $CF_3OCFClCF_2Cl$ on catalyst A

[0058] 1.0 g catalyst A was loaded in a Hastelloy C down-flow tubular reactor (length = 53 cm, internal diameter = 8 mm) equipped with an internal AISI 316 net to support the catalyst bed.

[0059] When the reactor temperature was equal to 250°C at a 10°/min rate under hydrogen/nitrogen flow, then $CF_3OCFClCF_2Cl$, manufactured according to **US 2007203368** (SOLVAY SOLEXIS SPA) 30/08/2007 was fed in the reactor at a space velocity of 7.4 g/h; the residence time was 5 seconds. Conversion and selectivity were calculated by gas-chromatography (GC) on an HP 5890 gas chromatographer equipped with a J&W Agilent Parabond Q semi-capillary column according to the internal standard method using nitrogen as internal standard and an autosampled calibrated injection loop.

[0060] The results are reported in Table 2 below. Selectivity is expressed as mole percentage with respect to the moles of reacted (or converted) $CF_3OCFClCF_2Cl$.

[0061]

Table 2

$CF_3OCFClCF_2Cl/H_2$ (mol/mol)	Conversion (% $CF_3OCFClCF_2Cl$)	Selectivity (% $CF_3OCF=CF_2$)	Selectivity (% $CF_3OCCl=CF_2$)
1	43	45	0
2	19	55	0

Example 2 - Hydrodechlorination of $CF_3OCFClCF_2Cl$ on catalyst B

[0062] Example 1 was repeated with the sole difference that Catalyst B was used. The results are reported in Table 3 below.

Table 3

$CF_3OCFClCF_2Cl/H_2$ (mol/mol)	Conversion (% $CF_3OCFClCF_2Cl$)	Selectivity (% $CF_3OCF=CF_2$)	Selectivity (% $CF_3OCCl=CF_2$)
1	35	87	0
2	21	85	0

Example 3 (comparative) - Hydrodechlorination of $CF_3OCFClCF_2Cl$ on catalyst C

[0063] Example 1 was repeated with the differences that catalyst C was used and $CF_3OCFClCF_2Cl$ was fed in the reactor at a space velocity of 7.7 g/h. The results are reported in Table 4 below.

Table 4

$CF_3OCFClCF_2Cl/H_2$ (mol/mol)	Conversion (% $CF_3OCFClCF_2Cl$)	Selectivity (% $CF_3OCF=CF_2$)	Selectivity (% $CF_3OCCl=CF_2$)
1	59	59	8
2	25	71	4

Example 4 (comparative) – Hydrodechlorination of $CF_3OCFClCF_2Cl$ on catalyst D

[0064] Example 1 was repeated with the differences that catalyst D was used, and $CF_3OCFClCF_2Cl$ was fed in the reactor at a space velocity of 1.4 g/h with a residence time of about 10 seconds. The results are reported in Table 5 below.

Table 5

$CF_3OCFClCF_2Cl/H_2$ (mol/mol)	Conversion % ($CF_3OCFClCF_2Cl$)	Selectivity (% $CF_3OCF=CF_2$)	Selectivity (% $CF_3OCCl=CF_2$)
1	67	88	3

[0065] The results reported in this Section demonstrate that the method according to the invention (Examples 1 and 2), wherein a Pd/K or Pd/Cs catalyst is used allows obtaining the desired perfluorovinyl ether free from the undesired chlorinated byproduct $CF_3OCCl=CF_2$. Instead, when a Pd monometallic catalyst (catalyst C, Comparative example 3) or a bimetallic Pd/Ru catalyst (catalyst D, Comparative example 4) is used, the undesired by-product forms, despite high conversion and selectivity.

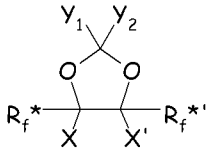
Claims

1. A method for the hydrodehalogenation of a halofluoroether (HaloFE) having general formula (I-A) or (I-B):

(I-A) $R_fO\text{-}CR_f'X\text{-}CR_f''R_f'''X'$

wherein R_f represents a C_1-C_6 perfluoroalkyl group or a C_1-C_6 perfluorooxyalkyl group; R_f', R_f'' and R_f''', equal or different from each other, independently represent fluorine atoms or C_1-C_5 perfluoroalkyl or C_1-C_5 perfluorooxyalkyl groups; X and X', equal or different from each other, are independently selected from Cl, Br or I;

(I-B)



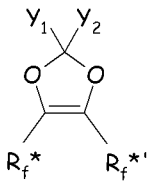
wherein:

- R_f^* and $R_f^{*'}$, equal or different from each other, independently represent fluorine atoms or C_1-C_3 perfluoroalkyl or C_1-C_3 perfluorooxyalkyl groups;
- Y_1 and Y_2, equal or different from each other, independently represent fluorine atoms or C_1-C_3 perfluoroalkyl groups;
- X and X' are as above defined;

to provide compounds of formulae (A*) and (B*), respectively:

(A*) $R_fO\text{-}CR_f'=CR_f''R_f'''$

(B*)



wherein R_f, R_f', R_f'', R_f''', Y_1, Y_2, R_f^* and $R_f^{*'}$ have the same meanings as above defined;

said method comprising contacting said halofluoroether (HaloFE) with hydrogen in the presence of a catalyst comprising at least one transition metal of group VIIIB [metal (M1)] and at least one alkali metal of group IA [metal (M2)].

2. The method according to claim 1 wherein metal (M1) is selected from Rh, Ir, Pd and Pt.
3. The method according to claim 2 wherein metal (M1) is Pd.
4. The method according to any one of claims 1 to 3 wherein metal (M2) is K or Cs.
5. The method according to claim 4 wherein metal (M2) is Cs.
6. The method according to any one of claims 1 to 5 wherein the halofluoroether (HaloFE) is a chlorofluoroether (HaloFE-1) having general formula (I-A), wherein X and X', equal or different from each other, are independently chosen among Cl, Br or I, with the proviso that at least one of X and X' in said formula (I-A) is a chlorine atom.
7. The method according to claim 6 wherein the halofluoroether (HaloFE) is a chlorofluoroether (HaloFE-2) having general formula (II-A):
$R_fO\text{-}CR_f'Cl\text{-}CR_f''R_f'''Cl$ (II-A)
wherein R_f represents a C_1-C_6 perfluoroalkyl group or a C_1-C_6 perfluorooxyalkyl group comprising more than one catenary oxygen atoms; R_f', R_f'' and R_f''', equal or different from each other, independently represent fluorine atoms or C_1-C_5 perfluoroalkyl or C_1-C_5 perfluorooxyalkyl groups.
8. The method according to any one of claims 1 to 7 wherein the catalyst comprises an inert carrier.
9. The method according to claim 8 wherein the inert carrier is activated carbon.
10. The method according to any one of claims 1 to 9 wherein the molar ratio between metal (M1) and (M2) ranges from 0.50 to 1.5.
11. The method according to claim 10 wherein the molar ratio between metal (M1) and (M2) ranges from 0.9 to 1.10.
12. The method according to any one of claims 8 to 11 wherein the catalyst comprises metal (M1) in an amount from 0.1% to 2% wt with respect to the inert carrier.
13. The method of any one of claims 1 to 12, said method being carried out at temperatures of at most 340°C.
14. The method of any one of claims 1 to 13, said method being carried out at temperatures of at least 170°C.

15. The method of any one of claims 1 to 14, wherein the hydrogen/halofluoroether (HaloFE) molar ratio is comprised between 0.25 and 4.

Abstract

A method for the hydrodehalogenation of a halofluoroether (HaloFE) having general formula (I-A) or (I-B):

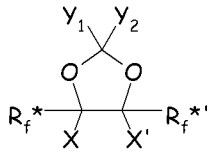
(I-A) $R_fO\text{-}CR_f'X\text{-}CR_f''R_f'''X'$

wherein

- R_f represents a C_1-C_6 perfluoroalkyl or a C_1-C_6 perfluorooxyalkyl group;

- R_f', R_f'' and R_f''', equal or different from each other, independently represent fluorine atoms or C_1-C_5 perfluoroalkyl or C_1-C_5 perfluorooxyalkyl groups; X and X', equal or different from each other, are independently selected from Cl, Br or I;

(I-B)



wherein:

- R_f* and R_f*', equal or different from each other, independently represent fluorine atoms or C_1-C_3 perfluoroalkyl or C_1-C_3 perfluorooxyalkyl groups;

- Y_1 and Y_2, equal or different from each other, independently represent fluorine atoms or C_1-C_3 perfluoroalkyl groups; X and X' are as above defined;

is herein disclosed, the method comprising contacting said halofluoroether (HaloFE) with hydrogen in the presence of a catalyst comprising at least one transition metal of group VIIIB and at least one alkali metal of group IA.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2017/068508

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07C41/24 C07C43/17 C07D317/34
ADD. C07D317/42

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)
C07D 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 practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2012/104365 A2 (SOLVAY SPECIALTY POLYMERS IT [IT]) 9 August 2012 (2012-08-09) cited in the application	1,2,4-15
A	claims; examples	3

Y	EP 0 434 408 A1 (DU PONT [US]) 26 June 1991 (1991-06-26) cited in the application page 6, lines 14-28; claim 1	1,2,4-15

☐ 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

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"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

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"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	Date of mailing of the international search report
17 October 2017	25/10/2017

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2017/068508

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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