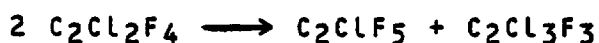


The present invention relates to the manufacture of chloropentafluoroethane C_2F_5Cl by a gas phase catalysed reaction of dichlorotetrafluoroethane $C_2F_4Cl_2$ with hydrofluoric acid HF.

5 Chloropentafluoroethane, which is used as a solvent, propellant or refrigerant fluid is prepared by known processes, for example from perchloroethylene, chlorine and hydrofluoric acid (East German Patent No. 117,580) or
10 by a gas phase reaction of trichlorotrifluoroethane $C_2F_3Cl_3$ with hydrofluoric acid in the presence of aluminium trifluoride (Japanese Publication 48-26,729/73).

US Patent 3,087,974 describes the vapour phase disproportionation of chlorofluoro compounds on a catalyst without the addition of hydrofluoric acid. The
15 disproportionation of dichlorotetrafluoroethane takes place according to the reaction:



This catalyst is activated alumina of high surface area which is treated with a fluorocarbon compound before
20 being used for the disproportionation reaction. The conversion of CF_2ClCF_2Cl to C_2ClF_5 does not exceed 34% on a molar basis and a high proportion of $C_2Cl_3F_3$ is produced as a by-product.

US Patent 3,258,500 describes a vapour phase
25 catalysed fluorination using hydrofluoric acid. The dichlorotetrafluoroethane CF_2Cl-CF_2Cl and hydrofluoric acid HF, in a molar ratio $\left[\frac{HF}{CF_2Cl-CF_2Cl} \right]$ of between 4 and 5,

react at 400°C on a chromium oxide catalyst. The proportion of hexafluoroethane C_2F_6 formed is 0.19 on a molar basis relative to C_2F_5Cl .

A paper by L. Marangoni et al., "Preparation of chloropentafluoroethane from dichlorotetrafluoroethane" (Journal of Fluorine Chemistry 19, 1981/82, pages 21 to 34) also describes a chromium oxide-based catalyst for the gas phase manufacture of C_2F_5Cl from $C_2F_4Cl_2$ and HF. The degree of conversion of $C_2Cl_2F_4$ is between 72 and 75%, the yield of C_2F_5Cl is between 89 and 92%, but the formation of hexafluoroethane is still 8% on a molar basis of the formation of C_2F_5Cl .

A paper by M. Vecchio et al., "Studies on a vapor-phase process for the manufacture of chlorofluoroethanes" (Journal of Fluorine Chemistry, 4, 1974, pages 111 to 139) describes the same reaction as the preceding paper but on a catalyst based on aluminium fluoride doped with nickel, iron and chromium halides. The degree of conversion of $C_2F_4Cl_2$ does not exceed 41% and the molar percentage of C_2F_5Cl at the reactor outlet is 38%.

The catalysts of the prior art are difficult to prepare, while the yields and selectivities for C_2F_5Cl are mediocre.

The present invention overcomes all these disadvantages by offering a simple, flexible and economical process for producing C_2F_5Cl .

The process according to the invention consists

in subjecting dichlorotetrafluoroethane $C_2Cl_2F_4$ to the action of hydrofluoric acid HF in gaseous phase in the presence of a catalyst prepared by reacting > in a gaseous phase, an activated alumina whose sodium oxide content
5 is less than 300ppm and in which the volume of the pores with a radius of 40 angstroms and more is greater than $0.7 \text{ cm}^3/\text{g}$ with hydrofluoric acid or with a mixture of hydrofluoric acid with air, nitrogen or a fluoro compound.

A high conversion, above 80%, of the starting
10 materials and a high yield of C_2F_5Cl are obtained. Another advantage of the process is the catalyst life.

The activated aluminas are produced by controlled heating of alumina hydrates so as to remove most of the water of formation (Kirk-Othmer, Encyclopedia of Chemical Technology, 3rd edition, vol. 2, page 225).
15

The alumina used to prepare the catalyst is a commercially available alumina. It suffices to choose an activated alumina in which the volume of the pores of 40 Å and more is greater than $0.7 \text{ cm}^3/\text{g}$ and is preferably between 0.75 and $1 \text{ cm}^3/\text{g}$. It is advantageous for the alumina
20 to be in the form of granules, beads or extrudates of a size smaller than a sphere with a diameter of 20 mm and preferably a few millimetres, to permit convenient handling during the loading and draining of the reactor.

25 As indicated above, the sodium oxide Na_2O content must be less than 300ppm, and should, preferably, be as low as possible.

It is also advantageous to choose an alumina containing, on a weight basis, not more than 0.5% of silica and not more than 0.2% of iron oxide Fe_2O_3 . This alumina is converted into a mixture of aluminium trifluoride AlF_3 and alumina by reaction with HF by
5 itself or mixed with air, nitrogen or a fluoro compound.

For example, it is possible to use a mixture of dichlorotetrafluoroethane $\text{C}_2\text{Cl}_2\text{F}_4$ and hydrofluoric acid,
10 which is passed over this alumina at a sufficient temperature to initiate a reaction which converts the alumina to aluminium trifluoride. It is advantageous to operate between 150 and 500°C. The operation is preferably performed at atmospheric pressure, with contact times of between 5
15 and 15 seconds. The specialist can easily carry out the reaction and adjust the proportions of $\text{C}_2\text{F}_4\text{Cl}_2$ and HF, the temperature, the pressure and the contact time so as to prevent the alumina being damaged by a high temperature due to the exothermicity of the reaction.

20 When the composition of the gases no longer changes after they have passed over this alumina, then the alumina has been converted to the catalyst. It can be employed, after being washed with water if appropriate, to effect the fluorination of $\text{C}_2\text{F}_4\text{Cl}_2$ to $\text{C}_2\text{F}_5\text{Cl}$ according to
25 the invention.

According to a preferred embodiment of the invention the catalyst may also be prepared by subjecting

alumina in a fluidized bed to the action of a stream of hot air or nitrogen containing hydrofluoric acid. It is advantageous to operate between 150 and 500°C. A mixture of between 0.1 and 30%, on a molar basis, of HF with air or nitrogen, and preferably between 1.5 and 3%, is advantageously employed. The throughput is advantageously between 200 and 250 moles/hour per litre of catalyst. The operation is preferably carried out at atmospheric pressure at 350°C or above. It is convenient to vary the HF concentration in the air or nitrogen to control the exothermicity of the reaction. When no more HF is consumed, the reaction is stopped and the catalyst is considered to be ready for the fluorination of $C_2F_4Cl_2$.

The reaction between dichlorotetrafluoroethane $C_2F_4Cl_2$ and anhydrous hydrofluoric acid HF is carried out in a gaseous phase over the catalyst which may be prepared according to either of the above two routes. The temperature is advantageously between 350 and 550°C and preferably between 380 and 500°C. The molar ratio $HF/C_2Cl_2F_4$ is advantageously between 0.5 and 1.5 and preferably between 0.9 and 1.1. While the operation may be carried out at any pressure, provided that it remains in a gaseous phase, it is nevertheless much simpler to operate between 0.5 and 4 bars absolute, and preferably at atmospheric pressure or thereabouts, and with a contact time of between 5 and 15 seconds and preferably between 6 and 13 seconds.

The following examples illustrate the invention

without limiting it.

In all these examples, the $C_2F_4Cl_2$ employed contains 92.7% of the symmetrical isomer.

Example 1

5 A pure activated alumina supplied by the Kaiser Company (ref. Al 4192) in the form of 0.8 mm (1/32") extrudates is employed, the characteristics of which are as follows:

10	Volume of pores with a radius greater than or equal to 40 Å	= 0.91 cm ³ /g
	Total BET specific surface	= 161 m ² /g
	Mean pore radius	= 106 Å
	Apparent density (compacted bulk)	= 0.47
15	Surface area of pores with a radius between 50 and 250 Å	= 105 m ² /g
	Fe ₂ O ₃ content: 0.08% by weight	
	SiO ₂ content: 0.13% by weight	
	Na ₂ O content: 0.015% by weight.	

20 0.12 litre of this alumina is charged as a fixed bed into a tubular reactor with an internal diameter of 28 mm, and it is then converted into catalyst by proceeding as in the table below.

Temperature in the reactor ° C	Absolute pressure (atmos- pheres)	Molar through- put of reactants in moles/(h x 100 ml of catalyst)		Contact time (seconds)	Life, hours cumulative
		C ₂ Cl ₂ F ₄	HF		
350	1	0.374	0.177	12.8	48
380	1	0.328	0.178	12.7	93
410	1	0.337	0.187	12.2	142

At the end of this treatment, after the oxygen-free acids have been scrubbed with water and with an aqueous sodium hydroxide solution, the proportion of C₂ClF₅ in the gas leaving the reactor reaches 23.6%, whereas it was only 0.7% at 350°C.

The reactor temperature is then raised to 450°C, the C₂Cl₂F₄ being of the same quality as before. The results are given in Table I below, where the molar throughputs are expressed per 0.1 litre of catalyst, the reactor pressure being 1 bar absolute, and the temperature being maintained at 450°C. The working life of the catalyst which is shown includes the preliminary step of conversion of alumina into catalyst.

In all the tests described above, the unconverted dichlorotetrafluoroethane (approximately 15% on a molar basis of the C₂Cl₂F₄ compound employed) contains 20 to 25% of the symmetrical isomer CF₂Cl-CF₂Cl.

After 550 hours' operation under the working conditions described above, and a regeneration with pure air at 450°C, the catalyst produces results which are absolutely identical to the above.

5 Example 2

The same activated alumina as in Example 1, in the same physical form of 0.8 mm extrudates, is taken and is converted into catalyst by a fluidized bed technique. 0.125 litre of Kaiser 4192 alumina, i.e. 51.3 g, is taken
10 and is heated to 350°C in a stream of nitrogen, and the following gas mixture is then introduced for 24 h at atmospheric pressure:

air ... 27.2 moles/h

HF ... 0.77 moles/h.

15 After 24 hours of this treatment, the catalyst contains 62% of fluorine, that is to say 91.4% of aluminium fluoride and 8.6% of unconverted alumina. Its weight rises to 77.9 grams.

68.1 grams of this catalyst (0.1 litre) are taken
20 to be tested in the same 28-mm diameter tubular reactor as in Example 1, and the procedure of Example 1 is followed. The results are shown in Table II below.

The catalyst working life which is shown in this table corresponds to the period beginning with the charging
25 of the reactor with a fixed bed and does not include the conversion of alumina into catalyst.

Example 3

The method of Example 2 is followed, starting with the same activated alumina, except that after the conversion of the alumina into catalyst and charging the reactor with a fixed bed for the fluorination of $C_2F_4Cl_2$, the reaction is started with a molar ratio $HF/C_2Cl_2F_4$ close to 1 instead of 0.4 in Example 2.

The results are shown in Table III.

The starting method does not alter the catalyst's activity or selectivity.

The working life shown is the period from the charging of the reactor with a fixed bed and does not include the conversion of alumina into catalyst.

Example 4 (comparative)

The procedure of Example 2 is followed but using an activated alumina whose pore volume is different from that of the activated alumina used in the process according to the invention; the alumina used is SCM 250, having the following characteristics:

Chemical purity

Na_2O 800 ppm

Fe_2O_3 300 ppm

SiO_2 200 ppm

Physical properties:

Form: beads, 2 to 4 mm in diameter

Specific surface (BET) = $270 m^2/g$

Total volume of pores of radius greater than

or equal to $40 \text{ \AA} = 0.63 \text{ cm}^3/\text{g}$

Mean pore diameter $90 \text{ \AA}$

Bulk density: 0.66 g/ml.

A catalyst is obtained whose AlF_3 content is 87.7%
5 by weight, the remainder being unconverted alumina. The
results are shown in Table IV,1; the working lives are
measured as in Example 2.

The same SCM 250 alumina is used as spheres of 2
to 4 mm and is converted into catalyst as before, but
10 after the conversion it is reduced mechanically into small
pieces of less than 1 mm to approach the size of the
Kaiser alumina of Examples 1, 2 and 3. This catalyst is
then used as before.

The results are shown in Table IV,2.

15 The working lives shown in the table do not in-
clude the time for converting the alumina to catalyst.

Example 5

CS 331-1 alumina sold by the Catalysts and Chemi-
cals Europe (CCE) company is employed, whose principal
20 physical characteristics are

the following:

form: extrudates $1/16''$ ($\approx 1.6 \text{ mm}$) in diameter

active surface area (BET): $255 \text{ m}^2/\text{g}$

mean pore diameter: $90 \text{ \AA}$

25 volume of pores of radius greater than or equal
to $40 \text{ \AA}$: $0.76 \text{ cm}^3/\text{g}$

bulk density: 0.60 g/ml.

Na₂O content: 0.02%

Fe₂O₃ content: 0.08%

SiO₂ content: 0.03%

The catalyst is prepared as in Example 2, the AlF₃
5 concentration of the catalyst is 92%, with 8% of unconverted alumina.

The results of the corresponding tests are shown in Table No. V below; the results obtained are found to be clearly superior to those obtained in comparative Example
10 No. 4 (SCM 250 alumina).

The working lives shown do not include the conversion of alumina into catalyst.

Example 6 (comparative)

Fluorination of C₂F₄Cl₂ with HF according to a process not in accordance with the invention.
15

Instead of taking an alumina and converting it into catalyst as previously, a commercial aluminium trifluoride powder containing approximately 8% of alumina is used.

Its chief physicochemical characteristics are as
20 follows:

mean particle size of the powder: 50 to 80
microns

total specific area (BET) = 1.6 m²/g

volume of pores of radius greater than or equal
25 to 40 Å: 0.25 cm³/g.

After this, the procedure is as in the preceding

examples of the fluorination of $C_2F_4Cl_2$ with HF, but in a fluid bed instead of a fixed bed.

The results are collated in Table VI.

Example 7

5 The procedure of Example 2 is followed, using the same type of alumina (Kaiser 4192), but working with a shorter contact time.

 The results are shown in Table VII, where the working lives do not include the time for converting the
10 alumina into catalyst.

 It is found that the specific output of C_2ClF_5 can be considerably increased without harming the yield.

 Table VIII, which gives results obtained in analogous operating conditions, shows the influence of
15 the Na_2O content.

OPERATING CONDITIONS					RESULTS OBTAINED						
Catalyst working life (cumulative hours)	Molar throughput of reactants (moles/hour)		Molar ratio HF/ $C_2Cl_2F_4$	Contact time (seconds)	Degree of conversion %		Degree of conversion of $C_2Cl_2F_4$ to C_2ClF_5 %	Molar ratio C_2F_6	Molar ratio $C_2F_3Cl_3$	Molar ratio $CF_4 + CF_3Cl$	Specific output in grams of C_2ClF_5 per hour per litre of catalyst
	HF	$C_2Cl_2F_4$			HF	$C_2Cl_2F_4$		C_2ClF_5 (x 100)	C_2ClF_5 (x 100)	C_2ClF_5 (x 100)	
165	0.132	0.330	0.40	13.1	90.0	76.9	62.0	0.5	20.1	0.2	316
257	0.268	0.257	1.04	11.6	79.3	85.2	81.4	0.6	3.9	0.1	310
445	0.254	0.283	0.90	11.3	73.1	85.5	81.7	0.5	4.0	0.1	351

TABLE I

TABLE II

OPERATING CONDITIONS			RESULTS OBTAINED						
Catalyst working life (cumulative hours)	Molar throughput of reactants (moles/hour)		Contact time (seconds)	Degree of conversion %		Degree of conversion of C_2F_4 to C_2ClF_5 %	Molar ratio C_2F_6 to C_2ClF_5 (x 100)	Molar ratio $C_2F_3Cl_3$ to C_2ClF_5 (x 100)	Specific output in grams of C_2ClF_5 per hour per litre of catalyst
	HF	$C_2Cl_2F_4$		HF	$C_2Cl_2F_4$				
23.5	0.140	0.377	11.8	89.3	80.4	64.7	1.1	19.2	377
46.5	0.149	0.365	11.8	91.1	80.5	65.1	1.2	18.8	367
66.5	0.140	0.360	12.2	93.4	79.6	63.8	0.7	20.0	354
89.5	0.244	0.247	12.4	79.5	87.9	80.8	1.0	5.5	309
111.5	0.223	0.247	12.9	80.2	87.2	79.6	1.0	6.0	304
133.5	0.218	0.247	13.0	83.1	85.8	77.2	1.0	7.5	295

Operating conditions

Fixed bed catalyst (volume = 0.1 litre)

Temperature: 450°C

Pressure: atmospheric

TABLE III

OPERATING CONDITIONS					Results obtained					
Catalyst working life (cumulative hours)	Molar throughput of reactants (moles/hour)		Molar ratio HF/ $C_2Cl_2F_4$	Contact time (seconds)	Degree of conversion %		Degree of conversion of $C_2Cl_2F_4$ to C_2ClF_5 %	Molar ratio C_2F_6 to C_2ClF_5 (x 100)	Molar ratio $C_2F_3Cl_3$ to C_2ClF_5 (x 100)	Specific output in grams of C_2ClF_5 per hour per litre of catalyst
	HF	$C_2Cl_2F_4$			HF	$C_2Cl_2F_4$				
24	0.255	0.243	1.05	13.2	75.4	86.5	79.8	1.2	4.5	300
47	0.240	0.245	0.98	12.5	76.8	86.7	79.9	0.9	5.2	302

Operating conditions

Fixed bed catalyst (volume = 0.1 litre) prepared as in

Example No. 2

Temperature = 450°C

Pressure: atmospheric

TABLE IV,1

OPERATING CONDITIONS					Results obtained					
Catalyst working life (cumulative hours)	Molar throughput of reactants (moles/hour)		Molar ratio HF/ $C_2Cl_2F_4$	Contact time (seconds)	Degree of conversion %		Degree of conversion of $C_2Cl_2F_4$ to C_2ClF_5 %	Molar ratio C_2F_6 to C_2ClF_5 (x 100)	Molar ratio $C_2F_3Cl_3$ to C_2ClF_5 (x 100)	Specific output in grams of C_2ClF_5 per hour per litre of catalyst
	HF	$C_2Cl_2F_4$			HF	$C_2Cl_2F_4$				
24	0.240	0.243	0.99	12.5	9.0	9.4	6.8	5.8	4.3	25
48	0.235	0.253	0.93	12.4	10.0	10.3	8.2	2.4	3.6	32
71	0.249	0.253	0.98	12.1	12.7	10.3	7.9	1.9	3.7	31

Operating conditions common to the tests

Fixed bed catalyst (volume = 0.1 litre) in the form of
2 to 4 mm beads

Temperature = 450°C

Atmospheric pressure

TABLE IV,2

OPERATING CONDITIONS					Results obtained					
Catalyst working life (cumulative hours)	Molar throughput of reactants (moles/hour)		Molar ratio HF/ $C_2Cl_2F_4$	Contact time (seconds)	Degree of conversion %		Degree of conversion of $C_2Cl_2F_4$ to C_2ClF_5 %	Molar ratio C_2F_6 to C_2ClF_5 (x 100)	Molar ratio $C_2F_3Cl_3$ to C_2ClF_5 (x 100)	Specific output in grams of C_2ClF_5 per hour per litre of catalyst
	HF	$C_2Cl_2F_4$			HF	$C_2Cl_2F_4$				
117	0.232	0.233	1.0	13.0	9.5	10.6	8.4	0.5	2.3	30
139	0.239	0.234	1.0	12.8	8.9	10.3	8.0	0.5	2.4	20
Temperature = 500°C after the 139th hour										
159	0.238	0.230	1.0	12.1	10.9	20.3	17.2	1.5	1.1	51

Operating conditions

Fixed bed catalyst (volume = 0.1 litre)

Temperature = 450°C up to the 139th hour, then 500°C

Atmospheric pressure

TABLE V

OPERATING CONDITIONS				Results obtained						
Catalyst working life (cumulative hours)	Molar throughput of reactants (moles/hour)		Molar ratio HF: $C_2Cl_2F_4$	Contact time (seconds)	Degree of conversion %		Degree of conversion of $C_2Cl_2F_4$ to C_2ClF_5 %	Molar ratio C_2F_6 to C_2ClF_5 (x 100)	Molar ratio C_2F_6 to C_2ClF_5 (x 100)	Specific output in grams of C_2ClF_5 per hour per litre of catalyst
	HF	$C_2Cl_2F_4$			HF	$C_2Cl_2F_4$				
25	0.245	0.242	1.0	12.5	67.7	76.9	71.5	1.7	5.3	268
48	0.245	0.245	1.0	12.4	66.4	77.0	71.0	1.0	5.4	268
71	0.245	0.245	1.0	12.4	66.3	76.9	70.7	1.0	5.7	268
36.5	0.194	0.243	0.8	13.9	66.2	78.3	70.3	1.2	7.5	266

Operating conditions

Fixed bed catalyst (volume = 0.1 litre) in the form of

1.6 mm extrudates, prepared as in Example No. 2

Temperature = 450°C

Atmospheric pressure

TABLE VI

OPERATING CONDITIONS					Results obtained					
Catalyst working life (cumulative hours)	Molar throughput of reactants (moles/hour)		Molar ratio HF/ $C_2Cl_2F_4$	Contact time (seconds)	Degree of conversion %		Degree of conversion of $C_2Cl_2F_4$ to C_2ClF_5 %	Molar ratio C_2F_6 to C_2ClF_5 (x 100)	Molar ratio $C_2F_3Cl_3$ to C_2ClF_5 (x 100)	Specific output in grams of C_2ClF_5 per hour per litre of catalyst
	HF	$C_2Cl_2F_4$			HF	$C_2Cl_2F_4$				
24	0.357	0.358	1.0	11.8	7.0	0.2	0.1	0	0	0.4
47	0.351	0.378	0.9	11.6	2.0	0.1	0.7	0	0	0.4
70	0.351	0.376	0.9	11.6	4.1	0.1	0.1	0	0	0.4
92	0.360	0.368	1.0	10.8	5.4	0.2	0.1	6	0	0.4

Operating conditions

Catalysts in the form of a fluid bed (volume = 0.14 litre)

with a mean particle size of 50 to 80 microns

Temperature = 450°C

Atmospheric pressure

TABLE VII

OPERATING CONDITIONS					Results obtained					
Catalyst working life (cumulative hours)	Molar throughput of reactants (moles/hour)		Molar ratio HF/ $C_2Cl_2F_4$	Contact time (seconds)	Degree of conversion %		Degree of conversion of $C_2Cl_2F_4$ to C_2ClF_5 %	Molar ratio C_2F_6 / C_2ClF_5 (x 100)	Molar ratio $C_2F_3Cl_3$ / C_2ClF_5 (x 100)	Specific output in grams of C_2ClF_5 per hour per litre of catalyst
	HF	$C_2Cl_2F_4$			HF	$C_2Cl_2F_4$				
24	0.349	0.375	0.93	8.4	60.3	65.4	60.2	1.0	7.5	348.8
48	0.367	0.373	0.98	8.2	59.5	67.2	62.5	0.5	7.0	360.2
72.45	0.521	0.501	1.04	5.9	51.7	60.9	57.1	0.5	6.1	442.0
95.45	0.500	0.495	1.01	6.4	54.4	62.7	58.5	0.7	6.7	447.4

Operating conditions

Fixed bed catalysts (volume = 0.1 litre) in the form of

0.8 mm extrudates

Temperature = 450°C

Atmospheric pressure

TABLE VIII

OPERATING CONDITIONS				Results obtained					
Na ₂ O content (ppm)	Molar through- out of reac- tants (moles/hour)		Molar ratio HF/ C ₂ Cl ₂ F ₄	Contact time (sec- onds)	Degree of conversion %		Degree of con- version of C ₂ Cl ₂ F ₄ to C ₂ ClF ₅ %	Molar ratio C ₂ F ₃ Cl ₃ C ₂ ClF ₅ (x 100)	Specific output in grams of C ₂ ClF ₅ per hour per litre of cata- lyst
	HF	C ₂ Cl ₂ F ₄			HF	C ₂ Cl ₂ F ₄			
150	0.449	0.429	1.05	7.4	52.1	61.1	57.9	5.5	383.8
930	0.411	0.428	0.96	7.2	7.8	8.1	7.7	5.2	50.9

Operating conditions

Fixed bed catalysts (volume = 0.1 litre) in the form of

0.8 mm extrudates

Temperature = 450°C

Atmospheric pressure

CLAIMS

1. Gas phase process for the manufacture of chloro-
pentafluoroethane by the action of hydrofluoric acid on
dichlorotetrafluoroethane in the presence of a catalyst,
characterized in that the catalyst is prepared by react-
5 ing, in a gaseous phase, an activated alumina in which
the volume of the pores with a radius of 40 angstroms and
more is greater than $0.7 \text{ cm}^3/\text{g}$ with hydrofluoric acid or
with a mixture of hydrofluoric acid either with air or
with a fluoro compound.
- 10 2. Process according to Claim 1, characterized in
that an alumina is used in which the volume of the pores
with a radius of 40 Å and more is between 0.75 and $1 \text{ cm}^3/\text{g}$.
3. Process according to Claim 1 or 2, characterized
in that the alumina has a purity greater than 99.2% by
15 weight.
4. Process according to one of Claims 1 to 3, charac-
terized in that the alumina is in the form of particles
of a size smaller than a sphere with a diameter of 20 mm.
5. Process according to one of Claims 1 to 4, charac-
20 terized in that the preparation of the catalyst is carried
out by the action of a mixture of air and hydrofluoric
acid on alumina at a temperature of between 150 and
500°C.
6. Process according to Claim 5, characterized in
25 that the HF content in the mixture of air and HF is bet-
ween 0.1 and 30% and preferably between 1.5 and 3% on a
molar basis.



7. Process according to Claim 5 or 6, in which the operation is carried out at atmospheric pressure at 350°C or above.

8. Process according to one of Claims 1 to 4, characterized in that the preparation of the catalyst is carried out by a gaseous phase reaction of a mixture of hydrofluoric acid and dichlorotetrafluoroethane over alumina at a temperature of between 150 and 500°C.

9. Process according to Claim 8, characterized in that the operation is carried out at atmospheric pressure with contact times of between 5 and 15 seconds.

10. Process according to one of Claims 1 to 9, characterized in that the fluorination of dichlorotetrafluoroethane with HF is carried out with a molar ratio HF/dichlorotetrafluoroethane of between 0.5 and 1.5 and preferably between 0.9 and 1.1, and at a temperature of between 350 and 550°C and preferably between 380 and 500°C.

11. Process according to Claim 10, characterized in that the operation is carried out between 0.5 and 4 bars absolute.

12. Process according to Claim 11, characterized in that the operation is carried out at atmospheric pressure with contact times of between 5 and 15 seconds and preferably between 6 and 13 seconds.



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Patentansprüche

1. Verfahren zur Herstellung von Chlorpentafluorethan in der Gasphase durch Einwirkung von Fluorwasserstoffsäure auf Dichlortetrafluorethan in Gegenwart eines Katalysators, dadurch gekennzeichnet, dass der Katalysator durch Reagieren

lases aktiven Aluminiumoxids in der Gasphase Gehalt an Natriumoxid geringer als ppm ist und dessen Volumen der Poren mit einem Radius von 40 Angström oder mehr grösser als 0,7 cm³/g, mit Fluorwasserstoffsäure oder einem Gemisch von Fluorwasserstoffsäure mit Luft, Stickstoff oder einer fluorierten Verbindung hergestellt wird.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, dass man ein Aluminiumoxid verwendet, dessen Volumen der Poren mit einem Radius von 40 Angström und mehr zwischen 0,75 und 1 cm³/g beträgt.

3. Verfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, dass das Aluminiumoxid eine Reinheit von mehr als 99,2 Gew.% hat.

4. Verfahren nach einem der Ansprüche 1 bis 3, dadurch gekennzeichnet, dass das Aluminiumoxid in Form von Partikeln einer Grösse kleiner als eine Kugel mit 20 mm Durchmesser vorliegt.

5. Verfahren nach einem der Ansprüche 1 bis 4, dadurch gekennzeichnet, dass die Herstellung des Katalysators durch Einwirkung eines Gemisches aus Fluorwasserstoffsäure und Luft oder Stickstoff auf Aluminiumoxid bei einer Temperatur zwischen 150 und 500° C erfolgt.

6. Verfahren nach Anspruch 5, dadurch gekennzeichnet, dass der Gehalt an HF in dem Gemisch HF-Luft oder -Stickstoff zwischen 0,1 und 30% und vorzugsweise zwischen 1,5 und 3 Mol.% liegt.

7. Verfahren nach Anspruch 5 oder 6, bei dem man bei atmosphärischem Druck bei einer Temperatur von 350° C oder mehr arbeitet.

8. Verfahren nach einem der Ansprüche 1 bis 4, dadurch gekennzeichnet, dass die Herstellung des Katalysators durch Einwirkung eines Gemisches von Fluorwasserstoffsäure und Dichlortetrafluorethan in der Gasphase auf Aluminiumoxid bei einer Temperatur zwischen 150 und 500° C geschieht.

9. Verfahren nach Anspruch 8, dadurch gekennzeichnet, dass man bei atmosphärischem Druck arbeitet mit einer Kontaktzeit von 5 bis 15 Sekunden.

10. Verfahren nach einem der Ansprüche 1 bis 9, dadurch gekennzeichnet, dass die Fluorierung des Dichlortetrafluorethans mit HF mit einem molaren Verhältnis HF/Dichlortetrafluorethan zwischen 0,5 und 1,5 und vorzugsweise zwischen 0,9 und 1,1 und bei einer Temperatur zwischen 350 und 550° C und vorzugsweise zwischen 380 und 500° C durchgeführt wird.

11. Verfahren nach Anspruch 10, dadurch gekennzeichnet, dass man zwischen 0,5 und 4 bar absolut arbeitet.

12. Verfahren nach Anspruch 11, dadurch gekennzeichnet, dass man bei atmosphärischem Druck mit einer Kontaktzeit von 5 bis 15 Sekunden und vorzugsweise zwischen 6 und 13 Sekunden arbeitet.

As printed

Claims

1. Gas phase process for the manufacture of chloropentafluoroethane by the action of hydrofluoric acid on dichlorotetrafluoroethane in the presence of a catalyst, characterized in that the catalyst is prepared by reacting, in a gaseous phase, an activated alumina whose sodium oxide content is less than 300 ppm and in which the volume of the pores with a radius of 40 angstroms and more is greater than 0.7 cm³/g with hydrofluoric acid or with a mixture of hydrofluoric acid with air, nitrogen or a fluoro compound.

2. Process according to Claim 1, characterized in that an alumina is used in which the volume of the pores with a radius of 40 A and more is between 0.75 and 1 cm³/g.

3. Process according to Claim 1 or 2, characterized in that the alumina has a purity greater than 99.2% by weight.

4. Process according to one of Claims 1 to 3, characterized in that the alumina is in the form of particles of a size smaller than a sphere with a diameter of 20 mm.

5. Process according to one of Claims 1 to 4, characterized in that the preparation of the catalyst is carried out by the action of a mixture of hydrofluoric acid and air or nitrogen on alumina at a temperature of between 150 and 500° C.

6. Process according to Claim 5, characterized in that the HF content in the mixture of HF and air or nitrogen is between 0.1 and 30% and preferably between 1.5 and 3% on a molar basis.

7. Process according to Claim 5 or 6, in which the operation is carried out at atmospheric pressure at 350° C or above.

8. Process according to one of Claims 1 to 4, characterized in that the preparation of the catalyst is carried out by a gaseous phase reaction of a mixture of hydrofluoric acid and dichlorotetrafluoroethane over alumina at a temperature of between 150 and 500° C.

9. Process according to Claim 8, characterized in that the operation is carried out at atmospheric pressure with contact times of between 5 and 15 seconds.

10. Process according to one of Claims 1 to 9, characterized in that the fluorination of dichlorotetrafluoroethane with HF is carried out with a molar ratio HF/dichlorotetrafluoroethane of between 0.5 and 1.5 and preferably between 0.9 and 1.1, and at a temperature of between 350 and 550° C and preferably between 380 and 500° C.

11. Process according to Claim 10, characterized in that the operation is carried out between 0.5 and 4 bar absolute.

12. Process according to Claim 11, characterized in that the operation is carried out at atmospheric pressure with contact times of between 5 and 15 seconds and preferably between 6 and 13 seconds.

