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Invention Title: Regeneration of Catalysts for Gas Phase Fluorination

The following statement is a full description of this invention, including the best method of performing it known to me/us:-

The present invention relates to the synthesis of hydrohaloalkanes by fluorination and more particularly to a process for regeneration of the catalysts for gas phase fluorination.

5 Intensive research into substitutes for chlorofluorocarbons (CFCs) is being directed, inter alia, towards the synthesis of hydrohaloalkanes. Some stages of these syntheses can be carried out by fluorination with hydrogen fluoride, using
10 heterogeneous gas-phase catalysis. Many fluorination catalysts have been developed for this purpose and are described in the literature.

The synthesis, using fluorination, of halogen compounds containing hydrogen atoms has been found to
15 be more complex than the synthesis of perhalogenated molecules (CFCs). In fact, the hydrogen-containing compounds (raw materials, reaction intermediates or finished products) are more fragile than perhalogenated compounds and the presence of hydrogen atoms can give
20 rise to dehydrohalogenation reactions, producing olefins which are liable to be decomposed and to foul the catalyst. Furthermore, the substitution of a chlorine by a fluorine on a carbon-based group also carrying hydrogen atoms is difficult and must often be
25 carried out under severe operational conditions, resulting in more rapid deactivation of the catalyst.

The fluorination of F133a ($\text{CF}_3\text{-CH}_2\text{Cl}$) to F134a

($\text{CF}_3\text{-CH}_2\text{F}$), an example widely described in the literature, is a good illustration of these difficulties. In this case the dehydrofluorination of F133a produces F1122 ($\text{CF}_2=\text{CHCl}$), which is one of the precursors of the "coke" resulting in catalyst fouling. Furthermore, this Cl/F substitution is difficult and unfavoured thermodynamically; it therefore requires relatively high temperatures ($> 300^\circ\text{C}$), which accelerate this coking and give rise to risks of deactivation due to change in the catalyst structure (crystallization etc.). Other fluorination reactions, in principle easier, are based on the fluorination of halogenated olefins (C_2HCl_3 , C_2Cl_4 , etc.) or of compounds liable to decompose thermally (F30, etc.); they therefore also present risks of coking.

The term "coke" is intended to mean not only the true coke deposited on the catalyst, but also all the heavy organic substances which foul the catalyst and have a chemical formula resembling that of halogenated polymers; they originate from the decomposition of the reactants and of the reaction products under the conditions of gas phase fluorination.

In order to improve the durability of the fluorination catalysts, various processes for regeneration or for maintenance of their activity have already been described in the literature. Thus, published Japanese Patent Application 1262946/89

describes the regeneration, in the absence of organic substances, of chromium-based fluorination catalysts by a treatment in the presence of oxygen.

Published European Patent Application

- 5 EP 475 693 also describes a process for regeneration of chromium-based catalysts, but this time using a treatment by means of a mixture of oxygen-containing oxidizing agent and of HF (more especially an air/HF mixture), at a temperature of between 300 and 500°C.
- 10 Similarly, US Patent 5 407 877 describes the regeneration of the same catalysts in the presence of water vapour.

- Continuous addition of chlorine during disproportionation reactions (absence of HF) in order
- 15 to maintain the activity of chromium-based catalysts is described in published Japanese Patent Application 49-134612/74.

- Finally, document H1129 (US Statutory Invention Registration) describes the continuous
- 20 addition of chlorine during fluorination of F133a, to maintain the catalytic activity of a chromium-based catalyst.

- These processes are not, however, completely satisfactory. In fact, those based on a regeneration in
- 25 the presence of oxygen by burning the "coke" require perfect control of the exothermicity, throughout the regeneration, to avoid the formation of hot spots in the catalyst bed, which are detrimental to the

catalyst.

As a result of chlorination of the organic products (replacement of a hydrogen atom by a chlorine atom), continuous addition of chlorine in order

- 5 possibly to improve the lifetime of the catalyst during the synthesis of hydrofluoroalkanes or of hydrochloro-fluoroalkanes is reflected in a loss of selectivity for the proper product and hence in a loss in yield.

- According to the invention, there is provided
10 a process for gas-phase regeneration of fluorination catalysts, which process comprises treating the deactivated catalyst with Cl_2 and HF, optionally in the presence of an inert substance, at a temperature of between 250 and 450°C.

- 15 The process for regeneration of deactivated fluorination catalysts according to the invention does not exhibit the above disadvantages of the prior art. The process of the invention, based on the treatment of the deactivated catalyst with chlorine and hydrogen
20 fluoride, makes it possible not only to restore the activity of the catalyst, but is easy to implement industrially and, as a result of very low exothermicity, makes it possible to avoid irreversible crystallization of the catalyst. In fact, apart from
25 the heat of adsorption of the reactants during the initial minutes, after they are introduced onto the catalyst from which HF and organic products have been desorbed, the regeneration using the Cl_2 /HF mixture is

practically not exothermic and in contrast to a regeneration by burning the "coke" (in the presence of oxygen) does not require a perfect control of the exothermicity throughout the regeneration.

5 The optimum temperature has to be chosen as a function of the conditions (nature of the organic compounds, temperature, etc.) of the fluorination which has preceded the regeneration. This optimum temperature is generally equal to or slightly higher than that used
10 in practice during the fluorination; it is therefore very often between 300 and 430°C.

 In the absence of organic compounds the introduction of hydrogen fluoride and of chlorine can be performed simultaneously or by alternate
15 introduction of either of the reactants. In this latter case the alternation must be frequent (for example every 10 minutes) to obtain an efficacious and rapid regeneration. However, where the efficiency of the regeneration is concerned, it has been found preferable
20 to work with a simultaneous introduction of HF and chlorine. During a simultaneous introduction the HF/HF + Cl₂ molar ratio (MR) can be variable ($0 < MR < 1$), but for reasons of efficiency it is preferable to work with an HF/HF + Cl₂ molar ratio of
25 between 0.05 and 0.995 and more particularly between 0.3 and 0.99. The value of the MR may even be modified during the regeneration; thus, for example, it is possible to start with a chlorine-rich mixture in order

to end with an HF-rich mixture.

The duration of the regeneration obviously depends on the deactivation state of the catalyst, the regeneration conditions and the degree of regeneration which is sought. It is generally between 10 and 300 hours and in most cases between 24 and 150 hours. It is preferable to regenerate the catalyst as soon as the first signs of deactivation appear ("preventive regeneration), rather than wait for a considerable deactivation and, hence, a more difficult regeneration. The frequency of these regenerations must be optimized as a function of the savings in the lifetime of the catalyst in relation to the losses of production which they cause.

During the regeneration the time of contact of the reactants with the catalyst can also be very variable and lie between 1 second and infinity (static regeneration). It is more generally between 5 and 300 seconds and preferably between 10 and 60 seconds.

The regeneration is often conducted at the same pressure as the fluorination reaction or at a lower pressure. It is even possible to envisage operating under a slight vacuum, so as better to desorb the heavy substances deposited on the catalyst. The regeneration is generally conducted at a pressure of between 10 kPa and 5 MPa and in most cases between 50 kPa and 2 MPa.

Bearing in mind its low exothermicity (apart

from the heat of adsorption of the HF and Cl₂ reactants onto the catalyst), the regeneration according to the invention can be conducted in the fluorination reactor, even if the latter is a monotubular reactor. Such a situation is very practical when it is intended to carry out preventive, and hence frequent, regenerations. On the other hand, in order to gain on plant output, it may be advantageous to discharge the catalyst and to regenerate it in equipment devised for this purpose, while a second catalyst charge is being recharged and then employed in the fluorination unit. Another possibility consists in working with two reactors alternately: one on fluorination, the other on regeneration, and then vice versa.

The Cl₂/HF regeneration according to the invention can be applied to any catalysts for gas phase fluorination which are described in the literature. It is particularly well suited to catalysts comprising at least one of the following metals: Cr, V, Co, Mg, Fe, Ni and Zn.

In the case of chromium-based catalysts the regeneration according to the present invention does not induce any chromium losses due to oxidation of Cr^{III}. Such losses can be observed when oxygen is employed, but the Cl₂/HF combination does not present this disadvantage.

As indicated above, continuous addition of chlorine during the fluorination of hydrogen-containing

organic compounds is generally not advantageous, because it results in a loss in yield. However, in the case of organic compounds which, like, for example, dichloromethane (F30) and/or chlorofluoromethane (F31),
5 react weakly with chlorine (chlorine conversion lower than 95 % in one pass over the catalyst), it may be found economically advantageous to regenerate the catalyst by noncontinuous addition of chlorine during the fluorination reaction. In contrast to regeneration
10 of the catalyst away from organic substances, this technique makes it possible not to interrupt the production of the unit; the momentary loss in selectivity, due to the portion of the chlorine which reacts with the organic substances, is then compensated
15 for by a gain in output.

An optimization of the frequency of the regenerations generally results in a regeneration being programmed when the catalyst has lost between 5 and 60 %, preferably between 10 and 30 %, of its activity.
20 This type of regeneration, without interrupting the production of the fluorination unit, is not recommended when the organic compounds are highly reactive towards chlorine (as in the fluorination of olefins like C_2Cl_4 or C_3HCl_3).

25 The following examples illustrate the invention without limiting it.

EXAMPLE 1: Cr_2O_3 catalyst (fluorination of F133a)

A Cr^{III} oxide-based catalyst (50 ml), deactivated after being used for the fluorination of F133a to F134a, is treated at 350°C, at atmospheric pressure, for 72 hours with a mixture of HF and chlorine with respective flow rates of 0.25 moles/hour and 0.01 mole/hour.

The activity of the catalyst before and after regeneration was tested in the conditions and with the results in Table I.

Quantitative determinations of chromium in the gas-scrubber water at the exit of the reactor, during the regeneration and during the fluorination sequence which follows it, have made it possible to conclude that there are no losses in chromium due to this regeneration technique.

EXAMPLE 2: Cr₂O₃ catalyst (fluorination of F133a)

A Cl₂/HF regeneration was tested on a 2 m³ charge of Cr₂O₃ catalyst in an industrial monotubular reactor. The fluorination of F133a is stopped by gradually raising the HF/organics molar ratio in order to finish under pure HF. The regeneration is ensured by adding chlorine to the HF flow. The flow rates employed are those of Example 1, but proportioned to the catalyst charge to be treated. No exotherm greater than 5°C was observed in this industrial regeneration. The results shown in Table I indicate that the regeneration has produced the same gain in conversion as during the

laboratory test (Example 1).

EXAMPLE 3: Cr-Zn/AlF₃ catalyst (fluorination of F133a)

A catalyst (50 ml) based on Cr and Zn which
5 are supported on a fluorinated alumina, deactivated
after being used for the fluorination of F133a to
F134a, was treated at 350°C, at atmospheric pressure,
for 72 hours with an HF/Cl₂ mixture with respective flow
rates of 0.25 moles/hour and 0.01 mole/hour. The
10 results of activity before and after regeneration are
shown in Table I.

EXAMPLE 4: Ni-Cr/AlF₃ catalyst (fluorination of F133a)

A catalyst (50 ml) based on Ni and Cr which
15 are supported on a fluorinated alumina, deactivated
after being used for the fluorination of F133a to
F134a, was treated at 350°C, at atmospheric pressure,
for 68 hours with an HF/Cl₂ mixture with respective flow
rates of 0.25 moles/hour and 0.01 mole/hour. The
20 results of activity before and after regeneration are
shown in Table I.

EXAMPLE 5: Ni/AlF₃ catalyst (fluorination of F133a)

A catalyst (50 ml) based on Ni supported on a
25 fluorinated alumina, deactivated after being used for
the fluorination of F133a to F134a, was treated at
350°C, at atmospheric pressure, for 90 hours with an
HF/Cl₂ mixture with respective flow rates of

0.25 moles/hour and 0.01 mole/hour. The results of activity before and after regeneration are shown in Table I.

EXAMPLE 6: Ni-Cr/AlF₃ catalyst (fluorination
5 of F1110)

A catalyst (50 ml) based on Ni and Cr which are supported on a fluorinated alumina, deactivated after being used for the fluorination of perchloro-ethylene, was treated at 350°C, at atmospheric
10 pressure, for 72 hours with an HF/Cl₂ mixture with respective flow rates of 0.25 moles/hour and 0.02 moles/hour. The results of activity before and after regeneration are shown in Table II.

EXAMPLE 7, comparative: Ni-Cr/AlF₃ catalyst in
15 fluorination of F1110 (regeneration with chlorine alone)

A sample (50 ml) of the same batch of spent catalyst as that described in Example 6 was treated in the same conditions as in Example 5, but without
20 introduction of HF (regeneration with Cl₂ alone). The results of activity before and after regeneration are shown in Table II.

EXAMPLE 8, comparative: Ni-Cr/AlF₃ catalyst in
fluorination of F1110 (regeneration with HF alone)

25 A sample (50 ml) of the same batch of spent catalyst as that described in Example 6 was treated in the same conditions as in Example 5, but without introduction of chlorine (regeneration with HF alone).

The results of activity before and after regeneration are shown in Table II.

EXAMPLE 9: Ni-Cr/ AlF_3 catalyst (fluorination of F123)

5 A catalyst (50 ml) based on Ni and Cr which are supported on a fluorinated alumina, deactivated after being used for the fluorination of F123 ($\text{CF}_3\text{-CHCl}_2$) was treated at 350°C , at atmospheric pressure, for 48 hours with an HF/Cl_2 mixture with
10 respective flow rates of 0.25 moles/hour and 0.02 moles/hour. The results of activity before and after regeneration are shown in Table II.

EXAMPLE 10: Ni-Cr/ AlF_3 catalyst (fluorination of F30)

15 A catalyst (50 ml) based on Ni and Cr which are supported on a fluorinated alumina, deactivated after being used for the fluorination of F30 (CH_2Cl_2) was treated at 350°C , at atmospheric pressure, for 96 hours with an HF/Cl_2 mixture with respective flow
20 rates of 0.25 moles/hour and 0.02 moles/hour. The results of activity before and after regeneration are shown in Table III.

EXAMPLE 11: Ni-Cr/ AlF_3 catalyst (regeneration during the fluorination of F30)

25 A catalyst (35 ml) based on Ni and Cr which are supported on a fluorinated alumina is employed at 15 bars, at 300°C and with an HF/F30 molar ratio of 3. When the activity has dropped by approximately 30 % the

catalyst is regenerated without interrupting the fluorination, by adding chlorine to the reactants for 12 hours ($\text{Cl}_2/\text{F30}$ molar ratio = 0.02).

The results of activity before and after regeneration are shown in Table III. The losses in selectivity are of the order of 1 %.

EXAMPLE 12: Cr/charcoal catalyst
(fluorination of F1216)

A catalyst (50 ml) based on Cr^{III} oxide supported on charcoal, deactivated by gas phase fluorination of F1216 ($\text{CF}_3\text{-CF=CF}_2$) to F227e ($\text{CF}_3\text{-CHF-CF}_3$) was regenerated at 350°C , at atmospheric pressure, for 72 hours with an HF/Cl_2 mixture with respective flow rates of 0.25 moles/hour and 0.01 mole/hour. The results of activity before and after regeneration are shown in Table III.

In contrast to regeneration in the presence of oxygen, Cl_2/HF regeneration does not present any risk of ignition (reactor placed under inert substance before the regeneration) of the catalyst charge, including with a catalyst supported on charcoal.

The examples described above show the effectiveness of a Cl_2/HF regeneration on various deactivated fluorination catalysts, after use on various fluorination reactions. Comparison Example 6 with Examples 7 and 8 expresses well the superior effectiveness of a Cl_2/HF regeneration when compared with those employing only one of the two reactants.

Finally, Examples 1 and 12 illustrate the advantages of this Cl_2/HF regeneration when compared with a regeneration in the presence of oxygen: no chromium losses, very little or no exothermicity, no risk of ignition of the catalyst charge, even in the presence of charcoal.

In Tables I to III the abbreviations employed have the following meanings:

- tc.(s) = Contact time in seconds
- MR = Molar ratio
- OC = Overall conversion

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TABLE I
Catalysts for fluorination of F133a

EXAMPLE (Catalyst)	CATALYST STATE	TEST CONDITIONS					ACTIVITY OC F133a (%)
		Temp. (°C)	tc. (s)	Pressure (in MPa)	HF/Org. MR		
1 (bulk Cr)	Initial	350	4.2	0.1	4	22.5	
	Spent	350	4.1	0.1	4	12.1	
	Regenerated	350	4.2	0.1	4	22.1	
2 (bulk Cr)	Initial	350	22	1.5	2	15.6	
	Spent	350	21.8	1.5	2	8.1	
	Regenerated	350	21.8	1.5	2	15.8	
3 (Cr-Zn/AlF ₃)	Initial	340	2.1	0.1	3.6	15.8	
	Spent	340	2	0.1	3.8	8.2	
	Regenerated	340	2	0.1	3.5	13.9	
4 (Ni-Cr/AlF ₃)	Initial	340	2.1	0.1	3.5	16.7	
	Spent	340	2.1	0.1	3.6	10.2	
	Regenerated	340	2.1	0.1	3.6	16.5	
5 (Ni/AlF ₃)	Initial	350	3.9	0.1	4.4	18.7	
	Spent	350	4.1	0.1	4.1	10.1	
	Regenerated	350	3.7	0.1	4.3	19.2	

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TABLE II

Catalysts for fluorination in F120 series

EXAMPLE (Catalyst)	CATALYST STATE	TEST CONDITIONS				ACTIVITY OC Org. (%)
		Temp. (°C)	tc. (s)	Pressure (in MPa)	HF/Org. MR	
6 (Ni-Cr/AlF ₃)	Initial	350	4.8	0.1	7.2	69.6
	Spent	350	5	0.1	6.9	31.5
	Regenerated	350	5.9	0.1	6.9	71.3
7 Comparative (Ni-Cr/AlF ₃)	Initial	350	4.8	0.1	7.2	69.6
	Spent	350	4.2	0.1	4.7	24.1
	Regenerated	350	4.1	0.1	4	28.2
8 Comparative (Ni-Cr/AlF ₃)	Initial	350	4.8	0.1	7.2	69.6
	Spent	350	4.2	0.1	4.7	24.1
	Regenerated	350	4	0.1	4	26.8
9 (Ni-Cr/AlF ₃)	Initial	350	14.7	0.1	2.1	74.3
	Spent	350	14.7	0.1	2	56.1
	Regenerated	350	14.3	0.1	2.3	71.6

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TABLE III

EXAMPLE (Catalyst)	CATALYST STATE	TEST CONDITIONS				ACTIVITY OC Org. (%)
		Temp. (°C)	tc. (s)	Pressure (in MPa)	HF/Org. MR	
10 (Ni-Cr/AlF ₃ in fluorination of F30)	Initial	250	0.5	0.1	3	53.6
	Spent	250	0.5	0.1	3.6	35.9
	Regenerated	250	0.5	0.1	3.1	55.2
11 (Ni-Cr/AlF ₃ in fluorination of F30)	Initial	300	5	1.5	3	43.4
	Spent	300	5	1.5	3	31.6
	Regenerated	300	4.9	1.5	2.9	44.3
12 Cr/C in fluorination of F1216)	Initial	330	20.5	0.1	2	99.9
	Spent	330	20.2	0.1	2.1	75.3
	Regenerated	330	19.9	0.1	1.9	98.1

The claims defining the invention are as follows:

1. Process for regeneration of a catalyst for gas phase fluorination, which process comprises treating the deactivated catalyst with chlorine and
5 hydrogen fluoride, at a temperature of between 250 and 450°C.
2. Process according to Claim 1, in which the operation is carried out at a temperature of between 300 and 430°C.
- 10 3. Process according to Claim 2, in which the operation is carried out with an HF/HF + Cl₂ molar ratio of between 0.05 and 0.995.
4. Process according to Claim 2 in which the operation is carried out with an HF/HF + Cl₂ molar
15 ratio of between 0.3 and 0.99.
5. Process according to any one of the preceding Claims, in which a chlorine-rich mixture is employed first and the regeneration is ended using an HF-rich mixture.
- 20 6. Process according to any one of the preceding Claims, in which the operation is carried out at a pressure of between 10 kPa and 5 MPa.
7. Process according to any one of Claims 1 to 5, in which the operation is carried out at a
25 pressure of between 50 kPa and 2 MPa.
8. Process according to any one of the preceding Claims, in which the time of contact of the

reactants with the catalyst is between 5 and 300 seconds.

9. Process according to any one of Claims 1 to 7, in which the time of contact of the reactants with the catalyst is between 10 and 60 seconds.

10. Process according to any one of the preceding Claims, in which the duration of regeneration is between 10 and 300 hours.

11. Process according to any one of Claims 1 to 9, in which the duration of regeneration is between 24 and 150 hours.

12. Process according to any one of the preceding Claims, in which the treatment is performed in the absence of organic compounds.

13. Process according to any one of the preceding Claims, in which the regeneration is performed by noncontinuous addition of chlorine during fluorination of an organic compound which is not very reactive towards chlorine.

14. Process according to Claim 13, in which the organic compound is dichloromethane and/or chlorofluoromethane.

15. Process according to Claim 1 substantially as herein described.

16. Process for regeneration of a catalyst substantially as described in any one of Examples 1 to 6 and 9 to 12.

17. Catalyst regenerated by the process

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