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PROCESS FOR THE REGENERATION OF A CATALYST BASED ON TRIVALENT CHROMIUM COMPOUNDS

ABSTRACT

Process for the regeneration of a fluorination catalyst based on Cr(III) compounds optionallay supported comprising a) the treatment at 350°C-400°C with an air/inert gas mixture and b) treatment at 300°C-380°C with a mixture of an inert gas containing from 1 to 10% by volume of hydrogen.

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Invention Title: PROCESS FOR THE REGENERATION OF A CATALYST BASED ON TRIVALENT CHROMIUM COMPOUNDS

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

GH REF: P17052-DL:VNV:RK

The present invention relates to a process for the regeneration of fluorination catalysts based on Cr(III) compounds, optionally supported.

The use of Cr(III)-based catalysts in various reactions of halogen-containing organic compounds at high temperatures is well known in the art.

In particular various fluorination catalysts of industrial interest are known, which are based on oxides/oxyfluorides of Cr(III) optionally supported on alumina, fluorinated alumina, aluminium trifluoride, in the reactions in gaseous phase, at high temperatures, between HF and halogen-containing hydrocarbons, with the purpose of introducing fluorine atoms.

From **USP 5,262,574 and from EP 408,005** it is known the use of Cr_2O_3 supported on AlF_3 in the fluorination in gaseous phase with HF respectively of $CCl_2=CCl_2$ to obtain CF_3CHCl_2 (HCFC-123) and of $CHCl=CCl_2$ and CF_3CH_2Cl (HCFC-133a) to obtain CF_3CH_2F (HFC-134a).

Such catalysts during their use in an industrial fluorination plant tend to deactivate owing to the deposit on their surface of organic contaminants comprising carbonaceous residues and/or organic oligomers deriving from cracking and/or oligomerization of the reacted organic compounds.

In order to reinstate the catalytic activity one generally proceeds to a treatment of the exhausted catalyst with oxidizing gas such as air or oxygen/nitrogen mixtures at sufficiently high temperatures (300-500°C) so as to cause the combustion of the organic contaminants.

However the above treatment causes also the partial oxidation of Cr(III) to Cr(VI) with consequent loss in the active metal Cr(III), wherefore the catalyst results less active and with a short lifetime.

Moreover the formation of toxic and volatile Cr(VI) compounds results highly undesirable since their dispersion in the environment is regulated by the laws in force which do not allow Cr(VI) concentrations higher than 1 ppm in the sewage waters and even lower concentrations in the gaseous effluents.

In case of use of the so reactivated catalyst in fluorination processes with HF, the Cr(VI) presence results even more undesirable since it reacts with HF by forming oxyfluoride of Cr(VI), CrO_2F_2, gaseous at room temperature and toxic, which contaminates the process effluents.

To obviate the loss of chromium of the catalyst during the regeneration with air and in the successive reaction with

HF, it has been proposed in 'EP 475,693 to regenerate the catalyst based on chromium compounds by a treatment with an HF/air mixture containing up to 30% by moles of air, at temperatures of 300°-500°C.

However such a process shows the drawback that to avoid the loss of the notable amounts of HF utilized in the regeneration mixture, it is necessary to employ two reactors in which, alternatively, in one reactor it occurs the regeneration of the exhausted catalyst and contemporaneously in the other reactor it occurs the fluorination of the halogen-containing organic compound by recycle of the hot HF directly coming from the reactor under regeneration.

It has now been found a process for the regeneration of exhausted or deactivated catalysts based on Cr(III) compounds which can be carried out in the same reactor containing the catalytic bed, which does not show the inconveniences and the drawbacks of the prior art and allows to obtain a regenerated highly active catalyst, which does not contain Cr(VI) compounds.

The process according to the invention comprises

a) a first phase of treatment with an oxidizing gas, in particular air, carried out with modalities known in the art, and

b) a successive phase of treatment with hydrogen mixed in particular ratios with an inert gas and at particular temperatures, until the disappearance of the Cr(VI) compounds formed during the previous oxidation phase.

The present invention provides a process for the regeneration of a fluorination catalyst, based on Cr(III) compounds optionally supported, exhausted owing to the presence on its surface of organic contaminants, comprising:

a) the treatment of the exhausted catalyst with an air flow or with an oxygen/inert gas mixture, at temperatures from 350°C to 400°C, until the organic contaminants disappear, and

b) the treatment of the catalyst obtained after phase a) with a flow of a gaseous mixture formed by an inert gas and from 1 to 10% by volume of hydrogen, at temperatures from 310°C to 340°C, until complete disappearance of the Cr(VI) compounds, formed during the oxidation phase.

The inert gas employed in phases a) and b) is preferably nitrogen.

The amount of hydrogen in admixture with the inert gas preferably ranges from 3 to 6% by volume.

The time of the treatment in phase b) is generally lower than 1 hour.

The process according to the invention is particularly suitable for the regeneration of a fluorination catalyst based on oxide and/or oxyfluoride of Cr(III) supported on AlF_3, Al_2O_3 or fluorinated Al_2O_3, which has been utilized in the fluorination in gaseous phase with HF of halogen-containing hydrocarbons.

In particular, a catalyst based on oxide and/or oxyfluoride of Cr(III) supported on AlF_3 can be continuously utilized for long periods of time in an industrial plant for preparing HCFC-123 from perchloroethylene and HF as described in USP 5,262,574, by alternating production periods with regeneration cycles according to the process of the invention, without undergoing substantial losses of chromium and of catalytic activity.

On the contrary, if regeneration is carried out by employing only the oxidation phase a), already after few production/regeneration cycles, substantial losses of chromium from the catalyst and a decay of its catalytic activity are noticed.

Some examples follow for illustrative purposes of the invention.

On the catalysts used in the examples were determined:

- the content of carbonaceous substances by TPO analysis (Temperature Programmed Oxidation)
- the content of Cr(VI) compounds by oxidimetric analysis by wet way
- the catalytic activity by catalytic test.

The TPO analysis, well known in the art, was carried out by letting flow an oxidizing gas on a catalyst sample while it is heated progressively from the room temperature to 700°C at a programmed speed of 10°C/min. and determining the variation of the composition of the analysis gas in comparison with a reference gas flow which does not pass on the sample.

For the TPO a flow of 40 cc/min. of an oxygen/helium mixture containing 5% by volume of oxygen was utilized.

In the oxidimetric analysis by wet way, well known in the art, the Cr(VI) compounds have been extractd from a catalyst sample by washing with acidified water and, successively, titred with KI/thiosulphate.

The catalytic test comprises the use of a catalyst sample in the standard fluorination of HCFC-133a (CF_3CH_2Cl) with anhydrous HF in a molar ratio 133a/HF of 1:4, at a temperature of 320°C.

EXAMPLE 1

A catalyst based on Cr(III) oxide supported on AlF_3, prepared as described in USP 5,262,574 containing 7.4% of chromium, was utilized in the continuous synthesis of HCFC-123 from perchloroethylene and HF according to the operating conditions described in Example 1 of the above US patent.

The catalyst, after continuous operation until its catalytic activity, determined by catalytic test, has dropped to 70% of its initial value, is regenerated in situ by means of the following treatments in sequence:

a) treatment with a flow of a nitrogen/air mixture containing 30% by volume of air, at a temperature of 380°C until disappearance of the organic contaminants, as by TPO analysis, and restoration of the catalytic activity.

   The TPR and oxidimetric analysis by wet way show that the catalyst contains 0.2% by weight of Cr(VI),

b) successive treatment with a nitrogen/hydrogen mixture containing 5% by volume of hydrogen, with a flow-rate of 150 Nl/hour per Kg of catalyst and at a temperature of 325°C for 50 minutes.

   By the oxidimetric analysis by wet way the catalyst does not show the presence of Cr(VI).

   The catalytic test shows that the catalyst has the same activity as the initial fresh catalyst.

The so regenerated catalyst is then put again on operation in the synthesis of HCFC-123 where it behaves in the same way as the initial fresh catalyst.

EXAMPLE 2

EXPERIMENT A

A catalyst based on Cr(III) oxide supported on AlF_3, prepared as described in ex. 1, col.4 of USP 5,262,574 and containing 7.4% of chromium, used in the synthesis in continuum of HCFC-123 from perchloroethylene and HF at 360°, was regenerated in situ with the method of the present invention, after that the catalytic activity, was dropped to 70% of the starting value.

The oxidation step was performed according to the invention, i.e. by treatment with a flow of a nitrogen/air mixture containing 30% by volume of air, at a temperature of 380°C until disappearance of the organic contaminants (TPO analysis) and restoration of the catalytic activity.

The TPR analysis showed that the catalyst contained approximately 0.2% by weight of Cr(VI).

The so regenerated catalyst was divided into 4 aliquots of a same weight, on which the treatment according to the second step of the invention with a nitrogen/hydrogen mixture containing 5% by volume of hydrogen, at a flow-rate of 150 Nl/hour per Kg of catalyst, was performed for a time of 50 minutes at the following different temperatures, respectively for each of the 4 aliquots :

Experiment A.1 : 280°C.
Experiment A.2 : 320°C.
Experiment A.3 : 360°C.
Experiment A.4 : 440°C.

It was found that by effecting the treatment with a nitrogen/hydrogen mixture at 280°C (Experiment A.1), i.e. below the instant limit of 310°C, at the end of the treatment the catalyst still contained a percentage comprised between 0.05-0.1% of Cr^{VI}, whereas at the temperature of 320°C (Experiment A.2), and above it (Experiments A.3 and A.4), no more Cr^{VI} was detectable in the catalyst.

It was also found at the TPR analysis that the signal of reducible (i.e. non-crystalline) Cr^{III} i.e. the active catalytic agent, at the end of the second step of the process of the invention decreased with increasing the temperature of said step above the instant limit of 340°C.

By assuming equal to unity the TPR signal of reducible Cr^{III} found at the temperature of 320°C, the relative values of TPR signals obtained at 360°C and 440°C were found to be those as reported in Table 1.

Table 1

Experiment	Temperature °C	Relative intensity of the TPR signal
A.2	320	1
A.3	360	0.74
A.4	440	0.63

The Table evidences that by increasing the temperature the quantity of reducible Chromium significantly diminished.

EXPERIMENT B

A catalyst based on Cr(III) oxide supported on AlF_3, prepared as above described, containing 7.4% of chromium and used in the same above said synthesis, was used for said fluorination reaction throughout 50 hours. At the end of said period the reactor was unloaded and the catalyst divided into two aliquots of the same weight.

Experiment B.1

100 g of the exhausted catalyst are charged in a tubular reactor of 40 mm diameter, equipped with a sintered filter and an electric heating system.

The oxidation step is performed with a flow of about 10 Nl/h air, at a temperature of 380°C until disappearance of the organic contaminants (TPO analysis).

The reduction step, to be performed according to Example 1 described above, was omitted due to time constraints.

The fluorination of PCE was performed at a temperature of 280°C, feeding a mixture containing 37 g/h HF and 51.5 g/h PCE. Thus the contact time was of 3 seconds and the molar ratio HF/PCE = 6.

The gas products leaving the reactor were bubbled into water to remove acid compounds, dehydrated and analyzed by gas chromatography. After 1.5 hours from the start the mixture of the gas products showed the following composition (% on a molar basis):

HFC-125	2.27	%
HCFC-124	15.06	%
HCFC-123	34.04	%
HCFC-121 + HCFC-122 + HCFC-1111 **	6.01	%
CFC-113 + CFC-114 +CFC-115 + HCFC-133a ***	0.92	%
PCE	41.70	%

** intermediate products

*** by-products

The main products are HCFC-123 and HCFC-124 and the conversion of PCE is of 58.30%.

Experiment B.2

An aliquot of 100 g of the same exhausted catalyst was regenerated as described in ex. B.1, but using in the oxidation step a temperature of 440°C.

The fluorination of PCE was performed in the same way. After 1 hour from the start the mixture of the gas products showed the following composition (% on a molar basis):

HFC-125	0.90	%
HCFC-124	9.65	%
HCFC-123	30.52	%
HCFC-121 + HCFC-122 + HCFC-1111 **	7.70	%
CFC-113 + CFC-114 +CFC-115 + HCFC-133a ***	0.98	%
PCE	50.25	%

The main products are still HCFC-123 and HCFC-124 and the conversion of PCE is of 49.75%.

Thus the conversion of PCE in experiment B.2 was lower than that obtained in exp. B.1.

The deactivation profile of the two catalysts was followed up to the end of the run (50 hours) monitoring HCl production (from PCE). It was found that the difference in activity between the two catalysts was maintained in time. See Figure 1, which is a graphical representation of HCl production against time.

It is to be understood that a reference herein to a prior art document does not constitute an admission that the document forms part of the common general knowledge in the art in Australia or in any other country.

In the claims which follow and in the preceding description of the invention, except where the context requires otherwise due to express language or necessary implication, the words "comprises" and "comprising" are used in the sense of "includes" and "including", i.e. the features specified may be associated with further features in various embodiments of the invention.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A process for the regeneration of a fluorination catalyst based on Cr(III) compounds optionally supported, exhausted for the presence on its surface of organic contaminants, comprising:
   a) the treatment of the exhausted catalyst with a flow of air or of an oxygen/inert gas mixture, at temperatures from 350°C to 400°C, until the organic contaminants disappear, and
   b) the treatment of the catalyst obtained after phase a) with a flow of a gaseous mixture formed by an inert gas and from 1 to 10% by volume of hydrogen, at temperatures from 310°C to 340°C, until complete disappearance of the Cr(VI) compounds, formed during the oxidation phase a).

2. Process according to claim 1, wherein the Cr(III) compounds are oxides and/or oxyfluorides and the support is chosen from AlF_3, Al_2O_3 and fluorinated Al_2O_3.

3. Process according to claim 1, wherein the catalyst consists of oxide and/or oxyfluoride of Cr(III) supported on AlF_3.

4. Process according to claim 1, wherein the hydrogen amount in admixture with the inert gas ranges from 3 to 6% by volume.

5. Process according to claim 1, wherein the inert gas employed in phases a) and b) is nitrogen.

6. Process for the fluorination of halogen-containing hydrocarbons with HF in gaseous phase in the presence of a catalyst, based on Cr(III) compounds optionally supported, which has been regenerated according to the process of claim 1.

7. Process according to claim 1 substantially as herein described with reference to the Example.

Dated this 24th day of January 2001
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By its Patent Attorneys
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Figure 1