EUROPEAN PATENT SPECIFICATION

PROCESS FOR PRODUCING 1,1,1,3,3-PENTAFUOROPROPANE
VERFAHREN ZUR HERSTELLUNG VON 1,1,1,3,3-PENTAFUOROPROPANE
PROCESSUS DE PRODUCTION DE 1,1,1,3,3-PENTAFUOROPROPANE

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Description

[0001] This invention relates to a method to produce 1,1,1,3,3-pentafluoropropane, which does not destroy the ozone layer and is important for industrial fields as HFC blowing agents, refrigerants and propellants.

Prior art

[0002] Because of these advantages, a method to produce 1,1,1,3,3-pentafluoropropane is urgently needed to be established.

[0003] The known methods of producing 1,1,1,3,3-pentafluoropropane are as follows. Carbon tetrachloride and vinylidene chloride are prepared and an addition reaction is triggered. The reaction product, 1,1,1,3,3,3-hexachloropropane, is fluorinated to produce 1,1,1,3,3-pentafluoro-3-chloropropane which is reduced with hydrogen to produce 1,1,1,3,3-pentafluoropropane (WO 95/04022).

[0004] Either 1,1,1,3,3-pentafluoro-2,3-dichloropropane or 1,1,1,3,3-pentafluoro-2,2,3-trichloropropane is reduced with hydrogen to produce 1,1,1,3,3-pentafluoropropane (EP 061174).

[0005] These well-known methods, however, present technical and cost problems because of the prolonged chemical processes including the process in which the chloride is fluorinated to produce a precursor, and the process in which the obtained compound is reduced with hydrogen.

Object of the Invention

[0006] The object of this invention is to provide a new cost-efficient method to produce 1,1,1,3,3-pentafluoropropane that gives high yield and selectivity without the disadvantages that are common with conventional production techniques.

Construction of the Invention

[0007] In order to solve these problems, a production method for 1,1,1,3,3-pentafluoropropane was thoroughly investigated.

As a result, the inventors found that when pentachloropropane is used as a starting material and this is reacted with hydrogen fluoride in the vapor phase, an important point is that an equilibrium exists between the reaction intermediates, 1,1,1-trifluoro-3-chloro-2-propene and 1,1,1,3-tetrafluoro-2-propene, and that when 1,1,1,3,3-pentachloropropane is fluorinated in the vapor phase, 1,1,1-trifluoro-3-chloro-2-propene is obtained and the by-product, hydrogen chloride, is removed and 1,1,1-trifluoro-2-propene is further fluorinated to produce 1,1,1,3,3-pentafluoropropane effectively.

As a result of this experiment, 1,1,1,3,3-pentafluoropropane is produced with high yield from 1,1,1,3,3-pentachloropropane simply through the process of fluorination. This gives a cost-effective method to produce 1,1,1,3,3-pentafluoropropane to complete this invention.

[0008] This invention provides a manufacturing method for 1,1,1,3,3-pentafluoropropane comprising the following two processes:

a first process to obtain a mixture, which contains mainly 1,1,1-trifluoro-3-chloro-2-propene, by inducing the reaction between 1,1,1,3,3-pentachloropropane and hydrogen fluoride in gaseous (vapor) phase, and a second process to remove the by-product, hydrogen chloride, from the mixture obtained in the first process, containing mainly 1,1,1-trifluoro-3-chloro-2-propene, and to obtain 1,1,1,3,3-pentafluoropropane by inducing a reaction between the remaining mixture and hydrogen fluoride in gaseous (vapor) phase.

According to the claimed manufacturing method, the chemical reaction is triggered in the following two stages.
First stage (first process)

[0009]

Second stage (second process)

[0010]

[0011] In the first stage (first process) in which 1,1,1,3,3-pentachloropropane is fluorinated with hydrogen fluoride in the vapor phase, there exists an equilibrium between 1,1,1-trifluoro-3-chloro-2-propene and 1,1,1,3-tetrafluoro-2-propene. Because the by-product of HCl promotes a strong tendency towards 1,1,1-trifluoro-3-chloro-2-propene, the main product is 1,1,1-trifluoro-3-chloro-2-propene even if excessive amounts of hydrogen fluoride are used. Although the intermediate, 1,1,1,3-tetrafluoropropene, and the target substance, 1,1,1,3,3-pentafluoropropane, can be obtained through these reactions, their amount is slight.

[0012] However, in this invention, after removing the by-product of HCl, the reaction product which mainly contains 1,1,1-trifluoro-3-chloro-2-propene is fluorinated with hydrogen fluoride in the vapor phase in the second stage (second process). Consequently the target substance, 1,1,1,3,3-pentafluoropropane, can be obtained with high yield and selectivity. In the first stage, 1,1,1-trifluoro-3-chloro-2-propene produced in the first stage is useful for an intermediate of medical drugs and agricultural chemicals for introducing a trifluoropropyl group into organic compounds.

Embodiments of the Invention

[0013] The claimed manufacturing method is explained in detail.
[0014] In the first stage described above, 1,1,1,3,3-pentachloropropane and hydrogen fluoride are added in a first reactor which is filled with a fluorinating catalyst to induce the reaction. In order to proceed the reaction, the molar ratio of hydrogen fluoride to the former should be more than three times that of 1,1,1,3,3-pentachloropropane. Adding ex-
cessive hydrogen fluoride is recommended to complete the reaction as well as it has no problem so as not to adversely affect the performance of the reactor. If the added excessive hydrogen fluoride is not sufficient, the remaining compound contains too much chlorine. Therefore, the molar ratio of the hydrogen fluoride is generally set at a level ranging from five to 20 times that of the 1,1,1,3,3-pentachloropropane.

[0015] A third stage follows the first and second stages (first and second processes) described in the above. The mixed gas which mainly contains 1,1,1,3,3-pentafluoropropane is obtained in the second stage. This gas contains 1,1,1,3-tetrafluoro-2-propene and 1,1,1-trifluoro-3-chloro-2-propene. After the separation of 1,1,1,3,3-pentafluoropropane, these two substances are recycled to the second process (the third process).

[0016] Because there exists an equilibrium between 1,1,1,3,3-pentafluoropropane and 1,1,1,3-tetrafluoro-2-propene, the third process described above is necessary to obtain 1,1,1,3,3-pentafluoropropane efficiently.

[0017] The following reaction formulae demonstrate these processes.

First stage (first process)

\[ \text{Cl} - C - C - C - H \xrightarrow{3 \text{HF}} \text{F} - C - C = C - \text{H} + 4 \text{HCl} \]

Second stage (second process)

\[ \text{F} - C - C = C - \text{Cl} \xrightarrow{} \text{F} - C - C - C - \text{F} + \]

Actually, the gas obtained in the second stage contains 1,1,1-trifluoro-3-chloro-2-propene, 1,1,1,3-tetrafluoro-2-propene, 1,1,1,3,3-pentafluoropropane, HCl, and excessively added hydrogen fluoride. After removal of the target substance, 1,1,1,3,3-pentafluoropropane and HCl from this mixture, the residual should be introduced into a second
The claimed manufacturing method comprises the following two processes. In the first process, 1,1,1,3,3-pentachloropropane and hydrogen fluoride are reacted in gaseous (vapor) phase to obtain 1,1,1-trifluoro-3-chloro-2-propene. In the second process, the 1,1,1-trifluoro-3-chloro-2-propene and hydrogen fluoride are reacted in gaseous (vapor) phase to produce 1,1,1,3,3-pentafluoropropane. The gas obtained in the first process, which mainly contains 1,1,1-trifluoro-3-chloro-2-propene, is supplied to the second process after removing the by-product, HCl. This technique is effective for the production of 1,1,1,3,3-pentafluoropropane with high selectivity. Consequently, 1,1,1,3,3-pentafluoropropane can be produced from 1,1,1,3,3-pentachloropropane economically and effectively simply through the fluorination process.

The claimed method is adopted to produce a substance: 1,1,1,3,3-pentafluoropropane that does not destroy the ozone layer and that is important for industrial use as HFC blowing agents, refrigerants and propellants. In the first process, 1,1,1-trifluoro-3-chloro-2-propene is produced. This substance is useful for an intermediate of medical drugs and agricultural chemicals for introducing the trifluoropropyl group into organic compounds.
Examples

[0035] The present invention will be explained in the following examples.

Example 1

A first reactor:

[0036] An aqueous solution of chromium nitrate and an aqueous ammonia were mixed to form a precipitate of chromium hydroxide. A fluorination catalyst was obtained by heat treating the chromium hydroxide. The catalyst was fluorinated by a pretreatment with only hydrogen fluoride passing therethrough before the reaction. A Hastelloy C reaction tube (internal diameter: 20 mm, length: 700 mm) was filled with 20 g of the catalyst and the temperature was increased at 250°C in a nitrogen stream.

[0037] After the nitrogen stream was terminated, 1,1,1,3,3-pentachloropropane and hydrogen fluoride were introduced at flow rates of 20 cc/min and 200 cc/min respectively. The obtained gas was washed with water and dried and then the composition of the produced gas was analyzed by gas chromatography. A mixed gas of the following composition was obtained:

- 1,1,1,3-tetrafluoro-2-propene 2.1%
- 1,1,1,3,3-pentafluoropropane 5.0%
- 1,1,1-trifluoro-3-chloro-2-propene 92.9%

A second reactor:

[0038] The gas obtained in the first reactor was washed with water to remove hydrogen chloride (HCl). After drying, the reaction mixture, which mainly contained 1,1,1-trifluoro-3-chloropropene, was added in a second reactor at flow rate of 20 cc/min accompanied with 200 cc/min of hydrogen fluoride. Conditions in the second reactor were adjusted to match those in the first reactor and a further reaction was induced.

[0039] The obtained gas was washed with water and the composition was analyzed by gas chromatography. The mixed gas of the following composition was obtained:

- 1,1,1,3-tetrafluoro-2-propene 23.4%
- 1,1,1,3,3-pentafluoropropane 52.3%
- 1,1,1-trifluoro-3-chloro-2-propene 24.3%

[0040] As demonstrated in this example, the target substance, 1,1,1,3,3-pentafluoropropane, was economically produced with high selectivity simply through the process of fluorination, using 1,1,1,3,3-pentachloropropane as the raw material.

Example 2

[0041] The reaction process adopted in this example was the same as that adopted in Example 1 except for the use of fluorinated alumina as the catalyst. The gas obtained in the second reactor was washed with water and its composition was analyzed by gas chromatography and a mixed gas of the following composition was obtained:

- 1,1,1,3-tetrafluoro-2-propene 22.9%
- 1,1,1,3,3-pentafluoropropane 51.8%
- 1,1,1-trifluoro-3-chloro-2-propene 25.3%

[0042] As demonstrated also in this example, the target substance, 1,1,1,3,3-pentafluoropropane, was economically produced with high selectivity simply through the process of fluorination, using 1,1,1,3,3-pentachloropropane as the raw material.
Example 3

[0043] As shown in Example 1, the first reactor was filled with a catalyst. An SUS made distiller (second reactor) was attached to the outlet of the first reactor so that the obtained gas could be rectified. In this system, 1,1,1-trifluoro-3-chloropropene and hydrogen fluoride were introduced at rates of 20 cc/min and 200 cc/min respectively. The products were introduced into the distillation column. In addition to the 1,1,1,3-tetrafluoropropene with low boiling point and unreacted 1,1,1-trifluoro-3-chloropropene with high boiling point, extra hydrogen fluoride was introduced into the distillation column for recycling.

[0044] As the reaction in the distillation column stabilized, the introduction amount of hydrogen fluoride was gradually decreased until the whole of the reaction system was stabilized. When the system was stable, the gas sample was collected from the outlet of the second reactor. The collected sample was washed with water and analyzed by gas chromatography and a mixed gas of the following composition was found to be obtained:

1,1,1,3-tetrafluoropropene 28.6%
1,1,1,3,3-pentafluoropropane 61.3%
1,1,1-trifluoro-3-chloro-2-propene 10.1%

[0045] The gas obtained from the middle outlet of the distillation column was washed with water and analyzed by gas chromatography and a mixed gas of the following composition was obtained:

1,1,1,3-tetrafluoropropene 1.6%
1,1,1,3,3-pentafluoropropane 98.4%

[0046] After collecting the gas produced during a specified period of time, the recovery rate was 97%.

[0047] As demonstrated in this example, the target substance, 1,1,1,3,3-pentafluoropropane, was economically produced with high selectivity, although the substances in the second reactor were recycled.

Claims

1. A manufacturing method of 1,1,1,3,3-pentafluoropropane comprising a first process in which 1,1,1-trifluoro-3-chloro-2-propene is mainly obtained by a reaction of 1,1,1,3,3-pentachloropropane and hydrogen fluoride in gaseous phase, and a second process in which 1,1,1,3,3-pentafluoropropane is obtained by a reaction of hydrogen fluoride and the gas obtained in the first process from which hydrogen chloride has been removed in gaseous phase.

2. A manufacturing method as defined by claim 1 having a third process in which 1,1,1,3,3-pentafluoropropane is recovered and hydrogen chloride is removed from the gas collected in the second process, and the residual gas mainly containing 1,1,1,3-tetrafluor-2-propene and 1,1,1-trifluoro-3-chloro-2-propene is recycled to the second process.

3. A manufacturing methods as defined by claim 1 or 2 in which the reactions are performed in the presence of fluorinating catalysts in the first and second processes.

Patentansprüche

1. Herstellungsverfahren für 1,1,1,3,3-Pentafluorpropan, umfassend ein erstes Verfahren, bei dem hauptsächlich 1,1,1-Trifluor-3-chlor-2-propen erhalten wird durch eine Umsetzung von 1,1,1,3,3-Pentachlorpropan und Wasserstofffluorid in der Gasphase, und ein zweites Verfahren, bei dem 1,1,1,3-Pentafluorpropan erhalten wird durch eine Umsetzung von Wasserstofffluorid und dem beim ersten Verfahren erhaltenen Gas, aus dem Wasserstoffchlorid entfernt worden ist, in der Gasphase.

2. Herstellungsverfahren nach Anspruch 1 mit einem dritten Verfahren, bei dem 1,1,1,3-Pentafluorpropan gewonnen und Wasserstoffchlorid aus dem beim zweiten Verfahren gesammelten Gas entfernt wird, und das hauptsächlich 1,1,1,3-Tetrafluor-2-propen und 1,1,1-Trifluor-3-chlor-2-propen enthaltende Restgas zu dem zweiten Verfahren rezykliert wird.
3. Herstellungsverfahren nach Anspruch 1 oder 2, wobei die Umsetzungen in Gegenwart von Fluorierungskatalysatoren beim ersten und zweiten Verfahren durchgeführt werden.

Revendications

1. Procédé de production de 1,1,1,3,3-pentafluoropropane comprenant une première opération dans laquelle du 1,1,1-trifluoro-3-chloro-2-propène est principalement obtenu en faisant réagir du 1,1,1,3,3-pentachloropropane et du fluorure d'hydrogène en phase gazeuse, et une deuxième opération dans laquelle on obtient du 1,1,1,3,3-pentafluoropropane en faisant réagir du fluorure d'hydrogène et le gaz obtenu dans la première opération dont le chlorure d'hydrogène a été éliminé, en phase gazeuse.

2. Procédé de production selon la revendication 1, comprenant une troisième opération dans laquelle on récupère le 1,1,1,3,3-pentafluoropropane et on élimine l'hydrogène du gaz recueilli dans la deuxième opération, et le gaz résiduel contenant principalement du 1,1,1,3-tétrafluoro-2-propène et du 1,1,1-trifluoro-3-chloro-2-propène, est recyclé dans la deuxième opération.

3. Procédé de production selon la revendication 1 ou 2, dans lequel les réactions sont effectuées en présence de catalyseurs de fluororation dans les première et deuxième opérations.