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(54) Title: PRODUCTION AND USE OF HEXAFLUOROETHANE

(57) Abstract: A process for production of high-purity hexafluoroethane, wherein a mixed gas containing hexafluoroethane and chlorotrifluoromethane is reacted with hydrogen fluoride in a gas phase in the presence of a fluorination catalyst at 200-450°C, for fluorination of the chlorotrifluoromethane, or wherein pentafluoroethane containing chlorine compounds with 1-3 carbon atoms is reacted with hydrogen in a gas phase in the presence of a hydrogenation catalyst at 150-400°C, and the product is then reacted with fluorine in a gas phase in the presence of a diluent gas.



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## DESCRIPTION

PRODUCTION AND USE OF HEXAFLUOROETHANE

5           Technical Field

The present invention relates to production and use of hexafluoroethane.

Background Art

10           Hexafluoroethane ( $\text{CF}_3\text{CF}_3$ ) is used, for example, as a cleaning gas or etching gas for semiconductors. Several processes have conventionally been known for the production of  $\text{CF}_3\text{CF}_3$ , such as

(1) electrolytic fluorination processes using ethane and/or ethylene as the starting material,

15           (2) thermal decomposition processes involving thermal decomposition of tetrafluoroethylene,

(3) processes in which acetylene, ethylene and/or ethane are fluorinated using metal fluorides,

20           (4) processes in which dichlorotetrafluoroethane or chloropentafluoroethane is fluorinated using hydrogen fluoride in the presence of a fluorination catalyst, and

(5) direct fluorination processes involving reaction of tetrafluoroethane and/or pentafluoroethane with fluorine.

25           However, when the process of (4) above is used, for example, the resulting  $\text{CF}_3\text{CF}_3$  contains impurities in the form of compounds derived from the starting material or compounds newly produced by the reaction. Particularly problematic among such impurities are chlorine compounds, which are difficult to separate from  $\text{CF}_3\text{CF}_3$ .

30           When the process of (5) above is used, for example, the resulting  $\text{CF}_3\text{CF}_3$  also contains impurities in the form of compounds derived from the starting material or compounds newly produced by the reaction. These  
35           impurities also include chlorine compounds which are difficult to separate from  $\text{CF}_3\text{CF}_3$ . Purification may be carried out before reaction with fluorine gas in order to

reduce the chlorine compounds in the starting material, but industrial application of conventionally known purification processes is difficult in most cases.

5 The chlorine compounds in  $\text{CF}_3\text{CF}_3$  include compounds such as chloromethane, chlorodifluoromethane, chlorotrifluoromethane, chloropentafluoroethane, dichlorotetrafluoroethane, chlorotetrafluoroethane, chlorotrifluoroethane, chlorotrifluoroethylene and the like.

10 Among these chlorine compounds, chlorotrifluoromethane is difficult to separate because it forms an azeotropic mixture with  $\text{CF}_3\text{CF}_3$ . Examples of methods of purifying  $\text{CF}_3\text{CF}_3$  containing chlorotrifluoromethane include the method described in  
15 U.S. Patent No. 5,523,499 in which  $\text{CF}_3\text{CF}_3$  containing impurities such as trifluoromethane ( $\text{CHF}_3$ ) and chlorotrifluoromethane ( $\text{CClF}_3$ ) is contacted with an adsorbing agent such as active carbon or a molecular sieve to adsorb and remove the impurities.

20 Purification methods using such adsorbing agents require special equipment for regeneration of the adsorbing agents at roughly consistent intervals in the case of constant operation, although this depends on the impurity content. For example, in a process wherein two  
25 adsorption towers are provided and operation alternately switches between a step of adsorption of impurities and a step of regeneration of the adsorbing agent, large amounts of gas may be continuously treated, but the adsorbed and removed chlorotrifluoromethane cannot be  
30 directly released into the atmosphere since it is a specific freon implicated in destruction of the ozone layer, and therefore some means must be used to render it harmless.

On the other hand, pentafluoroethane ( $\text{CF}_3\text{CHF}_2$ ) is  
35 used, for example, as a low-temperature refrigerant, or as a starting material for production of hexafluoroethane ( $\text{CF}_3\text{CF}_3$ ). As examples of conventionally known processes

for production of pentafluoroethane there may be mentioned the following:

(1) a process in which perchloroethylene ( $\text{CCl}_2=\text{CCl}_2$ ) or its fluorinated product is fluorinated with hydrogen fluoride (Japanese Unexamined Patent Publication No. 8-268932, Japanese Unexamined Patent Publication No. 9-511515),

(2) a process in which chloropentafluoroethane ( $\text{CClF}_2\text{CF}_3$ ) is subjected to hydrogenolysis (Japanese Patent No. 2540409), and

(3) a process in which fluorine gas is reacted with halogen-containing ethylene (Japanese Unexamined Patent Publication No. 1-38034).

When such processes are used, the major impurities in the target product, pentafluoroethane, are chlorine compounds which of course contain chlorine atoms in the molecules. Examples of such chlorine compounds include compounds with one carbon atom such as chloromethane, chlorodifluoromethane and chlorotrifluoromethane, compounds with two carbon atoms such as chloropentafluoroethane, dichlorotetrafluoroethane, chlorotetrafluoroethane and chlorotrifluoroethane, and unsaturated compounds such as chlorotrifluoroethylene.

When hexafluoroethane is produced by direct fluorination reaction with pentafluoroethane and fluorine gas ( $\text{F}_2$ ), any of these chlorine compounds included in the pentafluoroethane will react with the fluorine gas, producing chlorine, hydrogen chloride, chlorine fluorides, or various chlorofluorocarbons. While perfluorocarbons (PFCs) included in the pentafluoroethane do not present any notable problem, chloromethane ( $\text{CH}_3\text{Cl}$ ) and chlorodifluoromethane ( $\text{CHClF}_2$ ) will react with fluorine gas to produce chlorotrifluoromethane ( $\text{CClF}_3$ ). Hexafluoroethane and chlorotrifluoromethane form an azeotropic mixture, and therefore removal of chlorotrifluoromethane is difficult even by distillation or adsorption purification. Thus, when pentafluoroethane

and fluorine gas are reacted to produce hexafluoroethane, it is preferred to use pentafluoroethane with a minimal chlorine compound content.

5 With conventional processes for production of pentafluoroethane, the chlorine compound content in the pentafluoroethane can be as high as about 1 vol% in total. Repeated distillation has therefore been considered to remove the chlorine compounds in the pentafluoroethane and thus increase its purity, but  
10 because of the increased production cost of the distillation, as well as distillation loss, this procedure has been uneconomical, while some of the chlorine compounds also form azeotropic mixtures or azeotrope-like mixtures with pentafluoroethane and create  
15 a situation in which it is very difficult to separate the chlorine compounds by distillation procedures alone. In particular, chloropentafluoroethane ( $\text{CClF}_2\text{CF}_3$ ) is usually included in pentafluoroethane at a concentration of a few thousand ppm or greater, but since pentafluoroethane and  
20 chloropentafluoroethane form an azeotropic mixture, they are difficult to separate by distillation, which is the commonly employed separation and purification method.

#### Disclosure of the Invention

It is an object of the present invention, which was  
25 accomplished under the conditions described above, to provide an industrially advantageous process for production of high-purity hexafluoroethane, which can be used as an etching gas or cleaning gas for semiconductor device manufacturing steps, as well as the use of high-  
30 purity hexafluoroethane obtained by the process.

As a result of diligent research in light of the circumstances of the prior art as described above, the present inventors have completed the present invention upon finding that the above-mentioned problems can be  
35 solved by employing a step in which a mixed gas containing hexafluoroethane and chlorotrifluoromethane is reacted with hydrogen fluoride in a gas phase in the

presence of a fluorination catalyst and at a prescribed temperature, for fluorination of the chlorotrifluoromethane.

5 The invention therefore provides a process for production of hexafluoroethane which comprises a step in which a mixed gas containing hexafluoroethane and chlorotrifluoromethane is reacted with hydrogen fluoride in a gas phase in the presence of a fluorination catalyst at 200-450°C, for fluorination of the  
10 chlorotrifluoromethane.

The invention further provides a process for production of hexafluoroethane comprising the following steps (1) and (2):

(1) A step in which a mixed gas containing  
15 hexafluoroethane and chlorotrifluoromethane is reacted with hydrogen fluoride in a gas phase in the presence of a fluorination catalyst at 200-450°C to fluorinate the chlorotrifluoromethane to convert it to tetrafluoromethane.

20 (2) A step in which the mixed gas containing hexafluoroethane and tetrafluoromethane obtained in step (1) is distilled to obtain purified hexafluoroethane.

The invention still further provides a hexafluoroethane product containing hexafluoroethane at a  
25 purity of 99.9997 vol% or greater, obtained using the aforementioned process.

The invention still further provides an etching gas containing the aforementioned hexafluoroethane product.

30 The invention still further provides a cleaning gas containing the aforementioned hexafluoroethane product.

As a result of more detailed investigation, the present inventors have achieved completed the present invention upon finding that the above-mentioned problems can also be solved by employing a production process  
35 comprising a step (1) in which pentafluoroethane containing chlorine compounds with 1-3 carbon atoms is reacted with hydrogen in a gas phase in the presence of a

hydrogenation catalyst at a prescribed temperature, for hydrogenation of the chlorine compounds, and a step (2) in which the product of step (1) is reacted with fluorine in a gas phase in the presence of a diluent gas to  
5 produce hexafluoroethane.

The invention therefore provides a process for production of hexafluoroethane which comprises a step (1) in which pentafluoroethane containing chlorine compounds with 1-3 carbon atoms is reacted with hydrogen in a gas  
10 phase in the presence of a hydrogenation catalyst at 150-400°C, for hydrogenation of the chlorine compounds, and a step (2) in which the product of step (1) is reacted with fluorine in a gas phase in the presence of a diluent gas to produce hexafluoroethane.

15 The invention further provides a hexafluoroethane product containing hexafluoroethane at a purity of 99.9997 vol% or greater, obtained using the aforementioned process.

The invention still further provides an etching gas  
20 containing the aforementioned hexafluoroethane product.

The invention still further provides a cleaning gas containing the aforementioned hexafluoroethane product.

#### Best Mode for Carrying Out the Invention

A hexafluoroethane production process according to a  
25 first aspect of the invention will now be explained in detail.

As mentioned above, various processes are conventionally known for production of hexafluoroethane. As industrially safe and economical processes there may  
30 be mentioned the following:

(1) processes in which dichlorotetrafluoroethane or chloropentafluoroethane is fluorinated using hydrogen fluoride in the presence of a fluorination catalyst;

(2) processes involving reaction of  
35 tetrafluoroethane and/or pentafluoroethane with fluorine gas.

In these processes (1) and (2), compounds such as

dichlorotetrafluoroethane, chloropentafluoroethane or pentafluoroethane which are used as the starting materials can be produced using, for example, tetrachloroethylene ( $\text{CCl}_2=\text{CCl}_2$ ) as the starting material, while compounds such as tetrafluoroethane can be produced using trichloroethylene ( $\text{CHCl}=\text{CCl}_2$ ) as the starting material. Regardless of the method used, however, the resulting hexafluoroethane contains starting material-derived chlorine compounds as impurities, and the content of impurities tends to increase at a higher reaction temperature.

For example, pentafluoroethane ( $\text{CF}_3\text{CHF}_2$ ), which is commercially available as a refrigerant, contains these chlorine compounds as impurities. When chlorine compound-containing pentafluoroethane and fluorine gas are directly reacted for fluorination to produce  $\text{CF}_3\text{CF}_3$ , reaction between the chlorine compounds in the pentafluoroethane and the fluorine gas produces, among other compounds, chlorine, hydrogen chloride, chlorine fluorides, and various chlorofluorocarbons. For example, chlorodifluoromethane included as an impurity reacts with fluorine gas to produce chlorotrifluoromethane. The chlorotrifluoromethane forms an azeotropic mixture with  $\text{CF}_3\text{CF}_3$ , and is therefore a very difficult compound to separate, even by distillation.

The hexafluoroethane production process according to the first aspect of the invention comprises a step in which a mixed gas containing chlorotrifluoromethane and hexafluoroethane, which are extremely difficult to separate, is reacted with hydrogen fluoride in a gas phase in the presence of a fluorination catalyst at 200-450°C, for fluorination of the chlorotrifluoromethane. The mixed gas contains hexafluoroethane at 99.9 vol% or greater, while also containing chlorotrifluoromethane as an impurity.

The fluorination catalyst used in this process is preferably a catalyst with trivalent chromium oxide as



the major component, and contains nickel, zinc, indium and/or gallium in an atomic ratio of 0.01-0.6 with respect to chromium. The catalyst may be in the form of a supported catalyst or a bulk catalyst, and when it is in the form of a supported catalyst, the carrier is preferably active carbon, alumina, partially fluorinated alumina or the like, with a component-supporting rate of preferably no greater than 30 wt%.

The temperature for the reaction between the hydrogen fluoride and the mixed gas containing hexafluoroethane and chlorotrifluoromethane in the presence of the fluorination catalyst is 200-450°C, and preferably 250-400°C. If the reaction temperature is below 200°C, the chlorotrifluoromethane is not readily fluorinated, and if the reaction temperature is above 450°C the catalyst life is shortened, and the impurities will tend to increase.

In the fluorination reaction, the molar ratio of the hydrogen fluoride and the mixed gas (hydrogen fluoride/mixed gas containing hexafluoroethane and chlorotrifluoromethane) is preferably in the range of 0.05-10, and more preferably in the range of 0.05-5. If the molar ratio of the hydrogen fluoride and the mixed gas is smaller than 0.05, various chlorofluorocarbons will tend to be readily produced by side-reactions, and if it is greater than 10, an economically disadvantageous situation will result, such as increased reactor size and recovery of unreacted hydrogen fluoride.

The concentration of the chlorotrifluoromethane in the mixed gas is preferably no greater than 0.1 vol% and more preferably no greater than 0.05 vol% of the mixed gas.

The mixed gas is preferably obtained by reacting dichlorotetrafluoroethane and/or chloropentafluoroethane with hydrogen fluoride in a gas phase in the presence of a fluorination catalyst. Alternatively, the mixed gas may be obtained by reaction of tetrafluoroethane and/or

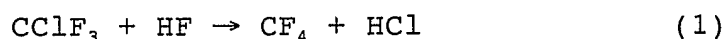
pentafluoroethane with fluorine gas.

The process for production of hexafluoroethane according to the first aspect of the invention may comprise the following steps (1) and (2).

5 (1) A step in which a mixed gas containing hexafluoroethane and chlorotrifluoromethane is reacted with hydrogen fluoride in a gas phase in the presence of a fluorination catalyst at 200-450°C to fluorinate the chlorotrifluoromethane and convert it to  
10 tetrafluoromethane.

(2) A step in which the mixed gas containing hexafluoroethane and tetrafluoromethane obtained in step (1) is distilled to obtain purified hexafluoroethane.

The chlorotrifluoromethane reacts with hydrogen  
15 fluoride in the presence of a fluorination catalyst to produce tetrafluoromethane (CF<sub>4</sub>), as shown in the following formula (1).



Instead of reaction of the hexafluoroethane, the  
20 chlorotrifluoromethane impurity reacts with the hydrogen fluoride. Since the difference in boiling points between the resulting CF<sub>4</sub> and the unreacted residual CF<sub>3</sub>CF<sub>3</sub> is about 50°C, and the CF<sub>4</sub> and CF<sub>3</sub>CF<sub>3</sub> therefore do not form an azeotropic mixture, they can be easily separated by  
25 any known distillation procedure.

The fluorination catalyst of step (1) is preferably a supported catalyst or a bulk catalyst with trivalent chromium oxide as the main component.

In step (1), the molar ratio of the hydrogen  
30 fluoride gas and mixed gas (hydrogen fluoride/mixed gas containing hexafluoroethane and chlorotrifluoromethane) is preferably in the range of 0.05-10, and the concentration of the chlorotrifluoromethane in the mixed gas of step (1) is preferably no greater than 0.1 vol%.

35 The mixed gas of step (1) is preferably obtained by reacting dichlorotetrafluoroethane and/or chloropentafluoroethane with hydrogen fluoride in a gas

phase in the presence of a fluorination catalyst. Alternatively, the mixed gas of step (1) may be obtained by reaction of tetrafluoroethane and/or pentafluoroethane with fluorine gas.

5           The method of removing the acid component consisting of the hydrochloric acid produced by the reaction of formula (1) and the excess hydrogen fluoride may be, for example, a method of contacting with a purifying agent or a method of contacting with water or an aqueous alkali  
10       solution. The gas composed mainly of  $\text{CF}_3\text{CF}_3$  after the acid component has been removed may be dehydrated using a dehydrating agent such as zeolite and subjected to a distillation procedure to cut the low boiling point fraction, in order to obtain high-purity  $\text{CF}_3\text{CF}_3$ .

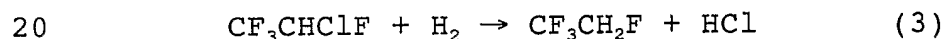
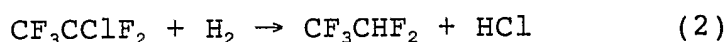
15           A hexafluoroethane production process according to a second aspect of the invention will now be explained in detail.

          This process is a process for production of hexafluoroethane which comprises a step (1) in which  
20       pentafluoroethane containing chlorine compounds with 1-3 carbon atoms is reacted with hydrogen in a gas phase in the presence of a hydrogenation catalyst at 150-400°C, for hydrogenation of the chlorine compounds, and a step (2) in which the product of step (1) is reacted with  
25       fluorine in a gas phase in the presence of a diluent gas to produce hexafluoroethane.

          As mentioned above, the pentafluoroethane used for this process is usually produced by fluorination of perchloroethylene ( $\text{CCl}_2=\text{CCl}_2$ ) or its fluorinated product  
30       with hydrogen fluoride (HF), and the pentafluoroethane will contain, as starting material-derived chlorine compounds, chloromethane, chlorodifluoromethane, chloropentafluoroethane, dichlorotetrafluoroethane, chlorotetrafluoroethane, chlorotrifluoroethane,  
35       chlorotrifluoroethylene and the like. A known distillation procedure may be employed for high purification of the pentafluoroethane containing these

compounds, but because the chlorine compounds and pentafluoroethane form azeotropic mixtures or azeotrope-like mixtures, their separation and purification is extremely difficult, requiring an increased number of  
5 distillation steps and distillation towers and thereby creating a problem, in economic terms, due to the added equipment and energy costs.

This process begins with step (1) in which the chlorine compounds containing chlorine atoms and included  
10 as impurities in the pentafluoroethane are first reacted with hydrogen in a gas phase in the presence of a hydrogenation catalyst at 150-400°C for hydrogenation, to convert them to hydrofluorocarbons (HFCs) and the like. For example, using hydrogen for hydrogenation of the  
15 chloropentafluoroethane ( $\text{CF}_3\text{CClF}_2$ ) and chlorotetrafluoroethane ( $\text{CF}_3\text{CHClF}$ ) included as impurities in the pentafluoroethane takes place the reactions represented by formulas (2) and (3) below.



The products are hydrofluorocarbons containing no chlorine atoms, with hydrochloric acid as a by-product.

Compounds which are converted to hydrofluorocarbons by the above hydrogenation reaction include the  
25 aforementioned chloromethane, chlorodifluoromethane, chlorotrifluoromethane, chloropentafluoroethane, dichlorotetrafluoroethane, chlorotetrafluoroethane, chlorotrifluoroethane, chlorotrifluoroethylene, etc., which are normally included in pentafluoroethane in a  
30 total amount of a few thousand volppm or greater. When pentafluoroethane containing these compounds is reacted directly with fluorine gas, the methane-based compounds are converted primarily to chlorotrifluoromethane while the ethane-based compounds are converted primarily to  
35 chloropentafluoroethane, and therefore the hexafluoroethane obtained after the reaction contains

chlorotrifluoromethane and chloropentafluoroethane as the major impurities.

The chloropentafluoroethane is virtually non-reactive with fluorine gas at low temperature.

5 Investigation by the present inventors, however, has indicated that when, for example, the reaction temperature is 400°C and the chloropentafluoroethane concentration in pentafluoroethane is no greater than about 800 volppm, the chloropentafluoroethane is cleaved,  
10 resulting in a chlorotrifluoromethane amount of no greater than 1 volppm, but when the chloropentafluoroethane concentration is greater than about 2000 volppm, the chlorotrifluoromethane content reaches about 2 volppm.

15 Since chlorotrifluoromethane forms an azeotropic mixture with hexafluoroethane, removal of this compound is very difficult by distillation or adsorption procedures even when the concentration is low. Consequently, it is preferred not only to remove, from  
20 the pentafluoroethane starting material, the compounds which produce chlorotrifluoromethane by reaction with fluorine gas, but also to reduce the chloropentafluoroethane content to as low a concentration as possible.

25 The chlorine compounds included in the pentafluoroethane used for this process are present at preferably no greater than 1 vol%, more preferably no greater than 0.5 vol% and even more preferably no greater than 0.3 vol%. If the chlorine compound content exceeds  
30 1 vol%, the reaction temperature must be increased, possibly resulting in a shorter life of the hydrogenation catalyst.

As hydrogenation catalysts for step (1) there are preferred catalysts containing at least one element from  
35 among platinum metals such as platinum, palladium, rhodium, iridium, ruthenium and osmium, and these metals or their metal oxides or salts may be used as the

starting materials. Carriers which may be used for these catalysts include active carbon, alumina and fluorinated alumina, and the element component-supporting rate is preferably at least 0.02 wt% in order to efficiently promote the intended reaction. The hydrogenation catalyst may be prepared, for example, by dissolving the metal salt in an aqueous solvent such as water, methanol or acetone, immersing the aforementioned carrier in the solution for adsorption of the necessary element, distilling off the solvent, and accomplishing heat reduction treatment with hydrogen or the like.

The reaction temperature for the hydrogenation reaction of step (1) is 150-400°C, and preferably 200-300°C. If the reaction temperature is higher than 400°C the catalyst life will tend to be shortened, often promoting excess reaction. Excessive promotion of the hydrogenation reaction is undesirable because of production of 1,1,1-trifluoroethane, etc. Reaction control is difficult in step (2) in which the organic compound and fluorine gas participate in direct fluorination reaction, because a very large amount of reaction heat is generated and, for example, a greater reaction heat results with a larger number of C-H bonds substituted with C-F bonds in the organic compound substrate, thus tending to produce partial heat generation (hot spots). Consequently, it is preferred to use pentafluoroethane containing minimal hydrofluorocarbons (HFCs), and especially 1,1,1-trifluoroethane which contains numerous C-H bonds. On the other hand, a reaction temperature of lower than 150°C will tend to inhibit the intended reaction.

The molar ratio of hydrogen and the mixed gas (hydrogen/chlorine compound and pentafluoroethane mixed gas) for the hydrogenation reaction of step (1) is preferably in the range of 1-20, and more preferably in the range of 2-10. The reaction pressure is preferably in a range from atmospheric pressure to 1.5 MPa. A

reaction pressure exceeding 1.5 MPa can be problematic since it necessitates pressure-resistant equipment.

In this process, step (1) is carried out under the reaction conditions described above, and the reaction product will contain, along with pentafluoroethane, also hydrofluorocarbons containing no chlorine atoms, and trace amounts of unreacted chlorine compounds and acid component by-products such as hydrochloric acid, which are preferably removed.

The method of removing the acid components may be, for example, a method of contacting with a purifying agent or a method of contacting with water or an aqueous alkali solution. The gas from which the acid components have been removed is preferably dehydrated using a dehydrating agent such as zeolite and then distilled before the direct fluorination step to obtain purified pentafluoroethane, and the unreacted hydrogen is preferably separated out. Hydrogen is preferably not included in the direct fluorination reaction of step (2), because it may react violently with fluorine gas.

The chlorine compounds in the mixed gas obtained by step (1) are preferably present in a total amount of no greater than 0.05 vol%, and 1,1,1-trifluoroethane is preferably present at no greater than 0.2 vol%.

The following explanation concerns step (2) in which the gas containing the pentafluoroethane obtained by step (1) as the major component is reacted with fluorine gas.

Step (2) is carried out in the presence of a diluent gas, in order to set the concentration of the mixed gas with pentafluoroethane as the major component to below the explosive range. Specifically, the concentration of the pentafluoroethane at the reactor inlet is preferably no greater than about 6 mole percent. The diluent gas used contains at least one selected from the group consisting of tetrafluoromethane, hexafluoroethane, octafluoropropane and hydrogen fluoride, and preferably a diluent gas rich in hydrogen fluoride is used. A diluent

gas rich in hydrogen fluoride is a diluent gas containing at least 50 mole percent hydrogen fluoride.

The amount of fluorine gas used may be in the range of 0.5-2.0 and preferably in the range of 0.9-1.3, in terms of the molar ratio with respect to the mixed gas containing pentafluoroethane as the major component (F<sub>2</sub>/hydrogenated compound-containing pentafluoroethane). The reaction temperature is preferably 250-500°C, and more preferably 350-450°C. If the reaction temperature is higher than 500°C, the target product, hexafluoroethane, may be cleaved, producing tetrafluoromethane (CF<sub>4</sub>). If the reaction temperature is below 250°C, the reaction rate may be slowed.

The method of purifying the effluent gas from step (2) is not particularly restricted, but preferably the residual unreacted fluorine gas is removed first. For example, a hydrofluorocarbon such as trifluoromethane may be added to react with and remove the excess fluorine gas. This is preferably followed by distillation, for example, distillation of the hydrogen fluoride and organic matter first. The separated hydrogen fluoride may be reused as diluent gas for the direct fluorination reaction of step (2), or it may be utilized for a different purpose.

The composition of the gas containing the separated organic matter will differ considerably depending on the diluent gas used for the reaction, and for example, when a hydrogen fluoride-rich gas or hexafluoroethane itself is used as the diluent gas, the gas obtained by the reaction will contain hexafluoroethane as the major component. When tetrafluoromethane or octafluoropropane is used as the diluent gas, purification is achieved by further distillation, but in either case, high-purity hexafluoroethane can be obtained by repeated distillation of the mixed gas which is obtained.

The distillation and purification of the mixed gas obtained by the reaction will depend on the compositional



ratio, but as an example, low boiling point components such as inert gases and tetrafluoromethane are extracted from the top of a first distillation tower, and a mixed gas composed mainly of hexafluoroethane is extracted from the bottom. The mixed gas extracted from the bottom is then introduced into a second distillation tower and the low boiling point components such as inert gases and trifluoromethane are extracted from the top of the second distillation tower, after which the mixed gas composed mainly of hexafluoroethane which is extracted from the bottom is introduced into a third distillation tower and high-purity hexafluoroethane is extracted from the top of the tower, thereby accomplishing purification.

The process of the invention described above may be used to obtain hexafluoroethane with a purity of 99.9997 vol% or greater. The chlorotrifluoromethane included as an impurity is therefore less than 1 volppm.  $\text{CF}_3\text{CF}_3$  with a purity of 99.9997 vol% or greater can be analyzed by gas chromatography (GC) methods such as TCD, FID (both including precut methods), ECD or with a gas chromatography-mass spectrometer (GC-MS).

The uses of high-purity hexafluoroethane obtained by the process of the invention will now be explained. High-purity  $\text{CF}_3\text{CF}_3$ , or mixed gases of high-purity  $\text{CF}_3\text{CF}_3$  with inert gases such as He,  $\text{N}_2$  and Ar or gases such as  $\text{O}_2$  and  $\text{NF}_3$  (for the purpose of the invention, these will be collectively referred to as "hexafluoroethane products") may be used as etching gases for etching steps in semiconductor device manufacturing processes or as cleaning gases for cleaning steps in semiconductor device manufacturing processes. In manufacturing processes for semiconductor devices such as LSIs and TFTs, thin-films and thick-films are formed using CVD, sputtering, vapor deposition and the like, and these are etched to form circuit patterns. The thin-film and thick-film forming apparatuses must be cleaned in order to remove unwanted accumulated matter in the apparatus inner walls, jigs,

etc. Production of unwanted accumulated matter can result in particle generation, requiring constant removal in order to produce satisfactory films.

Etching methods using  $\text{CF}_3\text{CF}_3$  may be carried out under various dry etching conditions such as plasma etching, microwave etching or the like, in which case the  $\text{CF}_3\text{CF}_3$  may be used as a mixture with inert gases such as He,  $\text{N}_2$  or Ar or gases such as  $\text{HCl}$ ,  $\text{O}_2$ ,  $\text{H}_2$ ,  $\text{F}_2$ ,  $\text{NF}_3$  or the like in appropriate proportions.

The present invention will now be explained in greater detail by way of examples, with the understanding that the invention is in no way limited by the examples.

Pentafluoroethane Production Example 1 (Starting Material Example 1)

Tetrachloroethylene ( $\text{CCl}_2=\text{CCl}_2$ ) was contacted with Molecular Sieve 4A (product of Union Showa Co., Ltd.) to remove the stabilizer and moisture in the tetrachloroethylene, and was then reacted with hydrogen fluoride ( $\text{HF}$ ) in the presence of a chromium-based fluorination catalyst (first reaction: Reaction pressure of 0.4 MPa, reaction temperature of  $320^\circ\text{C}$ ,  $\text{HF}/\text{tetrachloroethylene} = 8$  (molar ratio)). Next, the primarily dichlorotrifluoroethane ( $\text{CF}_3\text{CHCl}_2$ ) and chlorotetrafluoroethane ( $\text{CF}_3\text{CHClF}$ ) product obtained by the first reaction was reacted with hydrogen fluoride (second reaction: Reaction pressure of 0.45 MPa, reaction temperature of  $330^\circ\text{C}$ ,  $\text{HF}/(\text{CF}_3\text{CHCl}_2 + \text{CF}_3\text{CHClF}) = 6$  (molar ratio)). After completion of the second reaction, the acid component was removed by a known method, and distillation purification was performed to obtain a distillate containing pentafluoroethane as the major component. The distillate was analyzed by gas chromatography and identified as pentafluoroethane having the composition shown in Table 1.

Table 1

Compound	Purity (vol%)
CF <sub>3</sub> CHF <sub>2</sub>	99.7003
CH <sub>3</sub> Cl	0.0014
CHClF <sub>2</sub>	0.0009
CHF <sub>3</sub>	0.0127
CF <sub>3</sub> CClF <sub>2</sub>	0.2819
CF <sub>3</sub> CHClF	0.0008
CF <sub>3</sub> CCl <sub>2</sub> F	0.0009
Other	0.0011

5            Starting Material Hexafluoroethane Production  
Example 1 (Starting Material Example 2)

          Nitrogen gas was introduced into an Inconel 600  
reactor with an inner diameter of 20.6 mm and a length of  
500 mm (electric heater type: passivation treated with  
10    fluorine gas at a temperature of 500°C) through two gas  
inlets at a total flow rate of 30 NL/hr, and the  
temperature in the reactor was kept at 380°C. Next,  
hydrogen fluoride was introduced through the two gas  
inlets at a total flow rate of 50 NL/hr, and  
15    pentafluoroethane (Starting Material Example 1) obtained  
in Pentafluoroethane Production Example 1 was introduced  
through one of the gas inlets at a flow rate of 3.6  
NL/hr. Fluorine gas was introduced through the other gas  
inlet at a flow rate of 3.9 NL/hr for fluorination  
20    reaction. The outlet gas from the reactor was contacted  
with an aqueous potassium hydroxide solution and an  
aqueous potassium iodide solution, and the hydrogen  
fluoride and unreacted fluorine gas in the outlet gas  
were removed. After contact with a dehydrating agent for  
25    drying, the dried gas was cooled and collected, and  
distilled for purification. The purified  
hexafluoroethane was analyzed by gas chromatography,  
giving the results shown in Table 2.

Table 2

Compound	Purity (vol%)
CF <sub>3</sub> CF <sub>3</sub>	99.9972
CF <sub>4</sub>	<0.0001
CClF <sub>3</sub>	0.0025
CF <sub>3</sub> CHF <sub>2</sub>	0.0001
Other	0.0001

## 5 Catalyst Production Example 1 (Catalyst Example 1)

After placing 0.6 L of pure water in a 10 L vessel and stirring, a solution of 452 g of Cr(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O and 42 g of In(NO<sub>3</sub>)<sub>3</sub>·nH<sub>2</sub>O (where n is approximately 5) in 1.2 L of purified water and 0.31 L of 28% aqueous ammonia water were added dropwise thereto, to a reaction solution pH in the range of 7.5-8.5 over a period of about 1 hour while controlling the flow rate of the two aqueous solutions. The obtained slurry was filtered, and the filtered solid was thoroughly washed with purified water and then dried at 120°C for 12 hours. After pulverizing the dried solid, it was mixed with graphite and shaped into pellets using a tablet molding machine. The pellets were calcined for 4 hours under a nitrogen stream at 400°C to prepare a catalyst precursor. The catalyst precursor was filled into an Inconel reactor and subjected to fluorination treatment (catalyst activation) under a nitrogen-diluted hydrogen fluoride stream at 350°C and ordinary pressure. It was then subjected to fluorination treatment (catalyst activation) at 400°C under a 100% hydrogen fluoride stream and then under a nitrogen-diluted hydrogen fluoride stream, to prepare a catalyst (Catalyst Example 1).

## Example 1

A 150 ml portion of the catalyst (Catalyst Example 1) obtained in Catalyst Production Example 1 was filled into an Inconel 600 reactor with an inner diameter of 1 inch and a length of 1 m and the temperature was kept at 280°C while circulating nitrogen gas. Hydrogen fluoride

was then supplied at 1.5 NL/hr, and starting material hexafluoroethane having the composition shown in Table 2 (Starting Material Example 2) was supplied at 3.5 NL/hr. The supply of nitrogen gas was then suspended and  
5 reaction was initiated. After 3 hours, the outlet gas from the reactor was washed with an aqueous potassium hydroxide solution to remove the acid component, and the gas composition was analyzed by gas chromatography and identified as hexafluoroethane having the composition  
10 shown in Table 3.

Table 3

Compound	Purity (vol%)
CF <sub>3</sub> CF <sub>3</sub>	99.9972
CF <sub>4</sub>	0.0025
CClF <sub>3</sub>	<0.0001
CF <sub>3</sub> CHF <sub>2</sub>	0.0001
Other	<0.0001

15

As shown in Table 3, the chlorotrifluoromethane contained in hexafluoroethane can be converted to tetrafluoromethane.

The above reaction was then carried out and the acid  
20 component-removed gas was contacted with a dehydrating agent, dried, cooled and collected, and then distilled by a known method for purification. The hexafluoroethane obtained by the distillation was analyzed by gas chromatography, giving the results shown in Table 4.

25

Table 4

Compound	Purity
CF <sub>3</sub> CF <sub>3</sub>	≥99.9997 vol%
CF <sub>4</sub>	<0.5 volppm
CClF <sub>3</sub>	<0.5 volppm
CF <sub>3</sub> CHF <sub>2</sub>	<0.5 volppm
Other	<1.0 volppm

Based on the analysis results shown in Table 4, the purity of the hexafluoroethane was at least 99.9997 vol%, and the chlorotrifluoromethane content was less than 0.5 volppm. The impurities were analyzed by gas chromatography using TCD, FID, ECD and GC-MS.

#### Example 2

A 100 ml portion of the catalyst (Catalyst Example 1) obtained in Catalyst Production Example 1 was filled into an Inconel 600 reactor with an inner diameter of 1 inch and a length of 1 m and the temperature was kept at 400°C while circulating nitrogen gas. Hydrogen fluoride was then supplied at 10 NL/hr, and starting material hexafluoroethane having the composition shown in Table 2 (Starting Material Example 2) was supplied at 10 NL/hr. The supply of nitrogen gas was then suspended and reaction was initiated. After 3 hours, the outlet gas from the reactor was treated for removal of the acid component in the same manner as Example 1, and analysis was performed by gas chromatography. The results confirmed the product to be hexafluoroethane having the composition shown in Table 5.

Table 5

Compound	Purity (vol%)
CF <sub>3</sub> CF <sub>3</sub>	99.9972
CF <sub>4</sub>	0.0026
CClF <sub>3</sub>	ND
Other	0.0002

In Table 5, ND means "not detectable" by GC-MS, i.e. a value of less than 0.1 volppm. The CClF<sub>3</sub> content was therefore less than 0.1 volppm.

The product gas dehydrated in the same manner as Example 1 was cooled and collected, and distilled under the same conditions, and the resulting hexafluoroethane

was analyzed by gas chromatography, giving the results shown in Table 6.

Table 6

5

Compound	Purity
$\text{CF}_3\text{CF}_3$	>99.9998 vol%
$\text{CF}_4$	<0.5 volppm
$\text{CClF}_3$	<0.1 volppm
Other	<1.0 volppm

As clearly shown by the analysis results in Table 6, the  $\text{CClF}_3$  content was less than 0.1 volppm, and therefore high-purity hexafluoroethane had been obtained.

10 Pentafluoroethane Production Example 2 (Starting Material Example 3)

Tetrachloroethylene ( $\text{CCl}_2=\text{CCl}_2$ ) was contacted with Molecular Sieve 4A (product of Union Showa K.K.) to remove the stabilizer and moisture in the tetrachloroethylene, and was then reacted with hydrogen fluoride (HF) in the presence of a chromium-based fluorination catalyst (first reaction: Reaction pressure of 0.4 MPa, reaction temperature of 300°C, HF/tetrachloroethylene = 8 (molar ratio)). Next, the mixed gas containing primarily dichlorotrifluoroethane ( $\text{CF}_3\text{CHCl}_2$ ) and chlorotetrafluoroethane ( $\text{CF}_3\text{CHClF}$ ) obtained by the first reaction was reacted with hydrogen fluoride (second reaction: Reaction pressure of 0.4 MPa, reaction temperature of 330°C, HF/( $\text{CF}_3\text{CHCl}_2 + \text{CF}_3\text{CHClF}$ ) = 6 (molar ratio)). After completion of the second reaction, the acid component was removed by a known method, and distillation purification was performed to obtain a distillate containing mostly pentafluoroethane as the major component. The distillate was analyzed by gas chromatography and identified as a mixed gas having the composition shown in Table 7 (Starting Material Example 3).

Table 7

Compound	Purity (vol%)
CF <sub>3</sub> CHF <sub>2</sub>	99.4290
CH <sub>3</sub> Cl	0.0011
CHClF <sub>2</sub>	0.0008
CHF <sub>3</sub>	0.0218
CClF <sub>3</sub>	0.0006
CF <sub>3</sub> CClF <sub>2</sub>	0.5439
CF <sub>3</sub> CHClF	0.0007
CF <sub>3</sub> CCl <sub>2</sub> F	0.0011
CF <sub>3</sub> CH <sub>2</sub> Cl	0.0003
Other	0.0007

5

Pentafluoroethane Production Example 3 (Starting Material Example 4)

The mixed gas containing pentafluoroethane as the major component which was obtained by the process described above (Starting Material Example 3) was distilled by a known method. The distillate was analyzed by gas chromatography and identified as a mixed gas having the composition shown in Table 8 (Starting Material Example 4).

15

Table 8

Compound	Purity (vol%)
CF <sub>3</sub> CHF <sub>2</sub>	99.7984
CHClF <sub>2</sub>	0.0003
CHF <sub>3</sub>	0.0024
CF <sub>3</sub> CClF <sub>2</sub>	0.1989

20

Catalyst Production Example 2 (Catalyst Example 2)

Sodium palladium chloride was dissolved in water, and a 1.6 mmφ spherical alumina support was immersed therein for adsorption of the palladium salt, after which the solvent was distilled off at a temperature of 100°C,

25



calcining was conducted in air at 300°C, and hydrogen reduction was accomplished at 350°C. The supporting rate of the obtained palladium catalyst was 2.0%.

Catalyst Production Example 3 (Catalyst Example 3)

5       Platinic chloride was dissolved in water, and a 1.6 mmφ spherical alumina support was immersed therein for adsorption of the platinum salt, after which the solvent was distilled off at a temperature of 100°C, calcining was conducted in air at 300°C, and hydrogen reduction was  
10       accomplished at 350°C. The supporting rate of the obtained platinum catalyst was 2.0%.

Example 3

A 100 ml portion of the catalyst (Catalyst Example 2) obtained in Catalyst Production Example 2 was filled  
15       into an Inconel 600 reactor with an inner diameter of 1 inch and a length of 1 m and the temperature was kept at 280°C while circulating nitrogen gas. Hydrogen was then supplied at a flow rate of 0.36 NL/hr, the mixed gas having the composition shown in Table 7 (Starting  
20       Material Example 3) was supplied at 8.33 NL/hr, and then the supply of nitrogen gas was suspended and a reaction (step (1)) was initiated. After 2 hours, the outlet gas from the reactor was washed with an aqueous solution of potassium hydroxide for removal of the acid component,  
25       and then analysis of the gas composition by gas chromatography identified it as a mixed gas composed mainly of pentafluoroethane having the composition shown in Table 9.

Table 9

Compound	Purity (vol%)
CF <sub>3</sub> CHF <sub>2</sub>	99.9177
CH <sub>4</sub>	0.0013
CH <sub>2</sub> F <sub>2</sub>	0.0009
CHF <sub>3</sub>	0.0226
CF <sub>3</sub> CH <sub>2</sub> F	0.0126
CF <sub>3</sub> CH <sub>3</sub>	0.0386
CF <sub>3</sub> CClF <sub>2</sub>	0.0058
Other	0.0005

5           The mixed gas composed mainly of pentafluoroethane  
having the composition shown in Table 9, which was  
obtained by the process described above, was distilled by  
a known method, and after removing the low boiling point  
components such as the inert gas and hydrogen gas, a  
10       direct fluorination reaction (step (2)) was conducted  
with fluorine gas.

          Nitrogen gas was introduced into an Inconel 600  
reactor with an inner diameter of 20.6 mmφ and a length  
of 500 mm (electric heater type reactor: passivation  
15       treated with fluorine gas at a temperature of 500°C)  
through two gas inlets at a total flow rate of 30 NL/hr,  
and the temperature in the reactor was kept at 420°C.  
Next, hydrogen fluoride was introduced through the two  
gas inlets at a total flow rate of 50 NL/hr, and the  
20       above-mentioned mixed gas composed mainly of  
pentafluoroethane from which the low boiling point  
components had been removed was introduced through one of  
the gas inlets at a flow rate of 3.5 NL/hr. Fluorine gas  
was introduced through the other gas inlet at a flow rate  
25       of 3.85 NL/hr and reacted therewith. After 3 hours, the  
outlet gas from the reactor was contacted with an aqueous  
potassium hydroxide solution and an aqueous potassium  
iodide solution, and the hydrogen fluoride and unreacted  
fluorine gas were removed. After contact with a  
30       dehydrating agent for drying, the dried gas composition

was analyzed by gas chromatography. The analysis results are shown in Table 10.

Table 10

5

Compound	Purity (vol%)
$\text{CF}_3\text{CF}_3$	99.9541
$\text{CF}_4$	0.0388
$\text{CHF}_3$	0.0012
$\text{CF}_3\text{CHF}_2$	<0.0001
$\text{CF}_3\text{CH}_2\text{F}$	trace
$\text{CF}_3\text{CClF}_2$	0.0058

The dried gas composed mainly of hexafluoroethane was cooled and collected, and purified by distillation. The purified gas was analyzed by gas chromatography using TCD, FID, ECD and GC-MS, and the results shown in Table 11 were obtained.

10

Table 11

15

Compound	Purity volppm
$\text{CF}_3\text{CHF}_2$	<0.5 volppm
$\text{CF}_3\text{CH}_2\text{F}$	<0.5 volppm
$\text{CF}_4$	<0.4 volppm
$\text{SF}_6$	<0.4 volppm
$\text{CF}_3\text{CClF}_2$	<0.1 volppm
$\text{CF}_3\text{CF}_3$	>99.9998 vol%

As clearly seen by the analysis results in Table 11, the hexafluoroethane contained virtually no impurities, thus demonstrating that high-purity hexafluoroethane had been obtained, with a purity of at least 99.9997 vol%.

20

#### Example 4

A reaction (step (1)) was carried out with the same conditions and procedure as Example 3, except that 100 ml of catalyst (Catalyst Example 3) was filled in and the mixed gas of Starting Material Example 4 was used. The reactor outlet gas was treated in the same manner and

25

then analyzed, giving the results shown in Table 12.

Table 12

Compound	Purity (vol%)
$\text{CF}_3\text{CHF}_2$	99.9692
$\text{CH}_4$	0.0002
$\text{CH}_2\text{F}_2$	0.0002
$\text{CF}_3\text{CH}_2\text{F}$	0.0056
$\text{CF}_3\text{CH}_3$	0.0215
$\text{CF}_3\text{CClF}_2$	0.0012
$\text{CHF}_3$	0.0021

5

The mixed gas composed mainly of pentafluoroethane having the composition shown in Table 12, which was obtained by the process described above, was distilled by a known method, and after removing the low boiling point components such as the inert gas and hydrogen gas, a direct fluorination reaction (step (2)) was conducted with fluorine gas using the same conditions and procedure as Example 3. The gas obtained by treating the reactor outlet gas according to the same process as Example 3 was analyzed by gas chromatography, giving the results shown in Table 13.

15

Table 13

20

Compound	Purity (vol%)
$\text{CF}_3\text{CF}_3$	99.9680
$\text{CF}_4$	0.0314
$\text{CHF}_3$	0.0002
$\text{CF}_3\text{CHF}_2$	<0.0001
$\text{CF}_3\text{CH}_2\text{F}$	<0.0001
$\text{CF}_3\text{CH}_3$	<0.0001
$\text{CF}_3\text{CClF}_2$	<0.0001

The mixed gas composed mainly of hexafluoroethane was cooled and collected, and then purified by distillation. Analysis of the purified gas indicated a hexafluoroethane purity of at least 99.9998 vol%, a

25

chlorine compound impurity content of less than 1 volppm, and a starting material pentafluoroethane content of less than 1 volppm.

Comparative Example 1

5 A reaction (step (1)) was conducted using the same conditions and procedure as Example 3, except for a reaction temperature of 430°C, and the product was analyzed. The results are shown in Table 14.

10

Table 14

Compound	Purity (vol%)
CF <sub>3</sub> CHF <sub>2</sub>	99.5373
CH <sub>4</sub>	0.0134
C <sub>2</sub> H <sub>6</sub>	0.0098
CH <sub>2</sub> F <sub>2</sub>	0.0002
CHF <sub>3</sub>	0.0189
CF <sub>3</sub> CH <sub>2</sub> F	0.0043
CF <sub>3</sub> CH <sub>3</sub>	0.4150
CF <sub>3</sub> CClF <sub>2</sub>	0.0044
Other	0.0011

15 As clearly seen from the analysis results in Table 14, when step (1) was conducted at a reaction temperature of higher than 400°C, excess hydrogenation reaction was promoted, thereby notably increasing the amount of 1,1,1-trifluoroethane product. Methane and ethane were also produced, and deterioration of the catalyst was observed.

20 Comparative Example 2

A reaction (step (1)) was conducted with the same conditions and procedure as Example 3, except for a reaction temperature of 130°C, and the product was analyzed. When step (1) was conducted at a reaction  
25 temperature of lower than 150°C, hydrogenation reaction of the chlorine compounds was almost completely inhibited, resulting in a chloropentafluoroethane conversion rate of about 19%.

Comparative Example 3

30 A direct fluorination reaction (step (2)) was

conducted using the same conditions and procedure as Example 3, except for using the mixed gas of Starting Material Example 3, and after removing the hydrogen fluoride and unreacted fluorine gas contained in the reactor outlet gas, analysis was performed by gas chromatography. The results are shown in Table 15.

Table 15

Compound	Purity (vol%)
$\text{CF}_3\text{CF}_3$	99.4210
$\text{CF}_4$	0.0308
$\text{CClF}_3$	0.0046
$\text{CF}_3\text{CHF}_2$	0.0002
$\text{CF}_3\text{CClF}_2$	0.5419
$\text{CF}_3\text{CCl}_2\text{F}$	0.0009
Other	0.0006

As clearly seen in Table 15, direct fluorination reaction using pentafluoroethane with a high chlorine compound content produced chlorotrifluoromethane, which is difficult to separate.

#### Industrial Applicability

According to the procedure of the present invention, it is possible to obtain high-purity  $\text{CF}_3\text{CF}_3$  and the obtained  $\text{CF}_3\text{CF}_3$  is suitable for use as an etching gas or cleaning gas for semiconductor device manufacturing steps.

CLAIMS

1. A process for production of hexafluoroethane which comprises a step in which a mixed gas containing hexafluoroethane and chlorotrifluoromethane is reacted  
5 with hydrogen fluoride in a gas phase in the presence of a fluorination catalyst at 200-450°C, for fluorination of said chlorotrifluoromethane.

2. A process according to claim 1, wherein the fluorination catalyst is a supported catalyst or a bulk  
10 catalyst with trivalent chromium oxide as the major component.

3. A process according to claim 1 or 2, wherein the molar ratio of the hydrogen fluoride and said mixed gas (hydrogen fluoride/mixed gas containing  
15 hexafluoroethane and chlorotrifluoromethane) is in the range of 0.05-10.

4. A process according to any one of claims 1 to 3, wherein the concentration of the chlorotrifluoromethane in said mixed gas is no greater  
20 than 0.1 vol%.

5. A process according to any one of claims 1 to 4, wherein said mixed gas is obtained by reacting dichlorotetrafluoroethane and/or chloropentafluoroethane with hydrogen fluoride in a gas phase in the presence of  
25 a fluorination catalyst.

6. A process according to any one of claims 1 to 4, wherein said mixed gas is obtained by reacting tetrafluoroethane and/or pentafluoroethane with fluorine gas.

30 7. A process for production of hexafluoroethane which comprises the following steps (1) and (2):

(1) A step in which a mixed gas containing hexafluoroethane and chlorotrifluoromethane is reacted with hydrogen fluoride in a gas phase in the presence of  
35 a fluorination catalyst at 200-450°C to fluorinate said chlorotrifluoromethane and convert it to tetrafluoromethane.

(2) A step in which the mixed gas containing hexafluoroethane and tetrafluoromethane obtained in step (1) is distilled to obtain purified hexafluoroethane.

8. A process according to claim 7, wherein the fluorination catalyst of step (1) is a supported catalyst or a bulk catalyst with trivalent chromium oxide as the major component.

9. A process according to claim 7 or 8, wherein in step (1), the molar ratio of the hydrogen fluoride and said mixed gas (hydrogen fluoride/mixed gas containing hexafluoroethane and chlorotrifluoromethane) is in the range of 0.05-10.

10. A process according to any one of claims 7 to 9, wherein the concentration of the chlorotrifluoromethane in said mixed gas of step (1) is no greater than 0.1 vol%.

11. A process according to any one of claims 7 to 10, wherein said mixed gas of step (1) is obtained by reacting dichlorotetrafluoroethane and/or chloropentafluoroethane with hydrogen fluoride in a gas phase in the presence of a fluorination catalyst.

12. A process according to any one of claims 7 to 10, wherein said mixed gas of step (1) is obtained by reacting tetrafluoroethane and/or pentafluoroethane with fluorine gas.

13. A process for production of hexafluoroethane which comprises a step (1) in which pentafluoroethane containing chlorine compounds with 1-3 carbon atoms is reacted with hydrogen in a gas phase in the presence of a hydrogenation catalyst at 150-400°C for hydrogenation of said chlorine compounds, and a step (2) in which the product of step (1) is reacted with fluorine in a gas phase in the presence of a diluent gas to produce hexafluoroethane.

14. A process according to claim 13, wherein the product of step (1) used in step (2) is purified pentafluoroethane obtained by distillation of the crude



product of step (1).

15. A process according to claim 13 or 14, which comprises a further step in which the product obtained in step (2) is distilled to purify the hexafluoroethane.

5 16. A process according to any one of claims 13 to 15, which comprises a further step in which hydrochloric acid is removed from the reaction product obtained in step (1).

10 17. A process according to any one of claims 13 to 16, wherein said chlorine compounds are one or more compounds selected from the group consisting of chloromethane, chlorotrifluoromethane, chloropentafluoroethane, dichlorotetrafluoroethane, chlorotetrafluoroethane, chlorotrifluoroethane and  
15 chlorotrifluoroethylene.

18. A process according to any one of claims 13 to 17, wherein said chlorine compounds included in the chlorine compound-containing pentafluoroethane used in step (1) are present at no greater than 1 vol%.

20 19. A process according to claim 18, wherein said chlorine compounds included in the chlorine compound-containing pentafluoroethane used in step (1) are present at no greater than 0.5 vol%.

25 20. A process according to any one of claims 13 to 19, wherein the hydrogenation catalyst of step (1) contains at least one element selected from platinum metals.

30 21. A process according to claim 20, wherein the hydrogenation catalyst of step (1) is a catalyst having at least one element selected from platinum metals supported on at least one support selected from the group consisting of active carbon, alumina and fluorinated alumina.

35 22. A process according to any one of claims 13 to 21, wherein the amount of hydrogen used in step (1) is in a molar ratio of 1-20 with respect to the chlorine compound-containing pentafluoroethane.

23. A process according to any one of claims 13 to 22, wherein the trifluoroethane is included in an amount of no greater than 0.2 vol% in the product of step (1) used for step (2).

5        24. A process for production of hexafluoroethane according to any one of claims 13 to 23, wherein the chlorine compounds with 1-3 carbon atoms are included in an amount of no greater than 0.05 vol% in the product of step (1) used for step (2).

10       25. A process according to any one of claims 13 to 24, wherein the diluent gas of step (2) is a gas containing at least one selected from the group consisting of tetrafluoromethane, hexafluoroethane, octafluoropropane and hydrogen fluoride.

15       26. A process according to claim 25, wherein the diluent gas of step (2) is a hydrogen fluoride-rich gas.

27. A process according to any one of claims 13 to 26, wherein the reaction temperature in step (2) is 250-500°C.

20       28. A process according to claim 27, wherein the reaction temperature in step (2) is 350-450°C.

29. A process according to any one of claims 13 to 28, wherein the chlorine compound-containing pentafluoroethane used in step (1) is a gas composed  
25       mainly of pentafluoroethane obtained by reacting tetrachloroethylene or its fluorinated product with hydrogen fluoride.

30. A process according to claim 29, wherein the gas composed mainly of pentafluoroethane is a gas  
30       obtained by distillation of a gas obtained by reacting tetrachloroethylene or its fluorinated product with hydrogen fluoride.

31. A hexafluoroethane product comprising hexafluoroethane with a purity of 99.9997 vol% or greater  
35       obtained by using a process according to any one of claims 1 to 30.

32. A hexafluoroethane product according to claim

31, wherein the chlorotrifluoromethane content of said hexafluoroethane is no greater than 1 volppm.

33. An etching gas containing a hexafluoroethane product according to claim 31 or 32.

5        34. A cleaning gas containing a hexafluoroethane product according to claim 31 or 32.

## INTERNATIONAL SEARCH REPORT

INTERNATIONAL APPLICATION NO.

PCT/JP 02/08034

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC 7 C07C17/383 C07C17/20 C07C17/354 C07C19/08

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)

IPC 7 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 practical, search terms used)

EPO-Internal, WPI Data, CHEM ABS Data, BEILSTEIN Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 523 499 A (CORBIN DAVID R ET AL) 4 June 1996 (1996-06-04) cited in the application column 1, line 18-44 column 2, line 19,20 ---	31-34
X	DATABASE WPI Section Ch, Week 199749 Derwent Publications Ltd., London, GB; Class E16, AN 1997-532712 XP002222632 & JP 09 255596 A (SHOWA DENKO KK), 30 September 1997 (1997-09-30) abstract --- -/--	31-34

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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\*P\* document published prior to the international filing date but later than the priority date claimed

\*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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Date of the actual completion of the international search

27 November 2002

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## INTERNATIONAL SEARCH REPORT

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5 453 551 A (LACROIX ERIC ET AL) 26 September 1995 (1995-09-26) column 2, line 10 -column 3, line 2 claims 1-10 ----	1-12
Y	US 4 748 285 A (FOULLETIER LOUIS) 31 May 1988 (1988-05-31) examples 4-6 claim 11 ----	1-12
Y	US 5 710 351 A (NAKAJO TETSUO ET AL) 20 January 1998 (1998-01-20) claims 1-10 ----	13-30
Y	COQ, BERNARD ET AL: "Conversion under hydrogen of dichlorodifluoromethane over bimetallic palladium catalysts" APPLIED CATALYSIS, A: GENERAL , vol. 101, 1993, pages 41-50, XP001120714 see page 45 last paragraph -----	13-30

## INTERNATIONAL SEARCH REPORT

Information on patent family members

INTERNATIONAL APPLICATION NO.

PCT/JP 02/08034

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
US 5523499	A	04-06-1996	WO	9317988 A1	16-09-1993
			DE	69213029 D1	26-09-1996
			DE	69213029 T2	06-02-1997
			EP	0630362 A1	28-12-1994
			HK	1001476 A1	19-06-1998
			JP	7504435 T	18-05-1995
			JP	3130046 B2	31-01-2001
-----					
JP 9255596	A	30-09-1997	NONE		
-----					
US 5453551	A	26-09-1995	FR	2701943 A1	02-09-1994
			AU	652321 A1	18-08-1994
			CA	2115975 A1	25-08-1994
			CN	1099022 A	22-02-1995
			DE	69400036 D1	18-01-1996
			DE	69400036 T2	18-07-1996
			EP	0612709 A1	31-08-1994
			ES	2081226 T3	16-02-1996
			JP	6256234 A	13-09-1994
-----					
US 4748285	A	31-05-1988	FR	2501062 A1	10-09-1982
			AU	541788 B2	17-01-1985
			AU	7903781 A	08-07-1982
			BR	8108429 A	13-10-1982
			CA	1154425 A1	27-09-1983
			DD	208084 A5	28-03-1984
			DE	3169123 D1	28-03-1985
			EP	0055652 A1	07-07-1982
			ES	508385 D0	16-03-1983
			ES	8304903 A1	16-06-1983
			JP	1799947 C	12-11-1993
			JP	3072946 A	28-03-1991
			JP	5009135 B	04-02-1993
			JP	1654645 C	13-04-1992
			JP	3014498 B	26-02-1991
			JP	57119836 A	26-07-1982
			PL	234425 A1	16-08-1982
			US	4439534 A	27-03-1984
-----					
US 5710351	A	20-01-1998	JP	9241186 A	16-09-1997
			DE	19654720 A1	11-09-1997
			GB	2311287 A ,B	24-09-1997
			CN	1165803 A ,B	26-11-1997
			SG	48501 A1	17-04-1998
			TW	409114 B	21-10-2000