

DESCRIPTION

Title of Invention: METHOD FOR PURIFYING HEXAFLUOROBUTADIENE

Technical Field

5 [0001]

The present disclosure relates to a method for purifying hexafluorobutadiene.

Background Art

10 [0002]

Hexafluorobutadiene has been widely used as an etching gas in semiconductor production processes.

[0003]

Conventionally, hexafluorobutadiene is purified by removing impurities using a solid adsorbent such as a zeolite (e.g., Patent Literature 1 and 2). However, in the conventional technique, hexafluorobutadiene reacts with zeolite to cause isomerization of hexafluorobutadiene, which reduces the purity of hexafluorobutadiene.

20

Citation List

Patent Literature

[0004]

PTL 1: Japanese Patent No. 3866663

25 PTL 2: Japanese Patent No. 5607354

Summary

Technical Problem

[0005]

30 An object of the present disclosure is to purify hexafluorobutadiene to a high purity while inhibiting the isomerization of hexafluorobutadiene.

Solution to Problem

35 [0006]

The present disclosure includes the following.

[0007]

Item 1. A method for purifying hexafluorobutadiene, comprising bringing a composition containing hexafluorobutadiene into
5 contact with a zeolite having an $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 4.0 to 8.0.

[0008]

Item 2. The purification method according to Item 1, wherein an impurity other than the hexafluorobutadiene is adsorbed onto the zeolite to remove the impurity from the composition.

10 [0009]

Item 3. The purification method according to Item 1 or 2, wherein the purity of the hexafluorobutadiene in the composition after the purification is 99.99 volume% or more.

[0010]

15 Item 4. The purification method according to any of Items 1 to 3, wherein the zeolite has an average pore size of 5 Å to 9 Å.

[0011]

Item 5. A method for producing a composition containing hexafluorobutadiene, comprising bringing a composition containing
20 hexafluorobutadiene into contact with a zeolite having an $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 4.0 to 8.0,
wherein

the purity of the hexafluorobutadiene in the composition after the contact with the zeolite is 99.99 volume%
25 or more.

[0012]

Item 6. The production method according to Item 5, wherein an impurity other than the hexafluorobutadiene is adsorbed onto the zeolite to remove the impurity from the composition before the
30 contact with the zeolite.

[0013]

Item 7. The production method according to Item 5 or 6, wherein the zeolite has an average pore size of 5Å to 9Å.

[0014]

35 Item 8. A composition comprising hexafluorobutadiene having a

purity of 99.99 volume% or more.

[0015]

Item 9. The composition according to Item 8, which is used as an etching gas or a building block for organic synthesis.

5

[0015a]

In one aspect, there is provided a method for purifying hexafluorobutadiene, comprising bringing a composition containing hexafluorobutadiene into contact with a zeolite having an

10 $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 4.0 to 8.0 and having an average pore size of 5 Å to 9 Å.

[0015b]

In another aspect, there is provided a method for producing a composition containing hexafluorobutadiene, comprising bringing a composition containing hexafluorobutadiene into contact with a zeolite having an $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 4.0 to 8.0 and having an average pore size of 5 Å to 9 Å, wherein the purity of the hexafluorobutadiene in the composition after the contact with the zeolite is 99.99 volume% or more.

20

Advantageous Effects of Invention

[0016]

According to the present disclosure, the isomerization of hexafluorobutadiene can be inhibited, and the hexafluorobutadiene can be purified to a high purity.

25

Description of Embodiments

[0017]

As a result of extensive research, the present inventors found that the isomerization of hexafluorobutadiene can be inhibited by bringing a composition containing hexafluorobutadiene into contact with a zeolite having an $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 4.0 to 8.0, thereby purifying the hexafluorobutadiene to a high purity.

35

[0018]

The present disclosure was accomplished as a result of further research based on such findings.

[0019]

5 The present disclosure includes the following embodiments.

[0020]

In the present disclosure, hexafluorobutadiene refers to hexafluoro-1,3-butadiene.

10 [0021]

(1) Method for purifying hexafluorobutadiene

The method for purifying hexafluorobutadiene according to the present disclosure comprises the step of bringing a composition containing hexafluorobutadiene into contact with a
15 zeolite having an $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 4.0 to 8.0.

[0022]

According to the present disclosure, in the above step, an impurity other than the hexafluorobutadiene is adsorbed onto the zeolite to remove the impurity from the composition before the contact with the zeolite.

5 [0023]

According to the present disclosure, in the step, the purity of the hexafluorobutadiene in the composition after the contact with the zeolite is 99.99 volume% or more.

[0024]

10 The method for purifying hexafluorobutadiene according to the present disclosure has an advantage such that the isomerization of hexafluorobutadiene is inhibited and the hexafluorobutadiene is purified to a high purity by bringing the composition containing hexafluorobutadiene into contact with the
15 zeolite having an $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 4.0 to 8.0.

[0025]

(1-1) Composition containing hexafluorobutadiene

Hexafluorobutadiene is used as an etching gas for silicon oxide and related materials in the production of
20 semiconductors. The hexafluorobutadiene used in the semiconductor industry is required to have extremely high purity.

[0026]

The composition containing hexafluorobutadiene contains an impurity that is introduced during the production of
25 hexafluorobutadiene. Examples of the impurity include intermediates, isomers, and by-products (e.g., hydrogen fluoride, hydrofluorocarbons, hydrochlorofluorocarbons, chlorofluorocarbons, and fluoroalkenes).

[0027]

30 The composition containing hexafluorobutadiene contains an impurity that is introduced during the use of hexafluorobutadiene. Examples of the impurity include HF , SiF_4 , and O_2 when the hexafluorobutadiene is used as an etching gas for the production of semiconductors. Examples of the impurity
35 include moisture when the hexafluorobutadiene is used as a

refrigerant for refrigeration equipment.

[0028]

When water, hydrogen fluoride, or the like exist as an impurity, especially when a fluorine-containing compound is chemically unstable due to having a reactive moiety such as a double bond, alteration (decomposition, polymerization, or isomerization) of the fluorine-containing compound may occur, leading to a vicious cycle of further decrease in purity.

[0029]

Commercially available hexafluorobutadiene typically has a purity of 99.0 volume% to 99.9 volume%; and includes a partially fluorinated and chlorinated isomer of butadiene, a butadiene dimer, and a mixture of a starting material and a solvent.

[0030]

Hexafluorobutadiene having a higher purity is needed in the semiconductor industry.

[0031]

(1-2) Zeolite having an $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 4.0 to 8.0

Zeolites are one of the clay minerals. They are hydrous aluminosilicates that contain alkali or alkaline earth metals. Zeolites are composed of a rigid anionic framework with regular channels (tubular pores) and cavities (cavities).

[0032]

Zeolites are typically represented by the composition of $(\text{M}^{\text{I}}, \text{M}^{\text{II}}_{1/2})_m (\text{Al}_m \text{Si}_n \text{O}_{2(m+n)})_x \text{H}_2\text{O}$ ($n \geq m$) (M^{I} : Li^+ , Na^+ , K^+ , etc., M^{II} : Ca^{2+} , Mg^{2+} , Ba^{2+} , etc.). The cations compensate for the negative charge of the aluminosilicate framework.

[0033]

There is no limitation on the cation in the zeolite; H^+ , Li^+ , Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Ba^{2+} , and the like are usually used.

[0034]

The basic unit of the structure is a tetrahedral structure of SiO_4 or AlO_4 (TO_4 tetrahedron in combination). These structures are connected forever in the three-dimensional

direction to form a crystal. The crystal of zeolite is porous, and typically has a pore diameter of about 0.2 to 1.0 nm. The zeolite has a molecular sieving effect (molecular sieve), which means that a molecule having a size larger than the pore size of the zeolite cannot enter. The zeolite has properties such as solid acidity, ion exchange capacity, catalytic capacity, and adsorption capacity, in addition to the molecular sieving effect due to the pore derived from its framework structure.

[0035]

In the present disclosure, a zeolite having an $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio (molar ratio) of 4.0 to 8.0 is used because the isomerization of hexafluorobutadiene can be inhibited, and the hexafluorobutadiene can be purified to a high purity. In the present disclosure, it is preferable to use a zeolite having an $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio (molar ratio) of 5.0 to 7.0.

[0036]

If the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio (molar ratio) is smaller than 4.0, the polarity of the zeolite increases, and the zeolite itself is easily degraded by the reaction with hydrogen fluoride in the composition containing hexafluorobutadiene. If the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio (molar ratio) is larger than 8.0, the polarity of the zeolite is reduced, and the adsorption amount of water in the composition containing hexafluorobutadiene decreases.

[0037]

In the present disclosure, because the isomerization of hexafluorobutadiene can be inhibited and the hexafluorobutadiene can be purified to a high purity, a zeolite having an average pore size of 5Å to 9Å is preferable. Such a zeolite is preferably porous. Such a zeolite is commercially available.

[0038]

In the present disclosure, impurities to be adsorbed and removed by the zeolite include, *inter alia*, those containing water, those containing hydrogen fluoride, those containing hydrocarbons; those containing carbon halide compounds; those containing halogenated hydrocarbon compounds; and those

containing isomers of fluorine-containing compounds to be contacted with the zeolite, such as positional isomers of carbon-carbon double bonds and cyclic isomers of carbon-carbon double bonds. Examples of the aforementioned impurities include
5 heptafluorobutene, chloroheptafluorobutene, methyl iodide, chlorotrifluoroethylene, and the like.

[0039]

(1-3) Step of bringing the composition containing hexafluorobutadiene into contact with zeolite

10 The present disclosure includes the step of bringing the composition containing hexafluorobutadiene into contact with a zeolite having an $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 4.0 to 8.0. In the present disclosure, bringing the composition with the zeolite means allowing the composition to pass through a column or the like
15 filled with the zeolite, or introducing the composition into a container filled with the zeolite.

[0040]

 In the present disclosure, the zeolite is used as a material for adsorbing and removing an impurity, and the
20 composition containing hexafluorobutadiene is brought into contact with (allowed to pass through) the zeolite to remove an impurity contained in the composition.

[0041]

 In the present disclosure, for effective adsorption and
25 removal of impurities, it is preferable to bring the composition containing hexafluorobutadiene into contact with the zeolite in a mass ratio of about 100:1 to 1:10, more preferably in a ratio of about 50:1 to 1:5, and even more preferably in a ratio of about 10:1 to 1:3. In the present disclosure, the amount of the zeolite
30 to be used may be such that the amount of the composition containing hexafluorobutadiene is about 10 g to 100 g when a stainless cylinder or the like is filled with 10 g of zeolite (zeolite filling).

[0042]

35 In the present disclosure, the zeolite may be activated

and treated before the use thereof. As the condition for the activation treatment, a drying treatment in which heating is conducted in a vacuum (10^{-1} mmHg to 10^{-3} mmHg) at a temperature in the range of 300°C to 350°C overnight can be exemplified. In the present disclosure, zeolites that do not undergo the
5 aforementioned activation treatment can also be suitably used.
[0043]

 In the present disclosure, there is no limitation on the form of the zeolite to be used. The composition containing
10 hexafluorobutadiene may pass through a device filled with the zeolite; or the composition may be introduced into a device filled with the zeolite, and then removed after a predetermined time has passed.
[0044]

15 In the present disclosure, there is no limitation on the temperature at which the composition containing hexafluorobutadiene is brought into contact with the zeolite. The temperature may be determined considering the boiling point of hexafluorobutadiene contained in the composition including
20 hexafluorobutadiene. In general, contact at a low temperature is preferable because a side reaction such as isomerization during the contact is inhibited. The temperature is preferably in the range of about -50°C to 100°C.
[0045]

25 In the present disclosure, there is no limitation on the time for bringing the composition containing hexafluorobutadiene into contact with the zeolite.
[0046]

 In the present disclosure, the zeolite to be used may
30 be in the form of powders, granules, or pellets; or may be used as a molded body. From the industrial perspective, the zeolite to be used is preferably a molded body. Although there is no limitation on the shape of the molded body, a cylindrical shape having a diameter of about 0.5 to 5 mm and a length of about 1 to
35 15 mm, or a spherical shape having a diameter of about 0.5 to 10

mm is preferably used.

[0047]

In the present disclosure, the method for producing the molded body of the zeolite is not limited. For example, a conventional known method using kaolin clay as a binder can be used.

[0048]

According to the method for purifying hexafluorobutadiene of the present disclosure, by bringing the composition containing hexafluorobutadiene into contact with a zeolite having an $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 4.0 to 8.0, an impurity other than the hexafluorobutadiene can be adsorbed onto the zeolite, thereby removing the impurity from the composition.

[0049]

According to the method for purifying hexafluorobutadiene of the present disclosure, in the composition after purification, i.e., in the composition after the contact with the zeolite, the purity of the hexafluorobutadiene can be adjusted to 99.99 volume% or more. According to the method for purifying hexafluorobutadiene of the present disclosure, the purity of hexafluorobutadiene can be particularly adjusted to 99.995 volume% or more after purification.

[0050]

According to the present disclosure, by effectively removing various impurities in the composition containing hexafluorobutadiene, the composition from which the impurities have been removed can be suitably used as an etching gas for the production of semiconductors, thus allowing to inhibit corrosion and premature degradation of equipment.

[0051]

(2) Method for producing the composition containing hexafluorobutadiene

The method for producing a composition containing hexafluorobutadiene according to the present disclosure comprises the step of bringing the composition containing

hexafluorobutadiene into contact with a zeolite having an $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 4.0 to 8.0, wherein the purity of the hexafluorobutadiene in the composition after the contact with the zeolite is 99.99 volume% or more.

5 [0052]

According to the present disclosure, in the above step, it is preferable to adsorb an impurity other than the hexafluorobutadiene onto the zeolite, and remove the impurity from the composition before the contact with the zeolite.

10 [0053]

In the present disclosure, the purity of hexafluorobutadiene in the composition after the contact with the zeolite can be particularly adjusted to 99.995 volume% or more.

[0054]

15

In the method for producing a composition containing hexafluorobutadiene according to the present disclosure, the zeolite to be used, the composition containing hexafluorobutadiene that is brought into contact with the zeolite, and the like are as explained in the purification method of hexafluorobutadiene according to the present disclosure.

[0055]

(3) Composition containing hexafluorobutadiene

In the composition of the present disclosure, the purity of hexafluorobutadiene is 99.99 volume% or more. According to the present disclosure, it is particularly preferable that the purity of the hexafluorobutadiene in the composition is 99.995 volume% or more.

[0056]

In the present disclosure, the composition is used as an etching gas or a building block for organic synthesis. In the present disclosure, the composition can be effectively used for various applications such as building blocks for organic synthesis; as well as etching gases for forming state-of-the-art microstructures, such as semiconductors, liquid crystals, and the like.

35

[0057]

The building block for organic synthesis refers to a substance that can be a precursor for a compound having a highly reactive framework. For example, by the reaction of the
5 composition containing hexafluorobutadiene according to the present disclosure with a fluorine-containing organosilicon compound such as $\text{CF}_3\text{Si}(\text{CH}_3)_3$, a fluoroalkyl group such as a CF_3 group is introduced into the composition, thereby converting the composition into a substance that can become a detergent or a
10 fluorine-containing pharmaceutical intermediate.

[0058]

The embodiments of the present disclosure are described above; however, it can be understood that various changes in forms and details can be made without departing from the spirit
15 and scope of the claims.

Examples

[0059]

The present disclosure is explained in detail below
20 with reference to the following Examples; however, the present disclosure is not limited by these Examples.

[0060]

Measurement of purity of hexafluorobutadiene and impurity concentration

25 The purity was measured using the following measuring device and conditions.

[0061]

Measuring device: Gas chromatography (an FID detector is used)

Measuring conditions: Column/GS-GasPro, Column temperature/40°C

30 Calculation of purity: Quantified by a calibration curve using a hexafluorobutadiene standard gas.

[0062]

(1) Method for purifying hexafluorobutadiene in the Examples

A composition containing hexafluorobutadiene
35 (hexafluoro-1,3-butadiene) (purity of hexafluorobutadiene: 99.875

volume%) was brought into contact with a zeolite having an $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 4.0 to 8.0.

[0063]

Example 1

5 50 g of a composition containing hexafluorobutadiene was introduced into a stainless steel cylinder (100 mL) filled with 10 g of zeolite having an $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 6.1 and an average pore size of 5Å, and the cylinder was kept at -18°C for 20 hours. Gas chromatography analysis indicated that the purity
10 of hexafluorobutadiene in the composition after contact with the zeolite was 99.997 volume%. Since the concentration of the isomer of hexafluorobutadiene was below the detection limit, it was determined as 0 volume%.

[0064]

15 Example 2

 50 g of a composition containing hexafluorobutadiene was introduced into a stainless steel cylinder (100 mL) filled with 10 g of zeolite having an $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 5.5 and an average pore size of 9Å, and the cylinder was kept at -18°C for
20 20 hours. Gas chromatography analysis indicated that the purity of hexafluorobutadiene in the composition after contact with the zeolite was 99.995 volume%. Since the concentration of the isomer of hexafluorobutadiene was below the detection limit, it was determined as 0 volume%.

25 [0065]

(2) Method for purifying hexafluorobutadiene in the Comparative Examples

 The composition containing hexafluorobutadiene (purity of hexafluorobutadiene: 99.875 volume%) was brought into contact
30 with a zeolite having an $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 4.0 to 8.0.

[0066]

Comparative Example 1

 50 g of a composition containing hexafluorobutadiene was introduced into a stainless steel cylinder (100 mL) filled
35 with 10 g of zeolite having an $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 9.2 and an

average pore size of 4Å, and the cylinder was kept at -18°C for 20 hours. Gas chromatography analysis indicated that the purity of hexafluorobutadiene in the composition after contact with the zeolite was 99.151 volume%. The concentration of the isomer of
5 hexafluorobutadiene was detected as 0.724 volume%.

[0067]

Comparative Example 2

50 g of a composition containing hexafluorobutadiene was introduced into a stainless steel cylinder (100 mL) filled
10 with 10 g of zeolite having an SiO₂/Al₂O₃ ratio of 1.9 and an average pore size of 3Å, and the cylinder was kept at -18°C for 20 hours. Gas chromatography analysis indicated that the purity of hexafluorobutadiene in the composition after contact with the zeolite was 99.864 volume%. The concentration of the isomer of
15 hexafluorobutadiene was detected as 0.011 volume%.

[0068]

Comparative Example 3

50 g of a composition containing hexafluorobutadiene was introduced into a stainless steel cylinder (100 mL) filled
20 with 10 g of zeolite having an SiO₂/Al₂O₃ ratio of 2.6 and an average pore size of 3Å, and the cylinder was kept at -18°C for 20 hours. Gas chromatography analysis indicated that the purity of hexafluorobutadiene in the composition after contact with the zeolite was 99.782 volume%. The concentration of the isomer of
25 hexafluorobutadiene was detected as 0.093 volume%.

[0069]

Comparative Example 4

50 g of a composition containing hexafluorobutadiene was introduced into a stainless steel cylinder (100 mL) filled
30 with 10 g of zeolite having an SiO₂/Al₂O₃ ratio of 2.1 and an average pore size of 5Å, and the cylinder was kept at -18°C for 20 hours. Gas chromatography analysis indicated that the purity of hexafluorobutadiene in the composition after contact with the zeolite was 99.868 volume%. The concentration of the isomer of
35 hexafluorobutadiene was detected as 0.007 volume%.

[0070]

(3) Summary of method for purifying hexafluorobutadiene

Semiconductor integrated circuit devices undergo miniaturization of circuit patterns along with their acceleration
5 and high integration. Hexafluorobutadiene is an essential gas for etching the finest contact holes.

[0071]

According to the method for purifying hexafluorobutadiene of the present disclosure, by bringing the
10 composition containing hexafluorobutadiene into contact with a zeolite having an $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 4.0 to 8.0, an impurity other than the hexafluorobutadiene is adsorbed onto the zeolite to remove the impurity from the composition before the contact with the zeolite, thus adjusting the purity of
15 hexafluorobutadiene in the composition after the contact with the zeolite to 99.99 volume% or more.

[0072]

According to the method for purifying hexafluorobutadiene of the present disclosure,
20 hexafluorobutadiene can be purified to a high purity while inhibiting the isomerization of hexafluorobutadiene. Highly purified hexafluorobutadiene is advantageous for etching fine contact holes and forming fine circuit patterns in semiconductor integrated circuit devices.

25

CLAIMS

[Claim 1]

A method for purifying hexafluorobutadiene, comprising bringing a composition containing hexafluorobutadiene into
5 contact with a zeolite having an $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 4.0 to 8.0 and having an average pore size of 5 Å to 9 Å.

[Claim 2]

The purification method according to claim 1, wherein
10 an impurity other than the hexafluorobutadiene is adsorbed onto the zeolite to remove the impurity from the composition.

[Claim 3]

The purification method according to claim 1 or 2,
15 wherein the purity of the hexafluorobutadiene in the composition after the purification is 99.99 volume% or more.

[Claim 4]

The purification method according to claim 1 or 2,
20 wherein the purity of the hexafluorobutadiene in the composition after the purification is 99.995 volume% or more.

[Claim 5]

A method for producing a composition containing
25 hexafluorobutadiene, comprising bringing a composition containing hexafluorobutadiene into contact with a zeolite having an $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 4.0 to 8.0 and having an average pore size of 5 Å to 9 Å,

wherein the purity of the hexafluorobutadiene in the
30 composition after the contact with the zeolite is 99.99 volume% or more.

[Claim 6]

The production method according to claim 5, wherein an
35 impurity other than the hexafluorobutadiene is adsorbed onto the

zeolite to remove the impurity from the composition before the contact with the zeolite.

[Claim 7]

5 The production method according to claim 5 or 6,
wherein the purity of the hexafluorobutadiene in the composition
after the purification is 99.995 volume% or more.

10