

DESCRIPTION

Title of Invention: METHOD FOR PRODUCING PERFLUOROCYCLOALKENE
COMPOUND

5

Technical Field

[0001]

The present disclosure relates to a method for
producing a perfluorocycloalkene compound.

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Background Art

[0002]

Perfluorocycloalkene compounds are compounds that are
expected to be useful not only as a dry etching gas for
semiconductors, but also as a building block for organic
synthesis, and the like. Perfluorocycloalkene compounds are
cyclic compounds that have one carbon-carbon double bond.

15

[0003]

As a method for producing such a perfluorocycloalkene
compound, for example, Non-Patent Literature (NPL) 1 discloses
performing a batch reaction by heating hexafluorobutadiene at
300°C for 64 hours, to thereby obtain hexafluorocyclobutene with
a yield of 47%.

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25 Citation List

Non-patent Literature

[0004]

NPL 1: Journal of Fluorine Chemistry, 61 (1993) 57-83

30 Summary of Invention

Technical Problem

[0005]

An object of the present disclosure is to provide a
method capable of obtaining a perfluorocycloalkene compound with
a high yield and a high selectivity, at a high reaction

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conversion rate.

Solution to Problem

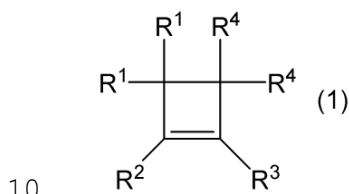
[0006]

5 This disclosure includes the following.

[0007]

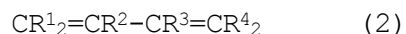
Item 1. A method for producing a perfluorocycloalkene compound represented by formula (1):

[0008]



[0009]

(wherein R¹ to R⁴ are the same or different and represent a fluorine atom or a perfluoroalkyl group),
the method comprising subjecting a perfluoroalkadiene compound to
15 a cyclization reaction in the presence of a catalyst,
the perfluoroalkadiene compound being represented by formula (2):

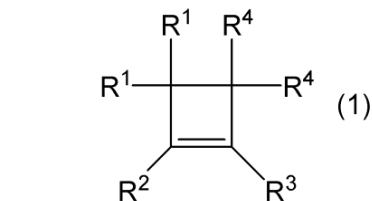


(wherein R¹ to R⁴ are the same or different and represent a fluorine atom or a perfluoroalkyl group).

20 [0010]

Item 2. A method for producing a perfluorocycloalkene compound represented by formula (1):

[0011]

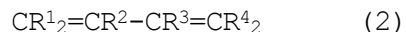


[0012]

(wherein R¹ to R⁴ are the same or different and represent a fluorine atom or a perfluoroalkyl group),
the method comprising subjecting a perfluoroalkadiene compound to

a cyclization reaction in a gas-phase continuous flow process,
and

the perfluoroalkadiene compound being represented by formula (2):

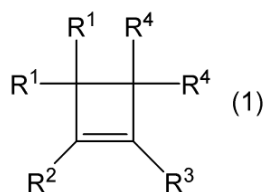


5 (wherein R^1 to R^4 are the same or different and represent a
fluorine atom or a perfluoroalkyl group).

[0013]

Item 3. A method for producing a perfluorocycloalkene compound
represented by formula (1):

10 [0014]



[0015]

(wherein R^1 to R^4 are the same or different and represent a
fluorine atom or a perfluoroalkyl group),

15 the method comprising subjecting a perfluoroalkadiene
compound to a cyclization reaction in the presence of a catalyst
in a gas-phase continuous flow process, and

the perfluoroalkadiene compound being represented by
formula (2):



(wherein R^1 to R^4 are the same or different and represent a
fluorine atom or a perfluoroalkyl group).

[0016]

Item 4. The method according to Item 1 or 3, wherein the catalyst
25 is a fluoride containing at least one metal element that belongs
to Groups 1 to 12 of the periodic table of elements.

[0017]

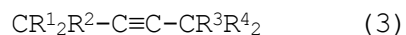
Item 5. The method according to Item 4, wherein the fluoride is a
fluoride containing at least one member selected from the group
30 consisting of alkali metals, alkaline earth metals, and metal
elements that belong to Group 4 of the periodic table.

[0018]

Item 6. The method according to any one of Items 1 to 5, wherein the cyclization reaction is performed at 270°C or more.

[0019]

Item 7. The method according to any one of Items 1 to 6, wherein
5 the cyclization reaction step produces, in addition to the perfluorocycloalkene compound represented by formula (1), a perfluoroalkyne compound represented by formula (3):



(wherein R¹ to R⁴ are as defined above).

10 [0020]

Item 8. A method for producing a perfluoroalkyne compound represented by formula (3):

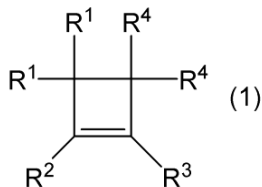


(wherein R¹ to R⁴ are the same or different and represent a
15 fluorine atom or a perfluoroalkyl group),
the method comprising obtaining the perfluoroalkadiene compound by using as a substrate the perfluorocycloalkene compound obtained by the production method of any one of Items 1 to 7.

20 [0021]

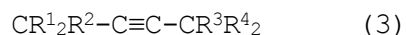
Item 9. A composition comprising a perfluorocycloalkene compound and a perfluoroalkyne compound,
the perfluorocycloalkene compound being represented by formula (1):

25 [0022]



[0023]

(wherein R¹ to R⁴ are the same or different and represent a
fluorine atom or a perfluoroalkyl group),
30 the perfluoroalkyne compound being represented by formula (3):



(wherein R¹ to R⁴ are as defined above), and

the composition containing the perfluorocycloalkene compound represented by formula (1) in an amount of 60 to 99.9 mol%, based on the total amount of the composition defined as 100 mol%.

[0024]

- 5 Item 10. The composition according to Item 9, which is for use as an etching gas or as a building block for organic synthesis.

Advantageous Effects of Invention

[0025]

- 10 According to the present disclosure, a perfluorocycloalkene compound can be obtained with a high yield and a high selectivity, at a high reaction conversion rate.

Description of Embodiments

- 15 [0026]

In the present specification, the terms "comprise," "contain," and "include" encompass the concepts of "comprising," "consisting essentially of," and "consisting of." In the present specification, a numerical range indicated by "A to B" means A or more and B or less.

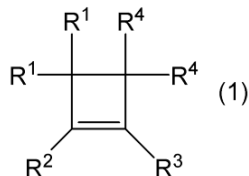
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[0027]

1. Method for Producing Perfluorocycloalkene Compound (No. 1: In the Presence of Catalyst)

The method for producing a perfluorocycloalkene compound according to the present disclosure is a method of producing a perfluorocycloalkene compound represented by formula (1):

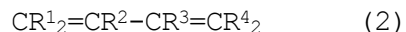
- 25 [0028]



- 30 [0029]

(wherein R¹ to R⁴ are the same or different and represent a fluorine atom or a perfluoroalkyl group),

the method comprising subjecting a perfluoroalkadiene compound to a cyclization reaction in the presence of a catalyst, and the perfluoroalkadiene compound being represented by formula (2):



5 (wherein R¹ to R⁴ are the same or different and represent a fluorine atom or a perfluoroalkyl group).

[0030]

Conventionally, as shown in Non-patent Literature (NPL) 1, even when the reaction was performed at a high temperature of 10 300°C, the yield of the perfluorocycloalkene compound was only 47%, which is not considered to be sufficient. Further, NPL 1 discloses cases where a fluorocycloalkene compound could not be produced in some heating conditions; and it was thus difficult to increase the yield. According to the present disclosure, a 15 perfluorocycloalkene compound can be obtained with a high yield and a high selectivity, at a high reaction conversion rate.

[0031]

Further, in the present disclosure, using a gas-phase continuous flow process is particularly economically 20 advantageous. As compared with a batch system in which the starting materials are charged all at once, a gas-phase continuous flow process in which the starting materials are always supplied can maintain a high reaction rate without decreasing the starting material concentrations over time, 25 thereby achieving a high yield per unit time.

[0032]

The perfluoroalkyl groups represented by R¹ to R⁴ in formulas (1) and (2) are not particularly limited. Examples include perfluoroalkyl groups having 1 to 6 carbon atoms 30 (particularly 1 to 4 carbon atoms). Specific examples include trifluoromethyl, pentafluoroethyl, and the like.

[0033]

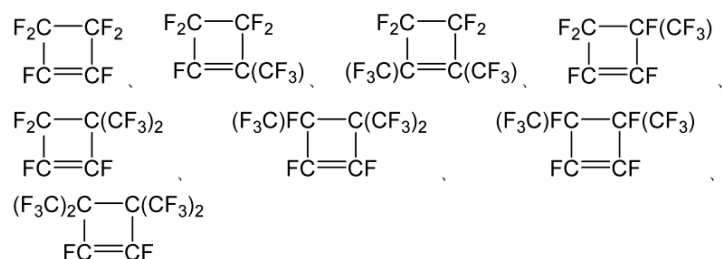
R¹ to R⁴ in formulas (1) and (2) are preferably all fluorine atoms in view of, for example, the conversion rate of 35 the reaction, and the high yield and high selectivity of the

obtained perfluorocycloalkene compound. R¹ to R⁴ may be the same or different.

[0034]

From the above, examples of the perfluorocycloalkene compound of formula (1) to be produced include

[0035]



[0036]

and the like.

10 [0037]

Examples of the perfluoroalkadiene compound of formula (2) that satisfies the above conditions include CF₂=CFCF=CF₂, CF₂=CFCF=CFCF₃, CF₃CF=CFCF=CFCF₃, CF(CF₃)=CFCF=CF₂, C(CF₃)₂=CFCF=CF₂, CF(CF₃)=CFCF=CF(CF₃), C(CF₃)₂=CFCF=CF(CF₃), C(CF₃)₂=CFCF=C(CF₃)₂, CF₂=C(CF₃)C(CF₃)=CF₂, and the like. These perfluoroalkadiene compounds represented by formula (2) can be used alone, or in a combination of two or more. Such perfluoroalkadiene compounds can be known or commercially available products. Perfluoroalkadiene compounds can also be produced in accordance with conventional methods, such as the method described in JP2001-192345A.

[0038]

In the present disclosure, the cyclization reaction catalyst is not particularly limited. In view of achieving a particularly high reaction conversion rate and obtaining a perfluorocycloalkene compound with a higher yield and higher selectivity, the catalyst is preferably a fluoride containing at least one metal element that belongs to Groups 1 to 12 of the periodic table of elements; more preferably a fluoride containing at least one member selected from the group consisting of alkali

metals, alkaline earth metals, and metal elements that belong to Group 4 of the periodic table; and even more preferably a fluoride containing at least one member selected from the group consisting of sodium, magnesium, zirconium, and the like. The
5 cyclization reaction catalyst may contain only one metal element, or two or more metal elements.
[0039]

Examples of the cyclization reaction catalyst that satisfies such conditions include NaF, MgF₂, ZrF₄, and the like.
10 Such fluorides used as cyclization reaction catalysts can be used alone, or in a combination of two or more.
[0040]

The amount of the cyclization reaction catalyst can be a catalytic amount, and is not particularly limited. In view of
15 achieving a particularly high reaction conversion rate and obtaining a perfluorocycloalkene compound with a higher yield and higher selectivity, the weight ratio (W/F) of the catalyst to the perfluoroalkadiene compound supply rate per hour is preferably 0.1 to 200 g·sec/cc, and more preferably 0.5 to 150 g·sec/cc.
20 When two or more cyclization reaction catalysts are used, the total amount of the catalysts is preferably adjusted to fall within the above range. The above W/F specifies the catalytic amount for the gas phase reaction, in particular. For the liquid phase reaction, the amount of the fluoride can also be a
25 catalytic amount, and can be appropriately adjusted.
[0041]

In the cyclization reaction step of the production method according to the present disclosure, in addition to the perfluoroalkadiene compound of formula (2) as a substrate and the
30 cyclization reaction catalyst, metal nickel (in particular, metal nickel beads), activated carbon, or the like can also be used for reducing heat transfer and the catalyst concentration in an amount to achieve a W/F of 0.1 to 200 g·sec/cc, and particularly 0.5 to 150 g·sec/cc. The above W/F specifies the amount of metal
35 nickel, activated carbon, or the like to be used for the gas

phase reaction, in particular. For the liquid phase reaction, the amount of metal nickel, activated carbon, or the like can also be appropriately adjusted.

[0042]

5 The production method according to the present disclosure can be performed in a liquid phase; however, the production process is preferably performed in a gas phase, and particularly preferably in a gas-phase continuous flow process using a fixed-bed reactor. Performing the production method in a
10 gas-phase continuous flow process can simplify equipment, operations, etc., and is also economically advantageous.

[0043]

 In the production method according to the present disclosure, the cyclization reaction step is preferably performed
15 with heating. More specifically, heating is preferably performed after the perfluoroalkadiene compound of formula (2), which is a substrate, is brought into contact with a cyclization reaction catalyst in the reaction system. The heating temperature in this process is preferably 270°C or more, and more preferably 320 to
20 800°C, in view of achieving a particularly high reaction conversion rate, and obtaining the perfluorocycloalkene compound with a higher yield and a higher selectivity.

[0044]

 In the production method according to the present
25 disclosure, the atmosphere in the cyclization reaction step is not particularly limited. For example, the reaction atmosphere is preferably an inert gas atmosphere (nitrogen gas atmosphere, argon gas atmosphere, etc.), and the reaction time (time of maintaining the maximum temperature) can be a period of time that
30 allows the reaction to sufficiently proceed.

[0045]

 The production method according to the present disclosure can produce, in addition to the perfluorocycloalkene compound represented by formula (1), a perfluoroalkyne compound
35 represented by formula (3):



(wherein R^1 to R^4 are as defined above). The details of the perfluoroalkyne compound represented by formula (3) are described later.

5 [0046]

Therefore, after completion of the reaction, a purification treatment is performed, if necessary, and the perfluorocycloalkene compound represented by formula (1) can be obtained.

10 [0047]

Further, the perfluorocycloalkene compound of formula (1) produced by the production method of the present disclosure can be purified in accordance with a conventional method, if necessary, and then used as a substrate to obtain a perfluoroalkyne compound represented by formula (3). The method, conditions, and the like in this process can be the same as those described in JP2014-058488A. Specific preferable examples can also be the same as those described in JP2014-058488A.

[0048]

20 Specifically, isomerization is performed using an isomerization catalyst and the perfluorocycloalkene compound of formula (1) as a substrate to thereby obtain a perfluoroalkyne compound represented by formula (3). This step can be performed in a gas phase, in particular, in a gas-phase continuous flow process using a fixed-bed reactor. It is also possible to perform this step by a batch reaction.

[0049]

The isomerization reaction catalyst is preferably sodium fluoride that is easy to handle in the atmosphere due to its low hygroscopicity, has high activity, and provides high selectivity. When sodium fluoride itself is used as a catalyst, it may be in powder form. Sodium fluoride in pellet form is preferable for the gas-phase continuous flow reaction. It is also possible to use sodium fluoride supported on a carrier, such as alumina, porous aluminum fluoride, activated carbon, silica, or

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zeolite. Sodium fluoride can also be mixed with other components, and then used.

[0050]

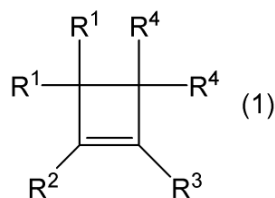
The isomerization reaction temperature is typically preferably 200 to 800°C, and more preferably 400 to 600°C.

[0051]

Method for Producing Perfluorocycloalkene Compound (No. 2: Gas-Phase Continuous Flow Process)

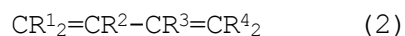
In the production method of the present disclosure, a perfluorocycloalkene compound can also be produced by a method of producing a perfluorocycloalkene compound represented by formula (1):

[0052]



15 [0053]

(wherein R¹ to R⁴ are the same or different and represent a fluorine atom or a perfluoroalkyl group), the method comprising subjecting a perfluoroalkadiene compound to a cyclization reaction in a gas-phase continuous flow process, the perfluoroalkadiene compound being represented by formula (2):



(wherein R¹ to R⁴ are the same or different and represent a fluorine atom or a perfluoroalkyl group). This method can also produce a perfluorocycloalkene compound with a high yield and a high selectivity.

[0054]

The perfluorocycloalkene compound represented by formula (1) and the perfluoroalkadiene compound represented by formula (2) can be the same as those described above in section "1. Method for Producing Perfluorocycloalkene Compound (No. 1: In the Presence of Catalyst)." Specific preferable examples can also

be the same.

[0055]

In the present disclosure, a cyclization reaction catalyst is preferably used. In view of achieving a particularly high reaction conversion rate and obtaining a perfluorocycloalkene compound with a higher yield and a higher selectivity, the catalyst is preferably a fluoride containing at least one metal element that belongs to Groups 1 to 12 of the periodic table of elements; more preferably a fluoride containing at least one member selected from the group consisting of alkali metals, alkaline earth metals, and metal elements that belong to Group 4 of the periodic table; and even more preferably a fluoride containing at least one member selected from the group consisting of sodium, magnesium, zirconium, and the like. The catalyst for the cyclization reaction may contain only one metal element or two or more metal elements, such as those mentioned above. Such cyclization reaction catalysts can be the same as those described above in section "1. Method for Producing Perfluorocycloalkene Compound (No. 1: In the Presence of Catalyst)." Preferable examples and the contents thereof can also be the same. When such a catalyst is used, the amount of the catalyst can be a catalytic amount, and is not particularly limited. In view of achieving a particularly high reaction conversion rate and obtaining a perfluorocycloalkene compound with a higher yield and a higher selectivity, the weight ratio (W/F) of the catalyst to the perfluoroalkadiene compound supply rate per hour is preferably 0.1 to 200 g·sec/cc, and more preferably 0.5 to 150 g·sec/cc. When two or more cyclization reaction catalysts are used, the total amount of the catalysts is preferably adjusted to fall within the above range.

[0056]

In the cyclization reaction step of the production method according to the present disclosure, in addition to the perfluoroalkadiene compound of formula (2) as a substrate and the cyclization reaction catalyst, metal nickel (in particular, metal

nickel beads), activated carbon, or the like can also be used for reducing heat transfer and the catalyst concentration in an amount to achieve a W/F of 0.1 to 200 g·sec/cc, and particularly 0.5 to 150 g·sec/cc.

5 [0057]

The production method according to the present disclosure is performed in a gas-phase continuous flow process using a fixed-bed reactor. Performing the production method in a gas-phase continuous flow process can simplify equipment,
10 operations, etc.; and is also economically advantageous.
[0058]

In the production method according to the present disclosure, the cyclization reaction step is preferably performed with heating. More specifically, heating is preferably performed
15 after the perfluoroalkadiene compound of formula (2), which is a substrate, is optionally brought into contact with a cyclization reaction catalyst in the reaction system. The heating temperature is preferably 270°C or more, and more preferably 320 to 800°C, in view of achieving a particularly high reaction conversion rate
20 and obtaining the perfluorocycloalkene compound with a higher yield and a higher selectivity. When no catalyst is used, the heating temperature is particularly preferably 280 to 800°C. When a catalyst is used, the heating temperature is particularly preferably 320 to 800°C.

25 [0059]

In the production method of the present disclosure, the atmosphere in the cyclization reaction step is not particularly limited. For example, the reaction atmosphere is preferably an inert gas atmosphere (nitrogen gas atmosphere, argon gas
30 atmosphere, etc.), and the reaction time (time of maintaining the maximum temperature) can be a period of time that allows the reaction to sufficiently proceed.

[0060]

The production method according to the present
35 disclosure can produce, in addition to the perfluorocycloalkene

compound represented by formula (1), a perfluoroalkyne compound represented by formula (3):



(wherein R^1 to R^4 are as defined above). The details of the

5 perfluoroalkyne compound represented by formula (3) are described later.

[0061]

Therefore, after completion of the reaction, a purification treatment is performed, if necessary, and a
10 perfluorocycloalkene compound represented by formula (1) can be obtained.

[0062]

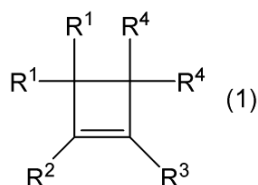
Further, the perfluorocycloalkene compound of formula (1) produced by the production method of the present disclosure
15 can be purified in accordance with a conventional method, if necessary, and then used as a substrate to obtain a perfluoroalkyne compound represented by formula (3). The method, conditions, etc. in this process can be the same as those described above.

20 [0063]

3. Method for Producing Perfluorocycloalkene Compound (No. 3: Gas-Phase Continuous Flow Process in the Presence of Catalyst)

In the production method according to the present disclosure, a perfluorocycloalkene compound can also be produced
25 by a method for producing a perfluorocycloalkene compound represented by formula (1):

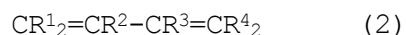
[0064]



[0065]

30 (wherein R^1 to R^4 are the same or different and represent a fluorine atom or a perfluoroalkyl group),
the method comprising subjecting a perfluoroalkadiene compound to

a cyclization reaction in a gas-phase continuous flow process, the perfluoroalkadiene compound being represented by formula (2):



(wherein R¹ to R⁴ are the same or different and represent a fluorine atom or a perfluoroalkyl group). This method can also achieve a high reaction conversion rate, and produce a perfluorocycloalkene compound with a high yield and a high selectivity.

[0066]

The perfluorocycloalkene compound represented by formula (1), the perfluoroalkadiene compound represented by formula (2), and the catalyst can be the same as those described above in section "1. Method for Producing Perfluorocycloalkene Compound (No. 1: In the Presence of Catalyst)." Preferred examples thereof can also be the same.

[0067]

In the cyclization reaction step of the production method according to the present disclosure, in addition to the perfluoroalkadiene compound of formula (2) as a substrate and the cyclization reaction catalyst, metal nickel (in particular, metal nickel beads), activated carbon, or the like can also be used for reducing heat transfer and the catalyst concentration to achieve a W/F of 0.1 to 200 g·sec/cc, and particularly 0.5 to 150 g·sec/cc.

[0068]

The production method according to the present disclosure is performed in a gas-phase continuous flow process using a fixed-bed reactor. Using a gas-phase continuous flow process can simplify equipment, operations, etc.; and is also economically advantageous.

[0069]

In the production method according to the present disclosure, the cyclization reaction step is preferably performed with heating. More specifically, heating is preferably performed after the perfluoroalkadiene compound of formula (2), which is a

substrate, is brought into contact with a cyclization reaction catalyst. The heating temperature is preferably 270°C or more, and more preferably 320 to 800°C, in view of achieving a particularly high reaction conversion rate, and obtaining the
5 perfluorocycloalkene compound with a higher yield and a higher selectivity.

[0070]

In the production method of the present disclosure, the atmosphere in the cyclization reaction step is not particularly
10 limited. For example, the reaction atmosphere is preferably an inert gas atmosphere (nitrogen gas atmosphere, argon gas atmosphere, etc.), and the reaction time (time of maintaining the maximum temperature) can be a period of time that allows the reaction to sufficiently proceed.

15 [0071]

The production method according to the disclosure can produce not only the perfluorocycloalkene compound represented by formula (1), but also a perfluoroalkyne compound represented by formula (3):

20 $CR^1_2R^2-C\equiv C-CR^3R^4_2$ (3)

(wherein R^1 to R^4 are as defined above). The details of the perfluoroalkyne compound represented by formula (3) are described later.

[0072]

25 Therefore, after completion of the reaction, a purification treatment is performed in accordance with a conventional method, if necessary, and a perfluorocycloalkene compound represented by formula (1) can be obtained.

[0073]

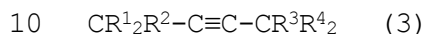
30 Further, the perfluorocycloalkene compound of formula (1) produced by the production method of the present disclosure can be purified in accordance with a conventional method, if necessary, and then used as a substrate to thereby obtain a perfluoroalkyne compound represented by formula (3). The method,
35 conditions, etc. in this process can be the same as those

described above.

[0074]

4. Perfluorocycloalkene Composition

The perfluorocycloalkene compounds represented by
5 formula (1) can be obtained as described above. However, the
compounds can also be obtained in the form of a
perfluorocycloalkene composition comprising a perfluoroalkadiene
compound represented by formula (1), and a perfluoroalkyne
compound represented by formula (3):



wherein R^1 to R^4 are as defined above.

In the perfluorocycloalkene composition of the present
disclosure, the perfluorocycloalkene compounds represented by
formula (1) can be used alone, or in a combination of two or
15 more.

[0075]

Examples of the perfluoroalkyne compound represented by
formula (3) include $CF_3C\equiv CCF_3$, $CF_3C\equiv CCF_2CF_3$, $CF_3C\equiv CCF(CF_3)_2$,
 $CF_3C\equiv CC(CF_3)_3$, $CF_3CF_2C\equiv CCF_2CF_3$, $CF_3CF_2C\equiv CCF(CF_3)_2$, $CF_3CF_2C\equiv CC(CF_3)_3$,
20 $(CF_3)_2CFC\equiv CCF(CF_3)_2$, $(CF_3)_2CFC\equiv CC(CF_3)_3$, and $(CF_3)_3CC\equiv CC(CF_3)_3$. The
perfluoroalkyne compounds represented by formula (3) can be used
alone, or in a combination of two or more.

[0076]

In the perfluorocycloalkene composition of the present
25 disclosure, the content of the perfluorocycloalkene compound
represented by formula (1) is preferably 60 to 99.9 mol%, more
preferably 70 to 99.8 mol%, and even more preferably 80 to 99.7
mol%, based on the total amount of the perfluorocycloalkene
composition of the present disclosure defined as 100 mol%.

30 Likewise, the content of the perfluoroalkyne compound represented
by formula (3) is preferably 0.1 to 40 mol%, more preferably 0.2
to 30 mol%, and even more preferably 0.3 to 20 mol%, based on the
total amount of the perfluorocycloalkene composition of the
present disclosure defined as 100 mol%.

35 [0077]

In addition to the perfluorocycloalkene compounds represented by formula (1) and the perfluoroalkyne compounds represented by formula (3), the production method according to the present disclosure can also produce, for example, a
5 perfluoroalkene compound represented by formula (4A):
$$\text{CR}^1_2=\text{CR}^2-\text{CFR}^3-\text{CFR}^4_2 \quad (4A),$$

wherein R^1 to R^4 are as defined above, and a fluoroalkene compound represented by formula (4B):
$$\text{CFR}^1_2-\text{CR}^2=\text{CH}-\text{CFR}^4_2 \quad (4B),$$

10 wherein R^1 to R^4 are as defined above.
[0078]

Therefore, the perfluorocycloalkene composition of the present disclosure can comprise a perfluoroalkene compound represented by formula (4A) and a fluoroalkene compound
15 represented by formula (4B). When a perfluoroalkene compound represented by formula (4A) is contained in the perfluorocycloalkene composition of the present disclosure, the content is preferably 0.05 mol% or less, and more preferably 0.03 mol% or less, based on the total amount of the
20 perfluorocycloalkene composition defined as 100 mol%, from the viewpoint of etchant performance. Further, in terms of production costs, the content is preferably 0.0001 mol% or more, and more preferably 0.0002 mol% or more. When a fluoroalkene compound represented by formula (4B) is contained in the
25 perfluorocycloalkene composition of the present disclosure, the content is preferably 0.3 mol% or less, and more preferably 0.2 mol% or less, based on the total amount of the perfluorocycloalkene composition defined as 100 mol%, from the viewpoint of etchant performance. Further, in terms of production
30 costs, the content is preferably 0.001 mol% or more, and more preferably 0.002 mol% or more.
[0079]

In the production method according to the present disclosure, the perfluorocycloalkene compound represented by
35 formula (1) can be obtained, in particular, with a high yield and

a high selectivity as described above, even when it is obtained as a perfluorocycloalkene composition. Therefore, the components other than the perfluorocycloalkene compound represented by formula (1) in the perfluorocycloalkene composition can be reduced, and the labor required for purification to obtain the perfluorocycloalkene compound represented by formula (1) can thus be reduced.

[0080]

As in the case of the perfluorocycloalkene compound described above alone, the perfluorocycloalkene composition of the present disclosure can also be effectively used for various applications, such as an etching gas used for forming state-of-the-art microstructures (e.g., semiconductors and liquid crystals), and a building block for organic synthesis. The term "building block for organic synthesis" means a substance that can serve as a precursor for a compound having a highly reactive skeleton. For example, the perfluorocycloalkene composition of the present disclosure can be converted into a substance that can serve as a detergent or a fluorine-containing medicinal intermediate by reacting with a fluorine-containing organosilicon compound, such as $\text{CF}_3\text{Si}(\text{CH}_3)_3$, and introducing fluoroalkyl, such as a CF_3 group.

[0081]

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

Examples

[0082]

The features of the present disclosure are clarified below with reference to Examples. However, the present disclosure is not limited to the Examples.

[0083]

Example 1: NaF Catalyst; W/F = 30 g·sec/cc; 350°C

Sodium fluoride (NaF) was filled in a metal tubular reactor as a catalyst. The reaction tube was heated to 350°C, and hexafluorobutadiene ($\text{CF}_2\text{CF}=\text{CFCF}_2$) was fed to the reaction tube to achieve a W/F of 30 g·sec/cc to allow a reaction to proceed in a gas-phase continuous flow process. About one hour later, the gas flowing out of the reaction tube was analyzed by gas chromatography, which revealed that the conversion rate was 99.2 mol%, and the selectivity of each component was as follows: 98.1 mol% for 1,2,3,3,4,4-hexafluoro-1-cyclobutene ($\text{c-C}_4\text{F}_6$), 1.60 mol% for 1,1,1,4,4,4-hexafluoro-2-butyne ($\text{CF}_3\text{C}\equiv\text{CCF}_3$), 0.00272 mol% for 1,1,2,3,3,4,4,4-octafluoro-1-butene ($\text{CF}_2=\text{CFCF}_2\text{CF}_3$) (the total amount of the E-isomer and Z-isomer), 0.0492 mol% for 1,1,1,2,4,4,4-heptafluoro-2-butene ($\text{CF}_3\text{CF}=\text{CHCF}_3$) (the total amount of the E-isomer and Z-isomer), and 0.245 mol% for the total of other by-products.

[0084]

Example 2: NaF Catalyst; W/F = 30 g·sec/cc; 400°C

The reaction proceeded in the same manner as in Example 1, except that the heating temperature was 400°C. About one hour later, the gas flowing out of the reaction tube was analyzed by gas chromatography, which revealed that the conversion rate was 99.3 mol%, and the selectivity of each component was as follows: 98.3 mol% for 1,2,3,3,4,4-hexafluoro-1-cyclobutene ($\text{c-C}_4\text{F}_6$), 0.696 mol% for 1,1,1,4,4,4-hexafluoro-2-butyne ($\text{CF}_3\text{C}\equiv\text{CCF}_3$), 0.00215 mol% for 1,1,2,3,3,4,4,4-octafluoro-1-butene ($\text{CF}_2=\text{CFCF}_2\text{CF}_3$) (the total amount of the E-isomer and Z-isomer), 0.0410 mol% for 1,1,1,2,4,4,4-heptafluoro-2-butene ($\text{CF}_3\text{CF}=\text{CHCF}_3$) (the total amount of the E-isomer and Z-isomer), and 0.956 mol% for the total of other by-products.

[0085]

Example 3: NaF Catalyst; W/F = 90 g·sec/cc; 400°C

The reaction proceeded in the same manner as in Example 1, except that the W/F was 90 g·sec/cc, and the heating temperature was 400°C. About one hour later, the gas flowing out of the reaction tube was analyzed by gas chromatography, which

revealed that the conversion rate was 98.9 mol%, and the selectivity of each component was as follows: 98.3 mol% for 1,2,3,3,4,4-hexafluoro-1-cyclobutene ($c\text{-C}_4\text{F}_6$), 0.941 mol% for 1,1,1,4,4,4-hexafluoro-2-butyne ($\text{CF}_3\text{C}\equiv\text{CCF}_3$), 0.0238 mol% for 1,1,2,3,3,4,4,4-octafluoro-1-butene ($\text{CF}_2=\text{CFCF}_2\text{CF}_3$) (the total amount of the E-isomer and Z-isomer), 0.0391 mol% for 1,1,1,2,4,4,4-heptafluoro-2-butene ($\text{CF}_3\text{CF}=\text{CHCF}_3$) (the total amount of the E-isomer and Z-isomer), and 0.695 mol% for the total of other by-products.

10 [0086]

Example 4: MgF_2 Catalyst; W/F = 30 g·sec/cc; 350°C

The reaction proceeded in the same manner as in Example 1, except that MgF_2 was used as the catalyst. About one hour later, the gas flowing out of the reaction tube was analyzed by gas chromatography, which revealed that the conversion rate was 99.7 mol%, and the selectivity of each component was as follows: 98.3 mol% for 1,2,3,3,4,4-hexafluoro-1-cyclobutene ($c\text{-C}_4\text{F}_6$), 1.21 mol% for 1,1,1,4,4,4-hexafluoro-2-butyne ($\text{CF}_3\text{C}\equiv\text{CCF}_3$), 0.00220 mol% for 1,1,2,3,3,4,4,4-octafluoro-1-butene ($\text{CF}_2=\text{CFCF}_2\text{CF}_3$) (the total amount of the E-isomer and Z-isomer), 0.0440 mol% for 1,1,1,2,4,4,4-heptafluoro-2-butene ($\text{CF}_3\text{CF}=\text{CHCF}_3$) (the total amount of the E-isomer and Z-isomer), and 0.414 mol% for the total of other by-products.

[0087]

25 Example 5: MgF_2 Catalyst; W/F = 30 g·sec/cc; 400°C

The reaction proceeded in the same manner as in Example 1, except that MgF_2 was used as the catalyst, and the heating temperature was 400°C. About one hour later, the gas flowing out of the reaction tube was analyzed by gas chromatography, which revealed that the conversion rate was 99.8 mol%, and the selectivity of each component was as follows: 99.0 mol% for 1,2,3,3,4,4-hexafluoro-1-cyclobutene ($c\text{-C}_4\text{F}_6$), 0.340 mol% for 1,1,1,4,4,4-hexafluoro-2-butyne ($\text{CF}_3\text{C}\equiv\text{CCF}_3$), 0.00190 mol% for 1,1,2,3,3,4,4,4-octafluoro-1-butene ($\text{CF}_2=\text{CFCF}_2\text{CF}_3$) (the total amount of the E-isomer and Z-isomer), 0.00440 mol% for

1,1,1,2,4,4,4-heptafluoro-2-butene ($\text{CF}_3\text{CF}=\text{CHCF}_3$) (the total amount of the E-isomer and Z-isomer), and 0.654 mol% for the total of other by-products.

[0088]

5 Example 6: ZrF_4 Catalyst; W/F = 15 g·sec/cc; 350°C

The reaction proceeded in the same manner as in Example 1, except that ZrF_4 was used as the catalyst, and W/F was 15 g·sec/cc. About one hour later, the gas flowing out of the reaction tube was analyzed by gas chromatography, which revealed
10 that the conversion rate was 99.1 mol%, and the selectivity of each component was as follows: 95.3 mol% for 1,2,3,3,4,4-hexafluoro-1-cyclobutene (C_4F_6), 3.71 mol% for 1,1,1,4,4,4-hexafluoro-2-butyne ($\text{CF}_3\text{C}\equiv\text{CCF}_3$), 0.0163 mol% for 1,1,2,3,3,4,4,4-octafluoro-1-butene ($\text{CF}_2=\text{CFCF}_2\text{CF}_3$) (the total amount of the E-isomer and Z-isomer),
15 0.0851 mol% for 1,1,1,2,4,4,4-heptafluoro-2-butene ($\text{CF}_3\text{CF}=\text{CHCF}_3$) (the total amount of the E-isomer and Z-isomer), and 0.923 mol% for the total of other by-products.

[0089]

Example 7: ZrF_4 Catalyst; W/F = 30 g·sec/cc; 350°C

20 The reaction proceeded in the same manner as in Example 1, except that ZrF_4 was used as the catalyst. About one hour later, the gas flowing out of the reaction tube was analyzed by gas chromatography, which revealed that the conversion rate was 99.5 mol%, and the selectivity of each component was as follows:
25 96.3 mol% for 1,2,3,3,4,4-hexafluoro-1-cyclobutene (C_4F_6), 2.68 mol% for 1,1,1,4,4,4-hexafluoro-2-butyne ($\text{CF}_3\text{C}\equiv\text{CCF}_3$), 0.0127 mol% for 1,1,2,3,3,4,4,4-octafluoro-1-butene ($\text{CF}_2=\text{CFCF}_2\text{CF}_3$) (the total amount of the E-isomer and Z-isomer), 0.118 mol% for
1,1,1,2,4,4,4-heptafluoro-2-butene ($\text{CF}_3\text{CF}=\text{CHCF}_3$) (the total amount
30 of the E-isomer and Z-isomer), and 0.916 mol% for the total of other by-products.

[0090]

Example 8: No catalyst; W/F = 30 g·sec/cc; 300°C

35 The reaction proceeded in the same manner as in Example 1, except that no catalyst was used, and the heating temperature

was 300°C. About one hour later, the gas flowing out of the reaction tube was analyzed by gas chromatography, which revealed that the conversion rate was 97.9 mol%, and the selectivity of each component was as follows: 77.8 mol% for 1,2,3,3,4,4-
5 hexafluoro-1-cyclobutene (c-C₄F₆) and 22.2 mol% for the total of other by-products.

[0091]

Example 9: No catalyst; W/F = 30 g·sec/cc; 400°C

The reaction proceeded in the same manner as in Example
10 1, except that no catalyst was used, and the heating temperature was 400°C. About one hour later, the gas flowing out of the reaction tube was analyzed by gas chromatography, which revealed that the conversion rate was 98.1 mol%, and the selectivity of each component was as follows: 67.4 mol% for 1,2,3,3,4,4-
15 hexafluoro-1-cyclobutene (c-C₄F₆) and 32.6 mol% for the total of other by-products.

[0092]

Table 1 shows the results.

[0093]

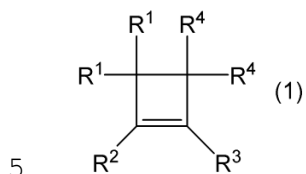
Table 1

[illegible]

CLAIMS

[Claim 1]

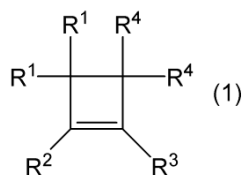
A method for producing a perfluorocycloalkene compound represented by formula (1):



wherein R^1 to R^4 are the same or different and represent a fluorine atom or a perfluoroalkyl group,
the method comprising subjecting a perfluoroalkadiene compound to a cyclization reaction in the presence of a catalyst,
10 the perfluoroalkadiene compound being represented by formula (2):
 $CR^1_2=CR^2-CR^3=CR^4_2$ (2)
wherein R^1 to R^4 are the same or different and represent a fluorine atom or a perfluoroalkyl group.

15 [Claim 2]

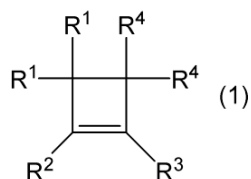
A method for producing a perfluorocycloalkene compound represented by formula (1):



wherein R^1 to R^4 are the same or different and represent a
20 fluorine atom or a perfluoroalkyl group,
the method comprising subjecting a perfluoroalkadiene compound to a cyclization reaction in a gas-phase continuous flow process,
the perfluoroalkadiene compound being represented by formula (2):
25 $CR^1_2=CR^2-CR^3=CR^4_2$ (2)
wherein R^1 to R^4 are the same or different and represent a fluorine atom or a perfluoroalkyl group.

[Claim 3]

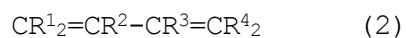
A method for producing a perfluorocycloalkene compound represented by formula (1):



wherein R¹ to R⁴ are the same or different and represent a
5 fluorine atom or a perfluoroalkyl group,

the method comprising subjecting a perfluoroalkadiene compound to a cyclization reaction in the presence of a catalyst in a gas-phase continuous flow process,

the perfluoroalkadiene compound being represented by
10 formula (2):



wherein R¹ to R⁴ are the same or different and represent a fluorine atom or a perfluoroalkyl group.

15 [Claim 4]

The method according to claim 1 or 3, wherein the catalyst is a fluoride containing at least one metal element that belongs to Groups 1 to 12 of the periodic table of elements.

20 [Claim 5]

The method according to claim 4, wherein the fluoride is a fluoride containing at least one member selected from the group consisting of alkali metals, alkaline earth metals, and metal elements that belong to Group 4 of the periodic table.

25

[Claim 6]

The method according to any one of claims 1 to 5, wherein the cyclization reaction is performed at 270°C or more.

30 [Claim 7]

The method according to any one of claims 1 to 6, wherein the cyclization reaction step produces, in addition to

the perfluorocycloalkene compound represented by formula (1), a perfluoroalkyne compound represented by formula (3):



wherein R^1 to R^4 are as defined above.

5

[Claim 8]

A method for producing a perfluoroalkyne compound represented by formula (3):



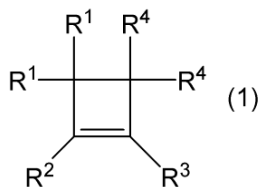
10 wherein R^1 to R^4 are the same or different and represent a fluorine atom or a perfluoroalkyl group,

the method comprising obtaining the perfluoroalkadiene compound by using as a substrate the perfluorocycloalkene compound obtained by the production method of any one of claims 1
15 to 7.

[Claim 9]

A composition comprising a perfluorocycloalkene compound and a perfluoroalkyne compound,

20 the perfluorocycloalkene compound being represented by formula (1):



wherein R^1 to R^4 are the same or different and represent a fluorine atom or a perfluoroalkyl group,

25 the perfluoroalkyne compound being represented by formula (3):



wherein R^1 to R^4 are as defined above, and

the composition containing the perfluorocycloalkene compound represented by formula (1) in an amount of 60 to 99.9 mol%, based on the total amount of the composition defined as 100 mol%.

30

[Claim 10]

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