DESCRIPTION

Title of Invention: METHOD FOR PRODUCING CYCLOBUTANE

Technical Field

[0001]

The present disclosure relates to a method for producing cyclobutane.

Background Art

[0002]

Cyclobutanes that contain halogen atoms are useful compounds, for example, in various refrigerants, foaming agents, and heat transfer mediums, as well as dry etching gas for semiconductors.

[0003]

NPL 1 discloses a method for producing 1H-heptafluorocyclobutane from 3,3,4,4,-tetrafluorocyclobutene by performing a fluorination reaction by using a fluorinating agent such as CoF_3 , MnF_3 , AgF_2 , CeF_4, or $KCoF_4$.

[0004]

NPL 2 discloses a method for producing 1Br,2H-hexafluorocyclobutane (cC_4F_6BrH) from hexafluorocyclobutene (cC_4F_6) by performing an addition reaction by using hydrogen bromide (HBr).

Citation List

Non-patent Literature

[0005]

NPL 1: Journal of Fluorine Chemistry, 2006, Vol. 127, 79-84, Fluorination of fluoro-cyclobutene with high-valency metal fluoride

NPL 2: Journal of American Chemistry, 1949, Vol. 71, 2339-2340, The Addition of Hydrogen Bromide to Fluorinated Olefins

Summary

Technical Problem

[0006]

An object of the present disclosure is to produce a halogen atom-containing cyclobutane at a high selectivity.

Solution to Problem

[0007]

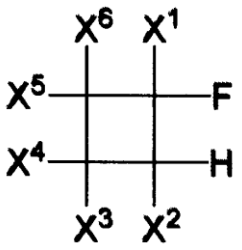
The present disclosure includes the following subject matter.

[0008]

Item 1.

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

[0009]



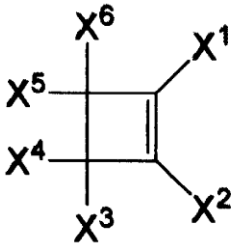
(1)

[0010]

wherein X^1, X^2, X^3, X^4, X^5, and X^6 are the same or different and represent a hydrogen atom, a halogen atom, or a perfluoroalkyl group,

the method comprising reacting a cyclobutene represented by formula (2):

[0011]



(2)

[0012]

wherein X^1, X^2, X^3, X^4, X^5, and X^6 are as defined above with hydrogen fluoride in the presence of a catalyst in a gas phase.

[0013]

Item 2.

The method according to Item 1, wherein 0.1 mol to 100 mol of the hydrogen fluoride is supplied per mol of the cyclobutene represented by formula (2) to perform the reaction.

[0014]

Item 3.

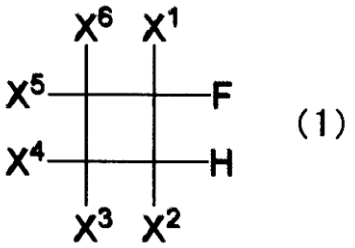
The method according to Item 1 or 2, wherein the catalyst is at least one member selected from the group consisting of activated carbon and chromium compounds.

[0015]

Item 4.

A composition comprising a cyclobutane represented by formula (1):

[0016]



(1)

[0017]

wherein X^1, X^2, X^3, X^4, X^5, and X^6 are the same or different and represent a hydrogen atom, a halogen atom, or a perfluoroalkyl group, wherein the cyclobutane represented by formula (1) is present in an amount of 99 mol% or more based on the total amount of the composition taken as 100 mol%.

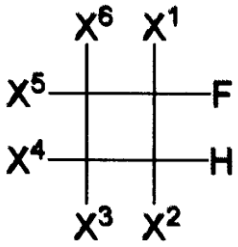
[0018]

Item 5.

The composition according to Item 4, which is for use in cleaning gas, etching gas, deposit gas, or a building block for organic synthesis.

[0018a]

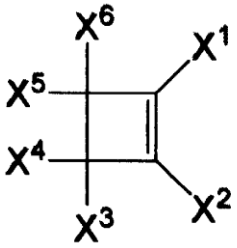
In one aspect, there is provided a method for producing a cyclobutane represented by formula (1):



(1)

wherein X^1, X^2, X^3, X^4, X^5, and X^6 are the same or different and represent a hydrogen atom, a halogen atom, or a perfluoroalkyl group,

the method comprising reacting a cyclobutene represented by formula (2):



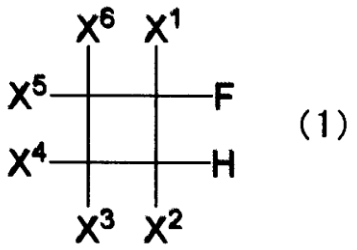
(2)

wherein X^1, X^2, X^3, X^4, X^5, and X^6 are as defined above with hydrogen fluoride in the presence of a catalyst in a gas phase,

wherein the reaction is an addition reaction of hydrogen fluoride.

[0018b]

In another aspect, there is provided a composition comprising a cyclobutane represented by formula (1):



(1)

wherein X^1, X^2, X^3, X^4, X^5, and X^6 are the same or different and represent a fluorine atom or a perfluoroalkyl group,

wherein the cyclobutane represented by formula (1) is present in an amount of 99 mol% or more based on the total amount of the composition taken as 100 mol%, and

wherein the composition is for use in cleaning gas or etching gas.

Advantageous Effects of Invention

[0019]

The present disclosure enables the production of a halogen atom-containing cyclobutane at a high selectivity.

Description of Embodiments

[0020]

The present inventors conducted extensive research and found that a fluorine atom-containing cyclobutane represented by formula (1) can be produced at a high selectivity by performing an addition reaction with hydrogen fluoride on a starting material compound in the presence of a catalyst in a gas phase.

[0021]

The inventors conducted further research on the basis of the finding and completed the present disclosure.

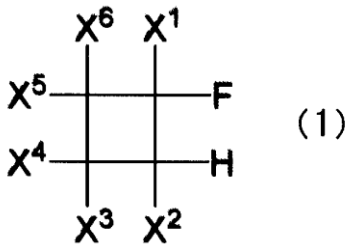
[0022]

The present disclosure includes the following embodiment.

[0023]

The method according to the present disclosure for producing a cyclobutane represented by formula (1):

[0024]

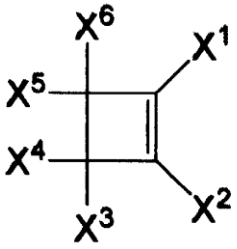


(1)

[0025]

wherein X^1, X^2, X^3, X^4, X^5, and X^6 are the same or different and represent a hydrogen atom, a halogen atom, or a perfluoroalkyl group comprises reacting a cyclobutene represented by formula (2):

[0026]



(2)

[0027]

wherein X^1, X^2, X^3, X^4, X^5, and X^6 are as defined above with hydrogen fluoride.

[0028]

In the present disclosure, the reaction is an addition reaction with hydrogen fluoride, and the reaction step is performed in the presence of a catalyst in a gas phase.

[0029]

In the present disclosure, a fluorine atom-containing cyclobutane can be produced at a high selectivity by satisfying the requirements above.

[0030]

In the present disclosure, "selectivity" refers to the percentage (mol%) of the total molar quantity of the target compound (a fluorine atom-containing cyclobutane) present in a gas outflowing from a reactor outlet relative to the total molar quantity of the compounds other than the starting material compounds (e.g., a fluorine atom-containing cyclobutane) in the gas outflowing from the reactor outlet.

[0031]

In the present disclosure, "conversion rate" refers to the percentage (mol%) of the total molar quantity of the compounds other than the starting material compounds (e.g., a fluorine atom-containing cyclobutane) present in a gas outflowing from a reactor outlet relative to the molar quantity of the starting material compound (cyclobutene) supplied to a reactor.

[0032]

The method for producing a cyclobutane according to the present disclosure is suitable for production on an industrial scale. The method for producing a cyclobutane according to the

present disclosure uses cyclobutene and hydrogen fluoride as starting materials, which are available on an industrial scale. The method for producing a cyclobutane according to the present disclosure can achieve a high selectivity when the target compound is 1H-heptafluorocyclobutane.

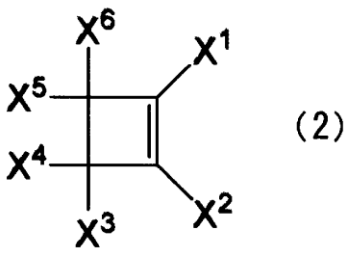
[0033]

(1) Starting Material Compound

Cyclobutene Represented by Formula (2)

In the present disclosure, the starting material compounds are hydrogen fluoride and cyclobutene represented by formula (2):

[0034]



(2)

[0035]

wherein X^1, X^2, X^3, X^4, X^5, and X^6 are the same or different and represent a hydrogen atom, a halogen atom, or a perfluoroalkyl group.

[0036]

X^1, X^2, X^3, X^4, X^5, and X^6 are the same or different and represent a hydrogen atom, a halogen atom, or a perfluoroalkyl group.

[0037]

The halogen atom represented by X^1, X^2, X^3, X^4, X^5, and X^6 includes a fluorine atom, a chlorine atom, a bromine atom, and an iodine atom.

[0038]

The perfluoroalkyl group represented by X^1, X^2, X^3, X^4, X^5, and X^6 is an alkyl group in which all of the hydrogen atoms are replaced with a fluorine atom. The perfluoroalkyl group has, for example, 1 to 20 carbon atoms, preferably 1 to 12 carbon

atoms, more preferably 1 to 6 carbon atoms, still more preferably 1 to 4 carbon atoms, and particularly preferably 1 to 3 carbon atoms. The perfluoroalkyl group is preferably a linear or branched perfluoroalkyl group. The perfluoroalkyl group is preferably a trifluoromethyl group (CF_3-) or a pentafluoroethyl group (C_2F_5-).

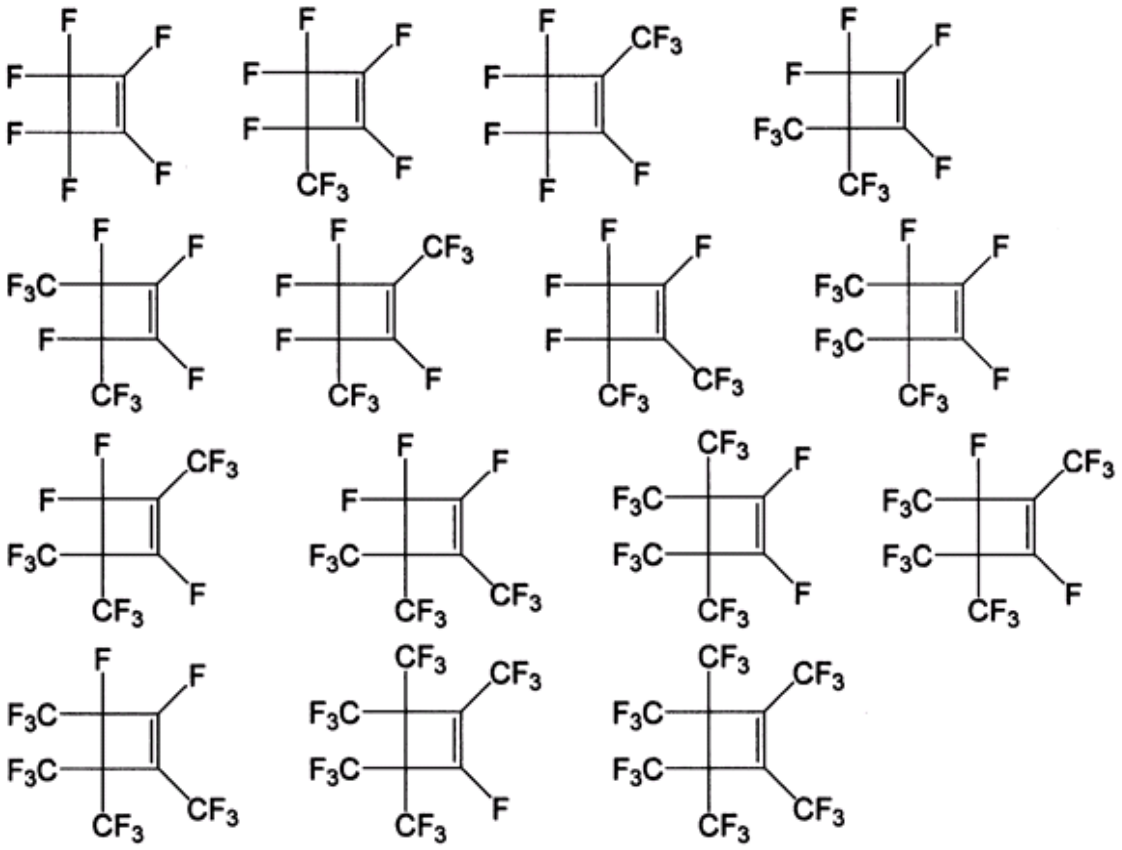
[0039]

From the standpoint of producing a fluorine atom-containing cyclobutane at a high selectivity, the cyclobutene represented by formula (2), which is a starting material compound, is more preferably a cyclobutene wherein X^1, X^2, X^3, X^4, X^5, and X^6 are the same or different and represent a fluorine atom or a perfluoroalkyl group.

[0040]

Examples of the cyclobutene represented by formula (2), which is a starting material compound, include the following compounds.

[0041]



[0042]

[0043]

These cyclobutenes represented by formula (2) may be used singly or in a combination of two or more. These cyclobutenes for use may be known or commercially available products.

[0044]

From the standpoint of producing a fluorine atom-containing cyclobutane at a high selectivity, the cyclobutene represented by formula (2) is more preferably a cyclobutene wherein X^1, X^2, X^3, X^4, X^5, and X^6 are a fluorine atom.

[0045]

Molar Ratio of Cyclobutene and Hydrogen Fluoride

Hydrogen fluoride (HF) is preferably supplied to a reactor together with a cyclobutene represented by formula (2) (starting material compound) in a gas phase. Regarding the amount of hydrogen fluoride to be supplied, hydrogen fluoride in an amount of about 0.1 mol to 100 mol is preferably reacted with one mol of the cyclobutene represented by formula (2) (starting material compound). The amount of hydrogen fluoride to be supplied is more preferably about 0.5 mol to 50 mol, still more preferably about 1 mol to 30 mol, and particularly preferably about 1 mol to 20 mol, per mol of the cyclobutene represented by formula (2) (starting material compound). The amount of hydrogen fluoride within these numerical ranges enables the addition reaction with hydrogen fluoride to proceed well, suppresses the formation of impurities, and enables the fluorine atom-containing cyclobutane (reaction product) to be recovered at a high selectivity and high yield.

[0046]

(2) Addition Reaction

The step of reacting cyclobutene with hydrogen fluoride according to the present disclosure is an addition reaction with hydrogen fluoride, and is performed in the presence of a catalyst in a gas phase. In the step of reacting cyclobutene with hydrogen

fluoride according to the present disclosure (addition reaction), the reaction is performed in a gas phase, particularly preferably in gas-phase continuous flow mode using a fixed bed reactor. The reaction performed in gas-phase continuous flow mode is advantageous because it can simplify the equipment, operation, etc., and it is also economical.

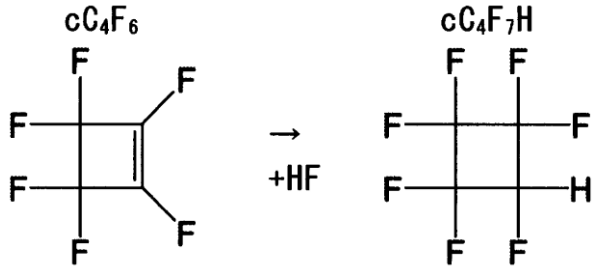
[0047]

In the step of reacting cyclobutene with hydrogen fluoride according to the present disclosure, for example, the starting material is more preferably a cyclobutene represented by formula (2) wherein X^1, X^2, X^3, X^4, and X^6 are a fluorine atom.

[0048]

In accordance with the following reaction scheme, the reaction is preferably an addition reaction with hydrogen fluoride.

[0049]



[0050]

Catalyst

The step of reacting cyclobutene with hydrogen fluoride according to the present disclosure is preferably performed as an addition reaction with hydrogen fluoride in the presence of a catalyst in a gas phase.

[0051]

The catalyst for use in this step is preferably activated carbon.

[0052]

The catalyst for use in this step is preferably a metal catalyst. The metal catalyst is preferably the following metal catalysts: chromium catalysts such as chromium oxide, fluorinated

chromium oxide, and chromium fluoride; aluminum catalysts such as aluminum oxide, fluorinated aluminum oxide, and aluminum fluoride; iron catalysts such as iron oxide, fluorinated iron oxide, and iron fluoride; nickel catalysts such as nickel oxide, fluorinated nickel oxide, and nickel fluoride; and magnesium catalysts such as magnesium oxide, fluorinated magnesium oxide, and magnesium fluoride. The catalyst is preferably at least one member selected from the group consisting of the metal catalysts described above.

[0053]

The catalyst for use in this step is preferably at least one member selected from the group consisting of activated carbon and the metal catalysts described above.

Of these catalysts, activated carbon and chromium catalysts such as chromium oxide, fluorinated chromium oxide, and chromium fluoride are more preferable from the standpoint of obtaining the target compound at a higher selectivity. These catalysts can also increase the conversion rate of the starting material compound.

[0054]

In this step, when bringing the starting material compound into contact with a catalyst in a gas phase, it is preferable to bring the starting material compound into contact with the catalyst in a slid form (solid phase).

[0055]

In this step, the catalyst may be in the form of a powder. However, the form of a pellet is preferable for the reaction in gas-phase continuous flow mode.

[0056]

The specific surface area ("BET specific surface area" below) of the catalyst according to the BET theory is typically 10 to 3,000 m^2/g, preferably 10 to 2,500 m^2/g, more preferably 20 to 2,000 m^2/g, and still more preferably 30 to 1,500 m^2/g. A catalyst having a BET specific surface area within these numerical ranges does not have an overly low particle density,

thus making it possible to obtain the target compound at a high selectivity. Such a catalyst can also increase the conversion rate of the starting material compound. For example, the catalyst for use is preferably activated carbon with a BET specific surface area of 800 m^2/g to 2,000 m^2/g.

[0057]

Activated carbon for use as a catalyst is preferably powdered activated carbon of crushed charcoal, briquette, granular charcoal, spherical charcoal, or the like. The powdered activated carbon for use preferably has a particle size of 4 mesh (4.76 mm) to 100 mesh (0.149 mm) in a JIS test. When activated carbon is used as a catalyst, activated carbon may be treated with heat at a temperature of, for example, 300 to 500°C by circulating nitrogen for a predetermined period of time before use (activated carbon treated with heat).

[0058]

The metal catalyst for use is preferably supported on a carrier. Examples of carriers include carbon, alumina (Al_2O_3), zirconia (ZrO_2), silica (SiO_2), and titania (TiO_2). The carbon for use includes activated carbon, amorphous carbon, graphite, and diamond.

[0059]

The following explains chromium oxide and fluorinated chromium oxide as an embodiment of the catalyst of the present disclosure. For example, when chromium oxide is represented by $Cr_2O_3 \cdot nH_2O$, n is preferably 3 or less, and more preferably 1 to 1.5. When chromium oxide is represented by formula: CrO_m, m is preferably within the range of $1.5<m<3$.

Fluorinated chromium oxide as a catalyst can be prepared by fluorinating chromium oxide. Fluorination includes fluorination by using hydrogen fluoride (HF) and fluorination by using a fluorocarbon or the like.

[0060]

Fluorinated chromium oxide as a catalyst can be obtained, for example, in accordance with the method disclosed in

Japanese Patent No. 3412165. Fluorinated chromium oxide can be obtained by subjecting chromium oxide to fluorination by hydrogen fluoride (HF treatment). The temperature of fluorination is, for example, preferably 100 to 460°C. The pressure of fluorination is preferably the pressure under a catalyst reaction. In the present disclosure, a highly fluorinated chromium oxide catalyst with a high fluorine content is particularly preferable for use. The highly fluorinated chromium oxide catalyst can be obtained by fluorinating chromium oxide at a temperature higher than usual for a long time.

[0061]

The highly fluorinated chromium oxide catalyst preferably contains fluorine in an amount of 30 mass% or more, and more preferably 30 to 45 mass%. The amount of fluorine can be determined from the change in mass of the catalyst, or measured according to typical quantitative analysis of chromium oxide.

[0062]

Temperature of Gas-Phase Reaction

In the step of reacting cyclobutene with hydrogen fluoride of the present disclosure, the lower limit of the reaction temperature is typically 50°C, preferably 200°C, more preferably 250°C, and still more preferably 300°C from the standpoint of more efficiently performing the addition reaction with hydrogen fluoride to obtain the target compound at a higher selectivity and suppressing a decrease in the conversion rate.

[0063]

When activated carbon is used as a catalyst, the reaction temperature is preferably 50°C to 400°C, more preferably 100°C to 350°C, and still more preferably 150°C to 300°C.

[0064]

When a chromium catalyst is used as a catalyst, the reaction temperature is preferably 50°C or more, more preferably 250°C or more, and still more preferably 300°C or more.

[0065]

The upper limit of the reaction temperature in the reaction of cyclobutene with hydrogen fluoride is typically 500°C, preferably 450°C, and more preferably 400°C from the standpoint of more efficiently performing the addition reaction with hydrogen fluoride to obtain the target compound at a higher selectivity and suppressing a decrease in selectivity due to decomposition or polymerization of the reaction product.

[0066]

Time Period of Gas-Phase Reaction

Regarding the time period of the reaction of cyclobutene with hydrogen fluoride, as the contact time (W/F_0)[W: weight of metal catalyst (g), F_0: flow rate of starting material compound (cc/sec)] between the starting material compound and the catalyst increases, the conversion rate of the starting material compound increases. However, due to the need for a larger amount of a catalyst, a longer reaction time requires larger equipment, and is thus inefficient.

[0067]

Thus, regarding the time period for the reaction of cyclobutene with hydrogen fluoride, the contact time (W/F_0) between the starting material compound and the catalyst is preferably 1 g·sec/cc to 30 g·sec/cc, more preferably 1.5 g·sec/cc to 10 g·sec/cc, and still more preferably 2.0 g·sec/cc to 5.0 g·sec/cc from the standpoint of increasing the conversion rate of the starting material compound and reducing equipment costs.

[0068]

The contact time between the starting material compound and the catalyst refers to the time period during which the starting material compound and the catalyst are in contact with each other.

[0069]

Molar Ratio of Cyclobutene and Hydrogen Fluoride

When activated carbon or / and a chromium catalyst is used as a catalyst, hydrogen fluoride in an amount of preferably

about 0.1 mol to 100 mol, more preferably about 0.5 mol to 75 mol, and still more preferably about 1 mol to 50 mol is reacted with one mol of the cyclobutene represented by formula (2) (starting material compound) from the standpoint of reaction costs and productivity.

[0070]

Pressure in Gash-Phase Reaction

The reaction pressure in the reaction of cyclobutene with hydrogen fluoride is preferably -0.05 MPa to 2 MPa, more preferably -0.01 MPa to 1 MPa, and still more preferably ordinary pressure to 0.5 MPa from the standpoint of more efficiently performing the addition reaction with hydrogen fluoride. In the present disclosure, the pressure is a gauge pressure unless indicated otherwise.

[0071]

In the reaction of cyclobutene with hydrogen fluoride, the reactor in which the starting material compound and a catalyst (e.g., activated carbon or a chromium catalyst) are brought into contact with each other and reacted is not limited in terms of shape and structure as long as the reactor is resistant to temperature and pressure. Examples of reactors include vertical reactors, horizontal reactors, and multi-tube reactors. Examples of reactor materials include glass, stainless steel, iron, nickel, and iron nickel alloy.

[0072]

Examples of Gas-Phase Reaction

The reaction of a cyclobutene with hydrogen fluoride (addition reaction with hydrogen fluoride) can be performed by a flow mode in which a starting material compound is continuously added to a reactor, and a target compound is continuously taken out from the reactor, or the reaction can be performed in batch mode. Because a target compound remaining in the reactor, on the contrary, allows the elimination reaction to further proceed, the reaction is preferably performed in flow mode. In the step of reacting cyclobutene with hydrogen fluoride according to the

present disclosure, the reaction is performed in a gas phase, particularly preferably in gas-phase continuous flow mode by using a fixed bed reactor. The reaction performed in gas-phase continuous flow mode can simplify the equipment, operation, etc., and is also economically advantageous.

[0073]

The atmosphere in which the reaction of cyclobutene with hydrogen fluoride is performed is preferably an atmosphere in which inert gas and/or hydrogen fluoride is present from the standpoint of suppressing the degradation of the catalyst (e.g., activated carbon and a chromium catalyst). The inert gas is preferably at least one member selected from the group consisting of nitrogen, helium, argon, and carbon dioxide. Of these inert gasses, nitrogen is more preferable from the standpoint of reducing costs. The concentration of the inert gas is preferably 0 to 50 mol% of the gas component introduced into the reactor.

[0074]

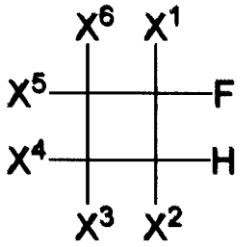
After completion of the reaction of cyclobutene with hydrogen fluoride (addition reaction with hydrogen fluoride), a purification treatment can be optionally performed in accordance with an ordinary method to obtain a fluorine atom-containing cyclobutane represented by formula (1).

[0075]

(3) Target Compound

The target compound according to the present disclosure is a fluorine atom-containing cyclobutane represented by formula (1):

[0076]



(1)

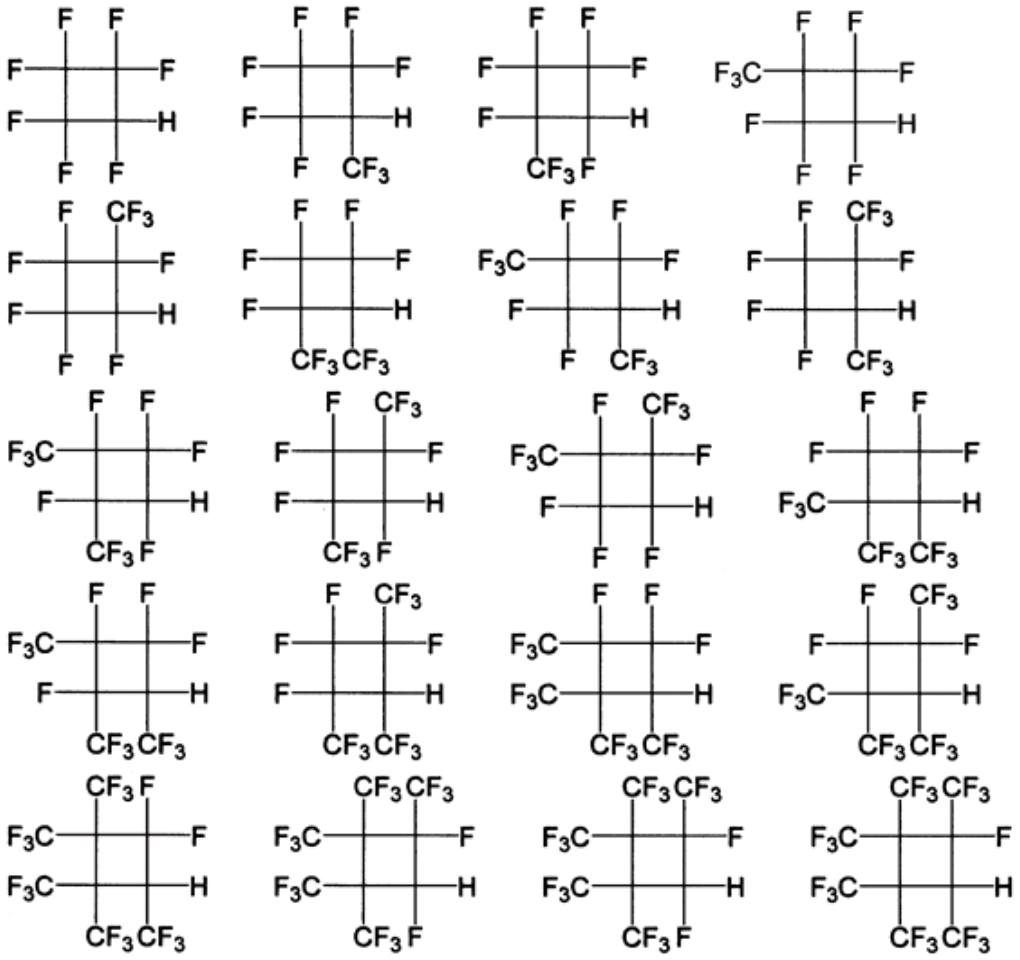
[0077]

wherein X^1, X^2, X^3, X^4, X^5, and X^6 are the same or different and represent a hydrogen atom, a halogen atom, or a perfluoroalkyl group.

[0078]

Examples of the fluorine atom-containing cyclobutane represented by formula (1) to be produced include the following.

[0079]



[0080]

[0081]

The fluorine atom-containing cyclobutane represented by formula (1) is a cyclobutane wherein X^1 , X^2, X^3, X^4 , X^5, and X^6 are the same or different and represent a hydrogen atom, a halogen atom, or a perfluoroalkyl group.

[0082]

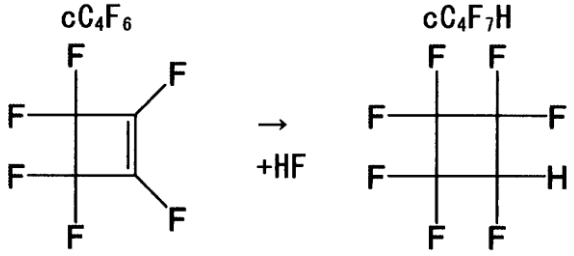
In the method for producing a cyclobutane according to

present disclosure, an addition reaction with hydrogen fluoride is performed on a starting material compound in the step of reacting a cyclobutene represented by formula (2) with hydrogen fluoride; for example, the cyclobutene represented by formula (2) as a starting material compound is more preferably a cyclobutene wherein X^1, X^2, X^3, X^4, and X^6 are a fluorine atom.

[0083]

In accordance with the following reaction scheme, the reaction is preferably an addition reaction with hydrogen fluoride.

[0084]



[0085]

The target compound is more preferably a fluorine atom-containing cyclobutane represented by formula (1) wherein X^1, X^2, X^3, X^4, X^5, and X^6 are a fluorine atom.

[0086]

The production method according to the present disclosure enables the production of a fluorine atom-containing cyclobutane represented by formula (1) as a target compound on an industrial scale at a high selectivity in an excellent manner.

[0087]

(4) Composition Containing Fluorine Atom-Containing Cyclobutane

In the manner described above, a fluorine atom-containing cyclobutane represented by formula (1) can be obtained. However, as described above, a fluorine atom-containing cyclobutane represented by formula (1) may also be obtained in the form of a composition containing a fluorine atom-containing cyclobutane represented by formula (1) and a cyclobutene represented by formula (2).

[0088]

The fluorine atom-containing cyclobutane represented by formula (1) contained in such a composition is preferably a cyclobutane wherein X^1, X^2 , X^3 , X^4 , X^5, and X^6 are a fluorine atom.

[0089]

In the composition containing the fluorine atom-containing cyclobutane represented by formula (1) according to present disclosure, the fluorine atom-containing cyclobutane represented by formula (1) is preferably present in an amount of 99 mol% or more based on the total amount of the composition taken as 100 mol%.

[0090]

In the composition containing the fluorine atom-containing cyclobutane represented by formula (1) according to present disclosure, the fluorine atom-containing cyclobutane represented by formula (1) is preferably present in an amount of 1 mol% to 99.9 mol%, more preferably 5 mol% to 99.9 mol%, and still more preferably 10 mol% to 99.9 mol% based on the total amount of the composition taken as 100 mol%.

[0091]

The production method according to present disclosure produces the fluorine atom-containing cyclobutane represented by formula (1) particularly at a high selectivity even when the fluorine atom-containing cyclobutane represented by formula (1) is obtained in the form of a composition containing the cyclobutane. Thus, it is possible to reduce the components other than the fluorine atom-containing cyclobutane represented by formula (1) in the composition. The production method according to the present disclosure can reduce labor for performing purification to obtain the fluorine atom-containing cyclobutane represented by formula (1).

[0092]

The composition containing the fluorine atom-containing cyclobutane represented by formula (1) according to the present disclosure can be used effectively in a variety of areas, such as

for etching gas for forming state-of-the-art microstructures, such as semiconductors and liquid crystals, as well as deposit gas, building blocks for organic synthesis, and cleaning gas, in the same manner as with the fluorine atom-containing cyclobutane represented by formula (1) alone.

[0093]

The deposit gas refers to a gas for depositing an etching-resistant polymer layer.

[0094]

The building blocks for organic synthesis refer to a substance that can serve as a precursor of a compound that has a highly reactive skeleton. For example, reacting the fluorine atom-containing cyclobutane represented by formula (1) according to present disclosure or the composition containing the fluorine atom-containing cyclobutane with a fluorine-containing organic silicon compound such as $CF_3Si(CH_3)_3$ introduces a fluoroalkyl group such as a CF_3 group, and this converts the cyclobutane or the composition into a substance that can be used as a cleaner or a fluorine-containing pharmaceutical intermediate.

[0095]

The above describes embodiments of the present disclosure. However, various modifications of the embodiments and details may be made without departing from the spirit and principal concept of the claims.

Examples

[0096]

The following describes the present disclosure in more detail with reference to Examples. However, the present disclosure is not limited to these Examples.

[0097]

Example

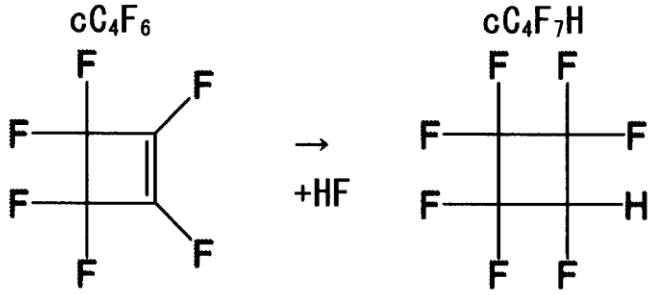
In the Examples, the method for producing a fluorine atom-containing cyclobutane used a cyclobutene represented by formula (2) wherein X^1, X^2, X^3, and X^4 are a fluorine atom as a

starting material compound.

[0098]

In accordance with the following reaction scheme, an addition reaction with hydrogen fluoride was performed on cyclobutene.

[0099]



[0100]

The target compound was a fluorine atom-containing cyclobutane represented by formula (1) wherein X^1, X^2, X^3, X^4, X^5 and X^6 are a fluorine atom.

[0101]

Example 1 (1-1 to 1-5): Activated Carbon (Catalyst)

10 g of activated carbon (catalyst) was placed in an SUS pipe (outer diameter: 1/2 inch) (reaction tube). The catalyst was used in an addition reaction with hydrogen fluoride. The activated carbon had a BET specific surface area of 850 m^2/g. 10 g of activated carbon (catalyst) was added to an SUS pipe (outer diameter: 1/2 inch) (reactor).

[0102]

The activated carbon was dried at 200°C for 2 hours in a nitrogen atmosphere, and then a starting material compound (cC_4F_6) was circulated in the reactor such that the pressure was ordinary pressure, and that the contact time (W/F_0) between the cyclobutene cC_4F_6 (starting material compound) and the activated carbon (catalyst) was 2.0 g·sec/cc.

[0103]

The amount of the hydrogen fluoride supplied was 1 mol or 15 mol per mol of the cyclobutene cC_4F_6 (starting material compound).

[0104]

The reaction was performed in gas-phase continuous flow mode.

[0105]

The reactor was heated at 150°C, 200°C, 250°C, or 300°C to start an addition reaction with hydrogen fluoride. After one hour from the start of the addition reaction with hydrogen fluoride, the distillate that passed through the abatement tower was collected.

[0106]

After that, mass spectrometry was performed by gas chromatography (trade name: GC-2014, produced by Shimadzu Corporation) in accordance with gas chromatography-mass spectrometry (GC-MS), and structural analysis based on an NMR spectrum was performed by using an NMR spectrometer (trade name: 400YH, produced by JEOL).

[0107]

The results of the mass spectrometry and structural analysis indicated that cC_4F_7H was formed as a target compound. In Example 1-1, the conversion rate from cC_4F_6 (starting material compound) was 0.364 mol%, and the selectivity (yield) for cC_4F_7H (target compound) was 18.6 mol%.

[0108]

In Example 1-2, the conversion rate was 11.6 mol%, and the selectivity was 96.2 mol%.

[0109]

In Example 1-3, the conversion rate was 4.57 mol%, and the selectivity was 84.9 mol%.

[0110]

In Example 1-4, the conversion rate was 2.30 mol%, and the selectivity was 38.8 mol%.

[0111]

In Example 1-5, the conversion rate was 0.6 mol%, and the selectivity was 94.2 mol%.

[0112]

Example 2 (2-1 to 2-8): Chromium Catalyst (Catalyst)

10 g of chromium oxide that contains Cr_2O_3 as the major component (catalyst) was placed in an SUS pipe (outer diameter: 1/2 inch; reaction tube). The catalyst was subjected to fluorination as a pretreatment before use in the addition reaction by circulating anhydrous hydrogen fluoride in the reactor and setting the reactor temperature to 200°C to 300°C. The fluorinated chromium oxide was taken out and used in the addition reaction. The fluorinated chromium oxide had a BET specific surface area of 75 m^2/g. 10 g of the fluorinated chromium oxide (catalyst) was placed in an SUS pipe (outer diameter: 1/2 inch; reactor).

[0113]

In a nitrogen atmosphere, the fluorinated chromium oxide was dried at 200°C for 2 hours, and a starting material compound ($cC_4F_6H_2$) was circulated in the reactor such that the pressure was ordinary pressure, and that the contact time (W/F_0) between the cyclobutene cC_4F_6 (starting material compound) and the fluorinated chromium oxide (catalyst) was 3.0 g·sec/cc, 4.0 g·sec/cc, or 5.0 g·sec/cc.

[0114]

The amount of the hydrogen fluoride supplied was 1 mol, 5 mol, or 20 mol, per mol of the cyclobutene cC_4F_6 (starting material compound).

[0115]

The reaction was performed in gas-phase continuous flow mode.

[0116]

The reactor was heated at 50°C, 200°C, 250°C, 300°C, or 350°C to start an addition reaction with hydrogen fluoride. After one hour from the start of the addition reaction with hydrogen fluoride, the distillate that passed through the abatement tower was collected.

[0117]

After that, mass spectrometry was performed by gas

chromatography (trade name: GC-2014, produced by Shimadzu Corporation,) in accordance with gas chromatography-mass spectrometry (GC-MS), and structural analysis based on an NMR spectrum was performed by using an NMR spectrometer (trade name: 400YH, produced by JEOL).

[0118]

The results of the mass spectrometry and structural analysis indicated that cC_4F_7H was formed as a target compound. In Example 2-1, the conversion rate from cC_4F_6 (starting material compound) was 0.942 mol%, and the selectivity (yield) for cC_4F_7H (target compound) was 0.7 mol%.

[0119]

In Example 2-2, the conversion rate was 0.183 mol%, and the selectivity was 1.6 mol%.

[0120]

In Example 2-3, the conversion rate was 0.506 mol%, and the selectivity was 2.4 mol%.

[0121]

In Example 2-4, the conversion rate was 0.396 mol%, and the selectivity was 0.7 mol%.

[0122]

In Examples 2-5, the conversion rate was 0.924 mol%, and the selectivity was 4.2 mol%.

[0123]

In Example 2-6, the conversion rate was 1.37 mol%, and the selectivity was 3.0 mol%.

[0124]

In Example 2-7, the conversion rate was 1.62 mol%, and the selectivity was 2.0 mol%.

[0125]

In Example 2-8, the conversion rate was 2.87 mol%, and the selectivity was 0.2 mol%.

[0126]

Comparative Examples 1 and 2

In accordance with the experiment in the Examples,

hydrogen fluoride was supplied to a cyclobutene cC_4F_6 (starting material compound) to perform a reaction without using a catalyst.

[0127]

The amount of the hydrogen fluoride supplied was 20 mol per mol of the cyclobutene cC_4F_6 (starting material compound).

[0128]

The reaction was performed in gas-phase continuous flow mode.

[0129]

The reactor was heated at 200°C or 350°C to start an addition reaction with hydrogen fluoride. After one hour from the start of the addition reaction with hydrogen fluoride, the distillate that passed through the abatement tower was collected.

[0130]

After that, mass spectrometry was performed by gas chromatography (trade name: GC-2014, produced by Shimadzu Corporation) in accordance with gas chromatography-mass spectrometry (GC-MS), and structural analysis based on an NMR spectrum was performed by using an NMR spectrometer (trade name: 400YH, produced by JEOL).

[0131]

The results of the mass spectrometry and structural analysis indicated that while the conversion rate from cC_4F_6 (starting material compound) was 0.801 mol% (Comparative Example 1) or 0.695 mol% (Comparative Example 2), the formation of cC_4F_7H (target compound) was not confirmed.

[0132]

Table 1 below illustrates the results of the Examples. In Table 1, the contact time (W/F_0) refers to the rate at which the starting material gas is circulated, i.e., the time period during which the catalyst and the starting material gas are in contact with each other. The molar ratio HF/cC_4F_6 refers to the amount of HF for use (mol) per mol of cC_4F_6.

[0133]

Table 1

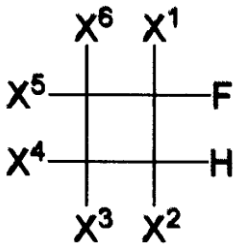
Table 1							
	Type of Catalyst	Reaction Temperature (°C)	Contact Time W/F0 (g·sec/cc)	Molar Ratio* HF/cC4F6	Conversion Rate from Starting Material Compound cC4F6 (mol%)	Selectivity for Target Compound cC4F7H (mol%)	Other Generated Products (mol%)
Example 1							
1-1	Activated Carbon	150	2.0	15	0.364	18.6	81.4
1-2	Activated Carbon	200	2.0	15	11.6	96.2	3.8
1-3	Activated Carbon	250	2.0	15	4.57	84.9	15.1
1-4	Activated Carbon	300	2.0	15	2.30	38.8	61.2
1-5	Activated Carbon	200	2.0	1	0.6	94.2	5.8
Example 2							
2-1	Chromium Oxide	50	4.0	20	0.942	0.7	99.3
2-2	Chromium Oxide	50	3.0	1	0.183	1.6	98.4
2-3	Chromium Oxide	200	5.0	5	0.506	2.4	97.6
2-4	Chromium Oxide	250	5.0	5	0.396	0.7	99.3
2-5	Chromium Oxide	300	5.0	5	0.924	4.2	95.8
2-6	Chromium Oxide	350	5.0	5	1.37	3.0	97.0
2-7	Chromium Oxide	350	4.0	20	1.62	2.0	98.0
2-8	Chromium Oxide	350	4.0	5	2.87	0.2	99.8
Comparative Example							
1	None	200	2.0	20	0.801	0	100
2	None	350	2.0	20	0.695	0	100

* Molar Ratio HF/cC4F6: The amount of HF for use per mol of cC4F6

CLAIMS

[Claim 1]

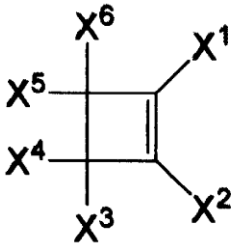
A method for producing a cyclobutane represented by formula (1):



(1)

wherein X^1, X^2, X^3, X^4, X^5, and X^6 are the same or different and represent a hydrogen atom, a halogen atom, or a perfluoroalkyl group,

the method comprising reacting a cyclobutene represented by formula (2):



(2)

wherein X^1, X^2, X^3, X^4, X^5, and X^6 are as defined above with hydrogen fluoride in the presence of a catalyst in a gas phase,

wherein the reaction is an addition reaction of hydrogen fluoride.

[Claim 2]

The method according to claim 1, wherein 0.1 mol to 100 mol of the hydrogen fluoride is supplied per mol of the cyclobutene represented by formula (2) to perform the reaction.

[Claim 3]

The method according to claim 1 or 2, wherein the catalyst is supported on a carrier selected from carbon, alumina, zirconia, silica, and titania,

where the carbon is selected from the group consisting of activated carbon, amorphous carbon, graphite, and diamond.

[Claim 4]

The method according to any one of claims 1 to 3, wherein the catalyst is at least one member selected from the group consisting of:

activated carbon;

chromium catalyst selected from the group consisting of chromium oxide, fluorinated chromium oxide, and chromium fluoride;

aluminum catalyst selected from the group consisting of aluminum oxide, fluorinated aluminum oxide, and aluminum fluoride;

iron catalyst selected from the group consisting of iron oxide, fluorinated iron oxide, and iron fluoride;

nickel catalyst selected from the group consisting of nickel oxide, fluorinated nickel oxide, and nickel fluoride; and

magnesium catalyst selected from the group consisting of magnesium oxide, fluorinated magnesium oxide, and magnesium fluoride,

provided that the combination, where the carrier is activated carbon when the catalyst is activated carbon, is excluded.

[Claim 5]

The method according to any one of claims 1 to 3, wherein the catalyst is at least one member selected from the group consisting of:

activated carbon; and

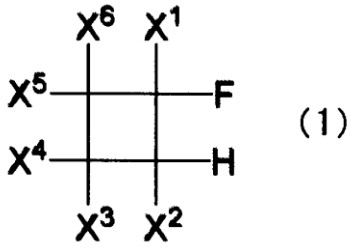
chromium catalyst selected from the group consisting of

chromium oxide, fluorinated chromium oxide, and chromium fluoride;

provided that the combination, where the carrier is activated carbon when the catalyst is activated carbon, is excluded.

[Claim 6]

A composition comprising a cyclobutane represented by formula (1):



(1)

wherein X^1, X^2, X^3, X^4, X^5, and X^6 are the same or different and represent a fluorine atom or a perfluoroalkyl group,

wherein the cyclobutane represented by formula (1) is present in an amount of 99 mol% or more based on the total amount of the composition taken as 100 mol%, and

wherein the composition is for use in cleaning gas or etching gas.

[Claim 7]

The composition according to claim 6,

wherein the cyclobutane represented by formula (1) is a fluorine atom-containing cyclobutane selected from the group consisting of

