

DESCRIPTION

METHOD OF PRODUCING ACETYLENE COMPOUND

TECHNICAL FIELD

[0001]

5 The present invention relates to a method of producing an acetylene compound by isomerizing an allene compound.

BACKGROUND ART

[0002]

10 JP-A-2-290831 describes, as a method of isomerizing an allene compound into an acetylene compound, a method of producing methylacetylene by reacting propadiene in the presence of a catalyst in which potassium carbonate is supported on γ -alumina.

15 PROBLEM TO BE SOLVED BY THE INVENTION

[0003]

20 The conventional production method as described in JP-A-2-290831, however, is not always satisfactory in terms of conversion of the allene compound and sustainability of the catalytic activity when carbon dioxide is present. For example, in the case of using as a feedstock an allene compound obtained by dehydration reaction of a ketone compound, the feedstock (allene compound) contains water produced in dehydration reaction, carbon dioxide as a by-product, etc., with the result that the problems of a

25

reduced conversion and sustainability of the catalytic activity occur remarkably.

In order to prevent carbon dioxide from being contained in the raw material (allene compound), complicated operations are required, leading to an increase in the number of manufacturing steps and an increase in cost.

[0004]

An object of the present invention is to provide a method of producing an acetylene compound stably in a favorable selectivity by isomerizing an allene compound at a high conversion, the method capable of stably maintaining the catalytic activity even in the condition that carbon dioxide is present as described above.

MEANS FOR SOLVING PROBLEM

[0005]

As a result of intensive study to solve the problem, the inventor has found out a solution composed of the following configurations and completed the present invention.

(1) A method of producing an acetylene compound by isomerizing an allene compound in a mixture containing the allene compound and carbon dioxide in the presence of a catalyst in which an alkali metal compound is supported on an alumina support, wherein the catalyst is used in an

amount of 10 molar times or more the alkali metal element contained in the catalyst relative to the number of moles of the carbon dioxide fed per hour.

(2) The method according to (1), wherein the mixture
5 is a mixture obtained by dehydration reaction of a ketone compound.

(3) The method according to (2), wherein the ketone compound is acetone.

(4) The method according to any one of (1) to (3),
10 wherein the catalyst is a catalyst obtained by subjecting the alumina support to a contact treatment with a solution containing the alkali metal compound and then calcining the support.

(5) The method according to any one of (1) to (4),
15 wherein the alkali metal compound is at least one compound selected from the group consisting of potassium compounds and cesium compounds.

(6) The method according to any one of (1) to (5),
wherein the allene compound is propadiene, and the
20 acetylene compound is methylacetylene.

(7) A method of producing a methacrylic acid ester, including reacting methylacetylene produced by the method according to (6) with carbon monoxide and alcohol in the presence of a catalyst comprising a Group 10 metal compound,
25 a protonic acid, and a phosphine compound.

MODE FOR CARRYING OUT THE INVENTION

[0006]

In a method of producing an acetylene compound according to the present invention (hereinafter, may be referred to simply as "production method of the present invention"), when isomerizing an allene compound in a mixture containing the allene compound and carbon dioxide in the presence of a catalyst in which an alkali metal compound is supported on an alumina support, the catalyst is used in an amount as much as the amount of an alkali metal element contained in the catalyst is 10 molar times or more the number of moles of carbon dioxide fed per hour.

[0007]

The production method of the present invention uses, as a catalyst, the catalyst in which an alkali metal compound is supported on an alumina support. Alumina is not particularly limited, but may be γ -alumina, α -alumina, θ -alumina, etc. Among them, γ -alumina is preferred. γ -alumina is easily available, and in the case of using alumina having a high-specific surface area in particular, γ -alumina is easy to obtain.

The alumina support contains alumina at a rate of preferably 50 wt% or more, and more preferably 90 wt% or more. The alumina support may further contain silica, zirconia, ceria, titania, magnesia, calcia, yttria, gallium

oxide, etc.

As necessary, these oxides may be used in the form of a composite oxide or a mixed oxide including two or more oxides. Alumina contained in the alumina support may be alumina having hydration water like boehmite.

[0008]

The specific surface area of the alumina support is preferably 50 m²/g or more, more preferably 100 m²/g or more, from the viewpoint of the supported amount of an alkali metal oxide. The specific surface area is a value as measured by nitrogen adsorption method (BET method), and normally is a value as measured by BET 1-point method.

[0009]

The alumina contained in the alumina support has an average pore radius of preferably 4.5 nm or more, more preferably 5.0 nm or more. This enables the acetylene compound to be produced in a high yield. The reason for this is presumably that the average pore radius of 4.5 nm or more provides a moderately increased pore volume, facilitating diffusion within pores of a reactant and a product, i.e., an allene compound and an acetylene compound, leading to an increased reaction rate. The upper limit of the average pore radius of the alumina is preferably 15 nm, more preferably 10 nm. The average pore radius of the alumina is a value as measured by the mercury intrusion

technique.

The alumina contained in the alumina support has a pore volume of preferably 0.40 mL/g or more, more preferably 0.50 mL/g or more. The pore volume of alumina is preferably 2.5 mL/g or less, more preferably 1.5 mL/g or less. If the pore volume lies within such a range, it is presumed that the reaction rate is improved as described above, enabling the acetylene compound to be produced in a higher yield. The pore volume of the alumina is a value as measured by the mercury intrusion technique.

[0010]

The alumina support may be subjected to a heat treatment before the alkali metal compound is deposited thereon. Application of the heat treatment removes impurities attaching to the surface of alumina to achieve activation of the surface. The heat treatment is performed in an atmosphere of oxidizing gas or inert gas, and it may be done in multiple stages by combining them. The oxidizing gas as used herein means a gas containing an oxidizing substance, and for example it may be an oxygen-containing gas such as air or pure oxygen. Examples of the inert gas include nitrogen gas, helium gas, and argon gas.

The gas for use in the heat treatment is preferably nitrogen gas, oxygen gas, air, or a mixture gas of nitrogen gas and oxygen gas.

[0011]

The heat treatment temperature is preferably 100 to 600°C. The heat treatment time is preferably 1 to 48 hours, more preferably 2 to 24 hours.

5 [0012]

Examples of the alkali metal compound supported on such an alumina support include alkali metal oxides, alkali metal halides, alkali metal hydroxides, alkali metal carbonates, alkali metal nitrates, alkali metal hydrides, 10 alkali metal alkoxides, and alkali metal acetates. If necessary, two or more of them may be supported on alumina. Examples of the alkali metal include potassium, cesium, lithium, and sodium.

Among these alkali metal compounds, a potassium 15 compound and/or a cesium compound is preferred. Furthermore, taking into consideration calcining after depositing the alkali metal compound on alumina as described later, it is preferred to use a thermally decomposable salt, and a carbonate or a hydride is more 20 preferable.

[0013]

The supported amount of alkali metal in the catalyst is preferably 0.01 to 6.7 mmol per gram of the catalyst, more preferably 0.15 to 4.0 mmol. The supported amount of 25 alkali metal can be measured by e.g., inductively coupled

plasma atomic emission spectrophotometry (hereinafter, may be described as "ICP spectroscopy").

[0014]

The catalyst is preferably used in the form of a
5 molded body, examples of the shape of which include a
spherical granular (spherical) shape, a cylindrical shape,
a pallet-like shape, an extruded shape, an annular shape, a
honeycomb shape, and a granular shape with a moderate size
pulverized and classified after molding. When the catalyst
10 is pulverized and classified into granules of a moderate
size after molding, the surface area of the catalyst
increases and the area of contact with the allene compound
also increases. Accordingly, the allene compound becomes
easier to isomerize, increasing the yield of the acetylene
15 compound.

[0015]

The method of supporting an alkali metal compound on
an alumina support is not particularly limited and may be,
for example, a method in which a contact treatment is
20 performed using a solution containing the alkali metal
compound. Examples of such a contact treatment include
impregnation, immersion, and kneading. The impregnation is
performed by, e.g., an evaporation to dryness method, a
pore-filling method, an incipient wetness method, or an
25 equilibrium adsorption method. In the contact treatment,

the treatment temperature is normally 0 to 100°C,
preferably 0 to 50°C. The treatment pressure is normally
0.1 to 1 MPa, preferably the atmospheric pressure. The
contact treatment may be performed in an air atmosphere or
5 in an inert gas atmosphere (e.g., in an atmosphere of
nitrogen gas, helium gas, argon gas, or carbon dioxide).
These atmospheres may contain water vapor. A solvent used
for preparing a solution is preferably water. The
supporting method is not limited to the contact treatment
10 and may be a coprecipitation method.

The evaporation to dryness method is a method
comprising immersing the alumina support in a solution
containing an alkali metal compound, and then heating and
drying the support under the atmospheric pressure or under
15 a reduced pressure, thereby supporting the metal on the
support. The pore-filling method is a method comprising
measuring the pore volume of the support then allowing the
support to absorb a solution containing the same volume of
an alkali metal compound, and then, under normal pressure
20 or under a reduced pressure, drying the support at normal
temperature or heating and drying the support, thereby
supporting the metal on the support.

[0016]

The catalyst is preferably calcined after supporting
25 the alkali metal compound on the alumina support. This

enables the supported alkali metal compound (except alkali metal oxides) to be converted into an alkali metal oxide.

[0017]

The calcination may be performed in an atmosphere of oxidizing gas, reducing gas, or inert gas, and it may be done in multiple stages by combining them. Examples of the oxidizing gas and the inert gas include the same gases as those provided as examples for the heat treatment of the alumina support described above. The reducing gas as used herein means a gas containing a reducing substance and examples thereof include hydrogen-containing gas, carbon monoxide-containing gas, and hydrocarbon-containing gas. Among them, nitrogen gas, oxygen gas, air, or a mixture gas of nitrogen gas and oxygen gas is preferred.

The calcination temperature is preferably 500 to 900°C, more preferably 550 to 700°C. The calcination time is preferably 0.5 to 48 hours, more preferably 2 to 24 hours.

[0018]

The catalyst is preferably dried before calcination. Removal of water by rapid heating like calcination possibly makes a supported alkali metal compound move together with water during movement of the water from the inside of the alumina support and, as a result, the supported state of the alkali metal compound is possibly rendered uneven. By drying the catalyst previous to calcination to remove water

to a moderate degree before the calcination, it is possible to suppress the movement of the alkali metal compound during the calcination to thereby render the supporting state of the catalyst even.

5 A conventionally known method may be employed as the drying method. The drying temperature is normally about from room temperature to 100°C, and the pressure is normally 0.001 to 1 MPa, preferably the atmospheric pressure. The drying may be performed in an air atmosphere
10 or in an atmosphere of inert gas such as nitrogen gas, helium gas, argon gas, and carbon dioxide. These atmospheres may contain water vapor.

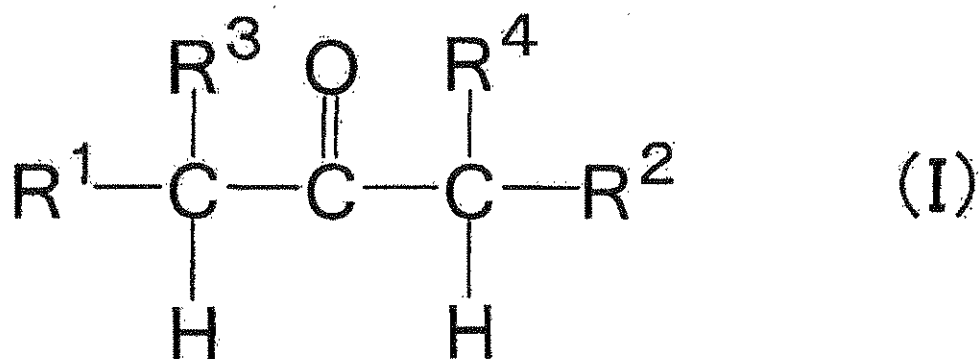
[0019]

 In the production method of the present invention, the
15 acetylene compound is produced by isomerizing an allene compound in a mixture containing an allene compound and carbon dioxide in the presence of the catalyst described above.

[0020]

20 The mixture containing an allene compound and carbon dioxide is not particularly limited and is preferably one obtained by dehydration reaction of a ketone compound. The ketone compound is not particularly limited and examples thereof include ketone compounds represented by following
25 Formulae (I) and (II).

[0021]



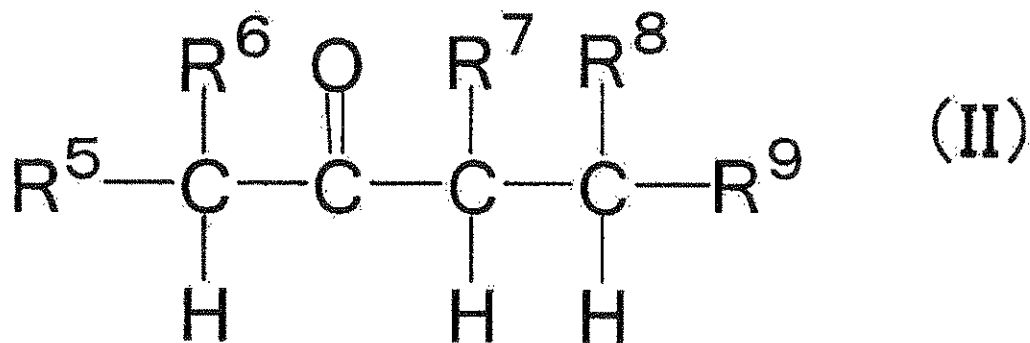
[0022]

In Formula (I), R¹, R², R³, and R⁴ each independently
5 denote a hydrogen atom, an alkylcycloalkyl group having 4
to 10 carbon atoms, or a phenyl group; or R¹ and R² are
combined together to form a ring having 5 to 15 carbon
atoms together with a carbon atom to which R¹ is bonded, a
carbon atom to which R² is bonded, and a carbon atom of a
10 carbonyl group, and R³ and R⁴ each independently denote a
hydrogen atom, an alkyl group having 1 to 6 carbon atoms, a
cycloalkyl group having 3 to 6 carbon atoms, an
alkylcycloalkyl group having 4 to 10 carbon atoms, a
cycloalkylalkyl group having 4 to 10 carbon atoms, an
15 aralkyl group having 7 to 10 carbon atoms, or a phenyl
group; or R¹ and R³ each independently denote a hydrogen
atom, an alkyl group having 1 to 6 carbon atoms, an
alkylcycloalkyl group having 4 to 10 carbon atoms, a

cycloalkylalkyl group having 4 to 10 carbon atoms, or an
aralkyl group having 7 to 10 carbon atoms, or a phenyl
group, and R² and R⁴ are combined together to form a ring
having 3 to 13 carbon atoms together with a carbon atom to
5 which R² and R⁴ are bonded; or

R¹ and R³ are combined together to form a ring having
3 to 13 carbon atoms together with a carbon atom to which
R¹ and R³ are bonded, and R² and R⁴ are combined together to
form a ring having 3 to 13 carbon atoms together with a
10 carbon atom to which R² and R⁴ are bonded.

[0023]



[0024]

In Formula (II),

15 R⁵, R⁶, R⁷, R⁸, and R⁹ each independently denote a
hydrogen atom, an alkyl group having 1 to 6 carbon atoms, a
cycloalkyl group having 3 to 6 carbon atoms, an
alkylcycloalkyl group having 4 to 10 carbon atoms, a
cycloalkylalkyl group having 4 to 10 carbon atoms, an

aralkyl group having 7 to 10 carbon atoms, or a phenyl group; or R^5 , R^6 , and R^7 each independently denote a hydrogen atom, an alkyl group having 1 to 6 carbon atoms, a cycloalkyl group having 3 to 6 carbon atoms, an alkylcycloalkyl group having 4 to 10 carbon atoms, a cycloalkylalkyl group having 4 to 10 carbon atoms, an aralkyl group having 7 to 10 carbon atoms, or a phenyl group, and R^8 and R^9 are combined together to form a ring having 3 to 13 carbon atoms together with a carbon atom to which R^8 and R^9 are bonded; or R^5 and R^6 are combined together to form a ring having 3 to 13 carbon atoms together with a carbon atom to which R^5 and R^6 are bonded, R^7 denote a hydrogen atom, an alkyl group having 1 to 6 carbon atoms, a cycloalkyl group having 3 to 6 carbon atoms, an alkylcycloalkyl group having 4 to 10 carbon atoms, a cycloalkylalkyl group having 4 to 10 carbon atoms, an aralkyl group having 7 to 10 carbon atoms, or a phenyl group, and R^8 and R^9 each independently denote a cycloalkyl group having 3 to 6 carbon atoms, an alkylcycloalkyl group having 4 to 10 carbon atoms, a cycloalkylalkyl group having 4 to 10 carbon atoms, an aralkyl group having 7 to 10 carbon atoms, or a phenyl group; or R^5 and R^6 are combined together to form a ring having 3 to 13 carbon atoms together with a carbon atom to which R^5 and R^6 are bonded, R^7 denote a hydrogen atom, an alkyl group having 1 to 6

carbon atoms, a cycloalkyl group having 3 to 6 carbon atoms, an alkylcycloalkyl group having 4 to 10 carbon atoms, a cycloalkylalkyl group having 4 to 10 carbon atoms, an aralkyl group having 7 to 10 carbon atoms, or a phenyl group, and R⁸ and R⁹ are combined together to form a ring having 3 to 13 carbon atoms together with a carbon atom to which R⁸ and R⁹ are bonded.

[0025]

In the ketone compounds (I) and (II), examples of the alkyl group having 1 to 6 carbon atoms include a methyl group, an ethyl group, a propyl group, a butyl group, a pentyl group, and a hexyl group. The alkyl group having 3 to 6 carbon atoms includes all structural isomers. For example, the propyl group includes an n-propyl group and an isopropyl group, and the butyl group includes an n-butyl group, an isobutyl group, a sec-butyl group, and a tert-butyl group.

[0026]

In the ketone compounds (I) and (II), examples of the cycloalkyl group having 3 to 6 carbon atoms include a cyclopropyl group, a cyclobutyl group, a cyclopentyl group, and a cyclohexyl group.

[0027]

In the ketone compounds (I) and (II), examples of the alkylcycloalkyl group having 4 to 10 carbon atoms include a

methylcyclopropyl group, a methylcyclobutyl group, a methylcyclopentyl group, a methylcyclohexyl group, a methylcyclooctyl group, an ethylcyclohexyl group, a trimethylcyclohexyl group, and an ethylcyclooctyl group.

5 [0028]

In the ketone compounds (I) and (II), examples of the cycloalkylalkyl group having 4 to 10 carbon atoms include a cyclopropylmethyl group, a cyclobutylmethyl group, a cyclopentylmethyl group, a cyclohexylmethyl group, a cyclooctylmethyl group, a cyclohexylethyl group, and a cyclooctylethyl group.

[0029]

In the ketone compounds (I) and (II), examples of the aralkyl group having 7 to 10 carbon atoms include a benzyl group, a phenethyl group, a trimethyl group, and a phenylbutyl group.

[0030]

In the ketone compound (I), when R^1 and R^2 are combined together to form a ring having 5 to 15 carbon atoms together with a carbon atom to which R^1 is bonded, a carbon atom to which R^2 is bonded, and a carbon atom of a carbonyl group, the ring is preferably a 5 to 15 membered alicyclic hydrocarbon ring, more preferably a 5 to 8 membered alicyclic hydrocarbon ring. Examples of the ring having 5-15 carbon atoms include a cyclopentane ring, a

cyclohexane ring, a cyclooctane ring, and a cyclopentdecane ring.

[0031]

In the ketone compound (I), when R^2 and R^4 are
5 combined together to form a ring having 3 to 13 carbon
atoms together with a carbon atom to which R^2 and R^4 are
bonded or when R^1 and R^3 are combined together to form a
ring having 3 to 13 carbon atoms together with a carbon
atom to which R^1 and R^3 are bonded, the ring having 3 to 13
10 carbon atoms is preferably a 3 to 13 membered alicyclic
hydrocarbon ring, more preferably a 3 to 8 membered
alicyclic hydrocarbon ring. Examples of the ring having 3
to 13 carbon atoms include a cyclopropane ring, a
cyclobutane ring, a cyclopentane ring, a cyclohexane ring,
15 a cyclooctane ring, and a cyclotridecane ring.

[0032]

When R^1 , R^2 , R^3 , and R^4 each independently denote a
hydrogen atom, an alkylcycloalkyl group having 4 to 10
carbon atoms, or a phenyl group, examples of the ketone
20 compound (I) include acetone and 1,3-diphenyl-2-propanone.

[0033]

When R^1 and R^2 are combined together to form a ring
having 5 to 15 carbon atoms together with a carbon atom to
which R^1 is bonded, a carbon atom to which R^2 is bonded,
25 and a carbon atom to which those carbon atoms are bonded,

and R^3 and R^4 each independently denote a hydrogen atom, an alkyl group having 1 to 6 carbon atoms, a cycloalkyl group having 3 to 6 carbon atoms, an alkylcycloalkyl group having 4 to 10 carbon atoms, a cycloalkylalkyl group having 4 to 10 carbon atoms, an aralkyl group having 7 to 10 carbon atoms, or a phenyl group, examples of the ketone compound (I) include cyclopentanone and cyclohexanone, cyclooctanone. [0034]

When R^1 and R^3 each independently denote a hydrogen atom, an alkyl group having 1 to 6 carbon atoms, an alkylcycloalkyl group having 4 to 10 carbon atoms, a cycloalkylalkyl group having 4 to 10 carbon atoms, an aralkyl group having 7 to 10 carbon atoms, or a phenyl group, and R^2 and R^4 are combined together to form a ring having 3 to 13 carbon atoms together with a carbon atom to which R^2 and R^4 are bonded, examples of the ketone compound (I) include 1-cyclopropylethanone, 1-cyclopropyl-1-propanone, and 1-cyclohexyl-1-propanone.

[0035]

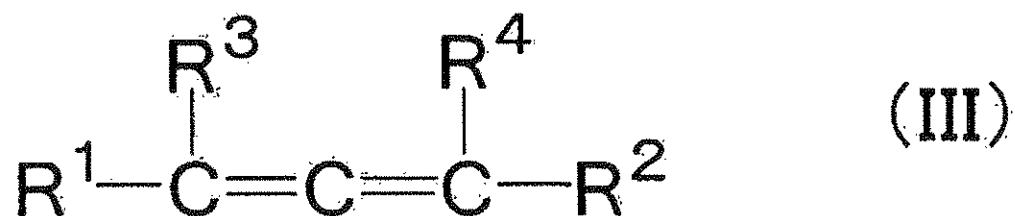
When R^1 and R^3 are combined together to form a ring having 3 to 13 carbon atoms together with a carbon atom to which R^1 and R^3 are bonded, and R^2 and R^4 are combined together to form a ring having 3 to 13 carbon atoms together with a carbon atom to which R^2 and R^4 are bonded, examples of the ketone compound (I) include

dicyclopropylketone and dicyclohexylketone.

[0036]

By subjecting the ketone compound (I) to dehydration reaction, an allene represented by the following Formula (III) is obtained.

[0037]



[0038]

In the formula, R¹, R², R³, and R⁴ individually express the same meanings as the above.

[0039]

In the ketone compound (II), when R⁸ and R⁹ are combined together to form a ring having 3 to 13 carbon atoms together with a carbon atom to which R⁸ and R⁹ are bonded or when R⁵ and R⁶ are combined together to form a ring having 3 to 13 carbon atoms together with a carbon atom to which R⁵ and R⁶ are bonded, the ring having 3 to 13 carbon atoms is preferably a 3 to 13 membered alicyclic hydrocarbon ring, more preferably a 3 to 8 membered alicyclic hydrocarbon ring. Examples of the ring having 3

to 13 carbon atoms include a cyclopropane ring, a cyclobutane ring, a cyclopentane ring, a cyclohexane ring, a cyclooctane ring, and a cyclotridecane ring.

[0040]

5 When R^5 , R^6 , R^7 , R^8 , and R^9 each independently denote a hydrogen atom, an alkyl group having 1 to 6 carbon atoms, a cycloalkyl group having 3 to 6 carbon atoms, an alkylcycloalkyl group having 4 to 10 carbon atoms, a cycloalkylalkyl group having 4 to 10 carbon atoms, an
10 aralkyl group having 7 to 10 carbon atoms, or a phenyl group, examples of the ketone compound (II) include 2-butanone, 2-pentanone, 3-pentanone, 3-methyl-2-butanone, 4-methyl-2-pentanone, 4-methyl-3-pentanone, 2,5-dimethyl-3-hexanone, 5-cyclohexyl-4-methyl-3-hexanone, and 3-methyl-4-
15 phenyl-2-butanone.

[0041]

 When R^5 , R^6 , and R^7 each independently denote a hydrogen atom, an alkyl group having 1 to 6 carbon atoms, a cycloalkyl group having 3 to 6 carbon atoms, an
20 alkylcycloalkyl group having 4 to 10 carbon atoms, a cycloalkylalkyl group having 4 to 10 carbon atoms, an aralkyl group having 7 to 10 carbon atoms, or a phenyl group, and R^8 and R^9 are combined together to form a ring having 3 to 13 carbon atoms together with a carbon atom to
25 which R^8 and R^9 are bonded, examples of the ketone compound

(II) include 1-cyclopropyl-2-propanone and 1-cyclohexyl-2-propanone.

[0042]

When R^5 and R^6 are combined together to form a ring
5 having 3 to 13 carbon atoms together with a carbon atom to
which R^5 and R^6 are bonded, R^7 denote a hydrogen atom, an
alkyl group having 1 to 6 carbon atoms, a cycloalkyl group
having 3 to 6 carbon atoms, an alkylcycloalkyl group having
4 to 10 carbon atoms, a cycloalkylalkyl group having 4 to
10 10 carbon atoms, an aralkyl group having 7 to 10 carbon
atoms, or a phenyl group, and R^8 and R^9 each independently
denote a cycloalkyl group having 3 to 6 carbon atoms, an
alkylcycloalkyl group having 4 to 10 carbon atoms, a
cycloalkylalkyl group having 4 to 10 carbon atoms, an
15 aralkyl group having 7 to 10 carbon atoms, or a phenyl
group, examples of the ketone compound (II) include 1-
cyclohexyl-2,3,3-triphenyl-1-propanone.

[0043]

When R^5 and R^6 are combined together to form a ring
20 having 3 to 13 carbon atoms together with a carbon atom to
which R^5 and R^6 are bonded, R^7 denote a hydrogen atom, an
alkyl group having 1 to 6 carbon atoms, a cycloalkyl group
having 3 to 6 carbon atoms, an alkylcycloalkyl group having
4 to 10 carbon atoms, a cycloalkylalkyl group having 4 to
25 10 carbon atoms, an aralkyl group having 7 to 10 carbon

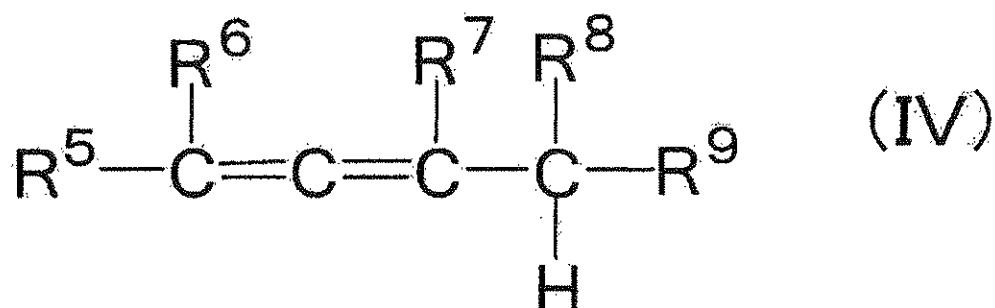
atoms, or a phenyl group, and R⁸ and R⁹ are combined together to form a ring having 3 to 13 carbon atoms together with a carbon atom to which R⁸ and R⁹ are bonded, examples of the ketone compound (II) include 1,2-

5 dicyclohexylethanone.

[0044]

By subjecting the ketone compound (II) to dehydration reaction, an allene represented by the following Formula (IV) is obtained.

10 [0045]



[0046]

In the formula, R⁵, R⁶, R⁷, and R⁸ individually express the same meanings as the above.

15 [0047]

Among them, acetone, 2-butanone, 2-pentanone, and 3-pentanone are preferable, and particularly acetone is advantageously employed in the production method of the present invention.

20 For example, if acetone is used as the ketone compound,

a reaction mixture containing propadiene and methylacetylene as its main ingredients is obtained as a result of dehydration reaction of acetone. The reaction mixture contains a small amount of unreacted acetone, water, carbon dioxide, a dimer of propadiene and a dimer of methylacetylene as byproducts, and the like. A mixture containing propadiene and carbon dioxide obtained by purifying this reaction mixture may be used as a starting material of the production method of the present invention.

[0048]

Dehydration reaction of a ketone compound is preferably carried out in the presence of a predetermined catalyst. The reaction temperature is preferably about 200 to 1200°C, and the pressure is preferably about 0.001 to 5 MPa.

Examples of the reaction system of dehydration reaction include a fixed bed system, a fluidized bed system, a moving bed system, and the like. Among them, the fixed bed system and the fluidized bed system are preferred. In the case of employing the fixed bed system, the ketone compound feed rate is normally about 1 to 20000h⁻¹ when expressed by a feed rate (L/h: in terms of 0°C, 1 atm.) of ketone compound per catalyst 1L, i.e., gas hourly space velocity (GHSV). A catalyst used in this dehydration reaction is preferably a catalyst containing silicon and at

least one selected from the group consisting of alkali metal elements and alkaline earth metal elements. Examples of such a catalyst include a catalyst in which a compound containing an alkali metal element (e.g., halides, oxides, hydroxides, silicates, etc., of alkali metal elements) is carried on a silica-containing support.

[0049]

The reaction mixture obtained by dehydration reaction is properly purified and thereafter is usable, for isomerization described later, as the mixture containing an allene compound and carbon dioxide obtained as a result of dehydration reaction of a ketone compound. The purification may be carried out by distillation, for example, to thereby achieve a reduction in the content of impurities such as carbon dioxide relative to the allene compound in the obtained mixture.

[0050]

The content of carbon dioxide relative to the allene compound in the mixture is preferably 0.0001 to 5 wt%, more preferably 0.0001 to 1 wt%, even more preferably 0.0001 to 0.1 wt%, most preferably 0.0001 to 0.01 wt%, with the total of the allene compound and carbon dioxide being 100 wt%.

[0051]

Isomerization of the allene compound in the mixture may be performed by either a semibatch system or a

continuous system as long as the system is a type of feeding the allene compound and carbon dioxide into a reactor loaded with a catalyst. It is preferred from the viewpoint of productivity to perform isomerization by the continuous system. The temperature for isomerization is normally -30 to 600°C, preferably 0 to 350°C, more preferably 0 to 200°C.

The pressure during the reaction is preferably 0.1 to 20 MPa.

The reaction system may be any flow system of the fixed bed system, the moving bed system, and the fluidized bed system, and the fixed bed flow system is preferred. The reactor for the fixed bed flow system is a reactor of a type of holding a granular catalyst by a predetermined member. The catalyst may be used solely or may be used diluted or mixed with a substance substantially inert to the reaction.

[0052]

In the case of performing isomerization by the continuous system, an inert gas or an oxidizing gas may be fed together with feedstock. The inert gas and the oxidizing gas have been described earlier. It is preferred in the continuous system reaction that isomerization is performed by employing the fixed bed system in liquid-phase or gas-phase conditions for example.

Weight hourly space velocity (WHSV) that is a feed rate of allene compound per catalyst weight is preferably 0.001 to 10000h^{-1} , more preferably 0.001 to 1000h^{-1} , most preferably 0.005 to 500h^{-1} .

5 [0053]

A diluent may be used in isomerization. Examples of the diluent include aliphatic hydrocarbons such as methane, ethane, propane, butane, pentane, hexane, octane, and propylene; alicyclic hydrocarbons such as cyclopentane and
10 cyclohexane; aromatic hydrocarbons such as benzene, toluene, and xylene; aprotic polar solvents such as N,N-dimethylformamide and N,N-dimethylacetamide; and the like, and as necessary, two or more of them may be used. Among them, aliphatic hydrocarbons are preferable, and propane or
15 propylene is more preferable.

[0054]

In the production method of the present invention, the amount of catalyst used is such that the amount of an alkali metal element contained in the catalyst is 10 molar
20 times or more the amount (the number of moles) of carbon dioxide fed per hour. If less than 10 molar times, it becomes difficult for isomerization to proceed at high efficiency. The amount of catalyst used is such that the amount of an alkali metal element contained in the catalyst
25 is preferably 20 molar times or more, more preferably 100

molar times or more the amount (the number of moles) of carbon dioxide fed per hour. The upper limit is properly set depending on the amount of carbon dioxide and allene compound to be fed. For example, it is set to 1000000

5 molar times or less.

[0055]

Post-treatment operations after reaction are properly selected. For example, an operation such as distillation may be performed so that an acetylene compound and an allene compound can be separated from each other.

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For example, if propadiene is used as the allene compound, methylacetylene is obtained as the acetylene compound. The obtained methylacetylene is preferably used as a raw material for producing a methacrylic acid ester for example. The methacrylic acid ester is obtained by reacting methylacetylene with carbon monoxide and alcohol in the presence of a catalyst comprising a Group 10 metal compound, a protonic acid, and a phosphine compound. This reaction may be achieved in accordance with a method described in JP-A-2010-120921, for example. Examples of a preferred embodiment include a mode of producing methyl methacrylate by using methanol as alcohol.

15

20

EXAMPLES

[0056]

25

The present invention will now be described

specifically based on examples and comparative examples,
but the present invention is not limited to these examples.

[0057]

<Catalyst Preparation>

5 Preparation Example 1

A spherical γ -alumina (2.0 to 4.0 mm sphere) was used
as a support. This support was heat-treated in an air
atmosphere at 500°C for 16 hours. The heat-treated γ -
alumina was brought into contact with a solution containing
10 an alkali metal compound. Specifically, 22.70 g of heat-
treated γ -alumina was brought into contact with an aqueous
solution in which 5.68 g of potassium carbonate (K_2CO_3 :
manufactured by WAKO PURE CHEMICAL INDUSTRIES, LTD.) is
dissolved in 10.36 g of pure water, to impregnate the heat-
15 treated γ -alumina with the aqueous solution. This contact
treatment was carried out in an air atmosphere (23°C, under
atmospheric pressure).

[0058]

The potassium-carbonate-supporting γ -alumina obtained
20 by the contact treatment was then dried (air-dried) for 15
hours or more in an air atmosphere (0 to 30°C, under
atmospheric pressure). After drying, the potassium-
carbonate-supporting γ -alumina was crushed and sized into
16 to 32 mesh granules. This granular γ -alumina was held
25 and calcined at 620°C for 6 hours under nitrogen gas flow.

The temperature was raised from room temperature (24°C) up to 620°C over 1 hour. In this manner, a potassium-supporting γ -alumina catalyst (A) was obtained.

The potassium supporting amount of the obtained catalyst (A) was calculated by ICP analysis using an ICP emission spectrometer (ICPS-8100: manufactured by Shimadzu Corporation). The potassium supporting amount per 1 g catalyst (A) was 2.56 mmol.

[0059]

<Catalytic Activity Testing>

Example 1

Methylacetylene (MA) was synthesized by isomerizing propadiene (PD) using a fixed bed flow reactor. 1.22 g of the catalyst (A) obtained in the preparation example 1 was loaded into a stainless steel (SUS) reaction tube with an outer diameter of 10 mm and an inner diameter of 8 mm. The amount of potassium in the catalyst loaded into the reaction tube was 3.12 mmol. Quartz wool was loaded on top of and under the catalyst bed and, in order to reduce the liquid residence time within the reaction tube, 2 mm dia glass beads were further loaded on top of and under the quartz wool. Liquefied propadiene (carbon dioxide concentration: approx. 400 wt.ppm) pressurized with 24°C, 1.5 MPaG nitrogen pressure was fed at 12.2 g/h through the inlet port of the reaction tube. The reaction was

performed in a liquid phase under 24°C, 0.8 to 1.2 MPaG pressure conditions. (Weight hourly space velocity (WHSV) = 10 h⁻¹). In this reaction, the amount of carbon dioxide fed per hour was 0.11 mmol, and the amount of potassium in the catalyst loaded into the reaction tube was 28-fold moles.

After the lapse of 0 hours, 1 hour, and 2 hours from the start of reaction, a reaction liquid from the outlet port of the reaction tube was sampled and analyzed by gas chromatography, to find a propadiene (PD) conversion and a methylacetylene (MA) selectivity from equations which follow. The results are shown in table 1.

The reaction liquid after 0 hours from the start of reaction refers to a reaction liquid first generated through the outlet port of the reaction tube.

[0060]

PD conversion (%) = (number of moles of reacted PD/number of moles of fed PD)×100

MA selectivity (%) = (number of moles of generated MA/number of moles of reacted PD)×100

[0061]

Example 2

The catalytic activity testing was carried out using the same method as in the example 1, with the exception that propadiene with an approximately 100 wt.ppm carbon

dioxide concentration was fed into the reaction tube at the rate of 12.4 g/h. In this reaction, the amount of carbon dioxide fed per hour was 0.028 mmol, and the amount of potassium in the catalyst loaded into the reaction tube was 111-fold moles. The results are shown in table 1.

[0062]

Comparative Example 1

The catalytic activity testing was carried out using the same method as in the example 1, with the exception that 1.21 g of the catalyst (A) was used and that propadiene with an approximately 5900 wt.ppm carbon dioxide concentration was fed into the reaction tube at the rate of 12.4 g/h. In this reaction, the amount of potassium in the catalyst loaded into the reaction tube was 3.10 mmol, and the amount of carbon dioxide fed per hour was 1.66 mmol, with the result that the amount of potassium in the catalyst loaded into the reaction tube was 1.9-fold moles. The results are shown in table 1.

[0063]

Comparative Example 2

The catalytic activity testing was carried out using the same method as in the example 1, with the exception that propadiene with an approximately 2200 wt.ppm carbon dioxide concentration was fed into the reaction tube at the rate of 12.5 g/h. In this reaction, the amount of carbon

dioxide fed per hour was 0.63 mmol, and the amount of potassium in the catalyst loaded into the reaction tube was 5.0-fold moles. The results are shown in table 1.

[0064]

5 Comparative Example 3

The catalytic activity testing was carried out using the same method as in the example 1, with the exception that 1.23 g of the catalyst (A) was used and that propadiene with an approximately 1300 wt.ppm carbon dioxide
10 concentration was fed into the reaction tube at the rate of 12.3 g/h. In this reaction, the amount of potassium in the catalyst loaded into the reaction tube was 3.15 mmol, and the amount of carbon dioxide fed per hour was 0.36 mmol, with the result that the amount of potassium in the
15 catalyst loaded into the reaction tube was 8.8-fold moles. The results are shown in table 1.

[0065]

[Table 1]

	Amount of Potassium relative to CO ₂ Flowrate (mmol-K/mmol-CO ₂ /h)	Time on Stream (h)	PD Conversion (%)	MA Selectivity (%)
Example 1	28	0	91.6	100
		1	82.3	100
		2	47.5	100
Example 2	111	0	91.6	100
		1	92.2	100
		2	92.1	100
Comparative Example 1	1.9	0	2.8	100
		1	0.1	100
		2	0.1	100
Comparative Example 2	5.0	0	62.9	100
		1	5.3	100
		2	1.9	100
Comparative Example 3	8.8	0	90.5	100
		1	18.3	100
		2	2.7	100

[0066]

As is apparent from Table 1, Examples 1 and 2 using the catalyst in an amount as much as the amount of the alkali metal element is 10 molar times or more the amount (the number of moles) of carbon dioxide fed per hour maintain a high PD conversion (i.e., maintain a high catalytic activity) even after a lapse of 2 hours from the start of reaction, so that methylacetylene is produced with a high efficiency.

It can be seen on the other hand that Comparative Examples 1 to 3 using a catalyst in an amount less than 10 molar times have significantly reduced PD conversions and cannot maintain the catalytic activity as the time on

stream becomes longer.

[0067]

Reference Example 1: Synthesis of Methylacetylene (Propyne) and Propadiene from Acetone

5 A catalyst was first prepared. Silica spheres (manufactured by FUJI SILYSIACHEMICAL LTD., Q50: 1.7 to 4.0 mm sphere) were used as a support. 32.6 g of this support was brought into contact with a solution in which 0.71 g of potassium hydroxide (KOH: manufactured by WAKO PURE
10 CHEMICAL INDUSTRIES, LTD.) was dissolved in 32.6 g of pure water, to impregnate the silica sphere with the solution. The support was then dried (air-dried) for 15 hours or more in an air atmosphere (20 to 30°C, under atmospheric pressure). After drying, it was held and calcined at 200°C
15 for 2 hours under air flow. The temperature was raised from room temperature (24°C) up to 200°C over 0.5 hours. The calcined material was pulverized and classified into a 0.85 to 1.4 mm grain diameter, to obtain a catalyst.

 The obtained catalyst was loaded into the reaction
20 tube. More specifically, a quartz reaction tube (14 mm in inner diameter) having equipped with a thermometer sheath tube having an outer diameter of 4 mm is loaded with, in order from the bottom, quartz wool as partition agents, SiC (7.1 mL), quartz wool, the catalyst (2.4 g (6.2 mL)),
25 quartz wool, and SiC (12.7 mL).

[0068]

The interior pressure of the reaction tube loaded with the catalyst was then reduced to 0.01 MPa or below using a diaphragm pump, while feeding nitrogen gas through the inlet port of the reaction tube at the rate of 2.7 mL/min.

Thereafter, the reaction tube was heated in an electric furnace to raise the temperature of the reaction tube.

Acetone (manufactured by WAKO PURE CHEMICAL INDUSTRIES, LTD.) was fed through the inlet port of the reaction tube using a pump and gasified to start a reaction under 0.008 MPa reaction pressure (acetone gas flowrate: 25.6 mL/min, acetone feed rate: 0.069 mol/h, acetone concentration in feed gas: 90.5 vol%). The ratio (GHSV) of total gas flow rate to catalyst volume was 257 h^{-1} .

[0069]

After the start of the reaction, the temperature of the catalyst bed was kept at $598 \pm 4^\circ\text{C}$. At the lapse of 60 minutes from the start of the reaction, outlet gas from the reactor was sampled by a gas-tight syringe. The sampled gas was analyzed with a gas chromatography having an FID detector. After filling the outlet gas from the reactor into a sampling loop, the gas was subjected to an online analysis with the gas chromatography having a TCD detector, to thereby quantify each of products.

A SUS trap connected to the reaction tube outlet port was cooled in an ethanol/dry ice bath to condense acetone and high-boiling components. The resultant condensate was analyzed with the gas chromatography having an FID detector, to quantify acetone and high-boiling components.

[0070]

The acetone conversion was found by the following equation.

$$\text{Acetone conversion (\%)} = [b/(a+b)] \times 100$$

a: acetone flow rate (mol/h) in reactor outlet gas

b: production rate (mol/h) of total product in reactor outlet gas

The selectivity (%) to each product was found by the following equation. The unit of the production rate is mol per hour.

$$\text{Selectivity (\%)} = (\text{production rate of each product} / \text{production rate of total product}) \times 100$$

The product contained methylacetylene, propadiene, methane, isobutylene, 2-methyl-1-penten-3-yne, 2-hexen-4-yne, 4-methyl-3-penten-2-one, 4-methyl-4-penten-2-one, 2-methylfuran, methylcyclopentadiene, 3,5,5-trimethyl-2-cyclohexen-1-one, phenol, methylphenol, 3,5-dimethylphenol, and carbon dioxide.

[0071]

In Reference Example 1 synthesizing methylacetylene

and propadiene from acetone, the conversion of acetone was 24.6%, and the selectivities to methylacetylene, propadiene, and carbon dioxide were 67.7%, 22.0%, and 0.8%, respectively.

5 INDUSTRIAL APPLICABILITY

[0072]

According to the present invention, the catalytic activity can stably be maintained even in the condition that carbon dioxide is present, and an allene compound is isomerized at a high conversion, so that acetylene compound can stably be produced with favorable selectivity.

CLAIMS

1. A method of producing an acetylene compound by isomerizing an allene compound in a mixture containing the allene compound and carbon dioxide in the presence of a catalyst in which an alkali metal compound is supported on an alumina support, wherein the catalyst is used in an amount as much as the amount of the alkali metal element contained in the catalyst is 10 molar times or more the number of moles of the carbon dioxide fed per hour.
2. The method according to claim 1, wherein the mixture is a mixture obtained by dehydration reaction of a ketone compound.
3. The method according to claim 2, wherein the ketone compound is acetone.
4. The method according to any one of claims 1 to 3, wherein the catalyst is a catalyst obtained by subjecting the alumina support to a contact treatment with a solution containing the alkali metal compound and then calcining the support.
5. The method according to any one of claims 1 to 4,

wherein the alkali metal compound is at least one compound selected from the group consisting of potassium compounds and cesium compounds.

5 6. The method according to any one of claims 1 to 5,
wherein the allene compound is propadiene, and the
acetylene compound is methylacetylene.

7. A method of producing a methacrylic acid ester,
10 comprising:

reacting methylacetylene produced by the method
according to claim 6 with carbon monoxide and an alcohol in
the presence of a catalyst comprising a Group 10 metal
compound, a protonic acid, and a phosphine compound.

15