

DESCRIPTION

METHOD FOR PRODUCING COMPOUND HAVING
ACETYLENIC BOND AND/OR DIENE

5 Technical Field

The present invention relates to a method for producing compound having acetylenic bond and/or diene.

10 Background Art

A compound having acetylenic bond is useful as a starting material for producing alkyl methacrylates for example, and, for example, there has been known a method for producing an alkyl methacrylate in which
15 carbon monoxide and an alcohol compound are reacted with propyne in the presence of a catalyst (for example, Patent Document 1). Further, diene, which is represented by butadiene, is useful as a starting material for producing synthetic rubbers, for example,
20 there has been known a method for producing a diene based polymer rubber in which butadiene and styrene are copolymerized (for example, Patent Document 2).

A method for producing compound having acetylenic bond and/or diene has been known a method
25 in which, for example, a compound having acetylenic

bond such as propyne, and diene such as propadiene and butadiene are obtained as by-products together with ethylene and propylene in an olefin production system (steam cracking) by thermal decomposition of naphtha. That is, in a method in which naphtha is introduced into a thermal cracking furnace together with steam and the obtained hydrocarbons are rapidly cooled and then introduced into a rectifying column to afford tar from a column bottom, gas oil from a column side, and hydrocarbons from a column top, a compound having acetylenic bond and diene are obtained as by-products as a part of the column top fraction.

However, a compound having acetylenic bond and diene are the by-products in steam cracking and thus the amount supplied varies depending on the working situation of a naphtha thermal decomposition plant, thereby raising a concern about unstable supply. To address this, there is a demand for a technique for producing a compound having acetylenic bond and diene except by the steam cracking.

Under these circumstances, as a method for producing compound having acetylenic bond and/or diene, for example, Patent Documents 3 and 4 disclose a method for producing propyne from 1,2-dichloropropane in the presence of a catalyst of iron

oxide and nickel oxide supported on activated carbon
or of a catalyst of a calcined iron hydroxide
supported on activated carbon, and Patent Document
5 discloses a method for producing propadiene and
propyne from acetone in the presence of an alumina
catalyst or of a catalyst of platinum, chromium oxide,
or a rare earth element supported on alumina, and
Patent Document 6 discloses a method for producing
butadiene by oxidative dehydrogenation of butene in
10 the presence of a complex oxide catalyst.

Citation List

- Patent Document 1: JP-A-No. 2007-269707
- Patent Document 2: JP-A-No. 2003-246816
- 15 • Patent Document 3: East German Patent Application
Publication No. 240740
- Patent Document 4: East German Patent Application
Publication No. 240741
- Patent Document 5: US Patent No. 4301319
- 20 • Patent Document 6: JP-A-No. 2012-77076

Summary of Invention

Technical Problem

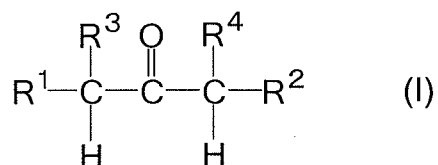
In view of the above circumstances, an object of
25 the present invention is to provide a novel method for

producing a method for producing compound having acetylenic bond and/or diene.

Solution to Problem

5 Under these circumstances, the present inventors have carried out intensive studies in order to solve the problems and, as a result, have completed the invention. That is, the present invention includes the following aspects.

- 10 (1) A method for producing compound having acetylenic bond and/or diene, in which at least one compound selected from the group consisting of the following compounds of formula (I), (II), (III), (IV) and (V) is dehydrated in the presence of a catalyst of at
- 15 least one selected from the group consisting of a compound containing a group 1 metallic element, a compound containing a group 2 metallic element, a group 1 metallic element, and a group 2 metallic element, supported on a carrier containing silica:
- 20 Compound represented by formula (I) (hereinafter, it may be abbreviated as "ketone compound (I).)



(wherein, in the formula, R^1 , R^2 , R^3 and R^4 each independently represent hydrogen atom, alkylcycloalkyl group having 4-10 carbon atoms or phenyl group; or

R^1 and R^2 , together with carbon atom to which they are

5 bonded, and also with carbon atom which those carbon atom are bonded, to form a ring having 5-15 carbon atoms, and R^3 and R^4 each independently represent

hydrogen atom, alkyl group having 1-6 carbon atoms,

cycloalkyl group having 3-6 carbon atoms,

10 alkylcycloalkyl group having 4-10 carbon atoms,

cycloalkylalkyl group having 4-10 carbon atoms,

aralkyl group having 7-10 carbon atoms or phenyl group; or

R^1 and R^3 each independently represent hydrogen atom,

15 alkyl group having 1-6 carbon atoms, alkylcycloalkyl group having 4-10 carbon atoms, cycloalkylalkyl group

having 4-10 carbon atoms, aralkyl group having 7-10

carbon atoms or phenyl group, and R^2 and R^4 , together

with carbon atom to which they are bonded, to form a

20 ring having 3-13 carbon atoms; or

R^1 and R^3 , together with carbon atom to which they are

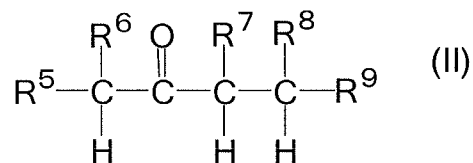
bonded, to form a ring having 3-13 carbon atoms, and

R^2 and R^4 , together with carbon atom to which they are

bonded, to form a ring having 3-13 carbon atoms);

25 Compound represented by formula (II) (hereinafter, it

may be abbreviated as "ketone compound (II).)



(wherein, in the formula, R⁵, R⁶, R⁷, R⁸ and R⁹ each independently represent hydrogen atom, alkyl group having 1-6 carbon atoms, cycloalkyl group having 3-6 carbon atoms, alkylcycloalkyl group having 4-10 carbon atoms, cycloalkylalkyl group having 4-10 carbon atoms, aralkyl group having 7-10 carbon atoms or phenyl group; or

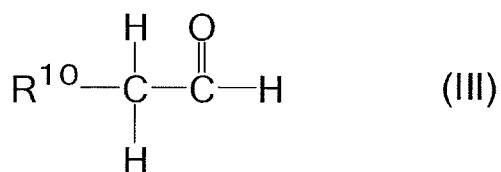
R⁵, R⁶ and R⁷ each independently represent hydrogen atom, alkyl group having 1-6 carbon atoms, cycloalkyl group having 3-6 carbon atoms, alkylcycloalkyl group having 4-10 carbon atoms, cycloalkylalkyl group having 4-10 carbon atoms, aralkyl group having 7-10 carbon atoms or phenyl group, and R⁸ and R⁹, together with carbon atom to which they are bonded, to form a ring having 3-13 carbon atoms; or

R⁵ and R⁶, together with carbon atom to which they are bonded, to form a ring having 3-13 carbon atoms, and R⁷ represents hydrogen atom, alkyl group having 1-6 carbon atoms, cycloalkyl group having 3-6 carbon atoms, alkylcycloalkyl group having 4-10 carbon atoms, cycloalkylalkyl group having 4-10 carbon atoms,

aralkyl group having 7-10 carbon atoms or phenyl group, and R⁸ and R⁹ each independently represent cycloalkyl group having 3-6 carbon atoms, alkylcycloalkyl group having 4-10 carbon atoms, 5 cycloalkylalkyl group having 4-10 carbon atoms, aralkyl group having 7-10 carbon atoms or phenyl group; or

R⁵ and R⁶, together with carbon atom to which they are bonded, to form a ring having 3-13 carbon atoms, and 10 R⁷ represents hydrogen atom, alkyl group having 1-6 carbon atoms, cycloalkyl group having 3-6 carbon atoms, alkylcycloalkyl group having 4-10 carbon atoms, cycloalkylalkyl group having 4-10 carbon atoms, aralkyl group having 7-10 carbon atoms or phenyl 15 group, and R⁸ and R⁹, together with carbon atom to which they are bonded, to form a ring having 3-13 carbon atoms);

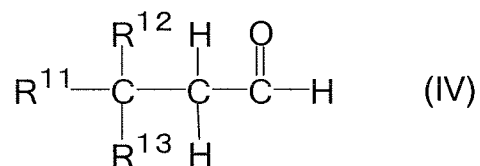
Compound represented by formula (III) (hereinafter, it may be abbreviated as "aldehyde compound (III).)



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(wherein, in the formula, R¹⁰ represents hydrogen atom or phenyl group);

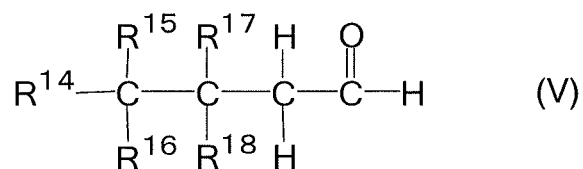
Compound represented by formula (IV) (hereinafter, it may be abbreviated as "aldehyde compound (IV).)



(wherein, in the formula, R^{11} , R^{12} and R^{13} each independently represent hydrogen atom or phenyl group; or

R^{11} and R^{12} , together with carbon atom to which they are bonded, to form a ring having 3-13 carbon atoms, and R^{13} represents hydrogen atom, alkyl group having 1-6 carbon atoms, cycloalkyl group having 3-6 carbon atoms, alkylcycloalkyl group having 4-10 carbon atoms, cycloalkylalkyl group having 4-10 carbon atoms, aralkyl group having 7-10 carbon atoms or phenyl group); and

Compound represented by formula (V) (hereinafter, it may be abbreviated as "aldehyde compound (V).)



(wherein, in the formula, R^{14} , R^{15} , R^{16} , R^{17} and R^{18} each independently represent hydrogen atom, alkyl group having 1-6 carbon atoms, cycloalkyl group having 3-6 carbon atoms, alkylcycloalkyl group having

4-10 carbon atoms, cycloalkylalkyl group having 4-10 carbon atoms, aralkyl group having 7-10 carbon atoms or phenyl group; or

5 R^{14} and R^{15} , together with carbon atom to which they are bonded, to form a ring having 3-13 carbon atoms, and R^{16} , R^{17} and R^{18} each independently represent hydrogen atom, alkyl group having 1-6 carbon atoms, cycloalkyl group having 3-6 carbon atoms, alkylcycloalkyl group having 4-10 carbon atoms, 10 cycloalkylalkyl group having 4-10 carbon atoms, aralkyl group having 7-10 carbon atoms or phenyl group).

(2) The production method according to the aspect (1), in which the catalyst is a catalyst of at least one 15 selected from the group consisting of a compound containing a group 1 metallic element and a group 1 metallic element, supported on the carrier containing silica.

(3) The production method according to the aspect 20 (2), in which the catalyst is a catalyst of a compound containing a group 1 metallic element supported on the carrier containing silica and the compound containing a group 1 metallic element is at least one compound selected from the group consisting of a halide of a 25 group 1 metallic element, a carbonate of a group 1

metallic element, an oxide of a group 1 metallic element, a hydroxide of a group 1 metallic element, and a silicate of a group 1 metallic element.

(4) The production method according to the aspect
5 (3), in which the group 1 metallic element is sodium, potassium, rubidium, or cesium.

(5) The production method according to any one of the aspects (1) to (4), in which the compound represented by formula (I) is acetone.

10 (6) The production method according to any one of the aspects (1) to (5), in which the compound represented by formula (II) is 2-butanone.

(7) The production method according to any one of the aspects (1) to (6), in which the compound
15 represented by formula (IV) is propanal.

(8) The production method according to any one of the aspects (1) to (7), in which the carrier is composed of silica.

20 Advantageous Effects of Invention

The present invention can provide a novel method for producing compound having acetylenic bond and/or diene.

25 Description of Embodiments

The present invention will be described in detail hereinbelow. The catalyst used in the production method of the present invention is a catalyst of at least one [hereinafter, also referred to as a metal

5 component] selected from the group consisting of a compound containing a group 1 metallic element, a compound containing a group 2 metallic element, a group 1 metallic element, and a group 2 metallic element, supported on a carrier containing silica.

10 Among at least one selected from the group consisting of a compound containing a group 1 metallic element, a compound containing a group 2 metallic element, a group 1 metallic element, and a group 2 metallic element, from the viewpoint of obtaining a compound

15 having acetylenic bond and/or diene at high selectivity, at least one selected from the group consisting of a compound containing a group 1 metallic element and a group 1 metallic element is preferred and a compound containing a group 1 metallic element is more preferred.

20 Examples of the compound containing a group 1 metallic element include a lithium compound, a sodium compound, a potassium compound, a rubidium compound, and a cesium compound. Among them, from the viewpoint of obtaining a compound having

25 acetylenic bond and/or diene at high selectivity, a

sodium compound, a potassium compound, a rubidium compound, and a cesium compound are preferred. Among the compounds containing a group 1 metallic element, a halide of a group 1 metallic element, a carbonate of a group 1 metallic element, an oxide of a group 1 metallic element, a hydroxide of a group 1 metallic element, and a silicate of a group 1 metallic element are preferred, and a halide of a group 1 metallic element, an oxide of a group 1 metallic element, a hydroxide of a group 1 metallic element, and a silicate of a group 1 metallic element are more preferred. Among the halides of a group 1 metallic element, a chloride of a group 1 metallic element is preferred.

Examples of the lithium compound include a lithium halide such as lithium fluoride (LiF), lithium chloride (LiCl), lithium bromide (LiBr), and lithium iodide (LiI); an oxoacid salt such as lithium carbonate (Li_2CO_3), lithium hydrogen carbonate (LiHCO_3), lithium sulfate (Li_2SO_4), lithium hydrogen sulfate (LiHSO_4), lithium sulfite (Li_2SO_3), lithium hydrogen sulfite (LiHSO_3), lithium nitrate (LiNO_3), lithium nitrite (LiNO_2), lithium thiosulfate ($\text{Li}_2\text{S}_2\text{O}_3$), lithium silicate ($\text{Li}_2\text{O} \cdot n\text{SiO}_2$, $n=1-4$ (molar ratio)), trilithium phosphate (Li_3PO_4), lithium borate (Li_3BO_3), lithium hypochlorite

(LiClO), lithium chlorite (LiClO₂), lithium chlorate (LiClO₃), and lithium perchlorate (LiClO₄); an oxide and a hydroxide such as lithium oxide (Li₂O), lithium peroxide (Li₂O₂), and lithium hydroxide (LiOH); an
5 organic acid salt such as lithium acetate (CH₃COOLi) and lithium citrate; lithium hydride (LiH); lithium sulfide (Li₂S); lithium hydrogen sulfide (lithium hydrosulfide) (LiHS); and lithium borohydride (LiBH₄). When a corresponding hydrate is present, such a
10 hydrate may also be used. As necessary, two or more of these compounds may also be used.

Examples of the sodium compound include a sodium halide such as sodium fluoride (NaF), sodium chloride (NaCl), sodium bromide (NaBr), and sodium
15 iodide (NaI); an oxoacid salt such as sodium carbonate (Na₂CO₃), sodium hydrogen carbonate (NaHCO₃), sodium sulfate (Na₂SO₄), sodium hydrogen sulfate (NaHSO₄), sodium sulfite (Na₂SO₃), sodium hydrogen sulfite (NaHSO₃), sodium nitrate (NaNO₃), sodium
20 nitrite (NaNO₂), sodium thiosulfate (Na₂S₂O₃), sodium silicate (Na₂O · nSiO₂, n=1-4 (molar ratio)), trisodium phosphate (Na₃PO₄), sodium borate (Na₃BO₃), sodium hypochlorite (NaClO), sodium chlorite (NaClO₂), sodium chlorate (NaClO₃), and sodium perchlorate (NaClO₄); an
25 oxide and a hydroxide such as sodium oxide (Na₂O),

sodium peroxide (Na_2O_2), and sodium hydroxide (NaOH); an organic acid salt such as sodium acetate (CH_3COONa) and sodium citrate; sodium hydride (NaH); sodium sulfide (Na_2S); sodium hydrogen sulfide (sodium hydrosulfide) (NaHS); and sodium borohydride (NaBH_4). When a corresponding hydrate is present, such a hydrate may also be used. As necessary, two or more of these compounds may also be used.

Examples of the potassium compound include a potassium halide such as potassium fluoride (KF), potassium chloride (KCl), potassium bromide (KBr), and potassium iodide (KI); an oxoacid salt such as potassium carbonate (K_2CO_3), potassium hydrogen carbonate (KHCO_3), potassium sulfate (K_2SO_4), potassium hydrogen sulfate (KHSO_4), potassium sulfite (K_2SO_3), potassium hydrogen sulfite (KHSO_3), potassium nitrate (KNO_3), potassium nitrite (KNO_2), potassium thiosulfate ($\text{K}_2\text{S}_2\text{O}_3$), potassium silicate ($\text{K}_2\text{O} \cdot n\text{SiO}_2$, $n=1-4$ (molar ratio)), tripotassium phosphate (K_3PO_4), potassium borate (K_3BO_3), potassium hypochlorite (KClO), potassium chlorite (KClO_2), potassium chlorate (KClO_3), and potassium perchlorate (KClO_4); an oxide and a hydroxide such as potassium oxide (K_2O), potassium peroxide (K_2O_2), and potassium hydroxide (KOH); an organic acid salt such

as potassium acetate (CH_3COOK) and potassium citrate; potassium hydride (KH); potassium sulfide (K_2S); potassium hydrogen sulfide (potassium hydrosulfide) (KHS); and potassium borohydride (KBH_4).

5 When a corresponding hydrate is present, such a hydrate may also be used. As necessary, two or more of these compounds may also be used.

Examples of the rubidium compound include a rubidium halide such as rubidium fluoride (RbF),
10 rubidium chloride (RbCl), rubidium bromide (RbBr), and rubidium iodide (RbI); an oxoacid salt such as rubidium carbonate (Rb_2CO_3), rubidium hydrogen carbonate (RbHCO_3), rubidium sulfate (Rb_2SO_4), rubidium hydrogen sulfate (RbHSO_4), rubidium sulfite
15 (Rb_2SO_3), rubidium hydrogen sulfite (RbHSO_3), rubidium nitrate (RbNO_3), rubidium nitrite (RbNO_2), rubidium thiosulfate ($\text{Rb}_2\text{S}_2\text{O}_3$), rubidium silicate ($\text{Rb}_2\text{O} \cdot n\text{SiO}_2$, $n=1-4$ (molar ratio)), trirubidium phosphate (Rb_3PO_4), rubidium borate (Rb_3BO_3),
20 rubidium hypochlorite (RbClO), rubidium chlorite (RbClO_2), rubidium chlorate (RbClO_3), and rubidium perchlorate (RbClO_4); an oxide and a hydroxide such as rubidium oxide (Rb_2O), rubidium peroxide (Rb_2O_2), and rubidium hydroxide (RbOH); an organic acid salt such
25 as rubidium acetate (CH_3COORb) and rubidium citrate;

rubidium hydride (RbH); rubidium sulfide (Rb_2S); rubidium hydrogen sulfide (rubidium hydrosulfide) (RbHS); and rubidium borohydride (RbBH_4). When a corresponding hydrate is present, such a hydrate may also be used. As necessary, two or more of these compounds may also be used.

Examples of the cesium compound include a cesium halide such as cesium fluoride (CsF), cesium chloride (CsCl), cesium bromide (CsBr), and cesium iodide (CsI); an oxoacid salt such as cesium carbonate (Cs_2CO_3), cesium hydrogen carbonate (CsHCO_3), cesium sulfate (Cs_2SO_4), cesium hydrogen sulfate (CsHSO_4), cesium sulfite (Cs_2SO_3), cesium hydrogen sulfite (CsHSO_3), cesium nitrate (CsNO_3), cesium nitrite (CsNO_2), cesium thiosulfate ($\text{Cs}_2\text{S}_2\text{O}_3$), cesium silicate ($\text{Cs}_2\text{O} \cdot n\text{SiO}_2$, $n=1-4$ (molar ratio)), tricesium phosphate (Cs_3PO_4), cesium borate (Cs_3BO_3), cesium hypochlorite (CsClO), cesium chlorite (CsClO_2), cesium chlorate (CsClO_3), and cesium perchlorate (CsClO_4); an oxide and a hydroxide such as cesium oxide (Cs_2O), cesium peroxide (Cs_2O_2), and cesium hydroxide (CsOH); an organic acid salt such as cesium acetate (CH_3COOCs) and cesium citrate; cesium hydride (CsH); cesium sulfide (Cs_2S); cesium hydrogen sulfide (cesium hydrosulfide) (CsHS); and cesium borohydride (CsBH_4).

When a corresponding hydrate is present, such a hydrate may also be used. As necessary, two or more of these compounds may also be used.

Examples of the compound containing a group 2
5 metallic element include a magnesium compound, a calcium compound, a strontium compound, and a barium compound. Among them, a barium compound is preferred.

Examples of the magnesium compound include a
10 magnesium halide such as magnesium fluoride (MgF_2), magnesium chloride (MgCl_2), magnesium bromide (MgBr_2), and magnesium iodide (MgI_2); an oxoacid salt such as magnesium carbonate (MgCO_3), magnesium sulfate (MgSO_4), magnesium sulfite (MgSO_3),
15 magnesium nitrate ($\text{Mg}(\text{NO}_3)_2$), magnesium nitrite ($\text{Mg}(\text{NO}_2)_2$), magnesium thiosulfate (MgS_2O_3), magnesium silicate ($\text{MgO} \cdot n\text{SiO}_2$, $n=1-4$ (molar ratio)), magnesium phosphate (MgHPO_4), and magnesium borate (MgB_2O_4); an oxide and a hydroxide such as
20 magnesium oxide (MgO), magnesium peroxide (MgO_2), and magnesium hydroxide ($\text{Mg}(\text{OH})_2$); an organic acid salt such as magnesium acetate ($\text{Mg}(\text{CH}_3\text{COO})_2$) and magnesium citrate; magnesium hydride (MgH_2); and magnesium sulfide (MgS). When a corresponding
25 hydrate is present, such a hydrate may also be used.

As necessary, two or more of these compounds may also be used.

Examples of the calcium compound include a calcium halide such as calcium fluoride (CaF_2),
5 calcium chloride (CaCl_2), calcium bromide (CaBr_2), and calcium iodide (CaI_2); an oxoacid salt such as calcium carbonate (CaCO_3), calcium sulfate (CaSO_4), calcium sulfite (CaSO_3), calcium nitrate ($\text{Ca}(\text{NO}_3)_2$), calcium nitrite ($\text{Ca}(\text{NO}_2)_2$), calcium thiosulfate (CaS_2O_3),
10 calcium silicate ($\text{CaO} \cdot n\text{SiO}_2$, $n=1-4$ (molar ratio)), calcium phosphate (CaHPO_4), and calcium borate (CaB_2O_4); an oxide and a hydroxide such as calcium oxide (CaO), calcium peroxide (CaO_2), and calcium hydroxide ($\text{Ca}(\text{OH})_2$); an organic acid salt such as
15 calcium acetate ($\text{Ca}(\text{CH}_3\text{COO})_2$) and calcium citrate; calcium hydride (CaH_2); and calcium sulfide (CaS). When a corresponding hydrate is present, such a hydrate may also be used. As necessary, two or more of these compounds may also be used.

20 Examples of the strontium compound include a strontium halide such as strontium fluoride (SrF_2), strontium chloride (SrCl_2), and strontium bromide (SrBr_2), and strontium iodide (SrI_2); an oxoacid salt such as strontium carbonate (SrCO_3), strontium sulfate
25 (SrSO_4), strontium sulfite (SrSO_3), strontium nitrate

($\text{Sr}(\text{NO}_3)_2$), strontium nitrite ($\text{Sr}(\text{NO}_2)_2$), strontium thiosulfate (SrS_2O_3), strontium silicate ($\text{SrO} \cdot n\text{SiO}_2$, $n=1-4$ (molar ratio)), strontium phosphate (SrHPO_4), and strontium borate (SrB_2O_4); an oxide and a
5 hydroxide such as strontium oxide (SrO), strontium peroxide (SrO_2), and strontium hydroxide ($\text{Sr}(\text{OH})_2$); an organic acid salt such as strontium acetate ($\text{Sr}(\text{CH}_3\text{COO})_2$) and strontium citrate; strontium hydride (SrH_2); and strontium sulfide (SrS). When a
10 corresponding hydrate is present, such a hydrate may also be used. As necessary, two or more of these compounds may also be used.

Examples of the barium compound include a barium halide such as barium fluoride (BaF_2), barium
15 chloride (BaCl_2), barium bromide (BaBr_2), and barium iodide (BaI_2); an oxoacid salt such as barium carbonate (BaCO_3), barium sulfate (BaSO_4), barium sulfite (BaSO_3), barium nitrate ($\text{Ba}(\text{NO}_3)_2$), barium nitrite ($\text{Ba}(\text{NO}_2)_2$), barium thiosulfate (BaS_2O_3), barium
20 silicate ($\text{BaO} \cdot n\text{SiO}_2$, $n=1-4$ (molar ratio)), barium phosphate (BaHPO_4), and barium borate (BaB_2O_4); an oxide and a hydroxide such as barium oxide (BaO), barium peroxide (BaO_2), and barium hydroxide ($\text{Ba}(\text{OH})_2$); an organic acid salt such as barium acetate
25 ($\text{Ba}(\text{CH}_3\text{COO})_2$) and barium citrate; barium hydride

(BaH₂); and barium sulfide (BaS). When a corresponding hydrate is present, such a hydrate may also be used. As necessary, two or more of these compounds may also be used.

5 In the catalyst in which a group 1 metallic element is supported, examples of the group 1 metallic element include lithium, sodium, potassium, rubidium, and cesium, and among them, sodium, potassium, rubidium, and cesium are preferred. In the catalyst in
10 which a group 2 metallic element is supported, examples of the group 2 metallic element include magnesium, calcium, strontium, and barium, and among them, barium is preferred.

 In the catalyst, a carrier containing silica is used.
15 The carrier may include an oxide such as titania, zirconia, niobium oxide, and tin oxide in addition to silica. The carrier may be a carrier containing silica alone, namely a carrier composed of silica, may be a composite oxide composed of silica and another oxide
20 than silica, and may be a mixture of silica and another oxide than silica. A carrier composed of silica is particularly preferred.

 In the catalyst, examples of the method for supporting a metal component on the carrier
25 containing silica include impregnating, coprecipitating,

and kneading. The catalyst can be prepared, for example, by supporting a metal component on a carrier by impregnating, coprecipitating, kneading, or the like, followed by heat treatment at 50°C to 1,000°C. The supported metal component may be oxidized to be used as a supported oxide. The supported metal component may be reduced to be used as a supported metal catalyst. The oxidation is performed, for example, by supporting a metal component on a carrier, followed by calcining the metal component in an oxidizing gas atmosphere. The oxidizing gas is a gas containing an oxidizing substance and examples of the oxidizing gas include a gas containing oxygen. The oxygen concentration is commonly about 1 to 30% by volume. As the oxygen source, air or pure oxygen is typically used and such a gas is diluted with an inert gas, as necessary. Among the oxidizing gases, air is preferred. The calcining temperature during the oxidation is commonly 100 to 1,000°C and preferably 200 to 800°C. The reduction is performed, for example, by supporting a metal component on a carrier, followed by calcining the metal component in a reducing gas atmosphere. The reducing gas is a gas containing a reducing substance and examples of the reducing gas include a gas containing hydrogen, a gas containing carbon

monoxide, and a gas containing a hydrocarbon. The concentration of hydrogen, carbon monoxide, or a hydrocarbon is commonly about 1 to 30% by volume and is adjusted, for example, with an inert gas or water vapor. Among the reducing gases, a gas containing hydrogen and a gas containing carbon monoxide are preferred. The calcining temperature during the reduction is commonly 100 to 1,000°C and preferably 200 to 800°C.

The amount of a metal component supported in the catalyst is 0.01 to 30% by weight, preferably 0.1 to 20% by weight, and more preferably 0.1 to 15% by weight, in terms of weight of a metallic element with respect to the total amount of the catalyst. When two or more metallic elements are contained, the total amount of metallic elements may be within the range in the catalyst.

The catalyst has a BET specific surface area of 1 to 800 m²/g and preferably 1 to 400 m²/g. A catalyst having a BET specific surface area of less than 1 m²/g may reduce the degree of dispersion of a supported metal component, while a catalyst having a BET specific surface area of more than 800 m²/g may have a reduced thermal stability. Here, the BET specific surface area is determined using a specific surface

area analyzer based on nitrogen adsorption method.

The catalyst has a pore volume of 0.05 to 2.5 ml/g and preferably 0.1 to 1.5 ml/g. A catalyst having a pore volume of less than 0.05 ml/g may have an
5 excessively small pore diameter, and this may reduce the activity. A catalyst having a pore volume of more than 2.5 ml/g may lead to reduction in the strength of a carrier, and this may readily deteriorate the catalyst. The pore volume is determined by mercury intrusion
10 method.

The catalyst is preferably used as a molded material. Examples of the molded shape include a spherical granular shape, a column shape, a pellet shape, an extrusion shape, a ring shape, a honeycomb
15 shape, and a granular shape having a moderate size by pulverization and classification after shape forming. The shape of the molded material is selected depending on a reaction manner to be used. For example, a molded material used as the catalyst for a fixed bed
20 reaction may have any shape among the various shapes above. At the time, the molded material preferably has a diameter of 5 mm or less. A molded material having an excessively large diameter may reduce the conversion rate of the dehydration. The lower limit of
25 the molded material diameter is not specifically limited,

but an excessively small diameter increases pressure loss in a catalyst layer, and hence a compact having a diameter of 0.5 mm or more is commonly used. A molded material used as the catalyst for a fluidized bed reaction or a moving bed reaction preferably has a spherical particle shape having an average particle diameter of about 1-1000 μm , especially for the fluidized bed reaction, has a spherical particle shape having an average particle diameter of about 10-500 μm . Here, the molded material diameter means the diameter of a sphere in a spherical granular shape, the diameter of a circular cross section in a column shape, and the maximum diameter of a cross section in other shapes.

At least one compound selected from the group consisting of ketone compound (I), ketone compound (II), aldehyde compound (III), aldehyde compound (IV) and aldehyde compound (V), in the presence of the supported catalyst are dehydrated.

In ketone compound (I), ketone compound (II), aldehyde compound (III), aldehyde compound (IV) and aldehyde compound (V), as alkyl group having 1-6 carbon atoms, for example, methyl group, ethyl group, propyl group, butyl group, pentyl group, and hexyl group can be given. Further, alkyl group having 3-6

carbon atoms includes all structural isomers. For example, propyl group includes n-propyl group and isopropyl group, butyl group includes n-butyl group, isobutyl group, secondary butyl group and tertiary butyl group.

In ketone compound (I), ketone compound (II), aldehyde compound (III), aldehyde compound (IV) and aldehyde compound (V), as cycloalkyl group having 3-6 carbon atoms, for example, cyclopropyl group, cyclobutyl group, cyclopentyl group and cyclohexyl group can be given.

In ketone compound (I), ketone compound (II), aldehyde compound (III), aldehyde compound (IV) and aldehyde compound (V), as alkylcycloalkyl group having 4-10 carbon atoms, for example, methylcyclopropyl group, methylcyclobutyl group, methylcyclopentyl group and methylcyclohexyl group, methylcyclooctyl group, ethylcyclohexyl group, trimethylcyclohexyl group and ethylcyclooctyl group can be given.

In ketone compound (I), ketone compound (II), aldehyde compound (III), aldehyde compound (IV) and aldehyde compound (V), as cycloalkylalkyl group having 4-10 carbon atoms, for example, cyclopropylmethyl group, cyclobutylmethyl group

cyclopentylmethyl group and cyclohexylmethyl group, cyclooctylmethyl group, cyclohexylmethyl group and cyclooctylethyl group can be given.

5 In the ketone compound (I), ketone compound (II), aldehyde compound (III), aldehyde compound (IV) and aldehyde compound (V), as aralkyl group having 7-10 carbon atoms, for example, benzyl group, phenethyl group, trimethyl group and phenylbutyl group can be given.

10 In the ketone compound (I), in case that R^1 and R^2 , together with carbon atom to which they are bonded, and also with carbon atom which those carbon atom are bonded, form a ring having 5-15 carbon atoms, the ring is preferably alicyclic hydrocarbon of 5-15
15 membered ring, more preferably alicyclic hydrocarbon of 5-8 membered ring. As 5-15 membered ring, for example, cyclopentane ring, cyclohexane ring, cyclooctane ring and cyclopentadecane ring can be given.

20 In the ketone compound (I), in each of both case that R^2 and R^4 , together with carbon atom to which they are bonded, form a ring having 3-13 carbon atoms, and R^1 and R^3 , together with carbon atom to which they are bonded, form a ring having 3-13 carbon atoms,
25 the ring having 3-13 carbon atoms is preferably

alicyclic hydrocarbon of 3-13 membered ring, more preferably alicyclic hydrocarbon of 3-8 membered ring. As for 3-13 membered ring, for example, such as cyclopropane ring, cyclobutane ring, cyclopentane ring and cyclohexane ring, cyclooctane ring and cyclotridecane ring can be given.

In case that R^1 , R^2 , R^3 and R^4 each independently represent hydrogen atom, alkylcycloalkyl group having 4-10 carbon atoms or phenyl group, as the ketone compound (I), for example, such as acetone and 1,3-diphenyl-2-propanone can be given.

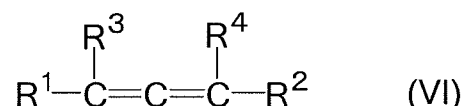
In case that R^1 and R^2 , together with carbon atom to which they are bonded, and also with carbon atom which those carbon atom are bonded, form a ring having 5-15 carbon atoms, and R^3 and R^4 each independently represent hydrogen atom, alkyl group having 1-6 carbon atoms, cycloalkyl group having 3-6 carbon atoms, alkylcycloalkyl group having 4-10 carbon atoms, cycloalkylalkyl group having 4-10 carbon atoms, aralkyl group having 7-10 carbon atoms or phenyl group, as the ketone compound (I), for example, such as cyclopentanone, cyclohexane and cyclooctanone can be given.

In case that R^1 and R^3 each independently represent hydrogen atom, alkyl group having 1-6

carbon atoms, alkylcycloalkyl group having 4-10 carbon atoms, cycloalkylalkyl group having 4-10 carbon atoms, aralkyl group having 7-10 carbon atoms or phenyl group, and R^2 and R^4 , together with carbon atom to which they are bonded, form a ring having 3-13 carbon atoms, as the ketone compound (I), for example, such as 1-cyclopropylethanone, 1-cyclopropyl-1-propanone and 1-cyclohexyl-1-propanone can be given.

In case that R^1 and R^3 , together with carbon atom to which they are bonded, form a ring having 3-13 carbon atoms, and R^2 and R^4 , together with carbon atom to which they are bonded, form a ring having 3-13 carbon atoms, as the ketone compound (I), for example, such as dicyclopropylketone and dicyclohexylketone can be given.

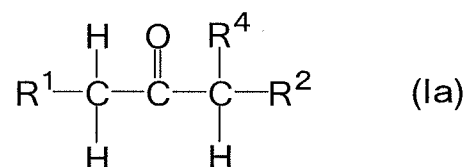
Diene represented by the following formula (VI) can be obtained by dehydrating the ketone compound (I):



(wherein, in the formula, R^1 , R^2 , R^3 and R^4 have the abovementioned meanings).

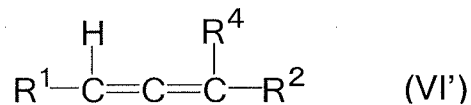
Furthermore, in case that, in the ketone compound (I), R^3 is hydrogen atom, that is, the ketone

compound (I) can be represented by the formula (Ia), diene represented by the following formula (VI') and/or compound having acetylenic bond represented by the following formula (VII) can be obtained:



- 5 (wherein, in the formula, R^1 , R^2 and R^4 each independently represent hydrogen atom, alkylcycloalkyl group having 4-10 carbon atoms or phenyl group; or R^1 and R^2 , together with carbon atom to which they are bonded, and also with carbon atom which those carbon
- 10 atom are bonded, to form a ring having 5-15 carbon atoms, and R^4 represents hydrogen atom, alkyl group having 1-6 carbon atoms, cycloalkyl group having 3-6 carbon atoms, alkylcycloalkyl group having 4-10 carbon atoms, cycloalkylalkyl group having 4-10
- 15 carbon atoms, aralkyl group having 7-10 carbon atoms or phenyl group; or R^1 represents hydrogen atom, alkyl group having 1-6 carbon atoms, alkylcycloalkyl group having 4-10 carbon atoms, cycloalkylalkyl group having 4-10
- 20 carbon atoms, aralkyl group having 7-10 carbon atoms or phenyl group, and R^2 and R^4 , together with carbon atom to which they are bonded, to form a ring having

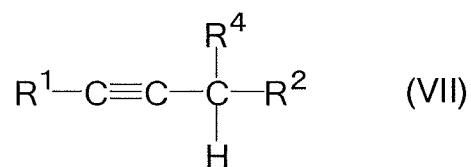
3-13 carbon atoms);



(wherein, in the formula, R^1 , R^2 and R^4 each independently represent hydrogen atom, alkylcycloalkyl group having 4-10 carbon atoms or phenyl group; or

5 R^1 and R^2 , together with carbon atom to which they are bonded, and also with carbon atom which those carbon atom are bonded, to form a ring having 5-15 carbon atoms, and R^4 represents hydrogen atom, alkyl group having 1-6 carbon atoms, cycloalkyl group having 3-6
10 carbon atoms, alkylcycloalkyl group having 4-10 carbon atoms, cycloalkylalkyl group having 4-10 carbon atoms, aralkyl group having 7-10 carbon atoms or phenyl group; or

R^1 represents hydrogen atom, alkyl group having 1-6
15 carbon atoms, alkylcycloalkyl group having 4-10 carbon atoms, cycloalkylalkyl group having 4-10 carbon atoms, aralkyl group having 7-10 carbon atoms or phenyl group, and R^2 and R^4 , together with carbon atom to which they are bonded, to form a ring having
20 3-13 carbon atoms); and



(wherein, in the formula, R^1 , R^2 and R^4 each independently represent hydrogen atom, alkylcycloalkyl group having 4-10 carbon atoms or phenyl group; or

R^1 and R^2 , together with carbon atom to which they are
5 bonded, and also with carbon atom which those carbon atom are bonded, to form a ring having 5-15 carbon atoms, and R^4 represents hydrogen atom, alkyl group having 1-6 carbon atoms, cycloalkyl group having 3-6 carbon atoms, alkylcycloalkyl group having 4-10
10 carbon atoms, cycloalkylalkyl group having 4-10 carbon atoms, aralkyl group having 7-10 carbon atoms or phenyl group; or

R^1 represents hydrogen atom, alkyl group having 1-6 carbon atoms, alkylcycloalkyl group having 4-10
15 carbon atoms, cycloalkylalkyl group having 4-10 carbon atoms, aralkyl group having 7-10 carbon atoms or phenyl group, and R^2 and R^4 , together with carbon atom to which they are bonded, to form a ring having 3-13 carbon atoms).

20 In case that the ketone compound (I) is acetone, the present invention can be usefully employed, because propyne and/ or propadiene can be obtained at high selectivity.

In the ketone compound (II), in each of both case
25 that R^8 and R^9 , together with carbon atom to which

they are bonded, form a ring having 3-13 carbon atoms, and R^5 and R^6 , together with carbon atom to which they are bonded, form a ring having 3-13 carbon atoms, the ring having 3-13 carbon atoms is preferably
5 alicyclic hydrocarbon of 3-13 membered ring, more preferably alicyclic hydrocarbon of 3-8 membered ring. As for 3-13 membered ring, for example, such as cyclopropane ring, cyclobutane ring, cyclopentane ring and cyclohexane ring, cyclooctane ring and
10 cyclotridecane ring can be given.

R^5 , R^6 , R^7 , R^8 and R^9 each independently represent hydrogen atom, alkyl group having 1-6 carbon atoms, cycloalkyl group having 3-6 carbon atoms, alkylcycloalkyl group having 4-10 carbon atoms,
15 cycloalkylalkyl group having 4-10 carbon atoms, aralkyl group having 7-10 carbon atoms or phenyl group, as the ketone compound (II), for example, such as 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, 3-methyl-4-phenyl-2-butanone can
20 be given.

R^5 , R^6 , and R^7 each independently represent hydrogen atom, alkyl group having 1-6 carbon atoms,
25 cycloalkyl group having 3-6 carbon atoms,

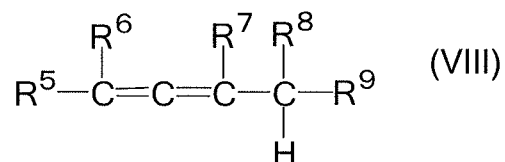
alkylcycloalkyl group having 4-10 carbon atoms,
 cycloalkylalkyl group having 4-10 carbon atoms,
 aralkyl group having 7-10 carbon atoms or phenyl
 group, and R^8 and R^9 , together with carbon atom to
 5 which they are bonded, form a ring having 3-13 carbon
 atoms, as the ketone compound (II), for example, such
 as 1-cyclopropyl-1-propanone and 1-cyclohexyl-1-
 propanone can be given.

R^5 and R^6 , together with carbon atom to which
 10 they are bonded, form a ring having 3-13 carbon atoms,
 R^7 represents hydrogen atom, alkyl group having 1-6
 carbon atoms, cycloalkyl group having 3-6 carbon
 atoms, alkylcycloalkyl group having 4-10 carbon atoms,
 cycloalkylalkyl group having 4-10 carbon atoms,
 15 aralkyl group having 7-10 carbon atoms or phenyl
 group, and R^8 and R^9 each independently represent
 cycloalkyl group having 3-6 carbon atoms,
 alkylcycloalkyl group having 4-10 carbon atoms,
 cycloalkylalkyl group having 4-10 carbon atoms,
 20 aralkyl group having 7-10 carbon atoms or phenyl
 group, as the ketone compound (II), for example, such
 as 1-cyclohexyl-2,3,3-triphenyl-1-propanone can be
 given.

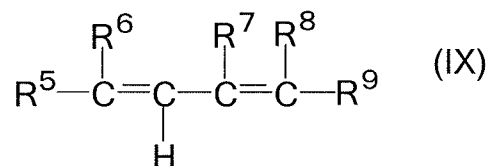
R^5 and R^6 , together with carbon atom to which
 25 they are bonded, form a ring having 3-13 carbon atoms,

R⁷ represents hydrogen atom, alkyl group having 1-6 carbon atoms, cycloalkyl group having 3-6 carbon atoms, alkylcycloalkyl group having 4-10 carbon atoms, cycloalkylalkyl group having 4-10 carbon atoms, aralkyl group having 7-10 carbon atoms or phenyl group, and R⁸ and R⁹, together with carbon atom to which they are bonded, form a ring having 3-13 carbon atoms, as the ketone compound (II), for example, such as 1,2-dicyclohexylethanone can be given.

Diene represented by the following formula (VIII) and/or formula (IX) can be obtained by dehydrating the ketone compound (II):



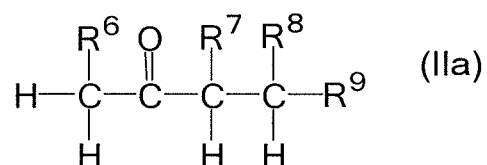
(wherein, in the formula, R⁵, R⁶, R⁷, R⁸ and R⁹ have the abovementioned meanings.); and



(wherein, in the formula, R⁵, R⁶, R⁷, R⁸ and R⁹ have the abovementioned meanings.)

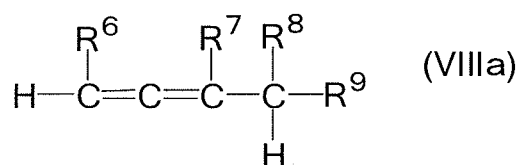
Furthermore, in case that, in the ketone compound (II), R⁵ is hydrogen atom, that is, the ketone compound (II) can be represented by the formula (IIa),

diene represented by the following formula (VIIIa), formula (IXa), and/or compound having acetylenic bond represented by the following formula (X) can be obtained:



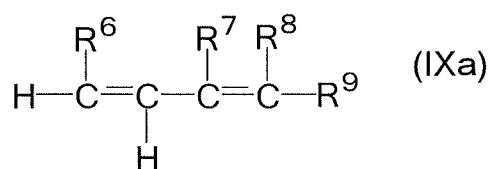
5 (wherein, in the formula, R⁶, R⁷, R⁸ and R⁹ each independently represent hydrogen atom, alkyl group having 1-6 carbon atoms, cycloalkyl group having 3-6 carbon atoms, alkylcycloalkyl group having 4-10 carbon atoms, cycloalkylalkyl group having 4-10 carbon atoms, aralkyl group having 7-10 carbon atoms or phenyl group; or

R⁶ and R⁷ each independently represent hydrogen atom, alkyl group having 1-6 carbon atoms, cycloalkyl group having 3-6 carbon atoms, alkylcycloalkyl group having 4-10 carbon atoms, cycloalkylalkyl group having 4-10 carbon atoms, aralkyl group having 7-10 carbon atoms or phenyl group, and R⁸ and R⁹, together with carbon atom to which they are bonded, form a ring having 3-13 carbon atoms);



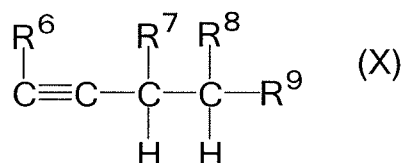
(wherein, in the formula, R^6 , R^7 , R^8 and R^9 each independently represent hydrogen atom, alkyl group having 1-6 carbon atoms, cycloalkyl group having 3-6 carbon atoms, alkylcycloalkyl group having 4-10 carbon atoms, cycloalkylalkyl group having 4-10 carbon atoms, aralkyl group having 7-10 carbon atoms or phenyl group; or

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



(wherein, in the formula, R^6 , R^7 , R^8 and R^9 each independently represent hydrogen atom, alkyl group having 1-6 carbon atoms, cycloalkyl group having 3-6 carbon atoms, alkylcycloalkyl group having 4-10 carbon atoms, cycloalkylalkyl group having 4-10 carbon atoms, aralkyl group having 7-10 carbon atoms or phenyl group; or

R⁶ and R⁷ each independently represent hydrogen atom, alkyl group having 1-6 carbon atoms, cycloalkyl group having 3-6 carbon atoms, alkylcycloalkyl group having 4-10 carbon atoms, cycloalkylalkyl group having 4-10 carbon atoms, aralkyl group having 7-10 carbon atoms or phenyl group, and R⁸ and R⁹, together with carbon atom to which they are bonded, form a ring having 3-13 carbon atoms); and

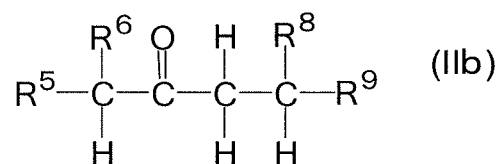


(wherein, in the formula, R⁶, R⁷, R⁸ and R⁹ each independently represent hydrogen atom, alkyl group having 1-6 carbon atoms, cycloalkyl group having 3-6 carbon atoms, alkylcycloalkyl group having 4-10 carbon atoms, cycloalkylalkyl group having 4-10 carbon atoms, aralkyl group having 7-10 carbon atoms or phenyl group; or

R⁶ and R⁷ each independently represent hydrogen atom, alkyl group having 1-6 carbon atoms, cycloalkyl group having 3-6 carbon atoms, alkylcycloalkyl group having 4-10 carbon atoms, cycloalkylalkyl group having 4-10 carbon atoms, aralkyl group having 7-10 carbon atoms or phenyl group, and R⁸ and R⁹, together with carbon atom which they are bonded, form a ring having 3-13

carbon atoms).

Furthermore, in case that, in the ketone compound (II), R^7 is hydrogen atom, that is, the ketone compound (II) can be represented by the formula (IIb),
 5 diene represented by the following formula (VIIIb), formula (IXb), and/or compound having acetylenic bond represented by the following formula (XI) can be obtained:



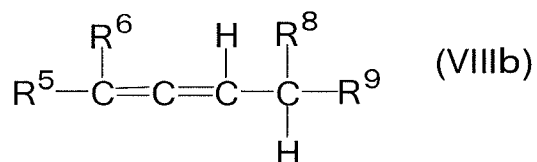
(wherein, in the formula, R^5 , R^6 , R^8 and R^9 each
 10 independently represent hydrogen atom, alkyl group having 1-6 carbon atoms, cycloalkyl group having 3-6 carbon atoms, alkylcycloalkyl group having 4-10 carbon atoms, cycloalkylalkyl group having 4-10 carbon atoms, aralkyl group having 7-10 carbon atoms
 15 or phenyl group; or

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

13 carbon atoms; or

R⁵ and R⁶, together with carbon atom to which they are bonded, form a ring having 3-13 carbon atoms, R⁸ and R⁹ each independently represent cycloalkyl group
 5 having 3-6 carbon atoms, alkylcycloalkyl group having 4-10 carbon atoms, cycloalkylalkyl group having 4-10 carbon atoms, aralkyl group having 7-10 carbon atoms or phenyl group; or

R⁵ and R⁶, together with carbon atom to which they are
 10 bonded, form a ring having 3-13 carbon atoms, and R⁸ and R⁹, together with carbon atom to which they are bonded, form a ring having 3-13 carbon atoms);



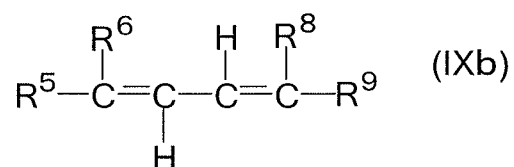
(wherein, in the formula, R⁵, R⁶, R⁸ and R⁹ each independently represent hydrogen atom, alkyl group
 15 having 1-6 carbon atoms, cycloalkyl group having 3-6 carbon atoms, alkylcycloalkyl group having 4-10 carbon atoms, cycloalkylalkyl group having 4-10 carbon atoms, aralkyl group having 7-10 carbon atoms or phenyl group; or
 20 R⁵ and R⁶ each independently represent hydrogen atom, alkyl group having 1-6 carbon atoms, cycloalkyl group having 3-6 carbon atoms, alkylcycloalkyl group having

4-10 carbon atoms, cycloalkylalkyl group having 4-10 carbon atoms, aralkyl group having 7-10 carbon atoms or phenyl group, and R⁸ and R⁹, together with carbon atom to which they are bonded, form a ring having 3-

5 13 carbon atoms; or

R⁵ and R⁶, together with carbon atom to which they are bonded, form a ring having 3-13 carbon atoms, R⁸ and R⁹ each independently represent cycloalkyl group having 3-6 carbon atoms, alkylcycloalkyl group having 4-10 carbon atoms, cycloalkylalkyl group having 4-10 carbon atoms, aralkyl group having 7-10 carbon atoms or phenyl group; or

10 R⁵ and R⁶, together with carbon atom to which they are bonded, form a ring having 3-13 carbon atoms, and R⁸ and R⁹, together with carbon atom to which they are bonded, form a ring having 3-13 carbon atoms);



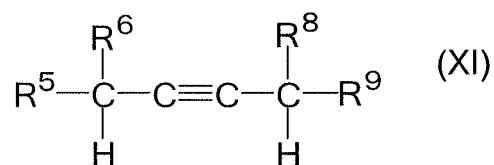
(wherein, in the formula, R⁵, R⁶, R⁸ and R⁹ each independently represent hydrogen atom, alkyl group having 1-6 carbon atoms, cycloalkyl group having 3-6 carbon atoms, alkylcycloalkyl group having 4-10 carbon atoms, cycloalkylalkyl group having 4-10 carbon atoms, aralkyl group having 7-10 carbon atoms

or phenyl group; or

R⁵ and R⁶ each independently represent hydrogen atom, alkyl group having 1-6 carbon atoms, cycloalkyl group having 3-6 carbon atoms, alkylcycloalkyl group having 4-10 carbon atoms, cycloalkylalkyl group having 4-10 carbon atoms, aralkyl group having 7-10 carbon atoms or phenyl group, and R⁸ and R⁹, together with carbon atom to which they are bonded, form a ring having 3-13 carbon atoms; or

R⁵ and R⁶, together with carbon atom to which they are bonded, form a ring having 3-13 carbon atoms, R⁸ and R⁹ each independently represent cycloalkyl group having 3-6 carbon atoms, alkylcycloalkyl group having 4-10 carbon atoms, cycloalkylalkyl group having 4-10 carbon atoms, aralkyl group having 7-10 carbon atoms or phenyl group; or

R⁵ and R⁶, together with carbon atom to which they are bonded, form a ring having 3-13 carbon atoms, and R⁸ and R⁹, together with carbon atom to which they are bonded, form a ring having 3-13 carbon atoms); and



(wherein, in the formula, R⁵, R⁶, R⁸ and R⁹ each independently represent hydrogen atom, alkyl group

having 1-6 carbon atoms, cycloalkyl group having 3-6 carbon atoms, alkylcycloalkyl group having 4-10 carbon atoms, cycloalkylalkyl group having 4-10 carbon atoms, aralkyl group having 7-10 carbon atoms or phenyl group; or

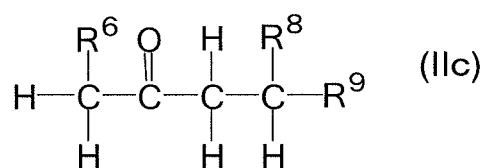
R⁵ and R⁶ each independently represent hydrogen atom, alkyl group having 1-6 carbon atoms, cycloalkyl group having 3-6 carbon atoms, alkylcycloalkyl group having 4-10 carbon atoms, cycloalkylalkyl group having 4-10 carbon atoms, aralkyl group having 7-10 carbon atoms or phenyl group, and R⁸ and R⁹, together with carbon atom to which they are bonded, form a ring having 3-13 carbon atoms; or

R⁵ and R⁶, together with carbon atom to which they are bonded, form a ring having 3-13 carbon atoms, R⁸ and R⁹ each independently represent cycloalkyl group having 3-6 carbon atoms, alkylcycloalkyl group having 4-10 carbon atoms, cycloalkylalkyl group having 4-10 carbon atoms, aralkyl group having 7-10 carbon atoms or phenyl group; or

R⁵ and R⁶, together with carbon atom to which they are bonded, form a ring having 3-13 carbon atoms, and R⁸ and R⁹, together with carbon atom to which they are bonded, form a ring having 3-13 carbon atoms).

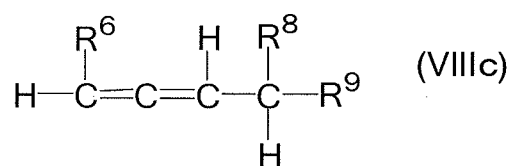
Furthermore, in case that, in the ketone

compound (II), R^5 and R^7 is hydrogen atom, that is, the ketone compound (II) can be represented by the formula (IIc), diene represented by the following formula (VIIIc), formula (IXc), and compound having
 5 acetylenic bond represented by the following formula (X') and/or formula (XI') can be obtained:



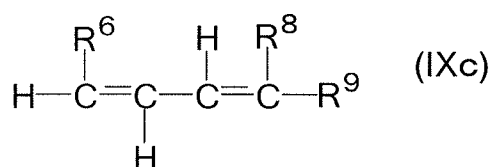
(wherein, in the formula, R^6 , R^8 and R^9 each independently represent hydrogen atom, alkyl group having 1-6 carbon atoms, cycloalkyl group having 3-6
 10 carbon atoms, alkylcycloalkyl group having 4-10 carbon atoms, cycloalkylalkyl group having 4-10 carbon atoms, aralkyl group having 7-10 carbon atoms or phenyl group; or

R^6 represents hydrogen atom, alkyl group having 1-6
 15 carbon atoms, cycloalkyl group having 3-6 carbon atoms, alkylcycloalkyl group having 4-10 carbon atoms, cycloalkylalkyl group having 4-10 carbon atoms, aralkyl group having 7-10 carbon atoms or phenyl group, and R^8 and R^9 , together with carbon atom to
 20 which they are bonded, form a ring having 3-13 carbon atoms);



(wherein, in the formula, R^6 , R^8 and R^9 each independently represent hydrogen atom, alkyl group having 1-6 carbon atoms, cycloalkyl group having 3-6 carbon atoms, alkylcycloalkyl group having 4-10 carbon atoms, cycloalkylalkyl group having 4-10 carbon atoms, aralkyl group having 7-10 carbon atoms or phenyl group; or

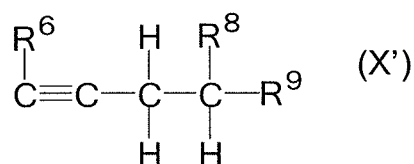
R^6 represents hydrogen atom, alkyl group having 1-6 carbon atoms, cycloalkyl group having 3-6 carbon atoms, alkylcycloalkyl group having 4-10 carbon atoms, cycloalkylalkyl group having 4-10 carbon atoms, aralkyl group having 7-10 carbon atoms or phenyl group, and R^8 and R^9 , together with carbon atom to which they are bonded, form a ring having 3-13 carbon atoms);



(wherein, in the formula, R^6 , R^8 and R^9 each independently represent hydrogen atom, alkyl group having 1-6 carbon atoms, cycloalkyl group having 3-6 carbon atoms, alkylcycloalkyl group having 4-10

carbon atoms, cycloalkylalkyl group having 4-10 carbon atoms, aralkyl group having 7-10 carbon atoms or phenyl group; or

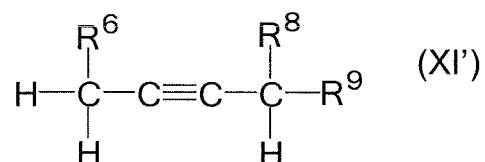
5 R^6 represents hydrogen atom, alkyl group having 1-6 carbon atoms, cycloalkyl group having 3-6 carbon atoms, alkylcycloalkyl group having 4-10 carbon atoms, cycloalkylalkyl group having 4-10 carbon atoms, aralkyl group having 7-10 carbon atoms or phenyl group, and R^8 and R^9 , together with carbon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



(wherein, in the formula, R^6 , R^8 and R^9 each independently represent hydrogen atom, alkyl group having 1-6 carbon atoms, cycloalkyl group having 3-6
15 carbon atoms, alkylcycloalkyl group having 4-10 carbon atoms, cycloalkylalkyl group having 4-10 carbon atoms, aralkyl group having 7-10 carbon atoms or phenyl group; or

R^6 represents hydrogen atom, alkyl group having 1-6
20 carbon atoms, cycloalkyl group having 3-6 carbon atoms, alkylcycloalkyl group having 4-10 carbon atoms, cycloalkylalkyl group having 4-10 carbon atoms,

aralkyl group having 7-10 carbon atoms or phenyl group, and R^8 and R^9 , together with carbon atom to which they are bonded, form a ring having 3-13 carbon atoms); and



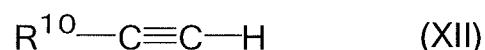
5 (wherein, in the formula, R^6 , R^8 and R^9 each independently represent hydrogen atom, alkyl group having 1-6 carbon atoms, cycloalkyl group having 3-6 carbon atoms, alkylcycloalkyl group having 4-10 carbon atoms, cycloalkylalkyl group having 4-10
10 carbon atoms, aralkyl group having 7-10 carbon atoms or phenyl group; or

R^6 represents hydrogen atom, alkyl group having 1-6 carbon atoms, cycloalkyl group having 3-6 carbon atoms, alkylcycloalkyl group having 4-10 carbon atoms, cycloalkylalkyl group having 4-10 carbon atoms, aralkyl group having 7-10 carbon atoms or phenyl group, and R^8 and R^9 , together with carbon atom to which they are bonded, form a ring having 3-13 carbon atoms).

20 In case that the ketone compound (II) is 2-butanone, the present invention can be usefully employed, because 1,3-butadiene, 1,2-butadiene, 1-

butyne and/or 2-butyne can be obtained at high selectivity.

As the aldehyde compound (III), acetaldehyde and phenylacetaldehyde can be given. A compound having
5 acetylenic bond represented by the following formula (XII) can be obtained by dehydrating the aldehyde compound (III):



(wherein, in the formula, R^{10} has the abovementioned meanings).

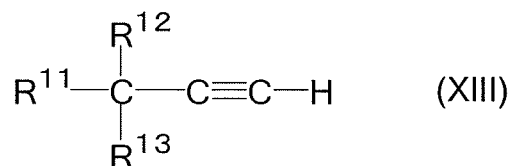
10 In the aldehyde compound (IV), in case that R^{11} and R^{12} , together with carbon atom to which they are bonded, form a ring having 3-13 carbon atoms, the ring having 3-13 carbon atoms is preferably alicyclic hydrocarbon of 3-13 membered ring, more preferably
15 alicyclic hydrocarbon of 3-8 membered ring. As for 3-13 membered ring, for example, such as cyclopropane ring, cyclobutane ring, cyclopentane ring and cyclohexane ring, cyclooctane ring and cyclotridecane ring can be given.

20 In case that R^{11} , R^{12} and R^{13} each independently represent hydrogen atom or phenyl group, as the aldehyde compound (IV), for example, such as propanal and 3-phenylpropanal can be given.

In case that R^{11} and R^{12} , together with carbon

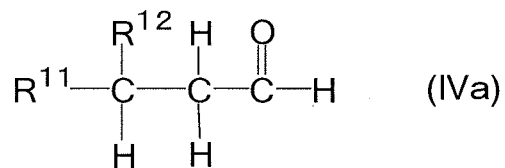
atom to which they are bonded, form a ring having 3-13 carbon atoms, and R^{13} represents hydrogen atom, alkyl group having 1-6 carbon atoms, cycloalkyl group having 3-6 carbon atoms, alkylcycloalkyl group having 4-10 carbon atoms, cycloalkylalkyl group having 4-10 carbon atoms, aralkyl group having 7-10 carbon atoms or phenyl group, as the aldehyde compound (IV), for example, such as cyclopropylacetaldehyde and cyclohexylacetaldehyde can be given.

10 A compound having acetylenic bond represented by the following formula (XIII) can be obtained by dehydrating the aldehyde compound (IV):



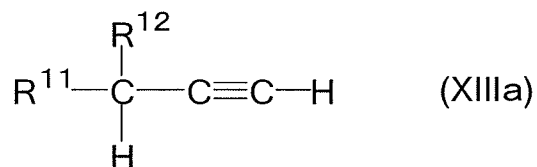
(wherein, in the formula, R^{11} , R^{12} and R^{13} have the abovementioned meanings).

15 Furthermore, in case that, in the aldehyde compound (IV), R^{13} is hydrogen atom, that is, the aldehyde compound (IV) can be represented by the formula (IVa), a compound having acetylenic bond represented by the following formula (XIIIa) and/or
20 diene represented by the following formula (XIX) can be obtained:



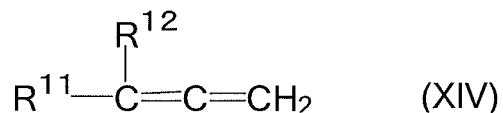
(wherein, in the formula, R^{11} and R^{12} each independently represent hydrogen atom or phenyl group; or

R^{11} and R^{12} , together with carbon atom to which they are bonded, form a ring having 3-13 carbon atoms);



(wherein, in the formula, R^{11} and R^{12} each independently represent hydrogen atom or phenyl group; or

R^{11} and R^{12} , together with carbon atom to which they are bonded, form a ring having 3-13 carbon atoms); and

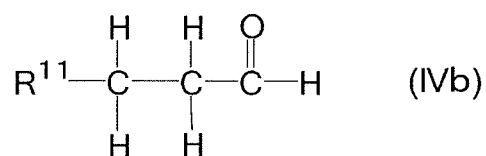


(wherein, in the formula, R^{11} and R^{12} each independently represent hydrogen atom or phenyl group; or

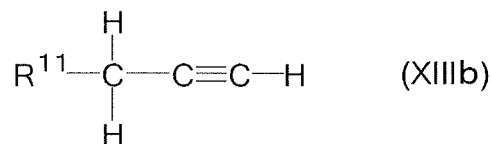
R^{11} and R^{12} , together with carbon atom to which they are bonded, form a ring having 3-13 carbon atoms).

Furthermore, in case that, in the aldehyde

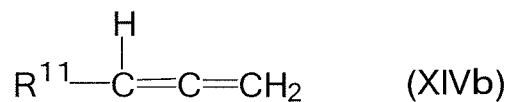
compound (IV), R^{11} is phenyl group, and R^{11} and R^{12} are hydrogen atoms, that is, the aldehyde compound (IV) can be represented by the formula (IVb), a compound having acetylenic bond represented by the following formula (XIIIb), diene represented by the following formula (XIVb), and a compound having acetylenic bond represented by the following formula (XV) can be obtained:



(wherein, in the formula, R^{11} represents phenyl group);

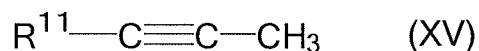


(wherein, in the formula, R^{11} represents phenyl group);



(wherein, in the formula, R^{11} represents phenyl group);

and



(wherein, in the formula, R^{11} represents phenyl group).

Furthermore, in case that, in the aldehyde compound (IV), R^{11} , R^{12} and R^{13} are hydrogen atoms, propyne and/or propadiene can be obtained.

In case that the aldehyde compound (IV) is propanal, the present invention can be usefully employed, because propyne and/or propadiene can be obtained at high selectivity.

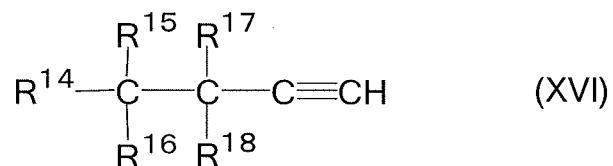
5 In the aldehyde compound (V), in case that R^{14} and R^{15} , together with carbon atom to which they are bonded, form a ring having 3-13 carbon atoms, the ring having 3-13 carbon atoms is preferably alicyclic hydrocarbon of 3-13 membered ring, more preferably
10 alicyclic hydrocarbon of 3-8 membered ring. As for 3-13 membered ring, for example, such as cyclopropane ring, cyclobutane ring, cyclopentane ring and cyclohexane ring, cyclooctane ring and cyclotridecane ring can be given.

15 In case that R^{14} , R^{15} , R^{16} , R^{17} and R^{18} each independently represent hydrogen atom, alkyl group having 1-6 carbon atoms, cycloalkyl group having 3-6 carbon atoms, alkylcycloalkyl group having 4-10 carbon atoms, cycloalkylalkyl group having 4-10
20 carbon atoms, aralkyl group having 7-10 carbon atoms or phenyl group, as for the aldehyde compound (V), for example, such as butanal, pentanal, 3-methylbutanal and 3, 3-dimethylbutanal can be given.

25 In case that R^{14} and R^{15} , together with carbon atom to which they are bonded, form a ring having 3-

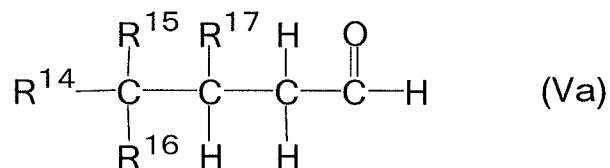
13 carbon atoms, and R^{16} , R^{17} and R^{18} each independently represent hydrogen atom, alkyl group having 1-6 carbon atoms, cycloalkyl group having 3-6 carbon atoms, alkylcycloalkyl group having 4-10 carbon atoms, cycloalkylalkyl group having 4-10 carbon atoms, aralkyl group having 7-10 carbon atoms or phenyl group, as for the aldehyde compound (V), for example, such as 3-cyclohexylpropanal and 3-phenyl-3-cyclohexylpropanal can be given.

10 A compound having acetylenic bond represented by the following formula (XVI) can be obtained by dehydrating the aldehyde compound (V):



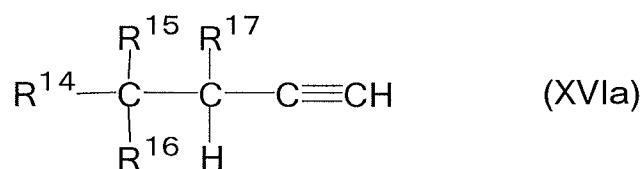
(wherein, in the formula, R^{14} , R^{15} , R^{16} , R^{17} and R^{18} have the abovementioned meanings).

15 Furthermore, in case that, in the aldehyde compound (V), R^{18} is hydrogen atom, that is, the aldehyde compound (V) can be represented by the formula (Va), a compound having acetylenic bond represented by the following formula (XVIa) and/or
20 diene represented by the following formula (XVII) can be obtained:



(wherein, in the formula, R^{14} , R^{15} , R^{16} and R^{17} each independently represent hydrogen atom, alkyl group having 1-6 carbon atoms, cycloalkyl group having 3-6 carbon atoms, alkylcycloalkyl group having 4-10 carbon atoms, cycloalkylalkyl group having 4-10 carbon atoms, aralkyl group having 7-10 carbon atoms or phenyl group; or

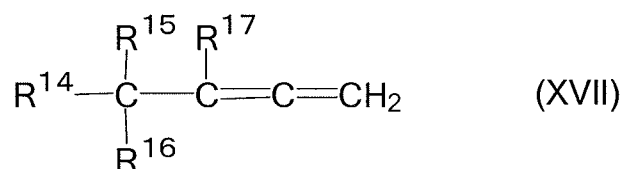
R^{14} and R^{15} , together with carbon atom to which they are bonded, form a ring having 3-13 carbon atoms, and R^{16} and R^{17} each independently represent hydrogen atom, alkyl group having 1-6 carbon atoms, cycloalkyl group having 3-6 carbon atoms, alkylcycloalkyl group having 4-10 carbon atoms, cycloalkylalkyl group having 4-10 carbon atoms, aralkyl group having 7-10 carbon atoms or phenyl group);



(wherein, in the formula, R^{14} , R^{15} , R^{16} and R^{17} each independently represent hydrogen atom, alkyl group having 1-6 carbon atoms, cycloalkyl group having 3-6 carbon atoms, alkylcycloalkyl group having 4-10

carbon atoms, cycloalkylalkyl group having 4-10 carbon atoms, aralkyl group having 7-10 carbon atoms or phenyl group; or

5 R^{14} and R^{15} , together with carbon atom to which they are bonded, form a ring having 3-13 carbon atoms, and R^{16} and R^{17} each independently represent hydrogen atom, alkyl group having 1-6 carbon atoms, cycloalkyl group having 3-6 carbon atoms, alkylcycloalkyl group having 4-10 carbon atoms, cycloalkylalkyl group
10 having 4-10 carbon atoms, aralkyl group having 7-10 carbon atoms or phenyl group); and

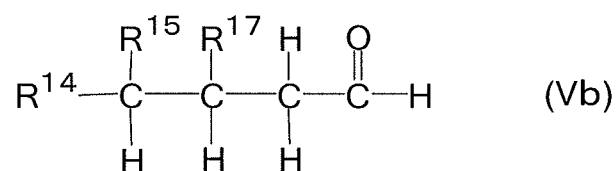


(wherein, in the formula, R^{14} , R^{15} , R^{16} and R^{17} each independently represent hydrogen atom, alkyl group having 1-6 carbon atoms, cycloalkyl group having 3-6
15 carbon atoms, alkylcycloalkyl group having 4-10 carbon atoms, cycloalkylalkyl group having 4-10 carbon atoms, aralkyl group having 7-10 carbon atoms or phenyl group; or

20 R^{14} and R^{15} , together with carbon atom to which they are bonded, form a ring having 3-13 carbon atoms, and R^{16} and R^{17} each independently represent hydrogen atom, alkyl group having 1-6 carbon atoms, cycloalkyl

group having 3-6 carbon atoms, alkylcycloalkyl group having 4-10 carbon atoms, cycloalkylalkyl group having 4-10 carbon atoms, aralkyl group having 7-10 carbon atoms or phenyl group).

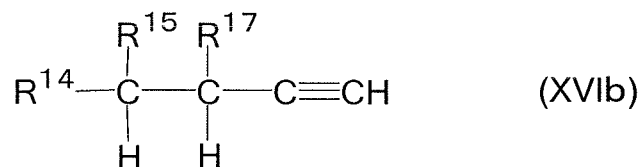
5 Furthermore, in case that, in the aldehyde compound (V), R^{16} and R^{18} are hydrogen atoms, that is, the aldehyde compound (V) can be represented by the formula (Vb), a compound having acetylenic bond represented by the following formula (XVIb), and diene
10 represented by the following formula (XVIIb) and/or formula (XVIII) can be obtained:



(wherein, in the formula, R^{14} , R^{15} and R^{17} each independently represent hydrogen atom, alkyl group having 1-6 carbon atoms, cycloalkyl group having 3-6
15 carbon atoms, alkylcycloalkyl group having 4-10 carbon atoms, cycloalkylalkyl group having 4-10 carbon atoms, aralkyl group having 7-10 carbon atoms or phenyl group; or

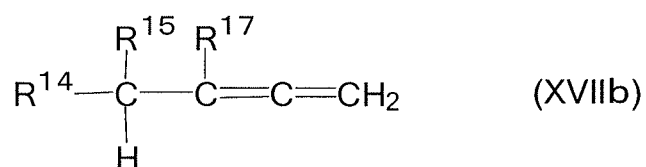
R^{14} and R^{15} , together with carbon atom to which they
20 are bonded, form a ring having 3-13 carbon atoms, and R^{17} represents hydrogen atom, alkyl group having 1-6 carbon atoms, cycloalkyl group having 3-6 carbon

atoms, alkylcycloalkyl group having 4-10 carbon atoms, cycloalkylalkyl group having 4-10 carbon atoms, aralkyl group having 7-10 carbon atoms or phenyl group);



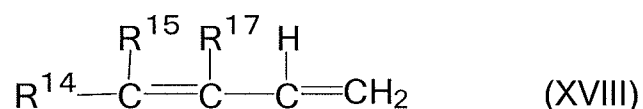
- 5 (wherein, in the formula, R^{14} , R^{15} and R^{17} each independently represent hydrogen atom, alkyl group having 1-6 carbon atoms, cycloalkyl group having 3-6 carbon atoms, alkylcycloalkyl group having 4-10 carbon atoms, cycloalkylalkyl group having 4-10 carbon atoms, aralkyl group having 7-10 carbon atoms or phenyl group; or
- 10

- R^{14} and R^{15} , together with carbon atom to which they are bonded, form a ring having 3-13 carbon atoms, and R^{17} represents hydrogen atom, alkyl group having 1-6 carbon atoms, cycloalkyl group having 3-6 carbon atoms, alkylcycloalkyl group having 4-10 carbon atoms, cycloalkylalkyl group having 4-10 carbon atoms, aralkyl group having 7-10 carbon atoms or phenyl group);
- 15



(wherein, in the formula, R^{14} , R^{15} and R^{17} each independently represent hydrogen atom, alkyl group having 1-6 carbon atoms, cycloalkyl group having 3-6 carbon atoms, alkylcycloalkyl group having 4-10 carbon atoms, cycloalkylalkyl group having 4-10 carbon atoms, aralkyl group having 7-10 carbon atoms or phenyl group; or

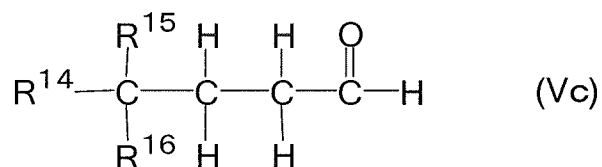
R^{14} and R^{15} , together with carbon atom to which they are bonded, form a ring having 3-13 carbon atoms, and R^{17} represents hydrogen atom, alkyl group having 1-6 carbon atoms, cycloalkyl group having 3-6 carbon atoms, alkylcycloalkyl group having 4-10 carbon atoms, cycloalkylalkyl group having 4-10 carbon atoms, aralkyl group having 7-10 carbon atoms or phenyl group); and



(wherein, in the formula, R^{14} , R^{15} and R^{17} each independently represent hydrogen atom, alkyl group having 1-6 carbon atoms, cycloalkyl group having 3-6 carbon atoms, alkylcycloalkyl group having 4-10 carbon atoms, cycloalkylalkyl group having 4-10 carbon atoms, aralkyl group having 7-10 carbon atoms or phenyl group; or

R¹⁴ and R¹⁵, together with carbon atom to which they are bonded, form a ring having 3-13 carbon atoms, and R¹⁷ represents hydrogen atom, alkyl group having 1-6 carbon atoms, cycloalkyl group having 3-6 carbon atoms, alkylcycloalkyl group having 4-10 carbon atoms, cycloalkylalkyl group having 4-10 carbon atoms, aralkyl group having 7-10 carbon atoms or phenyl group).

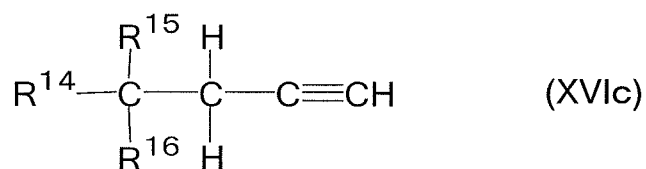
Furthermore, in case that, in the aldehyde compound (V), R¹⁷ and R¹⁸ are hydrogen atoms, that is, the aldehyde compound (V) can be represented by the formula (Vc), a compound having acetylenic bond represented by the following formula (XVIc), diene represented by the following formula (XVIIc), and a compound having acetylenic bond represented by the following formula (XVIId) can be obtained:



(wherein, in the formula, R¹⁴, R¹⁵ and R¹⁶ each independently represent hydrogen atom, alkyl group having 1-6 carbon atoms, cycloalkyl group having 3-6 carbon atoms, alkylcycloalkyl group having 4-10 carbon atoms, cycloalkylalkyl group having 4-10 carbon atoms, aralkyl group having 7-10 carbon atoms

or phenyl group; or

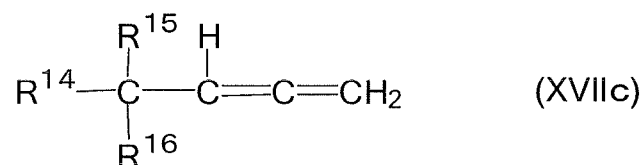
R^{14} and R^{15} , together with carbon atom to which they are bonded, form a ring having 3-13 carbon atoms, and R^{16} represents hydrogen atom, alkyl group having 1-6 carbon atoms, cycloalkyl group having 3-6 carbon atoms, alkylcycloalkyl group having 4-10 carbon atoms, cycloalkylalkyl group having 4-10 carbon atoms, aralkyl group having 7-10 carbon atoms or phenyl group);



(wherein, in the formula, R^{14} , R^{15} and R^{16} each independently represent hydrogen atom, alkyl group having 1-6 carbon atoms, cycloalkyl group having 3-6 carbon atoms, alkylcycloalkyl group having 4-10 carbon atoms, cycloalkylalkyl group having 4-10 carbon atoms, aralkyl group having 7-10 carbon atoms or phenyl group; or

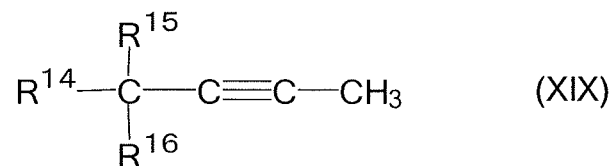
R^{14} and R^{15} , together with carbon atom to which they are bonded, form a ring having 3-13 carbon atoms, and R^{16} represents hydrogen atom, alkyl group having 1-6 carbon atoms, cycloalkyl group having 3-6 carbon atoms, alkylcycloalkyl group having 4-10 carbon atoms, cycloalkylalkyl group having 4-10 carbon atoms,

aralkyl group having 7-10 carbon atoms or phenyl group);



(wherein, in the formula, R^{14} , R^{15} and R^{16} each independently represent hydrogen atom, alkyl group having 1-6 carbon atoms, cycloalkyl group having 3-6 carbon atoms, alkylcycloalkyl group having 4-10 carbon atoms, cycloalkylalkyl group having 4-10 carbon atoms, aralkyl group having 7-10 carbon atoms or phenyl group; or

R^{14} and R^{15} , together with carbon atom to which they are bonded, form a ring having 3-13 carbon atoms, and R^{16} represents hydrogen atom, alkyl group having 1-6 carbon atoms, cycloalkyl group having 3-6 carbon atoms, alkylcycloalkyl group having 4-10 carbon atoms, cycloalkylalkyl group having 4-10 carbon atoms, aralkyl group having 7-10 carbon atoms or phenyl group); and

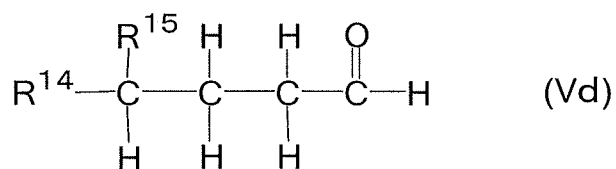


(wherein, in the formula, R^{14} , R^{15} and R^{16} each independently represent hydrogen atom, alkyl group

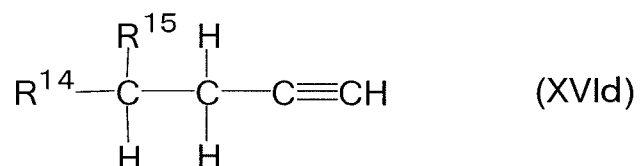
having 1-6 carbon atoms, cycloalkyl group having 3-6 carbon atoms, alkylcycloalkyl group having 4-10 carbon atoms, cycloalkylalkyl group having 4-10 carbon atoms, aralkyl group having 7-10 carbon atoms or phenyl group; or

R¹⁴ and R¹⁵, together with carbon atom to which they are bonded, form a ring having 3-13 carbon atoms, and R¹⁶ represents hydrogen atom, alkyl group having 1-6 carbon atoms, cycloalkyl group having 3-6 carbon atoms, alkylcycloalkyl group having 4-10 carbon atoms, cycloalkylalkyl group having 4-10 carbon atoms, aralkyl group having 7-10 carbon atoms or phenyl group).

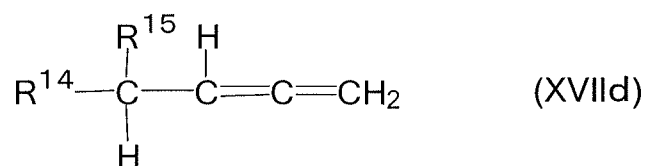
Furthermore, in case that, in the aldehyde compound (V), R¹⁶, R¹⁷ and R¹⁸ are hydrogen atoms, that is, the aldehyde compound (V) can be represented by the formula (Vd), a compound having acetylenic bond represented by the following formula (XVIId), diene represented by the following formula (XVIIId), diene represented by the following formula (XVIIIId), and/or a compound having acetylenic bond represented by the following formula (XIXd) can be obtained:



(wherein, in the formula, R^{14} and R^{15} each independently represent hydrogen atom, alkyl group having 1-6 carbon atoms, cycloalkyl group having 3-6 carbon atoms, alkylcycloalkyl group having 4-10 carbon atoms, cycloalkylalkyl group having 4-10 carbon atoms, aralkyl group having 7-10 carbon atoms or phenyl group; or R^{14} and R^{15} , together with carbon atom to which they are bonded, form a ring having 3-13 carbon);



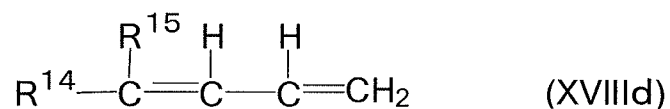
(wherein, in the formula, R^{14} and R^{15} each independently represent hydrogen atom, alkyl group having 1-6 carbon atoms, cycloalkyl group having 3-6 carbon atoms, alkylcycloalkyl group having 4-10 carbon atoms, cycloalkylalkyl group having 4-10 carbon atoms, aralkyl group having 7-10 carbon atoms or phenyl group; or R^{14} and R^{15} , together with carbon atom to which they are bonded, form a ring having 3-13 carbon);



(wherein, in the formula, R^{14} and R^{15} each

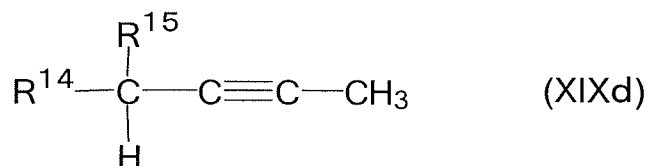
independently represent hydrogen atom, alkyl group having 1-6 carbon atoms, cycloalkyl group having 3-6 carbon atoms, alkylcycloalkyl group having 4-10 carbon atoms, cycloalkylalkyl group having 4-10 carbon atoms, aralkyl group having 7-10 carbon atoms or phenyl group; or

R^{14} and R^{15} , together with carbon atom to which they are bonded, form a ring having 3-13 carbon);



(wherein, in the formula, R^{14} and R^{15} each independently represent hydrogen atom, alkyl group having 1-6 carbon atoms, cycloalkyl group having 3-6 carbon atoms, alkylcycloalkyl group having 4-10 carbon atoms, cycloalkylalkyl group having 4-10 carbon atoms, aralkyl group having 7-10 carbon atoms or phenyl group; or

R^{14} and R^{15} , together with carbon atom to which they are bonded, form a ring having 3-13 carbon); and



(wherein, in the formula, R^{14} and R^{15} each independently represent hydrogen atom, alkyl group having 1-6 carbon atoms, cycloalkyl group having 3-6

carbon atoms, alkylcycloalkyl group having 4-10 carbon atoms, cycloalkylalkyl group having 4-10 carbon atoms, aralkyl group having 7-10 carbon atoms or phenyl group; or

- 5 R^{14} and R^{15} , together with carbon atom to which they are bonded, form a ring having 3-13 carbon).

In the dehydration reaction, a reaction system may include, together with at least one compound selected from the group consisting of ketone compound
10 (I), ketone compound (II), aldehyde compound (III), aldehyde compound (IV) and aldehyde compound (V) as the raw material, water vapor, carbon monoxide, carbon dioxide, methane, ethane, ethylene, acetylene, propane, propylene, propyne, propadiene, butane,
15 butene, butyne, isobutylene, butadiene, nitrogen, and the like.

In the dehydration reaction, the reaction temperature is typically 200 to 1,200°C, preferably 250 to 1,000°C, and more preferably 400 to 800°C. A
20 reaction temperature of lower than 200°C may reduce catalyst activity, while a reaction temperature of higher than 1,200°C may cause the deterioration of catalyst activity.

In the dehydration reaction, the reaction pressure
25 is 0.001 to 5 MPa and preferably 0.005 to 0.3 MPa. A

reaction pressure of lower than 0.001 MPa may reduce the productivity, while a reaction pressure of higher than 5 MPa may reduce an equilibrium conversion rate in the reaction.

5 The reaction of the present invention may be performed in various systems such as a fixed bed system, a fluidized bed system, and a moving bed system and the fixed bed system or the fluidized bed system is preferred. The catalyst may be used alone or
10 may be diluted or mixed with a substance that is substantially inert to the reaction to be used.

When the reaction is performed by the fixed bed system, the feed rate of a material gas containing at least one compound selected from the group consisting
15 of ketone compound (I), ketone compound (II), aldehyde compound (III), aldehyde compound (IV) and aldehyde compound (V) as the raw material, in terms of feed rate (L/h; 0°C, in terms of 0.1 MPa) of a material gas per liter of the catalyst, that is, in terms of GHSV (gas
20 hourly space velocity) is 1 to 20,000 h⁻¹ and preferably 10 to 10,000 h⁻¹. The concentration of at least one compound selected from the group consisting of ketone compound (I), ketone compound (II), aldehyde compound (III), aldehyde compound (IV) and aldehyde
25 compound (V) in the raw material including at least

one compound selected from the group consisting of ketone compound (I), ketone compound (II), aldehyde compound (III), aldehyde compound (IV) and aldehyde compound (V) is appropriately designed in consideration of productivity and catalyst activity.

The preferred embodiments of the present invention has been described hereinbefore, but the present invention is not limited to the embodiments, and it is needless to say that modifications and changes may be made to the embodiments without departing from the scope of the present invention.

Examples

The present invention will now be described in detail with reference to examples, but the present invention is not limited to the examples alone. In the examples below, the feed rate (mL/min) of a gas is a reduced value at 0°C and 0.1 MPa unless otherwise specified.

Example 1

<Production of Catalyst>

Silica spheres (1.7 to 4.0 mm sphere) [manufactured by Fuji Silysia Chemical Ltd., Q-50] were used as a carrier. Into 10.0 g of the carrier, an aqueous solution prepared by dissolving 0.095 g of potassium chloride [manufactured by Wako Pure

Chemical Industries, Ltd.] in 7.63 g of pure water was impregnated and the carrier was air-dried at 20 to 30°C for 15 hours or more. The temperature of the obtained solid was raised from room temperature to
5 400°C over 1.1 hours in an air stream and then was maintained at the same temperature for 2 hours for calcining the solid. Next, the obtained calcined product was crushed into a granular form having a size of 0.85 to 1.4 mm to afford a catalyst of potassium
10 chloride (potassium chloride content: 0.94% by weight) supported on silica.

<Catalyst Filling>

Into a lower part in a quartz reaction tube having an inner diameter of 14 mm equipped with a
15 thermometer well having an outer diameter of 4 mm, quartz wool was filled as a partition, and then 0.48 g (a volume of 1.2 mL) of the obtained catalyst was filled from the top of the reaction tube.

<Dehydration Reaction>

20 The reaction tube filled with the catalyst was heated in an electric furnace and the temperature of the reaction tube was raised while feeding a nitrogen gas at a rate of 156 mL/min from an inlet of the reaction tube through the reaction tube.

25 Next, acetone (a compound in which, in the

formula (I), R^1 , R^2 , R^3 and R^4 are hydrogen atom)(manufactured by Wako Pure Chemical Industries, Ltd.) was charged in a gas absorbing bottle and cooled to 0°C; then into the gas absorbing bottle, a nitrogen gas was fed at a rate of 32 mL/min to make a nitrogen gas stream in acetone; the obtained nitrogen gas accompanied with acetone was added to the feeding nitrogen gas at a rate of 156 mL/min at the time of temperature rise; and the whole was fed from the reaction tube inlet (acetone feed rate: 0.0088 mol/h, acetone concentration in the feeding gas: 1.7% by volume) to start the reaction at a reaction pressure of 0.1 MPa. The ratio (GHSV) of the total gas flow rate with respect to the catalyst volume was 9,564 h⁻¹.

After the start of reaction, the temperature of the catalyst layer was maintained at 600°C ± 2°C. After 90 minutes of the reaction start time, a gas from an outlet of the reactor was collected in a Tedlar bag and analyzed with gas chromatograph equipped with TCD and FID detectors to determine the amount of each product. Once the sampling was completed, next, acetone and high boiling components were absorbed using a two stage trap including monochlorobenzene. Each absorption liquid in the first stage trap and the second stage trap was analyzed with a gas

chromatograph equipped with a FID detector to determine the amounts of acetone and high boiling components. The results are shown in Table 1.

Here, the conversion rate (%) of acetone was
5 calculated in accordance with the following equation (i).

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

a: acetone feed rate (mol/h)

b: production rate (mol/h) of all products in gas
from the reaction tube outlet

10 The acetone feed rate was calculated from the change in weight of acetone in the gas absorbing bottle from the start to the end of feeding.

The selectivity (%) of each product was calculated in accordance with the following equation (ii).

15 Selectivity (%) of each product = [production rate (mol/h) of each product/total production rate (mol/h) of all products] $\times$ 100 (ii)

Here, the products are propyne, propadiene, propane, propylene, methane, ethane, ethylene,
20 isobutylene, carbon monoxide, and carbon dioxide.

Example 2

<Production of Catalyst>

Silica spheres (1.7 to 4.0 mm sphere)
[manufactured by Fuji Silysia Chemical Ltd., Q-50]
25 were used as a carrier. Into 10.0 g of the carrier, an

aqueous solution prepared by dissolving 0.29 g of potassium chloride [manufactured by Wako Pure Chemical Industries, Ltd.] in 8.16 g of pure water was impregnated and the carrier was air-dried at 20 to 30°C for 15 hours or more. The temperature of the obtained solid was raised from room temperature to 400°C over 1.1 hours in an air stream and then was maintained at the same temperature for 2 hours for calcining the solid. Next, the obtained calcined product was crushed into a granular form having a size of 0.85 to 1.4 mm to afford a catalyst of potassium chloride (potassium chloride content: 2.8% by weight) supported on silica.

<Catalyst Filling, Dehydration Reaction>

The catalyst filling and the reaction were carried out in the same manner as in Example 1 except that the catalyst obtained above was used. The results are shown in Table 1.

Example 3

<Production of Catalyst>

Silica spheres (1.7 to 4.0 mm sphere) [manufactured by Fuji Silysia Chemical Ltd., Q-50] were used as a carrier. Into 10.0 g of the carrier, an aqueous solution prepared by dissolving 1.04 g of potassium chloride [manufactured by Wako Pure

Chemical Industries, Ltd.] in 8.25 g of pure water was impregnated and the carrier was air-dried at 20 to 30°C for 15 hours or more. The temperature of the obtained solid was raised from room temperature to 400°C over 1.1 hours in an air stream and then was maintained at the same temperature for 2 hours for calcining the solid. Next, the obtained calcined product was crushed into a granular form having a size of 0.85 to 1.4 mm to afford a catalyst of potassium chloride (potassium chloride content: 9.4% by weight) supported on silica.

<Catalyst Filling, Dehydration Reaction>

The catalyst filling and the reaction were carried out in the same manner as in Example 1 except that the catalyst obtained above was used. The results are shown in Table 1.

Example 4

<Production of Catalyst>

Silica spheres (1.7 to 4.0 mm sphere) [manufactured by Fuji Silysia Chemical Ltd., Q-50] were used as a carrier. Into 10.0 g of the carrier, an aqueous solution prepared by dissolving 0.22 g of cesium chloride [manufactured by Wako Pure Chemical Industries, Ltd.] in 9.88 g of pure water was impregnated and the carrier was air-dried at 20 to

30°C for 15 hours or more. The temperature of the obtained solid was raised from room temperature to 400°C over 1.1 hours in an air stream and then was maintained at the same temperature for 2 hours for calcining the solid. Next, the obtained calcined product was crushed into a granular form having a size of 0.85 to 1.4 mm to afford a catalyst of cesium chloride (cesium chloride content: 2.2% by weight) supported on silica.

<Catalyst Filling, Dehydration Reaction>

The catalyst filling and the reaction were carried out in the same manner as in Example 1 except that the catalyst obtained above was used. The results are shown in Table 1.

Example 5

<Production of Catalyst>

Silica spheres (1.7 to 4.0 mm sphere) [manufactured by Fuji Silysia Chemical Ltd., Q-50] were used as a carrier. Into 10.0 g of the carrier, an aqueous solution prepared by dissolving 0.075 g of sodium chloride [manufactured by Wako Pure Chemical Industries, Ltd.] in 9.42 g of pure water was impregnated and the carrier was air-dried at 20 to 30°C for 15 hours or more. The temperature of the obtained solid was raised from room temperature to

400°C over 1.1 hours in an air stream and then was maintained at the same temperature for 2 hours for calcining the solid. Next, the obtained calcined product was crushed into a granular form having a size
5 of 0.85 to 1.4 mm to afford a catalyst of sodium chloride (sodium chloride content: 0.74% by weight) supported on silica.

<Catalyst Filling, Dehydration Reaction>

The catalyst filling and the reaction were carried
10 out in the same manner as in Example 1 except that the catalyst obtained above was used. The results are shown in Table 1.

Example 6

<Production of Catalyst>

15 Silica spheres (1.7 to 4.0 mm sphere)
[manufactured by Fuji Silysia Chemical Ltd., Q-50]
were used as a carrier. Into 10.0 g of the carrier, an aqueous solution prepared by dissolving 0.13 g of rubidium chloride [manufactured by Wako Pure
20 Chemical Industries, Ltd.] in 9.77 g of pure water was impregnated and the carrier was air-dried at 20 to 30°C for 15 hours or more. The temperature of the obtained solid was raised from room temperature to 400°C over 1.1 hours in an air stream and then was
25 maintained at the same temperature for 2 hours for

calcining the solid. Next, the obtained calcined product was crushed into a granular form having a size of 0.85 to 1.4 mm to afford a catalyst of rubidium chloride (rubidium chloride content: 1.3% by weight) supported on silica.

<Catalyst Filling, Dehydration Reaction>

The catalyst filling and the reaction were carried out in the same manner as in Example 1 except that the catalyst obtained above was used. The results are shown in Table 1.

Example 7

<Production of Catalyst>

Silica spheres (1.7 to 4.0 mm sphere) [manufactured by Fuji Silysia Chemical Ltd., Q-50] were used as a carrier. Into 10.0 g of the carrier, an aqueous solution prepared by dissolving 0.054 g of lithium chloride [manufactured by Wako Pure Chemical Industries, Ltd.] in 9.87 g of pure water was impregnated and the carrier was air-dried at 20 to 30°C for 15 hours or more. The temperature of the obtained solid was raised from room temperature to 400°C over 1.1 hours in an air stream and then was maintained at the same temperature for 2 hours for calcining the solid. Next, the obtained calcined product was crushed into a granular form having a size

of 0.85 to 1.4 mm to afford a catalyst of lithium chloride (lithium chloride content: 0.54% by weight) supported on silica.

<Catalyst Filling, Dehydration Reaction>

5 The catalyst filling and the reaction were carried out in the same manner as in Example 1 except that the catalyst obtained above was used. The results are shown in Table 1.

Example 8

10 <Production of Catalyst>

 Silica spheres (1.7 to 4.0 mm sphere)
[manufactured by Fuji Silysia Chemical Ltd., Q-50]
were used as a carrier. Into 10.0 g of the carrier, an
aqueous solution prepared by dissolving 0.31 g of
15 barium chloride [manufactured by Wako Pure Chemical
Industries, Ltd.] in 9.86 g of pure water was
impregnated and the carrier was air-dried at 20 to
30°C for 15 hours or more. The temperature of the
obtained solid was raised from room temperature to
20 400°C over 1.1 hours in an air stream and then was
maintained at the same temperature for 2 hours for
calcining the solid. Next, the obtained calcined
product was crushed into a granular form having a size
of 0.85 to 1.4 mm to afford a catalyst of barium
25 chloride (barium chloride content: 3.0% by weight)

supported on silica.

<Catalyst Filling, Dehydration Reaction>

The catalyst filling and the reaction were carried out in the same manner as in Example 1 except that
5 the catalyst obtained above was used. The results are shown in Table 1.

Example 9

<Production of Catalyst>

A catalyst of potassium chloride (potassium
10 chloride content: 2.8% by weight) supported on silica was obtained in the same manner as in <Production of Catalyst> in Example 2.

<Catalyst Filling>

The catalyst filling was carried out in the same
15 manner as in <Catalyst Filling> in Example 1 except the catalyst obtained above was used.

<Dehydration Reaction>

The reaction tube filled with the catalyst was heated in an electric furnace and the temperature of
20 the reaction tube was raised while feeding a nitrogen gas at a rate of 173.5 mL/min from an inlet of the reaction tube through the reaction tube.

Next, acetone (manufactured by Wako Pure
Chemical Industries, Ltd.) was charged in a gas
25 absorbing bottle and cooled to 0°C; then into the gas

absorbing bottle, a nitrogen gas was fed at a rate of 173.5 mL/min to make a nitrogen gas stream in acetone; and the obtained nitrogen gas accompanied with acetone was fed from the reaction tube inlet (acetone feed rate: 0.048 mol/h, acetone concentration in the feeding gas: 9.3% by volume) in place of the feeding nitrogen gas at the time of temperature rise to start the reaction at a reaction pressure of 0.1 MPa. The ratio (GHSV) of the total gas flow rate with respect to the catalyst volume was 9,564 h⁻¹.

After the start of reaction, the temperature of the catalyst layer was maintained at 600°C ± 2°C. After 90 minutes of the reaction start time, a gas from an outlet of the reactor was collected in a Tedlar bag and analyzed with gas chromatograph equipped with TCD and FID detectors to determine the amount of each product. Once the sampling was completed, next, acetone and high boiling components were absorbed using a two stage trap including monochlorobenzene. Each absorption liquid in the first stage trap and the second stage trap was analyzed with a gas chromatograph equipped with a FID detector to determine the amounts of acetone and high boiling components. The results are shown in Table 1.

Example 10

<Production of Catalyst>

Silica spheres (1.7 to 4.0 mm sphere)
[manufactured by Fuji Silysia Chemical Ltd., Q-50]
were used as a carrier. Into 10.0 g of the carrier, an
5 aqueous solution prepared by dissolving 0.27 g of
potassium carbonate [manufactured by Wako Pure
Chemical Industries, Ltd.] in 10.0 g of pure water was
impregnated and the carrier was air-dried at 20 to
30°C for 15 hours or more. The temperature of the
10 obtained solid was raised from room temperature to
400°C over 1.1 hours in an air stream and then was
maintained at the same temperature for 2 hours for
calcining the solid. Next, the obtained calcined
product was crushed into a granular form having a size
15 of 0.85 to 1.4 mm to afford a catalyst of potassium
carbonate (potassium carbonate content: 2.6% by
weight) supported on silica.

<Catalyst Filling, Dehydration Reaction>

The catalyst filling and the reaction were carried
20 out in the same manner as in Example 9 except that
the catalyst obtained above was used. The results are
shown in Table 1.

Comparative Example 1

<Production of Catalyst>

25 Silica spheres (1.7 to 4.0 mm sphere)

[manufactured by Fuji Silysia Chemical Ltd., Q-50] were crushed into a granular form having a size of 0.85 to 1.4 mm to afford a silica catalyst.

<Catalyst Filling, Dehydration Reaction>

5 The catalyst filling and the reaction were carried out in the same manner as in Example 1 except that the catalyst obtained above was used. The results are shown in Table 1.

Comparative Example 2

10 <Production of Catalyst>

γ -Alumina spheres (2 to 4 mm sphere)
[manufactured by Sumitomo Chemical Co., Ltd., GO-24] were crushed into a granular form having a size of 0.85 to 1.4 mm to afford an alumina catalyst.

15 <Catalyst Filling>

 Into a lower part in a quartz reaction tube having an inner diameter of 14 mm equipped with a thermometer well having an outer diameter of 4 mm, quartz wool was filled as a partition, and then 0.48 g
20 (a volume of 0.71 mL) of the obtained catalyst was filled from the top of the reaction tube.

<Dehydration Reaction>

 The reaction was carried out in the same manner as in Example 1 except that the catalyst obtained
25 above was used. The results are shown in Table 1.

The ratio (GHSV) of the total gas flow rate with respect to the catalyst volume was $16,164 \text{ h}^{-1}$.

[Table 1]

		Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Example 8	Example 9	Example 10	Comparative Example 1	Comparative Example 2
Catalyst	Supported metal component	KCl	←	←	CsCl	NaCl	RbCl	LiCl	BaCl ₂	KCl	K ₂ CO ₃	—	—
	Amount of the supported metal component (wt%)	0.94	2.8	9.4	2.2	0.74	1.3	0.54	3.0	2.8	2.6	—	—
	Carrier	SiO ₂	←	←	←	←	←	←	←	←	←	←	Al ₂ O ₃
Acetone conc. in feed gas (vol%)		1.7	←	←	←	←	←	←	←	9.3	←	1.7	←
Acetone conversion rate (%)		7.3	9.7	10.2	16.3	5.7	9.5	2.1	3.4	6.9	6.8	2.7	22.0
Selectivity (%)	propyne	61.1	64.4	69.0	69.5	66.9	67.1	55.5	53.1	61.5	59.2	23.4	45.3
	propadiene	21.1	22.4	23.9	23.1	23.7	22.9	17.7	18.0	20.6	19.5	6.9	14.0
	methane	12.8	9.7	5.1	4.9	7.3	6.7	26.8	16.6	11.0	13.3	46.8	10.7
	ethane	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.3	0.0	0.0
	ethylene	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.2	0.0	0.0
	propylene	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	2.4
	propane	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	isobutylene	0.0	0.0	0.0	0.0	0.0	0.0	0.0	8.4	3.4	4.2	17.0	19.9
	CO	0.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	2.3	2.7
	CO ₂	4.6	3.5	2.0	2.5	2.1	3.3	0.0	3.9	3.2	3.3	3.6	5.0
Total selectivity of propyne and propadiene (%)		82.2	86.8	92.9	92.6	90.6	90.0	73.2	71.1	82.1	78.7	30.3	59.3

As shown in Table 1, it is revealed that Examples 1 to 10 in which the catalyst of a metal component supported on silica was used showed high total selectivities of propyne and propadiene comparing with Comparative Examples 1 and 2 in which silica or alumina with no supported metal component was used as a catalyst.

Example 11

<Production of Catalyst>

10 Silica spheres (1.7 to 4.0 mm sphere)
[manufactured by Fuji Silysia Chemical Ltd., Q-50]
were used as a carrier. Into 20.0 g of the carrier, an
aqueous solution prepared by dissolving 4.54 g of
potassium silicate solution [manufactured by Wako
15 Pure Chemical Industries, Ltd., Aqueous solution of
 $K_2O \cdot 3.9SiO_2$, $K_2O \cdot 3.9SiO_2$ content: 28.1 % by weight)]
in 26.5 g of pure water was impregnated and the
carrier was air-dried at 20 to 30°C for 15 hours or
more. The temperature of the obtained solid was
20 raised from room temperature to 200°C over 0.5 hours
in an air stream and then was maintained at the same
temperature for 2 hours for calcining the solid. Next,
the obtained calcined product was crushed into a
granular form having a size of 0.85 to 1.4 mm to afford
25 a catalyst of potassium silicate (potassium silicate

content: 6.0% by weight) supported on silica.

<Catalyst Filling>

Into a lower part in a quartz reaction tube having an inner diameter of 14 mm equipped with a thermometer well having an outer diameter of 4 mm, quartz wool was filled as a partition, and then 7.1 mL of SiC, quartz wool as a partition, 2.4 g (a volume of 5.9 mL) of the obtained catalyst, quartz wool as a partition, and 7.1 mL of SiC was sequentially filled from the top of the reaction tube.

<Dehydration Reaction>

The reaction tube was reduced to 0.01MPa or less by using a diaphragm pump while feeding a nitrogen gas at a rate of 2.7 mL/min from an inlet of the reaction tube through the reaction tube, and then the reaction tube was heated in an electric furnace and the temperature of the reaction tube was raised.

Next, liquid acetone (manufactured by Wako Pure Chemical Industries, Ltd.) was charged into the inlet of the reaction tube by using the pump and thereby being evaporated (acetone gas flow rate: 34.2 mL/min, acetone feed rate: 0.092 mol/h, acetone concentration in the feeding gas: 92.7% by volume) to start the reaction at a reaction pressure of 0.008 MPa. The ratio (GHSV) of the total gas flow rate with respect to

the catalyst volume was 375 h^{-1} .

After the start of reaction, the temperature of the catalyst layer was maintained at $598^{\circ}\text{C} \pm 4^{\circ}\text{C}$. After 60 minutes of the reaction start time, a gas from an outlet of the reactor was gathered with a gas tight syringe and analyzed with a gas chromatograph equipped with a FID detector, and further the gas from an outlet of the reactor was filled into a loop for sampling and online analyzed with a gas chromatograph equipped with a TCD detector to determine the amount of each product. Once the sampling was completed, next, acetone and high boiling components were condensed and collected by introducing into a cold trap made of SUS connected to the outlet of the reactor and cooled with a freezing mixture of ethanol and dry ice. The collected condensate was analyzed with a gas chromatograph equipped with a FID detector to determine the amounts of acetone and high boiling components. The results are shown in Table 2.

Here, the conversion rate (%) of acetone was calculated in accordance with the following equation (iii).

$$\text{Acetone conversion rate (\%)} = [d/(c+d)] \times 100 \quad (\text{iii})$$

c: acetone feed rate from the reaction tube outlet

(mol/h)

d: production rate (mol/h) of all products in gas from the reaction tube outlet

The selectivity (%) of each product was calculated in accordance with the following equation (iv).

5 Selectivity (%) of each product = [production rate (mol/h) of each product/total production rate (mol/h) of all products] $\times$ 100 (iv)

Here, the products are propyne, propadiene, methane, ethane, ethylene, propylene, propane,
10 isobutylene, 2-methyl-1-pentene-3-yne, 2-hexen-4-yne, 4-methyl-3-pentene-2-one, 4-methyl-4-pentene-2-one, 2-methylfuran, methylcyclopentadiene, 3,5,5-trimethyl-2-cyclohexen-1-one, phenol, methylphenol, 3,5-dimethylphenol, carbon monoxide, and carbon dioxide.

15 Example 12

<Production of Catalyst>

Silica spheres (1.7 to 4.0 mm sphere) [manufactured by Fuji Silysia Chemical Ltd., Q-50] were used as a carrier. Into 30.2 g of the carrier, an
20 aqueous solution prepared by dissolving 0.71 g of sodium metasilicate [manufactured by Wako Pure Chemical Industries, Ltd., Na_2SiO_3 ($\text{Na}_2\text{O} \cdot \text{SiO}_2$)] in 30.0 g of pure water was impregnated and the carrier was air-dried at 20 to 30°C for 15 hours or more. The
25 temperature of the obtained solid was raised from room

temperature to 200°C over 0.5 hours in an air stream and then was maintained at the same temperature for 2 hours for calcining the solid. Next, the obtained calcined product was crushed into a granular form having a size of 0.85 to 1.4 mm to afford a catalyst of sodium metasilicate (sodium metasilicate content: 2.3% by weight) supported on silica.

<Catalyst Filling, Dehydration Reaction >

The catalyst filling was carried out in the same manner as in <Catalyst Filling> and <Dehydration Reaction > in Example 11 except the catalyst obtained above was used. The results are shown in Table 2.

Example 13

<Production of Catalyst>

Silica spheres (1.7 to 4.0 mm sphere) [manufactured by Fuji Silysia Chemical Ltd., Q-50] were used as a carrier. Into 32.6 g of the carrier, an aqueous solution prepared by dissolving 0.71 g of potassium hydroxide [manufactured by Wako Pure Chemical Industries, Ltd.] in 32.6 g of pure water was impregnated and the carrier was air-dried at 20 to 30°C for 15 hours or more. The temperature of the obtained solid was raised from room temperature to 200°C over 0.5 hours in an air stream and then was maintained at the same temperature for 2 hours for

calcining the solid. Next, the obtained calcined product was crushed into a granular form having a size of 0.85 to 1.4 mm to afford a catalyst of potassium hydroxide (potassium hydroxide content: 2.1% by weight) supported on silica.

<Catalyst Filling, Dehydration Reaction >

The catalyst filling was carried out in the same manner as in <Catalyst Filling> and <Dehydration Reaction > in Example 11 except 2.4 g (a volume of 6.2 mL) of the obtained catalyst obtained above was used, and acetone gas was charged at a flow rate of 25.6 mL/min (acetone feed rate: 0.069 mol/h, acetone concentration in the feeding gas: 90.5% by volume, The ratio (GHSV) of the total gas flow rate with respect to the catalyst volume: 257 h⁻¹). The results are shown in Table 2.

Example 14

<Production of Catalyst>

Silica powder [manufactured by Tosoh Silica Corp., ER-R] were used as a carrier. Into 30.2 g of the carrier, an aqueous solution prepared by dissolving 0.70 g of potassium hydroxide [manufactured by Wako Pure Chemical Industries, Ltd.] in 58.5 g of pure water was impregnated and the carrier was air-dried at 20 to 30°C for 15 hours or more. The temperature of the

obtained solid was raised from room temperature to 200°C over 0.5 hours in an air stream and then was maintained at the same temperature for 2 hours for calcining the solid. Next, the obtained calcined product was crushed into a granular form having a size of 0.85 to 1.4 mm to afford a catalyst of potassium hydroxide (potassium hydroxide content: 2.1% by weight) supported on silica.

<Catalyst Filling, Dehydration Reaction >

The catalyst filling was carried out in the same manner as in <Catalyst Filling> and <Dehydration Reaction > in Example 11 except 2.4 g (a volume of 6.7 mL) of the catalyst obtained above was used. The results are shown in Table 2.

Comparative Example 3

<Production of Catalyst>

Silica spheres (1.7 to 4.0 mm sphere) [manufactured by Fuji Silysia Chemical Ltd., Q-50] were crushed into a granular form having a size of 0.85 to 1.4 mm to afford a silica catalyst.

<Catalyst Filling, Dehydration Reaction>

The catalyst filling and the reaction were carried out in the same manner as in Example 1 except that the catalyst obtained above was used. The results are shown in Table 2.

[Table 2]

		Example 11	Example 12	Example 13	Example 14	Comparative Example 3
Catalyst	Supported metal component	$\text{K}_2\text{O} \cdot 3.9\text{SiO}_2$	Na_2SiO_3	KOH	←	—
	Amount of the supported metal component (wt%)	6.0	2.3	2.1	←	—
	Carrier	SiO_2	←	←	←	←
Acetone conc. in feed gas (vol%)		92.7	←	90.5	92.7	←
Acetone conversion rate (%)		14.0	7.9	24.6	15.5	4.3
Selectivity (%)	propyne	69.8	60.0	67.7	69.3	11.1
	propadiene	23.1	20.0	22.0	23.0	3.3
	methane	0.4	0.7	1.7	0.5	2.0
	ethane	0.0	0.0	0.0	0.0	0.0
	ethylene	0.0	0.0	0.0	0.0	0.0
	propylene	0.0	0.0	0.0	0.0	0.6
	propane	0.0	0.0	0.0	0.0	0.0
	isobutylene	0.0	0.9	0.8	0.0	22.1
	2-methyl-1-penten e-3-yne and 2-hexen-4-yne	1.2	1.8	3.6	1.3	9.2
	4-methyl-3-penten e-2-one and 4-methyl-4-penten e-2-one	1.2	9.1	1.6	1.3	33.3
	2-methylfuran	3.1	6.0	0.2	3.3	6.3
	CO	0.0	0.0	0.0	0.0	0.0
	CO ₂	0.0	0.0	0.8	0.0	0.0
the others*		1.2	1.5	1.6	1.3	12.1
Total selectivity of propyne and propadiene (%)		92.9	80.0	89.7	92.3	14.4

*) methylcyclopentadiene, 3,5,5-trimethyl-2-cyclohexen-1-one, phenol, methylphenol and 3,5-dimethylphenol.

Example 15

<Production of Catalyst>

5 The <Production of Catalyst> were carried out in

the same manner as in Example 14 to afford a catalyst of potassium hydroxide (potassium hydroxide content: 2.1% by weight) supported on silica.

<Catalyst Filling>

5 Into a lower part in a quartz reaction tube having an inner diameter of 14 mm equipped with a thermometer well having an outer diameter of 4 mm, quartz wool was filled as a partition, and then 7.1 mL of SiC, quartz wool as a partition, 2.4 g (a volume of
10 6.7 mL) of the obtained catalyst, quartz wool as a partition, and 12.7 mL of SiC was sequentially filled from the top of the reaction tube.

<Dehydration Reaction>

15 The reaction tube filled with the catalyst was heated in an electric furnace and the temperature of the reaction tube was raised while feeding a nitrogen gas at a rate of 189 mL/min from an inlet of the reaction tube through the reaction tube.

20 Next, 2-butanone (a compound in which, in the formula (II), R^5 , R^6 , R^7 , R^8 and R^9 are hydrogen atom)(manufactured by Wako Pure Chemical Industries, Ltd.) was charged in a gas absorbing bottle and cooled to 0°C; then into the gas absorbing bottle, a nitrogen gas was fed at a rate of 189 mL/min to make a nitrogen
25 gas stream in 2-butanone; the obtained nitrogen gas

accompanied with 2-butanone was fed from the reaction tube inlet instead of the feeding nitrogen gas at the time of temperature rise (2-butanone feed rate: 0.017 mol/h, 2-butanone concentration in the feeding gas: 3.2% by volume) to start the reaction at a reaction pressure of 0.1 MPa. The ratio (GHSV) of the total gas flow rate with respect to the catalyst volume was 1,747 h⁻¹.

After the start of reaction, the temperature of the catalyst layer was maintained at 550°C ± 3°C. After 60 minutes of the reaction start time, a gas from an outlet of the reactor was collected in a Tedlar bag and analyzed with gas chromatograph equipped with TCD and FID detectors to determine the amount of each product. Once the sampling was completed, next, 2-butanone and high boiling components were absorbed using a two stage trap including acetonitrile. Each absorption liquid in the first stage trap and the second stage trap was analyzed with a gas chromatograph equipped with a FID detector to determine the amounts of 2-butanone and high boiling components. The results are shown in Table 3.

Here, the conversion rate (%) of 2-butanone was calculated in accordance with the following equation (v).

2-butanone conversion rate (%) = $[f/e] \times 100$ (v)

e: 2-butanone feed rate (mol/h)

f: production rate (mol/h) of all products in gas from the reaction tube outlet

5 The 2-butanone feed rate was calculated from the change in weight of acetone in the gas absorbing bottle from the start to the end of feeding.

The selectivity (%) of each product was calculated in accordance with the following equation (vi).

10 Selectivity (%) of each product = [production rate (mol/h) of each product/total production rate (mol/h) of all products] $\times 100$ (vi)

Here, the products are 1,3-butadiene, 1,2-butadiene, 1-butyne, 2-butyne, propyne, propadiene, propane, propylene, methane, ethane, ethylene, isobutylene, carbon monoxide, and carbon dioxide.

Example 16

<Production of Catalyst>

20 The <Production of Catalyst> were carried out in the same manner as in Example 14 to afford a catalyst of potassium hydroxide (potassium hydroxide content: 2.1% by weight) supported on silica.

<Catalyst Filling>

25 The catalyst filling was carried out in the same manner as in <Catalyst Filling> in Example 15.

<Dehydration Reaction>

The reaction were carried out in the same manner as in Example 15 except that the temperature of the catalyst layer was maintained at $600^{\circ}\text{C} \pm 9^{\circ}\text{C}$. The results are shown in Table 3.

[Table 3]

		Example 15	Example 16
Catalyst	Supported metal component	KOH	←
	Amount of the supported metal component (wt%)	2.1	←
	Carrier	SiO ₂	←
Reaction temperature (°C)		550	600
2-butanone conversion rate (%)		12.9	44.4
Selectivity (%)	1,3-butadiene	9.2	28.1
	1,2-butadiene	23.3	17.4
	1-butyne	11.0	8.4
	2-butyne	52.9	40.0
	propyne	0.0	0.2
	propadiene	0.4	0.2
	methane	1.5	2.2
	ethane	0.0	0.0
	ethylene	1.7	3.0
	propylene	0.0	0.2
	propane	0.0	0.0
	isobutylene	0.0	0.3
	CO	0.0	0.0
	CO ₂	0.0	0.0
Total selectivity of butyne and butadiene (%)		96.4	93.9

Example 17

<Production of Catalyst>

5 Silica spheres (1.7 to 4.0 mm sphere)
[manufactured by Fuji Silysia Chemical Ltd., Q-50]
were used as a carrier. Into 30.0 g of the carrier, an

aqueous solution prepared by dissolving 0.66 g of cesium chloride [manufactured by Wako Pure Chemical Industries, Ltd.] in 30.0 g of pure water was impregnated and the carrier was air-dried at 20 to 30°C for 15 hours or more. The temperature of the obtained solid was raised from room temperature to 200°C over 0.5 hours in an air stream and then was maintained at the same temperature for 2 hours for calcining the solid. Next, the obtained calcined product was crushed into a granular form having a size of 0.85 to 1.4 mm to afford a catalyst of cesium chloride (cesium chloride content: 2.1% by weight) supported on silica.

<Catalyst Filling>

Into a lower part in a quartz reaction tube having an inner diameter of 14 mm equipped with a thermometer well having an outer diameter of 4 mm, quartz wool was filled as a partition, and then 2.4 g (a volume of 6.4 mL) of the obtained catalyst was filled from the top of the reaction tube.

<Dehydration Reaction>

The reaction tube filled with the catalyst was heated in an electric furnace and the temperature of the reaction tube was raised while feeding a nitrogen gas at a rate of 42 mL/min from an inlet of the

reaction tube through the reaction tube.

Next, propanal (a compound in which, in the formula (IV), R^{11} , R^{12} and R^{13} are hydrogen atom)(manufactured by Wako Pure Chemical Industries, Ltd.) was charged in a gas absorbing bottle and cooled to 0°C; then into the gas absorbing bottle, a nitrogen gas was fed at a rate of 132 mL/min to make a nitrogen gas stream in propanal; the obtained nitrogen gas accompanied with propanal was added to the feeding nitrogen gas at a rate of 42 mL/min at the time of temperature rise; and the whole was fed from the reaction tube inlet (propanal feed rate: 0.057 mol/h, propanal concentration in the feeding gas: 10.9% by volume) to start the reaction at a reaction pressure of 0.1 MPa. The ratio (GHSV) of the total gas flow rate with respect to the catalyst volume was 1,886 h⁻¹.

After the start of reaction, the temperature of the catalyst layer was maintained at 600°C ± 4°C. After 60 minutes of the reaction start time, a gas from an outlet of the reactor was collected in a Tedlar bag and analyzed with gas chromatograph equipped with TCD and FID detectors to determine the amount of each product. Once the sampling was completed, next, propanal and high boiling components were absorbed using a two stage trap including water. Each

absorption liquid in the first stage trap and the second stage trap was analyzed with a gas chromatograph equipped with a FID detector to determine the amounts of propanal and high boiling components. The results are shown in Table 4.

Here, the conversion rate (%) of 2-butanone was calculated in accordance with the following equation (vii).

$$\text{2-butanone conversion rate (\%)} = [h/g] \times 100$$

(vii)

g: propanal feed rate (mol/h)

h: production rate (mol/h) of all products in gas from the reaction tube outlet

The propanal feed rate was calculated from the change in weight of acetone in the gas absorbing bottle from the start to the end of feeding.

The selectivity (%) of each product was calculated in accordance with the following equation (viii).

$$\text{Selectivity (\%)} = [\text{production rate (mol/h) of each product} / \text{total production rate (mol/h) of all products}] \times 100 \quad \text{(viii)}$$

Here, the products are propyne, propadiene, methane, ethane, ethylene, propane, acetylene, propylene, isobutylene, carbon monoxide, and carbon dioxide.

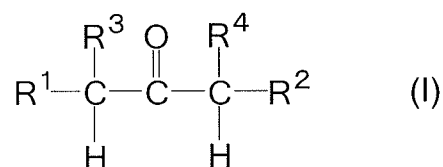
[Table 4]

		Example 17
Catalyst	Supported metal component	CsCl
	Amount of the supported metal component (wt%)	2.1
	Carrier	SiO ₂
propanal conversion rate (%)		36.7
Selectivity (%)	propyne	13.5
	propadiene	4.4
	methane	1.3
	ethane	7.2
	ethylene	3.4
	acetylene	0.2
	propylene	2.2
	propane	0.1
	isobutylene	2.6
	CO	57.1
	CO ₂	0.0
	high boiling component	8.0
Total selectivity of propyne and propadiene (%)		17.9

CLAIMS

1. A method for producing compound having acetylenic bond and/or diene, in which at least one compound selected from the group consisting of the following compounds of formula (I) and (II) is dehydrated in the presence of a catalyst of at least one selected from the group consisting of a compound containing a group 1 metallic element, a compound containing a group 2 metallic element, a group 1 metallic element, and a group 2 metallic element, supported on a carrier containing silica:

Compound represented by formula (I)

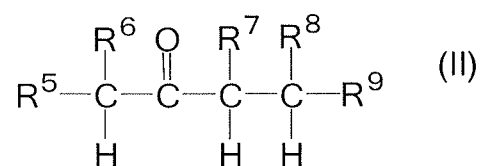


(wherein, in the formula, R¹, R², R³ and R⁴ each independently represent hydrogen atom, alkylcycloalkyl group having 4-10 carbon atoms or phenyl group; or R¹ and R², together with carbon atom to which they are bonded, and also with carbon atom which those carbon atom are bonded, to form a ring having 5-15 carbon atoms, and R³ and R⁴ each independently represent hydrogen atom, alkyl group having 1-6 carbon atoms, cycloalkyl group having 3-6 carbon atoms, alkylcycloalkyl group having 4-10 carbon atoms,

cycloalkylalkyl group having 4-10 carbon atoms,
 aralkyl group having 7-10 carbon atoms or phenyl
 group; or

R^1 and R^3 each independently represent hydrogen atom,
 5 alkyl group having 1-6 carbon atoms, alkylcycloalkyl
 group having 4-10 carbon atoms, cycloalkylalkyl group
 having 4-10 carbon atoms, aralkyl group having 7-10
 carbon atoms or phenyl group, and R^2 and R^4 , together
 with carbon atom to which they are bonded, to form a
 10 ring having 3-13 carbon atoms; or

R^1 and R^3 , together with carbon atom to which they are
 bonded, to form a ring having 3-13 carbon atoms, and
 R^2 and R^4 , together with carbon atom to which they are
 bonded, to form a ring having 3-13 carbon atoms); and
 15 Compound represented by formula (II)



(wherein, in the formula, R^5 , R^6 , R^7 , R^8 and R^9 each
 independently represent hydrogen atom, alkyl group
 having 1-6 carbon atoms, cycloalkyl group having 3-6
 carbon atoms, alkylcycloalkyl group having 4-10
 20 carbon atoms, cycloalkylalkyl group having 4-10
 carbon atoms, aralkyl group having 7-10 carbon atoms
 or phenyl group; or

R⁵, R⁶ and R⁷ each independently represent hydrogen atom, alkyl group having 1-6 carbon atoms, cycloalkyl group having 3-6 carbon atoms, alkylcycloalkyl group having 4-10 carbon atoms, cycloalkylalkyl group having 4-10 carbon atoms, aralkyl group having 7-10 carbon atoms or phenyl group, and R⁸ and R⁹, together with carbon atom to which they are bonded, to form a ring having 3-13 carbon atoms; or

R⁵ and R⁶, together with carbon atom to which they are bonded, to form a ring having 3-13 carbon atoms, and R⁷ represents hydrogen atom, alkyl group having 1-6 carbon atoms, cycloalkyl group having 3-6 carbon atoms, alkylcycloalkyl group having 4-10 carbon atoms, cycloalkylalkyl group having 4-10 carbon atoms, aralkyl group having 7-10 carbon atoms or phenyl group, and R⁸ and R⁹ each independently represent cycloalkyl group having 3-6 carbon atoms, alkylcycloalkyl group having 4-10 carbon atoms, cycloalkylalkyl group having 4-10 carbon atoms, aralkyl group having 7-10 carbon atoms or phenyl group; or

R⁵ and R⁶, together with carbon atom to which they are bonded, to form a ring having 3-13 carbon atoms, and R⁷ represents hydrogen atom, alkyl group having 1-6 carbon atoms, cycloalkyl group having 3-6 carbon

atoms, alkylcycloalkyl group having 4-10 carbon atoms, cycloalkylalkyl group having 4-10 carbon atoms, aralkyl group having 7-10 carbon atoms or phenyl group, and R^8 and R^9 , together with carbon atom to
5 which they are bonded, to form a ring having 3-13 carbon atoms).

2. The method according to claim 1, wherein the catalyst is a catalyst of at least one selected from the
10 group consisting of a compound containing a group 1 metallic element and a group 1 metallic element, supported on the carrier containing silica.

3. The method according to claim 2, wherein the
15 catalyst is a catalyst of a compound containing a group 1 metallic element supported on the carrier containing silica, and the compound containing a group 1 metallic element is at least one compound selected from the group consisting of a halide of a group 1 metallic
20 element, a carbonate of a group 1 metallic element, an oxide of a group 1 metallic element, a hydroxide of a group 1 metallic element, and a silicate of a group 1 metallic element.

25 4. The method according to claim 3, wherein the

group 1 metallic element is sodium, potassium, rubidium, or cesium.

5. The method according to any one of claims 1-4, in
5 which the compound represented by formula (I) is acetone.

6. The method according to any one of claims 1-5, in
10 which the compound represented by formula (II) is 2-butanone.

7. The method according to any one of claims 1 to 6, wherein the carrier is composed of silica.