

DESCRIPTION

PRODUCTION PROCESS OF ALLYL ALCOHOL, AND ALLYL
ALCOHOL OBTAINED BY THE PRODUCTION PROCESSES

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Cross-Reference to Related Application

This application is an application filed under 35 U.S.C. §111(a) claiming benefit pursuant to 35 U.S.C. §119(e)(1) of the filing date of the Provisional Application 60/455,589 filed March 19, 2003, pursuant to 35 U.S.C. §111(b).

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Technical Field

The present invention relates to the production of allyl alcohol.

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Background Art

In the production process of allyl acetate where an allyl acetate is obtained by a gas phase oxidation reaction starting from propylene, acetic acid and oxygen, a catalyst comprising a support having supported thereon a palladium as the main catalyst component and a compound containing alkali metal and/or alkaline earth metal, as a co-catalyst is widely used. For example, Japanese Unexamined Patent Publication No. 2-91045 (JP-A-2-91045) discloses the production of allyl acetate by using a catalyst comprising a support having supported thereon palladium/potassium acetate/copper components.

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Also, a method of hydrolyzing allyl acetate by using an acid catalyst to obtain allyl alcohol is known. Furthermore, a method of producing allyl acetate and then hydrolyzing the separated allyl acetate to obtain allyl alcohol is known, for example, as disclosed in Japanese Unexamined Patent Publication No. 61-238745 (JP-A-61-238745).

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In producing allyl alcohol continuously from the production step of allyl acetate, when acetic acid unreacted at the production of allyl acetate is present, the hydrolysis reaction rate decreases, because the

hydrolysis reaction of allyl acetate is a reversible reaction. Therefore, the reaction solution obtained in the production step of allyl acetate cannot be used as it is and in order to achieve an efficient hydrolysis reaction rate, the reaction product obtained in the production step of allyl acetate is separated and purified through a distillation tower and the resulting solution substantially comprising allyl acetate, water and allyl alcohol is hydrolyzed to produce allyl alcohol. Thus, expensive equipment is required for purifying the reaction solution. Furthermore, in the process for producing allyl acetate by using a catalyst comprising palladium/potassium acetate/copper, a phenomenon wherein a compound containing alkali metal and/or alkaline earth metal or a component derived from the compound as one component of the catalyst (hereinafter, these are collectively called an "alkali component(s)") desorbs and flows out from the catalyst during the reaction is seen. The mechanism of desorption is not particularly understood, but one reason for desorption occurring is believed to be that the acetic acid as starting material and the alkali component(s) react, producing a new compound (hereinafter referred to as an "acetic acid compound") and this acetic acid compound is more readily desorbed from the catalyst than the alkali component(s) present in the catalyst. Depending on the case, this potassium acetate-originated component outflowing at the production of allyl acetate poisons the catalyst in the hydrolysis step and if this occurs, a step of removing this component is required.

Disclosure of Invention

An object of the present invention is to provide a production process of allyl alcohol, where allyl alcohol can be efficiently obtained by hydrolyzing the reaction mixture from the production step of allyl acetate without requiring purification, separation and the like.

As a result of intensive investigations to overcome

these problems, the present inventors have found that when the conversion of the starting material acetic acid is elevated in the production step of allyl acetate, the resulting reaction mixture can be introduced into the hydrolysis step without passing through purification and separation. The present invention has been accomplished based on this finding.

Specifically, the present invention (I) is a process for producing allyl alcohol, comprising the following steps (1) and (2), with the conversion of the starting material acetic acid in the step (1), represented by formula (1), being 60% or more:

Step (1):

a step of producing allyl acetate from propylene, acetic acid and oxygen in a gas phase in the presence of a catalyst comprising a support having supported thereon a catalyst component containing (a) a compound containing alkali metal and/or alkaline earth metal, (b) an element belonging to Group 11 of the Periodic Table or a compound containing at least one of these elements, and (c) palladium; and

Step (2):

a step of hydrolyzing the allyl acetate obtained in the step (1), by using an acid catalyst to produce allyl alcohol:

Conversion (%) =

$$\frac{\{(\text{amount (mol) of acetic acid at reactor inlet} - \text{amount (mol) of acetic acid at reactor outlet}) / \text{amount (mol) of acetic acid at reactor inlet}\} \times 100}{(1)}$$

The present invention (II) is allyl alcohol produced by the production process of the present invention (I).

The present invention having such constitutions comprises, for example, the following.

[1] A process for producing allyl alcohol, comprising the following steps (1) and (2), with the conversion of the starting material acetic acid in the

step (1), represented by formula (1), being 60% or more:

Step (1):

5 a step of producing allyl acetate from propylene, acetic acid and oxygen in a gas phase in the presence of a catalyst comprising a support having supported thereon a catalyst component containing (a) a compound containing alkali metal and/or alkaline earth metal, (b) an element belonging to Group 11 of the Periodic Table or a compound containing at least one of these elements, and (c) a
10 palladium; and

Step (2):

a step of hydrolyzing the allyl acetate obtained in the step (1), by using an acid catalyst to produce allyl alcohol:

Conversion (%) =

$$\frac{\{(\text{amount (mol) of acetic acid at reactor inlet} - \text{amount (mol) of acetic acid at reactor outlet}) / \text{amount (mol) of acetic acid at reactor inlet}\} \times 100}{(1)}$$

15 [2] The production process as described in [1] above, wherein the outflow ratio per hour of (a) the compound containing alkali metal and/or alkaline earth metal, represented by formula (2), is from 1.0×10^{-5} to 0.01%/h:

Outflow ratio (%)/h =

$$\frac{\{\text{mass (kg/h) of alkali metal or alkaline earth metal detected} / \text{mass (kg) of alkali metal or alkaline earth metal in the entire catalyst packed}\} \times 100}{(2)}$$

20 [3] The production process as described in [1] or [2] above, wherein (a) the compound containing alkali metal and/or alkaline earth metal is a compound containing at least one member selected from the group consisting of lithium, sodium, potassium, cesium,
25 magnesium, calcium and barium.

[4] The production process as described in any one

of [1] to [3] above, wherein (a) the compound containing alkali metal and/or alkaline earth metal is a salt of a lower aliphatic carboxylic acid.

5 [5] The production process as described in [4] above, wherein the salt of a lower aliphatic carboxylic acid is at least one member selected from lithium, sodium, potassium, cesium, magnesium, calcium and barium salts of formic acid, acetic acid, propionic acid, acrylic acid or methacrylic acid.

10 [6] The production process as described in any one of [1] to [5] above, wherein (b) the element belonging to Group 11 of the Periodic Table or the compound containing at least one of these elements is an element of copper or gold or a compound containing one or more of copper and
15 gold.

[7] The production process as described in any one of [1] to [6] above, wherein propylene, acetic acid and oxygen are reacted in the presence of water.

20 [8] Allyl alcohol produced by the production process described in any one of [1] to [7] above.

Best Mode for Carrying Out the Invention

Preferred embodiments of the present invention are described in more detail below.

25 The compound containing alkali metal and/or alkaline earth metal (a) in the catalyst for use in the step (1) of the present invention (I) is not particularly limited and may be sufficient if it is a compound containing at least one of the elements belonging to Groups 1 and 2 of the Periodic Table according to IUPAC Nomenclature of
30 Inorganic Chemistry, Rules 1989. This compound is preferably a compound containing at least one element selected from the group consisting of lithium, sodium, potassium, cesium, magnesium, calcium and barium, more preferably a salt of a lower aliphatic carboxylic acid,
35 still more preferably at least one member selected from lithium, sodium, potassium, cesium, magnesium, calcium and barium salts of a formic acid, an acetic acid, a

propionic acid, an acrylic acid or a methacrylic acid, particularly preferably an acetate, and most preferably a potassium acetate.

5 Examples of (b) the element belonging to Group 11 of the Periodic Table according to IUPAC Nomenclature of Inorganic Chemistry, Rules 1989, or the compound containing at least one of these elements in the catalyst for use in the step (1) of the present invention (I) include Group 11 elements and nitrates, carbonates, 10 sulfates, organic acid salts and halides of a Group 11 element. This component is preferably one or more element(s) selected from copper and gold or a compound thereof, and most preferably copper alone and/or gold alone.

15 The palladium (c) in the catalyst for use in the step (1) of the present invention (I) may have any valence number but is preferably metal palladium. The "metal palladium" as used herein means palladium having 0 valence. This palladium can be usually obtained by 20 reducing a divalent and/or tetravalent palladium ion with hydrazine, hydrogen or ethylene as a reducing agent. At this time, the palladium need not be entirely in the metal state. The starting material of (c) the palladium is not particularly limited and metal palladium or a 25 palladium salt capable of converting into metal palladium can be used. Examples of the palladium salt capable of converting into metal palladium include, but are not limited to, palladium chloride, sodium chloropalladate, palladium nitrate and palladium sulfate.

30 The support used in the catalyst for use in the step (1) of the present invention (I) may be sufficient if it is a commonly employed porous material. Preferred examples thereof include silica, alumina, silica-alumina, kieselguhr, montmorillonite, titania and zirconia, with 35 silica being more preferred. The silica as used herein is not limited to SiO_2 , but silica containing impurities may also be used. The shape of the support is not

particularly limited and examples thereof include powder, sphere and pellet, but a spherical shape is preferred.

The size of the support used is also not particularly limited and the optimal size of the support varies, depending on the shape or reaction style. For example, when the support is spherical, the particle diameter, which is not particularly limited, is preferably from 1 to 10 mm, more preferably from 3 to 8 mm. In the case of performing a reaction by packing the catalyst in a tubular reactor, if the particle diameter is less than 1 mm, a large pressure loss occurs on passing a gas and the gas circulation may not be effectively performed, whereas if the particle diameter exceeds 10 mm, the reaction gas cannot diffuse into the inside of catalyst and the catalytic reaction may not proceed effectively.

As for the pore structure of the support, the average pore diameter is preferably from 0.1 to 1,000 nm, more preferably from 0.2 to 500 nm, and most preferably from 0.5 to 200 nm. If the average pore diameter is less than 0.1 nm, the gas may hardly diffuse, whereas if it exceeds 1,000 nm, the surface area of the support becomes too small and the catalytic activity may decrease.

The ratio between support and (c) palladium is, as the mass ratio, preferably support : (c) palladium = 10 to 1,000 : 1, more preferably support : (c) palladium = 30 to 500 : 1. If the ratio of support and (c) palladium is, in terms of the mass of support, less than support : (c) palladium = 10:1, the amount of palladium becomes excessively large for the support, resulting in a poor palladium dispersion state and the reaction yield may decrease, whereas if the ratio of support and (c) palladium is, in terms of the mass of support, larger than support : (c) palladium = 1,000:1, the mass of support becomes too large and this is not practical.

The ratio among (a) compound containing alkali metal and/or alkaline earth metal, (b) element belonging to

Group 11 of the Periodic Table or compound containing at least one of these elements and (c) palladium is, as the mass ratio, preferably (a) compound containing alkali metal and/or alkaline earth metal : (b) element belonging to Group 11 of the Periodic Table or compound containing at least one of these elements : (c) palladium = 0.1 to 100 : 0.001 to 10 : 1, more preferably (a) compound containing alkali metal and/or alkaline earth metal : (b) element belonging to Group 11 of the Periodic Table or compound containing at least one of these elements : (c) palladium = 1 to 50 : 0.05 to 5 : 1.

The catalyst for use in the step (1) of the present invention (I) can be obtained by loading (a) a compound containing alkali metal and/or alkaline earth metal, (b) an element belonging to Group 11 of the Periodic Table or a compound containing at least one of these elements and (c) a palladium on a support. In this case, the method for loading the components (a), (b) and (c) is not particularly limited, but examples thereof include a method of performing the following steps (A) to (F) in this order:

Step (A):

a step of impregnating a support with an aqueous solution of salt(s) of palladium and (b) an element belonging to Group 11 of the Periodic Table or a compound containing at least one of these elements to obtain Catalyst Precursor A;

Step (B):

a step of bringing Catalyst Precursor A obtained in the step (A) into contact with an aqueous solution of an alkali metal salt without drying the precursor A to obtain Catalyst Precursor B;

Step (C):

a step of bringing Catalyst Precursor B obtained in the step (B) into contact with a reducing agent such as hydrazine or formalin to obtain Catalyst Precursor C;

Step (D):

a step of water-washing Catalyst Precursor C obtained in the step (C);

Step (E):

5 a step of bringing Catalyst Precursor C obtained in the step (D) into contact with (a) a compound containing alkali metal and/or alkaline earth metal to obtain a catalyst; and

Step (F):

10 a step of drying the catalyst obtained in the step (E).

The catalyst for use in the step (1) of the present invention (I) is preferably, for example, a catalyst produced by this method and having a specific surface area of 10 to 250 m²/g and a pore volume of 0.1 to 1.5 ml/g.

15 The propylene for use in the step (1) of the present invention (I) is not particularly limited. In the propylene, a lower saturated hydrocarbon such as ethane, methane and propane, or a lower unsaturated hydrocarbon such as butadiene, may be mixed. The propylene is preferably high-purity propylene.

The acetic acid for use in the step (1) of the present invention (I) is not particularly limited and an acetic acid usually available on the market can be used.

25 The oxygen for use in the step (1) of the present invention (I) is not particularly limited and may be supplied in the form of being diluted with an inert gas such as nitrogen or carbon dioxide gas, for example, in the form of air, but oxygen having a purity of 99% or more is preferably used.

30 The ratio among acetic acid, propylene and oxygen for use in the step (1) of the present invention (I) is, as the molar ratio, preferably acetic acid : propylene : oxygen = 1 : 0.08 to 16 : 0.01 to 4, more preferably acetic acid : propylene : oxygen = 1 : 1 to 12 : 0.5 to 2.

The reaction starting material gas for use in the

step (1) of the present invention (I) contains propylene, acetic acid and oxygen and, for example, nitrogen, carbon dioxide or rare gas may be used as a diluent, if desired. When the propylene, acetic acid and oxygen are denoted as the reaction starting material, the ratio of reaction starting material and diluent is, as the molar ratio, preferably reaction starting material : diluent = 1 : 0.05 to 9, more preferably reaction starting material : diluent = 1 : 0.1 to 3.

The reaction starting material gas for use in the step (1) of the present invention (I) is preferably passed through the catalyst at a space velocity of, in the standard state, from 10 to 15,000 hr⁻¹, more preferably from 300 to 8,000 hr⁻¹. If the space velocity is less than 10 hr⁻¹, the heat of reaction may be difficult to remove, whereas if the space velocity exceeds 15,000 hr⁻¹, the equipment required, such as a compressor, becomes too large and this is not practical.

In the reaction starting material gas for use in the step (1) of the present invention (I), from 0.5 to 20 mol% of water can be added. Preferably, from 1 to 18 mol% of water is added. By virtue of the presence of water in the system, although the reasons are not clearly understood, the outflow of (a) the compound containing alkali metal and/or alkaline earth metal from the catalyst decreases. Even if water is added in an amount exceeding 20 mol%, the effect is not enhanced but rather hydrolysis of allyl acetate may proceed. Therefore, it is preferred that a large amount of water not be present.

In the step (1) of the present invention (I), the reaction of propylene, acetic acid and oxygen in the presence of a catalyst may be performed in any conventionally known form as long as it is in a gas phase, but the reaction is preferably a fixed-bed flow reaction.

The construction material of the reactor used in performing the step (1) of the present invention (I) is

not particularly limited but a reactor constituted by a material having corrosion resistance is preferred.

In performing the step (1) of the present invention (I), the reaction temperature is from 100 to 300°C, preferably from 120 to 250°C. If the reaction temperature is less than 100°C, this may disadvantageously cause the reaction to proceed at an excessively low rate, whereas if the reaction temperature exceeds 300°C, the heat of reaction may not be removed and this is not desirable.

In performing the step (1) of the present invention (I), the reaction pressure is from 0 to 3 MPaG, preferably from 0.1 to 1.5 MPaG. If the reaction pressure is less than 0 MPaG, this may disadvantageously cause reduction in the reaction rate, whereas if the reaction pressure exceeds 3 MPaG, the equipment such as reaction tube becomes expensive and this is not practical.

The conversion of the acetic acid for use in the step (1) of the present invention (I) is 60% or more. There is correlation between the concentration of the acetic acid and the amount of (a) the compound containing alkali metal and/or alkaline earth metal deposited in the vicinity of the outlet and as the concentration of the acetic acid decreases, the amount of (a) the compound containing alkali metal and/or alkaline earth metal deposited increases. Furthermore, due to the presence of a large amount of unreacted acetic acid, the equilibrium in the hydrolysis reaction of the step (2) may turn to be disadvantageous to the production of allyl alcohol and steps such as separation are undesirably required.

The outflow ratio specified by formula (2), that is, the ratio of the alkali metal and/or alkaline earth metal in the catalyst for use in the step (1) of the present invention (I) flowing out from the catalyst, is preferably from 1.0×10^{-5} to 0.01%/h. If the outflow

ratio is less than 1.0×10^{-5} %/h, the reaction tube may be clogged or the compound containing alkali metal and/or alkaline earth metal may deposit on the catalyst, and as a result, the production may not be stable. On the other hand, if the outflow ratio exceeds 0.01%/h, the catalytic performance may disadvantageously decrease at a high rate due to the large outflow of the compound containing alkali metal and/or alkaline earth metal. In this case, the activity may be maintained by feeding from the reaction inlet a compound containing alkali metal and/or alkaline earth metal in an amount large enough to compensate for the outflow of the compound containing alkali metal and/or alkaline earth metal, although this is unprofitable.

In formula (2), the mass of alkali metal or alkaline earth metal outflowing is the mass of alkali metal and/or alkaline earth metal contained in the gas at the reactor outlet. The alkali metal element or alkaline earth element as used herein indicates the alkali metal element or alkaline earth metal element contained as a catalyst component in the catalyst.

Outflow ratio (%)/h =

$$\frac{\{\text{mass (kg/h) of alkali metal or alkaline earth metal detected / mass (kg) of alkali metal or alkaline earth metal in the entire catalyst packed}\} \times 100}{(2)}$$

For example, in the production process of allyl acetate, potassium acetate is generally used as a co-catalyst and the potassium acetate is appropriately added to the reactor even during reaction, because this co-catalyst flows out from the reaction tube during reaction and is contained as potassium or a potassium compound in the gas at the reactor outlet.

The "catalyst packed" as used herein indicates a catalyst packed in the reactor and being in the state before passing a reaction starting material gas. In the

case where two or more reactors are present in series or in parallel in one apparatus (process), the total amount of catalyst packed in all reactors is indicated.

5 The alkali metal element and/or alkaline earth metal element in the gas at the reactor outlet may be detected by any method. Examples thereof include a method of detecting the element as a condensate at the time of separating and purifying the reactor outlet gas, and a method of adsorbing the element by contacting the
10 reaction mixture with an ion exchange resin or the like. Specific examples thereof include a method of cooling the reactor outlet gas to an extent wherein condensation occurs, and determining the potassium concentration in the obtained condensate by an analysis method such as
15 induction coupled plasma emission spectroscopic analysis (hereinafter referred to as "ICP spectroscopic analysis") or atomic absorption method. The determination method using ICP spectroscopic analysis is not particularly limited but, for example, an absolute calibration curve
20 method may be used.

In the outflow ratio used in the step (1) of the present invention (I), the mass of alkali metal or alkaline earth metal in the entire catalyst packed indicates the mass of alkali metal and/or alkaline earth
25 metal in the entire catalyst packed in the reactor, specifically, the mass of alkali metal and/or alkaline earth metal in the packed catalyst before the catalyst is used for the reaction. The mass of alkali metal and/or alkaline earth metal in the catalyst changes during
30 reaction due to outflowing or deposition of the component fed, but the mass of alkali metal and/or alkaline earth metal as used herein is calculated based on the catalyst before reaction.

The outflow ratio (%/h) can be controlled by the
35 reaction conditions such as reaction temperature, reaction pressure and starting material component, and the reaction conditions are set to give an outflow ratio

in the desired range. The controlling method is not particularly limited and, for example, the outflow ratio can be increased by elevating the reaction temperature or increasing the proportion of lower aliphatic carboxylic acid in the starting material component.

5 During the reaction, (a) a compound containing alkali metal and/or alkaline earth metal must be fed from the reactor inlet in an amount large enough to compensate for the mass of the alkali metal and/or alkaline earth metal outflowing. Preferably, the alkali metal and/or alkaline earth metal is added as (a) a compound containing the alkali metal and/or alkaline earth metal in an amount of 0.01 to 200 mass% based on the mass of the alkali metal and/or alkaline earth metal outflowed. 10 More preferably, (a) a compound containing alkali metal and/or alkaline earth metal is added in an amount equivalent to or greater than the mass of the alkali metal and/or alkaline earth metal outflowing. Although the reasons are not clearly understood, when (a) a compound containing alkali metal and/or alkaline earth metal is added in an equivalent amount or more, the reaction yield decreases less. 15 20

The compound containing alkali metal and/or alkaline earth metal (a) may be added by any method but is preferably added by mixing it in a reaction starting material gas. 25

The step (2) of the present invention (I) is described below.

The allyl acetate for use in the step (2) of the present invention (I) is not particularly limited as long as it is allyl acetate obtained in the step (1) of the present invention (I), and may contain impurities. 30

The pressure in the hydrolysis reaction is not particularly limited but is preferably, for example, from 0.0 to 1.0 MPaG. 35

The reaction temperature in the hydrolysis reaction is not particularly limited but is preferably from 20 to

300°C, more preferably from 50 to 250°C.

The hydrolysis reaction in the step (2) of the present invention (I) can be performed in any reaction system such as gas phase reaction, liquid phase reaction
5 and solid-liquid reaction.

The hydrolysis reaction is preferably performed by adding water to the allyl acetate so as to elevate the conversion of the allyl acetate in the hydrolysis reaction. The amount of water added is preferably from
10 1.0 to 60 mass%, more preferably from 5 to 40 mass%.

Also, the hydrolysis reaction is preferably performed while removing the produced allyl alcohol out of the reaction system. The method for removing the allyl alcohol out of the reaction system is not
15 particularly limited, but, for example, a method of adding a substance capable of forming an azeotropic mixture with the allyl alcohol and removing the allyl alcohol while performing distillation during the reaction, may be used.

20 Examples of the acid catalyst for use in the hydrolysis reaction of the allyl acetate include organic acids, inorganic acids, solid acids and salts thereof. Specific examples thereof include formic acid, acetic acid, propionic acid, tartaric acid, oxalic acid, butyric
25 acid, terephthalic acid, fumaric acid, heteropolyacid, hydrochloric acid, sulfuric acid, nitric acid, phosphoric acid, hydrobromic acid, hydrofluoric acid, silica alumina, silica titania, silica magnesia, acidic cation exchange resin and sodium salt, potassium salt, magnesium
30 salt and aluminum salt thereof. Among these, a solid acidic cation exchange resin is most preferred in view of easy separation from the allyl alcohol after reaction or acidity. This resin is more preferably, for example, an ion exchange resin where an acidic active functional
35 group such as sulfonic acid group is bonded to the styrene-divinylbenzene resin skeleton.

The apparatus of performing the hydrolysis reaction

for use in the step (2) of the present invention (I) is not particularly limited, but a fixed bed flow-type reactor is preferred. When two or more reactor units are used in parallel, a constant amount of allyl alcohol can be continuously obtained and therefore, this is preferred.

In the step (2) of the present invention (I), the method of producing allyl alcohol in a fixed bed flow-type reactor by using an acidic cation exchange resin as the hydrolysis catalyst is not particularly limited, but a method of causing an ascending flow to convey a reaction solution containing the allyl acetate and water from the bottom of the reactor into the reactor system is preferred. In this case, the coagulation of ion exchange resin and the drifting of reaction starting material, which may occur in the case of passing the reaction solution from the top to the bottom, can be suppressed.

The production process of the present invention (I) may contain any other steps as long as it contains the steps (1) and (2). For example, a step of treating the starting material before the step (1) or a step of separating the allyl alcohol after the step (2) may be of course provided, and a certain step may also be provided between the step (1) and the step (2).

The present invention (II) is described below. The present invention (II) is allyl alcohol obtained by the production process of the present invention (I). This allyl alcohol is advantageously free from mingling of halogen, because the allyl acetate as the starting material does not contain halogen. Therefore, when this allyl alcohol is used as a starting material, steps such as removal of halogen giving rise to corrosion of equipment can be dispensed with and the process can be advantageously simplified.

The present invention is described in greater detail below by referring to Examples. However, the present invention is not limited thereto.

The reactor outlet gas was analyzed by the following methods.

1. Propylene

5 An absolute calibration curve method was employed for analysis, where 50 ml of the outflow gas was sampled and the entire amount of the gas flowed into a 1-ml gas sampler attached to a gas chromatograph and analyzed under the following conditions.

Gas chromatography:

gas chromatograph (GC-7B manufactured by Shimadzu Corporation) with a gas sampler (MGS-4, measuring tube: 1 ml) for Shimadzu Gas Chromatograph

Column: packed column Unibeads IS, length: 3 m

Carrier gas: helium (flow rate: 35 ml/min)

Temperature conditions:

The detector temperature was 100°C, the vaporization chamber temperature was 140°C and the column temperature was constantly 140°C.

Detector: TCD (He pressure: 125 kPaG, current: 125 mA)

2. Oxygen

10 An absolute calibration curve method was employed for analysis, where 50 ml of the outflow gas was sampled and the entire amount of the gas flowed into a 1-ml gas sampler attached to a gas chromatograph and analyzed under the following conditions.

Gas chromatography:

gas chromatograph (GC-14B manufactured by Shimadzu Corporation) with a gas sampler (MGS-4, measuring tube: 1 ml) for Shimadzu Gas Chromatograph

Column: MS-5A IS, 60/80 mesh (3 mmφ × 3 m)

Carrier gas: helium (flow rate: 20 ml/min)

Temperature conditions:

The temperature of detector and vaporization chamber was 110°C and the column temperature was constantly 70°C.

Detector: TCD (He pressure: 70 kPaG, current: 100 mA)

15 3. Acetic Acid

An internal standard method was employed for analysis, where 1 ml of 1,4-dioxane was added as the internal standard to 10 ml of the reaction solution and 0.2 μ l of the resulting analysis solution was injected and analyzed under the following conditions.

5 Gas chromatography:

GC-14B manufactured by Shimadzu Corporation
Column: packed column Thermo 3000 (length: 3 m, inner diameter: 0.3 mm)

Carrier gas: nitrogen (flow rate: 20 ml/min)

Temperature conditions:

The temperature of detector and vaporization chamber was 180°C and the column temperature was kept at 50°C for 6 minutes from the start of analysis, then elevated to 150°C at a temperature rising rate of 10°C/min and kept at 150°C for 10 minutes.

Detector: FID (H_2 pressure: 40 kPaG, air pressure: 100 kPaG)

4. Allyl Acetate

An internal standard method was employed for analysis, where 1 g of pentyl acetate was added as the internal standard to 25 g of the reaction solution and 0.3 μ l of the resulting analysis solution was injected and analyzed under the following conditions.

10 Gas chromatography:

GC-9A manufactured by Shimadzu Corporation
Column: capillary column TC-WAX (length: 30 m, inner diameter: 0.25 mm, film thickness: 0.5 μ m)
Carrier gas: nitrogen (flow rate: 30 ml/min)

Temperature conditions:

The temperature of detector and vaporization chamber was 200°C and the column temperature was kept at 45°C for 2 minutes from the start of analysis, then elevated to 130°C at a temperature rising rate of 4°C/min, kept at 130°C for 15 minutes, again elevated to 200°C at a temperature rising rate of 25°C/min and kept at 200°C for 10 minutes.

Detector: FID (H₂ pressure: 60 kPaG, air pressure: 100 kPaG)

5. Allyl Alcohol

An internal standard method was employed for analysis, where 200 µl of n-amine acetate was added as the internal standard to 10 ml of the reaction solution, and 0.1 µl of the resulting analysis solution was injected and analyzed under the following conditions.

Gas chromatography:

GC-14B manufactured by Shimadzu Corporation
Column: packed column Thermon 3000 (length: 3 m, inner diameter: 0.3 mm)

Carrier gas: nitrogen (flow rate: 2.0 ml/min)

Temperature conditions:

The temperature of detector and vaporization chamber was 180°C and the column temperature was kept at 45°C for 5 minutes from the start of analysis, then elevated to 130°C at a temperature rising rate of 7°C/min and kept at 130°C for 13 minutes.

Detector: FID (H₂ pressure: 98 kPaG, air pressure: 98 kPaG)

Example 1

Preparation of Catalyst A:

Sodium chloropalladate crystal (56.4 mmol), 8.50 mmol of cupric chloride dihydrate and 18.4 mmol of zinc chloride were dissolved in pure water and the resulting solution was measured to 97% of the water absorption amount of the support.

The aqueous metal salt solution obtained above was uniformly impregnated into a silica support (KA-160 produced by Sud-chemi AG) which was previously dried at 110°C for 4 hours.

5 Subsequently, sodium metasilicate nonahydrate was dissolved in pure water and the amount of the solution was adjusted to 2 times the water absorption amount of the support. The resulting solution was added to the impregnated support and left standing at room temperature
10 for 20 hours to obtain a catalyst.

To this solution, 720 mmol of hydrazine monohydrate was further added and after stirring at room temperature for 4 hours, the catalyst was washed with pure water and dried by a hot air dryer at 110°C for 4 hours.

15 Thereafter, 509 mmol of potassium acetate was dissolved in pure water and the resulting solution was measured to about 97% of the water absorption amount of the catalyst. This solution was uniformly loaded on the catalyst and then dried at 110°C for 4 hours to obtain
20 Catalyst A for reaction.

Analysis of Potassium:

1. Analysis of Catalyst Before Use

The catalyst before use was finely ground in an agate mortar and then dried at 110°C for 2 hours to
25 prepare a powder sample. To 1 g of the powder sample, 100 ml of pure water was added and 10 ml of 35% hydrochloric acid was further added. Thereafter, the sample was boiled in a sand bath for 2 hours and then allowed to cool and thereto, pure water was added to make
30 500 ml. After filtering, the filtrate was subjected to ICP spectroscopic analysis and the amount of potassium was calculated.

2. Analysis of Potassium Detected After Reactor Outlet

35 The condensate obtained by cooling the reaction gas to 0°C was subjected to ICP analysis and the amount of potassium was calculated.

Synthesis of Allyl Acetate:

The obtained catalyst (20 ml) was packed in a stainless steel-made reaction tube having an inner diameter of 21.4 mm and by supplying a mixed gas containing 30 mol% of propylene, 7.0 mol% of oxygen, 5.5 mol% of acetic acid, 14.0 mol% of water and 43.5 mol% of nitrogen, the reaction was performed at a reaction temperature of 135°C and a pressure of 0.8 MPaG. The results are shown in Table 2. The concentration of each component in the reaction solution was measured by using a gas chromatography analyzer. The conversion of acetic acid was calculated according to formula (1) and the outflow ratio (%/h) was calculated according to formula (2) from the weight of potassium in the condensate obtained by cooling the gas at the outlet of the reaction tube and the weight of potassium in the catalyst before use.

Synthesis of Allyl Alcohol:

The condensate obtained in the synthesis of allyl acetate was directly hydrolyzed at 80°C and 0.5 MPaG by using an ion exchange resin (Diaion SK104H, produced by Mitsubishi Chemical Corporation) to obtain an allyl alcohol. The conversion was 98% and the selectivity was 98%.

Example 2:

The reaction was performed in the same manner as in Example 1, except that the conditions were changed as shown in Table 1. The results are shown in Table 2.

Comparative Example 1:

The reaction was performed in the same manner as in Example 1 except for changing the reaction conditions to give an acetic acid conversion of 45%. The results are shown in Table 2.

In the hydrolysis, the conversion was 75% and the selectivity was 96%. After 2,400 hours, the conversion in the hydrolysis was 65%, revealing a considerable decrease in conversion.

TABLE 1

	Catalyst	SV h ⁻¹	Reaction Temperature °C	Reaction Pressure MPaG	Reaction Gas					
					Olefin	Oxygen	mol%			
							Acetic Acid	Water	Nitrogen	
Example 1	A	1600	135	0.8	propylene	30	7	5.5	14	43.5
Example 2	A	1600	160	0.8	propylene	30	7	5.5	14	43.5
Comparative Example 1	A	1600	135	0.8	propylene	30	5	5	7	53

TABLE 2

	Allyl Acetate		Conversion of Acetic Acid	Outflow Ratio	Allyl Alcohol			
	STY	Sel			Conversion		Sel	
	g/L-cat	%			5 h	2400 h	5 h	2400 h
			%	%/h	%		%	
Example 1	355.7	92	70.3	6.5×10^{-4}	98	94	96	97
Example 2	425.4	91	85	2.2×10^{-4}	99	96	97	98
Comparative Example 1	204.8	91	45	0.008	75	65	96	95

Industrial Applicability

According to the present invention, in producing an allyl alcohol by producing an allyl acetate from acetic acid, propylene and oxygen and hydrolyzing the obtained allyl acetate, the reaction mixed solution after the reaction for producing an allyl acetate can be directly hydrolyzed without any purification through controlling the conversion of acetic acid during the production of allyl acetate, and therefore the process can be simplified.

CLAIMS

1. A process for producing allyl alcohol, comprising the following steps (1) and (2), with the conversion of the starting material acetic acid in the step (1), represented by formula (1), being 60% or more:
5 Step (1):

a step of producing allyl acetate from propylene, acetic acid and oxygen in a gas phase in the presence of a catalyst comprising a support having supported thereon a catalyst component containing (a) a
10 compound containing alkali metal and/or alkaline earth metal, (b) an element belonging to Group 11 of the Periodic Table or a compound containing at least one of these elements, and (c) a palladium; and

15 Step (2):

a step of hydrolyzing the allyl acetate obtained in the step (1), by using an acid catalyst to produce allyl alcohol:

Conversion (%) =

$$\frac{\{(\text{amount (mol) of acetic acid at reactor inlet} - \text{amount (mol) of acetic acid at reactor outlet}) / \text{amount (mol) of acetic acid at reactor inlet}\} \times 100}{(1)}$$

2. The production process as claimed in claim 1, wherein the outflow ratio per hour of (a) the compound containing alkali metal and/or alkaline earth metal, represented by formula (2), is from 1.0×10^{-5} to 0.01%/h:
20

Outflow ratio (%)/h =

$$\frac{\{\text{mass (kg/h) of alkali metal or alkaline earth metal detected} / \text{mass (kg) of alkali metal or alkaline earth metal in the entire catalyst packed}\} \times 100}{(2)}$$

3. The production process as claimed in claim 1 or 2, wherein (a) the compound containing alkali metal and/or alkaline earth metal is a compound containing at least one member selected from the group consisting of
25

lithium, sodium, potassium, cesium, magnesium, calcium and barium.

4. The production process as claimed in any one of claims 1 to 3, wherein (a) the compound containing alkali metal and/or alkaline earth metal is a salt of a lower aliphatic carboxylic acid.

5. The production process as claimed in claim 4, wherein the salt of a lower aliphatic carboxylic acid is at least one member selected from lithium, sodium, potassium, cesium, magnesium, calcium and barium salts of formic acid, acetic acid, propionic acid, acrylic acid or methacrylic acid.

6. The production process as claimed in any one of claims 1 to 5, wherein (b) the element belonging to Group 11 of the Periodic Table or the compound containing at least one of these elements is an element of copper or gold or a compound containing one or more of copper and gold.

7. The production process as claimed in any one of claims 1 to 6, wherein propylene, acetic acid and oxygen are reacted in the presence of water.

8. Allyl alcohol produced by the production process as set forth in any one of claims 1 to 7.