

PROCESS FOR PRODUCING α, β -UNSATURATED CARBOXYLIC ACID

Background of the Invention

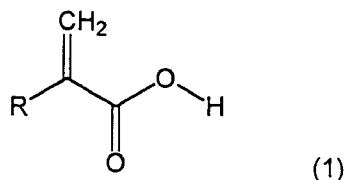
The present invention relates to a process for producing α, β -unsaturated carboxylic acid.

JP2001-507697T, which corresponds to WO98/29379, discloses a process for preparing α, β -unsaturated carboxylic acid or ester thereof from a carboxylic acid or ester and formaldehyde in the presence of a catalyst containing oxide of niobium, which was prepared from hygroscopic niobium fluoride.

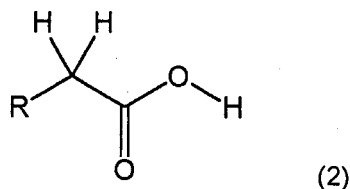
JP62-221651A discloses a process of using a catalyst obtained by adding a sulfur oxide to a solid catalyst having an acid strength showing an acid point of $\text{pK}_a \leq -3.0$ for the production of similar compounds, and ammonium sulfate, ammonium hydrogensulfate, sulfuric acid, ammonium sulfite or sulfurous acid is disclosed as raw material of sulfur oxide. It also discloses an oxidizing ability retaining component such as an oxide of V, Cr, Co, Ni, Mo, W or Pb or a heteropolyacid containing V, Mo or W or both as an additional component of the catalyst.

According to the present invention, α, β -unsaturated carboxylic acid can be readily prepared.

The present invention provides a process for producing α, β -unsaturated carboxylic acid of formula (1):



wherein R represents a hydrogen atom, an alkyl group, an aryl group, an aralkyl group, an alkenyl group or alkynyl group, which comprises reacting a carboxylic acid of formula (2):



- 5 wherein R represents the same as defined above, with formaldehyde or a precursor thereto in the presence of a sulfate of nickel, cobalt, iron, aluminum, copper, chromium, manganese, zirconium, zinc, silver, palladium, indium, or vanadyl, or mixtures thereof.

10 Examples of the alkyl group represented by R include, for example, a C1-10 alkyl group such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, or decyl.

Examples of the aryl group include, for example, a C6-10 aryl group such as phenyl, tolyl (e.g. p-tolyl) or naphthyl.

15 Examples of the aralkyl group include, for example, a C7-11 arylaralkyl such as benzyl, 3-phenylpropyl, or naphthylmethyl.

Examples of the alkenyl group include, for example, a C2-10 alkenyl group such as vinyl, propenyl, butenyl, pentenyl, hexenyl, heptenyl, octenyl, nonenyl, or decenyl.

20 Examples of the alkynyl group include, for example, a C2-10 alkynyl group such as ethynyl, propynyl, butynyl, pentynyl, hexynyl, heptynyl, octynyl, nonynyl, or decynyl.

Specific examples of the carboxylic acid of formula (2) include, for example, acetic acid, propionic acid, butyric acid, valeric acid, 3-methylbutanoic acid, caproic acid, heptanoic acid, caprylic acid, nonanoic acid, capric acid, undecanoic acid, phenylacetic acid, p-tolylacetic acid, naphthylacetic acid, vinylacetic acid, 4-pentenoic acid, 10-undecenoic acid, 3-butynoic acid, 3-pentynoic acid, and 3-hexynoic acid.

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Preferred are acetic acid and propionic acid, and more preferred is propionic acid.

Formaldehyde may be used in a form of a precursor thereto, for example, in a form of an aqueous solution thereof such as formaldehyde hydrate or oligomer thereof (e.g. formalim) or may be used as it is without
5 any diluent. The oligomer of formaldehyde such as trioxane or paraformaldehyde may be used. Preferred is trioxane. Formaldehyde and the oligomer may also be used with a diluent such as an organic or inorganic solvent.

10 The amount of the formaldehyde is usually 0.01 to 10 moles, preferably 0.03 to 3 moles, more preferably 0.1 to 1 mol per mol of the carboxylic acid (2).

Examples of the α , β -unsaturated carboxylic acid include, for example, methacrylic acid, which is produced from propionic acid and
15 formaldehyde.

Examples of the sulfate include, for example, nickel sulfate, cobalt sulfate such as cobaltous sulfate or cobaltic sulfate, iron sulfate such as ferrous sulfate or ferric sulfate, aluminum sulfate, copper sulfate such as cuprous sulfate or cupric sulfate, chromium sulfate such as chromous sulfate
20 or chromic sulfate, manganese sulfate such as manganous sulfate or manganic sulfate, zirconium sulfate, zinc sulfate, silver sulfate, palladium sulfate, indium sulfate, and nickel ammonium sulfate, and oxymetal sulfate such as vanadyl sulfate. Preferred are nickel sulfate, cobalt sulfate, aluminum sulfate, iron sulfate, and vanadyl sulfate. More preferred is nickel
25 sulfate. The sulfate may be used alone or may be used as a mixture thereof or as a complex thereof. The sulfate containing crystalline water may also be used, or the sulfate(s) may be used in a supported form on a support such as silica or alumina.

The sulfate can be readily prepared or may be commercially available
30 typically in a hydrated form, which are preferably calcined before use. The

calcination is usually conducted at a temperature range of from 50 to 1000°C, preferably 100 to 500°C, more preferably 150 to 450°C and yet more preferably 200 to 400°C.

5 The reaction of the carboxylic acid (2) and formaldehyde can be conducted by a batch process or by a continuous process. Preferred is the continuous process for industrial production. In the continuous process, the carboxylic acid to be reacted is usually fed in an amount of 0.1g/hr to 100g/hr, preferably 0.3g/hr to 20g/hr per 1 g of the metal sulfate.

10 The formaldehyde or the precursor thereto and the carboxylic acid (2) are usually fed into a reactor together with an inert gas such as nitrogen, helium, or argon. Nitrogen is preferably used for its cost.

The reaction of the formaldehyde or the precursor thereto with the carboxylic acid (2) is usually conducted at a temperature range of 150 to 500°C, preferably 200 to 400°C, more preferably about 250 to 350°C, and
15 usually at a gauge pressure of 0 MPa (i.e. atmospheric pressure) to a gauge pressure of 10MPa, preferably at a gauge pressure of 0.05MPa to a gauge pressure of 1MPa. After the reaction, the product is usually separated by distillation or extraction and may be further purified, if necessary.

20 Examples

The present invention is illustrated by way of the following examples, but are not to be construed to limit the scope of invention thereto.

Example 1

25 30g of nickel sulfate hexahydrate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$), available from Nacalai Tesque, Inc., placed on an evaporating dish was put into a Muffle oven kept at 350°C and maintained at the temperature for 5 hours. Obtained yellow solid was molded and screened to a 12 to 24 mesh size. 5g of thus obtained molded material were charged into a reactor made of SUS and
30 having a diameter of 1/2 inch. A vaporizing pipe provided at the upstream of

the reactor was filled with quartz granules with 20-28 mesh, available from Nacalai Tesque, Inc. A mixture solution of propionic acid, available from Kanto Kagaku, and trioxane, available from Kanto Kagaku, prepared by dissolving 20g of trioxane in 230g of propionic acid was fed into the vaporizing pipe and reactor pipe heated at 300°C at a flow amount of 0.1ml/min accompanied by nitrogen flow of 82ml/min. The pressure inside the reactor was kept at 2kg/cm², which corresponds to 0.2MPa, by adjusting a back pressure regulating valve provided at the downstream of the reactor. Reaction solution collected during a period of 2 hours to 4 hours after initiation of feeding was analyzed by gas-chromatography, which revealed that yield of methacrylic acid was 11% in terms of propionic acid and 47% in terms of formaldehyde contained in trioxane.

Example 2

The reaction was conducted in a similar manner as in Example 1 except that nickel sulfate hexahydrate was placed in the Muffle oven at room temperature and then heated to 350°C and thereafter kept for 5 hours at the temperature. Yield of methacrylic acid was 9% in terms of propionic acid and 40% in terms of formaldehyde contained in trioxane.

Example 3

The reaction was conducted in a similar manner as in Example 2 except that the Muffle oven was heated to 300°C. Yield of methacrylic acid was 11% in terms of propionic acid and 49% in terms of formaldehyde contained in trioxane.

Example 4

The reaction was conducted in a similar manner as in Example 1 except that the Muffle oven was heated to 400°C. Yield of methacrylic acid was 8% in terms of propionic acid and 37% in terms of formaldehyde

contained in trioxane.

Example 5

15g of nickel sulfate hexahydrate and 1.8 g of cobalt sulfate
5 heptahydrate ($\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$) were dissolved in 200 g of ion-exchange water
and evaporated at 50°C to dryness. The obtained solid material was put into
a Muffle oven kept at 350°C and maintained at the temperature for 5 hours.
Obtained material was molded and screened to a 12 to 24 mesh size. The
reaction was conducted in a similar manner as in Example 1 except that the
10 catalyst prepared from nickel sulfate and cobalt sulfate were used. Yield of
methacrylic acid was 7% in terms of propionic acid and 32% in terms of
formaldehyde contained in trioxane.

Example 6

15 30g of nickel sulfate hexahydrate, available from Nacalai Tesque, Inc.,
placed on an evaporating dish was put into a Muffle oven kept at 300°C and
maintained at the temperature for 5 hours. Obtained yellow solid was
molded and screened to a 12 to 24 mesh size. 5g of thus obtained molded
material were charged into a reactor made of SUS having a diameter of 3/4
20 inch. A vaporizing pipe was not provided at the upstream of the reactor. A
mixture solution of propionic acid, available from Kanto Kagaku, and
trioxane, available from Kanto Kagaku, prepared by dissolving 20g of
trioxane in 230g of propionic acid was fed into the reactor pipe heated at
300 $^\circ\text{C}$ at a flow amount of 0.2ml/min accompanied by nitrogen flow of
25 123ml/min. The pressure inside the reactor was kept at 2kg/cm², which
corresponds to 0.2MPa, by adjusting a back pressure regulating valve
provided at the downstream of the reactor. Reaction solution collected during
a period of 1 hour to 3 hour after initiation of feeding was analyzed by
gas chromatography, which revealed that yield of methacrylic acid was 12%
30 in terms of propionic acid and 54% in terms of formaldehyde contained in

trioxane.

Example 7

5 The reaction was conducted in a similar manner as in Example 6 except that nickel sulfate hexahydrate was put into a Muffle oven kept at 250°C and maintained for 5 hours at 250°C. Yield of methacrylic acid was 12% in terms of propionic acid and 54% in terms of formaldehyde contained in trioxane.

10 Example 8

30g of nickel sulfate hexahydrate, available from Nacalai Tesque, Inc., placed on an evaporating dish was put into a Muffle oven kept at 350°C and maintained at the temperature for 5 hours. Obtained yellow solid was molded and screened to a 12 to 24 mesh size. 5g of thus obtained molded
15 material were charged into a reactor made of SUS and having a diameter of 3/4 inch. A vaporizing pipe was not provided at the upstream of the reactor. A mixture solution of propionic acid, available from Kanto Kagaku, and trioxane, available from Kanto Kagaku, prepared by dissolving 20g of trioxane in 230g of propionic acid was fed into the reactor pipe heated at
20 330°C at a flow amount of 0.2ml/min accompanied by nitrogen flow of 82ml/min. The pressure inside the reactor was kept at 2kg/cm², which corresponds to 0.2MPa, by adjusting a back pressure regulating valve provided at the downstream of the reactor. Reaction solution collected during a period of 1 hour to 3 hour after initiation of feeding was analyzed by
25 gas-chromatography, which revealed that yield of methacrylic acid was 8% in terms of propionic acid and 35% in terms of formaldehyde contained in trioxane.

Reference Example

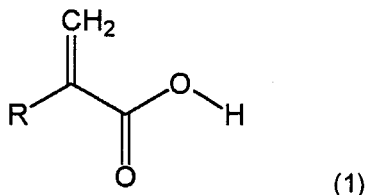
30 12.1 g of niobium fluoride, available from Aldrich Company, Limited,

were gradually added to 38.2 g of colloidal silica containing 40wt% SiO₂, available from Nissan Chemical Industries, Ltd under stirring and aged under stirring for 1 hour at room temperature. White solid obtained by evaporating water was calcined at 300°C for 4 hours and at 450°C for 6
5 hours. Obtained white solid was molded and screened to a 12 to 24 mesh size. 5 g of the molded particles were charged into a reactor made of a SUS pipe having a diameter of 3/4 inch, and cotton quartz was placed on top of the charged catalyst to hold it and thereafter 40 g of quartz granules were filled thereon. The vaporizing pipe provided at the upstream of the reactor was
10 filled with quartz granules.

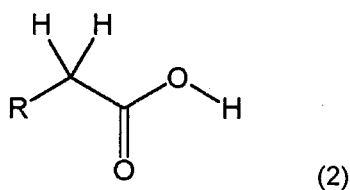
A mixture solution of propionic acid, available from Kanto Kagaku, and trioxane, available from Kanto Kagaku, prepared by dissolving 20g of trioxane in 230g of propionic acid was fed into the vaporizing pipe and reactor pipe heated at 300°C at a flow amount of 0.1ml/min accompanied by
15 nitrogen flow of 82ml/min. The pressure inside the reactor was kept at 2kg/cm², which corresponds to 0.2MPa, by adjusting a back pressure regulating valve provided at the downstream of the reactor. Reaction solution collected during a period of 2 hours to 4 hours after initiation of feeding was analyzed by gas chromatography, which revealed that yield of
20 methacrylic acid was 6% in terms of propionic acid and 27% in terms of formaldehyde contained in trioxane.

Claims:

1. A process for producing α, β -unsaturated carboxylic acid of formula (1):



wherein R represents a hydrogen atom, an alkyl group, an aryl group, an aralkyl group, an alkenyl group or an alkynyl group, which comprises reacting a carboxylic acid of formula (2):



- 10 wherein R represents the same as defined above, with formaldehyde or a precursor thereto in the presence of a sulfate of nickel, cobalt, iron, aluminum, copper, chromium, manganese, zirconium, zinc, silver, palladium, indium, or vanadyl, or mixtures thereof.
2. A process according to claim 1, wherein the sulfate is nickel sulfate, cobalt sulfate, aluminum sulfate, iron sulfate, or vanadyl sulfate.
- 15 3. A process according to claim 1, wherein the sulfate is nickel sulfate.
4. A process according to claim 1, wherein the carboxylic acid is acetic acid or propionic acid.
5. A process according to claim 1, wherein the precursor of
- 20 formaldehyde is trioxane.