

METHOD FOR PRODUCING UNSATURATED ALDEHYDE AND/OR UNSATURATED CARBOXYLIC ACID

FIELD OF THE INVENTION

5 The present invention relates to a method for producing an
unsaturated aldehyde and/or an unsaturated carboxylic acid comprising
supplying a feedstock gas containing at least one compound selected from the
group consisting of propylene, isobutylene and tert-butyl alcohol and
molecular oxygen into a reaction tube to catalytically oxidize said at least
10 one compound in a vapor phase to obtain an unsaturated aldehyde and/or an
unsaturated carboxylic acid.

DESCRIPTION OF THE RELATED ART

As an example of a method for producing an unsaturated aldehyde
15 and/or an unsaturated carboxylic acid comprising supplying a feedstock gas
containing at least one compound selected from the group consisting of
propylene, isobutylene and tert-butyl alcohol and molecular oxygen into a
reaction tube to catalytically oxidize said at least one compound in a vapor
phase, a method is proposed, in which after the preparation of plural kinds of
20 catalysts having different catalytic activities by changing the kinds or
amounts of metal elements constituting the catalysts, these catalysts are
filled in a reaction tube so that the catalyst activity increases from a
feedstock gas inlet toward a feedstock gas outlet and a feedstock gas is
supplied into the reaction tube (see U.S. Patent No. 5,276,178 and
25 JP-A-2000-351744).

However, such conventional methods are not necessarily satisfactory in the conversion of propylene, isobutylene or tert-butyl alcohol, or in the yield of an unsaturated aldehyde and/or an unsaturated carboxylic acid.

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SUMMARY OF THE INVENTION

An object of the present invention is to provide a method which can produce an unsaturated aldehyde and/or an unsaturated carboxylic acid by the catalytic vapor phase oxidization of at least one compound selected from the group consisting of propylene, isobutylene and tert-butyl alcohol at a
10 good conversion in a satisfactory yield.

The inventors of the present invention have found, through their intensive investigations, that the above object could be attained by filling plural kinds of catalysts composed of specific mixed oxides differing from each other in terms of the kinds and/or content ratios of the constituent
15 metal elements, which catalysts have been obtained by drying an aqueous solution or an aqueous slurry containing the components of each catalyst, followed by calcination in an atmosphere of a gas containing molecular oxygen and subsequent heat treatment in the presence of a reducing material, into a reaction tube so that the catalyst activity increases from an
20 feedstock gas inlet toward a feedstock gas outlet and then introducing a feedstock gas into the reaction tube. Thus, they have accomplished the present invention based on the above finding.

That is, the present invention provides a method for producing an unsaturated aldehyde and/or an unsaturated carboxylic acid comprising the
25 steps of:

supplying a feedstock gas containing at least one compound selected from the group consisting of propylene, isobutylene and tert-butyl alcohol, and molecular oxygen into a reaction tube, and

catalytically oxidizing said at least one compound in a vapor phase to
5 produce the unsaturated aldehyde and/or the unsaturated carboxylic acid corresponding thereto, wherein

(1) at least two kinds of catalysts having different catalytic activities are filled in the reaction tube so that the catalytic activity increases from a feedstock gas inlet toward a feedstock gas outlet of the reaction tube,

10 (2) the catalysts comprise each independently a mixed oxide represented by the following formula (I):



wherein

Mo, Bi and Fe represent molybdenum, bismuth and iron, respectively,

15 A represents nickel and/or cobalt,

B represents at least one element selected from the group consisting of manganese, zinc, calcium, magnesium, tin and lead,

C represents at least one element selected from the group consisting of phosphorus, boron, arsenic, tellurium, tungsten, antimony, silicon,

20 aluminum, titanium, zirconium and cerium,

D represents at least one element selected from the group consisting of potassium, rubidium, cesium and thallium,

O represents oxygen,

a, b, c, d, e, f and g satisfy the following relationships: $0 < b \leq 10$, $0 < c \leq 10$, 1
25 $\leq d \leq 10$, $0 \leq e \leq 10$, $0 \leq f \leq 10$ and $0 < g \leq 2$ when a is set equal to 12, , and

x is a value determined depending upon the oxidation states of other elements,

(3) the catalysts differ from each other in terms of the kinds and/or content ratios of the metal elements constituting the catalysts, and

5 (4) the catalysts are each independently obtained by drying an aqueous solution or an aqueous slurry containing the components of the catalyst, followed by calcination in an atmosphere of a gas containing molecular oxygen and subsequent heat treatment in the presence of a reducing material.

10 According to the present invention, an unsaturated aldehyde and/or an unsaturated carboxylic acid corresponding thereto can be produced in a satisfactory yield by the catalytic vapor phase oxidization of at least one compound selected from the group consisting of propylene, isobutylene and tert-butyl alcohol at a good conversion,.

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DETAILED DESCRIPTION OF THE INVENTION

In the present invention, a feedstock gas comprising at least one compound selected from the group consisting of propylene, isobutylene and tert-butyl alcohol, and molecular oxygen is supplied into a reaction tube
20 which is filled with plural kinds of catalysts having different catalytic activities so that the catalytic activity increases from a feedstock gas inlet toward a feedstock gas outlet. The more the kinds of catalysts, the more effective they are in terms of reaction results or controlling a temperature in the reaction tube, but the more complicated the preparation or filling of
25 catalysts is. By taking these factors into account, it is preferable to use two

kinds of catalysts.

The catalysts to be used in the present invention are each independently a mixed oxide represented by the following formula (I):



5 wherein

Mo, Bi and Fe represent molybdenum, bismuth and iron, respectively,

A represents nickel and/or cobalt,

B represents at least one element selected from the group consisting of manganese, zinc, calcium, magnesium, tin and lead,

10 C represents at least one element selected from the group consisting of phosphorus, boron, arsenic, tellurium, tungsten, antimony, silicon, aluminum, titanium, zirconium and cerium,

D represents at least one element selected from the group consisting of potassium, rubidium, cesium and thallium,

15 O represents oxygen,

a, b, c, d, e, f and g satisfy the following relationships: $0 < b \leq 10$, $0 < c \leq 10$, $1 \leq d \leq 10$, $0 \leq e \leq 10$, $0 \leq f \leq 10$ and $0 < g \leq 2$, when a is set equal to 12, and x is a value determined depending upon the oxidation states of other elements.

20 The catalysts differ from each other in terms of the kinds and/or content ratios of the metal elements constituting the catalysts. The "catalysts differing from each other in terms of the kinds of the metal elements constituting the catalysts" means that at least one element in Group A, B, C or D of one catalyst being compared is different from any
25 element in the corresponding group of other catalyst being compared. In

addition, "the catalysts differing from each other in terms of the content ratios of the metal elements constituting the catalysts" means that in a case where the values of b, c, d, e, f and g when a is set equal to 12 in one catalyst are compared with the values of b, c, d, e, f and g when a is set equal to 12 in another catalyst, respectively, at least one value among b, c, d, e, f and g of one catalyst is different from the value corresponding thereto of the other catalyst.

Preferably, the catalysts comprise a mixed oxide represented by the following formula (II):



wherein Mo, Bi, Fe, Co, Sb and Cs represent molybdenum, bismuth, iron, cobalt, antimony and cesium, respectively,

a, b, c, d, e, f and g satisfy the following relationships: $0 < b \leq 10$, $0 < c \leq 10$, $1 \leq d \leq 10$, $0 \leq f \leq 10$ and $0 < g \leq 2$, when a is set equal to 12, and

15 x is a value determined depending upon the oxidation states of other elements.

Also in such a case, the catalysts are different from each other in terms of the kinds and/or content ratios of the metal elements constituting the catalysts.

20 In a preferable embodiment of the catalysts and the filling state thereof in the reaction tube, two kinds of catalysts are filled in the reaction tube, and one catalyst comprising a mixed oxide of the formula (II) in which f is not zero is filled in the feedstock gas inlet-side reaction tube and the other catalyst comprising a mixed oxide of the formula (II) in which f is zero is
25 filled in the feedstock gas outlet-side reaction tube, and the content ratios of

molybdenum, bismuth, iron and cobalt of the catalyst in the feedstock gas inlet-side reaction tube are equal to those of the ~~other~~ catalyst in the feedstock gas outlet-side reaction tube, respectively.

Now, a method for preparing the catalysts used according to the present invention is described below. The catalysts having different catalytic activities to be used in the present invention are prepared independently from each other. As raw materials of such catalysts, compounds of the respective elements constituting the catalysts, such as oxides, nitrates, sulfates, carbonates, hydroxides, oxoacids and ammonium salts thereof, and halides, are used in ratios such that desired content ratios of the elements can be satisfied. For example, molybdenum trioxide, molybdic acid, ammonium paramolybdate and the like may be used as a molybdenum compound. Bismuth oxide, bismuth nitrate, bismuth sulfate and the like may be used as a bismuth compound. Iron (III) nitrate, iron (III) sulfate, iron (III) chloride and the like may be used as an iron compound. Cobalt nitrate, cobalt sulfate, cobalt chloride and the like may be used as a cobalt compound. Antimony trioxide, antimony (III) chloride and the like may be used as an antimony compound. Cesium nitrate, cesium carbonate, cesium hydroxide and the like may be used as a cesium compound.

In the present invention, an aqueous solution or an aqueous slurry is prepared by mixing the raw materials of the catalyst in water, followed by drying the solution or slurry. Then, the dried mixture is calcined in a molecular oxygen-containing gas atmosphere. Some of the raw materials of a catalyst, such as an antimony compound, may be added after drying.

Each of the steps can be conducted according to conventional methods (see,

for example, JP-A-59-46132, JP-A-60-163830 and JP-A-2000-288396). For example, the drying can be conducted using a kneader, a box dryer, a drum-type through-air dryer, a spray dryer, a flush dryer, or the like. The concentration of molecular oxygen in the molecular oxygen-containing gas is usually from 1 to 30 vol%, and preferably from 10 to 25 vol%. Ambient air or pure oxygen is usually used as the source of molecular oxygen. Such a source is used as a molecular oxygen-containing gas, if necessary, after being diluted with nitrogen, carbon dioxide, water, helium, argon, or the like. A calcination temperature is usually from 300 to 600°C, and preferably from 400 to 550°C. A calcination time is usually from 5 minutes to 40 hours, and preferably from 1 to 20 hours.

The calcined product resulting from the calcination is subjected to heat treatment in the presence of a reducing material. Such a treatment conducted in the presence of a reducing material will hereinafter be referred simply as a "reduction treatment".

Examples of the reducing material include such as hydrogen, ammonia, carbon monoxide, hydrocarbons, alcohols, aldehydes and amines. Optionally, two or more of such reducing materials may be used. Preferably, hydrocarbons, alcohols, aldehydes and amines each have 1 to about 6 carbon atoms. Examples of such hydrocarbons include saturated aliphatic hydrocarbons such as methane, ethane, propane, n-butane and isobutane, unsaturated aliphatic hydrocarbons such as ethylene, propylene, α -butylene, β -butylene and isobutylene, and aromatic hydrocarbons such as benzene. Examples of such alcohols include saturated aliphatic alcohols such as methanol, ethanol, n-propyl alcohol, isopropyl alcohol, n-butyl alcohol,

isobutyl alcohol, sec-butyl alcohol and tert-butyl alcohol, unsaturated aliphatic alcohols such as allyl alcohol, crotyl alcohol and methallyl alcohol, and aromatic alcohols such as phenol. Examples of such aldehydes include saturated aliphatic aldehydes such as formaldehyde, acetaldehyde, 5 propionaldehyde, n-butylaldehyde and isobutylaldehyde, and unsaturated aliphatic aldehydes such as acrolein, crotonaldehyde and methacrolein. Examples of such amines include saturated aliphatic amines such as methylamine, dimethylamine, trimethylamine, ethylamine, diethylamine and triethylamine, and unsaturated aliphatic amines such as allylamine and 10 diallylamine, and aromatic amines such as aniline.

The reduction treatment is usually conducted by subjecting the calcined product to heat treatment in an atmosphere of a gas containing the reducing material. The concentration of the reducing material in the gas is usually from 0.1 to 50 vol%, and preferably from 1 to 30 vol%. The reducing 15 material may be diluted with nitrogen, carbon dioxide, water, helium, argon, or the like so that such a concentration could be achieved. Molecular oxygen is allowed to exist unless the effect of the reduction treatment is affected. However, it may not allow molecular oxygen to exist.

A temperature for the reduction treatment is usually from 200 to 20 600°C, and preferably from 250 to 550°C. The time of the reduction treatment is usually from 5 minutes to 20 hours, and preferably from 30 minutes to 10 hours. It is preferable to conduct the reduction treatment by placing the calcined product in a tubular or box-shaped container and keeping the container ventilated with a gas containing the reducing material. 25 At this time, a gas discharged from the container may be circulated and

reused, if necessary.

The reduction treatment usually causes mass loss. This may be due to the loss of lattice oxygen atoms from a catalyst. It is preferable that the mass loss is from 0.05 to 6% by mass, and preferably from 0.1 to 5% by mass.

- 5 If the mass loss exceeds 6% by mass due to the excessive reduction, the mass loss may be recovered by conducting calcination again in a molecular oxygen-containing gas atmosphere. The mass loss can be calculated using the following equation:

$$\text{Mass loss (\%)} = 100 \times [(\text{weight of calcined product before reduction treatment}) - (\text{weight of catalyst after reduction treatment})] / (\text{weight of calcined product before reduction treatment})$$

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- In the reduction treatment, the reducing material itself, decomposition products derived from the reducing material or the like may remain in the catalyst after the reduction treatment according to the type of the reducing material used, heat treatment conditions or the like. In such a case, the mass loss can be calculated by measuring the weight of the residual material in the catalyst and then calculating the weight after the reduction treatment by subtracting the mass of the residual material from the weight of the catalyst including the residual material. A typical residual material is carbon and, therefore, the mass of the residual material can be determined, for example, by total carbon (TC) analysis.
- 15
- 20

- The catalysts are usually molded into a desired shape, and then used in the method of the present invention. In the molding, the catalysts may be molded in the form of a ring, a pellet, a sphere and the like by tablet compression, extrusion molding or the like. The shapes of the catalysts to
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be used in the present invention may be the same or different. The molding may be carried out before or after the calcination in a molecular oxygen-containing gas atmosphere, or after the reduction treatment. Upon the molding, for improving the mechanical strength of the catalysts,
5 inorganic fiber or the like which is substantially inert to the intended oxidation reaction may be added as described, for example, in JP-A-9-52053.

Thus, the catalysts having different catalytic activities are prepared. The catalytic activity of each catalyst can be evaluated by catalytically oxidizing at least one raw material compound selected from the group
10 consisting of propylene, isobutylene and tert-butyl alcohol with molecular oxygen in the presence of a catalyst in vapor phase and measuring the conversion of the compound. The vapor phase catalytic oxidation is conducted by filling such catalysts in a reaction tube so that the catalytic activity, namely, the conversion increases from a feedstock gas inlet toward a
15 feedstock gas outlet and supplying a feedstock gas containing the raw material compound and molecular oxygen. In the industrial production, it is preferable to use a fixed bed multitubular reactor comprising the above-mentioned reaction tubes.

The air is usually used as a source of molecular oxygen. Besides the
20 raw material compounds and molecular oxygen, the feedstock gas may contain nitrogen, carbon dioxide, carbon monoxide, water vapor and the like.

By the above-described vapor phase catalytic oxidation, acrolein and/or acrylic acid can be produced from propylene in a satisfactorily high yield. Alternatively, methacrolein and/or methacrylic acid can be produced
25 from isobutylene or tert-butyl alcohol in a satisfactory yield.

A reaction temperature is usually from 250 to 400°C. A reaction pressure may be reduced pressure, but it is usually from normal pressure to 500 kPa. The amount of molecular oxygen is usually from 1 to 3 moles per one mole of the raw material compound. The space velocity SV of the feedstock gas is usually from 500 to 5000 h⁻¹ at STP (standard temperature and pressure).

EXAMPLES

Examples of the present invention are shown below, but they do not limit the present invention in any way. In the examples, the unit "ml/min" indicating the flow rate of gas is at STP, unless otherwise stated. In the examples, the conversion (%) and the yield are defined as follows:

Conversion (%) = $100 \times [(\text{moles of introduced isobutylene}) - (\text{moles of unreacted isobutylene})] / (\text{moles of introduced isobutylene})$

Total yield (%) = $100 \times (\text{total moles of methacrolein and methacrylic acid}) / (\text{moles of introduced isobutylene})$

Referential Example 1

Preparation of Catalyst a (catalyst without reduction treatment)

4414 g of ammonium molybdate [(NH₄)₆Mo₇O₂₄ · 4H₂O] was dissolved in 5000 g of warm water to form Liquid A. Separately, 2020 g of iron (III) nitrate [Fe(NO₃)₃ · 9H₂O], 4366 g of cobalt nitrate [Co(NO₃)₂ · 6H₂O] and 195 g of cesium nitrate [CsNO₃] were dissolved in 2000 g of warm water and subsequently 970 g of bismuth nitrate [Bi(NO₃)₃ · 5H₂O] was further dissolved to form Liquid B. Liquid B was added to Liquid A while stirring to form a

slurry. The slurry was then dried with a flash dryer to obtain a dried product. Six parts by mass of silica alumina fiber (RFC400-SL produced by Saint-Gobain TM) was added to 100 parts of the dried material. The resulting mixture was molded into a ring form having an outer diameter of 6.3 mm, an inner diameter of 2.5 mm and a length of 6 mm, and then was calcined at 525°C for 6 hours in an air flow to obtain Catalyst a. This catalyst contained 0.96 bismuth atom, 2.4 iron atoms, 7.2 cobalt atoms and 0.48 cesium atom per 12 molybdenum atoms.

10

Example 1

Preparation of Catalyst A (catalyst with reduction treatment)

Catalyst A was prepared by filling Catalyst a into a glass tube, and then flowing a mixed gas of hydrogen/nitrogen (5/95 by volume) through the glass tube to conduct a reduction treatment at 350°C for 8 hours. This catalyst contained 0.96 bismuth atom, 2.4 iron atoms, 7.2 cobalt atoms and 0.48 cesium atom per 12 molybdenum atoms like Catalyst a, and the mass loss due to the reduction treatment was 0.90% by mass.

Referential Example 2

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Preparation of Catalyst b (catalyst without reduction treatment)

Catalyst b was prepared in the same manner as in Referential Example 1, except for adding 2.54 parts by mass of antimony trioxide (Sb_2O_3) to 100 parts by mass of the dried material in Referential Example 1 and changing the calcination temperature to 546°C. This catalyst contained 0.96 bismuth atom, 0.48 antimony atom, 2.4 iron atoms, 7.2 cobalt atoms and

0.48 cesium atom per 12 molybdenum atoms.

Example 2

Preparation of Catalyst B (catalyst with reduction treatment)

- 5 Catalyst B was prepared by filling Catalyst b into a glass tube, and then flowing a mixed gas of hydrogen/nitrogen (5/95 by volume) through the glass tube to conduct a reduction treatment at 350°C for 8 hours. This catalyst contained 0.96 bismuth atom, 0.48 antimony atom, 2.4 iron atoms, 7.2 cobalt atoms and 0.48 cesium atom per 12 molybdenum atoms like
- 10 Catalyst b, and the mass loss due to the reduction treatment was 1.28% by mass.

Referential Example 3

Preparation of Catalyst c (catalyst without reduction treatment)

- 15 Catalyst c was prepared in the same manner as in Referential Example 1, except for changing the amount of cesium nitrate for use to 273 g. This catalyst contained 0.96 bismuth atom, 2.4 iron atoms, 7.2 cobalt atoms and 0.67 cesium atom per 12 molybdenum atoms.

Example 3

- 20 Preparation of Catalyst C (catalyst with reduction treatment)

Catalyst C was prepared by filling Catalyst c into a glass tube, and then flowing a mixed gas of hydrogen/nitrogen (5/95 by volume) through the glass tube to conduct a reduction treatment at 350°C for 8 hours. This catalyst contained 0.96 bismuth atom, 2.4 iron atoms, 7.2 cobalt atoms and

25 0.67 cesium atom per 12 molybdenum atoms like Catalyst c, and the mass

loss due to reduction treatment was 0.77% by mass.

Referential Example 4

Preparation of Catalyst d (catalyst without reduction treatment)

5 Six parts by mass of silica alumina fiber (RFC400-SL produced by Saint-Gobain TM) and 2.54 parts by mass of antimony trioxide (Sb_2O_3) were added to 100 parts of the dried material produced in Referential Example 3. The resulting mixture was molded into a ring form having an outer diameter of 6.3 mm, an inner diameter of 2.5 mm and a length of 6 mm, and then was
10 calcined at 490°C for 6 hours in an air flow to obtain Catalyst d. This catalyst contained 0.96 bismuth atom, 0.29 antimony atom, 2.4 iron atoms, 7.2 cobalt atoms and 0.67 cesium atom per 12 molybdenum atoms.

Example 4

15 Preparation of Catalyst D (catalyst with reduction treatment)

Catalyst D was prepared by filling Catalyst d into a glass tube, and then flowing a mixed gas of hydrogen/nitrogen (5/95 by volume) through the glass tube to conduct a reduction treatment at 350°C for 8 hours. This catalyst contained 0.96 bismuth atom, 0.29 antimony atom, 2.4 iron atoms,
20 7.2 cobalt atoms and 0.67 cesium atom per 12 molybdenum atoms like Catalyst d, and the mass loss due to reduction treatment was 1.17% by mass.

Comparative Example 1

Oxidation using Catalyst A (Catalyst A monolayer)

25 Into a glass reaction tube having an inner diameter of 18 mm, 14.30

ml of Catalyst A was filled after being diluted with 30 g of silicon carbide (SHINANO-RUNDUM GC F16 produced by Shinano Electric Refining Co., Ltd.). An oxidation reaction was conducted at a reaction temperature of 330°C by supplying a mixed gas of isobutylene/oxygen/nitrogen/steam
5 (1.0/2.2/6.2/2.0 by mole) into the reaction tube at a flow rate of 157.5 ml/min. The conversion of isobutylene and the total yield of methacrolein and methacrylic acid are shown in Table 1.

Comparative Example 2

10 Oxidation using Catalyst A (Catalyst A monolayer)

An oxidation reaction was conducted in the same manner as in Comparative Example 1, except for changing the reaction temperature to 340°C. The conversion of isobutylene and the total yield of methacrolein and methacrylic acid are shown in Table 1.

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Comparative Example 3

Oxidation using Catalyst A (Catalyst A monolayer)

An oxidation reaction was conducted in the same manner as in Comparative Example 1, except for changing the reaction temperature to
20 350°C. The conversion of isobutylene and the total yield of methacrolein and methacrylic acid are shown in Table 1.

Comparative Example 4

Oxidation using Catalyst B (Catalyst B monolayer)

25 An oxidation reaction was conducted in the same manner as in

Comparative Example 1, except for changing Catalyst A to Catalyst B. The conversion of isobutylene and the total yield of methacrolein and methacrylic acid are shown in Table 1.

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Comparative Example 5

Oxidation using Catalyst C (Catalyst C monolayer)

An oxidation reaction was conducted in the same manner as in Comparative Example 1, except for changing Catalyst A to Catalyst C and the reaction temperature to 340°C. The conversion of isobutylene and the
10 total yield of methacrolein and methacrylic acid are shown in Table 1.

Comparative Example 6

Oxidation using Catalyst D (Catalyst D monolayer)

An oxidation reaction was conducted in the same manner as in
15 Comparative Example 1, except for changing Catalyst A to Catalyst D and the reaction temperature to 350°C. The conversion of isobutylene and the total yield of methacrolein and methacrylic acid are shown in Table 1.

Example 5

20 Oxidation using Catalysts B and A (Catalyst B/Catalyst A bilayer)

In a glass reaction tube having an inner diameter of 18 mm, 7.15 ml of Catalyst B was filled into a region on the side of the feedstock gas inlet after being diluted 15 g of silicon carbide (SHINANO-RUNDUM GC F16 produced by Shinano Electric Refining Co., Ltd.) and 7.15 ml of Catalyst A
25 was filled into a region side of the feedstock gas outlet after being diluted

with 15 g of silicon carbide (SHINANO-RUNDUM GC F16 produced by Shinano Electric Refining Co., Ltd.). An oxidation reaction was conducted at a reaction temperature of 330°C by supplying a mixed gas of isobutylene/oxygen/nitrogen/steam (1.0/2.2/6.2/2.0 by mole) into the reaction
5 tube at a flow rate of 157.5 ml/min. The conversion of isobutylene and the total yield of methacrolein and methacrylic acid are shown in Table 1.

Example 6

Oxidation using Catalysts C and A (Catalyst C/Catalyst A bilayer)

10 An oxidation reaction was conducted in the same manner as in Example 5, except for changing Catalyst B to Catalyst C and changing the reaction temperature to 340°C. The conversion of isobutylene and the total yield of methacrolein and methacrylic acid are shown in Table 1.

Example 7

15 Oxidation using Catalysts D and A (Catalyst D/Catalyst A bilayer)

An oxidation reaction was conducted in the same manner as in Example 5, except for changing Catalyst B to Catalyst D and changing the reaction temperature to 350°C. The conversion of isobutylene and the total yield of methacrolein and methacrylic acid are shown in Table 1.

20 Comparative Example 7

Oxidation using Catalysts b and a (Catalyst b/Catalyst a bilayer)

An oxidation reaction was conducted in the same manner as in Example 5, except for changing Catalyst B and Catalyst A to Catalyst b and Catalyst a, respectively. The conversion of isobutylene and the total yield of
25 methacrolein and methacrylic acid are shown in Table 1.

Comparative Example 8

Oxidation using Catalysts c and a (Catalyst c/Catalyst a bilayer)

- An oxidation reaction was conducted in the same manner as in Example 5, except for changing Catalyst B and Catalyst A to Catalyst c and Catalyst a, respectively, and changing the reaction temperature to 340°C. The conversion of isobutylene and the total yield of methacrolein and methacrylic acid are shown in Table 1.

Comparative example 9

Oxidation using Catalysts d and a (Catalyst d/Catalyst a bilayer)

- 10 An oxidation reaction was conducted in the same manner as in Example 5, except for changing Catalyst B and Catalyst A to Catalyst d and Catalyst a, respectively, and changing the reaction temperature to 350°C. The conversion of isobutylene and the total yield of methacrolein and methacrylic acid are shown in Table 1.

Table 1

	Catalyst		Reaction temperature (°C)	Conversion (%)	Total yield (%)
	Inlet/Outlet	Reduction treatment			
Comparative Example 1	Catalyst A monolayer	Yes	330	96.3	79.8
Comparative Example 2	Catalyst A monolayer	Yes	340	99.6	80.6
Comparative Example 3	Catalyst A monolayer	Yes	350	100.0	79.7
Comparative Example 4	Catalyst B monolayer	Yes	330	80.3	69.5
Comparative Example 5	Catalyst C monolayer	Yes	340	98.4	81.8
Comparative Example 6	Catalyst D monolayer	Yes	350	93.4	80.1
Example 5	Catalyst B/ Catalyst A	Yes/Yes	330	99.1	83.1
Example 6	Catalyst C/ Catalyst A	Yes/Yes	340	99.0	82.7
Example 7	Catalyst D/ Catalyst A	Yes/Yes	350	99.1	84.6
Comparative Example 7	Catalyst b/ Catalyst a	No/No	330	90.9	78.3
Comparative Example 8	Catalyst c/ Catalyst a	No/No	340	96.7	81.3
Comparative Example 9	Catalyst d/ Catalyst a	No/No	350	99.1	81.9

What is claimed is:

1. A method for producing an unsaturated aldehyde and/or an unsaturated carboxylic acid comprising the steps of:
 - 5 supplying a feedstock gas containing at least one compound selected from the group consisting of propylene, isobutylene and tert-butyl alcohol, and molecular oxygen into a reaction tube, and
 - catalytically oxidizing said at least one compound in a vapor phase to produce the unsaturated aldehyde and/or the unsaturated carboxylic acid
 - 10 corresponding thereto, wherein
 - (1) at least two kinds of catalysts having different catalytic activities are filled in the reaction tube so that the catalytic activity increases from a feedstock gas inlet toward a feedstock gas outlet of the reaction tube,
 - (2) the catalysts comprise each independently a mixed oxide represented by
 - 15 the following formula (I):
$$\text{Mo}_a\text{Bi}_b\text{Fe}_c\text{A}_d\text{B}_e\text{C}_f\text{D}_g\text{O}_x \quad (\text{I})$$
- wherein
- Mo, Bi and Fe represent molybdenum, bismuth and iron, respectively,
- A represents nickel and/or cobalt,
- 20 B represents at least one element selected from the group consisting of manganese, zinc, calcium, magnesium, tin and lead,
- C represents at least one element selected from the group consisting of phosphorus, boron, arsenic, tellurium, tungsten, antimony, silicon, aluminum, titanium, zirconium and cerium,
- 25 D represents at least one element selected from the group consisting of

potassium, rubidium, cesium and thallium,

O represents oxygen,

a, b, c, d, e, f and g satisfy the following relationships: $0 < b \leq 10$, $0 < c \leq 10$, $1 \leq d \leq 10$, $0 \leq e \leq 10$, $0 \leq f \leq 10$ and $0 < g \leq 2$ when a is set equal to 12, , and

5 x is a value determined depending upon the oxidation states of other elements,

(3) the catalysts differ from each other in terms of the kinds and/or content ratios of the metal elements constituting the catalysts, and

(4) the catalysts are each independently obtained by drying an aqueous
10 solution or an aqueous slurry containing the components of the catalyst, followed by calcination in an atmosphere of a gas containing molecular oxygen and subsequent heat treatment in the presence of a reducing material.

15 2. The method according to claim 1, wherein the catalysts comprise each independently a mixed oxide represented by the following formula (II):



wherein Mo, Bi, Fe, Co, Sb and Cs represent molybdenum, bismuth, iron, cobalt, antimony and cesium, respectively,

20 a, b, c, d, f and g satisfy the following relationships: $0 < b \leq 10$, $0 < c \leq 10$, $1 \leq d \leq 10$, $0 \leq f \leq 10$ and $0 < g \leq 2$, when a is set equal to 12, and x is a value determined depending upon the oxidation states of other elements.

25 3. The method according to claim 1 or 2, wherein the number of

kinds of the catalysts filled in the reaction tube is two.

4. The method according to claim 3, wherein
one catalyst comprising a mixed oxide of the formula (II) in which f is
5 not zero is filled in the feedstock gas inlet-side reaction tube and the other
catalyst comprising a mixed oxide of the formula (II) in which f is zero is
filled in the feedstock gas outlet-side reaction tube, and
the content ratios of molybdenum, bismuth, iron and cobalt of the
catalyst filled in the feedstock gas inlet-side reaction tube are equal to those
10 of the other catalyst filled in the feedstock gas outlet-side reaction tube,
respectively.

5. The method according to any one of claims 1 to 4, wherein the
calcination is conducted at 300 to 600°C.

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6. The method according to any one of claims 1 to 5, wherein the
heat treatment is conducted at 200 to 600°C.

7. The method according to any one of claims 1 to 6, wherein the
20 mass loss of the catalyst due to the heat treatment is from 0.05 to 6% by
mass.

8. The method according to any one of claims 1 to 7, wherein the
reducing material is at least one compound selected from the group
25 consisting of hydrogen, ammonia, carbon monoxide, hydrocarbons having 1

to 6 carbons, alcohols having 1 to 6 carbons, aldehydes having 1 to 6 carbons,
and amines having 1 to 6 carbons.