

Process for Producing Catalyst for Use in Producing Unsaturated Aldehyde and Unsaturated Carboxylic Acid, and Process for Producing Unsaturated Aldehyde and Unsaturated Carboxylic Acid

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BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a process for producing a catalyst for use in producing an unsaturated aldehyde and an unsaturated carboxylic acid. In addition, the present
10 invention relates to a process for producing an unsaturated aldehyde and an unsaturated carboxylic acid, using the catalyst obtained by the above process.

2. Description of the related art

It has been known for a long time that for catalysts used
15 in producing acrolein and acrylic acid by catalytically oxidizing propylene in gaseous phase with molecular oxygen, or for catalysts used in producing methacrolein and methacrylic acid by catalytically oxidizing isobutylene or t-butyl alcohol in gaseous phase with molecular oxygen, catalysts comprising a mixed
20 oxide which contains molybdenum, bismuth and iron are effective. Such catalysts for producing an unsaturated aldehyde and an unsaturated carboxylic acid are usually produced by drying an aqueous solution or aqueous slurry obtained by mixing raw
25 precursor. The calcination is generally performed under a gas

atmosphere containing molecular oxygen such as an air atmosphere,
as disclosed in, for example, JP-A-62-234548, JP-A-4-4048,
JP-A-7-124473, JP-A-2000-70719 and JP-A-2004-351295.

The catalysts for use in producing an unsaturated aldehyde
5 and an unsaturated carboxylic acid which are produced in
accordance with conventional processes, however, have
insufficient catalytic activity, and therefore, propylene,
isobutylene, and t-butyl alcohol may not be oxidized in good
conversion, and corresponding unsaturated aldehydes and
10 unsaturated carboxylic acids may not be obtained in satisfactory
yield. When the reaction temperature is raised in order to
increase the conversion, side reactions such as consecutive
oxidation easily proceed, whereby unsaturated aldehydes and
unsaturated carboxylic acids may not be obtained in satisfactory
15 yield.

Thus, the object of the present invention is to provide
a process for producing a catalyst for use in producing an
unsaturated aldehyde and an unsaturated carboxylic acid which
have excellent catalytic activity. In addition, the object of
20 the invention is to provide a production process in which
propylene, isobutylene or t-butyl alcohol is oxidized with the
catalyst obtained by the above process in a good conversion to
produce the corresponding unsaturated aldehyde and unsaturated
carboxylic acid in good yield.

SUMMARY OF THE INVENTION

The present invention provides a process for producing a catalyst for use in producing an unsaturated aldehyde and an unsaturated carboxylic acid by catalytically oxidizing a compound which is selected from propylene, isobutylene and t-butyl alcohol in gaseous phase with molecular oxygen, and comprising a mixed oxide which contains molybdenum, bismuth and iron, wherein a catalyst precursor is calcined under a gas atmosphere containing molecular oxygen; and then is heat-treated in the presence of a reducing substance.

Further, the present invention provides a process for producing an unsaturated aldehyde and an unsaturated carboxylic acid, which process comprises steps of producing a catalyst by the above-mentioned process and then catalytically oxidizing a compound selected from propylene, isobutylene and t-butyl alcohol in gaseous phase with molecular oxygen in the presence of the catalyst.

According to the present invention, catalysts for use in producing an unsaturated aldehyde and an unsaturated carboxylic acid, which have excellent catalytic activity, can be produced. Also, by using the thus obtained catalysts, propylene, isobutylene and t-butyl alcohol can be oxidized in good conversion to produce the corresponding unsaturated aldehydes and unsaturated carboxylic acids in good yield.

DETAILED DESCRIPTION OF THE INVENTION

The present invention will be described below in detail.

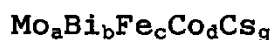
In the present invention, catalysts for use in producing an unsaturated aldehyde and an unsaturated carboxylic acid comprise a mixed oxide which contains molybdenum, bismuth and iron as essential components. The mixed oxide may contain an element(s) other than molybdenum, bismuth and iron, preferably nickel and/or cobalt and an element(s) selected from potassium, rubidium, cesium and thallium.

Preferable mixed oxides can be exemplified by the following general formula (1):



wherein Mo, Bi and Fe are molybdenum, bismuth and iron, respectively; A is nickel and/or cobalt; B is an element selected from manganese, zinc, calcium, magnesium, tin and lead; C is an element selected from phosphorus, boron, arsenic, tellurium, tungsten, antimony, silicon, aluminum, titanium, zirconium and cerium; D is an element selected from potassium, rubidium, cesium and thallium; when $a=12$, $0 < b \leq 10$, $0 < c \leq 10$, $1 \leq d \leq 10$, $0 \leq e \leq 10$, $0 \leq f \leq 10$, and $0 < g \leq 2$; and x is a value depending on the oxidation state of each element.

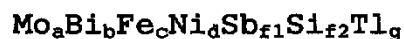
Among them, compounds having the following compositions (exemplified without oxygen atom) are preferably used.



($a=12$, $0.1 \leq b \leq 5$, $0.5 \leq c \leq 5$, $5 \leq d \leq 10$, $0.01 \leq g \leq 1$)



($a=12$, $0.1 \leq b \leq 5$, $0.5 \leq c \leq 5$, $5 \leq d \leq 10$, $0.1 \leq f \leq 5$, $0.01 \leq g \leq 1$)



($a=12$, $0.1 \leq b \leq 5$, $0.5 \leq c \leq 5$, $5 \leq d \leq 10$, $0.1 \leq f1 \leq 5$, $0.1 \leq f2 \leq 5$, $0.01 \leq g \leq 1$)

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As raw materials for the above-mentioned catalyst, compounds containing each of the elements contained in the catalyst, such as oxides, nitrates, sulfates, carbonates, hydroxides, oxo acids and ammonium salts thereof, and halides,
15 are used in ratio which satisfies prescribed atom ratios. For example, as molybdenum compounds, molybdenum trioxide, molybdic acid, ammonium molybdate and the like; as bismuth compounds, bismuth oxide, bismuth nitrate, bismuth sulfate and the like; and as iron compounds, iron(III) nitrate, iron(III) sulfate,
20 iron(III) chloride and the like can be used.

In the process for producing the catalyst of the present invention, a catalyst precursor produced from the above-mentioned raw materials is calcined under a gas atmosphere containing molecular oxygen, and then heat-treated in the
25 presence of a reducing substance. The catalyst precursor can

be usually produced by mixing the raw materials in water to give an aqueous solution or aqueous slurry, and then drying the aqueous solution or aqueous slurry. The solution or slurry can be dried using, for example, a kneader, box dryer, drum-type through-flow drying apparatus, spray dryer, flush dryer, and the like.

The thus obtained catalyst precursor is calcined under a gas atmosphere containing molecular oxygen. A concentration of the molecular oxygen in this gas is usually from 1 to 30% by volume, preferably from 10 to 25% by volume. As the source of molecular oxygen is usually used air or pure oxygen, and if necessary, is used with being diluted with nitrogen, carbon dioxide, water, helium, argon, and the like. The thus obtained gas is used as the molecular oxygen-containing gas. A calcining temperature is usually 300 to 600°C, preferably 400 to 550°C. A calcining time is usually 5 minutes to 40 hours, preferably 1 hour to 20 hours.

In the present invention, the calcined catalyst precursor obtained in the above-mentioned calcination is heat-treated in the presence of a reducing substance (hereinafter this treatment is sometimes referred to as reduction treatment). Such a reduction treatment can effectively improve the catalyst activity.

Examples of the reducing substance may include, for example, hydrogen, ammonia, carbon monoxide, hydrocarbons, alcohols, aldehydes, amines, and the like. These may be used in combination

therewith if necessary. Preferably, the hydrocarbons, alcohols, aldehydes and amines have each about 1 to about 6 carbon atoms. Examples of the hydrocarbon may 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; benzene, and the like. Examples of the alcohol may include saturated aliphatic alcohols such as methyl alcohol, ethyl alcohol, n-propyl alcohol, isopropyl alcohol, n-butyl alcohol, isobutyl alcohol, sec-butyl alcohol and t-butyl alcohol; unsaturated aliphatic alcohols such as allyl alcohol, crotyl alcohol and metallyl alcohol; phenol, and the like. Examples of the aldehyde may include saturated aliphatic aldehydes such as formaldehyde, acetaldehyde, propionaldehyde, n-butyl aldehyde and isobutyl aldehyde; unsaturated aliphatic aldehydes such as acrolein, croton aldehyde and methacrolein, and the like. Examples of the amine may include saturated aliphatic amines such as methyl amine, dimethyl amine, trimethyl amine, ethyl amine, diethyl amine and triethyl amine; unsaturated aliphatic amines such as allyl amine and diallyl amine; aniline, and the like.

The reduction treatment is usually performed by heat-treating the calcined catalyst precursor under a gas atmosphere containing the above-mentioned reducing substance. A concentration of the reducing substance in the gas is usually 0.1 to 50% by volume, preferably 1 to 50% by volume, more preferably

3 to 30% by volume. The reducing substance may be diluted with nitrogen, carbon dioxide, water, helium, argon, or the like so as to have the above-mentioned concentrations. The molecular oxygen may be present in the gas within a range in which the effect of the reduction treatment is not imparted, but usually an absence of molecular oxygen is preferable.

A reduction treatment temperature is usually 200 to 600°C, preferably 300 to 500°C. A reduction treatment time is usually 5 minutes to 20 hours, preferably 30 minutes to 10 hours. It is preferable that the reduction treatment is performed by putting the calcined catalyst precursor in a vessel such as tube-type vessel or box-type vessel, through which the gas containing the reducing substance is passed. In such a case, exhaust gas from the vessel may be recycled, if necessary. For example, the calcined catalyst precursor is filled in a reaction tube for gaseous catalytic oxidation, through which the gas containing the reducing substance is passed to perform the reduction treatment, after which the gas-phase catalytic oxidation can be subsequently performed.

In usual, the mass of a catalyst is decreased after reduction treatment, which is caused probably by loss of lattice oxygen from the calcined catalyst precursor. A loss of the mass is preferably 0.05 to 6%, more preferably 0.1 to 5%. When excessive reduction occurs and the loss of the mass is too high, the catalytic activity may lessen. In such a case, it is

preferable that the calcination is performed under a gas atmosphere containing molecular oxygen again to lower the loss of the mass. The loss of the mass is calculated from the following equation:

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$$\begin{aligned} \text{loss of the mass (\%)} = & (\text{mass of calcined catalyst precursor before} \\ & \text{reduction treatment} - \text{mass of catalyst after reduction treatment}) \\ & / \text{mass of calcined catalyst precursor before reduction treatment} \\ & \times 100 \end{aligned}$$

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When the reduction treatment is performed, the reducing substance itself and decomposition products thereof can remain in the catalyst after the treatment, depending on the kind of reducing substance used and the heat treatment condition. In such a case, the mass of the remaining products in the catalyst is separately measured, and a value which is obtained by subtracting it from the mass of the catalyst which contains the remaining products after the reduction treatment is used as the mass of catalyst after treatment. Since the remaining products are typically carbon, the mass thereof may be found by, for example, a total carbon (TC) measurement, and the like.

The catalysts are usually formed into desired shapes, which are used. Preferably, they are formed into rings, pellets, balls, and the like by tablet compression or extrusion molding. The formation may be performed in the state of a catalyst precursor

before the calcination under a molecular oxygen-containing gas atmosphere, and may be performed after the calcination, or after the reduction treatment. During the formation, in order to improve the mechanical strength of the catalyst, inorganic fibers and the like that are substantially inert to the oxidation reaction may be added, as described in JP-A-9-52053.

The thus obtained catalysts for use in producing an unsaturated aldehyde and an unsaturated carboxylic acid have excellent catalytic activity. By using the catalyst, propylene can be catalytically oxidized with molecular oxygen in gaseous phase to produce acrolein and acrylic acid in good yields. Further, by using the catalyst, isobutylene or t-butyl alcohol can be catalytically oxidized with molecular oxygen in gaseous phase to produce methacrolein and methacrylic acid in good yields.

According to the catalytic oxidation in gaseous phase, the catalyst is usually filled in a fixed-bed multi-tubular reaction vessel, to which a starting gas containing molecular oxygen and a starting compound selected from propylene, isobutylene and t-butyl alcohol are supplied. Fluid-bed and moving-bed reaction vessels can also be used. The molecular oxygen source is usually air, and the starting gas may contain nitrogen, carbon dioxide, carbon monoxide, steam and the like, in addition to the starting compound and molecular oxygen.

A reaction temperature is usually 250 to 400°C, and a

reaction pressure is usually 100 to 500 kPa, but also the reaction can be performed under reduced pressure. An amount of molecular oxygen is usually 1 to 3 moles per mole of the starting compound. A space velocity (SV) of the starting gas is usually 500 to 5,000/hour based on the STP (standard temperature and pressure).

EXAMPLES

Examples of the present invention will be shown below, but the present invention is not limited thereto. In Examples, 10 ml/min showing a gas flow rate is based on STP, unless otherwise noted.

Comparative Example 1

(a) Production of a catalyst

15 Ammonium molybdate $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}]$ of 13,241 g was dissolved in warm water of 15,000 g, which was named as the liquid A. On the other hand, iron(III) nitrate $[\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}]$ of 6,060 g, cobalt nitrate $[\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ of 13,096 g and cesium nitrate $[\text{CsNO}_3]$ of 585g were dissolved in warm water of 6,000g, next, 20 in which bismuth nitrate $[\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}]$ of 2,910 g was dissolved, which was named as the liquid B. The liquid A was stirred, to which the liquid B was added to give a slurry, and then the slurry was dried using a flash dryer to give a catalyst precursor. To the catalyst precursor of 100 parts by mass, silica alumina fiber 25 (made by ITM Co., Ltd., RFC400-SL) of 6 parts by mass was added,

and then was formed into rings having an outer diameter of 6.3 mm, an inner diameter of 2.5 mm, and a length of 6 mm. The rings were calcined in air stream at 516°C for 6 hours to give a catalyst. The catalyst has 0.96 bismuth atom, 2.4 iron atoms, 7.2 cobalt atoms and 0.48 cesium atom per 12 molybdenum atoms.

(b) Oxidation reaction

In a glass reaction tube having an inner diameter of 18 mm, the catalyst obtained in the step (a) of 13 ml, was filled and while a mixed gas of

isobutylene/oxygen/nitrogen/steam=1/2.2/6.7/2.1 (molar ratio) was supplied to the tube at a flow rate of 162.5 ml/min, the oxidation reaction was performed at a reaction temperature of 360°C. The conversion of isobutylene and the total yield of methacrolein and methacrylic acid are shown in Table 1.

Example 1

The catalyst obtained in Comparative Example 1 (a) of 50 g, was filled in a glass tube, and while a mixed gas of hydrogen/nitrogen = 10/90 (volume ratio) was supplied to the tube at a flow rate of 200 ml/min, reduction treatment was performed at 350°C for 5 hours. Then, the supply of hydrogen was stopped, which was then cooled to room temperature under nitrogen stream to give a reduction-treated catalyst. The loss of the mass of the catalyst by the reduction treatment was 0.84%.

The same oxidation reaction as in Comparative Example 1

(b) was performed except that the catalyst obtained above was used and the reaction temperature was changed to 320°C. The results are shown in Table 1.

5 Example 2

The same procedure as in Example 1 was performed, except that the gas used in the reduction treatment was changed to a mixed gas of hydrogen/nitrogen = 20/80 (volume ratio), the reduction treatment temperature was changed to 400°C, and the
10 reduction treatment time was changed to 3 hours to give a reduction-treated catalyst. The loss of the mass of the catalyst by the reduction treatment was 3.52%.

The same oxidation reaction as in Comparative Example 1 (b) was performed except that the catalyst obtained above was
15 used and the reaction temperature was changed to 320°C. The results are shown in Table 1.

Example 3

The same procedure as in Example 1 was performed, except
20 that the gas used in the reduction treatment was changed to a mixed gas of hydrogen/nitrogen = 20/80 (volume ratio) and the reduction treatment temperature was changed to 400°C to give a reduction-treated catalyst. The loss of the mass of the catalyst by the reduction treatment is 6.42%.

25 Then, the temperature was elevated to 200°C under nitrogen

stream of 200 ml/min, and was further elevated to 400°C over 8 hours while air was intermittently supplied at 200 ml/min. The supply of nitrogen was stopped at 400°C, the temperature was kept at 400°C under air stream for 1 hour, which was cooled
5 to room temperature to give an air-calcined catalyst after the reduction treatment. The loss of the mass of the catalyst was 0.36% in the total of the loss after the reduction treatment and the loss after the air-calcination.

The same oxidation reaction as in Comparative Example 1
10 (b) was performed except that the catalyst obtained above was used and the reaction temperature was changed to 320°C. The results are shown in Table 1.

Example 4

15 The catalyst obtained in Comparative Example 1 (a) of 25 g was filled in a glass tube, and while a mixed gas of isobutylene/nitrogen/steam = 6.8/80.6/12.6 (volume ratio) was supplied to the tube at a flow rate of 600 ml/min, the reduction treatment was performed at 366°C for 5 hours. Then the supply
20 of isobutylene and steam was stopped, which was then cooled to room temperature under nitrogen stream to give a reduction-treated catalyst. The loss of the mass of the catalyst by the reduction treatment was 1.18%.

The same oxidation reaction as in Comparative Example 1
25 (b) was performed except that the catalyst obtained above was

used and the reaction temperature was changed to 320°C. The results are shown in Table 1.

Example 5

5 The same procedure as in Example 4 was performed except that ethanol was used instead of isobutylene to give a reduction-treated catalyst. The loss of the mass of the catalyst by the reduction treatment was 3.11%.

10 The same oxidation reaction as in Comparative Example 1 (b) was performed except that the catalyst obtained above was used and the reaction temperature was changed to 300°C. The results are shown in Table 1.

Example 6

15 The catalyst obtained in Comparative Example 1 (a) of 25 g was filled in a glass tube, and while a mixed gas of methacrolein/nitrogen/steam = 4.3/78.2/17.5 (volume ratio) was supplied to the tube at a flow rate of 100 ml/min, the reduction treatment was performed at 366°C for 2.5 hours. Then, the supply
20 of methacrolein and steam was stopped, which was then cooled to room temperature under nitrogen stream to give a reduction-treated catalyst. The loss of the mass of the catalyst by the reduction treatment was 0.58%.

25 The same oxidation reaction as in Comparative Example 1 (b) was performed except that the catalyst obtained above was

used and the reaction temperature was changed to 320°C. The results are shown in Table 1.

Table 1

	Reduction treatment				Oxidation reaction		
	Reducing substance	Temperature (°C)	Time (hour)	Loss of the mass (%)	Temperature (°C)	Conversion (%)	Yield (%)
Comparative Example 1	-	-	-	-	360	99.0	76.6
Example 1	Hydrogen	350	5	0.84	320	99.4	79.0
Example 2	Hydrogen	400	3	3.52	320	99.3	77.6
Example 3	Hydrogen*	400*	5*	0.36*	320	99.1	78.1
Example 4	Isobutylene	366	5	1.18	320	99.5	77.4
Example 5	Ethanol	366	5	3.11	300	98.0	77.9
Example 6	Methacrolein	366	2.5	0.58	320	99.3	78.0

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*After the reduction treatment, the air-calcination was performed again.

According to the present invention, the following
10 inventions are provided.

[1] A process for producing a catalyst for use in producing an unsaturated aldehyde and an unsaturated carboxylic acid by catalytically oxidizing a compound which is selected from propylene, isobutylene and t-butyl alcohol in gaseous phase with
15 molecular oxygen, and comprising a mixed oxide which contains molybdenum, bismuth and iron, wherein a catalyst precursor is calcined under a gas atmosphere containing molecular oxygen; and then is heat-treated in the presence of a reducing substance.

[2] The process according to [1], wherein the mixed oxide

is shown by the following general formula (1):



5 wherein Mo, Bi and Fe are molybdenum, bismuth and iron,
respectively; A is nickel and/or cobalt; B is an element selected
from manganese, zinc, calcium, magnesium, tin and lead; C is
an element selected from phosphorus, boron, arsenic, tellurium,
tungsten, antimony, silicon, aluminum, titanium, zirconium and
10 cerium; D is an element selected from potassium, rubidium, cesium
and thallium; when $a=12$, $0 < b \leq 10$, $0 < c \leq 10$, $1 \leq d \leq 10$, $0 \leq e \leq 10$, $0 \leq f \leq 10$,
and $0 < g \leq 2$; and x is a value depending on the oxidation state
of each element.

[3] The process according to [1] or [2], wherein the
15 calcinations is performed at 300 to 600°C.

[4] The process according to any one of [1] to [3], wherein
the heat-treatment is performed at 200 to 600°C.

[5] The process according to any one of [1] to [4], wherein
a loss of the mass caused by the heat-treatment is 0.05 to 6%
20 by mass.

[6] The process according to any one of [1] to [5], wherein
the reducing substance is a compound selected from hydrogen,
ammonia, carbon monoxide, a hydrocarbon having 1 to 6 carbon
atoms, an alcohol having 1 to 6 carbon atoms, an aldehyde having
25 1 to 6 carbon atoms, and an amine having 1 to 6 carbon atoms.

[7] A process for producing an unsaturated aldehyde and an unsaturated carboxylic acid, which process comprises steps of producing a catalyst by the process according to any one of [1] to [6] and then catalytically oxidizing a compound selected from propylene, isobutylene and t-butyl alcohol in gaseous phase with molecular oxygen in the presence of the catalyst.

What is claimed is:

1. A process for producing a catalyst for use in producing an unsaturated aldehyde and an unsaturated carboxylic acid by
5 catalytically oxidizing a compound which is selected from propylene, isobutylene and t-butyl alcohol in gaseous phase with molecular oxygen, and comprising a mixed oxide which contains molybdenum, bismuth and iron, wherein a catalyst precursor is calcined under a gas atmosphere containing molecular oxygen;
10 and then is heat-treated in the presence of a reducing substance.

2. The process according to claim 1, wherein the mixed oxide is shown by the following general formula (1):



wherein Mo, Bi and Fe are molybdenum, bismuth and iron, respectively; A is nickel and/or cobalt; B is an element selected from manganese, zinc, calcium, magnesium, tin and lead; C is
20 an element selected from phosphorus, boron, arsenic, tellurium, tungsten, antimony, silicon, aluminum, titanium, zirconium and cerium; D is an element selected from potassium, rubidium, cesium and thallium; when $a=12$, $0 < b \leq 10$, $0 < c \leq 10$, $1 \leq d \leq 10$, $0 \leq e \leq 10$, $0 \leq f \leq 10$, and $0 < g \leq 2$; and x is a value depending on the oxidation state
25 of each element.

3. The process according to claim 1, wherein the calcinations is performed at 300 to 600°C.

5 4. The process according to claim 1, wherein the heat-treatment is performed at 200 to 600°C.

5. The process according to claim 1, wherein a loss of the mass caused by the heat-treatment is 0.05 to 6% by mass.

10 6. The process according to claim 1, wherein the reducing substance is a compound selected from hydrogen, ammonia, carbon monoxide, a hydrocarbon having 1 to 6 carbon atoms, an alcohol having 1 to 6 carbon atoms, an aldehyde having 1 to 6 carbon
15 atoms, and an amine having 1 to 6 carbon atoms.

7. A process for producing an unsaturated aldehyde and an unsaturated carboxylic acid, which process comprises steps of producing a catalyst by the process according to any one of
20 claims 1 to 6 and then catalytically oxidizing a compound selected from propylene, isobutylene and t-butyl alcohol in gaseous phase with molecular oxygen in the presence of the catalyst.