

A PROCESS FOR PRODUCING UNSATURATED ALDEHYDE AND
CARBOXYLIC ACID

Field of the Invention

5 The present invention relates to a process for producing
an unsaturated aldehyde and an unsaturated carboxylic acid by
vapor phase catalytic oxidation of isobutylene or tertiary
butanol with molecular oxygen using a fixed bed multi-tubular
reactor.

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Background of the Invention

It has been well known that an unsaturated aldehyde and
an unsaturated carboxylic acid are produced from isobutylene
or tertiary butanol by vapor phase catalytic oxidation using
15 a so-called bismuth molybdate based composite oxide catalyst.

The oxidation reaction is usually conducted using a fixed
bed multi-tubular reactor. In the reactor, hot spots are
liable to be generated particularly near the raw material gas
inlet because the reaction is very exothermic. The hot spots
20 raise such problems as decrease in yield of the resulting
reaction products due to its excessive oxidation reaction and
shortened catalytic lifetime due to deterioration of the
catalyst which is accelerated by the generation of hot spots.
In particular, when a concentration of raw material or a space
25 velocity is increased in order to improve the productivity per

unit catalyst, these problems become more serious.

Several proposals have been made to suppress the generation of hot spots and thereby improve the productivity and the catalytic lifetime. For example, in Japanese Patent Publication (JP-B) No. S53-30688, a process has been proposed for producing acrolein and acrylic acid by vapor phase catalytic oxidation of propylene with molecular oxygen, wherein the catalyst placed near the raw material gas inlet is diluted with a material inert to the reaction. With respect to catalysts for synthesis of methacrolein and methacrylic acid by vapor phase catalytic oxidation of isobutylene with molecular oxygen, for example, Japanese Patent Application Laid-Open (JP-A) No. S51-127013 describes a process in which a so-called supported-type catalyst is placed at a raw material gas inlet side and a conventional molded catalyst is placed at an outlet side, and JP-A No.H6-192144 describes a process in which a supported-type catalyst is packed so that the amount of supported catalyst increases in the direction from a raw material gas inlet side to an outlet side.

Furthermore, JP-A No.H4-217932 has proposed a process in which a plurality kinds of catalysts respectively having different exclusive volume, *i.e.*, different size, are packed so that the exclusive volume decreases in the direction from a raw material gas inlet side to an outlet side.

In addition, JP-A Nos.H3-176440 and H3-200733 disclose

processes in which multi-component bismuth molybdate catalysts are prepared by adjusting a kind and/or an amount of alkali metal elements and thallium group elements as well as alkaline earth metal elements in the catalysts to control catalytic activity of the catalysts and such catalysts are packed so that the catalytic activity increases in the direction from a raw material inlet gas side to an outlet side. Likewise, JP-A No.H3-294238 discloses a process in which multi-component bismuth molybdate catalysts are prepared by adjusting a kind and/or an amount of alkali metal elements and thallium group elements and further by adjusting a calcining temperature for preparing the catalysts to control catalytic activity of the catalysts and such catalysts are packed as described above. Furthermore, JP-A No.H3-215441 discloses a process in which multi-component bismuth molybdate catalysts, which comprise as their essential components tungsten, iron, nickel and/or cobalt and further comprise at least one element selected from phosphorus, tellurium, antimony, tin, cerium, lead, niobium, manganese, arsenic and zinc, are prepared by adjusting a kind and/or an amount of the elements in the catalyst to control catalytic activity thereof and such catalysts are packed as described above.

As mentioned above, in order to suppress the generation of hot spots at the raw material gas inlet part to improve the productivity and to prolong the catalytic lifetime, in the

vapor phase catalytic oxidation utilizing a fixed bed multi-tubular reactor, such methods have been applied in which the catalytic activity is controlled in some way and the activity-controlled catalysts are packed dividedly into the
5 reaction tubes.

All of these methods are effective in some degree. However, the methods have several problems. For example, the methods disclosed in JP-B No. S53-30688 and JP-A Nos. S51-127013 and H6-192144 wherein the inert diluents are used, are not
10 always advantageous in catalytic lifetime, since the amount of catalytic component packed in the reaction tubes is small and therefore the load per unit catalyst increases.

The method disclosed in JP-A H4-217932 wherein the size of catalyst is adjusted may not be advantageous in yield of
15 methacrolein and methacrylic acid, since the yield decreases as the size of the catalyst increases so long as the catalyst has the same shape, even if the catalyst has an ingenious shape such as a ring form.

In contrast, the methods disclosed in JP-A Nos. H3-176440,
20 H3-200733, H3-294238 and H3-215441 wherein the catalytic activity is controlled by adjusting the composition of catalyst may be superior to the others. However, the methods have problems such that the number of metal elements constituting the catalyst is so large, ex., the number ranging from 7 to
25 11, that it is complicated to recover the metal components from

the utilized catalyst or to conduct the catalyst preparation process, thereby ultimately increasing the cost. In addition, the hot spot generation is not always sufficiently suppressed and, therefore, the selectivities to an unsaturated aldehyde and an unsaturated carboxylic acid from isobutylene or tertiary butanol are not enough, which results in low productivity.

Summary and Objects of the Invention

Under these circumstances, the inventors of the present invention have made earnest studies to find a method for producing an unsaturated aldehyde and an unsaturated carboxylic acid by vapor phase catalytic oxidation of isobutylene and/or tertiary butanol with molecular oxygen using a fixed bed multi-tubular reactor comprising a plurality of tubes, which suppresses generation of hot spots and prolong lifetime of the catalyst in a simple and reliable way. As a result, the inventors have found that such a method can be provided when a molybdenum-bismuth based multi-component composite oxide catalyst containing antimony is placed at a raw material gas inlet side of each tube, while a molybdenum-bismuth based antimony-free multi-component composite oxide catalyst is placed at a gas outlet side. The present invention has been thus completed.

Thus, the present invention provides a process for producing an unsaturated aldehyde and an unsaturated

carboxylic acid which comprises subjecting isobutylene or tertiary butanol to vapor phase catalytic oxidation with molecular oxygen using fixed bed multi-tubular reactor comprising a plurality of tubes, each tube (i) being packed
5 at a gas outlet side of each tube with a composite oxide catalyst represented by the formula



wherein Mo, Bi, Fe and O represent molybdenum, bismuth, iron and oxygen, respectively; A represents nickel and/or cobalt;
10 B represents at least one kind of element selected from a group consisting of potassium, rubidium, cesium, and thallium; in the case of a being 12, $0 < b \leq 10$, $0 < c \leq 10$, $1 \leq d \leq 10$, and $0 < e \leq 2$; and x is a value dependent on the oxidation states of the respective elements, and (ii) being packed at a gas inlet side of each
15 tube with a composite oxide catalyst by the formula



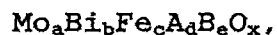
wherein A, B, a, b, c, d, and e are the same as defined above; Sb represents antimony; in the case of a being 12, $0.01 \leq f \leq 5$; and x is a value dependent on the oxidation states of the
20 respective elements.

Description of the Preferred Embodiment

In the present invention, an unsaturated aldehyde and an unsaturated carboxylic acid are produced from isobutylene
25 or tertiary butanol by vapor phase catalytic oxidation with

molecular oxygen using fixed bed multi-tubular reactor comprising a plurality of tubes. Each tube may be divided into two parts of reaction zone, i.e., into a gas inlet side and a gas outlet side. A molybdenum-bismuth based multi-component composite oxide catalyst containing antimony is placed at the raw material gas inlet side, while a molybdenum-bismuth based multi-component composite oxide catalyst containing no antimony is placed at the outlet side.

In the present invention, the catalyst to be placed at the gas outlet side of each tube is a composite oxide catalyst represented by the formula



wherein Mo, Bi, Fe and O represent molybdenum, bismuth, iron and oxygen, respectively; A represents nickel and/or cobalt; B represents at least one kind of element selected from a group consisting of potassium, rubidium, cesium, and thallium; in the case of a being 12, $0 < b \leq 10$, $0 < c \leq 10$, $1 \leq d \leq 10$, and $0 < e \leq 2$; and x is a value dependent on the oxidation states of the respective elements. The catalyst to be placed at the raw material gas inlet side of each tube is a composite oxide catalyst represented by the formula



wherein A, B, a, b, c, d, and e are the same as defined above; Sb represents antimony; in the case of a being 12, $0.01 \leq f \leq 5$; and x is a value dependent on the oxidation states of the

respective elements.

Examples of the catalyst to be placed at the raw material gas inlet side include catalysts having the following composition (oxygen atom being omitted):

- 5 $\text{Mo}_{12}\text{Bi}_{0.1-5}\text{Sb}_{0.1-5}\text{Fe}_{0.5-5}\text{Co}_{5-10}\text{Cs}_{0.01-1}$,
 $\text{Mo}_{12}\text{Bi}_{0.1-5}\text{Sb}_{0.1-5}\text{Fe}_{0.5-5}\text{Co}_{5-10}\text{K}_{0.01-1}$,
 $\text{Mo}_{12}\text{Bi}_{0.1-5}\text{Sb}_{0.1-5}\text{Fe}_{0.5-5}\text{Ni}_{5-10}\text{Tl}_{0.01-1}$, or the like.

- Examples of the catalyst to be placed at the gas outlet side include catalysts having the following composition (oxygen atom being omitted):
- 10

$\text{Mo}_{12}\text{Bi}_{0.1-5}\text{Fe}_{0.5-5}\text{Co}_{5-10}\text{Cs}_{0.01-1}$,
 $\text{Mo}_{12}\text{Bi}_{0.1-5}\text{Fe}_{0.5-5}\text{Co}_{5-10}\text{K}_{0.01-1}$,
 $\text{Mo}_{12}\text{Bi}_{0.1-5}\text{Fe}_{0.5-5}\text{Ni}_{5-10}\text{Tl}_{0.01-1}$, or the like.

- Methods for producing these composite oxide catalyst are
- 15 not restricted, and any conventional method can be adopted. Examples thereof include methods disclosed in JP-A Nos. S59-46132 and S60-163830.

- These composite oxide catalyst may be produced using raw materials such as oxides, nitrates, sulfates, carbonates,
- 20 hydroxides, ammonium salts and halides of respective elements of the catalyst components in combination thereof. In particular, molybdenum trioxide, molybdic acid, ammonium paramolybdate or the like may be used as a molybdenum material; bismuth oxide, bismuth nitrate, bismuth sulfate or the like
- 25 may be used as a bismuth material; iron (III) nitrate, iron

(III) sulfate, iron (III) chloride or the like may be used as an iron material; and antimony (III) oxide, antimony (III) chloride or the like may be used as an antimony material.

The catalysts of the present invention may be prepared
5 by dissolving the raw materials for catalyst in water to obtain aqueous solutions containing the catalyst components therein, mixing the solution with each other, drying the resulting mixture containing the catalyst components and calcining the obtained dried material. In the present invention, the order
10 and the method of mixing the raw materials for catalyst are not restricted. In order to obtain the inlet side catalyst, a method is preferably adopted wherein an antimony material is added in a given amount to the outlet side catalyst when the outlet side catalyst is molded, since such a method is
15 simple.

In the present invention, when the antimony content in the inlet side catalyst is too small, the effect attained by using an antimony material may not appear, whereas when the content is too large, the catalytic activity decreases so
20 markedly that an adequate activity may not be achieved when the catalysts is placed in the fixed bed multi-tubular reactor. Therefore, in the case that a molybdenum material is used in an amount of 12 mol in terms of molybdenum atom, an antimony material is preferably used in an amount of from about 0.01
25 to about 5 mol in terms of antimony atom.

In the present invention, there is no limitation on a method for drying the mixture containing the catalyst components, and various well-known methods, for example, a method of evaporation to dryness using a kneader and a method
5 of drying using an apparatus such as a chamber dryer, a drum-type through-flow drying, a spray dryer, an pneumatic conveying dryer, or the like may be used, so long as the method does not result in markedly uneven distribution of the catalyst components.

10 The resulting dried mixture (hereinafter, referred to as "catalyst precursor") is then finally calcined to obtain a final catalyst to be placed in the tubes. The final calcination may be conducted at a temperature of from about 350°C to about 700°C for the period of time of from about 1
15 to about 40 hours.

The catalyst precursor may be formed into a desired shape after being crushed if necessary or as it is, before the calcination. The catalyst precursor may also be calcined in advance and then formed. The forming may be conducted by
20 compression molding or extrusion to give, for example, a ring-, pellet-, or sphere-shape.

In the present invention, reaction zones of each tube is divided into two parts, and two kinds of catalysts which respectively have different activity are placed at each part
25 so that the catalytic activity increases in the direction from

the raw material inlet side to the outlet side. By placing the catalyst having a lower catalytic activity near the raw material inlet side, the reaction of the raw material moderately proceeds to effectively suppress the generation of hot spots, since the hot spots tend to be generated near the inlet side by the exothermic reaction enhanced by the high catalytic activity. In the present invention, the difference in catalytic activity is achieved using a simple method mainly based on the presence or absence of antimony in the catalyst components. An antimony-containing catalyst, which has higher selectivity as well as a lower activity, is placed at the inlet side, while an antimony-free, which has higher activity, is placed at the outlet side.

A ratio of antimony-containing catalyst to antimony-free catalyst placed in each reaction zone is not restricted and depends on the composition of catalyst, the reaction temperature, the gas flow rate in the tube, and the like. The ratio may be in the range of from 1 : 9 to 7 : 3 by weight, and preferably from 2 : 8 to 6 : 4 by weight.

The vapor phase catalytic oxidation reaction of isobutylene or tertiary butanol with molecular oxygen using the multi-tubular reactor prepared by placing the above catalysts therein may be conducted under the reaction conditions similar to those for conventionally known methods. For example, the reaction may be conducted at a temperature

of from about 300°C to about 400°C, under a pressure of from normal pressure to about 500 kPa (although a reduced pressure may also be acceptable) at an oxygen/isobutylene or tertiary butanol (molar ratio) of from 1 to 3, and at a space velocity
5 (SV) of from about 500 h⁻¹ to about 5000 h⁻¹ which is determined under standard temperature and pressure (STP) condition.

According to the present invention, an unsaturated aldehyde and an unsaturated carboxylic acid are produced with high yield by vapor phase catalytic oxidation of isobutylene
10 or tertiary butanol with molecular oxygen using a fixed bed multi-tubular reactor comprising a plurality of tubes, while suppressing generation of hot spots and prolonging lifetime of the catalyst, in a simple method such that the tube are packed with a molybdenum-bismuth based composite oxide containing
15 antimony at a raw material gas inlet side of each tube and with molybdenum-bismuth based antimony-free composite oxide catalyst at a gas outlet side. Therefore, the present invention has a great industrial utility.

20 EXAMPLES

The present invention is described in more detail by following Examples, which should not be construed as a limitation upon the scope of the present invention.

In Examples, conversion (%), selectivity (%), and yield
25 (%) are defined as follows. In the following formulas, "raw

material" means isobutylene or tert-butanol.

Conversion (%) = [(molar amount of raw material fed in the reaction) - (molar amount of unreacted raw material)] ÷ (molar amount of raw material fed in the reaction) × 100

5 Selectivity (%) = (molar amount of product) ÷ [(molar amount of raw material fed in the reaction) - (molar amount of unreacted raw material)] × 100

Yield (%) = (molar amount of product) ÷ (molar amount of raw material fed in the reaction) × 100

10 Example 1

Ammonium molybdate [(NH₄)₆Mo₇O₂₄·4H₂O] (12,711.7 g) was dissolved into warm water (15,000 g) to prepare Solution A. Into warm water (6,000 g), were dissolved iron (III) nitrate [Fe(NO₃)₃·9H₂O] (6,060.0 g), cobalt nitrate [Co(NO₃)₂·6H₂O] (13,096.4 g) and cesium nitrate (CsNO₃) (701.7 g), and then further dissolved bismuth nitrate [Bi(NO₃)₃·5H₂O] (2,910.4 g) to prepare Solution B. Solution B was added to Solution A while stirring to obtain a slurry which was then spray dried. The resulting dried material was preliminarily calcined at 360°C for 1 hour to obtain a catalyst precursor. The obtained catalyst precursor was formed into the shape of a ring having an outer diameter of 6 mm, an internal diameter of 2.5 mm and a length of 6 mm, then finally calcined at 530°C for 6 hours to obtain Catalyst A. The composition of the catalyst exclusive of oxygen was Mo₁₂Bi₁Fe_{2.5}Co_{7.5}Cs_{0.6}. Catalyst B was

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prepared by the same method as above-described for preparing Catalyst A except that antimony trioxide (Sb_2O_3) (72.9 g) was added to the catalyst precursor (3,000.0 g) before the forming and that a calcination temperature was changed to 550°C. The composition of Catalyst B exclusive of oxygen was

5 $\text{Mo}_{12}\text{Bi}_1\text{Sb}_{0.5}\text{Fe}_{2.5}\text{Co}_{7.5}\text{Cs}_{0.6}$.

In a glass reaction tube having an internal diameter of 18 mm, 3.48g of Catalyst B was placed at a raw material gas inlet side of the reaction tube together with 9 g of silicon carbide (having a 14 mesh size), while 8.12 g of Catalyst A was placed at a raw material gas outlet side together with 21 g of silicon carbide (having a 14 mesh size). A raw material gas (having a molar ratio of isobutylene : oxygen : nitrogen : steam of 1 : 2.2 : 6.2 : 2) was fed into the reaction tube at

10 to conduct vapor phase catalytic oxidation of isobutylene.

15 a space velocity determined under STP condition of 158 ml/min

The obtained result is shown in Table 1.

Example 2

The same oxidation reaction was conducted as in Example 1 except that 5.8 g of Catalyst B was placed at the raw material inlet side together with 15 g of silicon carbide (having a 14 mesh size) and 5.8 g of Catalyst A was placed at the raw material gas outlet side together with 15 g of silicon carbide (having a 14 mesh size).

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25 The obtained result is shown in Table 1.

Comparative Example 1

The same oxidation reaction was conducted as in Example 1 except that only 11.6 g of Catalyst A was placed together with 30 g of silicon carbide (having a 14 mesh size) without using catalyst B.

The obtained result is shown in Table 1.

Comparative Example 2

The same oxidation reaction was conducted as in Example 1 except that only 11.6 g of catalyst B was placed together with 30 g of silicon carbide (having a 14 mesh size) without using catalyst A.

The obtained result is shown in Table 1.

Example 3

Catalyst C was prepared in the same manner as described for preparing Catalyst A in Example 1 except that antimony trioxide (Sb_2O_3) (874.8 g) was added into Solution A. The composition of Catalyst C exclusive of oxygen was $\text{Mo}_{12}\text{Bi}_1\text{Sb}_{1.0}\text{Fe}_{2.5}\text{Co}_{7.5}\text{Cs}_{0.6}$.

In a glass reaction tube having an internal diameter of 18 mm, 3.48g of Catalyst C was placed at a raw material gas inlet side of the reaction tube together with 9 g of silicon carbide (having a 14 mesh size), while 8.12 g of Catalyst A was placed at a raw material gas outlet side together with 21 g of silicon carbide (having a 14 mesh size).

Using such a prepared reaction tube, vapor phase

catalytic oxidation of isobutylene was conducted under the same reaction conditions as in Example 1.

The obtained result is shown in Table 1.

Comparative Example 3

5 The oxidation reaction was conducted as in Example 3 except that only 11.6 g of catalyst C was placed together with 30 g of silicon carbide (having a 14 mesh size) without using catalyst A.

The obtained result is shown in Table 1.

10 Table 1

	Inlet Side Catalyst / Outlet Side Catalyst	Reaction Temperature, (°C)	Temperature * difference ΔT (°C)	Conversion of isobutylene, (%)	Selectivity to methacrolein and methacrylic acid (%)	Yield of methacrolein and methacrylic acid (%)
Example 1	Catalyst B(30wt%) / Catalyst A(70wt%)	354	36	99.2	83.4	82.7
Example 2	Catalyst B(50wt%) / Catalyst A(50wt%)	353	37	99.0	83.5	82.7
Comparative Example 1	Catalyst A (100 wt%)	341	49	99.1	82.0	81.3
Comparative Example 2	Catalyst B (100 wt%)	354	36	95.3	84.2	80.2
Example 3	Catalyst C(30wt%) / Catalyst A(70wt%)	354	37	99.1	83.2	82.5
Comparative Example 3	Catalyst C (100 wt%)	354	37	96.3	84.0	80.9

* Between reaction temperature and hot spots temperature.

Based on the results of Examples 1 to 3 and Comparative Examples 1 to 3, it is revealed that Catalysts B and C have very low activities, while Catalyst A has high activity but provides a low total yield of methacrolein and methacrylic acid. In the catalyst systems combining Catalysts A and B or A and C, it is shown that the temperature difference (ΔT) between the reaction temperature and the hot spot temperature is smaller than that observed in the case of catalyst A alone, demonstrating that generation of hot spots is suppressed and that the total yield becomes higher.



What is claimed is

1. A process for producing an unsaturated aldehyde and an unsaturated carboxylic acid which comprises subjecting isobutylene or tertiary butanol to vapor phase catalytic oxidation with molecular oxygen using fixed bed multi-tubular reactor comprising a plurality of tubes, each tube (i) being packed at a gas outlet side of each tube with a composite oxide catalyst represented by the formula
$$\text{Mo}_a\text{Bi}_b\text{Fe}_c\text{A}_d\text{B}_e\text{O}_x,$$
wherein Mo, Bi, Fe and O represent molybdenum, bismuth, iron and oxygen, respectively; A represents nickel and/or cobalt; B represents at least one kind of element selected from a group consisting of potassium, rubidium, cesium, and thallium; in the case of a being 12, $0 < b \leq 10$, $0 < c \leq 10$, $1 \leq d \leq 10$, and $0 < e \leq 2$; and x is a value dependent on the oxidation states of the respective elements, and (ii) being packed at a gas inlet side of each tube with a composite oxide catalyst by the formula
$$\text{Mo}_a\text{Bi}_b\text{Fe}_c\text{A}_d\text{B}_e\text{Sb}_f\text{O}_x$$
wherein A, B, a, b, c, d, and e are the same as defined above; Sb represents antimony; in the case of a being 12, $0.01 \leq f \leq 5$; and x is a value dependent on the oxidation states of the respective elements.