



PROCESS FOR PRODUCING ACROLEIN AND ACRYLIC ACID



G00002

Field of the Invention

5 This invention relates to a process for producing acrolein and acrylic acid. More particularly, it relates to a process for producing acrolein and acrylic acid by the vapor-phase oxidation of propylene in the presence of a molybdenum-bismuth-iron-based oxide catalyst.

Description of the Prior Art

10 In producing acrolein and acrylic acid by the vapor-phase oxidation of propylene, a compound oxide catalyst containing molybdenum, bismuth and iron is usually used.

15 One disadvantage of this molybdenum-bismuth-iron-based compound oxide catalyst is that, when water vapor is present in the reaction system, the molybdenum component thereof tends to be sublimated and the sublimation of the molybdenum component is promoted especially at high temperatures. Moreover, in the case of
20 exothermic reactions, such as the oxidation reaction of propylene, the catalyst bed tends to develop local areas having an abnormally high temperature (i.e., hot spots), which creates an environment in which the molybdenum component is more liable to sublimation. Furthermore, the sublimated molybdenum component tends to accumulate in
25 areas having lower temperatures, leading to an increase in the pressure drop of the catalyst bed and hence a further rise in hot spot temperature.

 In order to solve these problems, a variety of improvements in the molybdenum-bismuth-iron-based compound oxide
30 catalyst or the process for producing acrolein and acrylic acid have been proposed. For example, Japanese Patent Laid-Open No.

113730/ '80 discloses a process using two or more molybdenum-bismuth-iron-based compound oxide catalysts having different activities controlled by varying the content of an alkali metal (e.g., potassium or rubidium) wherein two or more axially disposed reaction zones of each reaction tube of a fixed-bed multitubular reactor are packed with the aforesaid catalysts in such a way that the activity increases from the gas inlet side of the reaction tube toward the gas outlet side thereof.

10 **Problem to Be Solved by the Invention**

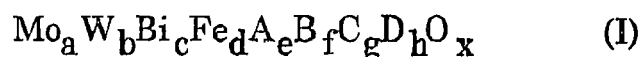
In these conventional molybdenum-bismuth-iron-based compound oxide catalysts or processes for producing acrolein and acrylic acid, the problems have been solved to some extent. However, it is still desired to develop a more improved process for producing acrolein and acrylic acid with aid of a molybdenum-bismuth-iron-based compound oxide catalyst.

Accordingly, an object of the present invention is to provide a process for producing acrolein and acrylic acid by the vapor-phase oxidation of propylene in the presence of molybdenum-bismuth-iron-based compound oxide catalysts wherein acrolein and acrylic acid can be stably produced in high yield for a long period of time.

Means for Solving the Problem

25 The above object of the present invention can be accomplished by a process for producing acrolein and acrylic acid by the vapor-phase catalytic oxidation of propylene with molecular oxygen or a molecular oxygen-containing gas in a fixed-bed multitubular reactor, which comprises

30 (a) using, as the catalysts therefor, compound oxide catalysts of the general formula



wherein Mo is molybdenum; W is tungsten, Bi is bismuth; Fe is iron;
 5 A is at least one element selected from the group consisting of cobalt
 and nickel; B is at least one element selected from the group consist-
 ing of phosphorus, antimony, boron, tin, cerium, niobium, lead,
 chromium and zinc; C is at least one element selected from the group
 consisting of alkali metals and thallium; D is at least one element
 10 selected from the group consisting of silicon, aluminum, titanium and
 zirconium; O is oxygen; a, b, c, d, e, f, g, h and x are the number of
 atoms of Mo, W, Bi, Fe, A, B, C, D and O, respectively; and when a is
 12, b has a value of 0 to 5, c has a value of 0.1 to 10, d has a value of
 0.1 to 10, e has a value of 1 to 20, f has a value of 0 to 5, g has a value
 15 of 0.001 to 3, h has a value of 0 to 30, and x has a value determined
 by the oxidation state of each element, and

(b) packing the catalysts in each reaction tube having two
 or more reaction zones disposed along its axis in such a way that the
 catalyst packed in the reaction zone on the gas outlet side has a lower
 20 ratio of the Bi and/or Fe content to the Mo content than the catalyst
 packed in the reaction zone on the gas inlet side.

Detailed Description of the Preferred Embodiments

The molybdenum-bismuth-iron-based compound oxide
 25 catalysts of the general formula (I) which are used in the present
 invention are well known per se and may be prepared according to
 well-known processes.

The essential feature of the present invention lies in the
 fact that each of the reaction tubes of a fixed-bed multitubular reac-
 30 tor is packed with molybdenum-bismuth-iron-based compound oxide
 catalysts in a specified manner. That is, according to the present
 invention, each reaction tube having two or more reaction zones

(usually two or three reaction zones) disposed along the axis of the tube is packed with two or more catalysts having different ratios of the bismuth and/or iron content to the Mo content (hereinafter referred to as "bismuth-iron proportion") in such a way that the
5 bismuth-iron proportion decreases from the gas inlet side toward the gas outlet side. For example, where each reaction tube has two reaction zones, two catalysts having different bismuth-iron proportions are prepared. Of these, the catalyst having a higher bismuth-iron proportion is packed in the reaction zone on the gas inlet side
10 (hereinafter referred to as "the former-stage reaction zone"), and the catalyst having a lower bismuth-iron proportion is packed in the reaction zone on the gas outlet side (hereinafter referred to as "the latter-stage reaction zone").

When the contents of constituent elements are expressed
15 as atomic ratios, the catalysts used in the present invention may contain 0.1 to 10 of Bi and 0.1 to 10 of Fe per 12 of molybdenum, as defined by the general formula (I). Accordingly, in the practice of the present invention, it is necessary to prepare two catalysts having different bismuth-iron proportions within these limits. Of these, the
20 catalyst having a higher bismuth-iron proportion must be packed in the former-stage reaction zone, and the catalyst having a lower bismuth-iron proportion must be packed in the latter-stage reaction zone.

When the bismuth-iron proportion (i.e., the atomic ratio of
25 bismuth and/or iron to 12 of molybdenum) for the catalyst packed in the former-stage reaction zone (hereinafter referred to as "the former-stage catalyst") is denoted by M_1 , and the bismuth-iron proportion (i.e., the atomic ratio of bismuth and/or iron to 12 of molybdenum) for the catalyst packed in the latter-stage reaction zone (hereinafter referred to as "the latter-stage catalyst") is denoted by M_2 , M_1
30 and M_2 preferably satisfy the relationship represented by $1 < M_1/M_2$

≤ 100 , more preferably $1.1 \leq M_1/M_2 \leq 20$, and most preferably $1.25 \leq M_1/M_2 \leq 10$.

If M_1 is equal to or less than M_2 (i.e., $M_1/M_2 \leq 1$), it will be difficult to control the sublimation of the molybdenum component.

5 On the other hand, if M_1 is excessively greater than M_2 (e.g., $100 < M_1/M_2$), the process will be disadvantageous in that the desired catalyst performance cannot be achieved, the reaction temperature will be raised, and the sublimation of the molybdenum component will be promoted.

10 Accordingly, in a preferred embodiment of the present invention, it is desirable to prepare the former-stage catalyst and the latter-stage catalyst so as to satisfy the relationship represented by $1 < M_1/M_2 \leq 100$, and pack them in the former-stage reaction zone and the latter-stage reaction zone, respectively.

15 In the present invention, no particular limitation is placed on the ratio of the group A element content to the Mo content (hereinafter referred to as "the proportion of the group A elements"). However, in a preferred embodiment of the present invention, two catalysts having different proportions of the group A elements are
20 prepared and packed in the reaction zones in such a way that the proportion of the group A elements increases from the gas inlet side toward the gas outlet side. That is, two catalysts having different proportions of the group A elements are prepared so that the atomic ratio of the group A elements to 12 of molybdenum is in the range of
25 1 to 20. Then, the catalyst having a lower proportion of the group A elements is packed in the former-stage reaction zone, and the catalyst having a higher proportion of the group A elements is packed in the latter-stage reaction zone. More specifically, when the proportion of the group A elements (i.e., the atomic ratio of the group A elements
30 to 12 of molybdenum) for the former-stage catalyst is denoted by N_1 , and the proportion of the group A elements (i.e., the atomic ratio of

the group A elements to 12 of molybdenum) for the latter-stage catalyst is denoted by N_2 , N_1 and N_2 should preferably satisfy the relationship represented by $0.01 \leq N_1/N_2 < 1$, more preferably $0.05 \leq N_1/N_2 < 1$, and most preferably $0.1 \leq N_1/N_2 < 1$.

5 Accordingly, in a more preferred embodiment of the present invention, it is desirable to prepare the former-stage catalyst and the latter-stage catalyst so that they satisfy both of the relationships represented by $1 < M_1/M_2 \leq 100$ and $0.01 \leq N_1/N_2 < 1$, and pack them in the former-stage reaction zone and the latter-stage reaction
10 zone, respectively.

Where each reaction tube has three reaction zones, the bismuth-iron proportions for the catalyst on the gas inlet side, the middle catalyst, and the catalyst on the gas outlet side are denoted by M_1 , M_2 and M_3 , respectively. Then, it is preferable that they satisfy
15 both of the relationships represented by $1 < M_1/M_2 \leq 100$ and $1 < M_2/M_3 \leq 100$. Similarly, when the proportions of the group A elements for the catalyst on the gas inlet side, the middle catalyst, and the catalyst on the gas outlet side are denoted by N_1 , N_2 and N_3 , respectively, it is preferable that they satisfy both of the relationships
20 represented by $0.01 \leq N_1/N_2 < 1$ and $0.01 \leq N_2/N_3 < 1$.

No particular limitation is placed on the shape and size of the catalysts used in the present invention, and any desired shape and size may be suitably chosen from well-known ones. For example, the catalysts may have any of various shapes such as balls, cylinders
25 and rings.

No particular limitation is placed on the method for preparing the catalysts for use in the present invention. For example, shaped catalysts may be obtained by dissolving or dispersing required amounts of source compounds containing respective constituent elements suitably in an aqueous medium, heating the resulting
30 solution or dispersion with stirring, evaporating it to dryness, pulver-

izing the resulting solid material to powder, shaping the powder into any desired shape according to a shaping technique such as extrusion molding or granulation shaping, and then firing the shaped pieces. During this shaping procedure, there may added materials which are
5 generally known to be effective in improving the strength and structural integrity of catalysts, such as inorganic fibers (e.g., glass fibers) and various whiskers. Moreover, in order to control catalyst properties with good reproducibility, there may also be used additives generally known as powder binders, such as ammonium nitrate,
10 cellulose, starch, polyvinyl alcohol and stearic acid.

The catalysts used in the present invention are not limited to the form of shaped catalysts as described above, but may also be in the form of supported catalysts. Supported catalysts may be obtained by depositing a source compound on a carrier generally known as an
15 inert carrier, such as alumina, silica, silica-alumina, silicon carbide, titanium oxide, magnesium oxide, sponge aluminum or silica-titania, and then firing the resulting supported pieces. Also in the case of supported catalysts, the above-described materials such as inorganic fibers and whiskers may be used to improve the strength and structural integrity of the catalysts. Moreover, the above-described powder
20 binders such as ammonium nitrate may also be used to control catalyst properties with good reproducibility.

In preparing the catalysts for use in the present invention, the firing of the precursor such as shaped pieces or supported pieces
25 may be carried out, for example, by heating the shaped pieces or loaded carrier in a stream of air at a temperature of 300 to 600°C for a period of about 1 to 10 hours.

No particular limitation is placed on the reaction conditions employed for the oxidation reaction of the present invention.
30 There may be employed any reaction conditions commonly known to be useful in a process for producing acrolein and acrylic acid by the

vapor-phase catalytic oxidation of propylene in a fixed-bed multi-tubular reactor. For example, the oxidation reaction of the present invention may be carried out by providing a gaseous mixture composed of 1 to 15% by volume of propylene, 3 to 30% by volume of molecular oxygen, 0 to 60% by volume of water vapor, and 20 to 80% by volume of an inert gas comprising nitrogen, carbon dioxide and the like, and passing this gaseous mixture through the reaction zones of the reaction tubes packed with the catalysts at a temperature of 250 to 450°C, a pressure of 0.1 to 1 MPa, and a space velocity (SV) of 300 to 5,000 hr⁻¹.

Effects of the Invention

The process of the present invention makes it possible to suppress the sublimation of the molybdenum component of the catalysts effectively and thereby maintain the catalyst performance stably for a long period of time. Consequently, the production of acrolein and acrylic acid from propylene can be stably continued in high yield for a long period of time. Moreover, the process of the present invention makes it possible to suppress the accumulation of sublimated molybdenum component and, in turn, an increase in the pressure drop of the catalyst bed, and thereby reduce utility costs such as electric power costs for the compressor.

Examples

The present invention is more specifically explained with reference to the following examples. The conversion of propylene, selectivity, yield and ΔP (kPa) are defined as follows.

Conversion of propylene (mole %) =
(Number of moles of propylene reacted) / (Number of moles of propylene fed) x 100

Selectivity (mole %) =

$$\frac{(\text{Number of moles of acrolein and acrylic acid formed})}{(\text{Number of moles of propylene reacted})} \times 100$$

Yield (mole %) =

5
$$\frac{(\text{Number of moles of acrolein and acrylic acid formed})}{(\text{Number of moles of propylene fed})} \times 100$$

ΔP (kPa) =

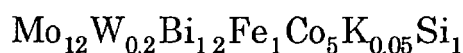
$$(\text{Inlet pressure of reactor}) - (\text{Outlet pressure of reactor})$$

10 Example 1

[Preparation of catalysts]

While 3,000 ml of water was being heated with stirring, 1,000 g of ammonium paramolybdate and 26 g of ammonium paratungstate were dissolved therein. Separately, 687 g of cobalt nitrate
 15 and 191 g of ferric nitrate were dissolved in 1,000 ml of water. Moreover, 275 g of bismuth nitrate was dissolved in an aqueous nitric acid solution composed of 50 g of concentrated nitric acid and 200 g of water. The foregoing three aqueous solutions were mixed by adding the second and third aqueous solutions dropwise to the first aqueous
 20 solution. Then, an aqueous solution prepared by dissolving 2.4 g of potassium nitrate in 50 ml of water, and 142 g of a silica sol having a concentration of 20% by weight were successively added to and mixed with the above mixed aqueous solution.

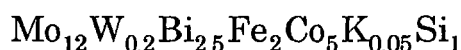
The suspension thus obtained was heated with stirring,
 25 evaporated to dryness, and dried. After the resulting solid material was pulverized to powder, this powder was shaped into cylinders having a diameter of 6 mm and a length of 6.6 mm, and fired in a stream of air at 460°C for 8 hours to obtain the catalyst (1). The composition (i.e., the atomic ratio of the constituent elements except
 30 oxygen; the same shall apply hereinafter) of this catalyst (1) was as follows.



In the catalyst (1), the bismuth-iron proportion is 2.2/12, and the proportion of the group A elements is 5/12.

5 Next, the catalyst (2) was prepared according to the same procedure as described above for the preparation of the catalyst (1), except that the amount of bismuth nitrate was changed to 572 g, and the amount of ferric nitrate was changed to 381 g. The composition of this catalyst (2) was as follows.

10



In the catalyst (2), the bismuth-iron proportion is 4.5/12, and the proportion of the group A elements is 5/12.

15 [Oxidation reaction]

A stainless steel tubular reactor having a diameter of 25 mm was packed with 500 ml of the catalyst (2) on the gas inlet side and 1,000 ml of the catalyst (1) on the gas outlet side. Then, a gaseous mixture composed of 8% by volume of propylene, 14% by volume of oxygen, 10% by volume of water vapor, and 68% by volume of an inert gas comprising nitrogen and the like was introduced through the inlet of the aforesaid tubular reactor at a contact time of 2.4 seconds, and the reaction was continued for 8,000 hours. The performance at the initial stage of the reaction and the performance after the lapse of 8,000 hours are shown in Table 1.

25

Comparative Example 1

Reaction was carried out in the same manner as in Example 1, except that 1,500 ml of the catalyst (1) alone was used. The results thus obtained are shown in Table 1.

30 Comparative Example 2

Reaction was carried out in the same manner as in Exam-

ple 1, except that 1,500 ml of the catalyst (2) alone was used. The results thus obtained are shown in Table 1.

Table 1

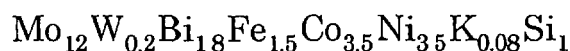
	Reaction time (hrs.)	Reaction temperature (°C)	Conversion (mole %)	Selectivity (mole %)	Yield (mole %)	ΔP (kPa)
Example 1	Initial stage	310	98.4	94.7	93.2	20.0
	8,000	325	98.2	94.9	93.2	22.0
Comparative Example 1	Initial stage	300	98.5	92.2	90.8	19.5
	8,000	315	98.4	90.4	89.0	30.0
Comparative Example 2	Initial stage	310	79.7	95.8	76.4	21.0
	8,000	325	81.0	95.6	77.4	21.5

Example 2

[Preparation of catalysts]

While 3,000 ml of water was being heated with stirring, 1,000 g of ammonium paramolybdate and 26 g of ammonium para-
 5 tungstate were dissolved therein. Separately, 481 g of cobalt nitrate, 480 g of nickel nitrate, and 286 g of ferric nitrate were dissolved in 1,000 ml of water. Moreover, 412 g of bismuth nitrate was dissolved in an aqueous nitric acid solution composed of 50 g of concentrated nitric acid and 200 g of water. The foregoing three aqueous solutions
 10 were mixed by adding the second and third aqueous solutions dropwise to the first aqueous solution. Then, an aqueous solution prepared by dissolving 3.8 g of potassium nitrate in 50 ml of water, and 142 g of a silica sol having a concentration of 20% by weight were successively added to and mixed with the above mixed aqueous
 15 solution.

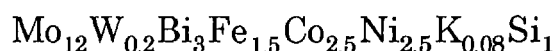
The suspension thus obtained was heated with stirring, evaporated to dryness, and dried. After the resulting solid material was pulverized to powder, this powder was shaped into rings having an outer diameter of 6 mm, an inner diameter of 2 mm, and a length
 20 of 6.6 mm, and fired in a stream of air at 480°C for 8 hours to obtain the catalyst (3). The composition of this catalyst (3) was as follows.



25 In the catalyst (3), the bismuth-iron proportion is 3.3/12, and the proportion of the group A elements is 7/12.

Next, the catalyst (4) was prepared according to the same procedure as described above for the preparation of the catalyst (3), except that the amount of cobalt nitrate was changed to 343 g, the
 30 amount of bismuth nitrate was changed to 687 g, and the amount of nickel nitrate was changed to 343 g. The composition of this catalyst

(4) was as follows.



- 5 In the catalyst (4), the bismuth-iron proportion is 4.5/12, and the proportion of the group A elements is 5/12.

[Oxidation reaction]

- Reaction was carried out in the same manner as in Example 1, except that the catalyst (4) was used in place of the catalyst (2),
 10 and the catalyst (3) was used in place of the catalyst (1). The results thus obtained are shown in Table 2.

Comparative Example 3

- Reaction was carried out in the same manner as in Example 2, except that 1,500 ml of the catalyst (3) alone was used. The
 15 results thus obtained are shown in Table 2.

Comparative Example 4

Reaction was carried out in the same manner as in Example 2, except that 1,500 ml of the catalyst (4) alone was used. The results thus obtained are shown in Table 2.

Table 2

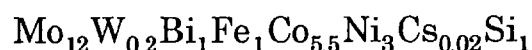
	Reaction time (hrs.)	Reaction temperature (°C)	Conversion (mole %)	Selectivity (mole %)	Yield (mole %)	ΔP (kPa)
Example 2	Initial stage	310	98.3	95.3	93.7	16.7
	8,000	320	98.2	95.2	93.5	17.5
Comparative Example 3	Initial stage	300	98.7	92.5	91.3	16.9
	8,000	310	98.8	90.8	89.7	23.7
Comparative Example 4	Initial stage	310	80.1	96.0	76.9	16.2
	8,000	320	77.4	96.3	74.5	16.4

Example 3

[Preparation of catalysts]

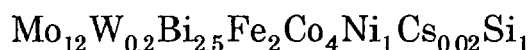
While 3,000 ml of water was being heated with stirring, 1,000 g of ammonium paramolybdate and 26 g of ammonium para-
 5 tungstate were dissolved therein. Separately, 756 g of cobalt nitrate, 412 g of nickel nitrate, and 191 g of ferric nitrate were dissolved in 1,000 ml of water. Moreover, 229 g of bismuth nitrate was dissolved in an aqueous nitric acid solution composed of 50 g of concentrated
 10 nitric acid and 200 g of water. The foregoing three aqueous solutions were mixed by adding the second and third aqueous solutions drop-
 wise to the first aqueous solution. Then, an aqueous solution pre-
 pared by dissolving 1.8 g of cesium nitrate in 50 ml of water, and 142 g of a silica sol having a concentration of 20% by weight were succes-
 sively added to and mixed with the above mixed aqueous solution.

15 The suspension thus obtained was heated with stirring, evaporated to dryness, and dried. After the resulting solid material was pulverized to powder, this powder was shaped into rings having an outer diameter of 6 mm, an inner diameter of 2 mm, and a length of 6.6 mm, and fired in a stream of air at 480°C for 8 hours to obtain
 20 the catalyst (5). The composition of this catalyst (5) was as follows.



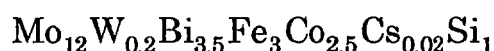
In the catalyst (5), the bismuth-iron proportion is 2/12, and the
 25 proportion of the group A elements is 8.5/12.

Next, the catalyst (6) was prepared according to the same procedure as described above for the preparation of the catalyst (5), except that the amount of bismuth nitrate was changed to 572 g, the amount of ferric nitrate was changed to 381 g, the amount of nickel
 30 nitrate was changed to 137 g, and the amount of cobalt nitrate was changed to 550 g. The composition of this catalyst (6) was as follows.



In the catalyst (6), the bismuth-iron proportion is 4.5/12, and the proportion of the group A elements is 5/12.

5 Furthermore, the catalyst (7) was prepared according to the same procedure as described above for the preparation of the catalyst (6), except that the amount of bismuth nitrate was changed to 801 g, the amount of ferric nitrate was changed to 572 g, the amount of nickel nitrate was changed to 0 g, and the amount of
10 cobalt nitrate was changed to 343 g. The composition of this catalyst (7) was as follows.



15 In the catalyst (7), the bismuth-iron proportion is 6.5/12, and the proportion of the group A elements is 2.5/12.

[Oxidation reaction]

A stainless steel tubular reactor having a diameter of 25 mm was packed with 500 ml of the catalyst (7), 500 ml of the catalyst
20 (6), and 500 ml of the catalyst (5) in such a way that they were arranged in that order from the gas inlet side toward the gas outlet side. Then, a gaseous mixture composed of 10% by volume of propylene, 16% by volume of oxygen, 10% by volume of water vapor, and 64% by volume of an inert gas comprising nitrogen and the like was
25 introduced through the inlet of the aforesaid tubular reactor at a contact time of 2.4 seconds, and the reaction was continued for 8,000 hours. The performance at the initial stage of the reaction and the performance after the lapse of 8,000 hours are shown in Table 3.

Comparative Example 5

30 Reaction was carried out in the same manner as in Example 3, except that 1,500 ml of the catalyst (5) alone was used. The

results thus obtained are shown in Table 3.

Comparative Example 6

Reaction was carried out in the same manner as in Example 3, except that 1,500 ml of the catalyst (6) alone was used. The results thus obtained are shown in Table 3.

Comparative Example 7

Reaction was carried out in the same manner as in Example 3, except that 1,500 ml of the catalyst (7) alone was used. The results thus obtained are shown in Table 3.

Table 3

	Reaction time (hrs.)	Reaction temperature (°C)	Conversion (mole %)	Selectivity (mole %)	Yield (mole %)	ΔP (kPa)
Example 3	Initial stage	310	98.1	94.3	92.5	17.3
	8,000	320	97.9	94.4	92.4	19.7
Comparative Example 5	Initial stage	The recitation could not be continued because of a marked in hot spot temperature				
Comparative Example 6	Initial stage	310	82.4	94.6	78.0	17.0
	8,000	320	80.4	95.3	76.6	17.8
Comparative Example 7	Initial stage	310	70.3	95.6	67.2	17.3
	8,000	320	68.7	95.7	65.7	17.5

Example 4

Reaction was carried out in the same manner as in Example 1, except that the catalyst (3) was used in place of the catalyst (1). The results thus obtained are shown in Table 4.

5 Example 5

Reaction was carried out in the same manner as in Example 1, except that the catalyst (6) was used in place of the catalyst (2). The results thus obtained are shown in Table 4.

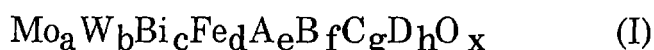
Table 4

	Reaction time (hrs.)	Reaction temperature (°C)	Conversion (mole %)	Selectivity (mole %)	Yield (mole %)	ΔP (kPa)
Example 4	Initial stage	310	98.1	94.7	92.9	17.7
	8,000	321	98.3	94.4	92.8	19.2
Example 5	Initial stage	310	98.0	94.6	92.7	18.9
	8,000	325	98.1	94.2	92.4	20.8

CLAIMS:

1. A process for producing acrolein and acrylic acid by the vapor-phase catalytic oxidation of propylene with molecular oxygen or a molecular oxygen-containing gas in a fixed-bed multitubular reactor, which comprises

(a) using, as the catalysts therefor, compound oxide catalysts of the general formula



wherein Mo is molybdenum; W is tungsten, Bi is bismuth; Fe is iron; A is at least one element selected from the group consisting of cobalt and nickel; B is at least one element selected from the group consisting of phosphorus, antimony, boron, tin, cerium, niobium, lead, chromium and zinc; C is at least one element selected from the group consisting of alkali metals and thallium; D is at least one element selected from the group consisting of silicon, aluminum, titanium and zirconium; O is oxygen; a, b, c, d, e, f, g, h and x are the number of atoms of Mo, W, Bi, Fe, A, B, C, D and O, respectively; and when a is 12, b has a value of 0 to 5, c has a value of 0.1 to 10, d has a value of 0.1 to 10, e has a value of 1 to 20, f has a value of 0 to 5, g has a value of 0.001 to 3, h has a value of 0 to 30, and x has a value determined by the oxidation state of each element, and

(b) packing said catalysts in each reaction tube having two or more reaction zones disposed along the axis of the tube in such a way that the catalyst packed in the reaction zone on the gas outlet side has a lower ratio of the Bi and/or Fe content to the Mo content than the catalyst packed in the reaction zone on the gas inlet side.

2. A process as claim in claim 1 wherein, when the ratio of the Bi and/or Fe content to the Mo content for the catalyst packed in the reaction zone on the gas inlet side is denoted by M_1 , and the ratio

of the Bi and/or Fe content to the Mo content for the catalyst packed in the reaction zone on the gas outlet side is denoted by M_2 , M_1 and M_2 satisfy the relationship represented by $1 < M_1/M_2 \leq 100$.

3. A process as claim in claim 1 or 2 wherein catalysts having different ratios of the group A element content to the Mo content are packed in the reaction zones in such a way that the ratio increases from the gas inlet side toward the gas outlet side.

4. A process as claim in claim 3 wherein, when the ratio of the group A element content to the Mo content for the catalyst packed in the reaction zone on the gas inlet side is denoted by N_1 , and the ratio of the group A element content to the Mo content for the catalyst packed in the reaction zone on the gas outlet side is denoted by N_2 , N_1 and N_2 satisfy the relationship represented by $0.01 \leq N_1/N_2 < 1$.

5. A process as claim in any of claims 1 to 4 wherein, when the number of the reaction zones is 2 or 3.