

PROCESS FOR PREPARING UNSATURATED ALDEHYDE AND UNSATURATED
CARBOXYLIC ACID

FIELD OF THE INVENTION

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[0001] The present invention relates to a process for preparing an unsaturated aldehyde and an unsaturated carboxylic acid by catalytically oxidizing a compound selected from the group consisting of propylene, 10 isobutylene and tert.-butyl alcohol with molecular oxygen in a gas phase.

BACKGROUND ART

15 [0002] It is well known in the art to prepare unsaturated aldehydes and unsaturated carboxylic acids by catalytically oxidizing propylene, isobutylene and/or tert.-butyl alcohol in a gas phase in the presence of a molybdenum-bismuth-iron mixed oxide catalyst.

20 [0003] Such an oxidation reaction is usually carried out by supplying raw material gas in a reactor tube packed with a catalyst. Commercially, the oxidation reaction is often carried out using a multitubular reactor. Since the oxidation reaction is a highly exothermic reaction, 25 localized high-temperature zones, which are usually called hot spots, tend to form near an inlet for introducing the raw material gas. Since the oxidation reaction excessively proceeds at the hot spots, the yields of the desired products often decrease. In addition, since large heat

load is applied to the catalyst, the catalyst may deteriorate and thus a catalyst lifetime may be shortened. These problems become more serious, particularly when the concentration of the raw material compounds in the raw material gas is increased or the space velocity of the raw material gas is increased to enhance the productivity per unit amount of the catalyst.

[0004] Accordingly, it is very important to suppress the excessive exothermic heat at the hot spots to lower the temperature of the hot spots, so that the desired products are obtained at high yields by the above oxidation reaction, and also commercial production facilities can be operated for a longer time with suppressing the deterioration of the catalyst.

[0005] To suppress the exothermic heat at hot spots, some proposals have been made. For example, JP-A-47-10614 discloses a method comprising diluting a catalyst present in a part of a reactor where a hot spot may easily be formed with a material inert to a reaction, GB 1529384 A discloses a method using a reactor in which an inlet for a raw material gas is packed with a supported catalyst, while an outlet is packed with a usual molded catalyst, and JP-A-06-192144 discloses a method for packing a reactor with supported catalysts having gradient support amounts of catalytic active components such that the support amounts of the catalytic active components increase from an inlet for a raw material gas to an outlet.

[0006] EP 0 450 596 A discloses a method for packing a reactor with a plurality of catalysts having different

occupying volumes such that the occupying volumes decrease from an inlet for a raw material gas to an outlet. US Patent No. 5,276,178 discloses a method comprising packing a reactor with a plurality of mixed oxide catalysts having controlled catalytic activities by varying the kind and/or amount of an element selected from the group consisting of alkali metals and thallium constituting the catalysts and also changing a calcination temperature during the preparation of the catalysts, so that the catalytic activity of the catalysts increases from an inlet for a raw material gas to an outlet.

[0007] However, none of the above methods can satisfactorily suppress the exothermic heat at hot spots, and the yields, catalyst lifetime and operation of the process may not necessarily be sufficient for commercial production.

SUMMARY OF THE INVENTION

[0008] An object of the present invention is to provide a process for preparing an unsaturated aldehyde and an unsaturated carboxylic acid by catalytically oxidizing a compound selected from the group consisting of propylene, isobutylene and tert.-butyl alcohol with molecular oxygen in a gas phase with sufficiently suppressing exothermic heat at hot spots during an oxidation reaction, whereby the yields of the products are increased and the heat load on the catalyst is reduced, which process is easily operated and advantageous from the viewpoint of commercial

production.

[0009] To achieve the above object, the present invention provides a process for preparing an unsaturated aldehyde and an unsaturated carboxylic acid comprising the steps of supplying a compound selected from the group consisting of propylene, isobutylene and tert.-butyl alcohol, and molecular oxygen in a reactor tube packed with mixed oxide catalysts and performing a catalytic oxidation reaction between the compound and molecular oxygen in a gas phase in the reactor tube, wherein the reactor tube is packed with a plurality of mixed oxide catalysts having different catalytic activities and each comprising molybdenum, bismuth and iron, which are heated in the presence of a reducing compound, such that the catalytic activities of the catalysts increase from an inlet for a raw material gas to an outlet of the reactor tube.

[0010] Furthermore, the present invention provides a process for preparing an unsaturated aldehyde and an unsaturated carboxylic acid comprising the steps of supplying a compound selected from the group consisting of propylene, isobutylene and tert.-butyl alcohol, and molecular oxygen in a reactor tube packed with mixed oxide catalysts and performing a catalytic oxidation reaction between the compound and molecular oxygen in a gas phase in the reactor tube, wherein the reactor tube is packed with at least one mixed oxide catalyst comprising molybdenum, bismuth and iron which is heated in the presence of a reducing compound and at least one mixed oxide catalyst comprising molybdenum, bismuth and iron which is not heated

in the presence of a reducing compound, such that the catalytic activities of the catalysts increase from an inlet for a raw material gas to an outlet of the reactor tube.

5 [0011] According to the present invention, during the preparation of an unsaturated aldehyde and an unsaturated carboxylic acid, the exothermic heat is thoroughly suppressed at hot spots, the temperature at the hot spots can be well decreased and thus the desired products can be prepared at high yields. Furthermore, the heat load on the catalysts at the hot spots can be reduced.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

15 [0012] The catalysts used for the preparation of an unsaturated aldehyde and an unsaturated carboxylic acid comprise a mixed oxide containing molybdenum, bismuth and iron as essential elements. The mixed oxide may contain one or more elements other than molybdenum (Mo), bismuth (Bi) and iron (Fe). Preferable examples of other elements include nickel, cobalt, potassium, rubidium, cesium, thallium, etc.

[0013] A preferable example of the mixed oxide used in the present invention may be represented by the formula

25 (1): $\text{Mo}_a\text{Bi}_b\text{Fe}_c\text{A}_d\text{B}_e\text{D}_f\text{D}_g\text{O}_x$ (1)

wherein A is an element selected from the group consisting of nickel and cobalt, B is an element selected from the group consisting of manganese, zinc, calcium, magnesium, tin and lead, C is an element selected from the group

consisting of phosphorus, boron, arsenic, tellurium, tungsten, antimony, silicon, aluminum, titanium, zirconium and cerium, D is an element selected from the group consisting of potassium, rubidium, cesium and thallium, and when $a = 12$, b , c , d , e , f and g respectively satisfy the equations: $0 < b \leq 10$, $0 < c \leq 10$, $1 \leq d \leq 10$, $0 \leq e \leq 10$, $0 \leq f \leq 1$, and $0 < g \leq 2$, and x is a value defined by the oxidation states of the elements other than oxygen.

[0014] Among the catalysts, those having the following compositions (except oxygen) are preferably used:

[0015] $\text{Mo}_{12}\text{Bi}_{0.1-5}\text{Fe}_{0.5-5}\text{Co}_{5-10}\text{Cs}_{0.01-1}$

[0016] $\text{Mo}_{12}\text{Bi}_{0.1-5}\text{Fe}_{0.5-5}\text{Co}_{5-10}\text{Sb}_{0.1-5}\text{Si}_{0.1-5}\text{K}_{0.01-1}$

[0017] $\text{Mo}_{12}\text{Bi}_{0.1-5}\text{Fe}_{0.5-5}\text{Ni}_{5-10}\text{Sb}_{0.1-5}\text{Tl}_{0.01-1}$

[0018] As raw materials for the preparation of the catalysts, compounds of the elements contained in the catalysts such as oxides, nitrates, sulfates, carbonates, hydroxides, oxo acids and their ammonium salts, halides, etc. may be used in amounts sufficient for satisfying the above atomic ratios. Specific examples of the molybdenum compounds include molybdenum trioxide, molybdic acid, ammonium paramolybdate, etc. Specific examples of the bismuth compounds include bismuth oxide, bismuth nitrate, bismuth sulfate, etc. Specific examples of the iron compounds include iron(III) nitrate, iron(III) sulfate, iron(III) chloride, etc.

[0019] The catalyst comprising the mixed oxide may usually be prepared by mixing the raw materials of the catalyst in water to obtain an aqueous solution or an aqueous slurry, drying the solution or slurry, and then

calcining the dried material in an atmosphere containing molecular oxygen (see JP-A-59-46132, JP-A-60-163830, JP-A-2000-288396, etc.). Here, the drying may be carried out using a conventional drying device such as a kneader, a box
5 type drier, a drum type through-flow drier, a spray drier, a flash drier, etc.

[0020] The concentration of molecular oxygen used in the above calcination process is usually from 1 to 30% by volume, preferably from 10 to 25% by volume. As the
10 molecular oxygen, an air or pure oxygen may be used. The molecular oxygen may optionally be diluted with nitrogen, carbon dioxide, water, helium, argon, etc.

[0021] The calcination temperature is usually from 300 to 600°C, preferably from 400 to 550°C. The calcination
15 time is usually from 5 minutes to 40 hours, preferably from 1 to 20 hours.

[0022] The catalyst is usually shaped in a desired form. Preferably, the catalyst is molded in the form of a ring, a pellet, a sphere, etc. by tableting, extrusion molding, etc.
20 The shaping may be carried out before or after the calcination in the atmosphere containing molecular oxygen, or after reduction treatment of the catalyst which is explained below. When the catalyst is shaped, inorganic fiber, which is substantially inert to the oxidation
25 reaction for which the catalyst is used, may be added to the catalyst to improve the mechanical strength of the catalyst (see, for example, JP-A-09-52053).

[0023] The activity of the catalyst can be controlled by heating the catalyst in the presence of a reducing compound

(hereinafter, this heating of the catalyst in the presence of a reducing compound may be simply referred to as "reduction treatment").

[0024] Examples of the reducing compound include

5 hydrogen, ammonia, carbon monoxide, hydrocarbons, alcohols, aldehydes, amines, etc. They may optionally be used as a mixture of two or more of them. Preferably, each of the hydrocarbons, alcohols, aldehydes and amines has 1 to about 6 carbon atoms. Specific examples of such hydrocarbons
10 include saturated aliphatic hydrocarbons such as methane, ethane, propane, n-butane, isobutane, etc.; unsaturated aliphatic hydrocarbons such as ethylene, propylene, α -butylene, β -butylene, isobutylene, etc.; benzene; and the like. Specific examples of such alcohols include saturated
15 aliphatic alcohols such as methanol, ethanol, n-propanol, isopropanol, n-butanol, isobutanol, sec.-butanol, tert.-butanol, etc.; unsaturated aliphatic alcohols such as allyl alcohol, crotyl alcohol, methallyl alcohol, etc.; and phenol. Specific examples of such aldehydes include
20 saturated aliphatic aldehydes such as formaldehyde, acetaldehyde, propionaldehyde, n-butyraldehyde, isobutyraldehyde, etc.; and unsaturated aliphatic aldehydes such as acrolein, crotonaldehyde, methacrolein, etc. Specific examples of such amines include saturated
25 aliphatic amines such as methylamine, dimethylamine, trimethylamine, ethylamine, diethylamine, triethylamine, etc.; unsaturated aliphatic amines such as allylamine, diallylamine, etc.; and aniline.

[0025] The catalyst is reduced by heating the catalyst

in a gas containing the above reducing compound. The concentration of the reducing compound in the gas is usually from 0.1 to 50% by volume, preferably from 1 to 30% by volume. The reducing compound is diluted with nitrogen, carbon dioxide, water, helium, argon, etc. to attain such a concentration. The molecular oxygen may be present in such an amount that the effect of the reduction of the catalyst is not impaired. Preferably, the molecular oxygen is not present.

[0026] The reduction temperature is usually from 200 to 600°C, preferably 250 to 550°C. The reduction time is usually from 5 minutes to 20 hours, preferably from 30 minutes to 10 hours. The reduction of the catalyst is preferably carried out by charging the catalyst in a container such as a tube-type container or a box-type container and flowing the gas containing the reducing compound through the container. In this case, the gas exhausted from the container may be recycled to the container, if desired.

[0027] In general, the weight of the catalyst decreases after the reduction treatment. The percentage of the weight loss of the catalyst is calculated according to the following equation:

$$[0028] \quad \text{Weight loss (\%)} = [(CW_b - CW_a)/CW_b] \times 100$$

[0029] in which CW_b is a weight of a catalyst before reduction treatment and CW_a is a weight of a catalyst after reduction treatment.

[0030] The weight loss of the catalyst may be caused by the loss of lattice oxygen atoms in the catalyst, and the

loss of the lattice oxygen atoms may change the catalytic activity. The degree of the reduction of the catalyst can be adjusted by selecting a reduction time and/or a reduction temperature. On one hand, as the reduction of

5 the catalyst proceeds, the weight loss of the catalyst tends to increase. On the other hand, the catalytic activity increases for a while and reaches the maximum and then gradually decreases, as the reduction of the catalyst proceeds. Accordingly, the catalyst activity does not

10 necessarily increases as the weight loss of the catalyst increases. In general, a catalyst having a weight loss of 0.01 to 6% has a higher catalytic activity than a catalyst which is not subjected to the reduction treatment.

Therefore, it is preferable to use such a catalyst having a
15 weight loss of 0.01 to 6% as one of the catalysts to be packed in the reactor tube. A catalyst having a weight loss of more than 6% may be used as such, but it is preferably again calcined in the molecular oxygen-containing gas and then reduced to adjust its catalytic
20 activity.

[0031] In the course of the reduction treatment, the reducing compound itself and/or decomposition materials derived from the reducing compound may remain in the catalyst after the reduction treatment depending the kind
25 of the reducing compound, heat treatment conditions, etc. In such a case, the weight of the remaining material is measured and subtracted from the whole weight of the catalyst to calculate the net weight of the catalyst. The weight of the remaining material may be measured by the

measurement of total carbons (TC), since the remaining material may typically be carbon.

[0032] In the process of the present invention, a plurality of catalysts having different catalytic

5 activities, which are obtained by the above reduction treatment, are packed in the reactor tube such that the catalytic activities of the catalysts increase from an inlet for a raw material gas to an outlet of the reactor tube. Alternatively, the catalyst(s) subjected to the

10 reduction treatment and a catalyst which has not been subjected to the reduction treatment are packed in the reactor tube such that the catalytic activities of the catalysts increase from the inlet for the raw material gas to the outlet of the reactor tube. Then, the catalytic
15 oxidation reaction between the raw material compound and molecular oxygen in a gas phase is carried out in the reactor tube. The catalyst may be charged from the inlet or the outlet of the reactor tube.

[0033] When the reactor tube is packed with the
20 plurality of the catalysts having the controlled catalytic activities in the specific order and then used for carrying out the catalytic oxidation reaction, the exothermic heat at the hot spots is effectively suppressed, and thus the desired products can be obtained in a high total yield.

25 [0034] In the process of the present invention, as the kinds of the catalysts increase, the temperature distribution in the reactor tube can more effectively be controlled. However, the increase of the kinds of the catalysts makes the production of the catalysts and the

packing procedure of the catalysts complicated. Therefore, preferably, two kinds of the catalysts are packed in the reactor tube.

[0035] The shapes of the catalysts packed in the reactor
5 may be the same or different. Any of conventional methods for suppressing exothermic heat at hot spots may be combined with the present invention.

[0036] In the process of the present invention, the gas-
phase catalytic oxidation reaction is carried out by
10 supplying the raw material compound selected from the group consisting of propylene, isobutylene and tert.-butyl alcohol, and molecular oxygen into the reactor tube. In the commercial production, a fixed bed multitubular reactor comprising the reactor tube explained above is used.

15 [0037] As the molecular oxygen, an air is usually used. Apart from the raw material compound and the molecular oxygen, the raw material gas may optionally contain other gaseous material such as nitrogen, carbon dioxide, carbon monoxide, steam, etc.

20 [0038] The reaction temperature is usually from 250 to 400°C. The reaction pressure is usually from an atmospheric pressure to 500 kPa, although a reduced pressure may be used. A molar ratio of the molecular oxygen to the raw material compound is usually from 1:1 to
25 3:1. The space velocity of the raw material gas is usually from 500 to 5,000 hr⁻¹ at a standard temperature and pressure (STP).

[0039] According to the process of the present invention, excessive exothermic heat at the hot spots can be

sufficiently suppressed and thus the temperature at the hot spots can effectively be lowered. Therefore, it is possible to produce acrolein and acrylic acid from propylene, or methacrolein and methacrylic acid from isobutylene or tert-butanol, in good yields.

[0040] The present invention will be illustrated by the following Examples, which do not limit the scope of the present invention in any way. Unless otherwise indicated, the volumes of gasses and a space velocity are those at STP.

10 In the following Examples, a conversion (%) and a total yield (%) are defined as follows:

[0041] $\text{Conversion (\%)} = 100 \times [(\text{Moles of supplied isobutylene}) - (\text{Moles of unreacted isobutylene})] / (\text{Moles of supplied isobutylene})$

15 [0042] $\text{Total yield (\%)} = 100 \times [\text{Total moles of methacrolein and methacrylic acid}] / (\text{Moles of supplied isobutylene})$

COMPARATIVE EXAMPLE 1

20 [0043] (a) Preparation of catalyst

[0044] Ammonium molybdate $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}]$ (13,241 g) was dissolved in warm water (15,000 g) at. This solution is referred to as "Solution A". Separately, iron(III) nitrate $[\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}]$ (6,060 g), cobalt nitrate $[\text{Co}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}]$ (13,096 g) and cesium nitrate $[\text{CsNO}_3]$ (585 g) were dissolved in warm water (6,000 g), and then bismuth nitrate $[\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}]$ (2,910 g) was dissolved. This solution is referred to as "Solution B". Solution B was poured in Solution A while stirring to obtain a slurry.

Then, the slurry was dried in a flash drier to obtain a dried material. To 100 parts by weight of the dried material, 6 parts by weight of silica-alumina fiber (RFC 400-SL manufactured by SAINT-GOBAIN TM) was added, and the mixture was molded in the form of rings each having an outer diameter of 6.3 mm, an inner diameter of 2.5 mm and a length of 6 mm, and calcined in an air stream at 516°C for 6 hours 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.

[0045] (b) Oxidation reaction

[0046] Catalyst A (13 ml) prepared in the previous step (a) was packed in a glass reactor tube having an inner diameter of 18 mm. Then, through the reactor tube packed with Catalyst A, a mixed gas of isobutylene, oxygen, nitrogen and steam in a molar ratio of 1:2.2:6.7:2.1 was supplied at a space velocity of 750 hr⁻¹ to oxidize isobutylene at a reaction temperature of 360°C (a temperature of a heat source for heating the reactor tube). The conversion of isobutylene and the total yield of methacrolein and methacrylic acid are shown in Table 1.

COMPARATIVE EXAMPLE 2

[0047] Catalyst A (50 g) prepared in the step (a) of Comparative Example 1 was packed in a glass tube, and a mixed gas of hydrogen and nitrogen in a volume ratio of 20:80 was supplied at a flow rate of 200 ml/min. into the glass tube to reduce Catalyst A at 400°C for 3 hours. Then, the supply of hydrogen was stopped, and the glass tube

containing Catalyst A was cooled to room temperature in a nitrogen stream. Thereby, the reduced catalyst, Catalyst B, was obtained. The weight loss of the catalyst caused by the reduction treatment was 3.52%.

- 5 [0048] The oxidation reaction was carried out in the same manner as in the step (b) of Comparative Example 1 except that Catalyst B was used in place of Catalyst A and the reaction temperature was changed from 360°C to 320°C. The results are shown in Table 1.

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COMPARATIVE EXAMPLE 3

- [0049] A reduced catalyst, Catalyst C, was prepared in the same manner as in Comparative Example 2 except that a mixed gas of hydrogen and nitrogen in a volume ratio of 10:90 was used in the reduction treatment, the reduction temperature was changed from 400°C to 250°C, and the reduction time was changed from 3 hours to 1 hour. The weight loss of the catalyst caused by the reduction treatment was 0.04%.

- 15 20 [0050] The oxidation reaction was carried out in the same manner as in the step (b) of Comparative Example 1 except that Catalyst C was used in place of Catalyst A. The results are shown in Table 1.

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EXAMPLE 1

- [0051] Catalyst A prepared in the step (a) of Comparative Example 1 (6.5 ml; 50% by volume of the whole catalysts) was packed in the inlet region for raw material gas of a glass reactor tube having an inner diameter of 18

mm, while Catalyst B prepared in Comparative Example 2 (6.5 ml; 50% by volume of the whole catalysts) was packed in the outlet region of the reactor tuber. Into the reactor tube, a mixed gas of isobutylene, oxygen, nitrogen and steam in a volume ratio of 1:2.2:6.7:2.1 was supplied at a space velocity of 750 hr⁻¹ to carry out the oxidation reaction at 330°C. The conversion of isobutylene and the total yield of methacrolein and methacrylic acid are shown in Table 1.

EXAMPLE 2

[0052] The oxidation reaction was carried out in the same manner as in Example 1 except that Catalyst C prepared in Comparative Example 3 (6.5 ml; 50% by volume of the whole catalysts) was used in place of Catalyst A. The results are shown in Table 1.

TABLE 1

	Catalyst Inlet/outlet	Reaction temp. (°C)	ΔT (°C)	Conversion (%)	Total yield (%)
Comparative Example 1	Single layer of Catalyst A	360	70	99.0	76.6
Comparative Example 2	Single layer of Catalyst B	320	66	99.3	77.6
Comparative Example 3	Single layer of Catalyst C	360	73	99.3	76.9
Example 1	Catalyst A/ Catalyst B	330	63	99.4	78.8
Example 2	Catalyst C/ Catalyst B	330	64	99.3	79.0

[0053] In Examples 1 and 2 and Comparative Examples 1 to 3, the reaction temperature (the temperature of a heat

source for heating the reactor tube) was controlled so that a conversion of isobutylene reached around 99% to evaluate the reaction results. In Table 1, ΔT indicates the difference of the temperature at the hot spot and the reaction temperature (ΔT = the former - the latter).

[0054] In Comparative Examples 1 and 3 in which Catalyst A and Catalyst C were used alone respectively, the reaction temperature should be made high to achieve a conversion of about 99%, and the total yield was low. In addition, in Comparative Examples 1 and 3, ΔT was large and thus the heat load on the catalyst was high. In Comparative Example 2 in which Catalyst B was used alone, the total yield was slightly low, although the reaction temperature and ΔT could be made low.

[0055] In contrast, when Catalysts A and B or Catalysts C and B were packed in the reactor tube so that the catalytic activities of the catalysts increased from the inlet to the outlet of the reactor tube, ΔT was smaller than that in Comparative Examples each using the single catalyst. Thus, the exothermic heat at the hot spots could be effectively suppressed and the total yield was higher.

What is claimed is:

1. A process for preparing an unsaturated aldehyde and an unsaturated carboxylic acid comprising the steps of supplying a compound selected from the group consisting of propylene, isobutylene and tert.-butyl alcohol, and molecular oxygen in a reactor tube packed with mixed oxide catalysts and performing a catalytic oxidation reaction between the compound and molecular oxygen in a gas phase in the reactor tube, wherein the reactor tube is packed with a plurality of mixed oxide catalysts having different catalytic activities and each comprising molybdenum, bismuth and iron, which are heated in the presence of a reducing compound, such that the catalytic activities of the catalysts increase from an inlet for a raw material gas to an outlet of the reactor tube.

2. A process for preparing an unsaturated aldehyde and an unsaturated carboxylic acid comprising the steps of supplying a compound selected from the group consisting of propylene, isobutylene and tert.-butyl alcohol, and molecular oxygen in a reactor tube packed with mixed oxide catalysts and performing a catalytic oxidation reaction between the compound and molecular oxygen in a gas phase in the reactor tube, wherein the reactor tube is packed with at least one mixed oxide catalyst comprising molybdenum, bismuth and iron which is heated in the presence of a reducing compound and at least one mixed oxide catalyst comprising molybdenum, bismuth and iron which is not heated in the presence of a reducing compound, such that the

catalytic activities of the catalysts increase from an inlet for a raw material gas to an outlet of the reactor tube.

5 3. The process according to claim 1 or 2, wherein the reducing compound is at least one compound selected from the group consisting of hydrogen, ammonia, carbon monoxide, hydrocarbons having 1 to 6 carbon atoms, alcohols having 1 to 6 carbon atoms, aldehydes having 1 to 6 carbon atoms and
10 amines having 1 to 6 carbon atoms.

 4. The process according to claim 1 or 2, wherein a weight loss of the catalyst caused by the heat treatment in the presence of a reducing compound is from 0.01 to 6%.

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 5. The process according to claim 1 or 2, wherein two kinds of the catalysts are packed in the reactor tube.

 6. The process according to claim 1 or 2, wherein the
20 mixed oxide is a compound represented by the formula (1):
$$\text{Mo}_a\text{Bi}_b\text{Fe}_c\text{A}_d\text{B}_e\text{D}_f\text{D}_g\text{O}_x \quad (1)$$

 wherein A is an element selected from the group consisting of nickel and cobalt, B is an element selected from the group consisting of manganese, zinc, calcium, magnesium,
25 tin and lead, C is an element selected from the group consisting of phosphorus, boron, arsenic, tellurium, tungsten, antimony, silicon, aluminum, titanium, zirconium and cerium, D is an element selected from the group consisting of potassium, rubidium, cesium and thallium, and

when $a = 12$, b , c , d , e , f and g respectively satisfy the equations: $0 < b \leq 10$, $0 < c \leq 10$, $1 \leq d \leq 10$, $0 \leq e \leq 10$, $0 \leq f \leq 1$, and $0 < g \leq 2$, and x is a value defined by the oxidation states of the elements other than oxygen.