

METHOD OF PRODUCING CATALYST USED IN THE PRODUCTION OF METHACRYLIC ACID AND METHOD OF PRODUCING METHACRYLIC ACID

TECHNICAL FIELD

5 [0001]

The present invention relates to a method of producing a catalyst used in the production of methacrylic acid, and a method of producing methacrylic acid using the catalyst obtained by the method.

Priority is claimed on Japanese Patent Application No. 2011-116925, filed
10 May 25, 2011, the content of which is incorporated herein by reference.

DESCRIPTION OF RELATED ART

[0002]

Conventionally, as a catalyst used in the production of methacrylic acid by a
15 gas-phase catalytic oxidation reaction of methacrolein or the like, a catalyst containing a heteropolyacid containing phosphorus and molybdenum or a salt thereof is known to be effective. In general, such a catalyst is produced by drying an aqueous mixture containing raw materials for the catalyst, followed by calcination. The calcination method is described in Patent Documents 1 to 5.

20 [0003]

Patent Document 1 discloses a method in which calcination is performed at 400 to 500°C in a non-oxidizing gas atmosphere, followed by calcination at 300 to 400°C in an oxidized gas atmosphere. Patent Document 2 discloses a method in which calcination is performed at 360 to 410°C in an oxidized gas atmosphere or a

non-oxidizing gas atmosphere, followed by calcination at 420 to 500°C in a non-oxidizing gas atmosphere, followed by calcination at 300 to 400°C in an oxidized gas atmosphere. Patent Document 3 discloses a method in which calcination is performed at 300 to 400°C in an atmosphere of an oxidized gas containing a water component of 10vol% or less, followed by calcination at 400 to 500°C in a non-oxidizing gas atmosphere, followed by calcination at 300 to 400°C in an atmosphere of an oxidized gas containing a water component of 30vol% or less. Patent Document 4 discloses a method in which calcination is performed at 300 to 400°C in an oxidized gas atmosphere, followed by calcination at 400 to 500°C in a non-oxidizing gas atmosphere, followed by cooling down to 280°C or lower in the non-oxidizing gas atmosphere. Patent Document 5 discloses a method which includes a first calcination at 300 to 400°C in an oxidized gas atmosphere, elevating the temperature to 420°C or higher in an atmosphere of a non-oxidizing gas containing a water component of 0.1 to 10vol%, and a second calcination at 420 to 500°C in a non-oxidizing gas atmosphere.

DOCUMENTS OF RELATED ART

[Patent Document]

[0004]

[Patent Document 1] Japanese Unexamined Patent Application, First Publication No. 2004-188231

[Patent Document 2] Japanese Unexamined Patent Application, First Publication No. 2005-21727

[Patent Document 3] Japanese Unexamined Patent Application, First

Publication No. 2005-131577

[Patent Document 4] Japanese Unexamined Patent Application, First

Publication No. 2007-90193

[Patent Document 5] Japanese Unexamined Patent Application, First

5 Publication No. 2008-284508

SUMMARY OF THE INVENTION

[0005]

However, catalysts used in the production of methacrylic acid obtained by the
10 conventional methods were not always satisfactory in terms of catalyst activity and
catalyst life.

An object of the present invention is to provide a method of producing a
catalyst used in the production of methacrylic acid which exhibits excellent catalyst
activity and catalyst life. Further, another object of the present invention is to provide
15 a method of producing methacrylic acid using a catalyst produced by the method, so as
to convert the raw materials with an excellent conversion and stably produce
methacrylic acid over a long period.

[0006]

As a result of intensive studies of the present inventors, they have found that
20 the following embodiments could solve the problems, and completed the present
invention based on these findings.

(1) A method of producing a catalyst used in the production of methacrylic
acid containing a heteropolyacid compound containing phosphorus and molybdenum,
the method including:

a first calcination step in which a catalyst precursor is subjected to calcination at 360 to 410°C in an atmosphere of a gas containing a water component of 0.1vol% to less than 2.0vol%;

a second calcination step in which a calcined product obtained in the first
5 calcination step is subjected to further calcination at 420 to 500°C in an atmosphere of a non-oxidizing gas; and

a cooling step in which a calcined product obtained in the second calcination step is cooled down to 280°C or lower in an atmosphere of a non-oxidizing gas.

(2) The method according to item (1) above, wherein the heteropolyacid
10 compound further contains:

vanadium;

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

at least one element selected from the group consisting of copper, arsenic,
15 antimony, boron, silver, bismuth, iron, cobalt, lanthanum and cerium.

(3) The method according to item (1) or (2) above, wherein the catalyst precursor is subjected to calcination for 1 to 20 hours in the first calcination step.

(4) The method according to any one of items (1) to (3) above, wherein the calcined product obtained in the first calcination step is subjected to calcination for 1 to
20 20 hours in the second calcination step.

(5) The method according to any one of items (1) to (4) above, wherein the non-oxidizing gas is at least one member selected from the group consisting of nitrogen, argon, helium and carbon dioxide.

(6) A method of producing methacrylic acid, comprising subjecting at least one

compound selected from the group consisting of methacrolein, isobutyraldehyde, isobutane and isobutyric acid to a gas-phase catalytic oxidation reaction in the presence of the catalyst used in the production of methacrylic acid obtained by the method according to any one of items (1) to (5) above.

5 [0007]

According to the present invention, an advantageous effect can be achieved in that a catalyst used in the production of methacrylic acid which exhibits excellent catalyst activity and catalyst life can be obtained. Further, by using the catalyst, an advantageous effect can be achieved in that the raw materials can be converted with an
10 excellent conversion, and methacrylic acid can be stably produced over a long period.

MODE FOR CARRYING OUT THE INVENTION

[0008]

The catalyst used in the production of methacrylic acid obtained by the
15 production method according to the present invention contains a heteropolyacid compound containing phosphorus and molybdenum. The heteropolyacid compound may be composed of a free heteropolyacid, or a salt of a heteropolyacid. Among these, a heteropolyacid compound composed of an acidic salt (partially neutralized salt) of a heteropolyacid is preferable, and a heteropolyacid compound composed of an acidic
20 salt of a Keggin-type heteropolyacid is more preferable.

[0009]

The heteropolyacid compound may contain any other element, as long as it contains phosphorus and molybdenum as essential elements and the catalyst activity is not obstructed by the other element. Examples of other elements include vanadium,

potassium, rubidium, cesium, thallium, copper, arsenic, antimony, boron, silver, bismuth, iron, cobalt, lanthanum and cerium. For example, a heteropolyacid compound containing the following elements is preferable.

Phosphorus;

5 molybdenum;

vanadium;

at least one element selected from the group consisting of potassium, rubidium, cesium and thallium (hereafter, sometimes referred to as “element X”); and

at least one element selected from the group consisting of copper, arsenic, 10 antimony, boron, silver, bismuth, iron, cobalt, lanthanum and cerium (hereafter, sometimes referred to as “element Y”).

[0010]

In particular, the heteropolyacid compound preferably contains 3 or less atoms of phosphorus, vanadium, an element X and an element Y, relative to 12 atoms of 15 molybdenum.

[0011]

As described above, the method of producing a catalyst used in the production of methacrylic acid according to the present invention (hereafter, sometimes referred to as “production method of the present invention”) includes a first calcination step, a 20 second calcination step and a cooling step.

[0012]

(First calcination step)

The first calcination step is a step in which a catalyst precursor is subjected to calcination at 360 to 410°C in an atmosphere of a gas containing a water component of

0.1vol% to less than 2.0vol%.

[0013]

The catalyst precursor is a mixture of compounds containing the elements that are contained in the catalyst used in the production of methacrylic acid. Examples of
5 such compounds include oxo acids, oxo-acid salts, oxides, nitrates, carbonates, bicarbonates, hydroxides and halides of each element. For example, as a compound containing phosphorus, phosphoric acid and phosphates can be mentioned. Examples of a compound containing molybdenum include molybdic acid, molybdates, molybdenum oxide and molybdenum chloride. Examples of a compound containing
10 vanadium include vanadic acid, vanadates, vanadium oxide and vanadium chloride. Examples of a compound containing the element X include oxides, nitrates, carbonates, bicarbonates, hydroxides and halides. Examples of a compound containing the element Y include oxo acids, oxo-acid salts, nitrates, carbonates, hydroxides and halides.

15 [0014]

The catalyst precursor is generally obtained by mixing the above compound with water to obtain an aqueous solution or a suspension, followed by drying the aqueous solution or suspension. As a method of drying, a spray drying using a spray drier can be mentioned. In general, the dried product is molded into a desired shape
20 (e.g., a cylindrical shape, a spherical shape, a ring shape or the like), and a mold aid agent may be used if necessary. The obtained molded article is preferably subjected to a heat treatment (precalcination) at a temperature of about 180 to 300°C in an atmosphere of an oxidized gas or a non-oxidizing gas. The molding may be conducted after subjecting the dried product to heat treatment (precalcination).

[0015]

In the preparation of the above aqueous solution or suspension, it is preferable to add ammonia or an ammonium salt, so as to obtain an aqueous solution or a suspension containing ammonium ion. Instead of adding ammonia or an ammonium salt, an ammonium compound may be used as at least one of the compounds containing
5 phosphorus, molybdenum, vanadium, an element X or an element Y. In such a case, as the dried product, a catalyst precursor composed of a non-Keggin-type heteropolyacid salt is obtained, and by subjecting the dried product to heat treatment (precalcination), a rearrangement reaction occurs to change from a non-Keggin-type to
10 a Keggin-type, thereby obtaining a catalyst precursor composed of a Keggin-type heteropolyacid salt.

[0016]

The obtained catalyst precursor is subjected to calcination at 360 to 410°C in an atmosphere of a gas containing a water component of 0.1 vol% to less than 2.0 vol%.
15 In the production method of the present invention, the gas is not particularly limited, as long as it contains the specific amount of a water component. Examples of the gas include an oxidized gas (air, oxygen or the like), a non-oxidizing gas (an inert gas (nitrogen, argon, helium, neon or the like)) and a reducing gas (carbon dioxide, hydrogen, ammonia or the like). Among these, nitrogen, air, argon, helium and
20 carbon dioxide are preferable, and air and nitrogen are more preferable. These gases may be used individually, or in a combination of two or more.

[0017]

The above gas contains a water component of 0.1 vol% to less than 2.0 vol%.
By containing a water component in a specific range, the catalyst activity and the

catalyst life of the obtained catalyst can be effectively improved. The amount of the water component is preferably from 0.8 to 1.8vol%.

[0018]

5 The first calcination is performed at 360 to 410°C. By performing the first calcination at 360 to 410°C, the catalyst activity and the catalyst life of the obtained catalyst can be effectively improved. The first calcination is preferably performed at 380 to 400°C.

[0019]

10 The first calcination is preferably performed for 1 to 20 hours, and more preferably for 1 to 5 hours. By performing the first calcination for 1 to 20 hours, calcination can be satisfactorily performed regardless of the composition of the catalyst precursor.

[0020]

15 The thus obtained calcined product in the first calcination step is subjected to the second calcination step.

[0021]

(Second calcination step)

20 The second calcination step is a step in which the calcined product obtained in the first calcination step is subjected to calcination at 420 to 500°C in an atmosphere of a non-oxidizing gas.

[0022]

Examples of the non-oxidizing gas used in the second calcination step include the aforementioned non-oxidizing gas (an inert gas (nitrogen, argon, helium, neon or the like)) and a reducing gas (carbon dioxide, hydrogen, ammonia or the like).

Among these non-oxidizing gases, nitrogen, argon, helium and carbon dioxide are preferable, and nitrogen is more preferable. The non-oxidizing gases may be used individually, or in a combination of two or more. Further, the non-oxidizing gas used in the second calcination step may or may not contain a water component, but a gas in a
5 dry state containing no water component is preferable.

[0023]

The second calcination is performed at 420 to 500°C. By performing the second calcination at 420 to 500°C, the catalyst activity and the catalyst life of the obtained catalyst can be effectively improved. The second calcination step is
10 preferably performed at 430 to 440°C.

[0024]

The second calcination is preferably performed for 1 to 20 hours, and more preferably for 1 to 5 hours. By performing the second calcination for 1 to 20 hours, calcination can be satisfactorily performed regardless of the composition of the catalyst
15 precursor.

[0025]

The calcined product obtained in the second calcination step is subjected to the cooling step.

[0026]

20 (Cooling step)

The cooling step is a step in which the calcined product obtained in the second calcination step is cooled down to 280°C or lower in an atmosphere of a non-oxidizing gas.

[0027]

Examples of the non-oxidizing gas used in the cooling step include the aforementioned non-oxidizing gas (an inert gas (nitrogen, argon, helium, neon or the like)) and a reducing gas (carbon dioxide, hydrogen, ammonia or the like). Among these non-oxidizing gases, nitrogen, argon, helium and carbon dioxide are preferable, and nitrogen is more preferable. In terms of workability, it is preferable to use the same non-oxidizing gas as that used in the second calcination step (i.e., the non-oxidizing gas used in the second calcination step is *in situ* used). The non-oxidizing gases may be used individually, or in a combination of two or more. Further, the non-oxidizing gas used in the cooling step may or may not contain a water component, but a gas in a dry state containing no water component is preferable.

[0028]

The cooling is performed to cool down to 280°C or lower, and preferably 250°C or lower. By preventing the catalyst from being exposed to an oxidized gas at a temperature higher than 280°C, the catalyst activity and the catalyst life can be effectively improved.

[0029]

(Production method of methacrylic acid)

The catalyst used in the production of methacrylic acid obtained by the production method of the present invention exhibits excellent catalyst activity and catalyst life. By subjecting a starting compound such as methacrolein, isobutyraldehyde, isobutane and/or isobutyric acid to a gas-phase catalytic oxidation reaction using the catalyst used in the production of methacrylic acid, the starting compound can be converted with an excellent conversion, and methacrylic acid can be stably produced over a long period.

[0030]

The production of methacrylic acid is generally performed by packing the catalyst in a fixed-bed multitubular reactor, followed by supplying a starting compound and a gas containing oxygen to the reactor. Instead of the fixed bed, a fluidized bed or
 5 a movable bed may be used. As the gas containing oxygen, air or pure oxygen is generally used. Nitrogen, carbon dioxide, carbon monoxide, water vapor or the like may be supplied to the reactor, apart from the starting compound and the gas containing oxygen.

[0031]

10 When methacrolein is used as the starting compound, the reaction is preferably performed under the following conditions. The space velocity is determined by dividing the feed rate (L/h) of the starting material (starting material and other gases) which passes through the reactor per 1 hour by the volume of the catalyst inside the reactor (L).

- 15 Concentration of methacrolein in the raw materials: 1 to 10vol%
 Concentration of water vapor in the raw materials: 1 to 30vol%
 Molar ratio of methacrolein to oxygen: 1/1 to 1/5 (methacrolein/oxygen)
 Space velocity: 500 to 5,000 h⁻¹ (in terms of standard state)
 Reaction temperature: 250 to 350°C
 20 Reaction pressure: 0.1 to 0.3MPa

[0032]

When isobutane is used as the starting compound, the reaction is preferably performed under the following conditions.

Concentration of isobutane in the raw materials: 1 to 85vol%

Concentration of water vapor in the raw materials: 3 to 30vol%

Molar ratio of isobutane to oxygen: 1/0.05 to 1/4 (isobutane /oxygen)

Space velocity: 400 to 5,000 h⁻¹ (in terms of standard state)

Reaction temperature: 250 to 400°C

5 Reaction pressure: 0.1 to 1MPa

[0033]

When isobutyraldehyde and/or isobutyric acid is used as the starting compound, the reaction is performed under substantially the same conditions as in the case of using methacrolein as the starting material. Further, the starting compounds
10 need not necessarily be a highly-purified product. For example, in the case of methacrolein, methacrolein obtained by a gas-phase catalytic oxidation reaction of isobutylene or t-butyl alcohol can be used without purification.

EXAMPLES

15 [0034]

As follows is a description of examples and comparative examples of the present invention, although the scope of the present invention is by no way limited by these examples. Nitrogen used in each of the examples and comparative examples contains substantially no water component.

20 [0035]

(Preparation Example 1: Preparation of catalyst precursor)

The following raw materials were mixed together to obtain liquid A and liquid

B.

<Liquid A>

Ion exchanged water (40°C): 224 kg

Cesium nitrate (CsNO_3): 38.2 kg

Orthophosphoric acid (an 85wt% product): 24.2 kg

Nitric acid (a 70wt% product): 25.2 kg

5 <Liquid B>

Ion exchanged water (40°C): 330 kg

Ammonium molybdate tetrahydrate: $((\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O})$: 297 kg

Ammonium metavanadate (NH_4VO_3): 8.19 kg

[0036]

10 Subsequently, Liquid A was dropwise added to liquid B while stirring. After the dropwise addition, stirring was conducted at 120°C for 5.8 hours in a sealed container. Then, 10.2 kg of antimony trioxide (Sb_2O_3) and 10.2 kg of cupric nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$) were suspended in 23 kg of an ion exchanged water, and the resulting suspension was added to the closed container, followed by stirring at

15 120°C for 5 hours.

[0037]

The obtained slurry was spray dried with a spray dryer, and to 100 parts by weight of the obtained dried product was added 4 parts by weight of a ceramic fiber (SiO_2 - Al_2O_3 system; fiber diameter: 2 to 4 μm ; average fiber length: 400 μm), 13 parts

20 by weight of ammonium nitrate and 9.7 parts by weight of an ion exchanged water, followed by kneading and extrusion molding to obtain a cylindrical molded article (diameter: 5 mm, height: 6 mm). Then, the obtained molded article was dried at 90°C for 3 hours in an atmosphere with a humidity of 30%RH. The obtained dried product was subjected to heat treatment (precalcination) at 220°C for 22 hours under air flow

and at 250°C for 1 hour, thereby obtaining a precalcined catalyst precursor composed of a Keggin-type heteropolyacid salt.

[0038]

(Example 1)

5 The catalyst precursor obtained in Preparation Example 1 was maintained at 390°C for 3 hours under flow of a mixed gas containing air and steam (water content: 1.0vol%) (first calcination). Then, the mixed gas containing air and steam was changed to nitrogen, and the catalyst precursor was further maintained at 435°C for 3 hours (second calcination). After the second calcination, the calcined product was
10 cooled down to 70°C under nitrogen flow, and was taken out to atmospheric air. The obtained calcined product (catalyst 1) was an acidic salt of a Keggin-type heteropolyacid containing phosphorus (1.5), molybdenum (12), vanadium (0.5), antimony (0.5), copper (0.3) and cesium (1.4). Each value in the brackets is the atomic ratio.

15 [0039]

(Example 2)

A calcined product (catalyst 2) was obtained by the same procedure as in Example 1, except that the water content was changed to 1.4vol% in the first calcination.

20 [0040]

(Example 3)

A calcined product (catalyst 3) was obtained by the same procedure as in Example 1, except that the water content was changed to 1.8vol% in the first calcination.

[0041]

(Example 4)

A calcined product (catalyst 4) was obtained by the same procedure as in Example 1, except that the mixed gas containing air and steam was changed to a mixed
5 gas containing nitrogen and steam (water content: 1.8vol%) in the first calcination..

[0042]

(Comparative Example 1)

A calcined product (catalyst 5) was obtained by the same procedure as in Example 1, except that the mixed gas containing air and steam was changed to just air
10 (water content: 0.0vol%) in the first calcination..

[0043]

(Comparative Example 2)

A calcined product (catalyst 6) was obtained by the same procedure as in Example 1, except that the mixed gas containing air and steam was changed to just
15 nitrogen (water content: 0.0vol%) in the first calcination..

[0044]

(Comparative Example 3)

A calcined product (catalyst 7) was obtained by the same procedure as in Example 1, except that the water content was changed to 2.8vol% in the first
20 calcination.

[0045]

(Comparative Example 4)

A calcined product (catalyst 8) was obtained by the same procedure as in Example 1, except that the water content was changed to 3.5vol% in the first

calcination.

[0046]

(Comparative Example 5)

A calcined product (catalyst 9) was obtained by the same procedure as in
5 Example 1, except that the water content was changed to 4.0vol% in the first
calcination.

[0047]

With respect to the catalysts (catalysts 1 to 9) obtained in each of the examples
and comparative examples, the catalyst activity test was conducted by the following
10 method.

[0048]

(Catalyst activity test)

9 g of the obtained catalyst was weighed, and was packed in a microreactor
made of glass and having an inner diameter of 16 mm, and the furnace temperature
15 (temperature of the furnace for heating the microreactor) was elevated to 280°C.
Then, a source gas prepared by mixing methacrolein, air, water vapor and nitrogen
(methacrolein: 4vol%, molecular oxygen: 12vol%, water vapor: 17vol%; nitrogen:
67vol%) was supplied to the microreactor at a space velocity of 670h⁻¹, and a reaction
was started. After 1 hour from the start of the reaction, the gas effused (gas after the
20 reaction) from the outlet of the microreactor was sampled, and analyzed by gas
chromatography. The conversion of methacrolein was determined from the following
formula.

$$\text{Conversion of methacrolein (\%)} = (A/B) \times 100$$

wherein,

A is the molar number of reacted methacrolein, and

B is the molar number of supplied methacrolein.

[0049]

Subsequently, the furnace temperature was elevated to 355°C, and the above
 5 source gas was supplied at the above space velocity (670h^{-1}), and a reaction was
 performed for 1 hour, so as to force deterioration of the catalyst. The furnace
 temperature was returned to 280°C, and the above source gas was supplied to the
 deteriorated catalyst at the above space velocity (670h^{-1}), so as to start a reaction.
 After 1 hour from the start of the reaction, the gas effused (gas after the reaction) from
 10 the outlet of the microreactor was sampled, and was analyzed by gas chromatography
 to determine the conversion of methacrolein in the same manner as described above.
 With respect to each catalyst (catalysts 1 to 9), the conversion of methacrolein before
 and after the forced deterioration are shown in Table 1.

[0050]

15 [Table 1]

	First calcination		Obtained catalyst	Conversion ratio (%)	
	Atmosphere	Water content (Vol%)		Before forced deterioration	After forced deterioration
Example 1	Air	1.0	Catalyst 1	91	91
Example 2	Air	1.4	Catalyst 2	94	91
Example 3	Air	1.8	Catalyst 3	93	91
Example 4	Nitrogen	1.8	Catalyst 4	93	91
Comparative Example 1	Air	0.0	Catalyst 5	95	81
Comparative Example 2	Nitrogen	0.0	Catalyst 6	76	65
Comparative Example 3	Air	2.8	Catalyst 7	92	89
Comparative Example 4	Air	3.5	Catalyst 8	92	86
Comparative Example 5	Air	4.0	Catalyst 9	90	79

[0051]

As shown in Table 1, the catalysts obtained in Examples 1 to 4 (catalysts 1 to 4) were able to maintain a high conversion of methacrolein even after the forced deterioration, and were capable of producing methacrolein over a long period with an excellent conversion, as compared to the catalysts obtained in Comparative Examples 1 to 5 (catalysts 5 to 9).

[0052]

While preferred embodiments of the invention have been described and illustrated above, it should be understood that these are exemplary of the invention and are not to be considered as limiting. Additions, omissions, substitutions, and other modifications can be made without departing from the spirit or scope of the present invention. Accordingly, the invention is not to be considered as being limited by the foregoing description, and is only limited by the scope of the appended claims.

What is claimed is:

1. A method of producing a catalyst used in the production of methacrylic acid comprising a heteropolyacid compound comprised of phosphorus and molybdenum, the method comprising:

a first calcination step in which a catalyst precursor is subjected to calcination at 360 to 410°C in an atmosphere of a gas containing a water component of 0.1 vol% to less than 2.0 vol%;

a second calcination step in which a calcined product obtained in the first calcination step is subjected to further calcination at 420 to 500°C in an atmosphere of a non-oxidizing gas; and

a cooling step in which a calcined product obtained in the second calcination step is cooled down to 280°C or lower in an atmosphere of a non-oxidizing gas.

2. The method according to claim 1, wherein the heteropolyacid compound further comprises:

vanadium;

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

at least one element selected from the group consisting of copper, arsenic, antimony, boron, silver, bismuth, iron, cobalt, lanthanum and cerium.

3. The method according to claim 1, wherein the catalyst precursor is subjected to calcination for 1 to 20 hours in the first calcination step.

4. The method according to claim 1, wherein the calcined product obtained in the first calcination step is subjected to calcination for 1 to 20 hours in the second calcination step.
5. The method according to claim 1, wherein the non-oxidizing gas is at least one member selected from the group consisting of nitrogen, argon, helium and carbon dioxide.
6. A method of producing methacrylic acid, comprising subjecting at least one compound selected from the group consisting of methacrolein, isobutyraldehyde, isobutane and isobutyric acid to a gas-phase catalytic oxidation reaction in the presence of the catalyst used in the production of methacrylic acid obtained by the method according to any one of claims 1 to 5.