

DESCRIPTION

METHOD FOR RECOVERING MOLYBDENUM AND COBALT

5 [TECHNICAL FIELD]

[0001]

The present invention relates to a method for recovering molybdenum and cobalt from a composite oxide containing molybdenum and cobalt, and to a method for
10 producing a composite oxide or a composite oxide catalyst, using the molybdenum and cobalt recovered by the above-described method, as raw materials. In addition, the present invention relates to a method for producing an unsaturated aldehyde and/or an unsaturated carboxylic acid
15 by using the catalyst obtained by the method for producing the composite oxide catalyst.

[RELATED ART]

[0002]

Composite oxides containing molybdenum and cobalt
20 conventionally have been widely used as catalysts for a variety of catalytic gas phase oxidation reactions. Generally, catalysts tend to degrade in their performance after used over a given period of time, and are then discarded as waste catalysts. Therefore, there arises a
25 demand for recovering and recycling molybdenum and cobalt

in such waste catalysts. As a method for recovering both of molybdenum and cobalt, there is proposed the method for recovering molybdenum and cobalt, respectively, as follows (Patent Publication 1): that is, a composite oxide
5 containing molybdenum and cobalt is leached in an aqueous solution of caustic soda to obtain a leachate containing molybdenum; and the insoluble residue is treated in an aqueous solution of sulfuric acid to obtain a leachate containing cobalt. There is also proposed the method for
10 recovering molybdenum, by mixing a composite oxide which contains molybdenum and cobalt, with an aqueous solution of alkali hydroxide, to obtain an aqueous solution containing molybdenum, so as to recover molybdenum (Patent Publication 2).

15

[PRIOR ART LITERATURE]

[Patent Publications]

[0003]

Patent Publication 1: JP-A-5-156375

20

Patent Publication 2: WO publication No. 2007/032228

[SUMMARY OF THE INVENTION]

[Problem to be Solved by the Invention]

[0004]

25

However, in any of the conventional methods for

recovering molybdenum and cobalt, described above, firstly, molybdenum is recovered, and then, cobalt is recovered from the residue. While these recovering methods are advantageous in case where the recovered molybdenum and cobalt are separately recycled, such methods are disadvantageous in view of facility and cost-effectiveness, since a number of steps are required for recovery. In the meantime, there are a lot of catalysts which contain both of molybdenum and cobalt as catalyst constitutive elements. In some cases, a method for recovering both of molybdenum and cobalt at once is advantageous so as to recycle molybdenum and cobalt as raw materials for such catalysts. Thus, a demand for such a method has been increasing.

[0005]

Objects of the present invention are therefore to provide a method for recovering both of molybdenum and cobalt at once at a higher recovery rate, and to provide a method for producing a composite oxide and a method for producing a composite oxide catalyst, using as raw materials the molybdenum and cobalt recovered by the above-described method. Other objects of the present invention are to provide a method for producing an unsaturated aldehyde and/or an unsaturated carboxylic acid by subjecting a compound selected from propylene, isobutylene and tert-butyl alcohol to a catalytic gas phase oxidation

with molecular oxygen in the presence of the composite oxide catalyst produced by the above-described method for producing the composite oxide catalyst.

5 [Means for solving the Problems]

[0006]

As a result of the present inventor's intensive studies for solving the foregoing problem, the followings are found out:

10 [0007]

That is, the present invention comprises the features as follows:

(1) A method for recovering molybdenum and cobalt, characterized in that a composite oxide containing molybdenum and cobalt is mixed with a ceramic compact and an aqueous extracting solution obtained by dissolving at least one of ammonia and an organic base in water, to thereby extract, from the composite oxide, molybdenum and cobalt into an aqueous phase.

20 (2) The recovering method according to the above item (1), wherein the amount of the ceramic compact is from 1 to 30 parts by mass, based on 100 parts by mass of the total amount of the composite oxide and the ceramic compact.

(3) The recovering method according to the above item
25 (1) or (2), wherein the ceramic compact is at least one

selected from the group consisting of a ceramic compact containing an oxide as a main component, a ceramic compact containing a carbide as a main component, and a ceramic compact containing a nitride as a main component.

5 (4) The recovering method according to the above item (3), wherein the oxide in the ceramic compact containing an oxide as a main component is at least one selected from the group consisting of silica, alumina, zirconia and mullite.

10 (5) The recovering method according to any one of the above item (1) to (4), wherein the composite oxide contains, together with molybdenum and cobalt, at least one selected from the group consisting of cesium, potassium and rubidium; and the at least one selected from the group consisting of cesium, potassium and rubidium is extracted
15 into the aqueous phase.

 (6) The recovering method according to any one of the above item (1) to (5), wherein the pH of the aqueous extracting solution is 8 or more.

20 (7) The recovering method according to any one of the above item (1) to (6), wherein a temperature for mixing the composite oxide with the ceramic compact and the aqueous extracting solution is from 0 to 100°C.

25 (8) The recovering method according to any one of the above item (1) to (7), wherein the organic base is at least one of an amine or a quaternary ammonium compound.

(9) A method for producing a composite oxide which contains molybdenum and cobalt, characterized in that the aqueous phase containing molybdenum and cobalt, which is obtained by the recovering method according to any one of the above items (1) to (8), is dried and is then calcined.

(10) A method for producing a composite oxide catalyst which contains molybdenum and cobalt, characterized in that molybdenum and cobalt contained in the aqueous phase, which was obtained by the recovering method according to any one of the above items (1) to (8), are used as raw materials for the catalyst so that an aqueous solution or aqueous slurry, containing the raw materials for the catalyst, is dried and is then calcined.

(11) A method for producing a composite oxide catalyst which contains molybdenum and cobalt, characterized in that molybdenum and cobalt contained in the aqueous phase, which was obtained by the recovering method according to any one of the above items (1) to (8), are used as raw materials for the catalyst so that an aqueous solution or aqueous slurry, containing the raw materials for the catalyst, is subjected to a first drying treatment and then to a first calcination treatment, followed by being mixed with an acid and water, subjected to a second drying treatment and then to a second calcination treatment.

(12) The method for producing a composite oxide

catalyst according to any one of the above item (10) or (11), wherein a catalyst for producing unsaturated aldehyde and unsaturated carboxylic acid is produced.

(13) A method for producing an unsaturated aldehyde and/or an unsaturated carboxylic acid, wherein a composite oxide catalyst is produced by the method according to any one of the above item (10) or (11), wherein a compound selected from propylene, isobutylene and tert-butyl alcohol is subjected to the catalytic gas phase oxidation with molecular oxygen in the presence of the composite oxide catalyst.

[Effect of the Invention]

[0008]

According to the present invention, it becomes possible to recover both of molybdenum and cobalt at once at a higher recovery rate, so that a composite oxide or a composite oxide catalyst, containing molybdenum and cobalt, can be produced at a lower cost by recycling such materials recovered by a simple method. In addition, an unsaturated aldehyde and/or an unsaturated carboxylic acid can be produced at a higher yield by subjecting a compound selected from propylene, isobutylene and tert-butyl alcohol to the catalytic gas phase oxidation with molecular oxygen in the presence of the obtained composite oxide catalyst.

[MODES FOR CARRYING OUT THE INVENTION]

[0009]

Hereinafter, the present invention will be described
5 in detail.

METHOD FOR RECOVERING MOLYBDENUM AND COBALT

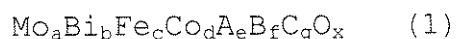
The method for recovering molybdenum and cobalt
according to the present invention, is intended to recover
10 molybdenum and cobalt from a composite oxide containing
molybdenum and cobalt.

[0010]

The composite oxide to be used in the recovering
method of the present invention is not limited, in so far
15 as the composite oxide contains molybdenum and cobalt. It
may be, for example, a composite oxide which contains
molybdenum and cobalt alone, or a composite oxide which
contains one or more other metal element as a constitutive
element, in addition to molybdenum and cobalt. As other
20 metal element, there are exemplified bismuth, iron, nickel,
manganese, zinc, calcium, magnesium, tin, lead, phosphorus,
boron, arsenic, tellurium, tungsten, antimony, silicon,
aluminum, titanium, zirconium, cerium, potassium, rubidium,
cesium, thallium, vanadium, copper, silver, lanthanum, etc.

25 [0011]

A preferable composition of the above-described composite oxide is represented by the following formula (1):



5 In the formula (1), Mo, Bi, Fe and Co represent molybdenum, bismuth, iron and cobalt, respectively; A represents at least one element selected from the group consisting of nickel, manganese, zinc, calcium, magnesium, tin and lead; B represents at least one element selected from the group
10 consisting of phosphorus, boron, arsenic, tellurium, tungsten, antimony, silicon, aluminum, titanium, zirconium and cerium; C represents at least one element selected from the group consisting of potassium, rubidium, cesium and thallium; and O represents oxygen, wherein the following
15 equations are satisfied when a is 12 ($a=12$): $0 < b \leq 10$, $0 < c \leq 10$, $1 \leq d \leq 10$, $0 \leq e \leq 10$, $0 \leq f \leq 10$ and $0 < g \leq 2$; and x is a value which is determined by the oxidized states of the respective elements. In the case where each of A, B and C contains two or more elements, the total amount of the two or more
20 elements may be within the range of $0 \leq e \leq 10$, $0 \leq f \leq 10$ and $0 < g \leq 2$, when a is 12.

[0012]

Among the composite oxides of the formula (1), the composite oxides of any of the following formulas (from
25 which oxygen atoms are excluded) are preferable:

$\text{Mo}_{12}\text{Bi}_{0.1-5}\text{Fe}_{0.5-5}\text{Co}_{5-10}\text{Cs}_{0.01-1}$; and

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

[0013]

The above-described composite oxide may be an unused
5 composite oxide or may be a composite oxide which already
has been used as a catalyst or the like, or may be a
composite oxide which has no required performance as a
catalyst although produced as a catalyst (The composite
oxide is, for example, a composite oxide which has powdered
10 during production thereof, or a composite oxide which has
degraded due to a thermal load or the like). However, a
composite oxide supported by a ceramic compact and a
Keggin-type heteropoly acid are excluded. The type of a
catalyst usable as the above-described composite oxide
15 includes, for example, a catalyst for production of an
unsaturated aldehyde and/or an unsaturated carboxylic acid,
a catalyst for production of an unsaturated carboxylic acid
and a catalyst for production of an unsaturated nitrile.
Among them, the catalyst for production of an unsaturated
20 aldehyde and an unsaturated carboxylic acid is preferable.

[0014]

In the method for recovering molybdenum and cobalt
according to the present invention, the above-described
composite oxides is mixed with a ceramic compact and an
25 aqueous extracting solution of at least one of ammonia and

an organic base (i.e., a basic component) in water.

By mixing the composite oxides with the ceramic compact and the aqueous extracting solution, molybdenum and cobalt are extracted from the composite oxide into the aqueous phase of the aqueous extracting solution at a high recovery rate (or a high extraction percentage).

[0015]

The ceramic compact includes, for example, a ceramic compact containing an oxide as a main component, a ceramic compact containing a carbide as a main component, and a ceramic compact containing a nitride as a main component, and two or more among the above may be used as necessary. Above all, the ceramic compact containing an oxide as a main component is preferable. The ratio of the oxide, carbide and nitride contained in the ceramic compact as a main component is preferably at least 60% by mass, more preferably at least 70% by mass, for example, at least 80% by mass, based on the ceramic compact. The oxide contained in the ceramic compact containing an oxide as a main component includes silica, alumina, zirconia, mullite and cordierite. Above all, silica and alumina are preferable. The ceramic compact containing an oxide as a main component may be the ceramic compact containing two or more oxides as a main component. Inter alia, the ceramic compact containing silica and alumina as a main component is

preferable. In the ceramic compact containing two or more oxides as a main component, the total amount of the two or more oxides in the ceramic compact may have the above range. The carbide in the ceramic compact containing a carbide as a main component includes silicon carbide and tungsten carbide. The ceramic compact containing a carbide as a main component may be the ceramic compact which contains silicon carbide and tungsten carbide as a main component. In the ceramic compact which contains silicon carbide and tungsten carbide as a main component, the total amount of silicon carbide and tungsten carbide in the ceramic compact may have the above range. The nitride contained in the ceramic compact containing a nitride as a main component includes silicon nitride and aluminum nitride. The ceramic compact containing a nitride as a main component may be the ceramic compact which contains silicon nitride and aluminum nitride as a main component. In the ceramic compact that contains silicon nitride and aluminum nitride as a main component, the total amount of silicon nitride and aluminum nitride in the ceramic compact may have the above range.

[0016]

The ceramic compact may be an unused one or may be a ceramic compact which already has been used as an inert filler together with the catalyst. The ceramic compact which already has been used as an inert filler together

with the catalyst means a ceramic compact which was used in a catalytic reaction as a filler inert to the catalytic reaction together with the composite oxide catalyst. In the case where the composite oxide is used as a catalyst and the ceramic compact is used as the inert filler in a catalytic reaction, the composite oxide and the ceramic compact after used may be subjected to the mixing treatment with the aqueous extracting solution without separating the composite oxide from the ceramic compact.

10 [0017]

The shape of the ceramic compact includes, for example, pellets, cylinders, spheres, rings, and granules obtained by being pulverized and classified after molded. When the ceramic compact is used, it is possible to contain a ceramic compact which has been pulverized, a ceramic compact which has been crushed and pulverized during the production process or the used process as the inert filler as well as an unshaped ceramics, in addition to the ceramic compact.

20 [0018]

The size of the ceramic compact is not particularly limited, but the compact preferably has a diameter from 1 to 20 mm. The diameter of the compact means a diameter of a sphere as to the spherical particle, a diameter of a circular cross-section as to the cylinder and a maximum

diameter of cross-section as to the other shapes. The ceramic compact preferably has a bulk density from 0.5 to 20 g/cm³, more preferably from 1.0 to 5 g/cm³.

[0019]

5 The amount of the ceramic compact when the composite oxide is mixed with the ceramic compact and the aqueous extracting solution is preferably from 1 to 30 parts by mass, based on 100 parts by mass of the total of the composite oxide and the ceramic compact. The ceramic
10 compact is dispersed as a solid phase in the mixed slurry containing the composite oxide, the ceramic compact and the aqueous extracting solution, wherein the ratio of the ceramic compact is preferably from 0.1 to 10% by mass, based on the mixed slurry containing the composite oxide,
15 the ceramic compact and the aqueous extracting solution.

[0020]

When the above-described basic component is ammonia, a compound which is decomposed to form ammonia (hereinafter, optionally referred to as "an ammonia-forming material")
20 may be dissolved in water, instead of ammonia. As the ammonia-forming material, there are exemplified ammonium carbonate, ammonium bicarbonate, urea, or the like. Any of these ammonia-forming materials may be used alone, or two or more selected therefrom may be used in combination.

25 [0021]

When the above-described basic component is an organic base, there are exemplified, as the organic base, amines including saturated aliphatic amines such as methylamine, dimethylamine, trimethylamine, ethylamine, diethylamine and triethylamine, unsaturated aliphatic amines such as allylamine, diallylamine and triallylamine, aromatic amine such as aniline; quaternary ammonium compounds including each of hydroxides or halides of those quaternary ammonium such as tetramethylammonium, tetraethylammonium, n-propyltrimethylammonium, tetra-n-propylammonium, tetra-n-butylammonium, 4,4'-trimethylenebis(dimethylpiperidinium), benzyltrimethylammonium, dibenzyltrimethylammonium, 1,1'-butylenebis(4-aza-1-azoniabicyclo[2,2,2]octane) and trimethyladamantyl ammonium; pyridine; pyrimidine; etc.

The use of at least one selected from the amines and the quaternary ammonium compounds among those organic bases are preferable. Any of these organic bases may be used alone, or two or more selected therefrom may be used in combination.

[0022]

The number of moles of the basic component to be dissolved in the aqueous extracting solution may be larger than the number of total moles of molybdenum and cobalt in the composite oxide to be mixed with the aqueous extracting solution. Specifically, a ratio of the number of moles of

the basic component to the number of the total moles of molybdenum and cobalt may be 1 or more, and preferably 2 or more.

The amount of the aqueous extracting solution can be
5 determined by considering e.g., the necessary amount of the basic component and a solubility of the basic component in water. The amount of the aqueous extracting solution may be from 50 to 5000 parts by mass, for example, 100 to 3000 parts by mass, particularly 200 to 2000 parts by mass,
10 based on 100 parts by mass of the composite oxide containing molybdenum and cobalt.

As the aqueous extracting solution, an aqueous ammonia solution is preferably used from the viewpoint of a lower cost.

15 [0023]

The pH of the aqueous extracting solution is preferably 8 or more. When the pH of the aqueous extracting solution is less than 8, the recovery rates of molybdenum and cobalt tend to be insufficient.

20 [0024]

The method for mixing the composite oxide with the ceramic compact and the aqueous extracting solution is not particularly limited, and may be appropriately selected, but the mixing treatment may be suitably performed by
25 immersing the composite oxide and the ceramic compact into

the aqueous extracting solution, followed by stirring with a stirrer. When the mixed slurry is prepared from the composite oxide, the ceramic compact and the aqueous extracting solution, the order for mixing the composite oxide, the ceramic compact and the aqueous extracting solution is not limited, and may be appropriately selected. Before the mixing, the composite oxide is preferably crushed or pulverized.

[0025]

The mixing may be performed batchwise or continuously. The temperature for mixing the composite oxide with the ceramic compact and the aqueous extracting solution is preferably from 0 to 100°C, more preferably from 10 to 80°C. The period of time for mixing may be appropriately selected in accordance with the mixing temperature, etc., and it is usually from one minute to 100 hours, preferably from 1 hour to 24 hours.

[0026]

In the method for recovering molybdenum and cobalt according to the present invention, as a result of mixing of the composite oxide with the ceramic compact and the aqueous extracting solution, there are obtained an aqueous phase containing the extracted molybdenum and cobalt (hereinafter optionally referred to as "a molybdenum-and-cobalt-containing aqueous solution") and a solid residue

derived from the composite oxide and the ceramic compact. The slurry containing the molybdenum-and-cobalt-containing aqueous solution and the residue, thus recovered, is separated by, for example, filtration treatment such as
5 decantation, natural filtration, vacuum filtration, pressure filtration, or centrifugal filtration, to thereby obtain only the molybdenum-and-cobalt-containing aqueous solution as the filtrate. When ammonia is used as the basic component, the ammonia may be separately recovered
10 and recycled.

[0027]

In the method for recovering molybdenum and cobalt according to the present invention, the molybdenum-and-cobalt-containing aqueous solution may be obtained as the
15 recovered material; or the molybdenum-and-cobalt-containing aqueous solution may be further dried and subjected to a heat treatment or the like to thereby obtain a solid material as the recovered material.

[0028]

20 The method for recovering molybdenum and cobalt according to the present invention, recovers particularly molybdenum and cobalt at a high recovery rate. When the composite oxide contains at least one element selected from the group consisting of cesium, potassium and rubidium
25 together with molybdenum and cobalt, the at least one

element selected from the group consisting of cesium, potassium and rubidium contained in the composite oxide can also be effectively extracted into the aqueous phase, and thus can be recovered at a good recovery rate. That is, when the composite oxide contains cesium, potassium and rubidium together with molybdenum and cobalt, the cesium, potassium or rubidium contained in the composite oxide can be effectively extracted into the aqueous phase and can be recovered at a good recovery rate. In addition, when the composite oxide contains at least two elements selected from the group consisting of cesium, potassium and rubidium together with molybdenum and cobalt, the at least two elements selected from the group consisting of cesium, potassium and rubidium contained in the composite oxide can also be effectively extracted into the aqueous phase, and thus can be recovered at a good recovery rate.

[0029]

Moreover, when the composite oxide contains tungsten together with molybdenum and cobalt, the tungsten contained in the composite oxide can also be effectively extracted into the aqueous phase and can be recovered at a good recovery rate.

[0030]

METHOD FOR PRODUCING COMPOSITE OXIDE CONTAINING MOLYBDENUM AND COBALT

In the method for producing a composite oxide which contains molybdenum and cobalt according to the present invention, the molybdenum-and-cobalt-containing aqueous solution obtained by the above-described recovering method of the present invention is dried and is then calcined to thereby obtain a composite oxide which contains at least molybdenum and cobalt.

[0031]

In the method for producing a composite oxide according to the present invention, the molybdenum-and-cobalt-containing aqueous solution obtained by the above-described recovering method of the present invention may be solely dried and calcined; or, a raw material compound for introducing a metal element other than molybdenum and cobalt may be added to the molybdenum-and-cobalt-containing aqueous solution at appropriate timing, i.e., before drying (in the state of the aqueous solution) or before calcination (in the state of the dried solid). When such a raw material compound is added to introduce a metal element other than molybdenum and cobalt, it becomes possible to control the composition rate of the resultant composite oxide to a desirable value. The composition of the composite oxide to be obtained by the composite oxide-producing method of the present invention may be the same as or different from that of the composite oxide used in

the above-described recovering method of the present invention.

[0032]

As the raw material compound for introducing a metal
5 element other than molybdenum and cobalt, there may be used
the compounds of other metal elements, described as the
constitutive elements of the composite oxides to be used in
the section of "Method for Recovering Molybdenum and
Cobalt", and examples of such compounds include oxides,
10 nitrates, sulfates, carbonates, hydroxides, oxo acids and
ammonium salts of the same acid, and halides.

In this regard, a raw material compound for
introducing molybdenum or cobalt may be added when the
metal element other than molybdenum and cobalt is
15 introduced, in order that the composition rate of the
resultant composite oxide may be controlled. As the raw
material compound for introducing molybdenum, there are
exemplified molybdenum compounds such as molybdenum
trioxide, molybdic acid and ammonium paramolybdate. As the
20 raw material compound for introducing cobalt, there are
exemplified cobalt compounds such as cobalt nitrate and
cobalt sulfate.

[0033]

In the method for producing the composite oxide
25 according to the present invention, the drying conditions

and the calcination conditions are not particularly limited, and thus may be appropriately selected according to known methods for producing the composite oxide or the composite oxide catalyst.

5 Generally, the drying may be performed at the temperature of 50 to 500°C, for example, 100 to 350°C, for 0.1 to 48 hours, for example, 0.5 to 24 hours. Generally, the calcination may be performed at the temperature of 100 to 650°C, for example, 250 to 550°C, for 0.2 to 24 hours,
10 for example, 0.5 to 12 hours.

[0034]

METHOD FOR PRODUCING COMPOSITE OXIDE CATALYST

 In a first embodiment of the method for producing a composite oxide catalyst according to the present invention,
15 the method comprising using molybdenum and cobalt contained in the aqueous phase (i.e., the molybdenum-and-cobalt-containing aqueous solution) obtained by the above-described recovering method of the present invention as a raw catalyst material, and drying and then calcining the
20 aqueous solution or aqueous slurry containing the raw catalyst material may be adopted. Thereby a composite oxide catalyst which contains at least molybdenum and cobalt can be obtained.

[0035]

25 In the first embodiment of the method for producing a

composite oxide catalyst according to the present invention, aqueous slurry or an aqueous solution may be prepared by adding other raw material compound for catalyst to the molybdenum-and-cobalt-containing aqueous solution obtained
5 by the recovering method of the present invention; or the molybdenum-and-cobalt-containing aqueous solution may be once dried to obtain a dried material, which may be then mixed with water and other raw material compound for catalyst, to prepare aqueous slurry or an aqueous solution
10 thereof.

[0036]

The other raw material compound for catalyst, to be used in the composite oxide catalyst-producing method of the present invention, may be the same one as any of the
15 raw material compounds described in the section of "Method for Producing Composite Oxide Containing Molybdenum and Cobalt". The amount of this raw material compound may be appropriately selected in accordance with the composition of a desired catalyst. Again, to control the composition
20 of the catalyst to be desirable, a molybdenum compound or a cobalt compound may be used as the raw material compound.

[0037]

In the first embodiment of the method for producing the composite oxide catalyst according to the present
25 invention, the conditions for preparing the aqueous slurry

or the aqueous solution and the conditions for calcining and baking the aqueous slurry or the aqueous solution are not particularly limited, and thus any known conditions may be appropriately adopted as the method for producing the composite oxide catalyst of the present invention according to the type (or use) of a desired catalyst. When an intended composite oxide catalyst is, for example, a catalyst for production of unsaturated aldehyde and unsaturated carboxylic acid, the procedure and conditions disclosed in, for example, JP-A-2007-117866, JP-A-2007-326787, JP-A-2008-6359 or JP-A-2008-231044 may be appropriately selected. When an intended composite oxide catalyst is a catalyst for production of unsaturated nitrile, the procedure and conditions disclosed in JP-B-48-43096, JP-B-59-16817 or the like may be appropriately selected.

[0038]

In a second embodiment of the method for producing a composite oxide catalyst according to the present invention, a method comprising mixing a composite oxide that contains at least molybdenum and cobalt, which composite oxide being obtained by using molybdenum and cobalt contained in the molybdenum-and-cobalt-containing aqueous solution mentioned above as a raw catalyst material, and drying and then calcining the aqueous solution or aqueous slurry containing

the raw catalyst material, with an acid and water to obtain an aqueous slurry, and drying and then calcining the aqueous slurry, may be adopted. That is, a composite oxide catalyst which contains at least molybdenum and cobalt is obtained by using molybdenum and cobalt contained in the molybdenum-and-cobalt-containing aqueous solution mentioned above as a raw catalyst material, subjecting the aqueous solution or aqueous slurry containing the raw catalyst material to a first drying treatment followed by a first calcination treatment, mixing the obtained calcined material with an acid and water, subjecting the mixture to a second drying treatment followed by a second calcination treatment.

[0039]

The acid to be used in the above includes inorganic acids such as nitric acid, sulfuric acid, hydrochloric acid, phosphoric acid and boric acid; and organic acids such as formic acid, acetic acid, propionic acid, butyric acid, valeric acid, hexanoic acid, benzoic acid, oxalic acid, malonic acid, succinic acid, adipic acid and phthalic acid. Particularly nitric acid is preferable. Any of these acids may be used alone, or two or more selected therefrom may be used in combination.

[0040]

The above acids may be used as it is, or as an aqueous

solution. The acid may be in such amount that the number of moles of the acid is higher than the number of moles of cobalt contained in the composite oxide. Specifically, the amount of the acid may be generally 1 to 20 moles, preferably from 2 to 10 moles, based on 1 mole of cobalt.

[0041]

In the second embodiment of the method for producing a composite oxide catalyst according to the present invention, the temperature for mixing the composite oxide with the acid and water to prepare an aqueous slurry is preferably from 0 to 100°C, more preferably from 10 to 80°C. The period of time for mixing may be appropriately selected in accordance with, for example, the mixing temperature, and it is usually from one minute to 100 hours, preferably from 1 hour to 24 hours.

[0042]

In the second embodiment of the method for producing a composite oxide catalyst according to the present invention, when the composite oxide is mixed with the acid and water to prepare the aqueous slurry, the mixing order and the mixing method are not limited, and each of the composite oxide, the acid and water may be mixed with each other in an arbitrary order. For example, to one of the acid and the aqueous dispersion in which the composite oxide has been previously dispersed in water, the other one may be

added; or to one of the composite oxide and the aqueous solution in which the acid has been previously dissolved in water, the other one may be added; or to one of the aqueous dispersion in which the composite oxide was previously dispersed in water and the aqueous solution in which the acid were previously dissolved in water, the other one may be added. Preferably, the composite oxide is preferably pulverized before it is mixed.

[0043]

10 In the second embodiment of the method for producing the composite oxide according to the present invention, the aqueous slurry alone obtained by mixing the composite oxide with the acid and water may be subjected to the second drying treatment, or a raw material compound for
15 introducing a metal element other than molybdenum and cobalt may be added to the aqueous slurry at appropriate timing, for example, before mixing, before the second drying treatment or before the second calcination treatment. The obtained composite oxide catalyst may be controlled so
20 that the resultant composite oxide has a desirable composition rate by adding the raw material compound for introducing a metal element other than molybdenum and cobalt.

[0044]

25 In the second embodiment of the method for producing

the composite oxide according to the present invention, as the raw material compound for introducing a metal element other than molybdenum and cobalt, the same one as any of the raw material compounds described in the section of
5 "Method for Producing Composite Oxide Containing Molybdenum and Cobalt" may be used. The amount of this raw material compound may be appropriately selected in accordance with the desirable composition of the catalyst. Again, to control the composition of the catalyst to be desirable, a
10 molybdenum compound or a cobalt compound may be used as a raw material compound as with the above-described method for producing the composite oxide.

[0045]

In the second embodiment of the method for producing
15 the composite oxide according to the present invention, the conditions during the preparation of the aqueous slurry or the aqueous solution, the drying conditions for the first and the second drying treatments, or the calcination conditions for the first and the second calcination
20 treatments are not particularly limited, and thus any known conditions may be appropriately adopted as the method for producing the catalyst according to the type (or use) of a desired catalyst. For example, when the intended composite oxide catalyst is, e.g., a catalyst for production of
25 unsaturated aldehyde and unsaturated carboxylic acid, the

procedure and conditions disclosed in, e.g., JP-A-2007-117866, JP-A-2007-326787, JP-A-2008-6359 and JP-A-2008-231044 may be appropriately selected. When an intended composite oxide catalyst is a catalyst for production of unsaturated nitrile, the procedure and conditions disclosed in, e.g., JP-B-48-43096 and JP-B-59-16817 may be appropriately selected.

[0046]

In the present invention, the drying treatment means a heat treatment for sufficiently decreasing a water content of the aqueous slurry or the aqueous solution, and the obtained dried material is preferably in a solid state. In the present invention, the calcination means an operation for heat-treating a dried material obtained after the drying treatment. The calcination may be performed under an atmosphere of an oxidizing gas such as oxygen or air, or under an atmosphere of a non-oxidizing gas such as nitrogen.

[0047]

In the method for producing a composite oxide catalyst according to the present invention, after the calcination in the first embodiment or after the second calcination in the second embodiment, a heat treatment is preferably performed in the presence of a reducing material (hereinafter, the heat treatment in the presence of a reducing material may be optionally simply referred to as

"reduction treatment"). Because of this reduction treatment, the catalytic activity of the resultant catalyst can be effectively improved. This effect is found to be remarkable especially in the production of the catalyst for
5 production of unsaturated aldehyde and unsaturated carboxylic acid.

[0048]

As the above-described reducing material, there are exemplified hydrogen, ammonia, carbon monoxide,
10 hydrocarbons, alcohols, aldehydes and amines as preferable ones. As to the hydrocarbons, the alcohols, the aldehydes and the amines, those having 1 to 6 carbon atoms are preferable, respectively. Examples of the C₁₋₆ hydrocarbons include saturated aliphatic hydrocarbons such as methane,
15 ethane, propane, n-butane and isobutane; unsaturated aliphatic hydrocarbons such as ethylene, propylene, .alpha.-butylene, .beta.-butylene and isobutylene; and benzene. Examples of the C₁₋₆ alcohols include saturated aliphatic alcohols such as methyl alcohol,
20 ethyl alcohol, n-propyl alcohol, isopropyl alcohol, n-butyl alcohol, isobutyl alcohol, secondary butyl alcohol and tertiary butyl alcohol; unsaturated aliphatic alcohols such as allyl alcohol, crotyl alcohol and methallyl alcohol; and phenols. Examples of the C₁₋₆ aldehydes include saturated
25 aliphatic aldehydes such as formaldehyde, acetaldehyde,

propionaldehyde, n-butyl aldehyde and isobutyl aldehyde; and unsaturated aliphatic aldehydes such as acrolein, crotonaldehyde and methacrolein. Examples of the C₁₋₆ amines include saturated aliphatic amines such as methylamine, dimethylamine, trimethylamine, ethylamine, diethylamine and triethylamine; unsaturated aliphatic amines such as allyamine and diallylamine; and aniline. Any of these reducing materials may be used alone, or two or more selected therefrom may be used in combination.

10 [0049]

The above-described reduction treatment is usually carried out by subjecting the catalyst to a heat treatment under an atmosphere of a gas which contains the above-described reducing material. The concentration of the reducing material in this gas is usually from 0.1 to 50% by vol., preferably from 3 to 30% by vol. The reducing material may be diluted with nitrogen, carbon dioxide, water, helium, argon or the like, to such a concentration. Although the molecular oxygen may be present within such a range that the effect of the reduction treatment is not impaired, no molecular oxygen is preferably allowed to be present,

[0050]

The temperature for the reduction treatment (i.e., a heat treatment temperature for the reduction treatment) is

25

preferably from 200 to 600°C, more preferably from 300 to 500°C. The period of time for the reduction treatment (i.e., a heat treatment time for the reduction treatment) is usually from 5 minutes to 20 hours, preferably from 30 minutes to 10 hours.

[0051]

Preferably, the above-described reduction treatment is carried out as follows: the calcined material (i.e., the composite oxide catalyst) obtained after the calcination is put in a container of tubular, box-type or the like, and is subjected to a heat treatment while a gas containing the reducing material is being allowed to flow into the container. During this treatment, the gas discharged from the container optionally may be recycled. For example, the catalyst may be packed in a reaction tube for catalytic gas phase oxidation, and a gas containing the reducing material may be allowed to pass through the tube for the reduction treatment, and the catalytic gas phase oxidation may be sequentially carried out.

[0052]

After the reduction treatment, the mass of the calcined material (i.e., the composite oxide catalyst) obtained after the calcination usually decreases. It is considered that this is because the catalyst would lose lattice oxygen. The rate of decrease in mass due to this

reduction treatment (or the heat treatment) is preferably from 0.05 to 6% by mass, more preferably from 0.1 to 5% by mass. When the reduction excessively proceeds with the result that the rate of decrease in mass becomes too high, the catalytic activity, on the contrary, tends to lower. In this case, the catalyst is again calcined under an atmosphere of a molecular oxygen-containing gas, to thereby lower the rate of decrease in mass. The rate of decrease in mass is determined by the following equation:

$$\text{Rate of Decrease in Mass (\%)} = \left[\frac{(\text{the mass of the catalyst determined before the reducing treatment}) - (\text{the mass of the catalyst determined after the reduction treatment})}{(\text{the mass of the catalyst determined before the reduction treatment})} \right] \times 100 \text{ (centupled)}$$

In this connection, depending on the type of the reducing material or the conditions for the heat treatment during the reduction treatment, the reducing material itself or a decomposed product derived from the reducing material is likely to remain in the catalyst after the reduction treatment. In such a case, the mass of such a remaining material in the catalyst is separately measured, and the measured mass value is subtracted from the mass of the catalyst containing the remaining material; and the mass of the catalyst after the reduction treatment may be calculated. Since the remaining material is typically

carbon, the mass of the remaining material can be determined, for example, by the measurement of total carbon (TC) or the like.

[0053]

5 After the above-described reduction treatment, the catalyst optionally may be again calcined under an atmosphere of a molecular oxygen-containing gas (this second calcination under the molecular oxygen-containing gas atmosphere is optionally referred to as "reoxidation").

10 [0054]

 The concentration of the molecular oxygen in the molecular oxygen-containing gas under which atmosphere the reoxidation is carried out is usually from 1 to 30% by vol., preferably from 10 to 25% by vol. As a molecular oxygen
15 source, an air or pure oxygen is usually used. This oxygen source is optionally diluted with nitrogen, carbon dioxide, water, helium, argon or the like, for use as the molecular oxygen-containing gas. The reoxidation temperature is usually from 200 to 600°C, preferably from 350 to 550°C.
20 The reoxidation time is from 5 minutes to 20 hours, preferably from 30 minutes to 10 hours.

[0055]

 In the composite oxide catalyst-producing method of the present invention, the catalyst is optionally subjected
25 to a molding process. The molding process may be carried

out according to a conventional method, for example, tablet compression or extrusion molding, to obtain a ring-shaped, pellet-like, spherical or granulated catalyst. The molding process may be carried out before the drying, the
5 calcination or the reduction treatment, or after the reduction treatment. Inorganic fibers or the like, which is substantially inactive to the intended reaction, may be added to the catalyst in the molding process, in order to improve the mechanical strength of the catalyst.

10 [0056]

The composite oxide catalyst-producing method of the present invention is intended to provide at least one composite oxide catalyst selected from the group consisting of a catalyst for production of unsaturated aldehyde and
15 unsaturated carboxylic acid, a catalyst for production of unsaturated carboxylic acid, and a catalyst for production of unsaturated nitrile. Above all, the composite oxide catalyst-producing method of the present invention is suitably employed to produce a catalyst for production of
20 unsaturated aldehyde and unsaturated carboxylic acid.

[0057]

As the catalyst for production of unsaturated aldehyde and unsaturated carboxylic acid, there is exemplified a catalyst for production of acrolein and acrylic acid by way
25 of catalytic gas phase oxidation of propylene with

molecular oxygen, or a catalyst for production of methacrolein and methacrylic acid by way of catalytic gas phase oxidation of isobutylene or tertiary butyl alcohol with molecular oxygen. As the catalyst for production of
5 unsaturated carboxylic acid, there is exemplified a catalyst for production of acrylic acid by way of oxidation of acrolein with molecular oxygen or a catalyst for production of methacrylic acid by way of oxidation of methacrolein with molecular oxygen. As the catalyst for
10 production of unsaturated nitrile, there is exemplified a catalyst for production of acrylonitrile by way of ammoxidation of propylene with molecular oxygen or a catalyst for production of methacrylonitrile by way of ammoxidation of isobutylene or tertiary butyl alcohol with
15 molecular oxygen.

[EXAMPLES]

[0058]

Hereinafter, the present invention will be more
20 specifically described by way of Examples thereof, which however should not be construed as limiting the scope of the present invention in any way. In Examples, the unit mL/min., which expresses the flow rate of the gas, is based on STP unless otherwise described. The activities of the
25 catalysts in the following Examples were evaluated by the

method set forth below.

[0059]

<Catalytic Activity Test>

A glass reaction tube with an inner diameter of 18 mm
 5 was charged with a catalyst (1 g), and a gas mixture of
 isobutylene/oxygen/nitrogen/steam (=1/2.2/6.2/2.0 in molar
 ratio) was fed into the reaction tube at a flow rate of
 87.5 mL/min, to carry out an oxidation reaction at 350°C
 for one hour. A gas from the outlet of the tube (i.e., a
 10 gas obtained after the reaction) was analyzed by gas
 chromatography, and a conversion of isobutylene, and a
 total selectivity for methacrolein and methacrylic acid
 were calculated according to the following formulae.

[0060]

15 A conversion (%) of isobutylene = [(the number of
 moles of fed isobutylene) - (the number of moles of
 unreacted isobutylene)] / (the number of moles of fed
 isobutylene) x 100

A total selectivity (%) for methacrolein and
 20 methacrylic acid = (the number of moles of methacrolein and
 methacrylic acid) / [(the number of moles of fed
 isobutylene) - (the number of moles of unreacted
 isobutylene)] x 100

A total yield (%) for methacrolein and methacrylic
 25 acid = (the number of moles of methacrolein and methacrylic

acid) / (the number of moles of fed isobutylene) x 100

[0061]

Reference Example 1 (Preparation of fresh catalyst (a1))

5 Ammonium molybdate $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}]$ (441.4 parts by mass) was dissolved in hot water (500 parts by mass) to obtain a liquid A. On the other hand, iron nitrate (III) $[\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}]$ (202.0 parts by mass), cobalt nitrate $[\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ (436.6 parts by mass) and cesium nitrate
10 $[\text{CsNO}_3]$ (19.5 parts by mass) were dissolved in hot water (200 parts by mass), and then, bismuth nitrate $[\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}]$ (97.0 parts by mass) was dissolved in the resulting liquid to obtain a liquid B.

[0062]

15 Next, the liquid A was stirred, and the liquid B was added to the liquid A to obtain a slurry. Then, this slurry was dried at 250°C with a flash drier, to obtain a catalyst precursor. To this catalyst precursor (100 parts by mass) were added silica alumina fibers (RFC400-SL
20 manufactured by ITM ASSOCIATES) (18 parts by mass) and antimony trioxide $[\text{Sb}_2\text{O}_3]$ (2.54 parts by mass); and the resulting mixture was molded into a ring-shaped material with an outer diameter of 6.3 mm, an inner diameter of 2.5 mm and a length of 6 mm. This molded material (compact)
25 was calcined at 545°C for 6 hours under a stream of an air,

to obtain a fresh composite oxide catalyst (a1).

[0063]

This fresh catalyst (a1) was found to contain bismuth (0.96 atom), antimony (0.48 atom), iron (2.4 atoms), cobalt
5 (7.2 atoms), cesium (0.48 atom), silicon (4.6 atoms) and aluminum (5.0 atoms) per molybdenum (12 atoms).

[0064]

Reference Example 2 (Preparation of used catalyst (b) and used ceramic compact)

10 A reaction tube was charged with a ceramic compact having a spherical shape (11 parts by mass) (ceramic balls (Z-10) manufactured by Iwao Jiki Kogyo Co. Ltd., the total content of silica and alumina: 90% by mass, diameter: 6.4 mm) as an inert filler, and further charged with a fresh
15 catalyst (a2) (100 parts by mass) which was prepared according to the similar process as Reference Example 1. To the reaction tube, a gas mixture of isobutylene/oxygen/nitrogen/steam was continuously fed for a given period of time, and the catalytic gas phase
20 oxidation reaction to methacrolein and methacrylic acid was performed, to obtain a used catalyst (b) and a used ceramic compact.

[0065]

Reference Example 3 (Preparation of used catalyst (c))

25 A reaction tube was charged with a fresh catalyst (a1)

and a gas mixture of isobutylene/oxygen/nitrogen/steam was continuously fed for a given period of time, thereby the catalytic gas phase oxidation reaction to methacrolein and methacrylic acid was performed, to obtain a used catalyst (c).

[0066]

Example 1

(Recovery of Molybdenum and Cobalt)

The fresh catalyst (a1) (100 parts by mass) (which contained 34.6% by mass of molybdenum, 4.0% by mass of iron, 12.8% by mass of cobalt and 1.9% by mass of cesium, and which was obtained in Reference Example 1) was pulverized, and was then mixed into a ceramic compact having a spherical shape (10 parts by mass) (ceramic balls (Z-10) manufactured by Iwao Jiki Kogyo Co. Ltd., the total content of silica and alumina: 90% by mass, diameter: 6.4 mm), water (200 parts by mass) and a 25% by mass aqueous ammonia solution (272 parts by mass). This mixture was stirred for 1 hour while the liquid temperature of the mixture was kept at 40°C, and was then filtered under reduced pressure. The resulting filtrate was subjected to a heat treatment at 420°C in an air for 2 hours, to obtain a solid material (d) (64.0 g) as a recovered material.

A part of the resultant solid material (d) was subjected to an elemental analysis with an X-ray

fluorescence spectrometer (ZSX Primus II manufactured by Rigaku Corporation). As a result, it was found to contain 48.5% by mass of molybdenum, 0.0% by mass of iron, 18.8% by mass of cobalt and 2.9% by mass of cesium. Therefore, the recovery rates of the respective elements from the fresh catalyst (a1) were 89.7% in molybdenum, 0.0% in iron, 94.0% in cobalt and 97.7% in cesium.

The recovery rate (%) of each element was calculated by the equation:

$$(x1 / y1) \times 100$$

wherein x1 represents the mass (g) of the element in the resultant solid material (d); and y1 represents the mass (g) of the element in the fresh catalyst (a1).

[0067]

Comparative Example 1

(Recovery of Molybdenum and Cobalt)

The fresh catalyst (a1) (100 parts by mass) (which contained 34.6% by mass of molybdenum, 4.0% by mass of iron, 12.8% by mass of cobalt and 1.9% by mass of cesium), which was obtained in Reference Example 1, was pulverized, and was then mixed into water (200 parts by mass) and a 25% by mass aqueous ammonia solution (272 parts by mass). This mixture was stirred for 1 hour while the liquid temperature of the mixture was kept at 40°C, and was then filtered

under reduced pressure. The resulting filtrate was subjected to a heat treatment at 420°C in an air for 2 hours, to obtain a solid material (e) (60.8 g) as a recovered material.

5 A part of the solid material (e) was subjected to an elemental analysis with an X-ray fluorescence spectrometer (ZSX Primus II manufactured by Rigaku Corporation). As a result, it was found to contain 48.7% by mass of molybdenum, 0.6% by mass of iron, 19.1% by mass of cobalt and 3.0% by
10 mass of cesium. Therefore, the recovery rates of the respective elements from the fresh catalyst (a1) were 85.6% in molybdenum, 9.3% in iron, 90.7% in cobalt and 96.0% in cesium.

The recovery rate (%) of each element was calculated
15 by the equation:

$$(x2 / y1) \times 100$$

wherein x2 represents the mass (g) of the element in the resultant solid material (e); and y1 represents the mass (g) of the element in the fresh catalyst (a1).

20 [0068]

Example 2

(Recovery of Molybdenum and Cobalt)

A mixture of the used catalyst (b) (100 parts by mass) (which contained 39.6% by mass of molybdenum, 4.6% by mass
25 of iron, 14.5% by mass of cobalt and 2.3% by mass of

cesium) and the used ceramic compact (11 parts by mass), which was obtained in Reference Example 2, was mixed into water (200 parts by mass) and a 25% by mass aqueous ammonia solution (272 parts by mass). This mixture was stirred for 4 hours while the liquid temperature of the mixture was kept at 40°C, and was then filtered under reduced pressure. The resulting filtrate was subjected to a heat treatment at 420°C in an air for 2 hours, to obtain 69.9 parts by mass of a solid material (f) as a recovered material.

A part of the resultant solid material (f) was subjected to an elemental analysis with an X-ray fluorescence spectrometer (ZSX Primus II manufactured by Rigaku Corporation). As a result, it was found to contain 48.5% by mass of molybdenum, 0.01% by mass of iron, 18.7% by mass of cobalt and 3.0% by mass of cesium. Therefore, the recovery rates of the respective elements from the used catalyst (b) were 85.6% in molybdenum, 0.2% in iron, 90.1% in cobalt and 91.2% in cesium. The recovery rate (%) of each element was calculated by the equation:

$$(x3 / y2) \times 100$$

wherein x3 represents the mass (g) of the element in the resultant solid material (f); and y2 represents the mass (g) of the element in the used catalyst (b).

[0069]

(Evaluation of Recovered Molybdenum and Cobalt)

The solid material (f) thus obtained was used for preparation of a composite oxide catalyst containing molybdenum and cobalt, and the catalytic activity of the catalyst was evaluated.

5 Thus obtained solid material (f) (30 parts by mass) was pulverized, and was then mixed into water (25 parts by mass) and a 60% by mass nitric acid (32 parts by mass). This aqueous slurry was stirred for 1 hour while the liquid temperature of the slurry was kept at 50°C, cesium nitrate
10 [CsNO₃] (0.27 parts by mass), iron (III) nitrate [Fe(NO₃)₃·9H₂O] (16.19 parts by mass), cobalt nitrate [Co(NO₃)₂·6H₂O] (6.40 parts by mass) and bismuth nitrate [Bi(NO₃)₂·5H₂O] (7.78 parts by mass) were added to the aqueous slurry with continuation of stirring, to obtain a liquid C.

15 [0070]

On the other hand, ammonium molybdate [(NH₄)₆Mo₇O₂₄·4H₂O] (8.88 parts by mass) was dissolved in a mixture liquid containing a 25% by mass aqueous ammonia solution (8.76 parts by mass) and water (100 parts by mass) to
20 obtain a liquid D.

[0071]

Next, the liquid D was stirred, and the liquid C was added to the liquid D to obtain an aqueous slurry. Then, this aqueous slurry was transferred into a stainless steel
25 container and was dried at 250°C with a box-type drier, to

obtain a catalyst precursor. Thus obtained catalyst precursor was made into tablets under a pressure of about 40 MPa; and the resulting tablets were pulverized and were then allowed to pass through a sieve having a sieve opening of from 2 mm to 710 μ m to obtain granules with a grain size of from 2 mm to 710 μ m. This granulated catalyst precursor was calcined at 525°C for 6 hours under a stream of an air, to obtain a composite oxide catalyst (g). This composite oxide catalyst (g) was found to contain bismuth (0.96 atoms), iron (2.5 atoms), cobalt (7.2 atoms) and cesium (0.49 atom) per molybdenum (12 atoms).

[0072]

The catalytic activity of this composite oxide catalyst (g) was evaluated according to the above-described catalytic activity test. As a result, the conversion of isobutylene was 79.7%, the total selectivity for methacrolein and methacrylic acid was 78.7%, and the total yield for methacrolein and methacrylic acid was 62.7%.

[0073]

A glass reaction tube was charged with thus obtained composite oxide catalyst (g) (10.00 g) and a gas mixture of hydrogen/steam/nitrogen was fed at a flow rate of 200 mL/min. (based on STP) to the reaction tube, thereby the reduction treatment was carried out at 375 °C for 8 hours. The rate of decrease in mass due to this reduction

treatment was 0.86%. Thereafter, the resultant was reoxidized by heating under a stream of an air at 350 °C for 1 hour, to obtain a composite oxide catalyst (h).

[0074]

5 The catalytic activity of the composite oxide catalyst (h) was evaluated according to the above-described catalytic activity test. As a result, the conversion of isobutylene was 80.8%, the total selectivity for methacrolein and methacrylic acid was 77.9%, and the total
10 yield for methacrolein and methacrylic acid was 62.9%.

[0075]

Comparative Example 2

A recovering experiment was conducted as follows, using the fresh composite oxide catalyst (a1) obtained in
15 Reference Example 1, under the same conditions as those for Example 1 of Patent Publication 2 (WO Publication No. 2007/032228). That is, the composite oxide catalyst (a1) (300 parts by mass) was dispersed in pure water (1,200 parts by mass), and a 45% by mass aqueous sodium hydroxide
20 solution (400 parts by mass) was added to this dispersion. The resulting aqueous solution containing the catalyst component was stirred at 60°C for 3 hours, and then, insoluble materials were removed by filtration, to obtain an aqueous solution containing catalyst component. To this
25 aqueous solution was added a 36% by mass hydrochloric acid

to adjust the pH of the solution to 1.0. After that, the solution was maintained at 30°C for 3 hours while being stirred. A precipitate thus formed was separated by filtration and was rinsed with a 2% by mass aqueous ammonium nitrate solution to obtain a precipitate (53.2 parts by mass) containing catalyst component (1).

A part of the precipitate containing catalyst component (1) was subjected to an elemental analysis with an X-ray fluorescence spectrometer (ZSX Primus II manufactured by Rigaku Corporation). As a result, it was found to contain 60.1% by mass of molybdenum, 0.7% by mass of cobalt and 6.3% by mass of cesium. Therefore, the recovery rates of the respective elements from the fresh catalyst (a1) were 30.8% in molybdenum, 1.0% in cobalt and 57.8% in cesium.

The recovery rate (%) of each element was calculated by the equation:

$$(x4 / y1) \times 100$$

wherein x4 represents the mass (g) of the element in the precipitate containing catalyst component (1); and y1 represents the mass (g) of the element in the fresh catalyst (a1).

[0076]

The obtained precipitate containing catalyst component (1) (30 parts by mass) was pulverized, and was then mixed

into water (25.0 parts by mass) and a 60% by mass nitric acid (3.35 parts by mass). This aqueous slurry was stirred for 1 hour while the liquid temperature of the slurry was kept at 50°C and to which, cesium nitrate $[\text{CsNO}_3]$ (0.18 parts by mass), iron nitrate $[\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}]$ (30.37 parts by mass) and cobalt nitrate $[\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ (64.59 parts by mass) were added and dissolved and then bismuth nitrate $[\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}]$ (14.59 parts by mass) was added and dissolved, to obtain a liquid E.

On the other hand, ammonium molybdate $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}]$ (33.18 parts by mass) was dissolved in a mixture liquid containing a 25% by mass aqueous ammonia solution (10.97 parts by mass) and water (100 parts by mass) to obtain a liquid F.

[0077]

Next, the liquid F was stirred, and the liquid E was added to the liquid F to obtain an aqueous slurry. Then, this aqueous slurry was transferred into a stainless steel container and was dried at 250°C with a box-type drier, to obtain a catalyst precursor. Thus obtained catalyst precursor was made into tablets under a pressure of about 40 MPa; and the resulting tablets were pulverized and were then allowed to pass through a sieve having a sieve opening of from 2 mm to 710 μm to obtain granules with a grain size of from 2 mm to 710 μm . This granulated catalyst precursor

was calcined at 525°C for 6 hours under a stream of an air,
to obtain a composite oxide catalyst (i). This composite
oxide catalyst (i) was found to contain bismuth (0.96 atom),
iron (2.5 atoms), cobalt (7.2 atoms) and cesium (0.49 atom)
5 per molybdenum (12 atoms).

[0078]

The catalytic activity of this composite oxide
catalyst (i) was evaluated according to the above-described
catalytic activity test. As a result, the conversion of
10 isobutylene was 71.8%, the total selectivity for
methacrolein and methacrylic acid was 83.9%, and the total
yield for methacrolein and methacrylic acid was 60.2%.

[0079]

Comparative Example 3

15 (Recovery of Molybdenum and Cobalt)

The used catalyst (c) (100 parts by mass) (which
contained 34.6% by mass of molybdenum, 4.0% by mass of iron,
12.8% by mass of cobalt and 1.9% by mass of cesium), which
was obtained in Reference Example 3, was mixed into water
20 (200 parts by mass) and a 25% by mass aqueous ammonia
solution (272 parts by mass). This mixture was stirred for
4 hours while the liquid temperature of the mixture was
kept at 40°C, and was then filtered under reduced pressure.
The resulting filtrate was subjected to a heat treatment at
25 420°C in an air for 2 hours, to obtain 58.1 parts by mass

of a solid material (j) as a recovered material.

A part of the solid material (j) was subjected to an elemental analysis with an X-ray fluorescence spectrometer (ZSX Primus II manufactured by Rigaku Corporation). As a
5 result, it was found to contain 47.1% by mass of molybdenum, 0.3% by mass of iron, 19.8% by mass of cobalt and 3.2% by mass of cesium. Therefore, the recovery rates of the respective elements from the used catalyst (c) were 79.1% in molybdenum, 4.4% in iron, 89.9% in cobalt and 97.9% in
10 cesium.

The recovery rate (%) of each element was calculated by the equation:

$$(x_5 / y_3) \times 100$$

wherein x_5 represents the mass (g) of the element in the
15 resultant solid material (j); and y_3 represents the mass (g) of the element in the used catalyst (c).

CLAIMS

1. A method for recovering molybdenum and cobalt, characterized in that a composite oxide containing
5 molybdenum and cobalt is mixed with a ceramic compact and an aqueous extracting solution obtained by dissolving at least one of ammonia and an organic base in water, to thereby extract, from the composite oxide, molybdenum and cobalt into an aqueous phase.

10

2. The recovering method according to claim 1, wherein the amount of the ceramic compact is from 1 to 30 parts by mass, based on 100 parts by mass of the total amount of the composite oxide and the ceramic compact.

15

3. The recovering method according to claim 1 or 2, wherein the ceramic compact is at least one selected from the group consisting of a ceramic compact containing an oxide as a main component, a ceramic compact containing a carbide as a main component, and a ceramic compact
20 containing a nitride as a main component.

4. The recovering method according to any one of claims 1 to 3, wherein the oxide in the ceramic compact
25 containing the oxide as a main component is at least one

selected from the group consisting of silica, alumina, zirconia and mullite.

5 5. The recovering method according to any one of
claims 1 to 4, wherein the composite oxide contains,
together with molybdenum and cobalt, at least one element
selected from the group consisting of cesium, potassium and
rubidium; and the at least one element selected from the
group consisting of cesium, potassium and rubidium is also
10 extracted into the aqueous phase.

6. The recovering method according to any one of
claims 1 to 5, wherein the pH of the aqueous extracting
solution is 8 or more.

15

7. The recovering method according to any one of
claims 1 to 6, wherein a temperature for mixing the
composite oxide with the ceramic compact and the aqueous
extracting solution is from 0 to 100 °C

20

8. The recovering method according to any one of
claims 1 to 7, wherein the organic base is at least one of
an amine or a quaternary ammonium compound.

25

9. A method for producing a composite oxide which

contains molybdenum and cobalt, characterized in that the aqueous phase containing molybdenum and cobalt, which is obtained by the recovering method according to any one of claims 1 to 8, is dried and is then calcined.

5

10. A method for producing a composite oxide catalyst which contains molybdenum and cobalt, characterized in that molybdenum and cobalt contained in the aqueous phase which was obtained by the recovering method according to any one of claims 1 to 8, are used as raw materials for the catalyst so that an aqueous solution or aqueous slurry, containing the raw materials for the catalyst, is dried and is then calcined.

15 11. A method for producing a composite oxide catalyst which contains molybdenum and cobalt, characterized in that molybdenum and cobalt contained in the aqueous phase which was obtained by the recovering method according to any one of claims 1 to 8, are used as raw materials for the catalyst so that an aqueous solution or aqueous slurry, containing the raw materials for the catalyst, is subjected to a first drying treatment and then to a first calcination treatment, followed by being mixed with an acid and water, subjected to a second drying treatment and then to a second
25 calcination treatment.

12. The method for producing a composite oxide catalyst according to claim 10 or 11, wherein a catalyst for producing an unsaturated aldehyde and/or an unsaturated
5 carboxylic acid is produced.

13. A method for producing an unsaturated aldehyde and/or an unsaturated carboxylic acid, wherein a composite oxide catalyst is produced by the method according to claim
10 10 or 11, and wherein at least one compound selected from the group consisting of propylene, isobutylene and tert-butyl alcohol is subjected to a catalytic gas phase oxidation with molecular oxygen in the presence of the composite oxide catalyst.

15