according to the following formulae (4) to (5).

(4) Acrolein yield (mol%) = 100 × (molar number of produced acrolein)/(molar number of fed propylene)

(5) Acrylic acid yield (mol%) = 100 × (molar number of produced acrylic acid)/(molar number of fed propylene)

In addition, the methacrolein conversion and the methacrylic acid yield are defined according to the following formulae (6) to (7).

(6) Methacrolein conversion (mol%) = 100 × [(molar number of fed methacrolein) – (molar number of unreacted methacrolein)]/(molar number of fed methacrolein)

(7) Methacrylic acid yield (mol%) = 100 × (molar number of produced methacrylic acid)/(molar number of fed methacrolein)

[0039]

EXAMPLE 1

In a mixing tank (A) equipped with an agitation motor, 600 parts of pure water at 95°C and 16.26 parts of ammonium tungstate were added and agitated. Subsequently, 18.22 parts of ammonium metavanadate and 110 parts of ammonium molybdate were dissolved therein. Subsequently, 3.88 parts of antimony trioxide was added. In a mixing tank (B) charged with 96 parts of deionized water, 15.56 parts of copper sulfate was dissolved, and the resulting solution was added in the mixing tank (A) to obtain a slurry solution. The thus obtained slurry solution was dried by adjusting a liquid sending amount such that an outlet temperature of a spray dryer was about 100°C. The thus obtained granule was subjected to preliminary calcination under air circulation at 390°C for 5 hours.

[0040]

Subsequently, the preliminarily calcined granule was pulverized by a ball mill, to obtain a powder (hereinafter referred to as “preliminarily calcined powder”). 300 parts of an alundum carrier having a diameter of 4.5 mm was charged into a rolling granulator having a diameter of a bottom plate of 23 cm, and the bottom plate was rotated at 100 rpm, thereby regulating a centrifugal acceleration to 1.3 G. The above-obtained preliminarily calcined powder was supported at a supporting rate of 30% by weight while sprinkling 50 parts of a 20% by weight glycerin aqueous solution thereover. The resulting shaped article was calcined under air circulation at 390°C for 5 hours, thereby obtaining a catalyst A1. An active component ratio of the catalyst A1 was $Mo_{12}V_3W_{1.2}Cu_{1.2}Sb_{0.5}$ when the ratio of molybdenum was defined as 12.

Table 1

Catalyst name	Relative centrifugal acceleration (G)	Attrition resistance (%)	Acrolein yield (mol%)	Acrylic acid yield (mol%)
A1	1.3	0.46	0.65	87.5
A2	4.2	0.52	0.51	87.2
A3	14	0.97	0.45	87.2
A4	21	1.95	0.49	87.2
B1	0.32	4.31	Not carried out	Not carried out
B2	31	Not carried out	Not carried out	Not carried out

[0051]

EXAMPLE 5

To 5,680 ml of pure water, 800 parts of molybdenum trioxide, 30.33 parts of vanadium pentoxide, and 76.87 parts of an 85% by mass orthophosphoric acid were added, and the contents were heated and agitated at 92°C for 3 hours to obtain a reddish brown transparent solution. Subsequently, this solution was cooled to 0 to 20°C, to which was then gradually added 661.32 parts of a 9.1% by mass cesium hydroxide aqueous solution, and the contents were aged at 15 to 20°C for 1 hour to obtain a yellow slurry solution. Subsequently, 196.86 parts of a 50.0% by mass ammonium acetate aqueous solution was gradually added to the slurry, and the resultant was further aged at 0 to 30°C for 1 hour. Subsequently, 22.18 parts of cupric acetate was further added to the resulting slurry, and the contents were agitated and mixed until the cupric acetate was completely dissolved. Subsequently, this slurry was spray dried to obtain a catalytic active component solid. A formulation of the catalytic active component solid as determined from the charged amounts of the raw materials is $Mo_{10}V_{0.6}P_{1.1}Cs_{0.7}(NH_4)_{2.3}Cu_{0.3}$.

[0052]

The resulting active component granule was calcined at 300°C over 6 hours to obtain a preliminarily calcined powder.

200 parts of a spherical porous alumina carrier having a diameter of 4.5 mm and having a cumulative specific surface area of 1.1 m^2/g, and a cumulative pore volume of 0.21 m^2/g, measured by a mercury porosimeter was charged into a rolling granulator having a diameter of a bottom plate of 23 cm. By rotating the bottom plate at 75 rpm, the centrifugal acceleration was

A catalyst A11 was prepared in the same method as in Example 10, except that in Example 10, the revolution rate of the bottom plate of the rolling granulator was set to 260 rpm, thereby regulating the centrifugal acceleration to 8.7 G, and the same evaluations as in Example 10 were carried out. The oxidation reaction results and the strength measurement results of the catalyst A11 are shown in Table 2.

[0064]

Table 2

Catalyst name	Relative centrifugal acceleration (G)	Attrition resistance (%)	Methacrolein conversion (mol%)	Methacrylic acid yield (mol%)
A5	0.72	0.69	92.1	76.0
A6	3.3	0.55	94.5	75.2
A7	5.1	0.58	94.6	76.2
A8	10	0.67	94.0	74.8
A9	21	0.31	93.3	76.2
A10	1.3	0.27	83.1	66.8
A11	8.7	0.34	83.7	67.1
B3	0.32	2.21	89.9	76.1
B4	31	Not carried out	Not carried out	Not carried out

[0065]

While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

It is to be noted that the present application is based on a Japanese patent application filed on October 10, 2013 (Japanese Patent Application No. 2013-212622), and the contents are incorporated herein by reference. In addition, all the references cited herein are incorporated as a whole.

Industrial Applicability

[0066]

The present invention is useful in industrial plants of producing unsaturated carboxylic

CLAIMS

[Claim 1]
A method for producing acrylic acid, comprising:
partially oxidizing acrolein in the presence of molecular oxygen and using a supported catalyst obtained by feeding a liquid binder component and a catalytic active component containing molybdenum and vanadium and/or a precursor thereof into a rolling granulator and conducting granulation at a relative centrifugal acceleration of 0.5 G to 30 G, said obtained catalyst having a formulation of a composite metal oxide represented by the following formula (1):

$$(Mo)_{12}(V)_a(W)_b(Cu)_c(Sb)_d(X)_e(Y)_f(Z)_g(O)_h \qquad (1)$$

wherein Mo, V, W, Cu, Sb and 0 represent molybdenum, vanadium, tungsten, copper, antimony and oxygen, respectively;
X represents at least one element selected from the group consisting of an alkali metal and thallium;
Y represents at least one element selected from the group consisting of magnesium, calcium, strontium, barium and zinc;
Z represents at least one element selected from the group consisting of niobium, cerium, tin, chromium, manganese, iron, cobalt, samarium, germanium, titanium and arsenic; and a, b, c, d, e, f, g, and h represent atomic ratios of the respective elements, in which a is ($0<a\leq10$), b is ($0\leq b\leq10$), c is ($0<c\leq6$), d is ($0\leq d\leq10$), e is ($0\leq e\leq0.5$), f is ($0\leq f\leq l$) and g is ($0\leq g<6$) relative to 12 of the molybdenum atom, and h is a number of oxygen atoms necessary for satisfying valences of the above-described respective components.

[Claim 2]
A supported catalyst, which is obtained by feeding a liquid binder component and a catalytic active component containing molybdenum and vanadium and/or a precursor thereof into a rolling granulator and conducting granulation at a relative centrifugal acceleration of 0.5 G to 30 G.

[Claim 3]
The supported catalyst according to claim 2,
wherein the catalytic active component and/or the precursor thereof contains molybdenum, vanadium and copper.

[Claim 4]
The supported catalyst according to claim 2,
wherein the catalytic active component and/or the precursor thereof contains molybdenum, vanadium and phosphorus.

[Claim 5]
A method for producing methacrylic acid comprising:
partially oxidizing methacrolein in the presence of molecular oxygen and using a supported catalyst obtained by feeding a liquid binder component and a catalytic active component containing molybdenum and vanadium and/or a precursor thereof into a rolling granulator and conducting granulation at a relative centrifugal acceleration of 0.5 G to 30 G, said obtained catalyst having a formulation of a composite metal oxide represented by the following formula (3):

$$(Mo)_{10}V_aP_b(NH_4)_c(X)_d(Y)_e(Z)_g(O)_f \qquad (3)$$

wherein Mo represents molybdenum; V represents vanadium;
P represents phosphorus; (NH_4) represents an ammonium group;
X represents at least one element selected from the group consisting of K, Rb and Cs; Y represents at least one element selected from the group consisting of Sb, As, Cu, Ag, Mg, Zn, AI, B, Ge, Sn, Pb, Ti, Zr, Cr, Re, Bi, W, Fe, Co, Ni, Ce and Th;
and a to e represent atomic ratios of the respective elements, in which a is ($0.1\leq a\leq6.0$), b is ($0.5\leq b\leq6.0$), c is ($0\leq c\leq10.0$), d is ($0\leq d\leq3.0$), e is ($0\leq e\leq3$), and f is a numerical value determined by oxidized states of the respective elements other than O and atomic ratios thereof.

[Claim 6]
The method of claim 5, wherein a is ($0.3 \leq a \leq 2.0$), b is ($0.7 \leq b \leq 2.0$), c is ($0 \leq c \leq 5$), d is ($0 \leq d \leq 1.5$), and e is ($0.01 \leq e \leq 0.5$).