

DESCRIPTION

Title of Invention:

CATALYST FOR PRODUCING UNSATURATED CARBOXYLIC ACID, METHOD FOR PRODUCING UNSATURATED CARBOXYLIC ACID, AND METHOD FOR PRODUCING UNSATURATED CARBOXYLIC ESTER

Technical Field

[0001]

The present invention relates to a catalyst for producing an unsaturated carboxylic acid, a method for producing an unsaturated carboxylic acid, and a method for producing an unsaturated carboxylic acid ester.

Background Art

[0002]

A catalyst carrying a component having oxidative ability and a component having an acid property is used for various reactions. For example, Patent Literature 1 proposes a method of mixing an oxide carrying platinum and a solid acid particle as a method for producing a solid acid catalyst useful for a conversion reaction of hydrocarbon, etc. Patent Literature 2 discloses a catalyst carrying zeolite and metal oxides of gold and iron on a ceramic fibre as a deodorizing catalyst. Patent Literature 3 discloses a catalyst carrying platinum and iridium on a carrier comprising acid type zeolite and zirconium oxide as a catalyst for oxidative removal of methane in a flue gas.

Citation List

Patent Literature

[0003]

Patent Literature 1: JP2000-102729A

Patent Literature 2: JP05-131138A

Patent Literature 3: JP2009-56455A

Summary of Invention

Technical Problem

[0004]

The catalysts described in Patent Literatures 1 to 3 are used for isomerization or oxidative degradation. An object of the present invention is to provide a new catalyst which is used for obtaining an unsaturated carboxylic acid from an unsaturated aldehyde, a method for producing an unsaturated carboxylic acid using the catalyst, and a method for producing an unsaturated carboxylic acid ester.

Solution to Problem

[0005]

The present invention relates to the following [1] to [18] and [1'] to [8']:

[1] A catalyst for producing an unsaturated carboxylic acid, wherein the catalyst is used for obtaining an unsaturated carboxylic acid from an unsaturated aldehyde, and comprises Component A represented by Formula (I) and Component B that is a compound containing an inorganic acid or an organic acid,



wherein in the Formula (I), M is at least one element selected from metal elements in the 4th period of the periodic table, M' is at least one element selected from metal elements other than the metal elements in the 4th period of the periodic table, O is oxygen, x, x' and y represent atomic ratios of the respective components, x is an integer of 1 or more, x' satisfies $0 < x' \leq 0.4$ for $x = 1$, and y is 0 or an atomic ratio of oxygen required for satisfying the atom ratios of the respective components.

[0006]

[2] The catalyst for producing an unsaturated carboxylic acid according to [1], wherein in the Formula (I), M is at least one element selected from transition metal elements in the 4th period of the periodic table.

[3] The catalyst for producing an unsaturated carboxylic acid according to [1], wherein in the Formula (I), M is at least one selected from Cr, Mn, Co, Cu and Fe.

[4] The catalyst for producing an unsaturated carboxylic acid according to any one of [1] to [3], wherein in the Formula (I), x' satisfies $0 < x' < 0.1$.

[5] The catalyst for producing an unsaturated carboxylic acid according to any one of [1] to [4], wherein the Component B is a compound containing an inorganic acid.

[6] The catalyst for producing an unsaturated carboxylic acid according to [5], wherein the inorganic acid contains at least one element selected from the group consisting of B, Si, Ge, N, P, As, Sb, Bi and S.

[7] The catalyst for producing an unsaturated carboxylic acid according to [5], wherein

the inorganic acid contains at least one selected from the group consisting of a borate ion, a phosphate ion, a sulfate ion, a nitrate ion and a heteropolyacid ion.

[8] The catalyst for producing an unsaturated carboxylic acid according to [7], wherein the heteropolyacid ion is a phosphotungstate ion.

[9] The catalyst for producing an unsaturated carboxylic acid according to any one of [1] to [8], further including an insoluble or slightly soluble Component C.

[10] The catalyst for producing an unsaturated carboxylic acid according to [9], wherein the Component C is at least one selected from the group consisting of SiO_2 , Al_2O_3 , $\text{SiO}_2\text{-Al}_2\text{O}_3$, ZrO_2 , zeolites and activated carbon.

[11] The catalyst for producing an unsaturated carboxylic acid according to any one of [1] to [10], wherein a mass ratio (A/B) of the Component A to the Component B is 0.0001 to 1000.

[12] The catalyst for producing an unsaturated carboxylic acid according to [11], wherein the mass ratio (A/B) is 0.1 to 300.

[0007]

[13] A catalyst for producing an unsaturated carboxylic acid, wherein the catalyst is used for obtaining an unsaturated carboxylic acid from an unsaturated aldehyde, and includes: Component A composed of at least one selected from Cr, Mn, Co and oxides thereof; and Component B containing an inorganic acid.

[14] The catalyst for producing an unsaturated carboxylic acid according to [13], wherein the inorganic acid contains at least one selected from the group consisting of H_3BO_3 , H_3PO_4 , H_2SO_4 , HNO_3 and a heteropolyacid.

[15] The catalyst for producing methacrylic acid according to any one of [1] to [14], in which the unsaturated aldehyde is methacrolein and the unsaturated carboxylic acid is methacrylic acid.

[0008]

[16] A method for producing an unsaturated carboxylic acid, including: performing catalytic gas phase oxidation of an unsaturated aldehyde with molecular oxygen or a gas containing molecular oxygen in the presence of the catalyst for producing an unsaturated carboxylic acid according to any one of [1] to [15].

[17] A method for producing an unsaturated carboxylic acid ester, including: esterifying an unsaturated carboxylic acid produced by the method for producing an unsaturated carboxylic acid according to [16].

[18] A method for producing an unsaturated carboxylic acid ester, including: producing

an unsaturated carboxylic acid by performing catalytic gas phase oxidation of an unsaturated aldehyde with molecular oxygen or a gas containing molecular oxygen in the presence of the catalyst for producing an unsaturated carboxylic acid according to any one of [1] to [15]; and esterifying the unsaturated carboxylic acid.

[0009]

[1'] A catalyst for producing an unsaturated carboxylic acid, wherein the catalyst is used for obtaining an unsaturated carboxylic acid from an unsaturated aldehyde, and includes Component A having an oxidative ability and Component B having an acid property.

[2'] The catalyst for producing an unsaturated carboxylic acid according to [1'], further containing Component C that is an insoluble or slightly soluble component as a catalytic component.

[3'] The catalyst for producing an unsaturated carboxylic acid according to [1'] or [2'], in which the Component A is a metal or a metal oxide.

[4'] The catalyst for producing an unsaturated carboxylic acid according to any one of [1'] to [3'], including at least one selected from Cr, Mn and Co as the Component A.

[5'] The catalyst for producing an unsaturated carboxylic acid according to any one of [1'] to [4'], including an inorganic acid as the Component B.

[6'] The catalyst for producing an unsaturated carboxylic acid according to any one of [1'] to [5'], including at least one selected from the group consisting of H_3BO_3 , H_3PO_4 , H_2SO_4 , HNO_3 and a heteropolyacid as the Component B.

[7'] A method for producing an unsaturated carboxylic acid, including: performing catalytic gas phase oxidation of unsaturated aldehyde with molecular oxygen or a gas containing molecular oxygen in the presence of the catalyst for producing an unsaturated carboxylic acid according to any one of [1'] to [6'].

[8'] A method for producing an unsaturated carboxylic acid ester, including: esterifying an unsaturated carboxylic acid produced by the method for producing an unsaturated carboxylic acid according to [7'].

Advantageous Effects of Invention

[0010]

According to the present invention, it is possible to provide a new catalyst which is used for obtaining an unsaturated carboxylic acid from an unsaturated aldehyde, a method for producing an unsaturated carboxylic acid using the catalyst, and a method for producing an unsaturated carboxylic acid ester.

Description of Embodiments

[0011]

[Catalyst for Producing Unsaturated Carboxylic Acid]

The present inventors have earnestly investigated a catalyst that can be suitably used for producing an unsaturated carboxylic acid from an unsaturated aldehyde and, as a result, they have found that it is possible to produce an unsaturated carboxylic acid from unsaturated aldehyde by using a catalyst that contains an oxidative component and an acid component, in which the oxidative component and the acid component are chemical species different from each other, and they have thus completed the present invention.

[0012]

In other words, the catalyst for producing an unsaturated carboxylic acid according to the present invention is a catalyst for producing an unsaturated carboxylic acid, wherein the catalyst is used for producing an unsaturated carboxylic acid from an unsaturated aldehyde, and contains at least two different components, Component A and Component B. The above-mentioned Component A is a component having oxidative ability, and the above-mentioned Component B has a component having an acid property. In the reaction of producing an unsaturated carboxylic acid from an unsaturated aldehyde, since Component A and Component B coexist as different kinds of components, it is considered that Component A essentially functions as an oxidation catalyst while Component B essentially functions as an acid catalyst. Specifically, it is thought that Component B contributes to protonation of unsaturated aldehyde. Moreover, it is thought that Component A contributes to an addition of oxygen atoms to the protonated unsaturated aldehyde. Therefore, it is presumed that the reaction from an unsaturated aldehyde to an unsaturated carboxylic acid progresses by using the catalyst according to the present invention.

[0013]

(Component A)

Component A is a component that has oxidative ability and that can oxidize a reactant (unsaturated aldehyde) represented by the following Formula (I) and used for a catalytic reaction. Moreover, for the purpose of function as a catalyst, it is preferable that its own redox reaction occurs reversibly.

[0014]



(In Formula (I), M is at least one element selected from metal elements in the 4th period of the

periodic table, M' is at least one element selected from metal elements other than metal elements in the 4th period of the periodic table, O is oxygen, x, x' and y represent atomic ratios of the respective components, x is an integer of 1 or more, x' satisfies $0 \leq x' \leq 0.4$ for $x = 1$, and y is 0 or an atomic ratio of oxygen required for satisfying the atom ratios of the components.)

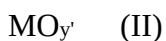
[0015]

Component A includes a metal or a metal oxide and contains the above-mentioned M as a main component. Specifically, M is at least one element selected from K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn and Ga, which are metal elements in the 4th period of the periodic table. Among these, from the viewpoint that the reaction from an unsaturated aldehyde to an unsaturated carboxylic acid more easily progresses, it is preferable that M is at least one element selected from Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Zn which are transition metal elements in the 4th period of the periodic table, and it is more preferable that M is at least one element selected from Cr, Mn, Co, Cu and Fe, and it is still more preferable that M is at least one element selected from Cr and Fe. For M, one kind may be used, or two or more kinds may be used in combination.

M' is at least one element selected from metal elements other than metals in the 4th period of the periodic table and, especially, M is preferably an element that can form an alloy with M or an element that can form a composite metal oxide with M. It is more preferable that M' is at least one element selected from Zr, Nb, Mo, Ru, Rh, Pd, Ag, Cd, Ta, W, Re, Os, Ir, Pt and Au.

In Formula (I), x' satisfies $0 \leq x' \leq 0.4$ for $x = 1$, preferably $0 \leq x' < 0.1$, more preferably $0 \leq x' \leq 0.01$ and especially preferably $x' = 0$.

Although Component A may be only M element (metal simple substance), an alloy consisting of two or more kinds of M, an alloy represented by $M_xM'^{x'}$, or a metal oxide (including a composite metal oxide), from the viewpoint that the reaction from unsaturated aldehyde to an unsaturated carboxylic acid progresses more easily, it is preferable that Component A is a metal oxide. In particular, the metal oxide represented by the following Formula (II) is preferable.



(In Formula (II), M is at least one element selected from metal elements in the 4th period of the periodic table, and y' is an atom ratio of oxygen corresponding to the valence of M.)

As for M in Formula (II), the same elements as M explained by Formula (I) are exemplified. In particular, an oxide of one M element such as Cr_2O_3 , Mn_2O_3 , Co_3O_4 , CuO and

Fe_2O_3 is preferable, and Cr_2O_3 and Fe_2O_3 is more preferable.

[0016]

(Component B)

The Component B is: a component having an acid property; an inorganic acid or an organic acid; and a component exhibiting a Brønsted acidity, a Lewis acidity, or the both. Specifically, the inorganic acid includes, for example, H_3PO_4 , H_3BO_3 , HNO_3 , H_2SO_4 , a heteropolyacid, etc. The organic acid includes, for example, formic acid, acetic acid, propionic acid, butyric acid, valeric acid, citric acid, malic acid, succinic acid, etc. The heteropolyacid includes, for example, $\text{H}_3\text{PW}_{12}\text{O}_{40}$, $\text{H}_4\text{SiW}_{12}\text{O}_{40}$, $\text{H}_3\text{PMo}_{12}\text{O}_{40}$, $\text{H}_6\text{PV}_3\text{Mo}_9\text{O}_{40}$, $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$, $\text{H}_5\text{PV}_2\text{W}_{10}\text{O}_{40}$, $\text{H}_4\text{PVMo}_{11}\text{O}_{40}$, $\text{H}_4\text{PVW}_{11}\text{O}_{40}$, etc. Since an oxidizing reaction of unsaturated aldehyde is generally carried out at a high temperature of about 200 to 450 °C, it is preferable that Component B is an inorganic acid. Moreover, it is preferable that the above-mentioned inorganic acid contains at least one element selected from the group consisting of boron (B), silicon (Si), germanium (Ge), nitrogen (N), phosphorous (P), arsenic (As), antimony (Sb), bismuth (Bi) and sulfur (S). Among these, it is more preferable that the above-mentioned inorganic acid contains at least one selected from the group consisting of H_3BO_3 , H_3PO_4 , H_2SO_4 , HNO_3 and a heteropolyacid for the viewpoint that the reaction from an unsaturated aldehyde to an unsaturated carboxylic acid progresses more easily. Moreover, it is preferable that the above-mentioned inorganic acid contains at least one selected from the group consisting of a borate ion, a phosphate ion, a sulfate ion, a nitrate ion and a heteropolyacid ion. In addition, the larger acid strength the above-mentioned inorganic acid has, the more protonation of the aldehyde group of unsaturated aldehyde is promoted so that subsequent oxidation by Component A may easily progress, and therefore it is preferable to use a heteropolyacid containing Mo or W in its constituent elements, and it is especially preferable to use the heteropolyacid containing phosphotungstate ion. For Component B, one kind may be used or two or more kinds may be used in combination.

[0017]

There is a component corresponding to both Component A and Component B. In other words, there is a case where both Component A and Component B are contained in one compound. However, in the present invention, the Component A and Component B must exist as different components, and Component A and Component B are contained as different components, respectively. In other words, when a catalyst contains only one component corresponding to both the Component A and Component B, the effects of the present invention cannot be caused, and it is required to further contain Components A or Component B other than

the one component.

[0018]

(Component C)

It is preferable that the catalyst according to the present invention further contains Component C, which is an insoluble or slightly soluble component, as a catalyst component in addition to Component A and Component B. Component C is a solid component that is different from Component A and Component B and for holding Component A and Component B and that serves as a catalyst carrier. In other word, Component C is a carrier component and Component A and Component B can be carried on Component C. "Insoluble" herein means being completely insoluble in water. Moreover, "slight soluble" means that the solubility to water at 25 °C is 100 mg / 100 mL or less. When Component A and Component B are dissolved or dispersed in water or other solvents, Component A and Component B in a solution state or a slurry state can be held on Component C. Therefore, it is preferable that Component C is hardly dissolved even when mixed with a solution or a slurry of Component A and Component B.

[0019]

Component C is not particularly limited, but an inorganic compound and a substance having high thermal stability is preferable. Specifically, it is possible to use SiO₂, Al₂O₃, SiO₂-Al₂O₃, ZrO₂, various zeolites (zeolites), activated carbon, etc. These may be used singly, or in combination of two or more thereof.

[0020]

Although there are some metal oxides that can be used as both Component A and Component C, when these exist together, one that has stronger oxidative ability acts on an oxidizing reaction. Therefore, the one that has stronger oxidative ability is considered as Component A, while one that has weaker oxidative ability is considered as Component C. Oxidative ability of metal oxide is herein estimated by heat of formation - H^0_f per oxygen atom, and smaller - H^0_f means stronger oxidative ability. Incidentally, - H^0_f of various metal oxides is described in, for example, Y. Morooka and A. Ozaki, *J.Catal.*, 5, 116 (1966); Tetsuro Seiyama et al., *Shokubai (Catalysts & Catalysis)*, 8, 306 (1966), etc.

[0021]

(Content Ratio)

When the masses of the Component A and Component B contained in the catalyst according to the present invention are respectively denoted as m_A and m_B , the content ratio of Component A and Component B (m_A/m_B , hereinafter also referred to as A/B mass ratio) is

preferably 0.0001 to 1000 from a viewpoint of yield of unsaturated carboxylic acid, more preferably 0.001 to 500, still more preferably 0.01 to 400, and especially preferably 0.1 to 300.

[0022]

In case that the catalyst according to the present invention contains Component C, when each mass of the Component A, Component B and Component C is defines as to m_A , m_B and m_C , respectively, the content ratio of Component A ($m_A/(m_A+m_C) \times 100$) is preferably 1 to 99 mass%, more preferably 5 to 90 mass%, still more preferably 10 to 85 mass%, especially preferably 20 to 80 mass%, and most preferably 30 to 60 mass%. The content ratio of Component B ($m_B/(m_A+m_B+m_C) \times 100$) is preferable 0.001 to 99 mass%, more preferably 0.01 to 90 mass%, still more preferably 0.1 to 70 mass%, and especially preferably 0.1 to 50 mass%. A preferable range of content ratio of Component C is naturally determined based on the above-mentioned preferable ranges of content ratios of Component A and Component B.

[0023]

[Method for Producing Catalyst]

The production method of the catalyst according to the present invention is not particularly limited, but the catalyst can be prepared by, for example, the method including the following steps.

Step (A): dissolving or dispersing Component A in a solvent to obtain a solution or a solvent dispersion.

Step (B): adding Component C to the solution or solvent dispersion obtained in the step (A) with stirring, and removing the solvent by reduced pressure evaporation, etc. to obtain a solid content.

Step (C): firing the solid content obtained in the step (B) to obtain a fired substance.

Step (D): dissolving or dispersing Component B in a solvent to obtain a solution or a solvent dispersion.

Step (E): adding the solution or solvent dispersion obtained in the step (D) to the fired substance obtained in the step (C) with stirring, and drying and removing the solvent to obtain a solid content.

Step (F): firing the solid content obtained in the step (E) to obtain a fired product.

[0024]

A source compound of each component is not particularly limited. Source materials of Component A and Component B are not particularly limited, but include, for example, hydroxides, chlorides, sulfates, nitrates, oxides, acetates, etc. of the component element. When using Component C, considering ease of mixing with Component C, a source material having a high solubility to the used solvent is preferable. For example, when using water as a solvent, a

source material of Component A includes $\text{Cr}(\text{NO}_3)_3$, $\text{Mn}(\text{NO}_3)_2$, $\text{Co}(\text{NO}_3)_2$, and hydrates thereof, etc. Moreover, a source material of Component B includes Component B, as it is, such as $\text{H}_3\text{PW}_{12}\text{O}_{40}$, $\text{H}_4\text{SiW}_{12}\text{O}_{40}$, $\text{H}_3\text{PMo}_{12}\text{O}_{40}$, $\text{H}_6\text{PV}_3\text{Mo}_9\text{O}_{40}$, $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$, $\text{H}_5\text{PV}_2\text{W}_{10}\text{O}_{40}$, $\text{H}_4\text{PVMo}_{11}\text{O}_{40}$, $\text{H}_4\text{PVW}_{11}\text{O}_{40}$, H_3BO_3 , H_3PO_4 , H_2SO_4 , HNO_3 , etc. or dilutions thereof by a solvent. The solvent is not particularly limited, but includes, for example, water and organic solvents such as ethanol and acetone.

[0025]

Moreover, when using Component C, as shown in the step (C), it is preferable to fire a solid content after drying the solution or solvent dispersion containing Component A and Component C. Component A is sufficiently fixed on Component C by firing. The firing is carried out, for example, at 200 to 600 °C under air atmosphere for 1 to 100 hours. Moreover, as shown in step (F), it is preferable that after a fired substance containing Component A and Component C is obtained, Component B is mixed with the fired substance and fired again.

The obtained catalyst can be used for a reaction from an unsaturated aldehyde to an unsaturated carboxylic acid directly or after firing. The firing is carried out, for example, at 200 to 600 °C for 1 to 100 hours.

[0026]

In addition, the catalyst according to the present invention can be produced by, for example, a method including the following steps.

Step (1): dissolving or dispersing a source material of Component A in a solvent to obtain a solution or a solvent dispersion.

Step (2): adding Component C to the above-mentioned solution or solvent dispersion and removing the solvent to obtain a solid content i.

Step (3): adding a compound containing a source material of Component B to the above-mentioned solid content i to obtain a solid content ii containing Component A, Component B and Component C.

[0027]

(Step (1))

A source material of the above-mentioned Component A is not particularly limited, but includes, for example, a hydroxide, a chloride, a sulfate, a nitrate, an oxide, an acetate, etc. of the component element. When using Component C, considering ease of mixing with Component C, a source material having a high solubility to the used solvent is preferable. For example, when using water as a solvent, a source material of Component A includes $\text{Cr}(\text{NO}_3)_3$, $\text{Mn}(\text{NO}_3)_2$, $\text{Co}(\text{NO}_3)_2$, $\text{Fe}(\text{NO}_3)_3$, $\text{Cu}(\text{NO}_3)_2$, and hydrates thereof, etc. The solvent is not particularly

limited, but includes, for example, water and organic solvents such as ethanol and acetone.

[0028]

(Step (2))

As mentioned above, it is possible to use SiO_2 , Al_2O_3 , $\text{SiO}_2\text{-Al}_2\text{O}_3$, ZrO_2 , various zeolites, activated carbon, etc. as the above-mentioned Component C. One of these may be used, or two or more thereof may be used in combination.

Moreover, it is preferable to use a reduced pressure evaporation as a method for removing a solvent from the above-mentioned solution or solvent dispersion.

Moreover, when using Component C, it is preferable to fire the solid content i in this step. The Component A is sufficiently fixed on Component C by firing. The firing is carried out, for example, at 200 to 600 °C under an air environment for 1 to 100 hours.

[0029]

(Step (3))

The source material of Component B includes $\text{H}_3\text{PW}_{12}\text{O}_{40}$, $\text{H}_4\text{SiW}_{12}\text{O}_{40}$, $\text{H}_3\text{PMo}_{12}\text{O}_{40}$, $\text{H}_6\text{PV}_3\text{Mo}_9\text{O}_{40}$, $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$, $\text{H}_5\text{PV}_2\text{W}_{10}\text{O}_{40}$, $\text{H}_4\text{PVMo}_{11}\text{O}_{40}$, $\text{H}_4\text{PVW}_{11}\text{O}_{40}$, H_3BO_3 , H_3PO_4 , H_2SO_4 , HNO_3 , etc.

In this step, the source material of Component B can be added to the solid content i by dissolution or dispersion in a solvent. The solvent is not particularly limited, but includes, for example, water and organic solvents such as ethanol and acetone. In this case, after the source material of Component B is dissolved or dispersed in a solvent and added to the solid content i, the solid content ii can be obtained by removing the solvent.

Moreover, the solid content ii can be also obtained by mixing the solid content i with a substance of which the Component B is carried on the Component C.

[0030]

(Firing Step)

Although the solid content ii may be directly used for the reaction from unsaturated aldehyde to unsaturated carboxylic acid, a usage after firing is preferable. The firing is carried out, for example, at 200 to 600 °C for 1 to 100 hours.

[0031]

Moreover, the catalyst according to the present invention can be produced by, for example, a method including the following steps.

Step (1)': dissolving or dispersing a source material of Component A in a solvent to obtain a solution or a solvent dispersion.

Step (2)': adding Component C and source materials of Component B to the solution or solvent

dispersion, and removing the solvent to obtain a solid content iii containing Component A, Component B and Component C.

[0032]

(Step (1'))

A source material of the Component A is not particularly limited, but includes, for example, a hydroxide, a chloride, a sulfate, a nitrate, an oxide, an acetate, etc. of the component element. When using Component C, considering ease of mixing with Component C, a source material having a high solubility to the used solvent is preferable. For example, when using water as a solvent, a source material of Component A includes $\text{Cr}(\text{NO}_3)_3$, $\text{Mn}(\text{NO}_3)_2$, $\text{Co}(\text{NO}_3)_2$, $\text{Fe}(\text{NO}_3)_3$, $\text{Cu}(\text{NO}_3)_2$, and hydrates thereof, etc. The solvent is not particularly limited, but includes, for example, water and organic solvents such as ethanol and acetone.

[0033]

(Step (2'))

As mentioned above, as the Component C, it is possible to use SiO_2 , Al_2O_3 , $\text{SiO}_2\text{-Al}_2\text{O}_3$, ZrO_2 , various zeolites and activated carbon, etc. One of these may be used, or two or more thereof may be used in combination.

The above-mentioned source material of Component B includes $\text{H}_3\text{PW}_{12}\text{O}_{40}$, $\text{H}_4\text{SiW}_{12}\text{O}_{40}$, $\text{H}_3\text{PMo}_{12}\text{O}_{40}$, $\text{H}_6\text{PV}_3\text{Mo}_9\text{O}_{40}$, $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$, $\text{H}_5\text{PV}_2\text{W}_{10}\text{O}_{40}$, $\text{H}_4\text{PVMo}_{11}\text{O}_{40}$, $\text{H}_4\text{PVW}_{11}\text{O}_{40}$, H_3BO_3 , H_3PO_4 , H_2SO_4 , HNO_3 , etc. These can be added to the solid content i by dissolution or dispersion in a solvent. The solvent is not particularly limited, but includes, for example, water and organic solvents such as ethanol and acetone.

Moreover, it is preferable to obtain a solid content iii by removing the solvent using reduced pressure evaporation.

[0034]

(Firing Step)

Although the solid content iii may be directly used for the reaction from unsaturated aldehyde to unsaturated carboxylic acid, a usage after firing is preferable. The firing is carried out, for example, at 200 to 600 °C for 1 to 100 hours.

Moreover, the catalyst obtained in the firing step of the solid content ii or the solid content iii can be used by crushing and sizing for making its particle size into tens to hundreds of micrometers (μm) or by pelletizing the catalyst. The catalyst according to the present invention is applicable to any reaction modes such as a fixed bed, a fluidized bed and a moving bed, but a usage for a reaction in a fixed bed is preferable. In case of the usage in a fixed bed, it is preferable to mix the catalyst with inert diluents such as sea sand and silicon carbide for the

purpose of heat removal.

[0035]

[Method for Producing Unsaturated Carboxylic Acid]

In the method for producing an unsaturated carboxylic acid according to the present invention, a catalytic gas phase oxidation reaction is performed by molecular oxygen or a molecular oxygen-containing gas of an unsaturated aldehyde in the presence of the catalyst for producing an unsaturated carboxylic acid according to the present invention. According to the method, an unsaturated carboxylic acid can be obtained from an unsaturated aldehyde. Examples of the unsaturated aldehyde include, for example, (meth)acrolein, crotonaldehyde (alias: -methylacrolein), cinnamaldehyde (alias: -phenylacrolein), etc. Among these, (meth)acrolein is suitable. An unsaturated carboxylic acid produced from an unsaturated aldehyde is an unsaturated carboxylic acid in which the aldehyde group of the unsaturated aldehyde changes to a carboxyl group, and, for example, when the unsaturated aldehyde is (meth)acrolein, (meth)acrylic acid is obtained. Incidentally, "(meth)acrolein" denotes acrolein and methacrolein, and "(meth)acrylic acid" denotes acrylic acid and methacrylic acid.

[0036]

The source gas composition in the catalytic gas phase oxidation reaction is not particularly limited, but unsaturated aldehyde: oxygen: water vapor: dilution gas = 1 : 0.1 to 10 : 0 to 30 : 0 to 60 (molar ratio) are preferable. In this case, nitrogen and CO₂, etc. are preferable as the dilution gas. A catalytic gas phase oxidation reaction may be carried out under pressurization or reduced pressure, but operation under pressure near atmospheric pressure is preferable. The reaction temperature is preferably 200 to 400 C and more preferably 220 to 350 C. As for supply of the source gas, its space velocity (SV) is preferably 100 to 100,000 hr⁻¹ and more preferably 400 to 30,000 hr⁻¹.

[0037]

[Method for Producing Unsaturated Carboxylic Acid Ester]

In the method for producing an unsaturated carboxylic acid ester according to the present invention, esterification of an unsaturated carboxylic acid obtained by the method according to the present invention is performed. According to the method, an unsaturated carboxylic acid ester can be obtained using an unsaturated carboxylic acid obtained from an unsaturated aldehyde. An alcohol reacted with an unsaturated carboxylic acid includes methanol, ethanol, isopropanol, n-butanol, isobutanol, etc. The obtained unsaturated carboxylic acid ester includes, for example, methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, butyl (meth)acrylate, etc. The reaction can be performed in the presence of an

acid catalyst such as a sulfonic acid type cation exchange resin. The reaction temperature is preferably 50 to 200 °C.

Examples

[0038]

Hereinafter, the present invention will be more specifically explained by Examples, but the present invention is not limited to the following Examples unless it exceeds the gist. The content ratio of Component A and the content ratio of Component B in the following Examples are defined as follows. All of Cr, Mn, Co, Cu and Fe carried on the carrier (Component C) are herein calculated as Cr₂O₃, Mn₂O₃, Co₃O₄, CuO and Fe₂O₃, respectively, based on the results of X-ray diffraction measurement.

[0039]

$$\text{Content ratio of Component A (mass\%)} = m_A / (m_A + m_C) \times 100.$$

$$\text{Content ratio of Component B (mass\%)} = m_B / (m_A + m_B + m_C) \times 100.$$

m_A : Mass of Component A (metal oxide)

m_B : Mass of Component B (H₃PW₁₂O₄₀, H₃PO₄ or H₂SO₄)

m_C : Mass of Component C (SiO₂ or SiO₂-Al₂O₃)

Moreover, m_A , m_B and m_C are values calculated from charged amounts of the source materials.

[0040]

Moreover, the content ratio of the Component A and Component B (A/B mass ratio) is defined as follows.

$$\text{A/B mass ratio} = m_A / m_B.$$

Moreover, the methacrylic acid yield in the following Examples is defined as follows.

$$\text{Methacrylic acid yield (mol\%)} = (\text{number of moles of methacrylic acid generated}) / (\text{number of moles of methacrolein supplied}) \times 100.$$

[0041]

[Example 1]

(Preparation of Catalyst)

To 100 mL of ultrapure water, 9.895 g (0.02474 mol, mass of Cr: 1.286 g) of Cr(NO₃)₃·9H₂O (formula weight 400) was added and completely dissolved by stirring. To this aqueous solution, 3 g of SiO₂ (product name: Aerosil 300, manufactured by Nippon Aerosil Co., Ltd.) was added and stirred at room temperature for 1 hour. The mixture was transferred to an eggplant flask, and the solvent was evaporated to dryness using an evaporator under reduced

pressure of about 5 Torr (about 7×10^2 N/m²) at a water bath temperature of 50 C. The obtained solid was dried overnight at 100 C. Firing was performed at 550 C (heating rate 10 C/min) in the air with a muffle furnace for 5 hours to obtain CrO_x/SiO₂ (solid content i) with a content ratio of Component A being 38.52 mass%.

[0042]

To 30 mL of ultrapure water, 100 g of phosphotungstic acid (manufactured by Nippon Inorganic Colour & Chemical Co., Ltd.) was added and completely dissolved by stirring. When the dissolution was insufficient, ultrapure water was added portion-wise until complete dissolution. The mixture was transferred to a separatory funnel, and 50 mL of diethyl ether was added and shaken while removing a gas and then left overnight. The ether phase of the lower layer was transferred to another separatory funnel, and 50 mL of ultrapure water was added thereto and shaken while removing a gas and then left overnight. This operation was repeated 5 times in total. The ether phase of the lower layer was transferred to an eggplant flask, and 50 mL of ultrapure water was added. The solvent was evaporated using an evaporator under reduced pressure of about 5 Torr (about 7×10^2 N/m²) at a water bath temperature of 40 C. When a solid was deposited and the solution became sherbet-like, the evaporator was once stopped and 50 mL of ultrapure water was added thereto. The solvent was again evaporated using a rotary evaporator under reduced pressure. This operation was repeated 5 times. When a small amount of crystal was deposited on the liquid surface in the fifth operation, the reduced pressure evaporation was stopped. The eggplant flask was soaked in a hot bath to dissolve the deposited crystal again. The obtained saturated aqueous solution was left overnight at room temperature. After the crystal generated was separated by decantation from the mother liquid and dried overnight at 60 C, air drying was further performed for two days at room temperature to obtain H₃PW₁₂O₄₀nH₂O. TG-DTA profile of the H₃PW₁₂O₄₀nH₂O was measured to calculate the number of hydrate water (value of n). Based on this value, 50 mL of 0.08 mol/L aqueous solution of H₃PW₁₂O₄₀ was prepared.

[0043]

On the previously prepared CrO_x/SiO₂ (1.8 g) with a content ratio of Component A being 38.52 mass%, 3.91 mL (amount of substance of H₃PW₁₂O₄₀: 0.3128 mmol, mass of H₃PW₁₂O₄₀: 0.901 g) of the previously prepared 0.08 mol/L H₃PW₁₂O₄₀ aqueous solution was deposited by the incipient wetness method. Specifically, to powder of CrO_x/SiO₂ weighed in a beaker, a small amount, which is enough to moderately moisten the whole of the powder, of H₃PW₁₂O₄₀ aqueous solution was dropped using a Pasteur pipette and stirred well with a glass rod. Thereafter, drying was performed at 100 C for about 15 to 30 minutes. This operation

was repeated until the whole quantity of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ aqueous solution was dropped. The obtained powder (solid content ii) was dried overnight at 60 °C and then fired at 250 °C (heating rate 10 °C/min) for 2 hours using a muffle furnace in the air to obtain $\text{H}_3\text{PW}_{12}\text{O}_{40}\text{-CrO}_x/\text{SiO}_2$ catalyst with a content ratio of Component B being 33.35 mass%. When X-ray diffraction (using a Cu-K α ray) of the obtained catalyst was measured, a crystal structure of trivalent chromic oxide and $\text{H}_3\text{PW}_{12}\text{O}_{40}$ was acknowledged, and it was confirmed that there were at least Cr_2O_3 , which is Component A having oxidative ability, and $\text{H}_3\text{PW}_{12}\text{O}_{40}$ which is Component B having an acid property.

[0044]

(Catalyst Evaluation Test)

The obtained $\text{H}_3\text{PW}_{12}\text{O}_{40}\text{-Cr}_2\text{O}_3/\text{SiO}_2$ catalyst was sized to 250 to 500 μm . One gram of the catalyst and 3 g of sea sand (manufactured by Wako Pure Chemical Industries, Ltd.) sized to 250 to 500 μm were physically mixed, charged into a glass reaction tube, and connected with a reaction apparatus. The temperature was raised to 320 °C while a mixed gas of $\text{O}_2:\text{H}_2\text{O}:\text{N}_2 = 10.7:17.9:71.4$ (volume ratio) was flowed at a space velocity (SV) of 1680 hr^{-1} , and heating was performed for 1 hour. Thereafter, at the reaction bath temperature (reaction temperature) of 300 °C, a source gas of methacrolein : oxygen : water vapor : nitrogen = 3:6:13:78 (molar ratio) was flowed at a space velocity (SV) of 4320 hr^{-1} to estimate a methacrylic acid yield. The result of the evaluation test is shown in Table 1.

[0045]

[Example 2]

$\text{H}_3\text{PW}_{12}\text{O}_{40}\text{-Cr}_2\text{O}_3/\text{SiO}_2$ catalyst with a content ratio of Component B being 10.00 mass% was prepared in the same manner as in Example 1 except that the quantity of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ aqueous solution used for depositing on $\text{CrO}_x/\text{SiO}_2$ was changed into 0.868 mL (mass of $\text{H}_3\text{PW}_{12}\text{O}_{40}$: 0.20 g). The catalyst evaluation test was performed in the same manner as in Example 1 except for using said catalyst. The result of the evaluation test is shown in Table 1.

[0046]

[Example 3]

$\text{H}_3\text{PW}_{12}\text{O}_{40}\text{-Cr}_2\text{O}_3/\text{SiO}_2$ catalyst with a content ratio of Component B being 49.99 mass% was prepared in the same manner as in Example 1 except that the quantity of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ aqueous solution used for depositing on $\text{CrO}_x/\text{SiO}_2$ was changed into 7.81 mL (mass of $\text{H}_3\text{PW}_{12}\text{O}_{40}$: 1.80 g). The catalyst evaluation test was performed in the same manner as in Example 1 except for using said catalyst. The result of the evaluation test is shown in Table 1.

[0047]

[Example 4]

H₃PW₁₂O₄₀-Cr₂O₃/SiO₂ catalyst with a content ratio of Component B being 69.97 mass% was prepared in the same manner as in Example 1 except that the quantity of H₃PW₁₂O₄₀ aqueous solution used for carrying on CrO_x/SiO₂ was changed into 18.2 mL (mass of H₃PW₁₂O₄₀: 4.19 g). The catalyst evaluation test was performed in the same manner as in Example 1 except for using said catalyst. The result of the evaluation test is shown in Table 1.

[0048]

[Comparative Example 1]

The catalyst evaluation test was performed in the same manner as in Example 1 except for using CrO_x/SiO₂ (solid content i) with a content ratio of Component A being 38.52 mass%, which was prepared in Example 1, as a catalyst. The result of the evaluation test is shown in Table 1.

[0049]

[Comparative Example 2]

H₃PW₁₂O₄₀ aqueous solution is deposited to SiO₂ that does not carry CrO_x in the same manner as in Example 1 by the incipient wetness method to obtain H₃PW₁₂O₄₀/SiO₂ catalyst with a content ratio of Component B being 33.35 mass%. The catalyst evaluation test was performed in the same manner as in Example 1 except for using said catalyst. The result of the evaluation test is shown in Table 1.

[0050]

[Example 5]

The catalyst evaluation test was performed in the same manner as in Example 1 except that the reaction temperature was changed to 350 C. The result of the evaluation test is shown in Table 1.

[0051]

[Example 6]

The catalyst evaluation test was performed in the same manner as in Example 1 except that the reaction temperature was changed to 400 C. The result of the evaluation test is shown in Table 1.

[0052]

[Example 7]

After the catalyst evaluation test in Example 1, feeding of water vapor was stopped with the temperature kept at 300 C, the source gas composition was changed to methacrolein : oxygen : nitrogen = 3:6:76 (molar ratio), the space velocity (SV) was changed into 3670 hr⁻¹, and

the methacrylic acid yield was evaluated. The result of the evaluation test is shown in Table 1.
[0053]

[Example 8]

MnO_x/SiO₂ (solid content i) with a content ratio of Component A being 38.11 mass% was prepared in the same manner as in the preparation of CrO_x/SiO₂ in Example 1 except for using 6.717 g (0.0234 mol, mass of Mn: 1.286 g) of Mn(NO₃)₂·6H₂O (formula weight 287) instead of Cr(NO₃)₃·9H₂O. H₃PW₁₂O₄₀-MnO_x/SiO₂ catalyst with a content ratio of Component B being 33.35 mass% was prepared in the same manner as in the preparation of H₃PW₁₂O₄₀-Cr₂O₃/SiO₂ in Example 1 except for using the aforementioned MnO_x/SiO₂ instead of CrO_x/SiO₂. When X-ray diffraction (using a Cu-K rays) of the obtained catalyst was measured, a crystal structure of trivalent manganese oxide and H₃PW₁₂O₄₀ was acknowledged, and it was confirmed that there were at least Mn₂O₃, which is Component A having oxidative ability, and H₃PW₁₂O₄₀ which is Component B having an acid property. The catalyst evaluation test was performed in the same manner as in Example 1 except for using the above-mentioned catalyst. The result of the evaluation test is shown in Table 1.

[0054]

[Comparative Example 3]

The catalyst evaluation test was performed in the same manner as in Example 1 except for using MnO_x/SiO₂ (solid content i) with a content ratio of Component A being 38.11 mass%, which was prepared in Example 8, as a catalyst. The result of the evaluation test is shown in Table 1.

[0055]

[Example 9]

CrO_x/SiO₂ (solid content i) with a content ratio of Component A being 59.37 mass% was prepared in the same manner as in the preparation of CrO_x/SiO₂ in Example 1 except that the used amount of Cr(NO₃)₃·9H₂O was changed to 23.083 g and that the used amount of ultrapure water was changed to 233.28 mL. H₃PW₁₂O₄₀-Cr₂O₃/SiO₂ catalyst with a content ratio of Component B being 33.35 mass% was prepared in the same manner as in the preparation of H₃PW₁₂O₄₀-Cr₂O₃/SiO₂ catalyst in Example 1 except for using the aforementioned CrO_x/SiO₂. The catalyst evaluation test was performed in the same manner as in Example 1 except for using said catalyst. The result of the evaluation test is shown in Table 1.

[0056]

[Example 10]

CrO_x/SiO₂-Al₂O₃ (solid content i) with a content ratio of Component A being 38.52

mass% was prepared in the same manner as in the preparation of $\text{CrO}_x/\text{SiO}_2$ in Example 1 except for using $\text{SiO}_2\text{-Al}_2\text{O}_3$ (reference catalyst of the Catalysis Society of Japan, JRC-SAL-2) instead of SiO_2 . $\text{H}_3\text{PW}_{12}\text{O}_{40}\text{-Cr}_2\text{O}_3/\text{SiO}_2\text{-Al}_2\text{O}_3$ catalyst with a content ratio of Component B being 33.35 mass% was prepared in the same manner as in the preparation of $\text{H}_3\text{PW}_{12}\text{O}_{40}\text{-Cr}_2\text{O}_3/\text{SiO}_2$ catalyst in Example 1 except for using said $\text{CrO}_x/\text{SiO}_2\text{-Al}_2\text{O}_3$. The catalyst evaluation test was performed in the same manner as in Example 1 except for using said catalyst. The result of the evaluation test is shown in Table 1.

[0057]

[Example 11]

$\text{CrO}_x/\text{SiO}_2$ (solid content i) with a content ratio of Component A being 77.33 mass% was prepared in the same manner as in the preparation of $\text{CrO}_x/\text{SiO}_2$ in Example 1 except that the used amount of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was changed to 53.869 g and that the used amount of ultrapure water was changed to 544.32 mL. $\text{H}_3\text{PW}_{12}\text{O}_{40}\text{-Cr}_2\text{O}_3/\text{SiO}_2$ catalyst with a content ratio of Component B being 33.35 mass% was prepared in the same manner as in the preparation of $\text{H}_3\text{PW}_{12}\text{O}_{40}\text{-Cr}_2\text{O}_3/\text{SiO}_2$ catalyst in Example 1 except for using said $\text{CrO}_x/\text{SiO}_2$. The catalyst evaluation test was performed in the same manner as in Example 1 except for using said catalyst. The result of the evaluation test is shown in Table 1.

[0058]

[Example 12]

$\text{CoO}_x/\text{SiO}_2$ (solid content i) with a content ratio of Component A being 53.85 mass% was prepared in the same manner as in the preparation of $\text{CrO}_x/\text{SiO}_2$ in Example 1 except for using 12.69 g (0.04360 mol and mass of Co: 2.570 g) of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (formula weight 291.03) instead of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. $\text{H}_3\text{PW}_{12}\text{O}_{40}\text{-CoO}_x/\text{SiO}_2$ catalyst with a content ratio of Component B being 33.35 mass% was prepared in the same manner as in the preparation of $\text{H}_3\text{PW}_{12}\text{O}_{40}\text{-Cr}_2\text{O}_3/\text{SiO}_2$ catalyst in Example 1 except for using $\text{CoO}_x/\text{SiO}_2$ instead of $\text{CrO}_x/\text{SiO}_2$. When X-ray diffraction (using a Cu-K α rays) of the obtained catalyst was measured, a crystal structure of spinel type cobalt oxide having a mixed valence of divalence and trivalence and $\text{H}_3\text{PW}_{12}\text{O}_{40}$ was acknowledged, and it was confirmed that there were at least Co_3O_4 , which is Component A having oxidative ability, and $\text{H}_3\text{PW}_{12}\text{O}_{40}$ which is Component B having an acid property. The catalyst evaluation test was performed in the same manner as in Example 1 except for using said catalyst. The result of the evaluation test is shown in Table 1.

[0059]

[Comparative Example 4]

The catalyst evaluation test was performed in the same manner as in Example 1 except

for using $\text{CoO}_x/\text{SiO}_2$ (solid content i) with a content ratio of Component A being 53.85 mass%, which was prepared in Example 12, as a catalyst. The result of the evaluation test is shown in Table 1.

[0060]

[Example 13]

$\text{H}_3\text{PO}_4\text{-Cr}_2\text{O}_3/\text{SiO}_2$ catalyst with a content ratio of Component B being 0.15 mass% was prepared in the same manner as in Example 1 except for using 0.343 mL of 0.08 mol/L H_3PO_4 aqueous solution instead of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ aqueous solution. The catalyst evaluation test was performed in the same manner as in Example 1 except for using said catalyst. The result of the evaluation test is shown in Table 1.

[0061]

[Example 14]

$\text{H}_2\text{SO}_4\text{-Cr}_2\text{O}_3/\text{SiO}_2$ catalyst with a content ratio of Component B being 0.22 mass% was prepared in the same manner as in Example 1 except for using 0.515 mL of 0.08 mol/L H_2SO_4 aqueous solution instead of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ aqueous solution. The catalyst evaluation test was performed in the same manner as in Example 1 except for using said catalyst. The result of the evaluation test is shown in Table 1.

[0062]

[Example 15]

$\text{H}_3\text{PO}_4\text{-Cr}_2\text{O}_3/\text{SiO}_2$ catalyst with a content ratio of Component B being 1.43 mass% was prepared in the same manner as in Example 1 except for using 3.34 mL of 0.08 mol/L H_3PO_4 aqueous solution instead of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ aqueous solution. The catalyst evaluation test was performed in the same manner as in Example 1 except for using said catalyst. The result of the evaluation test is shown in Table 1.

[0063]

[Example 16]

$\text{H}_2\text{SO}_4\text{-Cr}_2\text{O}_3/\text{SiO}_2$ catalyst with a content ratio of Component B being 2.14 mass% was prepared in the same manner as in Example 1 except for using 5.01 mL of 0.08 mol/L H_2SO_4 aqueous solution instead of the $\text{H}_3\text{PW}_{12}\text{O}_{40}$ aqueous solution. The catalyst evaluation test was performed in the same manner as in Example 1 except for using said catalyst. The result of the evaluation test is shown in Table 1.

[0064]

[Example 17]

To 100 mL of ultrapure water, 9.895 g (0.02474 mol, mass of Cr: 1.286 g) of

$\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (formula weight 400) was added and stirred until complete dissolution. To this aqueous solution, 3 g of SiO_2 (trade name: Aerosil 300, manufactured by Nippon Aerosil Co., Ltd.) was added, and 9.02 mL (amount of substance of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ 0.7216 mmol, mass of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ 2.078 g) of 0.08 mol/L $\text{H}_3\text{PW}_{12}\text{O}_{40}$ aqueous solution was further added and stirred at the room temperature for 1 hour. Thereafter, the mixture was transferred to an eggplant flask, and the solvent was evaporated to dryness using an evaporator under reduced pressure of about 5 Torr at a water bath temperature of 50 C. The obtained solid (solid content iii) was dried overnight at 100 C and fired at 250 C in the air with a muffle furnace for 1 hour to obtain of $\text{H}_3\text{PW}_{12}\text{O}_{40}\text{-CrO}_x/\text{SiO}_2$ catalyst having a content ratio of Component A being 38.52 mass% and a content ratio of Component B being 29.87 mass%. The catalyst evaluation test was performed in the same manner as in Example 1 except for using said catalyst. The result of the evaluation test is shown in Table 1.

[0065]

[Example 18]

$\text{CuO}_x/\text{SiO}_2$ (solid content i) with a content ratio of Component A being 34.92 mass% was prepared in the same manner as in the preparation of $\text{CrO}_x/\text{SiO}_2$ in Example 1 except for using 4.889 g (0.020 mol, mass of Cu 1.286 g) of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (formula weight 241.6) instead of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. $\text{H}_3\text{PW}_{12}\text{O}_{40}\text{-CuO}_x/\text{SiO}_2$ catalyst with a content ratio of Component B being 33.35 mass% was prepared in the same manner as in the preparation of $\text{H}_3\text{PW}_{12}\text{O}_{40}\text{-CrO}_x/\text{SiO}_2$ in Example 1 except for using the $\text{CuO}_x/\text{SiO}_2$ instead of $\text{CrO}_x/\text{SiO}_2$. When X-ray diffraction (using a Cu-K rays) of the obtained catalyst was measured, a crystal structure of divalent copper oxide and $\text{H}_3\text{PW}_{12}\text{O}_{40}$ was acknowledged, and it was confirmed that there were at least CuO, which is Component A having oxidative ability, and $\text{H}_3\text{PW}_{12}\text{O}_{40}$ which is Component B having an acid property. The catalyst evaluation test was performed in the same manner as in Example 1 except for using said catalyst. The result of the evaluation test is shown in Table 1.

[0066]

[Example 19]

$\text{FeO}_x/\text{SiO}_2$ (solid content i) with a content ratio of Component A being 37.99 mass% was prepared in the same manner as in the preparation of $\text{CrO}_x/\text{SiO}_2$ in Example 1 except for using 9.301 g (0.023 mol, mass of Fe 1.286 g) of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (formula weight 404.0) instead of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. $\text{H}_3\text{PW}_{12}\text{O}_{40}\text{-FeO}_x/\text{SiO}_2$ with a content ratio of Component B being 33.35 mass% was prepared in the same manner as in the preparation of $\text{H}_3\text{PW}_{12}\text{O}_{40}\text{-CrO}_x/\text{SiO}_2$ catalyst in Example 1 except for using said $\text{FeO}_x/\text{SiO}_2$ instead of $\text{CrO}_x/\text{SiO}_2$. When X-ray diffraction

(using a Cu-K α rays) of the obtained catalyst was measured, a crystal structure of trivalent iron oxide and $\text{H}_3\text{PW}_{12}\text{O}_{40}$ was acknowledged, and it was confirmed that there were at least Fe_2O_3 , which is Component A having oxidative ability, and $\text{H}_3\text{PW}_{12}\text{O}_{40}$ which is Component B having an acid property. The catalyst evaluation test was performed in the same manner as in Example 1 except for using said catalyst. The result of the evaluation test is shown in Table 1.

[0067]

[Example 20]

$\text{CrO}_x/\text{SiO}_2$ (solid content i) with a content ratio of Component A being 38.52 mass%, which was prepared in Example 1, and $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{SiO}_2$ with a content ratio of Component B being 33.35 mass%, which was prepared in the same manner as in Comparative Example 2, were respectively sized to 250 to 500 μm . Physical mixing of 0.5 g of $\text{CrO}_x/\text{SiO}_2$ and 0.5 g of $\text{H}_3\text{PW}_{12}\text{O}_{40}-\text{Cr}_2\text{O}_3/\text{SiO}_2$ was performed to obtain $\text{CrO}_x/\text{SiO}_2-\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{SiO}_2$ (solid content ii) with a content ratio of Component A (mass of Component A / (mass of component A + mass of Component C (total SiO_2) $\times$ 100) being 23.11 mass% and a content ratio of Component B being 16.68 mass%. Furthermore, 3.0 g of sea sand sized to 250 to 500 μm was physically mixed to this catalyst and charged in a glass reaction tube. Then, the catalyst evaluation test was performed in the same manner in Example 1. The result of the evaluation test is shown in Table 1.

[0068]

[Table 1]

Example and Comparative Example	Component A		Component B		Component C	A/B mass ratio	Reaction temp. (□)	Yield of methacrylic acid (%)
	Kind	Content ratio ^{*1} (mass%)	Kind	Content ratio ^{*2} (mass%)	Kind			
Example 1	Cr ₂ O ₃	38.52	H ₃ PW ₁₂ O ₄₀	33.35	SiO ₂	0.77	300	3.3
Example 2	Cr ₂ O ₃	38.52	H ₃ PW ₁₂ O ₄₀	10.00	SiO ₂	3.47	300	1.4
Example 3	Cr ₂ O ₃	38.52	H ₃ PW ₁₂ O ₄₀	49.99	SiO ₂	0.39	300	0.6
Example 4	Cr ₂ O ₃	38.52	H ₃ PW ₁₂ O ₄₀	69.97	SiO ₂	0.17	300	0.1
Comparative Example 1	Cr ₂ O ₃	38.52	-	0	SiO ₂	-	300	0.0
Comparative Example 2	-	0	H ₃ PW ₁₂ O ₄₀	33.35	SiO ₂	-	300	0.0
Example 5	Cr ₂ O ₃	38.52	H ₃ PW ₁₂ O ₄₀	33.35	SiO ₂	0.77	350	16.5
Example 6	Cr ₂ O ₃	38.52	H ₃ PW ₁₂ O ₄₀	33.35	SiO ₂	0.77	400	7.6
Example 7	Cr ₂ O ₃	38.52	H ₃ PW ₁₂ O ₄₀	33.35	SiO ₂	0.77	300 ^{*3}	1.1
Example 8	Mn ₂ O ₃	38.11	H ₃ PW ₁₂ O ₄₀	33.35	SiO ₂	0.76	300	0.1
Comparative Example 3	Mn ₂ O ₃	38.11	-	0	SiO ₂	-	300	0.0
Example 9	Cr ₂ O ₃	59.37	H ₃ PW ₁₂ O ₄₀	33.35	SiO ₂	1.19	300	5.4
Example 10	Cr ₂ O ₃	38.52	H ₃ PW ₁₂ O ₄₀	33.35	SiO ₂ -Al ₂ O ₃	0.77	300	2.2
Example 11	Cr ₂ O ₃	77.33	H ₃ PW ₁₂ O ₄₀	33.35	SiO ₂	1.55	300	3.2
Example 12	Co ₃ O ₄	53.85	H ₃ PW ₁₂ O ₄₀	33.35	SiO ₂	1.08	300	2.2
Comparative Example 4	Co ₃ O ₄	53.85	-	0	SiO ₂	-	300	0.0
Example 13	Cr ₂ O ₃	38.52	H ₃ PO ₄	0.15	SiO ₂	257.82	300	2.5
Example 14	Cr ₂ O ₃	38.52	H ₂ SO ₄	0.22	SiO ₂	171.57	300	2.3
Example 15	Cr ₂ O ₃	38.52	H ₃ PO ₄	1.43	SiO ₂	26.48	300	1.9
Example 16	Cr ₂ O ₃	38.52	H ₂ SO ₄	2.14	SiO ₂	17.64	300	3.3
Example 17	Cr ₂ O ₃	38.52	H ₃ PW ₁₂ O ₄₀	29.87	SiO ₂	0.90	300	2.8
Example 18	CuO	34.92	H ₃ PW ₁₂ O ₄₀	33.35	SiO ₂	0.70	300	0.2
Example 19	Fe ₂ O ₃	37.99	H ₃ PW ₁₂ O ₄₀	33.35	SiO ₂	0.76	300	7.1
Example 20	Cr ₂ O ₃	23.11	H ₃ PW ₁₂ O ₄₀	16.68	SiO ₂	1.15	300	1.1

*1 Content ratio in Component A and Component C

*2 Content ratio in components A to C

*3 Source gas composition Methacrolein: Oxygen: Nitrogen =3:6:76 (molar ratio). In others, methacrolein: oxygen: water vapor: nitrogen = 3:6:13:78 (molar ratio).

[0069]

In all Examples using the catalyst containing Component A having oxidative ability and Component B having an acid property, it was possible to obtain methacrylic acid from methacrolein. On the other hand, in Comparative Examples 1, 3 and 4 in which Component B was not contained in the catalyst, and in Comparative Example 2 in which Component A was not contained in the catalyst, it was not possible to obtain methacrylic acid from methacrolein, and it was found that the reaction of producing methacrylic acid from methacrolein progressed because of coexistence of Component A and Component B as different kinds of components.

[0070]

The present application claims priority based on Japanese Patent Application No. 2017-070810 filed on March 31, 2017, Japanese Patent Application No. 2017-095617 filed on May 12, 2017, and Japanese Patent Application No. 2017-225100 filed on November 22, 2017,

the disclosures of which are all incorporated herein by reference.

CLAIMS

1. A catalyst for producing an unsaturated carboxylic acid, wherein the catalyst is used for obtaining an unsaturated carboxylic acid from an unsaturated aldehyde, and comprises Component A represented by Formula (I) and Component B that is a compound containing an inorganic acid or an organic acid,



wherein in the Formula (I), M is at least one element selected from metal elements in the 4th period of the periodic table, M' is at least one element selected from metal elements other than the metal elements in the 4th period of the periodic table, O is oxygen, x, x' and y represent atomic ratios of the respective components, x is an integer of 1 or more, x' satisfies $0 < x' \leq 0.4$ for $x = 1$, and y is 0 or an atomic ratio of oxygen required for satisfying the atom ratios of the respective components.

2. The catalyst for producing an unsaturated carboxylic acid according to claim 1, wherein in the Formula (I), M is at least one element selected from transition metal elements in the 4th period of the periodic table.

3. The catalyst for producing an unsaturated carboxylic acid according to claim 1, wherein in the Formula (I), M is at least one selected from Cr, Mn, Co, Cu and Fe.

4. The catalyst for producing an unsaturated carboxylic acid according to any one of claim 1 to 3, wherein in the Formula (I), x' satisfies $0 < x' < 0.1$.

5. The catalyst for producing an unsaturated carboxylic acid according to any one of claims 1 to 4, wherein the Component B is a compound containing an inorganic acid.

6. The catalyst for producing an unsaturated carboxylic acid according to claim 5, wherein the inorganic acid contains at least one element selected from the group consisting of B, Si, Ge, N, P, As, Sb, Bi and S.

7. The catalyst for producing an unsaturated carboxylic acid according to claim 5, wherein the inorganic acid contains at least one selected from the group consisting of a borate ion, a phosphate ion, a sulfate ion, a nitrate ion and a heteropolyacid ion.

8. The catalyst for producing an unsaturated carboxylic acid according to claim 7, wherein the heteropolyacid ion is a phosphotungstate ion.
9. The catalyst for producing an unsaturated carboxylic acid according to any one of claims 1 to 8, further comprising an insoluble or slightly soluble Component C.
10. The catalyst for producing an unsaturated carboxylic acid according to claim 9, wherein the Component C is at least one selected from the group consisting of SiO_2 , Al_2O_3 , $\text{SiO}_2\text{-Al}_2\text{O}_3$, ZrO_2 , zeolites and activated carbon.
11. The catalyst for producing an unsaturated carboxylic acid according to any one of claims 1 to 10, wherein a mass ratio (A/B) of the Component A to the Component B is 0.0001 to 1000.
12. The catalyst for producing an unsaturated carboxylic acid according to claim 11, wherein the mass ratio (A/B) is 0.1 to 300.
13. A catalyst for producing an unsaturated carboxylic acid, wherein the catalyst is used for obtaining an unsaturated carboxylic acid from an unsaturated aldehyde, and comprises: Component A composed of at least one selected from Cr, Mn, Co and oxides thereof; and Component B containing an inorganic acid.
14. The catalyst for producing an unsaturated carboxylic acid according to claim 13, wherein the inorganic acid contains at least one selected from the group consisting of H_3BO_3 , H_3PO_4 , H_2SO_4 , HNO_3 and a heteropolyacid.
15. The catalyst for producing methacrylic acid according to any one of claim 1 to claim 14, wherein the unsaturated aldehyde is methacrolein and the unsaturated carboxylic acid is methacrylic acid.
16. A method for producing an unsaturated carboxylic acid, comprising: performing catalytic gas phase oxidation of an unsaturated aldehyde with molecular oxygen or a gas containing molecular oxygen in the presence of the catalyst for producing an unsaturated

carboxylic acid according to any one of claims 1 to 15.

17. A method for producing an unsaturated carboxylic acid ester, comprising: esterifying an unsaturated carboxylic acid produced by the method for producing an unsaturated carboxylic acid according to claim 16.

18. A method for producing an unsaturated carboxylic acid ester, comprising: producing an unsaturated carboxylic acid by performing catalytic gas phase oxidation of an unsaturated aldehyde with molecular oxygen or a gas containing molecular oxygen in the presence of the catalyst for producing an unsaturated carboxylic acid according to any one of claims 1 to 15; and esterifying the unsaturated carboxylic acid.