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,

$$M_xM'_{x'}O_y \qquad (I)$$

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 $0 \leq x' \leq 0.4$ for $x = 1$, and y is 0 or an atomic ratio of oxygen required for satisfying the atom ratios of the 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 $0 \leq x' < 0.1$.

[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

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.

$MO_{y'}$ (II)

(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

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,

$$M_xM'_{x'}O_y \quad (I)$$

wherein in the Formula (I), M is at least one element selected from transition 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 $0 \leq x' \leq 0.4$ for $x = 1$, and y is 0 or an atomic ratio of oxygen required for satisfying the atom ratios of the respective components, and
wherein the inorganic acid is an inorganic acid except for containing a phosphomolybdate ion.

2. The catalyst for producing an unsaturated carboxylic acid according to claim 1, 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.

3. The catalyst for producing an unsaturated carboxylic acid according to claim 1, 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.

4. The catalyst for producing an unsaturated carboxylic acid according to claim 3, wherein the heteropolyacid ion is a phosphotungstate ion.

5. 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,

$$M_xM'_{x'}O_y \quad (I)$$

wherein in the Formula (I), M is at least one element selected from transition 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 $0 \leq x' \leq 0.4$ for x = 1, and y is 0 or an atomic ratio of oxygen required for satisfying the atom ratios of the respective components, and 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 phosphotungstate ion.

6. The catalyst for producing an unsaturated carboxylic acid according to claim 5, wherein in the Formula (I), M is at least one selected from Cr, Mn, Co, Cu and Fe.

7. The catalyst for producing an unsaturated carboxylic acid according to claim 5 or 6, wherein in the Formula (I), x' satisfies $0 \leq x' < 0.1$.

8. The catalyst for producing an unsaturated carboxylic acid according to any one of claims 5 to 7, wherein the Component B is a compound containing an inorganic acid.

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, SiO_2-Al_2O_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 phosphotungstic acid.

15. The catalyst for producing an unsaturated carboxylic 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: 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.