CATALYST FOR OXIDATION OF SATURATED AND UNSATURATED ALDEHYDES TO UNSATURATED CARBOXYLIC ACID COMPRISING A HETEROPOLY ACID, METHOD OF MAKING AND METHOD OF USING THEREOF

SPECIFICATION

BACKGROUND OF THE INVENTION

FIELD OF THE INVENTION

[0001] : This invention relates to heteropoly acid catalyst compositions, a method of making such catalyst compositions and a process for the oxidation of unsaturated aldehydes, such as methacrolein, to unsaturated carboxylic acids, such as methacrylic acid, in a vapor phase reaction using such catalyst compositions.

DESCRIPTION OF THE PRIOR ART

[0002] : Various catalysts are known for the gas phase catalytic oxidation of unsaturated aldehydes to unsaturated carboxylic acids. Included are molybdenum-based mixed metal oxides compound which can contain oxides of metals such as phosphorus, arsenic, cesium, rubidium, cobalt, nickel, iron, chromium, antimony, tellurium and silicon in addition to molybdenum. These same metals and others may occur in heteropoly acid compounds as metal oxide clusters forming heteropolyoxoanions in acid form instead of simple metal oxides. Heteropoly acid compounds are also known as catalysts for the gas phase catalytic oxidation of unsaturated aldehydes to unsaturated carboxylic acids. Heteropoly acid compounds have a central metal atom surrounded by a framework of other metal atoms connected to each other and the central metal atom through oxygen atoms. The central metal atom is different ("hetero") from the framework metal atoms.

[0003] One problem of heteropoly acid compounds as catalysts is thermal stability. In process operating temperatures, the heteropoly acid compound catalysts tend to deactivate by chemically and physically breaking down. Commercially useful heteropoly acid compound catalysts compound catalysts must have thermal stability for acceptable catalyst lifetime.

SUMMARY ~~OF THE INVENTION~~

[0004] The present disclosure provides~~invention is for~~ a heteropoly acid catalyst composition, a method of making the catalyst composition and a process of using the catalyst composition for the oxidation of unsaturated aldehydes, such as methacrolein, to unsaturated carboxylic acids, such as methacrylic acid, in a vapor phase reaction. The catalyst composition has the general formula

$Mo_{12}V_aP_bCs_cBi_dCu_eSb_fO_x$ where Mo is molybdenum, V is vanadium, P is phosphorus, Cs is cesium, Bi is bismuth, Cu is copper, Sb is antimony and O is oxygen, a is 0.01 to 5.0, b is 0.5 to 3.5, c is 1.5 to 2.75, d is 0.05 to 0.5, e is 0.05 to 0.5, f is 0.1 to 0.5 and x satisfies the valences. Presence of cesium along with bismuth, copper and antimony is required for a heteropoly acid compound catalyst with good thermal stability and catalytic performance. This catalyst composition is essentially insoluble in water.

[0004a] In a first aspect, there is provided a catalyst comprising a heteropoly acid compound of the general formula:

$Mo_{12}V_aP_bCs_cBi_dCu_eSb_fO_x$

where Mo is molybdenum, V is vanadium, P is phosphorus, Cs is cesium, Bi is bismuth, Cu is copper, Sb is antimony and O is oxygen, a is 0.01 to 5.0, b is 0.5 to 3.5, c is 1.5 to 2.75, d is 0.05 to 0.5, e is 0.05 to 0.5, f is 0.1 to 0.5 and x satisfies the valences.

[0005] In general, the method of making the catalyst is to dissolve compounds of the catalyst components of the heteropoly acid compound in an acidified aqueous solution, precipitating particles of the catalyst precursor, drying the solid particles and calcining the solid particles.

[0005a] In a second aspect, there is provided a process of preparing a heteropoly acid compound catalyst comprising:

a) mixing the solution of a molybdenum compound, a vanadium compound, a phosphorus compound, a cesium compound, a bismuth compound, a copper compound and an antimony compound;

b) precipitating solid particles

c) removing liquid to leave the solid particles;

d) drying the solid particles;

e) calcining the solid particles; and

f) forming a heteropoly acid compound catalyst comprising the general formula:

$Mo_{12}V_aP_bCs_cBi_dCu_eSb_fO_x$

where Mo is molybdenum, V is vanadium, P is phosphorus, Cs is cesium, Bi is bismuth, Cu is copper, Sb is antimony and O is oxygen, a is 0.01 to 5.0, b is 0.5 to 3.5, c is 1.5 to 2.75, d is 0.05 to 0.5, e is 0.05 to 0.5, f is 0.1 to 0.5 and x satisfies the valences.

[0006] In general, the process of using the catalyst compositions for the oxidation of unsaturated aldehydes to unsaturated carboxylic acids in a vapor phase reaction is to contact the unsaturated aldehyde, such as methacrolein, with an oxidizing agent, such as air or another oxygen-containing gas, in the presence of the heteropoly acid compound catalyst at conditions to produce an unsaturated carboxylic acid, such as methacrylic acid.

[0006a] In a third aspect, there is provided a process for converting saturated and/or unsaturated aldehydes to unsaturated carboxylic acids comprising contacting a saturated and/or unsaturated aldehyde with an oxidizing agent in the presence of a supported or bound heteropoly acid catalyst comprising a heteropoly acid compound comprising the general formula:

$Mo_{12}V_aP_bCs_cBi_dCu_eSb_fO_x$

where Mo is molybdenum, V is vanadium, P is phosphorus, Cs is cesium, Bi is bismuth, Cu is copper, Sb is antimony and O is oxygen, a is 0.01 to 5.0, b is 0.5 to 3.5, c is 1.5 to 2.75, d is 0.05 to 0.5, e is 0.05 to 0.5, f is 0.1 to 0.5 and x satisfies the valences.

BRIEF DESCRIPTION OF THE DRAWINGS

[0007] A more complete appreciation of the invention and many of the attendant advantages thereof will be readily understood by reference to the following detailed description when considered in connection with the accompanying drawings.

[0008] Figure 1 shows catalytic activities obtained from high and low Cs content catalysts under different calcination temperatures.

[0009] Figure 2 shows XRD of low Cs content and high Cs content catalysts at 380°C.

[0010] Figure 3 shows XRD of low Cs content and high Cs content catalysts at different temperatures.

[0011] Figure 4 shows a comparison of catalyst activities of heteropoly acid compound catalysts with various promoters.

[0012] Figure 5 shows a comparison of catalyst activities of heteropoly acid compound (HPA) catalysts with various promoters.

[0013] Figure 6A-1 shows lifetime tests of low Cs catalyst.

[0014] Figure 6A-2 shows lifetime tests of high Cs catalyst.

[0015] Figure 6B shows lifetime tests of low Cs and high Cs catalysts.

CLAIMS

1. A catalyst comprising a heteropoly acid compound of the general formula:

$Mo_{12}V_aP_bCs_cBi_dCu_eSb_fO_x$

where Mo is molybdenum, V is vanadium, P is phosphorus, Cs is cesium, Bi is bismuth, Cu is copper, Sb is antimony and O is oxygen, a is 0.01 to 5.0, b is 0.5 to 3.5, c is 1.5 to 2.75, d is 0.05 to 0.5, e is 0.05 to 0.5, f is 0.1 to 0.5, and x satisfies the valences.

2. The catalyst of Claim 1, wherein the heteropoly acid compound contains one or more element selected from the group consisting of boron, tungsten, cerium, niobium, indium, iron, chromium, cobalt, nickel, manganese, arsenic, silver, zinc, lead, tin, titanium, aluminum, silicon, tantalum, germanium, gallium, zirconium, magnesium, barium, and lanthanum.

3. The catalyst of Claim 1, wherein the heteropoly acid compound has the general formula:

$Mo_{12}V_aP_bCs_cBi_dCu_eSb_fM'_gO_x$

where Mo is molybdenum, V is vanadium, P is phosphorus, Cs is cesium, Bi is bismuth, Cu is copper, M' is one or more of boron, tungsten, cerium, niobium, indium, iron, chromium, cobalt, nickel, manganese, arsenic, silver, zinc, lead, tin, titanium, aluminum, silicon, tantalum, germanium, gallium, zirconium, magnesium, barium and lanthanum, O is oxygen, a is 0.01 to 5.0, b is 0.5 to 3.5, c is 1.5 to 2.75, d is 0.05 to 0.5, e is 0.05 to 0.5, f is 0.1 to 0.5, g is 0 to 0.5, and x satisfies the valences.

4. A process of preparing a heteropoly acid compound catalyst comprising:

a) mixing the solution of a molybdenum compound, a vanadium compound, a phosphorus compound, a cesium compound, a bismuth compound, a copper compound, and an antimony compound;

b) precipitating solid particles;

c) removing liquid to leave the solid particles;

d) drying the solid particles;

e) calcining the solid particles; and

f) forming a heteropoly acid compound catalyst comprising the general formula:

$Mo_{12}V_aP_bCs_cBi_dCu_eSb_fO_x$

where Mo is molybdenum, V is vanadium, P is phosphorus, Cs is cesium, Bi is bismuth, Cu is copper, Sb is antimony and O is oxygen, a is 0.01 to 5.0, b is 0.5 to 3.5, c is 1.5 to 2.75, d is 0.05 to 0.5, e is 0.05 to 0.5, f is 0.1 to 0.5, and x satisfies the valences.

5. The process of Claim 4, wherein the molybdenum compound is ammonium

paramolybdate, molybdenum trioxide, molybdenum chloride or mixtures or combinations thereof, the vanadium compound is ammonium metavanadate, vanadium pentoxide, vanadium chloride or mixtures or combinations thereof, the phosphorus compound is phosphoric acid, ammonium phosphite or mixtures or combinations thereof, the copper compound is copper nitrate, copper chloride or mixtures or combinations thereof, the bismuth compound is bismuth nitrate, bismuth oxide, bismuth chloride or mixtures or combinations thereof, the cesium compound is cesium nitrate, cesium oxide, cesium chloride or mixtures or combinations thereof, and the antimony compound is antimony nitrate, antimony oxide, antimony chloride, or mixtures or combinations thereof.

6. The process of any of Claims 4 – 5, wherein the calcining is at a temperature of about 350°C to about 450 °C for about 2 to about 12 hours.

7. The process of any of Claims 4 – 6, wherein the calcining is in two stages, one at a temperature lower than about 350°C for about 1 to about 8 hours and another at a temperature above about 350°C for about 2 to about 12 hours.

8. A process for converting saturated and/or unsaturated aldehydes to unsaturated carboxylic acids comprising contacting a saturated and/or unsaturated aldehyde with an oxidizing agent in the presence of a supported or bound heteropoly acid catalyst comprising a heteropoly acid compound comprising the general formula:

$$Mo_{12}V_aP_bCs_cBi_dCu_eSb_fO_x$$

where Mo is molybdenum, V is vanadium, P is phosphorus, Cs is cesium, Bi is bismuth, Cu is copper, Sb is antimony and O is oxygen, a is 0.01 to 5.0, b is 0.5 to 3.5, c is 1.5 to 2.75, d is 0.05 to 0.5, e is 0.05 to 0.5, f is 0.1 to 0.5, and x satisfies the valences.

9. The process of Claim 8, wherein the oxidizing agent is air or another oxygen-containing gas.

10. The process of Claim 9, wherein the oxygen-containing gas additionally comprises nitrogen, carbon dioxide, noble gases, and/or steam.

11. The process of any of Claims 8 – 10, wherein the converting is at a pressure of about 0 atm to about 5 atm.

12. The process of Claim 11, wherein the pressure is about 1 atm.

13. The process of any of Claims 8 – 12, wherein the converting is at a temperature of about 230°C to about 450°C.

14. The process of Claim 13, wherein the temperature is about 250°C to about 400°C.

15. The process of Claim 14, wherein the temperature is about 250°C to about 350°C.

16. The process of any of Claims 8 –15, wherein the unsaturated aldehyde is methacrolein.

17. The process of any of Claims 8 – 15, wherein the saturated aldehyde is isobutanal or isobutyraldehyde.

18. The process of any of Claims 8 – 17, wherein the heteropoly acid compound contains one or more element selected from the group consisting of boron, tungsten, cerium, niobium, indium, iron, chromium, cobalt, nickel, manganese, arsenic, silver, zinc, lead, tin, titanium, aluminum, silicon, tantalum, germanium, gallium, zirconium, magnesium, barium, and lanthanum.

19. The process of any of Claims 8 – 17, wherein the heteropoly acid compound has the general formula:

$$Mo_{12}V_aP_bCs_cBi_dCu_eSb_fM'_gO_x$$

where Mo is molybdenum, V is vanadium, P is phosphorus, Cs is cesium, Bi is bismuth, Cu is copper, M' is one or more of boron, tungsten, cerium, niobium, indium, iron, chromium, cobalt, nickel, manganese, arsenic, silver, zinc, lead, tin, titanium, aluminum, silicon, tantalum, germanium, gallium, zirconium, magnesium, barium and lanthanum, O is oxygen, a is 0.01 to 5.0, b is 0.5 to 3.5, c is 1.5 to 2.75, d is 0.05 to 0.5, e is 0.05 to 0.5, f is 0.1 to 0.5, g is 0 to 0.5 and x satisfies the valences.

CLAIMS

1. A catalyst comprising a heteropoly acid compound of the general formula:

$Mo_{12}V_aP_bCs_cBi_dCu_eSb_fO_x$

where Mo is molybdenum, V is vanadium, P is phosphorus, Cs is cesium, Bi is bismuth, Cu is copper, Sb is antimony and O is oxygen, a is 0.01 to 5.0, b is 0.5 to 3.5, c is 1.5 to 2.75, d is 0.05 to 0.5, e is 0.05 to 0.5, f is 0.1 to 0.5 and x satisfies the valences.

2. The catalyst of Claim 1 wherein the heteropoly acid compound contains one or more element selected from the group consisting of boron, tungsten, cerium, niobium, indium, iron, chromium, cobalt, nickel, manganese, arsenic, silver, zinc, lead, tin, titanium, aluminum, silicon, tantalum, germanium, gallium, zirconium, magnesium, barium and lanthanum.

3. The catalyst of Claim 1 wherein the heteropoly acid compound has the general formula:

$Mo_{12}V_aP_bCs_cBi_dCu_eSb_fM'_gO_x$

where Mo is molybdenum, V is vanadium, P is phosphorus, Cs is cesium, Bi is bismuth, Cu is copper, M' is one or more of boron, tungsten, cerium, niobium, indium, iron, chromium, cobalt, nickel, manganese, arsenic, silver, zinc, lead, tin, titanium, aluminum, silicon, tantalum, germanium, gallium, zirconium, magnesium, barium and lanthanum, O is oxygen, a is 0.01 to 5.0, b is 0.5 to 3.5, c is 1.5 to 2.75, d is 0.05 to 0.5, e is 0.05 to 0.5, f is 0.1 to 0.5, g is 0 to 0.5 and x satisfies the valences.

4. The catalyst of Claim 1 wherein c is greater than 1.5 to 2.75.

5. The catalyst of Claim 1 wherein c is 2.0 to 2.75.

6. A process of preparing a heteropoly acid compound catalyst comprising:

a) mixing the solution of a molybdenum compound, a vanadium compound, a phosphorus compound, a cesium compound, a bismuth compound, a copper compound and an antimony compound;

b) precipitating solid particles

c) removing liquid to leave the solid particles;

d) drying the solid particles;

e) calcining the solid particles; and

f) forming a heteropoly acid compound catalyst comprising the general formula:

$Mo_{12}V_aP_bCs_cBi_dCu_eSb_fO_x$

where Mo is molybdenum, V is vanadium, P is phosphorus, Cs is cesium, Bi is bismuth, Cu is copper, Sb is antimony and O is oxygen, a is 0.01 to 5.0, b is 0.5 to 3.5, c is 1.5 to 2.75, d is 0.05 to 0.5, e is 0.05 to 0.5, f is 0.1 to 0.5 and x satisfies the valences.

7. The process of Claim 6 wherein the molybdenum compound is ammonium paramolybdate, molybdenum trioxide, molybdenum chloride or mixtures or combinations thereof, the vanadium compound is ammonium metavanadate, vanadium pentoxide, vanadium chloride or mixtures or combinations thereof, the phosphorus compound is phosphoric acid, ammonium phosphite or mixtures or combinations thereof, the copper compound is copper nitrate, copper chloride or mixtures or combinations thereof, the bismuth compound is bismuth nitrate, bismuth oxide, bismuth chloride or mixtures or combinations thereof, the cesium compound is cesium nitrate, cesium oxide, cesium chloride or mixtures or combinations thereof and the antimony compound is antimony nitrate, antimony oxide, antimony chloride or mixtures or combinations thereof.

8. The process of Claim 6 wherein calcining is at a temperature of about 350°C to about 450 °C for about 2 to about 12 hours.

9. The process of Claim 6 wherein calcining is in two stages, one at a temperature lower than about 350°C for about 1 to about 8 hours and another at a temperature above about 350°C for about 2 to about 12 hours.

10. The process of Claim 6 wherein c is greater than 1.5 to 2.75.

11. A process for converting saturated and/or unsaturated aldehydes to unsaturated carboxylic acids comprising contacting a saturated and/or unsaturated aldehyde with an oxidizing agent in the presence of a supported or bound heteropoly acid catalyst comprising a heteropoly acid compound comprising the general formula:

$Mo_{12}V_aP_bCs_cBi_dCu_eSb_fO_x$

where Mo is molybdenum, V is vanadium, P is phosphorus, Cs is cesium, Bi is bismuth, Cu is copper, Sb is antimony and O is oxygen, a is 0.01 to 5.0, b is 0.5 to 3.5, c is 1.5 to 2.75, d is 0.05 to 0.5, e is 0.05 to 0.5, f is 0.1 to 0.5 and x satisfies the valences.

12. The process of Claim 11 wherein the oxidizing agent is air or another oxygen-containing gas.

13. The process of Claim 11 wherein the oxygen-containing gas additionally comprises nitrogen, carbon dioxide, noble gases or steam.

14. The process of Claim 11 wherein pressure is from about 0 atm to about 5 atm.

15. The process of Claim 11 wherein the pressure is about 1 atm.

16. The process of Claim 11 wherein temperature is from about 230°C to about 450°C.

17. The process of Claim 11 wherein the temperature is from about 250°C to about 400°C.

18. The process of Claim 11 wherein the temperature is from about 250°C to about 350°C.

19. The process of Claim 11 wherein the unsaturated aldehyde is methacrolein.

20. The process of Claim 11 wherein the saturated aldehyde is isobutanal or isobutyraldehyde.