

Process for preparing an oxygen-containing organic compound through hydroformylation reaction

Technical Field

5 The present application relates to the field of hydroformylation reaction, and specifically relates to a process for preparing an oxygen-containing organic compound through hydroformylation reaction.

Background Art

10 Organic compounds having a carbon-carbon double bond such as olefins can undergo hydroformylation with carbon monoxide and hydrogen under the action of a catalyst to obtain aldehydes and/or alcohols that contain an additional carbon atom. Conventional hydroformylation processes includes contacting and reacting an ethylenically unsaturated
15 compound with carbon monoxide and hydrogen in the presence of a catalyst under reaction conditions to produce one or more aldehydes and/or alcohols. The catalysts used in hydroformylation reaction in industrial production are generally cobalt (Co)-based or rhodium (Rh)-based catalysts.

 CN102123978A discloses a process for hydroformylating α -olefins to
20 produce two or more aldehydes including normal aldehydes and one or more isomeric aldehydes, the target molar ratio of the normal aldehydes to the one or more isomeric aldehydes is within a selectable range of 3/1-60/1. This process uses a transition metal-ligand complex catalyst containing a symmetric calixarene diphosphite ligand.

25 CN108586219A discloses a process for preparing aldehydes by hydroformylation of olefins. The preparation process is as follows: Step 1: performing continuous hydroformylation reaction of C2-C4 olefins, carbon monoxide and hydrogen in the first reaction kettle under the action of a catalyst to prepare aldehyde at a temperature of 90 °C and a pressure of
30 2.5MPa; Step 2: Heating in the second reaction kettle, the heating temperature is 70-80 °C, and at the same time, inert gas is introduced into the second reaction kettle; Step 3: Connecting the first reaction kettle to the

second reaction kettle, and introducing the aldehyde prepared in the first reaction kettle into the second reaction kettle; Step 4: When introducing in step 3, conducting it under the conditions of isobaric and unequal temperature; after the introducing, and then conducting a secondary introduction; the reaction process of this technology is complex, and it uses
5 a rhodium-phosphine complex catalyst, which is expensive.

Compared with cobalt catalysts, rhodium complexes are more reactive and can react at milder temperatures and pressures. However, rhodium catalysts have poor high-temperature performance and are difficult to use in
10 the carbonylation of higher olefins; the existing rhodium catalysts have better catalytic effects on terminal olefins, but have poor activity on internal olefins; the catalyst is oil-soluble and product separation is also difficult, making the post treatment is more complex. As a precious metal, rhodium is scarce and expensive, and its recycling and reuse costs are higher.

15 CN1370137A discloses a continuous process for hydroformylation of olefins with 6-20 carbon atoms, wherein: a) an aqueous solution of cobalt (II) salt is fully contacted with hydrogen and carbon monoxide to form a hydroformylation active cobalt catalyst, the aqueous phase containing the cobalt catalyst is then fully contacted with the olefins and optionally organic
20 solvents as well as hydrogen and carbon monoxide in at least one reaction zone, where the cobalt catalyst is extracted into the organic phase and the olefins are hydroformylated, b) the effluent from the reaction zone is treated with oxygen in the presence of an acidic aqueous solution of cobalt (II) salt, wherein the cobalt catalyst decomposes to form cobalt (II) salts and these
25 materials are back-extracted into the aqueous phase; and subsequently separated each phase, c) the solution of cobalt (II) salt is recycled to step a) in unchanged form. The process of this process is complex.

In the hydroformylation reaction process, higher alkane selectivity reduces the economic benefits of the unit. Reducing the alkane selectivity
30 and increasing the selectivity of alcohols and aldehydes can improve the unit economy; reducing the content of heavy matter in the reaction product can reduce the amount of discarded heavy matter and the amount of waste liquid

discarded from the device, which is beneficial to environmental protection. The amount of discarded materials also determines the industrial implementation prospects of the hydroformylation process.

Therefore, there is still a need for a process that can convert an organic
5 compound having a carbon-carbon double bond into target aldehydes and/or alcohol products at low cost and with high efficiency.

Summary of the Invention

The object of the present application is to provide an improved process
10 for preparing an oxygen-containing organic compound through hydroformylation reaction, which process can achieve reduced alkane selectivity and increased alcohol and aldehyde selectivity.

In order to achieve the above object, the present application provides a process for preparing an oxygen-containing organic compound through
15 hydroformylation reaction, including the following steps:

1) hydroformylation is carried out by contacting an organic compound having 2 to 60 carbon atoms and at least one carbon-carbon double bond with a syngas containing CO and H₂ in the presence of a hydroformylation catalyst and at a first reaction temperature to obtain a reaction mass
20 containing the oxygen-containing organic compound and heavy matter, wherein the oxygen-containing organic compound is an alcohol, an aldehyde, or a combination thereof that have one more carbon atom than the organic compound having a carbon-carbon double bond, wherein the first reaction temperature is 60-150°C; and

25 2) in the presence of syngas containing CO and H₂ and at a second reaction temperature, the reaction mass obtained in step 1) is continued to react, to decompose the heavy matter contained therein, resulting in a reaction product with a decrease in the content of the heavy substances and an increase in the content of the oxygen-containing organic compound,
30 wherein the second reaction temperature is 140-200°C, and the second reaction temperature is higher than the first reaction temperature by 20-100°C.

Compared with the process of the prior art, the process of the present application can achieve a reduced alkane selectivity and an increased alcohol selectivity, and can reduce the content of heavy matter in the product, thereby significantly reducing the amount of discarded materials and
5 reducing the discharge of waste liquid, which is beneficial for environmental protection.

At the same time, the process of the present application has a simple process flow, can be implemented in a continuous manner, has high raw materials conversion rate, high target product yield, low alkane selectivity,
10 and low waste liquid discharge, and has good industrial application prospects.

Other characters and advantages of the present invention will be described in detail in the section of detailed description of embodiments that follows.

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Detailed Description of the Invention

The present application will be further described in detail below through specific embodiments. It should be understood that the specific embodiments described herein are only used to illustrate and explain the
20 application, but do not limit the application in any way.

Any specific numerical value disclosed herein, including the endpoints of a numerical range, is not limited to the precise value of that numerical value, but is to be understood to encompass the values approaching that precise value. Moreover, for the disclosed numerical range, one or more new
25 value range(s) can be obtained by any combination of the endpoint values of the range, of the endpoint value of the range with a specific point value within the range, and of each specific point value within the range. These new numerical ranges should also be deemed to be specifically disclosed herein.

30 Unless otherwise stated, the terms used herein have the same meanings as commonly understood by those skilled in the art. If a term is defined herein and its definition is different from the common understanding in the

art, the definition herein shall prevail.

In the present application, the term "olefin" has the meaning generally understood in the art, that is, an unsaturated hydrocarbon compound having a carbon-carbon double bond (C=C bond). The olefin may be a chain olefin or a cyclic olefin, and the number of its carbon-carbon double bonds may be one (i.e., monoolefin), two (i.e., diolefin), or more, and the carbon-carbon double bond can be at the end of the carbon chain (i.e., terminal olefin, such as α -olefin) or in the middle of the carbon chain (i.e., internal olefin). In addition, olefin can contain other functional groups, such as hydroxyl group, aromatic ring, etc. In the process of the present application, the olefin is preferably a monoolefin, and more preferably a linear or branched monoolefin.

In the present application, the expression "C8 " means having 8 carbon atoms, and similarly the expression "C9 " means having 9 carbon atoms.

In the present application, the term "C8 olefin " refers to an olefin compound having 8 carbon atoms, preferably a linear or branched monoolefin having 8 carbon atoms, including 1-octene and its various isomers, such as 2,4,4-trimethyl-1-pentene, 2,4,4-trimethyl-2-pentene, 3,4,4-trimethyl-2-pentene, 2,3,3-trimethyl-1-pentene, 5,5-dimethyl-2-hexene, 3,5-dimethyl-2-hexene, 2,4-dimethyl-2-Hexene, 2,3-dimethyl-3-hexene, 3,4-dimethyl-2-hexene, etc.

In the present application, the term "hydroformylation catalyst" generally refers to various catalysts suitable for catalyzing the hydroformylation reaction to produce aldehydes. Such catalysts are well known in the art, such as those mentioned in Chinese Patent Application Publication CN106103399A, the contents of which are incorporated herein by reference in their entirety.

In the present application, the term "organic phosphorus-containing ligand" has the meaning commonly understood in the art, and particularly refers to a ligand containing phosphorus and a group bonded to phosphorus in molecular structure, the group being selected from hydrocarbyl group, hydrocarbyloxy group, heterocyclic group, or combination thereof, wherein

the hydrocarbyl in the hydrocarbyloxy group and the hydrocarbyl group can be various aliphatic hydrocarbyl groups, alicyclic hydrocarbyl groups and aromatic hydrocarbyl groups, such as alkyl, cycloalkyl and aryl groups, the heterocyclic groups can be a variety of organic group having one or more
5 heteroatoms selected from O, N, S...in the ring. The group may also optionally have various substituents that do not adversely affect the properties of the resulting complex, such as sulfonic acid group, halogen, amino, nitro, hydroxyl, carbonyl, etc. For example, the organic phosphorus-containing ligand may be a ligand containing phosphorus and a hydrocarbyl
10 group bonded to the phosphorus by a "P-C" bond and/or a hydrocarbyloxy group bonded to the phosphorus by a "P-O" bond in the molecular structure. Specific examples of the organic phosphorus-containing ligand include various phosphine ligands known in the art, especially phosphine ligand having alkyl, aryl and/or heterocyclic groups, such as trialkyl phosphine
15 ligand. Preferably, the organic phosphorus-containing ligand has a general formula PR_3 , wherein each group R is independently selected from a hydrocarbyl group, a hydrocarbyloxy group and a heterocyclic group, preferably is independently selected from an alkyl, a cycloalkyl, aryl, alkoxy, cycloalkoxy and aryloxy. The group R may also optionally have various
20 substituents that do not adversely affect the properties of the resulting complex, such as sulfonic acid group, halogen, amino, nitro, hydroxyl, carbonyl, etc. Examples of the organic phosphorus-containing ligands include, but are not limited to, phosphite ligand, triarylphosphine ligand, trialkylphosphine ligand, and alkylarylphosphine ligand, etc., such as
25 triphenylphosphine ligand, tributylphosphine ligand, tri-tert-butylphosphine ligand, tricyclohexylphosphine ligand, sec-butyldiphenylphosphine ligand, di-tert-butylneopentylphosphine ligand, trioctylphosphine ligand etc..

In the present application, the term "cobalt-phosphine complex" refers broadly to a variety of cobalt complexes containing an organic phosphorus-
30 containing ligand, wherein the organic phosphorus-containing ligand is as defined above. For example, the cobalt-phosphine complex may be cobalt complex containing various phosphine ligands known in the art (such as

triphenylphosphine ligand, tributylphosphine ligand, tri-tert-butylphosphine ligand, etc.). In particular, when used as a hydroformylation catalyst, the cobalt-phosphine complex preferably also contains a carbonyl ligand in addition to the organic phosphorus-containing ligand.

5 In the present application, the term "organic phosphorus-containing ligand compound" refers to a compound capable of obtaining a metal complex comprising a metal and the above-mentioned organic phosphorus-containing ligand by reacting with a metal source.

10 In the present application, the "heavy matter" refers to the product obtained by a further reaction between the oxygen-containing organic compounds or between the oxygen-containing organic compound and other compounds, especially refers to a reaction product derived from at least two molecules of the oxygen-containing organic compound, i.e. a reaction product obtained by at least two molecules of the oxygen-containing organic
15 compound through one or more chemical reaction processes, such as an acetal compound, a hydroxyaldehyde compound, an ether compound, an ester compound etc. or a combination thereof obtained by aldol condensation reaction, acetalization reaction, etherification reaction, oxidation reaction, esterification reaction, etc. . For example, when C8
20 olefin is used as the raw material, the heavy matter may be an acetal compound, a hydroxyaldehyde compound, an ether compound, an ester compound, etc. or their combinations, obtained by at least two molecules of C9 aldehyde and/or C9 alcohol through one or more chemical reaction processes.

25 In the present application, except as explicitly stated, any matters or items not mentioned are directly applicable to those known in the art without the need for any changes. Moreover, any embodiments described herein can be freely combined with one or more other embodiments described herein, and the technical solutions or technical ideas formed thereby are regarded
30 as a part of the original disclosure or original record of the present application and shall not be regarded as new contents that have not been disclosed or expected in this description, unless those skilled in the art

believe that the combination is obviously unreasonable.

All patent and non-patent documents mentioned herein, including but not limited to textbooks and journal articles, are incorporated by reference in their entirety.

5 As described above, the present application provides a process for preparing an oxygen-containing organic compound through hydroformylation reaction, including the following steps:

1) hydroformylation is carried out by contacting an organic compound having 2 to 60 carbon atoms and at least one carbon-carbon double bond
10 with a syngas containing CO and H₂ in the presence of a hydroformylation catalyst and a first reaction temperature to obtain a reaction mass containing the oxygen-containing organic compound and heavy matter, wherein the oxygen-containing organic compound is an alcohol, an aldehyde or a combination thereof that have one more carbon atom than the organic
15 compound having a carbon-carbon double bond, the first reaction temperature being 60-150 °C; and

2) in the presence of syngas containing CO and H₂ and at the second reaction temperature, the reaction mass obtained in step 1) is continued to react, so that the heavy matter therein is(are) decomposed, and a reaction
20 product with a reduced content of the heavy matter and an increased content of oxygen-containing organic compound is obtained, wherein the second reaction temperature is 140-200 °C, and the second reaction temperature is higher than the first reaction temperature by 20-100 °C.

In a preferred embodiment, the first reaction temperature in step 1) is
25 100-145 °C, the second reactant temperature in step 2) is 170-200 °C, and the second reaction temperature is higher than the first reaction temperature by 30-70 °C, preferably by 40-60 °C.

The inventor of the present application has found during research that according to the two-stages reaction process of the present application, the
30 hydroformylation reaction in step 1) is carried out at a lower temperature and in the presence of syngas, which not only produces the target oxygen-containing organic compound, but also produces heavy matter formed by at

least two molecules of the oxygen-containing organic compound through one or more chemical reaction processes; while the reaction in step 2) is carried out at a higher temperature and in the presence of syngas, which can make the heavy matter be re-decomposed into the target oxygen-containing organic compound, but the by-product alkane basically does not increase during the reaction process of step 2), thereby significantly reducing the content of heavy matter in the final product, reducing the alkane selectivity and increasing the alcohol selectivity.

In a preferred embodiment, the reaction conditions of step 1) include: reaction temperature is 60-150 °C, preferably 100-145 °C, more preferably from 100 °C to less than 130°C; reaction pressure is 1-12MPa, preferably 2-10MPa; and reaction time is 1-60 h, preferably 2-25 h.

In a preferred embodiment, the reaction conditions of step 2) include: reaction temperature is 140-200 °C, preferably 170-200 °C; reaction pressure is 1-12MPa, preferably 2-10MPa; and reaction time is 1-40h, preferably 2-25 h.

In some preferred embodiments, the ratio of the molar amount of syngas to the molar amount of organic compound having a carbon-carbon double bond in step 1) of the process of the present application is (0.1-12):1, preferably (3-6): 1, wherein the molar amount of the syngas is the sum of the molar amounts of each gas in the syngas.

In a particularly preferred embodiment, steps 1) and 2) are performed in a syngas atmosphere. At this time, the amount of CO and H₂ in the reaction system is significantly excessive compared to the required amount for the reaction.

In a preferred embodiment, the reaction time of step 1) is longer than the reaction time of step 2). Further preferably, the reaction temperature in step 1) is lower than 130 °C, thereby further reducing the alkane selectivity.

In the present application, there is no particular limitations on the hydroformylation catalyst, as long as it can effectively catalyze the hydroformylation reaction of the organic compound having a carbon carbon double bond to generate aldehyde. In a preferred embodiment, the

hydroformylation catalyst is a transition metal complex catalyst suitable for catalyzing the hydroformylation reaction of olefins.

In a further preferred embodiment, the transition metal in the transition metal complex is selected from Group VIII metals, more preferably selected from rhodium (Rh), cobalt (Co), iridium (Ir), ruthenium (Ru) or their combination, more preferably selected from rhodium, cobalt, or their combination, particularly preferably cobalt.

In a further preferred embodiment, the transition metal complex comprises a carbonyl ligand, an organic phosphorus-containing ligand or a combination thereof, wherein the organic phosphorus-containing ligand is as defined above. Preferably, the organic phosphorus-containing ligand has a general formula PR_3 , wherein each group R is independently selected from a hydrocarbyl group, an hydrocarbyloxy group and a heterocyclic group, preferably is independently selected from alkyl, cycloalkyl, aryl, alkoxy, cycloalkoxy and aryloxy. The group R may also optionally have various substituents that do not adversely affect the properties of the resulting complex, such as sulfonic acid group, halogen, amino, nitro, hydroxyl, carbonyl, etc. Particularly preferably, the organic phosphorus-containing ligand is selected from phosphite ester ligand, triarylphosphine ligand, trialkylphosphine ligand, alkylarylphosphine ligand or a combination thereof, for example, selected from triphenylphosphine ligand, tributylphosphine ligand, tri-tert-butylphosphine ligand, tricyclohexylphosphine ligand, sec-butyldiphenylphosphine ligand, di-tert-butylneopentylphosphine ligand, trioctylphosphine ligand, or a combination thereof.

In a preferred embodiment of the process of the present application, the hydroformylation catalyst is used in the form of a solution of the transition metal complex in an organic solvent, and the concentration by mass of the transition metal in the solution is preferably 0.01-3 %, more preferably 0.2-2%. In the present application, there is no particular limitations on the organic solvent, as long as it can dissolve the transition metal complex and has no adverse effect on the hydroformylation reaction. Preferably, the

organic solvent is selected from alkanes, aromatic hydrocarbons, alcohols, ethers, aldehydes, ketones, nitriles, esters or a combination thereof, more preferably selected from alcohols, aldehydes or a combination thereof, particularly preferably selected from alcohols or aldehydes having the same
5 number of carbon atoms as the oxygen-containing organic compound as the target product.

In a further preferred embodiment, the transition metal complex is a cobalt complex comprising organic phosphorus-containing ligands (also referred to herein as a "cobalt-phosphine complex"), and the
10 hydroformylation catalyst is used in the form of a solution of the cobalt complex. Preferably, the concentration by mass of cobalt in the cobalt complex solution is 0.01-3%, preferably 0.2-2%, more preferably 0.3-1.5%, wherein the concentration by mass of cobalt = (mass of cobalt / mass of catalyst solution) $\times$ 100%; more preferably, in the cobalt complex solution,
15 the mass ratio of cobalt element to phosphorus element is (0.1-10):1, preferably (0.1-3):1, more preferably (0.2-2):1, most preferably (0.3-1):1. In a further preferred embodiment, the cobalt complex further contains a carbonyl ligand.

In a further preferred embodiment, the process of the present
20 application further includes a step of pretreating the hydroformylation catalyst in the form of a cobalt complex solution in the presence of a syngas containing CO and H₂ before step 1), preferably the pretreatment conditions include: temperature is 50-150 °C, preferably 75-130 °C; pressure is 0.1-12MPa, preferably 1-9 MPa, more preferably 3-8 MPa; pre-treatment time
25 is 0.1-10 h, preferably 1-3 h. In this preferred embodiment, the pretreatment step is beneficial to the formation of active unit of the hydroformylation catalyst, reduces catalyst decomposition, improves the activity and stability of the catalyst, and extends the service life of the catalyst.

In a particularly preferred embodiment, the cobalt complex solution is
30 obtained by contacting cobalt-containing raw materials with the organic phosphorus-containing ligand compound in the presence of an organic solvent, wherein the cobalt-containing raw materials are selected from

cobalt salts, cobalt oxides or their combination, preferably selected from cobalt carbonate, cobalt nitrate, cobalt acetate, cobalt levulinate, cobalt formate, dicobalt octacarbonyl, cobalt naphthenate or their combination; the organic phosphorus-containing ligand compound is as above defined.

5 Preferably, the organic phosphorus-containing ligand compound is a compound containing phosphorus and a group bonded to the phosphorus and selected from a hydrocarbyl group, a hydrocarbyloxy group, a heterocyclic group or a combination thereof, and more preferably is a compound of general formula PR_3 , wherein each group R is independently selected from

10 hydrocarbyl group, hydrocarbyloxy group and heterocyclic groups, preferably independently selected from alkyl, cycloalkyl, aryl, alkoxy, cycloalkoxy and aryloxy. Particularly preferably, the organic phosphorus-containing ligand compound is selected from phosphite ester, triarylphosphine, trialkylphosphine, alkylarylphosphine or a combination

15 thereof, for example, selected from triphenylphosphine, tributylphosphine, tri-tert-butylphosphine, tricyclohexylphosphine, sec-butylidiphenylphosphine, di-tert-butylneopentylphosphine, trioctylphosphine, or a combination thereof. Preferably, the conditions for the contact reaction include: temperature is 80-180 °C, preferably 100-150

20 °C; pressure is 0.1-6MPa, preferably 1-4MPa; time is 0.5-24h, preferably 1-15h. More preferably, the contact reaction is carried out in the presence of CO, in particular in the presence of syngas containing CO and H₂.

According to the present application, the organic compound having a carbon-carbon double bond used as a raw material for the hydroformylation

25 reaction can be a variety of organic compounds having at least one carbon-carbon double bond in the carbon chain, and the position of the carbon-carbon double bond can be at the end of the carbon chain or in the middle of the carbon chain, and the organic compound can have a hydroxyl group, an aromatic ring, etc. In a preferred embodiment, the organic compound

30 having a carbon-carbon double bond is a hydrocarbon compound, such as an olefin. In a further preferred embodiment, the organic compound having a carbon-carbon double bond is an olefin having 3-60 carbon atoms, further

preferably an olefin having 4-30 carbon atoms, even more preferably an olefin having 6-20 carbon atoms, particularly preferably an olefin having 8 to 12 carbon atoms. The olefin may be a linear olefin, a branched olefin, a cyclic olefin, or mixed olefins containing any two or three of them, and the branched olefin may have one or more branches. Most preferably, the olefin is C8 olefin, such as an olefin selected from 1-octene and its various isomers, such as 2,4,4-trimethyl-1-pentene, 2,4,4-trimethyl-2-pentene, 3,4,4-trimethyl-2-pentene, 2,3,3-trimethyl-1-pentene, 5,5-dimethyl-2-hexene, 3,5-dimethyl-2-hexene, 2,4-dimethyl-2-hexene, 2,3-dimethyl-3-hexene and 3,4-dimethyl-2-hexene. Generally, trimethylpolybranched olefins are more difficult to hydroformylate than the olefins with fewer branches due to their large steric hindrance.

In a particularly preferred embodiment, step 1) of the process of the present application includes: in the presence of a solution of the cobalt complex and at the first reaction temperature, contacting C8 olefin with the syngas to perform hydroformylation reaction to obtain a reaction mass containing the oxygen-containing organic compound and heavy matter.

In a preferred embodiment, in step 1) of the process of the present application, the dosage ratio of the transition metal complex solution used as a hydroformylation catalyst to the organic compound with carbon carbon double bonds by mass is (0.1-10):1, preferably (2-5):1.

In a preferred embodiment, the molar ratio of carbon monoxide to hydrogen in the syngas containing CO and H₂ used in each step of the process of the present application is independently 10:1 to 1:10, preferably 4:1 to 1: 4, more preferably 3:1 to 1:3, such as 3:1 to 1:1, or 1:2 to 1:3. In each step, such as step 1) and step 2), the ratio of CO to H₂ in the syngas used can be the same or different, which facilitates the adjustment of the ratios between organic compound having a carbon-carbon double bond to CO, H₂ in each step to achieve the optimal ratio and is beneficial to achieve a better conversion rate and a better selectivity.

The inventor of the present application unexpectedly discovered that in step 1), using a syngas with a higher molar ratio of carbon monoxide to

hydrogen, such as CO/H₂ molar ratio of 3:1 to 1:1, can increase the aldehyde content in the reaction product of step 1), although at this time, the amount of carbon monoxide and hydrogen in the syngas is still significantly excessive for the reaction in step 1). Therefore, when aldehyde is the target product, it is advantageous to adopt such an embodiment because the aldehyde product can be separated from the reaction product of step 1) after the reaction of step 1), thereby increasing the yield of the target aldehyde product.

In addition, the inventor of the present application also unexpectedly discovered that when part of the original organic compounds remains in the reaction product of step 1), the aldehyde content in the product is higher; but when the conversion rate of the original organic compounds is higher or the original organic compounds is completely converted, the aldehyde content in the product is significantly reduced. Therefore, by controlling the conversion rate of the raw materials of step 1) to < 100%, in particular, controlling the conversion rate of the raw materials of step 1) to < 95%, and after the reaction of step 1), separating the unreacted original organic compounds from the reaction product of step 1) and recycling them back to step 1) for further reaction can increase the aldehyde yield of the reaction in step 1).

In the present application, there are no special restrictions on the reactor for carrying out the reactions of steps 1) and 2), as long as the reaction can be carried out and the temperature can be freely controlled. In a preferred embodiment, the reaction of step 1) and the reaction of step 2) are carried out in the same or different tubular reactors, more preferably the process is carried out in a continuous manner, and the reaction of step 1) and the reaction of step 2) are carried out in different tubular reactors or in different zones of the same tubular reactor. During the reaction process, it is possible that the reaction raw materials (such as olefin, syngas and catalyst solution) flow in from the lower part of the tubular reactor, and the reaction products flow out from the upper part of the tubular reactor; or it is also possible that the reaction raw materials flow in from the upper part of

the tubular reactor, and the reaction products flow out from the lower part of the tubular reactor.

In some preferred embodiments, the reaction in step 2) is performed with the addition of water.

5 In other preferred embodiments, the reaction in step 2) is performed without adding water.

In certain embodiments, the process of the present application further includes, before step 2): separate the reaction mass obtained in step 1) to separate the oxygen-containing organic compound such as aldehyde from
10 the reaction mass, and then let the separated residue to continue to react in step 2).

In a preferred embodiment, the process of the present application further includes, after step 2):

3) separate the reaction product obtained in step 2) to obtain light
15 components including the oxygen-containing organic compound and heavy components including the hydroformylation catalyst and optional residual heavy matter; and

4) return at least part of the heavy components obtained in step 3) to step 1) for further reaction.

20 According to the present application, after the reaction in step 2) is completed, part of the organic oxygen-containing compound products (such as alcohols and aldehydes), the by-product alkanes and the unreacted original organic compound can be separated from the crude reaction products (such as through distillation), and the remaining catalyst-
25 containing materials are recycled to step 1) for further reaction. Or alternatively, the remaining catalyst-containing materials are recycled to the pretreatment step, and then are returned to step 1) for further reaction after the pretreatment.

In a preferred embodiment, in step 4), the recycled heavy components
30 contain 0.1-99.9 wt%, preferably 3-70 wt%, more preferably 3-30 wt% of the heavy matter.

In certain preferred embodiments, the process of the present application

may also include hydrogenating the separated oxygen-containing organic compound product, thereby obtaining alcohol in high yield.

In certain preferred embodiments, the process of the present application is performed in a continuous manner and includes the following steps:

- 5 i) in the presence of the hydroformylation catalyst and at the first reaction temperature, the C8 olefin is subjected to a hydroformylation reaction in a syngas atmosphere containing CO and H₂, to obtain the first stream containing C9 aldehyde and C9 alcohol, the first stream also contains heavy matter;
- 10 ii) in the syngas atmosphere containing CO and H₂ and at the second reaction temperature, the first stream obtained in step i) is continued to react, so that the heavy matter in the first stream is decomposed to obtain a second stream with reduced heavy matter content;
- iii) the second stream is separated to obtain light components and heavy
15 components, the light components contain C9 alcohol, C9 aldehyde and C8 alkane, and the heavy components contain the hydroformylation catalyst and optional residual heavy matter; and
- iv) at least part of the heavy components is recycled back to step i) to perform the hydroformylation reaction;
- 20 preferably, in step iii), the separation can be performed firstly by gas-liquid separation, and then by distillation separation.

In further preferred embodiment, the gas-liquid separation is carried out under the conditions of cooling but not reducing pressure in the gas-liquid separation tank, the gas-liquid separation temperature being 0-100 °C,
25 preferably 20-80 °C, and more preferably 20-40 °C.

In a further preferred embodiment, the gas phase stream obtained after gas-liquid separation is essentially syngas; after condensation and/or absorption, the remaining syngas can be recycled to the pretreatment reactor and/or the inlet of the reactor used in step i) to be reused.

30 The liquid phase stream after gas-liquid separation can be distilled and separated by a distillation device; the top discharge is a mixed product containing C9 alcohol, C8 alkane and C9 aldehyde, and the heavy

components containing the hydroformylation catalyst, and solvent are obtained at the bottom.

In a preferred embodiment, in step iv), the amount of the heavy components recycled back to step i) accounts for 0.1-90 wt% of all the heavy components obtained in step iii), preferably 0.1-40 wt%, more preferably 0.1-20 wt%. Further preferably, the heavy components recycled back to step i) contain a certain amount of the heavy matter, for example, 0.1-99.9wt%, preferably 3-70 wt%, more preferably 3-30 wt% of heavy matter, relative to the mass of the recycled heavy components. The inventor of the present application has unexpectedly discovered that including a certain amount of heavy matter in the recycled heavy components can increase the solubility of the catalyst, which is beneficial to reducing the reaction temperature and alkane selectivity of step i).

In a preferred embodiment, when the heavy components are returned to the reactor used in step i) and/or the pretreatment reactor inlet to participate in the hydroformylation reaction, a small amount of fresh catalyst can be added as needed.

In a particularly preferred embodiment, the process of the present application is carried out in a continuous manner and includes the following steps:

A) introduce the solution of cobalt complex catalyst containing organic phosphorus-containing ligand and the C8 olefin into the first tubular reactor, and perform the hydroformylation reaction at the first reaction temperature and in a syngas atmosphere;

B) let the reaction product obtained in step A) enter the second tubular reactor for further reaction at the second reaction temperature and in a syngas atmosphere;

C) separate the reaction product obtained in step B) to obtain light components and heavy components, wherein the light components include C9 alcohol, C9 aldehyde and C8 alkane, and the heavy components include the cobalt complex catalyst; and

D) return at least part of the heavy components obtained in step C) to

the inlet of the first tubular reactor for recycling.

In the above particularly preferred embodiment, in step A), C8 olefin is firstly converted into C8 alkane, C9 aldehyde, C9 alcohol and heavy matter at a lower reaction temperature; then, in step B), at a higher reaction temperature, the heavy matter is converted into C9 alcohol. Analysis shows that the hydroformylation reaction in step A) obtains a reaction product containing heavy matter; and through the reaction in step B), the heavy matter is unexpectedly re-decomposed into products such as C9 alcohol, while essentially no C8 alkane is produced.

It is further preferred that a part of the heavy components obtained in step C) is discarded from the reaction system; it is particularly preferred that this part of the heavy components is sent to the downstream reaction unit before being discarded from system, and syngas is injected into the downstream reaction unit but no original organic compound is introduced into it; this part of the heavy components are post-treated at higher temperature, in which the residual heavy matter will be decomposed into products such as C9 alcohol; this not only further increases the yield of the target product, but also significantly reduces the amount of the discarded materials, thereby significantly reducing waste liquid emissions and alleviating environmental issues in the hydroformylation process.

The process for preparing an oxygen-containing organic compound through hydroformylation reaction of the present application has one or more of the following advantages:

1. significantly reduce alkane selectivity, improve alcohol selectivity, and significantly improve the economic benefits of the process;

2. by re-decomposing the heavy matter into products such as alcohol in the reaction of the second step, the alcohol selectivity can be improved, the amount of discarded materials can be significantly reduced, and waste liquid emissions can be reduced, which is beneficial to environmental protection and has industrial prospects;

3. the process is suitable for a wide range of raw materials, especially for the hydroformylation reaction of multi-branched olefins with high steric

hindrance; the reaction pressure is low, and the investment of equipment and the processing cost are significantly reduced;

4. a cobalt catalyst that is cheaper than a rhodium catalyst can be used in the hydroformylation reaction in the first step, and the temperature of the hydroformylation reaction in the first step is significantly lowered, which is beneficial to the stability of the cobalt catalyst;

5. in the preferred embodiment, the pretreatment process of the catalyst can reduce the decomposition of the cobalt complex catalyst, facilitate the formation of active units of the cobalt complex catalyst, improve the activity and stability of the catalyst, and extend the service life of the catalyst;

6. in some preferred embodiments, extending the reaction time of the second step can reduce the aldehyde content in the reaction product of the second step to < 0.1 wt%, which is advantageous when alcohol is the target product because subsequent hydrogenation step to convert aldehydes to alcohols can be omitted.

7. by changing the composition of the syngas used in the hydroformylation reaction in the first step, the ratio of alcohol to aldehyde in the reaction product of the first step can be adjusted, and more aldehydes can be produced as needed, which is beneficial for product diversification.

Example

The present application will be further described below through examples, but the present application is not subject to any limitations thereby.

In the following examples and comparative examples, unless otherwise specified, the raw materials used are all commercially available products with industrial purity.

In the following Examples 1 to 5 and Comparative Examples 1 to 2, the olefin raw materials used are commercially available C8 olefins, and the composition is: 75.1wt% of 2,4,4-trimethyl-1-pentene, 21.2wt% of 2,4,4-trimethyl-2-pentene, the rest are multi-branched olefins; the CO/H₂ molar ratio in the syngas used is 1:2.

In the following examples and comparative examples, the calculation formula of the conversion rate of the raw materials is as follows:

Raw materials conversion rate = $[1 - (\text{total mass of 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene in the reaction product}) / (\text{the total mass of 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene})] \times 100\%$.

Catalyst Preparation Example 1

In a reaction kettle, cobalt naphthenate and triphenylphosphine were dissolved in isononanol in amounts such that the cobalt element content in the resulting solution was 0.13 wt% and the content of phosphorus element was 0.07 wt%; the air was replaced by syngas, and syngas was charged until the pressure was 1.7 Mpa; after the reaction was conducted at 140 °C for 9 hours under stirring at 400 rpm, a cobalt-phosphine complex solution was obtained, and was recorded as catalyst solution A1, of which the composition was shown in Table 1.

Catalyst Preparation Example 2

In a reaction kettle, cobalt naphthenate and triphenylphosphine were dissolved in isononanol in amounts such that the cobalt element content in the resulting solution was 0.1 wt% and the content of phosphorus element was 0.06 wt%; the air was replaced by syngas, and syngas was charged until the pressure was 1.8 Mpa; after the reaction was conducted at 140 °C for 9 hours under stirring at 400 rpm, a cobalt-phosphine complex solution was obtained, and was recorded as catalyst solution A2, of which the composition was shown in Table 1.

Catalyst Preparation Example 3

In a reaction kettle, cobalt naphthenate and triphenylphosphine were dissolved in isononanol in amounts such that the cobalt element content in the resulting solution was 0.077 wt% and the phosphorus element content was 0.069 wt%; the air was replaced by syngas, and syngas was charged until the pressure was 2Mpa; after the reaction was conducted at 140 °C for

9 hours under stirring at 400 rpm, a cobalt-phosphine complex solution was obtained, and was recorded as catalyst solution A3, of which the composition was shown in Table 1.

5 Catalyst Preparation Example 4

In a reaction kettle, cobalt naphthenate and triphenylphosphine were dissolved in isononanol in amounts such that the cobalt element content in the resulting solution was 0.11 wt% and the phosphorus element content was 0.07 wt%, the air was replaced by syngas, and syngas was charged until the
10 pressure was 2Mpa; after the reaction was conducted at 140 °C for 9 hours under stirring at 400 rpm, a cobalt-phosphine complex solution was obtained, and was recorded as catalyst solution A4, of which the composition was shown in Table 1.

15 Catalyst Preparation Example 5

In a reaction kettle, cobalt naphthenate and triphenylphosphine were dissolved in isononanol in amounts such that the cobalt element content in the resulting solution was 0.1 wt% and the phosphorus content was 0.1 wt%; the air was replaced by syngas, and syngas was charged until the pressure
20 was 3 MPa; after the reaction was conducted at 110 °C for 20 hours under stirring at 400 rpm, a cobalt-phosphine complex solution was obtained, and was recorded as catalyst solution A5, of which the composition was shown in Table 1.

25 Table 1 Composition of catalyst solutions A1 to A4

	complex		Solvent
	cobalt	phosphorus	
A1	0.13wt%	0.07wt%	isononanol
A2	0.10wt%	0.06wt%	isononanol
A3	0.077wt%	0.069wt%	isononanol
A4	0.11wt%	0.07wt%	isononanol
A5	0.1wt%	0.1wt%	isononanol

Example 1

Catalyst solution A1 (it was recycled during the reaction) and syngas were charged into the pretreatment reactor. The temperature of the pretreatment reactor was 125 °C, the pressure was 8MPa, and the pretreatment time was 0.5h. The pretreated catalyst solutions A1 and the C8 olefin were introduced into the first tubular reactor at a ratio of 83g : 30g; the temperature of the first tubular reactor was 120 °C and the pressure was 8MPa. Syngas was introduced into the reactor to conduct the reaction for 15 hours. After the reaction, the product was analyzed by chromatography, and the results were shown in Table 2-1.

The effluent materials from the first tubular reactor entered the second tubular reactor. The temperature of the second tubular reactor was 153-155 °C and the pressure was 8MPa. Syngas was introduced into the reactor to conduct the reaction for 4 hours. After the reaction, the product was analyzed by chromatography, and the results were shown in Table 2-1.

Table 2-1 Reaction results of Example 1

	2,2,4-trimethylpentane	heavy matter	isonononal	isononanol	conversion rate of raw materials
Step 1) Product	2.5 wt%	47.4wt%	11.3 wt%	35.7wt%	92.8 wt%
Step 2) Product	2.6 wt%	18.9wt%	9 wt%	68.8wt%	99.7 wt%

As shown in Table 2-1, compared with the product of step 1), the content of heavy matter in the product of step 2) is reduced, and the reduced heavy matter is essentially converted into isononanol, while the amount of the by-product 2,2,4-trimethylpentane remains essentially unchanged. Moreover, through step 2), the conversion rate of the raw materials is increased from 92.8 wt% to 99.7 wt%, essentially achieving complete conversion of the raw materials.

Comparative Example 1

The experiment was carried out with reference to Example 1, except

that the temperature of the second tubular reactor was 120°C, the pressure was 8MPa, and the synthesis gas was introduced to conduct the reaction for 4 hours. After the reaction, the product was analyzed by chromatography. The results show that, compared with the product of step 1), the content of heavy matter in the product of step 2) increased by 1 wt%, while the content of isononanol was essentially the same as that of the product of step 1). This showed that when reaction in the second tubular reactor was conducted at a lower temperature, the heavy matter could not be well converted into isononanol, but its content was increased.

Example 2

Catalyst solution A2 (it was recycled during the reaction) and syngas were charged into the pretreatment reactor. The temperature of the pretreatment reactor was 150 °C, the pressure was 8MPa, and the pretreatment time was 0.5h. The pretreated catalyst solutions A2 and the C8 olefin were introduced into the first tubular reactor at a ratio of 83g : 30g; the temperature of the first tubular reactor was 150 °C and the pressure was 8MPa. Syngas was introduced into the reactor to conduct the reaction for 12 hours. After the reaction, the product was analyzed by chromatography, and the results were shown in Table 2-2.

The effluent materials from the first tubular reactor entered the second tubular reactor. The temperature of the second tubular reactor was 180 °C and the pressure was 8MPa. Syngas was introduced into the reactor to conduct the reaction for 2 hours. After the reaction, the product was analyzed by chromatography, and the results were shown in Table 2-2.

Table 2-2 Reaction results of Example 2

	2,2,4-trimethylpentane	heavy matter	isononanal	isononanol	conversion rate of raw materials
Step 1) Product	3.2 wt%	20.7 wt%	3.4 wt%	69.3 wt%	91.6 wt%
Step 2) Product	3.3 wt%	8 wt%	0.5 wt%	87.1 wt%	99.7 wt%

As shown in Table 2-2, compared with the product of step 1), the content of heavy matter in the product of step 2) is reduced, and the reduced heavy matter is essentially converted into isononanol, while the amount of the by-product 2,2,4-trimethylpentane remains essentially unchanged. Moreover, through step 2), the conversion rate of the raw materials is increased from 91.6 wt% to 99.7 wt%, essentially achieving complete conversion of the raw materials.

Comparative Example 2

The experiment was carried out with reference to Example 2, except that the temperatures of the first and second tubular reactors were both 180 °C. After the reaction, the product was analyzed by chromatography. The results show that the content of the by-product 2,2,4-trimethylpentane in the final product of Comparative Example 2 was as high as 7wt%, and the content of 2,2,4-trimethylpentane was significantly increased.

Example 3

Catalyst solution A3 (it was recycled during the reaction) and syngas were charged into the pretreatment reactor. The temperature of the pretreatment reactor was 130 °C, the pressure was 8MPa, and the pretreatment time was 0.5h. The pretreated catalyst solutions A3 and the C8 olefin were introduced into the first tubular reactor at a ratio of 330g : 30g; the temperature of the first tubular reactor was 130 °C and the pressure was 8MPa. Syngas was introduced into the reactor to conduct the reaction for 8 hours. After the reaction, the product was analyzed by chromatography, and the results were shown in Table 2-4.

The effluent materials from the first tubular reactor entered the second tubular reactor. The temperature of the second tubular reactor was 155 °C and the pressure was 8MPa. Syngas was introduced into the reactor to conduct the reaction for 5 hours. After the reaction, the product was analyzed by chromatography, and the results were shown in Table 2-3.

Table 2-3 Reaction results of Example 3

	2,2,4-trimethylpentane	heavy matter	isonononal	isononanol	conversion rate of raw materials
Step 1) Product	1.1 wt%	59.6 wt%	5.9 wt%	31.3 wt%	88.3 wt%
Step 2) Product	1.4 wt%	49.3 wt%	0.7 wt%	47.6 wt%	98.9 wt%

As shown in Table 2-3, compared with the product of step 1), the content of heavy matter in the product of step 2) is reduced, and the reduced heavy matter is essentially converted into isononanol, while the amount of the by-product 2,2,4-trimethylpentane remains essentially unchanged. Moreover, through step 2), the conversion rate of raw materials is increased from 88.3 wt% to 98.9 wt%, essentially achieving complete conversion of raw materials.

Example 4

The experiment was carried out with reference to Example 1, except that catalyst solution A4 was used instead of catalyst solution A1, the reaction time in the first tubular reactor was 23h, and the temperature of the second tubular reactor was 150 °C, the pressure of the second tubular reactor was 8MPa, and 2.5wt% water was added and syngas was introduced to conduct the reaction for 5 hours. After the reaction, the product was analyzed by chromatography. The results were shown in Tables 2-4.

Table 2-4 Reaction results of Example 4

	2,2,4-trimethylpentane	heavy matter	isonononal	isononanol	conversion rate of raw materials
Step 1) Product	2.0 wt%	16.7 wt%	7.9 wt%	70.9 wt%	91.8 wt%
Step 2) Product	2.2 wt%	14.9 wt%	1.3 wt%	80.9 wt%	99.9 wt%

As shown in Table 2-4, compared with the product of step 1), the content of heavy matter in the product of step 2) is reduced, and the reduced heavy matter is essentially converted into isononanol, while the amount of

the by-product 2,2,4-trimethylpentane remains essentially unchanged. Moreover, through step 2), the conversion rate of raw materials is increased from 91.8wt% to 99.9wt%, essentially achieving complete conversion of raw materials.

5

Example 5

The experiment was carried out with reference to Example 2, except that the reaction temperature of the higher reaction temperature section of the second tubular reaction zone was 180 °C and the pressure was 8Mpa; 10 the reaction was conducted for 2h, and then 3wt% water was added at a reaction temperature of 180 °C under a pressure of 8MPa, and syngas was introduced to conduct the reaction for 2 hours. After the reaction, the product was analyzed by chromatography, and the results were shown in Tables 2-5.

15

Table 2-5 Reaction results of Example 5

	2,2,4-trimethylpentane	heavy matter	isononanal	isononanol	conversion rate of raw materials
Step 1) Product	3.2 wt%	20.7 wt%	3.4wt%	69.3wt%	91.6wt%
Step 2) Product	2.7wt%	5.3 wt%	0.04wt%	91wt%	99.9wt%

As shown in Table 2-5, compared with the product of step 1), the content of heavy matter in the product of step 2) is reduced, and the reduced 20 heavy matter is essentially converted into isononanol, while the content of the by-product 2,2,4-trimethylpentane is slightly reduced, and isononanal can be reduced to < 0.1 wt%. This is advantageous when isononanol is the target product because there is no need for a subsequent hydrogenation step for converting isononanaldehyde into isononanol (the aldehyde content 25 in the isononanol standard needs to be < 0.1 wt%). Moreover, through step 2), the conversion rate of raw materials is increased from 91.6 wt% to 99.9 wt%, essentially achieving complete conversion of the raw materials.

In the following Examples 6 to 8, the olefin raw materials used was commercially available C8 olefin, and its composition is: 64.7wt% of 2,4,4-trimethyl-1-pentene, 18.5 wt% of 2,4,4-trimethyl-2-pentene, and the rest were essentially multi-branched olefins.

5

Example 6

Catalyst solution A5 (it was recycled during the reaction) and syngas (CO/H₂ molar ratio was 1: 2) were added into a pretreatment reactor. The temperature of the pretreatment reactor was 100 °C, the pressure was 8 MPa, and the pretreatment time was 1 h. The pretreated catalyst solution A5 and the C8 olefin were introduced into the first tubular reactor at a ratio of 110 g: 73.4 g. The temperature of the first tubular reactor was 130 °C and the pressure of the first tubular reactor was 8MPa. Syngas (CO/H₂ molar ratio was 1: 2) was introduced to conduct the reaction for 15h. After the reaction, the product was analyzed by chromatography. The results were shown in Tables 2-7.

The effluent materials from the first tubular reactor entered the second tubular reactor. The temperature of the second tubular reactor was 180 °C and the pressure of the second tubular reactor was 8 MPa. Syngas (CO/H₂ molar ratio was 1: 2) was introduced to conduct the reaction for 7h. After the reaction, the product was analyzed by chromatography, and the results were shown in Tables 2-6.

Table 2-6 Reaction results of Example 6

	2,2,4-trimethylpentane	heavy matter	isonononal	isononanol	conversion rate of raw materials
Step 1) Product	5.7wt%	21.6wt%	10.2wt%	45.3wt%	98.2wt%
Step 2) Product	5.8wt%	2.6wt%	0.15wt%	74.2wt%	100wt%

25

As shown in Table 2-6, compared with the product of step 1), the content of heavy matter in the product of step 2) is reduced, and the reduced

heavy matter is essentially converted into isononanol, while the amount of the by-product 2,2,4-trimethylpentane remains essentially unchanged. Moreover, through step 2), the conversion rate of raw materials is increased from 98.2 wt% to 100 wt%, achieving complete conversion of raw materials.

5 At the same time, by extending the reaction time of step 2) to 10 h, the isononanal content in the product can be reduced to 0 wt%; other components don't change much.

Example 7

10 The experiment was carried out with reference to Example 6, except that the CO/H₂ molar ratio of the syngas used in each step was 1:1, the temperature of the second tubular reactor was 180°C, and the pressure was 8Mpa; 1.5wt% water was added and the syngas was introduced to conduct the reaction for 7 h. After the reaction, the product was analyzed by
15 chromatography. The results were shown in Tables 2-7.

Table 2-7 Reaction results of Example 7

	2,2,4-trimethylpentane	heavy matter	Isononanal	isononanol	conversion rate of raw materials
Step 1) Product	3.7wt%	22.6wt%	20.7wt%	33.5wt%	92.4wt%
Step 2) Product	3.3wt%	3wt%	0.1wt%	77wt%	100wt%

As shown in Table 2-7, compared with the product of step 1), the
20 content of heavy matter in the product of step 2) is reduced, and the reduced heavy matter is essentially converted into isononanol, while the amount of the by-product 2,2,4-trimethylpentane is slightly reduced. Moreover, through step 2), the conversion rate of the raw materials is increased from 92.4 wt% to 100 wt%, and the isononanal could be reduced to 0.1 wt%, i.e.
25 the subsequent hydrogenation step of isononanal to isononanol can be omitted, achieving complete conversion of raw materials.

At the same time, by extending the reaction time of step 2) to 10 h, the

isonononal content in the product can be reduced to 0wt%, and other components does not change much.

Example 8

The experiment was carried out with reference to Example 6, except
 5 that the CO/H₂ molar ratio of the syngas used in each step was 2:1, the temperature of the second tubular reactor was 180°C, and the pressure was 8Mpa; 1.5wt% water was added and the syngas was introduced to conduct the reaction for 7 h. After the reaction, the product was analyzed by chromatography. The results were shown in 2-8.

10

Table 2-8 Reaction results of Example 8

	2,2,4-trimethylpentane	heavy matter	isonononal	isononanol	conversion rate of raw materials
Step 1) Product	4.1wt%	27.6 wt%	21.0 wt%	29.5wt%	96.6wt%
Step 2) Product	3.8wt%	4.5wt%	2.5wt%	72.5wt%	100wt%

As shown in Table 2-8, compared with the product of step 1), the content of heavy matter in the product of step 2) is reduced, and the reduced
 15 heavy matter is essentially converted into isononanol, while the amount of the by-product 2,2,4-trimethylpentane is slightly reduced. Moreover, through step 2), the conversion rate of raw materials is increased from 96.6 wt% to 100 wt%, thereby achieving complete conversion of the raw materials.

20 By comparing the data in Tables 2-6 to 2-8, it can be found that, compared with Example 6 wherein the syngas with a CO/H₂ molar ratio being the normal stoichiometric ratio (i.e. CO/H₂=1:2) is used to conduct the reaction, Examples 7 to 8 conduct the reaction under the conditions that the CO/H₂ molar ratio in the syngas is higher than the normal stoichiometric ratio;
 25 under the conditions that the conversion rate of raw materials in step 1) is >95% (such as Example 8), the product of step 1) still contains a higher content of isonononal and the content of alkanes is lower; while in general,

when the olefin conversion rate is high, the aldehyde selectivity is low. This result is unexpected, because the reaction in step 1) is carried out in a syngas atmosphere, so that the amount of carbon monoxide and hydrogen in the reaction system is far excessive compared to that required for the reaction of olefin. In the case that isononanal is the target product, it is more advantageous to adopt the conditions that the molar ratio of CO/H₂ in the syngas is higher than the normal stoichiometric ratio; at this time, the reaction product of step 1) can be separated before step 2) to separate the aldehyde product, thereby increasing the yield of the isononanal product.

It can be seen from the above experimental results that the two-step reaction process of the present application can significantly reduce the alkane selectivity in the preparation of oxygen-containing organic compound through hydroformylation of olefin, and improve the alcohol selectivity.

The preferred embodiments of the present application have been described in detail above, however, the present application is not limited to the specific details in the above-mentioned embodiments. Within the scope of the technical concept of the present application, a variety of simple modifications can be made to the technical solutions of the present application, and all these simple modifications fall within the protection scope of the present application.

In addition, it should be noted that the various the specific technical features described in the above-mentioned specific embodiments can be combined in any suitable manner without contradiction. In order to avoid unnecessary repetition, various possible combinations will not be described further in this application.

In addition, various different embodiments of the present application can also be combined arbitrarily, as long as they do not violate the ideas of the present application, they should also be regarded as the content disclosed in the present application.

Claims

1. A process for preparing an oxygen-containing organic compound through hydroformylation reaction, comprising the following steps:

5 1) an organic compound having 2 to 60 carbon atoms and at least one carbon-carbon double bond is contacted with a syngas containing CO and H₂ in the presence of a hydroformylation catalyst and at a first reaction temperature to conduct hydroformylation reaction to obtain a reaction mass containing the oxygen-containing organic compound and heavy matter,
10 wherein the oxygen-containing organic compound is an alcohol, an aldehyde, or a combination thereof that have one more carbon atom than the organic compound having a carbon-carbon double bond, wherein the first reaction temperature is 60-150°C, preferably 100-145 °C; and

 2) in the presence of syngas containing CO and H₂ and at a second
15 reaction temperature, the reaction mass obtained in step 1) is continued to react, to decompose the heavy matter contained therein, resulting in a reaction product with a decrease in the content of the heavy substances and an increase in the content of the oxygen-containing organic compound, wherein the second reaction temperature is 140-200°C, preferably 170-200
20 °C, and the second reaction temperature is higher than the first reaction temperature by 20-100°C, preferably 30-70 °C, more preferably 40-60 °C.

2. The process according to claim 1, wherein:

 the reaction conditions of step 1) include: reaction temperature is 60-150 °C, preferably 100-145 °C; reaction pressure is 1-12MPa, preferably 2-
25 10MPa; and reaction time is 1-60 h, preferably 2-25 h; and

 the reaction conditions of step 2) include: reaction temperature is 140-200 °C, preferably 170-200 °C; reaction pressure is 1-12MPa, preferably 2-10MPa; and reaction time is 1-40h, preferably 2-25 h;

 preferably, step 1) and step 2) are performed in a syngas atmosphere.

30 3. A process according to any one of the preceding claims, wherein the hydroformylation catalyst is a transition metal complex catalyst,

preferably, the transition metal in the transition metal complex is selected from Group VIII metals, more preferably selected from rhodium (Rh), cobalt (Co), iridium (Ir), ruthenium (Ru) or their combination, more preferably selected from rhodium, cobalt, or their combination, particularly preferably cobalt;

more preferably, the transition metal complex includes a carbonyl ligand, an organic phosphorus-containing ligand, or a combination thereof, the organic phosphorus-containing ligand preferably is a ligand containing phosphorus and a group bonded to phosphorus and selected from hydrocarbyl group, hydrocarbyloxy group, heterocyclic group or their combination, more preferably a ligand of general formula PR_3 , wherein each group R is independently selected from a hydrocarbyl group, an hydrocarbyloxy group and a heterocyclic group, preferably is independently selected from alkyl, cycloalkyl, aryl, alkoxy, cycloalkoxy and aryloxy.

4. The process according to claim 3, wherein the hydroformylation catalyst is used in the form of a solution of the transition metal complex in an organic solvent, and the concentration by mass of the transition metal in the solution is preferably 0.01-3%, more preferably 0.2-2%,

the organic solvent is preferably selected from alkane, aromatic hydrocarbon, alcohol, ether, aldehyde, ketone, nitrile, ester or a combination thereof, more preferably selected from alcohol, aldehyde or a combination thereof, and particularly preferably selected from alcohol or aldehyde having the same number of carbon atoms as the oxygen-containing organic compound.

5. The process according to claim 4, wherein the transition metal complex is a cobalt complex containing the organic phosphorus-containing ligand, and the concentration by mass of cobalt in the cobalt complex solution is 0.01-3%, preferably 0.2-2%, more preferably the cobalt complex also contains a carbonyl ligand.

6. The process according to claim 5, wherein the cobalt complex solution is obtained by contacting and reacting a cobalt-containing raw material with an organic phosphorus-containing ligand compound in the

presence of an organic solvent, wherein the cobalt-containing raw material is selected from cobalt salt, cobalt oxide or a combination thereof, preferably selected from cobalt carbonate, cobalt nitrate, cobalt acetate, cobalt levulinate, cobalt formate, dicobalt octacarbonyl, cobalt naphthenate
5 or a combination thereof; and the organic phosphorus-containing ligand compound is a compound containing phosphorus and a group bonded to the phosphorus and selected from a hydrocarbyl group, a hydrocarbyloxy group, a heterocyclic group or a combination thereof, and more preferably is a compound of a general formula PR_3 , wherein each group R is independently
10 selected from hydrocarbyl group, hydrocarbyloxy group and heterocyclic group, preferably independently selected from alkyl, cycloalkyl, aryl, hydrocarbyloxy, cycloalkoxy and aryloxy;

preferably, the conditions for the contact reaction include: temperature is 80-180 °C, preferably 100-150 °C; pressure is 0.1-6MPa, preferably 1-
15 4MPa; time is 0.5-24h, preferably 1-15 h;

more preferably, the contact reaction is carried out in the presence of CO, in particular in the presence of syngas containing CO and H₂.

7. The process according to claim 5 or 6, wherein the process further comprises a step of pretreating the hydroformylation catalyst in the presence
20 of syngas containing CO and H₂ before step 1), preferably, the pretreatment conditions include: temperature is 50-150°C, preferably 75-130°C; pressure is 0.1-12MPa, preferably 1-9MPa, more preferably 3-8MPa; pretreatment time is 0.1-10 h, preferably 1-3 h.

8. The process according to any one of the preceding claims, wherein
25 the organic compound having a carbon-carbon double bond is an olefin having from 3 to 60 carbon atoms, preferably an olefin having from 4 to 30 carbon atoms, more preferably an olefin having from 6 to 20 carbon atoms, particularly preferably an olefin having from 8 to 12 carbon atoms, most preferably an C8 olefin.

30 9. The process according to claim 6, wherein step 1) includes: contacting an C8 olefin with the syngas to perform hydroformylation reaction in the presence of the cobalt complex solution and at the first

reaction temperature to obtain a reaction mass containing the oxygen-containing organic compound and heavy matter,

preferably, the C8 olefin is selected from 1-octene and its various isomers, such as 2,4,4-trimethyl-1-pentene, 2,4,4-trimethyl-2-pentene, 5 3,4,4-trimethyl-2-pentene, 2,3,3-trimethyl-1-pentene, 5,5-dimethyl-2-hexene, 3,5-dimethyl-2-hexene, 2,4-dimethyl-2-hexene, 2,3-dimethyl-3-hexene and 3,4-dimethyl-2-hexene.

10 10. The process according to any one of claims 4-7 and 9, wherein, the dosage ratio by mass of the transition metal complex solution used as a hydroformylation catalyst in step 1) to the organic compound having a carbon-carbon double bond is (0.1-10):1, preferably (2-5):1.

11. The process according to any one of the preceding claims, wherein the molar ratio of carbon monoxide to hydrogen in the syngas containing CO and H₂ used in each step is independently 10:1 to 1:10, preferably 4:1 to 15 1:4, more preferably 3:1 to 1:3.

12. The process according to any one of the preceding claims, wherein the reaction of step 1) and the reaction of step 2) are carried out in the same or different tubular reactors, preferably the process is carried out in a continuous manner, and the reaction of step 1) and the reaction of step 2) 20 are carried out in different tubular reactors or in different zones of the same tubular reactor.

13. The process according to any one of the preceding claims, wherein the process further comprises before step 2): separating the reaction mass obtained in step 1) to separate the oxygen-containing organic compound 25 therefrom, and then continuing the reaction of the separated residue in step 2).

14. The process according to any one of the preceding claims, wherein the process further comprises after step 2):

3) separating the reaction product obtained in step 2) to obtain a light 30 component containing the oxygen-containing organic compound and a heavy component containing the hydroformylation catalyst and optional residual heavy matter; and

4) returning at least part of the heavy component obtained in step 3) to step 1) for further reaction, preferably, the recycled heavy component contains 0.1-99.9 wt%, preferably 3-70 wt%, more preferably 3-30 wt% of the heavy matter.

- 5 15. The process according to any one of the preceding claims, wherein the reaction in step 2) is carried out with the addition of water.