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(71) Applicant: **EASTMAN CHEMICAL COMPANY**
[US/US]; 200 South Wilcox Drive, Kingsport, TN 37660 (US).(72) Inventors: **BOPPANA, Venkata Bharat, Ram**; 5773 McClintock Drive, Denver, NC 28037 (US). **NORMAN, David, William**; 3413 Bailey Ranch Road, Kingsport, TN 37662 (US). **TUSTIN, Gerald, Charles**; 1065 Rotherwood Drive, Kingsport, TN 37660 (US). **STEFFEY, Melissa, Page**; 2291 Addington Frame Road, Nickelsville, VA 24271 (US).(74) Agent: **OWEN, Steven, A.**; P.O. Box 511, Kingsport, TN 37662-5075 (US).

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(54) Title: EFFICIENT SYNTHESIS OF METHACROELIN AND OTHER ALPHA, BETA-UNSATURATED ALDEHYDES FROM METHANOL AND AN ALDEHYDE

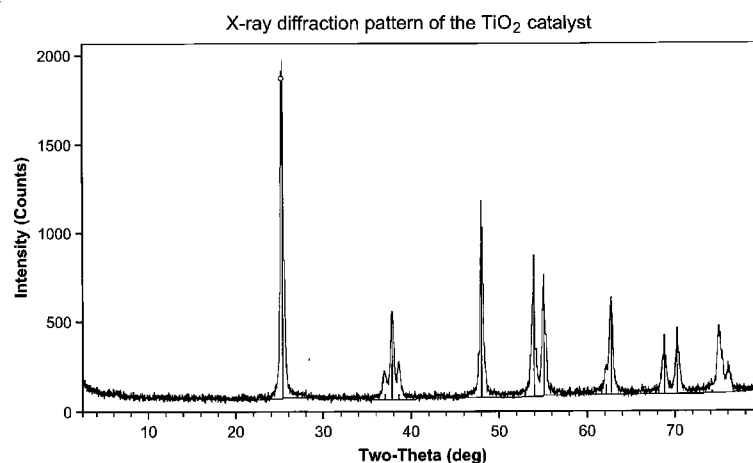


FIG. 1

(57) Abstract: A process is described that uses a silver catalyst to convert methanol into formaldehyde in the presence of less than a stoichiometric amount of oxygen. The resulting formaldehyde is reacted without isolation with propionaldehyde over a commercially available anatase titania catalyst that is shown to be catalytically active towards the formation of methacrolein from formaldehyde and propionaldehyde with conversions and selectivities close to 90%. This titania catalyst is readily available, non-toxic, and can be used with formaldehyde and a variety of other aldehyde compounds to make α,β -unsaturated aldehyde compounds. This process benefits from low raw material costs and is economically advantaged due to the elimination of catalyst separation. This process shows promising stability and selectivity during lifetime studies, particularly when performed in the presence of a hydrogen carrier gas.

EFFICIENT SYNTHESIS OF METHACROELIN AND OTHER ALPHA, BETA - UNSATURATED ALDEHYDES FROM METHANOL AND AN ALDEHYDE

FIELD OF THE INVENTION

5 [0001] This invention generally relates to a zoned process for the preparation of formaldehyde to be used in the synthesis of α,β -unsaturated aldehyde compounds using a heterogeneous anatase titania catalyst and an aldehyde under vapor-phase condensation conditions to obtain the α,β -unsaturated aldehyde compound with high conversion and selectivity values.

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BACKGROUND OF THE INVENTION

[0002] Methacrolein (or methacrylaldehyde) is an industrially useful chemical for the synthesis of a multitude of acrylate based polymers and resins. Among these applications, it is an intermediate for the production of methacrylonitrile and methacrylic acid. The latter is produced in an oxidation process and is a precursor for large scale applications such as methyl methacrylate and other esters.

15 [0003] The known process for methacrolein production involves the formation of propionaldehyde from ethylene hydroformylation (ethylene oxo) followed by the coupling of propionaldehyde with formaldehyde to form methacrolein. The yields for this synthetic approach are often greater than 95%. The major drawback of this process is that it requires a homogeneous Mannich base (typically a primary or a secondary amine) and an organic acid. While earlier patents detailed batch processes for the aldol reaction limiting their industrial applicability, latter patents revealed methods for a continuous process although the need for huge quantities of Mannich base and organic acid requires that the continuous process be run diluted at high atmospheric pressures. Although research in this area has developed the use of solid acid catalysts such as Amberlyst for the aldol condensation of formaldehyde and propionaldehyde, the process still requires one equivalent of a secondary amine. In many cases, this amine catalyst is consumed by the reaction which adds to the separation and feed costs.

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[0004] The art additionally details various vapor-phase condensation reactions involving formaldehyde and other aldehydes or ketones over an unmodified silica gel catalyst. Although methacrolein was produced in some of this work, there are at least three technical requirements that limit the commercial ability of this process: 1) The ratios of the aldehyde to formaldehyde were not 1:1 and in many examples were as high as 20:1, thus increasing the feedstock costs, separation costs, or both; 2) The need for high temperatures for the condensation reaction, for example, the condensation of propionaldehyde and formaldehyde over the silica gel catalyst required temperatures in excess of 460 °C; and 3) Despite the high temperatures required to give appreciable amounts of methacrolein, the highest recorded conversions were only about 45%.

[0005] In an ideal methacrolein process, a continuous 1:1 reactant stream of only formaldehyde and propionaldehyde would be condensed together over a simple regenerable heterogeneous catalyst. This idealized process would aid downstream separations since the catalyst would not be part of the reactor effluent. Noting these advantages, research in developing this type of ideal process has progressed in the direction of designing an efficient heterogeneous catalyst. For example, the prior art teaches the synthesis of methacrolein from acetaldehyde or propionaldehyde and methanol over a $Bi_aMo_bX_cO_d$ catalyst (where, $X = Al, Si, Ti, Fe, Co, Ag, W, V$ and/or P and a, b, c, d are the atomic ratios). Although these 3-metal catalysts had limited examples of acceptable runs with 86.6% selectivity at 67.5% conversion, the drawbacks for successful industrial implementation of this process include the synthesis of the complicated 3-metal catalyst along with the low yields obtained in all cases. Related catalyst work with borosilicate catalysts provided only low single pass yields of 56.6% with 57.5% conversion and 98% selectivity. Nearly 40% of the propionaldehyde used had to be recycled after each pass increasing separation volumes and costs. Similarly in other research, the aldol condensation of propionaldehyde and formaldehyde over a sodium oxide and silicic acid catalyst systems also showed poor yields of only 46%.

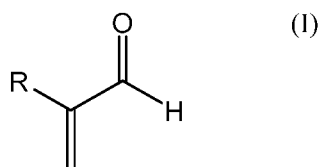
[0006] In addition to developing an effective regenerable heterogeneous

- catalyst, being able to supply a clean and reliable formaldehyde source can be problematic. Besides safety concerns, the main complicating issue with formaldehyde as a starting material is that it cannot be isolated in pure form since formaldehyde is notoriously unstable and frequently reacts with itself to form oligomers and polymers of paraformaldehyde. Paraformaldehyde can result from the evaporation of aqueous solutions of formaldehyde and cannot be used as a feed in vapor-phase reactions. The formation of paraformaldehyde can additionally contribute to yield losses and increased maintenance costs as the paraformaldehyde deposits on equipment and piping.
- 5
- 10 **[0007]** The most common commercial forms of formaldehyde are formalin or the 52% to 55% by weight aqueous solution. It would be preferred to avoid these forms of formaldehyde in the synthesis of methacrolein and/or related α,β -unsaturated aldehydes because of potential issues involving safety, expense, and handling difficulties. Formalin and the 52% to 55% by weight
- 15 aqueous solutions are toxic and suspected carcinogens. Although trioxane is a convenient form of formaldehyde, it is too expensive for use in a commercial process. The presence of an excessive amount of water or other hydroxylic compounds is undesirable since it would be expensive to separate these components from the desired aldol reaction products.
- 20 **[0008]** The present invention teaches that the oxidative dehydration of methanol to make formaldehyde can be used with propionaldehyde in the vapor-phase over an unmodified anatase titania catalyst for the facile synthesis of methacrolein. Moreover, it was surprisingly discovered that an α,β -unsaturated aldehyde such as methacrolein is stable over a titania catalyst
- 25 given the potential for this molecule to undergo further aldol condensation and oligomerization. The present invention's use of a silver catalyst to convert methanol to formaldehyde and a titania catalyst to synthesize methacrolein and other α,β -unsaturated aldehyde compounds offers multiple advantages not previously addressed by the prior art. These advantages include: 1) a reliable
- 30 and high quality formaldehyde stream; 2) improved aldol selectivity and conversion; 3) high single pass yields; 4) regenerable catalyst activity; 5) cleaner downstream separations due to the heterogeneous titania catalyst; and

6) efficient reactivity at atmospheric pressures.

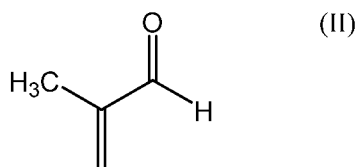
SUMMARY OF THE INVENTION

5 **[0009]** The present invention provides in a first embodiment a process for preparing an α,β -unsaturated aldehyde compound, comprising: contacting methanol with a silver catalyst and an oxygen source in a first zone to produce a vapor-phase formaldehyde source at a temperature from 450 °C to 750 °C; reducing the temperature of the vapor-phase formaldehyde source to
10 a temperature from 100 °C to 400 °C in a second zone; and contacting the vapor-phase formaldehyde source exiting the second zone, a diluent gas, and an aldehyde with a heterogeneous anatase titania catalyst in a third zone under vapor-phase condensation conditions to obtain the α,β -unsaturated aldehyde compound; wherein the α,β -unsaturated aldehyde compound has
15 the general formula (I):

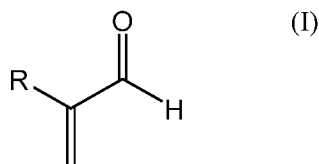


wherein R is a hydrogen or a hydrocarbon group having 1-12 carbons.

[0010] The present invention provides in a second embodiment a
20 process for preparing methacrolein, comprising: contacting methanol with a silver catalyst and an oxygen source in a first zone to produce a vapor-phase formaldehyde source at a temperature from 450 °C to 750 °C; reducing the temperature of the vapor-phase formaldehyde source to a temperature from 100 °C to 400 °C in a second zone; and contacting the vapor-phase
25 formaldehyde source exiting the second zone, a hydrogen containing diluent gas, and a propionaldehyde with a heterogeneous anatase titania catalyst in a third zone under vapor-phase condensation conditions to obtain methacrolein; wherein methacrolein has the general formula (I):



[0011] The present invention provides in a third embodiment a process for preparing an α,β -unsaturated aldehyde compound, comprising: contacting
 5 methanol with a silver catalyst and an oxygen source in a first zone to produce a vapor-phase formaldehyde source at a temperature from 450 °C to 750 °C; reducing the temperature of the vapor-phase formaldehyde source to a temperature from 100 °C to 400 °C in a second zone; and contacting the vapor-phase formaldehyde source exiting the second zone, a hydrogen containing
 10 diluent gas, and an aldehyde with a heterogeneous anatase titania catalyst in a third zone under vapor-phase condensation conditions to obtain the α,β -unsaturated aldehyde compound; wherein the α,β -unsaturated aldehyde compound has the general formula (I):



15 wherein R is a hydrogen or a hydrocarbon group having 1-12 carbons.

BRIEF DESCRIPTION OF THE DRAWINGS

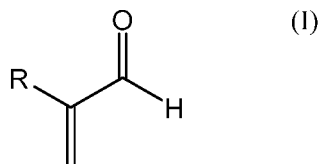
[0012] FIG. 1 is an X-ray diffraction pattern of the titania (TiO₂) catalyst.

DETAILED DESCRIPTION OF THE INVENTION

[0013] It has been surprisingly discovered that a zoned approach can be used for the efficient and regenerable production of α,β -unsaturated aldehydes. The first zone generates formaldehyde from the partial oxidative dehydrogenation of methanol over a silver catalyst and an oxygen source, the
 25 second zone reduces the temperature of the reactor effluent or formaldehyde from the first zone while maintaining vapor-phase conditions, and the third zone

combines the reactor effluent or cooled formaldehyde from the second zone with an aldehyde feedstock in the vapor-phase over a commercially available titania catalyst and diluent gas to produce the α,β -unsaturated aldehydes. One such example that works particularly well with this zoned process is the production of methacrolein from formaldehyde and propionaldehyde. The major advantages of this invention is an efficient and ready supply of formaldehyde to be used in the synthesis of α,β -unsaturated aldehydes over a catalyst that is readily available, non-toxic, and stable against additional unwanted aldol condensation reactions. The simplistic nature of anatase catalysts precludes the design and synthesis of complicated multi metal acid catalysts or homogeneous catalysts that typically increase downstream separation costs. The present invention is also advantageous as the aldol condensation of formaldehyde and propionaldehyde proceeds with highly reproducible yields over the titania catalyst with only a marginal drop in space time yields over the course of the reaction when hydrogen is used as part of a diluent gas.

[0014] The present invention provides in a first embodiment a process for preparing an α,β -unsaturated aldehyde compound, comprising: contacting methanol with a silver catalyst and an oxygen source in a first zone to produce a vapor-phase formaldehyde source at a temperature from 450 °C to 750 °C; reducing the temperature of the vapor-phase formaldehyde source to a temperature from 100 °C to 400 °C in a second zone; and contacting the vapor-phase formaldehyde source exiting the second zone, a diluent gas, and an aldehyde with a heterogeneous anatase titania catalyst in a third zone under vapor-phase condensation conditions to obtain the α,β -unsaturated aldehyde compound; wherein the α,β -unsaturated aldehyde compound has the general formula (I):



wherein R is a hydrogen or a hydrocarbon group having 1-12 carbons.

[0015] The first zone, or zone 1, operates as an area to contact methanol with a silver catalyst and an oxygen source to produce a vapor-phase formaldehyde source. This first zone can be used as a commercial formaldehyde process proceeding via the oxidative dehydrogenation of methanol without a water scrubber. This process comprises feeding an oxygen source to a reactor containing a shallow bed of a silver containing catalyst. In some embodiments, the ratio of methanol to molecular oxygen is about 2.5. The oxidation reaction is very exothermic, and large temperature rises occur in the catalyst bed. In some embodiments, the reactors can be run adiabatically. In some cases multiple stages of reactors are used with cooling sections between the reactors. The gas exiting the first zone is then cooled in a second zone, or zone 2. In the commercial process the gases exiting the cooling section are fed to a water scrubber, but the process of the present invention omits this scrubber. The omission of the scrubber makes the formaldehyde generation of the present invention more economical than the commercial process due to the elimination of equipment, and the formaldehyde is not isolated but fed directly into the third zone, or zone 3, at a reduced temperature.

[0016] The catalyst used for the methanol oxidation reaction can be silver or a silver mixture, although other materials such as copper, platinum, gold, or combinations thereof can also be used. In some embodiments, a silver catalyst is contacted with methanol and an oxygen source to make formaldehyde. The silver can be utilized in bulk form such as gauze, screens, powder or shot. The silver can also be used as 0.5 to 10.0 weight % metal supported on a refractory non-porous support such as pumice, alumina-silica refractory, or alundum. Although the diameter of the silver catalyst bed is not critical, the average depth should normally not exceed about 6 inches (15 cm) and in some embodiments be between about 0.25 inches (0.6 cm) and 1.5 inches (3.8 cm). The space velocity to the oxidation reactor of the first zone can range between about 10,000 and 600,000 hr⁻¹.

[0017] The methanol oxidation reaction using a silver catalyst is performed at temperatures ranging from 450 °C to 750 °C, from 500 °C to 700 °C, and from 550 °C to 650 °C. The reaction is performed between one and

three atmospheres pressure absolute, normally at about one atmosphere pressure absolute or slightly above due to fluctuations in the reaction system.

[0018] In some embodiments, the gas mixture fed to the reactor of the first zone comprises the following ranges in volume percent: 0.1 to 50 methanol, 0.1 to 30 oxygen, and 0 to 60 water. In other embodiments, the gas mixture fed to the reactor of the first zone comprises the following ranges in volume percent: 10 to 40 methanol, 5 to 20 oxygen, and 10 to 50 water.

[0019] An oxygen source can be any gas containing oxygen that is introduced to the reaction of methanol with the silver catalyst. If air is the source of the oxygen containing gas, then the inerts are comprised mostly of nitrogen. The oxygen source can contain any percentage of oxygen from 0.1% to pure oxygen. Recycled gases from the process also can be used as inert components. The addition of water to the reactant mixture can act as a temperature moderator and can also extend the catalyst life. In some embodiments, the mole ratio of methanol to molecular oxygen is between 1.67 and 4. In other embodiments, the mole ratio of methanol to molecular oxygen is between 2 and 3. It is important for the efficient reaction of methanol that nearly all of the oxygen is consumed. In some embodiments, when excessive combustion is occurring, lower ranges of methanol to oxygen molar ratios should only be used.

[0020] The oxidation of methanol to make formaldehyde using a silver catalyst can be performed with yields ranging from 80% to 99%, 85% to 95%, or 86% to 93%. Other products from the oxidation include water, carbon monoxide, carbon dioxide, methyl formate, formic acid and hydrogen. Although the product can also contain small amounts of unreacted methanol, the amount of unreacted methanol can be less than 5%, less than 3%, or less than 1%.

[0021] The second zone, or zone 2, in the process of the invention is essentially a cooling zone much like that used in a commercial formaldehyde process. Since the silver-catalyzed partial oxidation in the first zone is performed at temperatures between 450 °C and 750 °C, the temperatures of the exiting formaldehyde vapor stream is too high for the subsequent aldol reaction. In some embodiments, the heat removed in this second zone can be

used to generate steam to provide heat for other parts of the process such as the heating of reactants or operation of distillation columns. In some embodiments, the reactor effluent or vapor-phase formaldehyde from the first zone, or zone 1, can be cooled to temperatures ranging from 100 °C to 500 °C, from 100 °C to 400 °C, from 100 °C to 350 °C, and from 100 °C to 300 °C. In some embodiments, the temperature of the vapor-phase formaldehyde source exiting the second zone should be close to the temperature desired for the aldol condensation catalyst in the third zone.

[0022] The aldehyde to be used with the formaldehyde in the vapor-phase condensation reaction can be introduced near the exit of the second zone or at the entrance of the third zone.

[0023] The reactions occurring in the third zone, or zone 3, described herein are vapor-phase reactions catalyzed by heterogeneous aldol condensation catalysts. The term “heterogeneous aldol condensation catalyst”, as used herein, refers to a solid catalyst useful in the aldol condensation of lower aldehydes to higher aldehydes. The term “vapor-phase”, as used herein, refers to reactor conditions wherein the feed aldehydes and ensuing products are above their dew point. Dew point is defined as the temperature below which liquid condensation takes place for a gaseous mixture having a condensable material at a given pressure.

[0024] The vapor-phase formaldehyde source exiting the second zone, diluent gas, and aldehyde are contacted in a third zone bearing the heterogeneous anatase titania condensation catalyst. The third zone is a reaction zone that can be oriented vertically or horizontally. For vertically oriented reactor zones, the vapor feed may enter at the bottom of the zone and move up the reactor or the vapor feed may enter at the top of the zone and move down the reactor. The type of reactor is not particularly limiting. Examples of suitable reactors include, but are not limited to, fixed bed reactors, fluidized bed reactors, tubular reactors, stirred tank reactors, Berty reactors, and the like.

[0025] The term, “formaldehyde”, as used herein, represents the molecule HCHO and can be in a gaseous, aqueous, or anhydrous form. The

formaldehyde source for use in the present invention is not particularly limiting although in some embodiments, the formaldehyde source is made and delivered from the first zone. The formaldehyde source can also be 1,3,5-trioxane (sometimes referred to herein as simply "trioxane") or dimethoxymethane. Alternatively, the formaldehyde source may also be an aqueous solution of formaldehyde. The aqueous formaldehyde solution can contain, for example, from 30 to 65 weight % formaldehyde, many of these commercial stock solutions are readily available. Examples of such solutions include Formalin (37 wt % formaldehyde in water which may contain up to 15% methanol) and industrial grade aqueous formaldehyde (55 wt % formaldehyde). The aqueous formaldehyde solution may be obtained commercially, by oxidation of methanol, or by heating water with trioxane, for example, in a molar ratio of approximately 4:1.

[0026] The vapor-phase formaldehyde source can be fed directly from the first zone or as anhydrous formaldehyde in the form of trioxane or paraformaldehyde dissolved in the aldehyde. The aqueous formaldehyde solution can be fed to the reaction zone separate from or as a mixture with the aldehyde. Feeding the formaldehyde and aldehyde to the reactor zone can occur in conjunction with a diluent gas.

[0027] The molar ratio of the formaldehyde to aldehyde reagents may be from 0.2 to 5, from 0.2 to 2, or 1 to 1. The molar ratio of water to the formaldehyde component may be from 0 to 5, from 0 to 3, or from 0 to 1.5.

[0028] The term, "diluent gas", as used herein, is a gas that is introduced with the reagent streams so that this gas quantitatively lowers the concentration of the reactants in feed. The composition of the "diluent gas" can comprise steam, methane, carbon dioxide, carbon monoxide, nitrogen, argon, oxygen, air, hydrogen, helium, or mixtures thereof. The molar ratio of the diluent gas to the total moles of reactant aldehydes can range from 0.01:1 to 20:1, 0.01:1 to 10:1, 0.01:1 to 5:1, 0.1:1 to 20:1, 0.1:1 to 10:1, or 0.1:1 to 1:1.

[0029] An additional aspect of the invention detailed herein is the utilization of hydrogen as a carrier gas. Typically, nitrogen or an inert gas is used as a carrier/diluent gas but the use of hydrogen unexpectedly increases

the space time yields of methacrolein possibly due to the hydrogenation of inhibitory carbonaceous species. The reaction occurring in the first zone produces molecular hydrogen in addition to formaldehyde.

[0030] In some embodiments of the process of the invention, the vapor-phase formaldehyde and aldehyde reactants can be fed to the third zone with hydrogen along with an inert carrier gas such as nitrogen or oxygen-depleted air. Gases recycled from the process can be used. The inert gas component can be present at concentrations ranging from 0 to 90 mole % of the total feed, from 25 to 85 mole %, or from 30 to 80 mole %. The concentration of the hydrogen gas component can range from 10 to 90 mole %, 15 to 75 mole %, 20 to 70 mole %, 0.5 to 6 mole %, from 2 to 5 mole %, or from 3 to 4 mole %. Oxygen can additionally be added to the diluent gas for the reaction since low levels or a lack of oxygen allow for coke to build up on the catalyst. On the other hand, high levels of oxygen can lead to excessive combustion of reactants and products. In some examples, the concentration of the oxygen component can be 0.5 to 6 mole %, from 2 to 5 mole %, or 3 to 4 mole %.

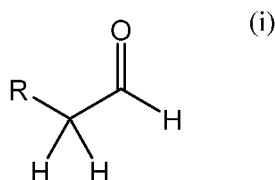
[0031] The space velocity for these condensation reactions should range from 50 to 400 moles of feed/(kg catalyst/hr), from 100 to 300 moles of feed/(kg catalyst/hr), or from 125 and 200 moles of feed/(kg catalyst/hr). The term “moles of feed” is meant to be inclusive of all of the species being fed to the catalyst including organics, solvents, and diluent gases. These embodiments of the invention take advantage of the combined effects of feeding the correct levels of reagents, diluent gases, water, and elevated space velocity to increase rate and selectivity without significantly affecting the yield. Any differences in formaldehyde conversion are primarily the result of formaldehyde destruction when the space velocity is too low. In the event of inhibitory coke formation, the catalyst may be regenerated between reaction runs in air at, for example, 400 °C.

[0032] Generally, increasing the space velocity of reactants increases the rate of a reaction, but this is normally accompanied with a corresponding decrease in the yield and conversion. It has been unexpectedly discovered that certain conditions of the process can actually allow for increased rate without a

decrease in yield as the space velocity is increased.

[0033] The term, “aldehyde”, as used herein, represents the broad class of organic compounds having the generic formula $RCHO$, and characterized by an unsaturated carbonyl functionality ($C=O$). Other than formaldehyde, which
5 will be referred to specifically in this specification, aldehyde will refer to a molecule having at least 2 hydrogen atoms in the alpha position to the aldehyde carbonyl group which will form the alkene or double bonded carbon added through the formaldehyde in the aldol condensation reaction.

[0034] The aldehyde has at least 2 hydrogen atoms in the position alpha
10 to the aldehyde carbonyl group as shown below:



The aldehyde is fed to the reactor zone of the third zone comprising a heterogeneous anatase titania condensation catalyst and contacted with a vapor-phase formaldehyde source. The aldehyde can be any aldehyde
15 wherein R is a hydrogen or a hydrocarbon group having 1 to 12 carbon atoms amenable to aldol condensation reactions. For example, this aldehyde comprises acetaldehyde, propionaldehyde, n-butyraldehyde, pentanal, hexanal, heptanal, octanal, nonanal, decanal, undecanal, dodecanal, 3-methylbutyraldehyde, 3-ethylbutyraldehyde and 3-ethylpentanal, but-3-enal,
20 pent-3-enal, 2-cyclohexylacetaldehyde, 2-phenylacetaldehyde, or a combination thereof. In some examples, the aldehyde can be a linear saturated aldehyde such as acetaldehyde, propionaldehyde, n-butyraldehyde, pentanal, hexanal, heptanal, octanal, nonanal, decanal, undecanal, dodecanal, or a combination thereof. In other examples, the aldehyde can be
25 a branched saturated aldehyde comprising 3-methylbutyraldehyde, 3-ethylbutyraldehyde, 3-ethylpentanal, or a combination thereof. In yet other examples, the aldehyde can be unsaturated non-conjugated aldehydes comprising but-3-enal, pent-3-enal, or combinations thereof. In another set of examples, the aldehyde can have cyclic or aromatic substituents and

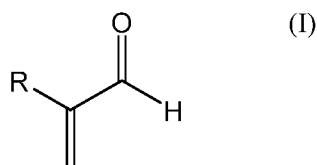
comprise 2-cyclohexylacetaldehyde, 2-phenylacetaldehyde, or combinations thereof. Heteroatom functional groups such as alcohols, ethers, esters, amines, amides, thiols and halogens may also be present as substituents in the aldehyde in some examples.

- 5 **[0035]** In some examples, the aldehyde can be an aldehyde wherein R is a hydrocarbon group having 1-2, 1-3, 1-4, 1-5, 1-6, 1-7, 1-8, 2-3, 2-4, 2-5, 2-6, 2-7, 2-8, 3-4, 3-5, 3-6, 3-7, 3-8, 3-9, 4-5, 4-6, 4-7, 4-8, 4-9, 4-10, 5-6, 5-7, 5-8, 5-9, 5-10, 6-7, 6-8, 6-9, 6-10, 7-8, 7-9, 7-10, 8-9, 8-10, 9-10, 9-11, or 10-12 carbon atoms.
- 10 **[0036]** The heterogeneous anatase titania catalyst comprises titanium dioxide, titanium IV oxide, titania, or TiO₂. Each of these titanium dioxide, titanium IV oxide, titania, and TiO₂ materials may exist and can be used in the anatase, rutile, and brookite mineral forms although the anatase polymorph of titania is the crystalline phase found to be active towards the formaldehyde and
- 15 aldehyde condensation reaction. In some embodiments, the titanium dioxide, titanium IV oxide, titania, and TiO₂ materials are used entirely in the anatase form. In other embodiments, the titanium dioxide, titanium IV oxide, titania, and TiO₂ materials are used as a mixture of the anatase and rutile forms. In some
- 20 embodiments, the heterogeneous titania catalyst is used in the anatase mineral form. The titania catalyst should be physically robust and pre-shaped. The term “pre-shaped” is used in this context to mean that the shape of the final catalyst is essentially the same as the starting material. The titania catalyst typically can have average particle diameter sizes ranging from about 0.1 millimeter (mm) to about 20 mm. The catalyst can be in any common form such
- 25 as extrudates, compressed pellets, or bulk solid that has been pulverized to the desired mesh size. The formed catalyst may also be in a variety of shapes such as rods, stars, cylinders, spheres, or broken chunks. Many of these anatase titania catalysts are available commercially, and their use simplifies the preparation of the catalyst composition of the invention, although this is not a
- 30 requirement of the invention.
- [0037]** The reactions described herein are vapor-phase reactions catalyzed by heterogeneous aldol condensation catalysts. The term

“heterogeneous aldol condensation catalyst”, as used herein, refers to a solid catalyst useful in the aldol condensation of lower aldehydes to higher aldehydes. The term “vapor-phase”, as used herein, refers to reactor conditions wherein the feed aldehydes and ensuing products are above their dew point. Dew point is defined as the temperature below which liquid condensation takes place from a gaseous mixture having a condensable material at a given pressure.

[0038] Vapor-phase condensation conditions are the temperature and pressure parameters that promote the chemical reaction of formaldehyde with the aldehyde in the gaseous state to form α,β -unsaturated compounds with the loss of a water molecule. The temperature used for the vapor-phase condensation is from 100 °C to 500 °C, from 100 °C to 400 °C, from 100 °C to 350 °C, and from 100 °C to 300 °C. In some embodiments, the condensation reaction is performed at a temperature of 250 °C, 290 °C, or 320 °C. The reaction is normally run between 0.1 and 10.0 bars absolute (bara), between 0.5 and 5.0 bara, or at atmospheric pressure.

[0039] The condensation reaction described herein produces α,β -unsaturated aldehydes from the aldol condensation of formaldehyde with an aldehyde. The α,β -unsaturated aldehydes produced through this reaction have the general formula:



in which the aldehydic C=O function is conjugated to an unsaturated C-C bond at the alpha, beta positions and wherein the R group is a hydrogen or a hydrocarbon group having 1-12 carbons. The R group can be an alkyl, aryl, alkoxy or aryloxy group. These α,β -unsaturated aldehydes may also be referred to as α -substituted acrolein compounds or 2-methylene substituted aldehydes. As previously described, in addition to formaldehyde, the aldehyde fed to the reactor zone with a heterogeneous anatase titania catalyst can be any primary aldehyde comprising 2 to 12 carbon atoms

amenable to aldol condensation reactions. The α,β -unsaturated aldehyde compounds synthesized from the reaction of formaldehyde with an aldehyde are acrolein (2-methyleneethanal), methacrolein (2-methylenepropanal), 2-methylenebutanal, 2-methylenepentanal, 2-methylenehexanal, 2-methyleneheptanal, 2-methyleneoctanal, 2-methylenenonanal, 2-methylenedecanal, 2-methyleneundecanal, 2-methylenedodecanal, 3-methyl-2-methylenebutanal, 3-methyl-2-methylenepentanal, 3-ethyl-2-methylenepentanal, 2-methylenebut-3-enal, 2-methylenepent-3-enal, 2-cyclohexylacrylaldehyde, or 2-phenylacrylaldehyde. Heteroatom functional groups such as alcohols, ethers, esters, amines, amides, thiols and halogens may also be present as substituents in the α,β -unsaturated aldehyde depending on the aldehyde used.

[0040] In some examples, the α,β -unsaturated aldehyde can have the general formula (I) wherein R is a hydrocarbon group having 1-2, 1-3, 1-4, 1-5, 1-6, 1-7, 1-8, 2-3, 2-4, 2-5, 2-6, 2-7, 2-8, 3-4, 3-5, 3-6, 3-7, 3-8, 3-9, 4-5, 4-6, 4-7, 4-8, 4-9, 4-10, 5-6, 5-7, 5-8, 5-9, 5-10, 6-7, 6-8, 6-9, 6-10, 7-8, 7-9, 7-10, 8-9, 8-10, 9-10, 9-11, or 10-12 carbon atoms.

[0041] The α,β -unsaturated aldehydes can be prepared with good yield, conversion, and selectivity. The term “yield”, as used herein, is meant to be the (moles of product)/(moles of reactant fed)*100. For example, the percent yield of methacrolein from formaldehyde is the (moles of methacrolein)/(moles of formaldehyde fed)*100. The term “conversion”, as used herein, is meant to be the (moles of reactant fed – moles of unreacted reactant)/(moles of reactant fed)*100. For example, the percent formaldehyde conversion is (moles of formaldehyde fed – moles of unreacted formaldehyde)/(moles of formaldehyde fed)*100. The term “selectivity”, as used herein, is meant to be (moles of product)/(moles of reactant fed – moles of unreacted reactant)*100. For example, the percent selectivity to methacrolein from formaldehyde is (moles of methacrolein)/(moles of formaldehyde fed – moles of unreacted formaldehyde)*100. One skilled in the art recognizes that yield is also equal to conversion times selectivity. When comparing examples, such as, Example B having an 80% formaldehyde conversion and Example C having a 60%

formaldehyde conversion, the formaldehyde conversion of Example B is said to be 20% higher than Example C. In other words, comparisons are simply the mathematical difference in the percentages from one example to another.

5 [0042] Inhibitors such as hydroquinone may be added to the α,β -unsaturated aldehyde product to minimize oligomerization or polymerization.

[0043] The aldehyde conversion in the vapor-phase condensation reaction of a formaldehyde source, a diluent gas, and an aldehyde is greater than 80%. The aldehyde conversion in the vapor-phase condensation reaction of a formaldehyde source, a diluent gas, and an aldehyde is greater than 70%,
10 greater than 75%, greater than 80%, greater than 85%, or greater than 90%. At 290 °C, using 8/14 mesh heterogeneous anatase titania catalyst, the aldehyde conversion in the vapor-phase condensation reaction of a formaldehyde source, a diluent gas, and an aldehyde is greater than 80%, greater than 85%, or greater than 90%. At 310 °C, using 8/14 mesh
15 heterogeneous anatase titania catalyst, the aldehyde conversion in the vapor-phase condensation reaction of a formaldehyde source, a diluent gas, and an aldehyde is greater than 80%, or greater than 85%.

[0044] The α,β -unsaturated aldehyde selectivity in the vapor-phase condensation reaction of a formaldehyde source, a diluent gas, and an
20 aldehyde is greater than 70%, greater than 75%, greater than 80%, or greater than 85%. The α,β -unsaturated aldehyde selectivity in the vapor-phase condensation reaction of a formaldehyde source, a diluent gas, and an aldehyde is greater than 70%, greater than 75%, greater than 80%, greater than 85%, or greater than 90%. At 290 °C, using 8/14 mesh heterogeneous
25 anatase titania catalyst, the α,β -unsaturated aldehydes selectivity in the vapor-phase condensation reaction of a formaldehyde source, a diluent gas, and an aldehyde is greater than 80%, or greater than 85%. At 310 °C, using 8/14 mesh heterogeneous anatase titania catalyst, the α,β -unsaturated aldehyde selectivity in the vapor-phase condensation reaction of a formaldehyde source,
30 a diluent gas, and an aldehyde is greater than 75%, greater than 80%, or greater than 85%.

[0045] The α,β -unsaturated aldehyde space time yield (STY) in the

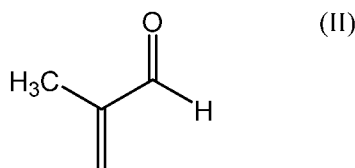
vapor-phase condensation reaction of a formaldehyde source, a diluent gas, and an aldehyde is 8.0, 8.5, or 9.0 moles of α,β -unsaturated aldehyde/(kg catalyst/hr). The α,β -unsaturated aldehyde space time yield in the vapor-phase condensation reaction of a formaldehyde source, a diluent gas, and an aldehyde is 7.5, 8.0, 8.5, 9.0, 9.5, or 10.0 moles of α,β -unsaturated aldehyde/(kg catalyst/hr). At 290 °C, using 8/14 mesh heterogeneous anatase titania catalyst, the α,β -unsaturated aldehydes space time yield in the vapor-phase condensation reaction of a formaldehyde source, a diluent gas, and an aldehyde is 10.0 moles of α,β -unsaturated aldehyde/(kg catalyst/hr). At 310 °C, using 8/14 mesh heterogeneous anatase titania catalyst, the α,β -unsaturated aldehyde space time yield in the vapor-phase condensation reaction of a formaldehyde source, a diluent gas, and an aldehyde is 8.5, or 9.0 moles of α,β -unsaturated aldehyde/(kg catalyst/hr).

[0046] In the event of inhibitory coke formation on the heterogeneous anatase titania catalyst, the catalyst may be regenerated between reaction runs in air at 450 °C.

[0047] Many uses exist for methacrolein and the other α,β -unsaturated aldehydes described herein such as for the synthesis of a multitude of acrylate based polymers and resins. For example, methacrolein can be used to produce or synthesize isobutyraldehyde, methacrylonitrile, methacrylic acid, and methyl methacrylate as monomers or other reagent chemicals. In industrial applications, methacrolein can be used to synthesize or produce methacrylic acid through an oxidation process; this methacrylic acid can then be esterified to synthesize or produce methyl methacrylate and/or a variety other methacrylate esters. The methyl methacrylate synthesized from methacrolein can be polymerized or copolymerized to produce polymethyl methacrylate (PMMA) or copolymers of PMMA, or a combination thereof. The other types of methacrylate esters synthesized from methacrolein can be polymerized or copolymerized to produce homopolymers of the methacrylate ester or esters used, copolymers of the methacrylate ester or esters used, or a combinations thereof. Methacrolein can be used to synthesize or produce methacrylonitrile;

this methacrylonitrile can then be used to make homopolymers, copolymers, or elastomers of polymethacrylonitrile. In some examples, methacrolein can be used to synthesize or produce isobutyraldehyde.

[0048] The present invention provides in a second embodiment a process for preparing methacrolein, comprising: contacting methanol with a silver catalyst and an oxygen source in a first zone to produce a vapor-phase formaldehyde source at a temperature from 450 °C to 750 °C; reducing the temperature of the vapor-phase formaldehyde source to a temperature from 100 °C to 400 °C in a second zone; and contacting the vapor-phase formaldehyde source exiting the second zone, a hydrogen containing diluent gas, and a propionaldehyde with a heterogeneous anatase titania catalyst in a third zone under vapor-phase condensation conditions to obtain methacrolein; wherein methacrolein has the general formula (I):



[0049] It is understood that the descriptions outlining and teaching the method for preparing α,β -unsaturated aldehydes previously discussed, which can be used in any combination, apply equally well to the second embodiment of the invention, where applicable, disclosing a process for preparing methacrolein.

[0050] The vapor-phase formaldehyde source exiting the second zone, hydrogen containing diluent gas, and propionaldehyde are contacted in a reactor zone of the third zone bearing the heterogeneous anatase titania condensation catalyst. The type of reactor is not particularly limiting. Examples of suitable reactors include, but are not limited to, fixed bed reactors, fluidized bed reactors, tubular reactors, stirred tank reactors, Berty reactors, and the like.

[0051] The formaldehyde source for use in the present invention is not particularly limiting. The formaldehyde source can be in a gaseous, aqueous, or an anhydrous form such as trioxane or paraformaldehyde dissolved in the aldehyde. The aqueous formaldehyde solution can be fed to the reaction zone

of the third zone separate from or as a mixture with the aldehyde. Feeding the formaldehyde and propionaldehyde to the reactor zone can occur in conjunction with a hydrogen containing diluent gas.

5 **[0052]** The molar ratio of the formaldehyde to propionaldehyde reagents may be from 0.2 to 5, from 0.2 to 2, or 1 to 1. The molar ratio of water to the formaldehyde component may be from 0 to 5, from 0 to 3, or from 0 to 1.5.

10 **[0053]** The term, "hydrogen containing diluent gas", as used herein, is a gas that contains at least some hydrogen gas that is introduced to the third zone with the vapor-phase formaldehyde and aldehyde reagent streams so that this gas quantitatively lowers the concentration of the reactants in the feed. The composition of the "hydrogen containing diluent gas" has at least some hydrogen gas and may additionally comprise steam, methane, carbon dioxide, carbon monoxide, nitrogen, argon, oxygen, air, helium, or mixtures thereof. The molar ratio of the hydrogen containing diluent gas to the total moles of reactant propionaldehyde can range from 0.01:1 to 20:1, 0.01:1 to 10:1, 0.01:1 to 5:1, 0.1:1 to 20:1, 0.1:1 to 10:1, or 0.1:1 to 1:1. In some embodiments, nitrogen or an inert gas is used as part of the hydrogen containing diluent gas because the use of hydrogen unexpectedly increases the space time yields of methacrolein possibly due to the hydrogenation of inhibitory carbonaceous species.

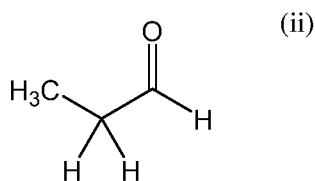
20 **[0054]** In some embodiments of the invention, the formaldehyde and propionaldehyde can be fed to the reactor zone of the third zone with hydrogen along with an inert carrier gas such as nitrogen or oxygen-depleted air. Gases recycled from the process can be used. The inert gas component can be present at concentrations ranging from 0 to 90 mole % of the total feed, from 25 to 85 mole %, or from 30 to 80 mole %. The concentration of the hydrogen gas component can range from 10 to 90 mole %, 15 to 75 mole %, 20 to 70 mole %, 0.5 to 6 mole %, from 2 to 5 mole %, or from 3 to 4 mole %.

30 **[0055]** In other embodiments, oxygen can additionally be added to the hydrogen containing diluent gas with the reactants since low levels or a lack of oxygen allow for coke to build up on the catalyst. On the other hand, high levels of oxygen can lead to excessive combustion of reactants and products. In some examples, the concentration of the oxygen component can be 0.5 to 6

mole %, from 2 to 5 mole %, or 3 to 4 mole %.

[0056] The space velocity for these condensation reactions should range from 50 to 400 moles of feed/(kg catalyst/hr), from 100 to 300 moles of feed/(kg catalyst/hr), or from 125 and 200 moles of feed/(kg catalyst/hr). The term “moles of feed” is meant to be inclusive of all of the species being fed to the catalyst including organics, solvents, and diluent gases. These embodiments of the invention take advantage of the combined effects of feeding the correct levels of reagents, diluent gases, water, and elevated space velocity to increase rate and selectivity without significantly affecting the yield. Any differences in formaldehyde conversion are primarily the result of formaldehyde destruction when the space velocity is too low. In the event of inhibitory coke formation, the catalyst may be regenerated between reaction runs in air at, for example, 450 °C.

[0057] The propionaldehyde has 2 hydrogen atoms in the position alpha to the aldehyde carbonyl group as shown below:



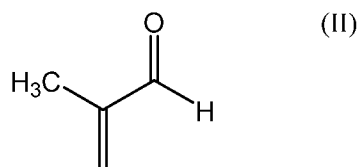
The propionaldehyde is fed to the reactor zone comprising a heterogeneous anatase titania condensation catalyst and contacted with a formaldehyde source.

[0058] The heterogeneous anatase titania catalyst comprises titanium dioxide, titanium IV oxide, titania, or TiO_2 . In some embodiments, the heterogeneous titania catalyst is used in the anatase mineral form. The titania catalyst should be physically robust and pre-shaped. The term “pre-shaped” is used in this context to mean that the shape of the final catalyst is essentially the same as the starting material. The titania catalyst typically can have average particle diameter sizes ranging from about 0.1 millimeter (mm) to about 20 mm. The catalyst can be in any common form such as extrudates, compressed pellets, or bulk solid that has been pulverized to the desired mesh size. They may also be in a variety of shapes such as rods, stars, cylinders,

spheres, or broken chunks. Many of these anatase titania catalysts are available commercially, and their use simplifies the preparation of the catalyst composition of the invention, although this is not a requirement of the invention.

[0059] Vapor-phase condensation conditions are the temperature and pressure parameters that promote the chemical reaction of formaldehyde with the propionaldehyde in the gaseous state to form methacrolein with the loss of a water molecule. The temperature used for the vapor-phase condensation is from 100 °C to 500 °C, from 100 °C to 400 °C, from 100 °C to 350 °C, and from 100 °C to 300 °C. In some embodiments, the condensation reaction is performed at a temperature of 250 °C, 290 °C, or 320 °C. The reaction is normally run between 0.1 and 10.0 bars absolute (bara), between 0.5 and 5.0 bara, or at atmospheric pressure.

[0060] The condensation reaction described herein with propionaldehyde as the reagent produces methacrolein from the aldol condensation of formaldehyde and propionaldehyde. The α,β -unsaturated aldehydes produced through this reaction have the general formula:



in which the aldehydic C=O function is conjugated to an unsaturated C-C bond at the alpha, beta positions.

[0061] The methacrolein can be prepared with good yield, conversion, and selectivity. The term “yield”, as used herein, is meant to be the (moles of product)/(moles of reactant fed)*100. For example, the percent yield of methacrolein from formaldehyde is the (moles of methacrolein)/(moles of formaldehyde fed)*100. The term “conversion”, as used herein, is meant to be the (moles of reactant fed – moles of unreacted reactant)/(moles of reactant fed)*100. For example, the percent formaldehyde conversion is (moles of formaldehyde fed – moles of unreacted formaldehyde)/(moles of formaldehyde fed)*100. The term “selectivity”, as used herein, is meant to be (moles of product)/(moles of reactant fed – moles of unreacted reactant)*100. For

example, the percent selectivity to methacrolein from formaldehyde is (moles of methacrolein)/(moles of formaldehyde fed – moles of unreacted formaldehyde)*100. One skilled in the art recognizes that yield is also equal to conversion times selectivity. When comparing examples, such as, Example B
5 having an 80% formaldehyde conversion and Example C having a 60% formaldehyde conversion, the formaldehyde conversion of Example B is said to be 20% higher than Example C. In other words, comparisons are simply the mathematical difference in the percentages from one example to another.

[0062] Inhibitors such as hydroquinone may be added to the
10 methacrolein product to minimize oligomerization and polymerization products.

[0063] The propionaldehyde conversion in the vapor-phase condensation reaction of a formaldehyde source, a hydrogen containing diluent gas, and an aldehyde is greater than 80%. The propionaldehyde conversion in the vapor-phase condensation reaction of a formaldehyde source, a hydrogen
15 containing diluent gas, and propionaldehyde is greater than 70%, greater than 75%, greater than 80%, greater than 85%, or greater than 90%. At 290 °C, using 8/14 mesh heterogeneous anatase titania catalyst, the propionaldehyde conversion in the vapor-phase condensation reaction of a formaldehyde source, a hydrogen containing diluent gas, and propionaldehyde is greater than
20 80%, greater than 85%, or greater than 90%. At 310 °C, using 8/14 mesh heterogeneous anatase titania catalyst, the propionaldehyde conversion in the vapor-phase condensation reaction of a formaldehyde source, a hydrogen containing diluent gas, and propionaldehyde is greater than 80%, or greater than 85%.

[0064] The methacrolein selectivity in the vapor-phase condensation reaction of a formaldehyde source, a hydrogen containing diluent gas, and propionaldehyde is greater than 70%, greater than 75%, greater than 80%, or greater than 85%. The methacrolein selectivity in the vapor-phase condensation reaction of a formaldehyde source, a hydrogen containing diluent
30 gas, and propionaldehyde is greater than 70%, greater than 75%, greater than 80%, greater than 85%, or greater than 90%. At 290 °C, using 8/14 mesh heterogeneous anatase titania catalyst, the methacrolein selectivity in the

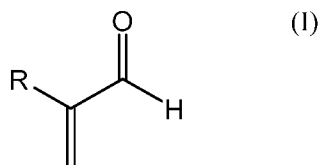
vapor-phase condensation reaction of a formaldehyde source, a hydrogen containing diluent gas, and propionaldehyde is greater than 80%, or greater than 85%. At 310 °C, using 8/14 mesh heterogeneous anatase titania catalyst, the methacrolein selectivity in the vapor-phase condensation reaction of a formaldehyde source, a hydrogen containing diluent gas, and propionaldehyde is greater than 75%, greater than 80%, or greater than 85%.

[0065] The methacrolein space time yield (STY) in the vapor-phase condensation reaction of a formaldehyde source, a hydrogen containing diluent gas, and propionaldehyde is 8.0, 8.5, or 9.0 moles of methacrolein/(kg catalyst/hr). The methacrolein space time yield in the vapor-phase condensation reaction of a formaldehyde source, a hydrogen containing diluent gas, and propionaldehyde is 7.5, 8.0, 8.5, 9.0, 9.5, or 10.0 moles of methacrolein/(kg catalyst/hr). At 290 °C, using 8/14 mesh heterogeneous anatase titania catalyst, the methacrolein space time yield in the vapor-phase condensation reaction of a formaldehyde source, a hydrogen containing diluent gas, and propionaldehyde is 10.0 moles of α,β -unsaturated aldehyde/(kg catalyst/hr). At 310 °C, using 8/14 mesh heterogeneous anatase titania catalyst, the methacrolein space time yield in the vapor-phase condensation reaction of a formaldehyde source, a hydrogen containing diluent gas, and propionaldehyde is 8.5 or 9.0 moles of methacrolein/(kg catalyst/hr).

[0066] In the event of inhibitory coke formation on the heterogeneous anatase titania catalyst, the catalyst may be regenerated between reaction runs in air at 450 °C.

[0067] The present invention provides in a third embodiment a process for preparing an α,β -unsaturated aldehyde compound, comprising: contacting methanol with a silver catalyst and an oxygen source in a first zone to produce a vapor-phase formaldehyde source at a temperature from 450 °C to 750 °C; reducing the temperature of the vapor-phase formaldehyde source to a temperature from 100 °C to 400 °C in a second zone; and contacting the vapor-phase formaldehyde source exiting the second zone, a hydrogen containing diluent gas, and an aldehyde with a heterogeneous anatase titania catalyst in a third zone under vapor-phase condensation conditions to obtain the α,β -

unsaturated aldehyde compound; wherein the α,β -unsaturated aldehyde compound has the general formula (I):



wherein R is a hydrogen or a hydrocarbon group having 1-12 carbons.

- 5 **[0068]** It is understood that the descriptions outlining and teaching the method for preparing α,β -unsaturated aldehydes, including methacrolein, previously discussed, which can be used in any combination, apply equally well to the third embodiment of the invention, where applicable, disclosing a process for preparing α,β -unsaturated aldehydes.
- 10 **[0069]** There are also many different variations on the composition elements, reductants, reaction conditions, and reactants used that could be employed and would be obvious to one skilled in the art.
- 15 **[0070]** Unless otherwise indicated, all numbers expressing quantities of ingredients, properties such as molecular weight, reaction conditions, and so forth used in the specification and claims are to be understood as being modified in all instances by the term “about.” Accordingly, unless indicated to the contrary, the numerical parameters set forth in the following specification and attached claims are approximations that may vary depending upon the desired properties sought to be obtained by the present invention. At the very
- 20 least, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques. Further, the ranges stated in this disclosure and the claims are intended to include the entire range specifically and not just the endpoint(s). For example, a range stated to be 0 to 10 is intended to disclose all whole
- 25 numbers between 0 and 10 such as, for example 1, 2, 3, 4, etc., all fractional numbers between 0 and 10, for example 1.5, 2.3, 4.57, 6.1113, etc., and the endpoints 0 and 10. Also, a range associated with chemical substituent groups such as, for example, “C₁ to C₅ hydrocarbons”, is intended to specifically include and disclose C₁ and C₅ hydrocarbons as well as C₂, C₃, and C₄ hydrocarbons.

[0071] Notwithstanding that the numerical ranges and parameters setting forth the broad scope of the invention are approximations, the numerical values set forth in the specific examples are reported as precisely as possible. Any numerical value, however, inherently contains certain errors necessarily
5 resulting from the standard deviation found in their respective testing measurements.

[0072] It is to be understood that the mention of one or more process steps does not preclude the presence of additional process steps before or after the combined recited steps or intervening process steps between those steps
10 expressly identified. Moreover, the lettering of process steps or ingredients is a convenient means for identifying discrete activities or ingredients and the recited lettering can be arranged in any sequence, unless otherwise indicated.

[0073] As used herein the term “and/or,” when used in a list of two or more items, means that any one of the listed items can be employed by itself,
15 or any combination of two or more of the listed items can be employed. For example, if a composition is described as containing components A, B, and/or C, the composition can contain A alone; B alone; C alone; A and B in combination; A and C in combination; B and C in combination; or A, B, and C in combination.

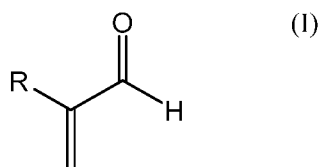
[0074] As used in the specification and claims, the singular forms “a,” “an” and “the” include their plural referents unless the context clearly dictates otherwise. For example, a reference to “a catalyst” or “a reductant” is synonymous with “at least one” or “one or more” catalysts or reductants and is thus intended to refer to both a single or a plurality of catalysts or reductants.
20 In addition, references to a composition containing or including “an” ingredient is intended to include other ingredients or elements in addition to the one named.
25

[0075] The terms “containing” or “including” are intended to be synonymous with the word “comprising,” meaning that at least the named compound, element, particle, or method step, etc., is present in the composition or article or method, but does not exclude the presence of other compounds,
30

catalysts, materials, particles, method steps, etc., even if such compounds, materials, particles, method steps, etc., have the same function as what is named, unless expressly excluded in the claim.

5 Listing of non-limiting Embodiments

[0076] Embodiment A is a process for preparing an α,β -unsaturated aldehyde compound, comprising: contacting methanol with a silver catalyst and an oxygen source in a first zone to produce a vapor-phase formaldehyde source at a temperature from 450 °C to 750 °C; reducing the temperature of the vapor-phase formaldehyde source to a temperature from 100 °C to 400 °C in a second zone; and contacting the vapor-phase formaldehyde source exiting the second zone, a diluent gas, and an aldehyde with a heterogeneous anatase titania catalyst in a third zone under vapor-phase condensation conditions to obtain the α,β -unsaturated aldehyde compound; wherein the α,β -unsaturated aldehyde compound has the general formula (I):



wherein R is a hydrogen or a hydrocarbon group having 1-12 carbons.

[0077] The process of Embodiment A, wherein the vapor-phase formaldehyde source and the aldehyde are contacted with the heterogeneous anatase titania catalyst at a temperature of 100 °C to 350 °C.

[0078] The process of Embodiment A or Embodiment A with one or more of the intervening features wherein the vapor-phase formaldehyde source and the aldehyde are contacted with the heterogeneous anatase titania catalyst at a temperature of 100 °C to 300 °C.

25 [0079] The process of Embodiment A or Embodiment A with one or more of the intervening features wherein the diluent gas comprises nitrogen, hydrogen, air, or a combination thereof.

[0080] The process of Embodiment A or Embodiment A with one or more of the intervening features wherein the vapor-phase formaldehyde source is

made in the first zone in an 80-99% yield.

[0081] The process of Embodiment A or Embodiment A with one or more of the intervening features wherein the aldehyde comprises acetaldehyde, propionaldehyde, n-butyraldehyde, pentanal, hexanal, heptanal, octanal, 5 nonanal, decanal, undecanal, dodecanal, 3-methylbutyraldehyde, 3-ethylbutyraldehyde and 3-ethylpentanal, but-3-enal, pent-3-enal, 2-cyclohexylacetaldehyde, 2-phenylacetaldehyde, or a combination thereof.

[0082] The process of Embodiment A or Embodiment A with one or more of the intervening features wherein the aldehyde is a linear saturated aldehyde 10 comprising acetaldehyde, propionaldehyde, n-butyraldehyde, pentanal, hexanal, heptanal, octanal, nonanal, decanal, undecanal, dodecanal, or a combination thereof.

[0083] The process of Embodiment A or Embodiment A with one or more of the intervening features wherein the aldehyde is a branched saturated 15 aldehyde comprising 3-methylbutyraldehyde, 3-ethylbutyraldehyde and 3-ethylpentanal, or a combination thereof.

[0084] The process of Embodiment A or Embodiment A with one or more of the intervening features wherein the aldehyde is a cyclic or an aromatic substituted aldehyde comprising 2-cyclohexylacetaldehyde, 2- 20 phenylacetaldehyde, or a combination thereof.

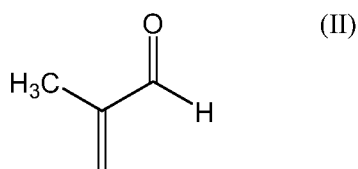
[0085] The process of Embodiment A or Embodiment A with one or more of the intervening features wherein the heterogeneous anatase titania catalyst is regenerated with a calcination step at 450 °C in air.

[0086] The process of Embodiment A or Embodiment A with one or more 25 of the intervening features wherein the α,β -unsaturated aldehyde compound is produced with a conversion and a selectivity above 80%.

[0087] The process of Embodiment A or Embodiment A with one or more of the intervening features wherein the α,β -unsaturated aldehyde compound is produced with a space time yield greater than 8 moles aldehyde/kg catalyst/hr.

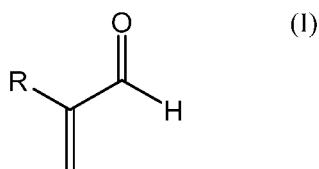
30 **[0088]** Embodiment B is a process for preparing methacrolein, comprising: contacting methanol with a silver catalyst and an oxygen source in a first zone to produce a vapor-phase formaldehyde source at a temperature

from 450 °C to 750 °C; reducing the temperature of the vapor-phase formaldehyde source to a temperature from 100 °C to 400 °C in a second zone; and contacting the vapor-phase formaldehyde source exiting the second zone, a hydrogen containing diluent gas, and a propionaldehyde with a
 5 heterogeneous anatase titania catalyst in a third zone under vapor-phase condensation conditions to obtain methacrolein; wherein methacrolein has the



general formula (I):

- [0089]** The process of Embodiment B, wherein the vapor-phase formaldehyde source is made in the first zone in an 80-99% yield.
- 10 **[0090]** The process of Embodiment B or Embodiment B with one or more of the intervening features wherein the α,β -unsaturated aldehyde compound is produced with a conversion and a selectivity above 80%.
- [0091]** The process of Embodiment B or Embodiment B with one or more of the intervening features wherein the α,β -unsaturated aldehyde compound is
 15 produced with a space time yield greater than 8 moles aldehyde/kg catalyst/hr.
- [0092]** The process of Embodiment B or Embodiment B with one or more of the intervening features wherein the methacrolein is used to produce isobutyraldehyde, methacrylonitrile, methacrylic acid, methyl methacrylate, poly(methyl methacrylate), or a combination thereof.
- 20 **[0093]** Embodiment C is a process for preparing an α,β -unsaturated aldehyde compound, comprising: contacting methanol with a silver catalyst and an oxygen source in a first zone to produce a vapor-phase formaldehyde source at a temperature from 450 °C to 750 °C; reducing the temperature of the vapor-phase formaldehyde source to a temperature from 100 °C to 400 °C
 25 in a second zone; and contacting the vapor-phase formaldehyde source exiting the second zone, a hydrogen containing diluent gas, and an aldehyde with a heterogeneous anatase titania catalyst in a third zone under vapor-phase condensation conditions to obtain the α,β -unsaturated aldehyde compound; wherein the α,β -unsaturated aldehyde compound has the general



wherein R is a hydrogen or a hydrocarbon group having 1-12 carbons.

[0094] The process of Embodiment C, wherein the α,β -unsaturated aldehyde compound is produced with a conversion and a selectivity above 80%.

[0095] The process of Embodiment C or Embodiment C with one of the intervening features wherein the α,β -unsaturated aldehyde compound is produced with a space time yield greater than 8 moles aldehyde/kg catalyst/hr.

Examples

Materials

[0096] The methanol, trioxane, propionaldehyde, anatase titania catalyst, solvents, additional reagents, and gases were purchased from commercial suppliers and used as received. The titania catalyst's crystal structure was determined using X-ray diffraction and was noted to be the pure anatase polymorph of TiO_2 as shown in Figure 1. The surface area of the catalyst was $36.8 \text{ m}^2/\text{g}$ as calculated by the Brunnauer, Emmett and Teller (BET) theory using nitrogen gas as the adsorbent. The pore volume and pore diameter of the catalyst as determined from N_2 physisorption measurements was found to be $0.14 \text{ cm}^3/\text{g}$ and $150 \text{ \AA}$ respectively.

XRD Measurements

[0097] All XRD measurements were performed on a Rigaku Miniflex X-Ray Diffraction Spectrometer using a Copper anode X-Ray tube operated at 30kV and 15mA. Diffraction patterns were collected from 5 degree two theta angle to 75 degree two theta angle with a sampling width of 0.02 degrees and a scan speed of 1.00 degrees/min.

[0098] Crystallite size was calculated based on the measurement of the

full width half maximum for peaks in the diffraction pattern and use of the Scherrer equation (P.N. Scherrer, *Ges. Wiss. Gottingen, Math.- Phys. Kl.* **2**, 96-100 (1918)). Quantitative phase analysis was calculated using a refinement algorithm base on the Rietveld method (H.M. Rietveld, *J. Applied*
5 *Crystallography* **21**, 86-91 (1988)). Percent crystallinity was calculated based on integrated intensities from the individual diffraction patterns with peaks of crystallite size greater than 30Å defined as crystalline and peaks of crystallite size less than or equal to 30Å defined as amorphous (N.S. Murthy et al., *Polymers* **31**, 996-1002 (1990)).

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Gas Chromatography Measurements

[0099] Liquid product samples were collected over a measured time period, weighed and analyzed by gas chromatography. THF was added to the products to homogenize the organic and the water layers. Samples were
15 weighed into a gas chromatography (GC) vial to a recorded weight of 0.1XXX g (where X is the actual number shown on the balance). Initially a stock ISTD solution comprising 75 g of cyclohexanone in acetonitrile was made-up. To 1.0XX g of the THF homogenized reaction product, approximately 7.86XX gram of ISTD solution was added. The vial was then capped and gently mixed. The
20 contents were then transferred into a 2-mL GC vial. The vials were then placed on a heat plate at 80 °C for 30 minutes. To separate the components, each sample was injected on two BD-Wax/DB-1301 columns (60 mx0.32 mmx1.00µm) running in parallel at 40 °C on a Shimadzu 2010 gas chromatograph with an AOC-20 autosampler. The concentration of
25 propionaldehyde, methacrolein, water, iso-butyraldehyde and other analytes were detected using this approach using the TCD and/or FID detectors.

Setup and Parameters for Zoned Approach

[00100] The three zone reaction processes were conducted in a 25 mm
30 outer diameter (21 mm inner diameter) quartz reactor tube with length = 42 inches (107 cm). The reactor tube had indentations located 11.5 inches (29 cm) up from the base. The purpose of the indentations was to provide a

physical means to support the solid materials in the reactor. The top of the reactor was fitted with a reactor head with openings for a 9 mm outer diameter quartz thermowell and for liquid and gas feeds. The thermowell extended into the reactor to a point approximately 1 inch (2.54 cm) below the indentations.

5 **[00101]** Heat to the reactor was supplied by a Lindberg three element electric furnace having a total heated section length of 24 inches (61 cm). Each zone was 8 inches (20.3) cm long. Control thermocouples were located in the center of each zone. The diameter of the furnace was approximately 5.5 inches (14 cm).

10 **[00102]** The reactor was placed in the furnace with the level of the indentations at the same level as the bottom of the furnace heated region. The base of the reactor was attached to a jacketed three necked 500 mL flask fitted with stopcock drain, a septum and a transfer line attached to an initial condenser. The initial condenser was attached to a 500 mL collection flask
15 fitted with a stopcock drain. Both the jacketed three necked 500 mL flask and condenser were cooled by a water-ethylene glycol chiller held at approximately zero degrees C. Vapor exiting the initial condenser entered a second condenser held at -78 °C by a mixture of dry ice and acetone. The second condenser also was fitted with a 500 mL collection flask with a stopcock drain.
20 Vapor exiting the second condenser was vented through an oil bubbler into the hood.

[00103] One end of a hollow 1/16 inch (0.16 cm) OD stainless steel tube was inserted through the septum attached to one of the necks of the jacketed three necked 500 mL flask at the base of the reactor. The tube was pulled into
25 the flask and then bent upward and the end pulled upward into the quartz reactor to a distance 7.5 inches (19 cm) from the base of the bottom of the heat zone 3. This tube was used to feed the propionaldehyde to zone 3. Propionaldehyde liquid feed to the reactor was provided by a high pressure liquid chromatography pump connected to the other end of the 1/16 inch tube.
30 During the operation of the process of the invention the liquid flowing through the 1/16 inch tube would be vaporized as it entered through the base of zone 3 and would be delivered as vapor in a region of zone 3 above the titania catalyst.

[00104] The reactor containing the thermowell and stainless steel tube was loaded with inert packing (fused silica chunks, -4+10 mesh) and catalysts by pouring them through an opening in the reactor head. The reactor was first loaded with fused silica to a height of 4 inches (10.1 cm) up from the bottom of the reactor indentations followed by 10 mL (10.2 g) of -8+14 mesh titania catalyst. The bed height of the titania catalyst was 1.5 inches (3.8 cm), and a thermocouple in the quartz thermowell was placed 0.75 inches (1.9 cm) up from the base of the titania catalyst bed.

[00105] The reactor was then further loaded with fused silica up to a position directly opposite the top furnace control thermocouple [approximately 20 inches (51 cm) up from the base of the furnace] extending through zone 3 through zone 2 and up into zone 1. One of the silver catalysts detailed in Examples 1-3 was then loaded and an additional thermocouple centered in the silver catalyst bed was placed in the thermowell. Quartz chips were placed on top of the silver catalyst and extended up to the top of zone 1.

[00106] The outside of the region of quartz reactor located in zone 2 was wrapped with quartz wool to minimize heat transfer from zone 1 to zone 3. Zone 2 was not heated, and the insulation was sufficient to allow the temperature of the gases entering zone 3 to be such that little or no furnace heat was required for zone 3.

Example 1: Zoned Approach to the Synthesis of Formaldehyde and Methacrolein with Silver Shot in First Zone

[00107] This Example illustrates the process of the invention using silver shot catalyst for the generation of formaldehyde in zone 1 and its subsequent reaction with propionaldehyde in zone 3. While this example illustrates the concept of the invention, it also demonstrates the detrimental effect of an incomplete reaction in zone 1. The reactor was loaded with the titania catalyst and fused silica as described in the apparatus section. Silver shot (3 mL, 18.9g) was loaded into reactor so that the base of the catalyst was directly opposite the control thermocouple for zone 1. The bed height was approximately 0.25 inch (0.64 cm), and the thermocouple in the thermowell was placed 1/8 inch

(0.32 cm) up from the base of the silver catalyst. Four inches (10.2 cm) of quartz chips were placed on top of the silver catalyst. Zone 1 was set for 650 °C and zone 3 was set for 290 °C. Zone 2 was not heated. A mixture of 5 volume % oxygen in nitrogen was fed to the reactor head at 539 standard cubic centimeters per minute (SCCM). Methanol was fed to the reactor head above zone 1 at 3.0 mmoles/minute. The mole ratio of methanol to molecular oxygen was about 2.5. Propionaldehyde was fed into zone 3 at 3.0 mmoles/minute. Both catalysts exhibited about 10 °C exotherms. The reactor was operated in this fashion for three hours, and the liquid products were collected and discarded. The reaction was continued for an additional hour, and the product (16.75 g, 2 phases) was collected and analyzed. Some of the methanol and oxygen were not reacted in zone 1, and this situation was manifested by the presence of methyl propionate resulting from the oxidation of propionaldehyde and the subsequent esterification of the propionic acid. Methanol conversion (including that present as ester) was 99.4 % and the propionaldehyde conversion was 70.8 %. Selectivity to methacrolein from propionaldehyde was 35.0 %. Selectivity to methyl propionate from propionaldehyde was 13.4 % and the selectivity to 2-methyl-2-pentenals was 26.8 %. The 2-methyl-2-pentenals resulted from the aldol condensation of two molecules of propionaldehyde.

20 **[00108]** Examination of the reactor revealed that there was no visible coke present in zone 1 or in the upper region of zone 2. Coke was visible in the lower part of zone 2 and in zone 3. The coke was removed by heating all three zones to 450 °C in flowing air overnight.

25 *Example 2: Zoned Approach to the Synthesis of Formaldehyde and Methacrolein with Silver Wool Catalyst in First Zone*

[00109] This Example illustrates the process of the invention using silver wool catalyst for the generation of formaldehyde in zone 1 and its subsequent reaction with propionaldehyde in zone 3. While this example also illustrates the concept of the invention, it also demonstrates the detrimental effect of incomplete reaction in zone 1. The reactor was loaded as per Example 1 except that silver wool was used in place of silver shot. Silver wool (0.05 mm diameter,

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approximately 1.1 g) was cut up and loaded into the reactor in portions using a wire to make the bed as even as possible. The base of the catalyst was directly opposite the control thermocouple for zone 1. The catalyst was carefully compressed using the wire to provide a bed height of 0.75 inches (1.9 cm, volume = approximately 5 mL). The thermocouple in the thermowell was placed 3/8 inch (0.95 cm) up from the base of the silver catalyst. Four inches of quartz chips were placed on top of the silver catalyst. Zone 1 was set for 650 °C and zone 3 was set for 290 °C. Zone 2 was not heated. A mixture of 5 volume % oxygen in nitrogen was fed to the reactor head at 539 SCCM. Methanol was fed to the reactor head above zone 1 at 3.0 mmoles/minute. The mole ratio of methanol to molecular oxygen was about 2.5. Propionaldehyde was fed into zone 3 at 3.0 mmoles/minute. The silver catalyst exhibited about a 2-3 °C exotherm and the titania catalyst exhibited about a 2 °C exotherm. The reactor was operated in this fashion for two hours, and the liquid products were collected and discarded. The reaction was continued for an additional hour, and the product (15.4 g, 1 phase) was collected and analyzed. Some of the methanol and oxygen were not reacted in zone 1, but data for methyl propionate were not provided by the GC program. Thus the amount of methyl propionate present in the product could not be quantified in this example. The methanol conversion was 98.9 % and the propionaldehyde conversion was 37.5 %. Selectivity to methacrolein from propionaldehyde was 28.6 %, and the selectivity to 2-methyl-2-pentenals was 23.7 %.

[00110] Examination of the reactor revealed that there was no visible coke present in zones 1 or 2. Coke was visible on the titania catalyst in zone 3. The coke was removed by heating all three zones to 450 °C in flowing air overnight.

Example 3: Zoned Approach to the Synthesis of Formaldehyde and Methacrolein with No Oxygen Added to First Zone

[00111] This example illustrates that when no oxygen is delivered to zone 1 only negligible amounts of methacrolein are produced. The same reactor and catalysts used in Example 2 were used in Example 3. Zone 1 was set for 650 °C and zone 3 was set for 290 °C. Zone 2 was not heated. Nitrogen was fed to

the reactor head at 76 SCCM. Methanol was fed to the reactor head above zone 1 at 4.1 mmol/min. Propionaldehyde was fed into zone 3 at 3.0 mmol/min. The silver catalyst exhibited about a 2 °C exotherm and the titania catalyst exhibited about a 10-15 °C exotherm. The reactor was operated in this fashion for one hour, and the liquid products were collected and discarded. The reaction was continued for an additional 2 hours, and the product (28.7 g) was collected and analyzed. Data for methyl propionate were not provided by the GC program. Thus the amount of methyl propionate present in the product could not be quantified in this example. The methanol conversion was 65.8 % and the propionaldehyde conversion was 86.4 %. Selectivity to methacrolein from propionaldehyde was 1.5 %, and the selectivity to 2-methyl-2-pentenals was 28.6 %.

[00112] A light gray coke was visible in zone 1 above and below the silver catalyst. The top half of zone 2 also contained the light gray coke. A darker coke was visible on the titania catalyst in zone 3. The coke was removed by heating all three zones to 450 °C in flowing air over night.

Examples 4 – 5: Methacrolein Production Using TiO₂ Catalyst (in 3.2 mm Pellets Form) from Propionaldehyde and Formaldehyde in Nitrogen Flow

[00113] **Reaction:** The vapor-phase condensation reactions of formaldehyde (as trioxane) with propionaldehyde were performed at temperatures ranging from 290 °C to 310 °C, using a 0.2 mL liquid feed/minute for 4 or 6 hours. The residence time was maintained constant at approximately 1 second by changing the diluent N₂ gas flow rate. The performance of the catalyst is summarized in performance Table 1. The conversions presented in Table 1 are based on moles of propionaldehyde converted to initial moles of propionaldehyde and the space time yield (STY) of acrylic acid is equal to the moles of methacrolein produced per kg of catalyst per hour. The selectivities are based on the final moles of methacrolein relative to the reacted moles of propionaldehyde. The reacted moles of propionaldehyde are the difference between the initial and final moles of propionaldehyde. The yield percentage detailed in the introduction is the product of the conversion and selectivity.

[00114] The vapor-phase condensation reaction of formaldehyde (fed as trioxane) with propionaldehyde was performed in a 25 mm outer diameter (21 mm inner diameter) quartz reactor tube with length = 79 cm (31 inches). Heat to the reactor was provided by an Applied Test Systems series 3210 three element electric furnace having a heated zone 54 cm (21.25 inches) in length. Liquid products were collected in a three necked flask fitted with a glycol chilled (0 °C) jacket and an additional dry ice trap. The third neck of the flask was connected to a side arm which was connected to a dry ice trap. The base of the main receiver flask and dry ice trap were fitted with a stopcock to allow for draining of the liquid products.

[00115] The quartz reactor had indentations 16 cm (6.25 inches) up from the base of the tube. The region of the reactor with the indentations was situated near the base of the heated section of the furnace. The reactor was also fitted with a thermowell that extended from the top of the reactor to about an inch below the indentations. The reactor was first loaded with quartz chips to about 8 inches (20.3 cm) in height above the indentations to allow the catalyst to be positioned in the middle of the 3 element furnace. The reactor was then loaded with an approximately 10.0 mL charge of catalyst. The three point thermocouple in the thermowell was placed 1.5 inches (3.8 cm) up from the base of the catalyst bed. Sufficient quartz chips were added to the region above the catalyst charge to reach the top of the heated region of the 3 element furnace. Liquid samples were collected over a measured time period, weighed and analyzed by gas chromatography.

[00116] As a substantial exotherm was observed in the first 3 to 10 minutes of the reaction, the sample collected during the first hour of reaction was discarded. The reaction activities and yields presented in Table 1 were collected over a period of 2 to 4 hours after the initial 1 hour temperature stabilization period. The residence time for the reaction was kept constant at approximately 1 second by varying the nitrogen gas flow rate. The catalyst was regenerated at 450 °C in air overnight.

Table 1: Methacrolein production from condensation of formaldehyde (HFr) and propionaldehyde (HPr) using nitrogen as a carrier gas – TiO₂ Catalyst was 3.2 mm pellets

Example	HPr/HFr	Furnace Temp (°C)	Reaction Time (hrs)	HPr Conversion (%)	Methacrolein Selectivity (%)	Methacrolein STY moles/kg catalyst/hr
4	1/1	310	2	81	81	8.8
			4	74	82	8.2
5	1/1	290	2	87	72	8.4
			4	79	85	9.1

[00117] Table 1 illustrates that the efficient synthesis of methacrolein from formaldehyde and propionaldehyde can be obtained over an unmodified commercially available titania catalyst.

Examples 6 – 7: Methacrolein Production Using TiO₂ Catalyst (in 3.2 mm Pellets Form) from Propionaldehyde and Formaldehyde in Hydrogen Flow

[00118] Examples 6 - 7 were conducted as described above in Examples 4 and 5 except that the diluent gas was changed from nitrogen to hydrogen. The results are presented below in Table 2.

Table 2: Methacrolein production from condensation of formaldehyde (HFr) and propionaldehyde (HPr) using hydrogen as a carrier gas – TiO₂ Catalyst was 3.2 mm pellets

Example	HPr/HFr	Furnace Temp (°C)	Reaction Time (hrs)	HPr Conversion (%)	Methacrolein Selectivity (%)	Methacrolein STY moles/kg catalyst/hr
6	1/1	310	2	85	79	9
			4	74	89	8.9
7	1/1	290	2	87	78	9.1
			4	79	89	9.5

[00119] Comparing the results in Tables 1 and 2, the space time yields are higher when the diluent gas is hydrogen compared with an inert gas like nitrogen. This increased yield could be attributed to less coke formation on the

catalyst due to the hydrogenation of inhibitory carbonaceous species. Less catalyst coking could potentially lead to an increase in the catalytically active sites resulting in higher space time yields of methacrolein. When the diluent gas used was hydrogen, the space time yields increased or remained constant with reaction time unlike when nitrogen was used as the carrier gas, wherein the space time yields dropped as the reaction time was increased from 2 hours to 4 hours (at 310 °C). To further illustrate the importance of hydrogen, the following experiments were conducted.

Examples 8 – 9: Methacrolein Production Using TiO₂ Catalyst (in 8/14 Mesh Form) from Propionaldehyde and Formaldehyde in Nitrogen Flow

[00120] Examples 8 - 9 were conducted as described above in Examples 4 and 5 except the catalyst used had smaller particle size. To mitigate mass transfer effects of the catalyst and to illustrate the importance of hydrogen, the anatase TiO₂ catalyst was crushed and sieved into 8/14 mesh sized particles which were used as the catalyst material for this set of experiments. The results are presented below in Table 3.

Table 3: Methacrolein production from condensation of formaldehyde (HFr) and propionaldehyde (HPr) using nitrogen as a carrier gas – TiO₂ Catalyst was 8/14 mesh sized particles

Example	Pr/HFr	Furnace Temp (°C)	Reaction Time (hrs)	HPr Conversion (%)	Methacrolein Selectivity (%)	Methacrolein STY moles/kg catalyst/hr
8	1/1	310	2	82	70	7.7
			4	74	84	8.4
9	1/1	290	2	92	76	9.4
			4	86	87	10.1

Examples 10 – 11: Methacrolein Production Using TiO₂ Catalyst (in 8/14 Mesh Form) from Propionaldehyde and Formaldehyde in Hydrogen Flow

Examples 10 - 11 were conducted as described above in Examples 8 and 9 except that the diluent gas was changed from nitrogen to hydrogen. The catalyst used was anatase TiO₂ catalyst in the form of 8/14 mesh sized particles. The results are presented below in Table 4.

Table 4: Methacrolein production from condensation of formaldehyde (HFr) and propionaldehyde (HPr) using hydrogen as a carrier gas – TiO₂ Catalyst was 8/14 mesh sized particles

Example	HPr/HFr	Furnace Temp (°C)	Reaction Time (hrs)	HPr Conversion (%)	Methacrolein Selectivity (%)	Methacrolein STY (moles/kg catalyst/hr)
10	1/1	310	2	86	75	8.8
			4	80	85	9.1
11	1/1	290	2	91	81	10.0
			4	86	87	10.1

[00121] Tables 2 and 4 demonstrate that higher space time yields were obtained in the presence of hydrogen as a carrier gas. The use of hydrogen is an unexpected aspect of this invention since most condensation experiments are conducted in the presence of nitrogen or an equivalent inert gas.

Example 12: Reproducibility of Example 11 and Longer Term Stability of the Catalyst

[00122] Experiment 12 was conducted as described above in Examples 10 - 11 with a hydrogen flow. Prior experiments demonstrated that 290 °C is a more optimal operating temperature than 310 °C since the space time yields were higher at the former temperature. Therefore, the longer term stability test was conducted at 290 °C. The experiment was continued for 2 more hours to analyze a longer reaction window to determine stability of the catalyst. The results are presented below in Table 5.

Table 5: Methacrolein production from condensation of formaldehyde (HFr) and

propionaldehyde (HPr) using hydrogen as a carrier gas – TiO₂ Catalyst was 8/14 mesh sized particles

Example	HPr/HFr	Furnace Temp (°C)	Reaction Time (hrs)	HPr Conversion (%)	Methacrolein Selectivity (%)	Methacrolein STY (moles/kg catalyst/hr)
12	1/1	290	2	91	82	10.0
			4	86	88	10.2
			6	80	92	9.9

[00123] The methacrolein production reaction was performed in accordance to conditions presented in Example 11 in Table 4. The catalyst was regenerated overnight at 450 °C in a continuous flow of 100 standard cubic centimeters per minute (SCCM) air. Comparing Examples 11 and 12 in Tables 4 and 5 above, the catalyst activity is completely reproducible after the regeneration step in air. For example, after 4 hours of reaction, the same propionaldehyde conversion (80 %) was observed and the space time yields of methacrolein were almost the same as those presented in the earlier Example 11 at approximately 10.15 moles/kg catalyst/hr. These results highlight the stability of the catalyst. Furthermore, Example 12 shows that the drop in space time yields over 6 hours is only 3 % (from 10.2 units to 9.9 units). These Examples highlight the importance of using hydrogen as a carrier gas and are further corroborated by Example 13.

Example 13: Reproducibility of Example 11 with Regenerated Catalyst

[00124] Example 13 was conducted as described above in Example 12 with a hydrogen flow. As presented in Table 6, the catalytic activity is highly reproducible and the catalyst is completely regenerable upon a calcination step in air at 450 °C.

Table 6: Methacrolein production from condensation of formaldehyde (HFr) and propionaldehyde (HPr) using hydrogen as a carrier gas – TiO₂ Catalyst was 8/14 mesh sized particles

Example	HPr/HFr	Furnace Temp (°C)	Reaction Time (hrs)	HPr Conversion (%)	Methacrolein Selectivity (%)	Methacrolein STY (moles/kg catalyst/hr)
13	1/1	290	2	92	81	10.0
			4	87	85	10.0
			6	78	92	9.7

5 Examples 14 – 15: Methacrolein Production Using TiO₂ Catalyst (in 8/14 Mesh Form) from Propionaldehyde and Formaldehyde in Hydrogen Flow in the Presence of Water

[00125] Examples 14 - 15 were carried out with an anatase titania catalyst. The earlier experiments were conducted with trioxane (containing 0% water) as the source of formaldehyde while the most commonly available grade of formaldehyde is approximately 55% by weight in water. To simulate this, appropriate amounts of water were added to a solution of 1/1 formaldehyde (trioxane) and propionaldehyde to simulate a formaldehyde solution containing approximately 55% by weight water. As displayed in Table 7, only a small drop of 5% in space time yields was observed at 290 °C. This suggests that the catalytic reaction to methacrolein proceeds efficiently over the titania catalyst in the presence of water.

15 **Table 7:** Methacrolein production from condensation of formaldehyde (HFr) and propionaldehyde (HPr) using hydrogen as a carrier gas – TiO₂ Catalyst was 8/14 mesh sized particles in the presence of water

Example	HPr/HFr	Furnace Temp (°C)	Reaction Time (hrs)	HPr Conversion (%)	Methacrolein Selectivity (%)	Methacrolein STY (moles/kg catalyst/hr)
14	1/1	310	2	81	84	8.4
			4	74	86	7.9
15	1/1	290	2	88	87	9.5

			4	83	94	9.6
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Example 16 – 18: Additional Examples with other Titania Sources

[00126] Examples 16 - 18 were carried out with an anatase titania catalyst. In these examples the residence time was maintained at approximately 0.6 seconds by varying the diluent nitrogen gas flowrate.

Table 8: Methacrolein production from condensation of formaldehyde (HFr) and propionaldehyde (HPr) using nitrogen as a carrier gas – TiO₂ Catalyst was 8/14 mesh sized particles

Example	HPr/HFr	Furnace Temp (°C)	Reaction Time (hrs)	HPr Conversion (%)	Methacrolein Selectivity (%)	Methacrolein STY moles/kg catalyst/hr
16	1/1	325	4	49	77	9.6
17	1/1	300	4	55	80	11.2
18	1/1	275	4	49	79	9.9

Example 19: Application of Rutile TiO₂

[00127] The Examples performed above were all carried out with titania obtained from multiple sources but each sample consisted of the anatase polymorph as the major crystalline phase. To broaden the use of any titania as a potential catalyst, the following examples are catalyzed with a rutile polymorph of titania purchased from a commercial source. In Example 19, the residence time was maintained at approximately 1 second by varying the diluent nitrogen gas flowrate. As can be seen from Table 9 below, rutile titania was determined to not perform as well as the anatase polymorph of TiO₂.

Table 9: Methacrolein production from condensation of formaldehyde (HFr) and propionaldehyde (HPr) with hydrogen as a carrier gas using the rutile form of titania as the catalyst

Example	HPr/HFr	Furnace Temp (°C)	Reaction Time (hrs)	HPr Conversion (%)	Methacrolein Selectivity (%)	Methacrolein STY (moles/kg catalyst/hr)
19	1/1	290	2	35	69	3.0
			4	22	87	2.4

- 5 **[00128]** It is not intended that the scope of the invention is to be limited by the Examples described and illustrated above, but instead it is intended the scope of the invention will be determined by the appended claims and their equivalents.

We claim:

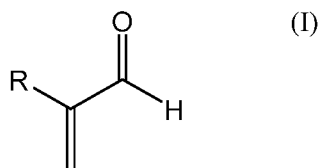
1. A process for preparing an α,β -unsaturated aldehyde compound, comprising:

5 (i) contacting methanol with a silver catalyst and an oxygen source in a first zone to produce a vapor-phase formaldehyde source at a temperature from 450 °C to 750 °C;

(ii) reducing the temperature of the vapor-phase formaldehyde source to a temperature from 100 °C to 400 °C in a second zone; and

10 (iii) contacting the vapor-phase formaldehyde source exiting the second zone, a diluent gas, and an aldehyde with a heterogeneous anatase titania catalyst in a third zone under vapor-phase condensation conditions to obtain the α,β -unsaturated aldehyde compound;

wherein the α,β -unsaturated aldehyde compound has the general formula (I):



wherein R is a hydrogen or a hydrocarbon group having 1-12 carbons.

2. The process according to claim 1, wherein the vapor-phase
20 formaldehyde source and the aldehyde are contacted with the heterogeneous anatase titania catalyst at a temperature of 100 °C to 350 °C.

3. The process according to claim 1, wherein the vapor-phase
formaldehyde source and the aldehyde are contacted with the heterogeneous
25 anatase titania catalyst at a temperature of 100 °C to 300 °C.

4. The process according to claim 1, wherein the diluent gas comprises nitrogen, hydrogen, air, or a combination thereof.
5. The process according to claim 1, wherein the vapor-phase
5 formaldehyde source is made in the first zone in an 80-99% yield.
6. The process of claim 1, wherein the aldehyde comprises acetaldehyde, propionaldehyde, n-butyraldehyde, pentanal, hexanal, heptanal, octanal, nonanal, decanal, undecanal, dodecanal, 3-methylbutyraldehyde, 3-
10 ethylbutyraldehyde and 3-ethylpentanal, but-3-enal, pent-3-enal, 2-cyclohexylacetaldehyde, 2-phenylacetaldehyde, or a combination thereof.
7. The process according to claim 1, wherein the aldehyde is a linear saturated aldehyde comprising acetaldehyde, propionaldehyde, n-
15 butyraldehyde, pentanal, hexanal, heptanal, octanal, nonanal, decanal, undecanal, dodecanal, or a combination thereof.
8. The process according to claim 1, wherein the aldehyde is a branched saturated aldehyde comprising 3-methylbutyraldehyde, 3-ethylbutyraldehyde
20 and 3-ethylpentanal, or a combination thereof.
9. The process according to claim 1, wherein the aldehyde is a cyclic or an aromatic substituted aldehyde comprising 2-cyclohexylacetaldehyde, 2-phenylacetaldehyde, or a combination thereof.
25
10. The process according to claim 1, wherein the heterogeneous anatase titania catalyst is regenerated with a calcination step at 450 °C in air.

11. The process according to claim 1, wherein the α,β -unsaturated aldehyde compound is produced with a conversion and a selectivity above 80%.

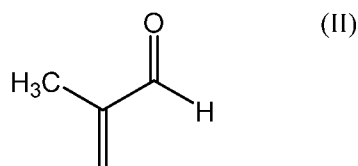
5 12. The process according to claim 1, wherein the α,β -unsaturated aldehyde compound is produced with a space time yield greater than 8 moles aldehyde/kg catalyst/hr.

13. A process for preparing methacrolein, comprising:

10 (i) contacting methanol with a silver catalyst and an oxygen source in a first zone to produce a vapor-phase formaldehyde source at a temperature from 450 °C to 750 °C;

(ii) reducing the temperature of the vapor-phase formaldehyde source to a temperature from 100 °C to 400 °C in a second zone; and

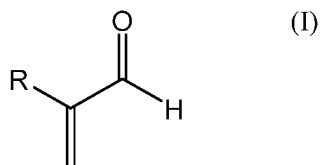
15 (iii) contacting the vapor-phase formaldehyde source exiting the second zone, a hydrogen containing diluent gas, and a propionaldehyde with a heterogeneous anatase titania catalyst in a third zone under vapor-phase condensation conditions to obtain methacrolein; wherein methacrolein has the general formula (I):



14. The process according to claim 13, wherein the vapor-phase formaldehyde source is made in the first zone in an 80-99% yield.

15. The process according to claim 13, wherein the α,β -unsaturated aldehyde compound is produced with a conversion and a selectivity above 80%.
- 5 16. The process according to claim 13, wherein the α,β -unsaturated aldehyde compound is produced with a space time yield greater than 8 moles aldehyde/kg catalyst/hr.
17. The process according to claim 13, wherein the methacrolein is used to
10 produce isobutyraldehyde, methacrylonitrile, methacrylic acid, methyl methacrylate, poly(methyl methacrylate), or a combination thereof.
18. A process for preparing an α,β -unsaturated aldehyde compound, comprising:
- 15 (i) contacting methanol with a silver catalyst and an oxygen source in a first zone to produce a vapor-phase formaldehyde source at a temperature from 450 °C to 750 °C;
- (ii) reducing the temperature of the vapor-phase formaldehyde source to a temperature from 100 °C to 400 °C in a second zone; and
- 20 (iii) contacting the vapor-phase formaldehyde source exiting the second zone, a hydrogen containing diluent gas, and an aldehyde with a heterogeneous anatase titania catalyst in a third zone under vapor-phase

condensation conditions to obtain the α,β -unsaturated aldehyde compound;
wherein the α,β -unsaturated aldehyde compound has the general formula (I):



5 wherein R is a hydrogen or a hydrocarbon group having 1-12 carbons.

19. The process according to claim 18, wherein the α,β -unsaturated aldehyde compound is produced with a conversion and a selectivity above 80%.

10

20. The process according to claim 18, wherein the α,β -unsaturated aldehyde compound is produced with a space time yield greater than 8 moles aldehyde/kg catalyst/hr.

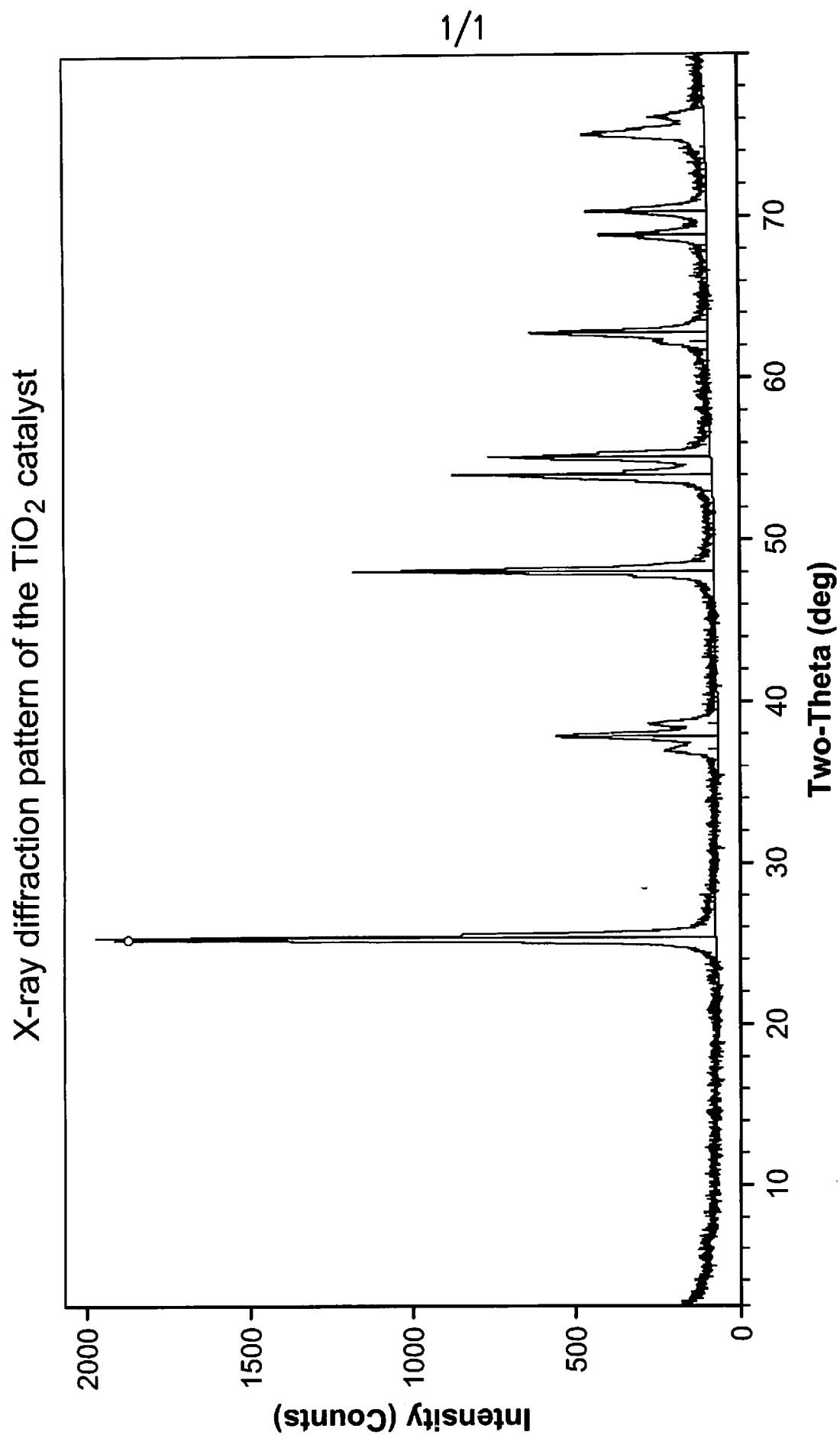


FIG. 1

A. CLASSIFICATION OF SUBJECT MATTER

C07C 45/86(2006.01)i, C07C 45/71(2006.01)i, C07C 47/22(2006.01)i, B01J 23/50(2006.01)i, C07C 31/04(2006.01)i, C07C 47/04(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C07C 45/86; C07C 45/75; C07C 51/16; C07C 45/72; C07C 47/20; C07C 45/71; C07C 47/22; B01J 23/50; C07C 31/04; C07C 47/04

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKOMPASS(KIPO internal), STN(Registry, Caplus), Google & keywords: α,β -unsaturated aldehyde, formaldehyde, aldehyde, methanol, silver, catalyst, heterogeneous anatase titania, hydrogen, propionaldehyde, methacrolein

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2012-0283479 A1 (DUBOIS, J. L.) 8 November 2012 See abstract; paragraphs [0053], [0057], [0064]-[0069] ; and claims 1, 6.	1-20
Y	US 4316990 A (MORRIS, D. L.) 23 February 1982 See abstract; column 1, lines 19-27; and claims 1-15.	1-20
Y	US 7012156 B2 (LEE, K.-H. et al.) 14 March 2006 See claim 1.	17
A	AI, M., "Formation of Acrylaldehyde by Vapor-Phase Aldol Condensation II. Phosphate Catalysts", Bulletin of the Chemical Society of Japan, 1991, Vol. 64, No. 4, pp. 1346-1350 See abstract; and table 1.	1-20
A	QIAN, M. et al.. "Formaldehyde synthesis from methanol over silver catalysts", Applied Catalysis A: General, 20 January 2003, Vol. 238, No 2, pp. 211-222 See abstract; and table 2.	1-20
A	GB 513772 A (DEUTSCHE GOLD-UND SILBER-SCHNEIDANSTALT) 20 October 1939 See claims 1-5, 12, 16.	1-20



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

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Name and mailing address of the ISA/KR

International Application Division

Korean Intellectual Property Office

189 Cheongsa-ro, Seo-gu, Daejeon, 35208, Republic of Korea



Facsimile No. +82-42-481-8578

Authorized officer

CHO, Han Sol

Telephone No. +82-42-481-5580



INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2017/014824

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