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(54) Title: PROCESS FOR THE CONVERSION OF ONE OR MORE POLYOLS

(57) Abstract: The invention relates to a process for the conversion of one or more polyols including the steps of: (i) reacting one or more polyols chosen from the group consisting of sorbitol, glycerol, and erythritol, at a temperature in the range from equal to or more than 200°C to equal to or less than 280°C, in the presence of hydrogen and in the presence of a homogeneous catalyst, which homogeneous catalyst contains tungsten, in a reactor comprising a fixed bed of heterogeneous catalyst, which heterogeneous catalyst contains one or more transition metals from groups 8, 9 and 10 of the Periodic Table of the Elements, yielding one or more reaction products and a spent heterogeneous catalyst; (ii) regenerating the spent heterogeneous catalyst by washing the fixed bed of heterogeneous catalyst with a washing liquid and subsequently drying the fixed bed of heterogeneous catalyst under an atmosphere and/or in a flow of inert gas, yielding a regenerated heterogeneous catalyst; and (iii) optionally re-using at least a portion of the regenerated heterogeneous catalyst as heterogeneous catalyst.



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PROCESS FOR THE CONVERSION OF ONE OR MORE POLYOLS

FIELD OF THE INVENTION

[0001] The present invention relates to a process for the conversion of one or more polyols.

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BACKGROUND TO THE INVENTION

[0002] Alkylene glycols, such as ethylene glycol, are bulk chemicals that can be used in a wide variety of applications. They can be used as monomer in the preparation of polyesters, such as poly(ethylene terephthalate), poly(ethylene naphthenate) or poly(ethylene furandicarboxylate), but ethylene glycol can also be used for example in heat transfer media and anti-freeze compositions.

[0003] Recently, increased efforts are being made to produce alkylene glycols from sustainable resources, such as carbohydrates. By enabling the preparation of alkylene glycols, such as ethylene glycol, from sustainable resources, the dependence of fossil fuel resources is advantageously reduced.

[0004] WO2016/114658 describes a process for preparing ethylene glycol from a carbohydrate source. The carbohydrate source is reacted with hydrogen in the presence of a diluent and a catalyst system comprising a tungsten compound and at least one hydrogenolysis metal selected from the groups 8, 9 or 10 of the Periodic Table of the Elements. WO2016/114658 indicates that higher polyols, such as glycerol, erythritol, or sorbitol, tend to be produced as by-products in a process for preparing ethylene glycol from carbohydrates.

[0005] Although higher polyols, such as sorbitol, can be recycled as described in WO2016/114658, a substantial recycle of such higher polyols is not desirable. At the reactor conditions for converting a carbohydrate source, higher polyols such as sorbitol cannot be completely converted. As a result the concentration of such higher polyols would slowly build up, making the process less suitable for continuous operation.

[0006] Non-prepublished patent application PCT/EP2019/056518 mentions the possibility of separating, for example by distillation, a sorbitol-rich fraction and reacting, in a subsequent second reactor, at least a part of such sorbitol-rich fraction in the presence of a concentrated amount of homogeneous catalyst containing tungsten and a heterogeneous catalyst containing one or more transition metals from groups 8, 9 and 10 of the Periodic Table of the Elements.

[0007] In its examples, non-prepublished patent application PCT/EP2019/056518 illustrates interesting results. However, as illustrated in the examples of this current invention, conversion rates slowly decrease due to catalyst deactivation.

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[0008] It would be an advancement in the art to provide a process for the conversion of one or more polyols chosen from the group consisting of sorbitol, glycerol, and erythritol that would allow for a prolonged runtime with economically interesting conversion rates.

5 SUMMARY OF THE INVENTION

Such a process has been obtained with the process according to the invention. Accordingly the present invention provides a process for the conversion of one or more polyols including the steps of:

- 10 (i) reacting one or more polyols chosen from the group consisting of sorbitol, glycerol, and erythritol, at a temperature in the range from equal to or more than 200°C to equal to or less than 280°C, in the presence of hydrogen and in the presence of a homogeneous catalyst, which homogeneous catalyst contains tungsten, in a reactor comprising a fixed bed of heterogeneous catalyst, which heterogeneous catalyst contains one or more transition metals from groups 8, 9 and 10 of the Periodic Table of the Elements, yielding one or more
15 reaction products and a spent heterogeneous catalyst;
- (ii) regenerating the spent heterogeneous catalyst by washing the fixed bed of heterogeneous catalyst with a washing liquid and subsequently drying the fixed bed of heterogeneous catalyst under an atmosphere and/or in a flow of inert gas, yielding a regenerated heterogeneous catalyst; and
- 20 (iii) optionally re-using at least a portion of the regenerated heterogeneous catalyst as heterogeneous catalyst.

[0009] The above process advantageously allows one to operate the process for the conversion of one or more polyols chosen from the group consisting of sorbitol, glycerol, and erythritol for a prolonged period of time with economically interesting conversion rates. The
25 process according to the invention may advantageously have a runtime of equal to or more than 50 hours and even equal to or more than 100 hours.

[0010] Without wishing to be bound to any kind of theory, inventors believe that the heterogeneous catalyst, comprising one or more transition metals from groups 8, 9 and 10 of the Periodic Table of the Elements, is important in catalyzing a reduction of hexavalent
30 tungsten to pentavalent tungsten. It is further believed that, if operated for a prolonged period of time, an increasing amount of tungsten species can deposit onto the surface of the heterogeneous catalyst, increasingly preventing the heterogeneous catalyst from being an active catalyst.

[0011] The discovery of this previously unrecognized problem caused the inventors to
35 recognize the need for the removal of deposited tungsten species from the heterogeneous catalyst.

DETAILED DESCRIPTION OF THE INVENTION

[0012] Preferably step (i) is preceded by a step wherein: a feed of the one or more polyols; hydrogen; and the homogeneous catalyst are provided to the reactor. If not already present
5 (for example in a fixed bed reactor) also a heterogeneous catalyst, which heterogeneous catalyst contains one or more transition metals from groups 8, 9 and 10 of the Periodic Table of the Elements, can be provided to such reactor.

[0013] The feed of one or more polyols may contain or consist of one or more polyols chosen from the group consisting of sorbitol, glycerol, and erythritol. Suitably the feed may
10 contain or consist of mixtures of such sorbitol, glycerol, and erythritol. In addition to the one or more polyols chosen from the group consisting of sorbitol, glycerol, and erythritol, other compounds may be present. For example the feed may further comprise alkylene glycols, such as ethylene glycol, propylene glycol and/or butylene glycol.

[0014] Preferably the reactor is supplied with a feed comprising the one or more polyols
15 chosen from the group consisting of sorbitol, glycerol, and erythritol in an amount in the range from equal to or more than 10 wt. %, more preferably equal to or more than 20 wt. %, still more preferably equal to or more than 30 wt. %, even more preferably equal to or more than 40 wt. %, even still more preferably equal to or more than 50 wt. %, yet still more preferably equal to or more than 60 wt. % and most preferably equal to or more than 70 wt.
20 % to equal to or less than 100 wt. %, based on the total weight of the feed.

[0015] By a polyol is herein understood an organic compound comprising multiple, suitably three or more, hydroxyl groups. Sorbitol (hexane-1,2,3,4,5,6-hexol), erythritol (butane-1,2,3,4-tetraol) and glycerol (propane-1,2,3-triol) have boiling points above 250°C at atmospheric pressure of 0.1 Megapascal absolute. Sorbitol, glycerol and erythritol are
25 therefore herein also referred to as "heavy polyols".

[0016] Preferably the one or more polyols are chosen from the more limited group of sorbitol, and erythritol. More preferably the one or more polyols are chosen from the group of sorbitol, erythritol and mixtures thereof. Still more preferably the one or more polyols are sorbitol and/or erythritol. Most preferably the one or more polyols is sorbitol.

[0017] That is, most preferably the process according to the invention is a process for the
30 conversion of sorbitol including the steps of:

(i) reacting sorbitol, at a temperature in the range from equal to or more than 200°C to equal to or less than 280°C, in the presence of hydrogen and in the presence of a homogeneous catalyst, which homogeneous catalyst contains tungsten, in a reactor comprising a fixed bed
35 of heterogeneous catalyst, which heterogeneous catalyst contains one or more transition

metals from groups 8, 9 and 10 of the Periodic Table of the Elements, yielding one or more reaction products and a spent heterogeneous catalyst;

(ii) regenerating the spent heterogeneous catalyst by washing the fixed bed of heterogeneous catalyst with a washing liquid and subsequently drying the fixed bed of heterogeneous catalyst under an atmosphere and/or in a flow of inert gas, yielding a regenerated heterogeneous catalyst; and

(iii) optionally re-using at least a portion of the regenerated heterogeneous catalyst as heterogeneous catalyst.

[0018] A feed to the reactor containing the above sorbitol may suitably also contain other compounds such as erythritol, glycerol and/or alkylene glycols. Preferably the reactor is supplied with a feed comprising sorbitol in an amount in the range from equal to or more than 5 wt. %, more preferably equal to or more than 10 wt. %, still more preferably equal to or more than 20 wt. %, and most preferably equal to or more than 30 wt. % to equal to or less than 100 wt. %, suitably equal to or less than 90 wt. % and more suitably equal to or less than 80 wt. %, based on the total weight of such feed.

[0019] As the polyol can act as its own solvent, no solvent is necessary. Step (i) can therefore be carried out in the presence or in the absence of any additional solvent such as water. More preferably, any feed to the reactor contains preferably equal to or less than 20 wt. %, more preferably equal to or less than 10 wt. %, still more preferably equal to or less than 5 wt. % and even more preferably equal to or less than 1 wt. % of water. Still more preferably, any feed to the reactor contains equal to or less than 0.1 wt. % water. Most preferably the feed to the reactor contains no or essentially no water.

[0020] The reaction in step (i) is preferably carried out in a reaction mixture containing equal to or less than less than 20 wt. %, more preferably equal to or less than 10 wt. %, still more preferably equal to or less than 5 wt. % and even more preferably equal to or less than 1 wt. % of water. Still more preferably, the reaction in step (i) is preferably carried out in a reaction mixture containing equal to or less than 0.1 wt. % water. Most preferably the reaction in step (i) is carried out in a reaction mixture containing no or essentially no water.

[0021] Also the presence of alkylene glycols is not necessary in step (i), although such alkylene glycols can be formed in the conversion of the one or more polyols. Any feed to the reactor therefore preferably contains equal to or less than 20 wt. %, more preferably equal to or less than 10 wt. %, still more preferably equal to or less than 5 wt. % and even more preferably equal to or less than 1 wt. % of alkylene glycols. Still more preferably, any feed to the reactor contains equal to or less than 0.1 wt. % alkylene glycols. Most preferably the feed to the reactor contains no or essentially no alkylene glycols.

[0022] Preferably the one or more polyols, more preferably the sorbitol, can be continuously or periodically added to the reactor. At the same time one or more reaction products may be continuously or periodically withdrawn from the reactor.

[0023] The hydrogen can be provided to the reactor as substantially pure hydrogen.

5 Alternatively, the hydrogen may be supplied in the form of a mixture of hydrogen and an inert gas. The inert gas can suitably be selected from nitrogen, argon, helium, neon and mixtures thereof. The volume ratio of hydrogen to the inert gas may vary between wide ranges. Suitably, the volume ratio is not very low, since the reaction proceeds well when the hydrogen partial pressure is sufficiently high. Accordingly, the volume ratio between
10 hydrogen and the inert gas may be from 1:1 to 1:0.01. More preferably, only hydrogen is used as gas in the process according to the invention. Preferably the hydrogen is continuously or periodically added to the reactor.

[0024] The homogeneous catalyst and heterogeneous catalyst are together herein also referred as the catalyst system.

15 [0025] The homogeneous catalyst contains tungsten and is herein also referred to as tungsten-comprising homogenous catalyst.

[0026] The tungsten can be present as elemental tungsten or as a tungsten compound. Such a tungsten compound can for example be a tungstic acid or a tungstate salt. The homogeneous catalyst can suitably contain one or more tungsten compounds. The tungsten
20 or tungsten compound(s) can suitably be dissolved in the reaction mixture. Preferably, the tungsten has an oxidation state of at least +2. More preferably the tungsten has an oxidation state of +4, +5 or +6. When dissolved in the feed or in the reaction mixture, the dissolved tungsten or dissolved tungsten compound may form complexes with (other) components of the feed, or respectively the reaction mixture.

25 [0027] The homogeneous catalyst provided to the reactor can be freshly made homogeneous catalyst or recycled homogeneous catalyst. Freshly made homogeneous catalyst is herein also referred to as "virgin" homogeneous catalyst. Such virgin homogeneous catalyst is preferably selected from the group consisting of tungstic acid (H_2WO_4) and tungstate compounds, such as tungstic salts, for example comprising at least
30 one Group 1 or 2 element, such as for example sodium tungstate (Na_2WO_4) or potassium tungstate (K_2WO_4) or for example comprising ammonium tungstate. It is also possible to use a combination of one or more of these.

[0028] Suitably the homogeneous catalyst provided to the reactor can contain recycled homogeneous catalyst or a combination of virgin homogeneous catalyst and recycled
35 homogeneous catalyst. Hence, the homogeneous catalyst provided to the reactor in the current invention can contain or consist of recycled tungsten species recovered, directly or indirectly (for example via a distillation), from the effluent of the same or another reactor.

[0029] Any recycled homogeneous catalyst may contain tungsten as a complex with components from the feed or the reaction mixture in which such homogeneous catalyst may be dissolved. The recycled homogeneous catalyst may therefore suitably comprise tungsten in a form derived from a precursor tungsten compound, such as the above virgin
5 homogeneous catalyst, as originally provided.

[0030] Preferably the homogeneous catalyst contains a tungsten compound or tungsten derived from a tungsten compound, wherein such tungsten compound is selected from the group consisting of tungstic acid (H_2WO_4), tungsten bronze (present as H_xWO_3 or M_xWO_3 , wherein x is a variable smaller than 1 (<1) and M is a metal, for example an alkali or alkali
10 earth metal), ammonium tungstate, ammonium metatungstate, ammonium paratungstate, tungstate compounds comprising at least one Group 1 or 2 element, metatungstate compounds comprising at least one Group 1 or 2 element, paratungstate compounds comprising at least one Group 1 or 2 element, tungsten oxide (WO_3), heteropoly compounds of tungsten, and combinations thereof. Tungstic acid (H_2WO_4), tungsten bronze (H_xWO_3) and
15 tungstate compounds comprising at least one Group 1 or 2 element, such as for example sodium tungstate (Na_2WO_4) or potassium tungstate (K_2WO_4), are preferred. Most preferably the homogeneous catalyst contains a tungsten compound or tungsten derived from a tungsten compound, wherein such tungsten compound is sodium tungstate and/or tungstic acid and/or tungsten bronze.

[0031] It has been found that the catalytic activity of the tungsten or tungsten compound advantageously increases if the tungsten or suitably the tungsten compound is dissolved, for example in the feed of polyols or in the reaction mixture. Preferably the homogeneous catalyst is continuously or periodically added to the reactor together with a feed comprising one or more polyols chosen from the group consisting of sorbitol, erythritol, glycerol and/or
25 derivatives thereof. More preferably the homogeneous catalyst is continuously or periodically added to the reactor together with a feed comprising sorbitol. Preferably such homogeneous catalyst that is continuously or periodically added contains tungsten that has an oxidation state of at least +2. Preferably the homogeneous catalyst is chosen from the group consisting of tungstic acid (H_2WO_4), tungsten bronze (H_xWO_3), sodium tungstate, a dissolved
30 tungstate ion, a dissolved metatungstate ion and a dissolved paratungstate ion.

[0032] As the tungsten can be present in so many forms, the tungsten and/or tungsten compounds are herein also referred to as tungsten species. By a tungsten species is herein understood any compound containing or consisting of tungsten element in any kind of form or oxidation state.

[0033] When (partly) oxidized, the tungsten species is herein also referred to as tungstate species. By a tungstate species is herein understood any compound comprising a tungsten-

oxide bond. Examples of tungstate species include tungsten dioxide and tungsten trioxide and tungsten bronze.

[0034] Preferably the homogeneous catalyst is dissolved in a feed comprising the one or more polyols, or more preferably in a feed comprising sorbitol, or in the reaction mixture.

5 [0035] The amount of tungsten, calculated as metal, that is provided to the reactor is preferably such that the concentration thereof in the reactor is maintained substantially constant. By substantially constant is herein understood that the difference between the highest and the lowest amounts of tungsten, calculated as metal, does not vary more than 10% from the average amount of tungsten in the reactor. Preferably the process according
10 to the invention is a continuous or semi-continuous process. Preferably a tungsten species is continuously or periodically added to the reactor. At the same time a portion of the tungsten species inside the reactor may be continuously or periodically withdrawn from the reactor, suitably via the reactor product stream. Whereas it is feasible to add tungsten periodically, it is preferred to provide for a continuous addition of tungsten to the reactor.

15 [0036] Preferably any concentration of tungsten species in a feed comprising the one or more polyols, or more preferably in a feed comprising sorbitol, as supplied to the reactor, ranges from equal to or more than 0.1 wt. % to equal to or less than 20.0 wt. % of tungsten (calculated as tungsten metal), based on the total weight of such feed. More preferably the concentration of tungsten species in any such feed ranges from equal to or more than 0.5
20 wt. %, preferably equal to or more than 1.0 wt. %, to equal to or less than 20.0 wt. %, to equal to or less than 10.0 wt. %, or even equal to or less than 5.0 wt. %, of tungsten (calculated as tungsten metal), based on the total weight of such feed.

[0037] Preferably the concentration of tungsten species in the reaction mixture during the reaction ranges from equal to or more than 0.1 wt. % to equal to or less than 20.0 wt. % of
25 tungsten (calculated as tungsten metal), based on the total weight of the reaction mixture. More preferably the concentration of tungsten species in the reaction mixture during the reaction ranges from equal to or more than 0.5 wt. %, preferably equal to or more than 1.0 wt. %, to equal to or less than 20.0 wt. %, to equal to or less than 10.0 wt. %, or even equal to or less than 5.0 wt. %, of tungsten (calculated as tungsten metal), based on the total
30 weight of the reaction mixture.

[0038] The heterogeneous catalyst contains one or more transition metals from groups 8, 9 and 10 of the Periodic Table of the Elements. The transition metal(s) can be selected from a wide range of transition metals. Preferably the one or more transition metal(s) is/are selected from the group consisting of Cu, Fe, Ni, Co, Pt, Pd, Ru, Rh, Ir, Os and combinations thereof.
35 More preferably the one or more transition metal(s) is/are selected from the group consisting of Ni, Pd, Pt, Ru, Rh, Ir and combinations thereof. Most preferred are nickel, ruthenium and combinations thereof. It has been found that these metals give good yields. The transition

metal can suitably be present in its metallic form or as its hydride or oxide or as another compound. As explained below, it is also possible for the transition metal to be present in a partly tungstated form.

[0039] The heterogeneous catalyst preferably comprises one or more transition metals from groups 8, 9 and 10 of the Periodic Table of the Elements, supported on a carrier. The carrier may be selected from a wide range of known carrier materials. Suitable carriers include activated carbon (also referred to as "active carbon"), silica, zirconia, alumina, silica-alumina, titania, niobia, iron oxide, tin oxide, zinc oxide, silica-zirconia, zeolitic aluminosilicates, titanosilicates, magnesia, silicon carbide, clays and combinations thereof. By activated carbon is herein understood an amorphous form of carbon with a surface area of at least 800 m²/g. Such activated carbon suitably has a porous structure. Most preferred carriers are activated carbon, silica, silica-alumina and alumina. Even more preferably, the catalyst comprises ruthenium and/or nickel as the transition metal and activated carbon as the carrier. Most preferably the heterogeneous catalyst contains ruthenium and/or nickel supported on activated carbon. Most preferably the heterogeneous catalyst contains ruthenium, preferably supported on activated carbon.

[0040] Preferably the heterogeneous catalyst comprises in the range from equal to or more than 1.0 wt. %, more preferably equal to or more than 2.0 wt. %, still more preferably equal to or more than 5.0 wt. %, to equal to or less than 50.0 wt. %, more preferably equal to or less than 20.0 wt. % of transition metal, on the basis of the total weight of transition metal and carrier.

[0041] It is possible for the heterogeneous catalyst to comprise more than one metal. Suitably, the heterogeneous catalyst can comprise at least one noble metal, selected from the group consisting of Pd, Pt, Ru, Rh and Ir, in combination with a second transition metal selected from the group of transition metals from groups 8, 9 or 10 of the Periodic Table of the Elements. The heterogeneous catalyst can for example comprise a combination of metals, such as for example Ni/Ir, Ni/Pt, Ni/Pd, Ni/Ru, Ru/Ir, Ru/Pt or Ru/Pd.

[0042] As explained in more detail below, it is believed that during the reaction tungsten species becomes deposited onto the heterogeneous catalyst. Therefore at least a portion of the heterogeneous catalyst can contain tungsten in addition to the one or more transition metals from groups 8, 9 and 10 of the Periodic Table of the Elements.

[0043] The heterogeneous catalyst is present within a fixed bed in the reactor.

[0044] Step (i) suitably comprises reacting one or more polyols chosen from the group consisting of sorbitol, glycerol, and erythritol, at a temperature in the range from equal to or more than 200°C to equal to or less than 280°C, in the presence of hydrogen and in the presence of a homogeneous catalyst, which homogeneous catalyst contains tungsten, in a reactor comprising a fixed bed of heterogeneous catalyst, which heterogeneous catalyst

contains one or more transition metals from groups 8, 9 and 10 of the Periodic Table of the Elements. Such step (i) suitably yields one or more reaction products and a spent heterogeneous catalyst.

5 [0045] The reactor can for example be a fixed bed reactor, a trickle flow reactor, a plug flow reactor or an external recycle loop reactor. Most preferably the reactor is a fixed bed reactor operated in plug flow.

[0046] Preferably the process is a continuous process. Preferably a continuous process is operated at a weight hourly space velocity (WHSV), expressed as the mass of per mass of transition metal, expressed as metal, per hour, in the range of 0.01 to 100 hr⁻¹, preferably 10 from 0.05 to 10 hr⁻¹. For practical purposes a WHSV in the range between 0.5 to 2.0 hr⁻¹ can be used.

[0047] The hydrogen partial pressure applied during step (i) preferably lies in the range from equal to or more than 1.0 Megapascal (MPa), preferably equal to or more than 2.0 MPa, more preferably equal to or more than 3.0 MPa to equal to or less than 16.0 MPa, preferably 15 equal to or less than 12.0 MPa, more preferably equal to or less than 8.0 MPa. All pressures herein are absolute pressures.

[0048] The total pressure applied during the reaction is suitably at least 1.0 MPa, preferably at least 2.0 MPa, more preferably at least 3.0 MPa. The total pressure applied during the reaction is suitably at most 16.0 MPa, more preferably at most 10.0 MPa. Preferably the 20 reactor is pressurized with hydrogen before addition of any starting material. The person skilled in the art will understand that the pressure at 20 °C will be lower than the actual pressure at the reaction temperature. The pressure applied during the reaction when converted back to 20 °C, preferably equals a pressure in the range from equal to or more than 0.7 MPa to equal to or less than 8.0 MPa.

25 [0049] As explained before, the total pressure may be applied by hydrogen gas or a hydrogen-containing gas, optionally in combination with the partial pressures of the contents of the reaction mixture.

[0050] It is preferred to maintain the partial hydrogen pressure at the reaction temperature within such range from 1.0 MPa to 16.0 MPa, preferably during the entire reaction. Therefore 30 hydrogen or a hydrogen-containing gas is preferably introduced into the reaction mixture during reaction as explained above.

[0051] During the reaction hydrogen is consumed. If the process is a continuous or semi-continuous process, the hydrogen is therefore preferably supplied in a continuous or semi-continuous manner.

35 [0052] In the reactor at least a portion of the one or more polyols is reacted in the presence of the hydrogen, or with the hydrogen, at a temperature in the range from equal to or more

than 200°C to equal to or less than 280 °C. More preferably a temperature in the range from equal to or more than 210°C to equal to or less than 270 °C is applied. The reactor may be brought to a temperature within these ranges before addition of any feed and can be maintained at a temperature within the range.

5 [0053] Without wishing to be bound to any theory it is believed that in the environment that is created in the reaction zone, hexavalent tungsten compounds and pentavalent tungsten compounds may exist. It is further believed that both the hexavalent and the pentavalent tungsten compounds may deposit, for example by adsorption, onto the surface of the heterogeneous catalyst and may thereby inactivate the heterogeneous catalyst.

10 [0054] It is believed that hexavalent tungsten may adsorb at the surface of the heterogeneous catalyst, and especially the transition metal thereof, and is reduced to the pentavalent tungsten, which pentavalent tungsten subsequently may desorb again from the surface. In solution subsequently a $H_xW_3O_{10}$ species may be formed, a complex of hexavalent tungsten and pentavalent tungsten.

15 [0055] The present inventors have found that, if operated for a prolonged period of time an increased amount of tungsten species may become deposited onto the surface of the heterogeneous catalyst, and especially the transition metal thereof, resulting in a decrease in conversion rates. Such tungsten species may become adsorbed, may become complexed or may in another manner become deposited onto the surface of the transition metal.

20 [0056] Hence, by reacting a portion of the one or more polyols in the presence of hydrogen in the process according to the invention, not only ethylene glycol is produced, but also spent heterogeneous catalyst is generated, which spent heterogeneous catalyst is believed to be enriched in deposited tungsten species.

[0057] The molar ratio of moles tungsten to moles transition metal, all calculated as metal, 25 of the spent heterogeneous catalyst may thus, suitably on average, be higher than the molar ratio of moles tungsten to moles transition metal, all calculated as metal, of the heterogeneous catalyst with which the reaction was started.

[0058] When a plug flow reactor is used comprising a fixed bed of heterogeneous catalyst, the heterogeneous catalyst after use in the reaction (i.e. the spent heterogeneous catalyst in 30 such a case) is believed to contain, suitably on average, a higher amount of tungsten species deposited onto its surface than the heterogeneous catalyst with which the use was started.

[0059] After the reaction a reactor product stream can be withdrawn from the reactor. This reactor product stream suitably contains ethylene glycol (ethane-1,2-diol) and/or propylene 35 glycol (propane-1,2-diol and/or propane-1,3-diol), yielded by the reaction. In addition, the reactor product stream can contain other compounds, such as unreacted sorbitol, erythritol or glycerol and one or more by-products such as diethylene glycol (2,2'-oxydi(ethan-1-ol)),

butane-1,2-diol, butane-1,3-diol, butane-2,3-diol, butane-1,4-diol, methanol, ethanol, propanol, butanol.

[0060] Step (ii) may suitably comprise regenerating the spent heterogeneous catalyst by removing at least a portion of deposited tungsten species from the spent heterogeneous catalyst.

[0061] In (ii) the spent heterogeneous catalyst is regenerated by washing the fixed bed of heterogeneous catalyst with a washing liquid and subsequently drying the fixed bed of heterogeneous catalyst under an atmosphere and/or in a flow of inert gas. Step (ii) suitably yields a regenerated heterogeneous catalyst.

[0062] Step (ii) is preferably carried out in the absence or essential absence of hydrogen.

[0063] The washing liquid preferably comprises or consists of an alkylene glycol, glycerol or other polyol, an alkali metal hydroxide solution or an alkali earth metal hydroxide solution or a combination of any of these. Preferably such washing liquid is chosen from the group consisting of alkylene glycols, a mixture of water and alkylene glycol, glycerol, a mixture of water and glycerol, an alkali metal hydroxide solution or an alkali earth metal hydroxide solution. More preferably the washing liquid is an alkylene glycol or a mixture of alkylene glycol and water. Examples of suitably alkylene glycols are ethylene glycol, propylene glycol and butylene glycol. Most preferably the washing liquid comprises or consists of ethylene glycol, propylene glycol, butylene glycol or a mixture thereof, such as an ethylene glycol/propylene glycol mixture, an ethylene glycol/butylene glycol mixture or an propylene glycol/butylene glycol mixture.

[0064] The washing liquid preferably contains no, or essentially no, tungsten species.

[0065] Preferred alkali metal hydroxide solutions include aqueous solutions of sodium hydroxide, potassium hydroxide and combinations thereof. An aqueous solution of sodium hydroxide is most preferred.

[0066] The washing can be carried out at a wide range of temperatures. Preferably, the washing of the spent heterogeneous catalyst is carried out at a temperature, herein also referred to as the "washing temperature", in the range from equal to or more than 100 °C, more preferably equal to or more than 150 °C, still more preferably equal to or more than 170 °C, and most preferably equal to or more than 180 °C, to equal to or less than 300 °C, more preferably equal to or less than 250 °C and most preferably equal to or less than 230 °C.

[0067] The amount of washing liquid applied may vary widely. Preferably the volume of washing liquid applied per weight of catalyst ranges from equal to or more than 2 ml washing liquid per gram of catalyst (2 ml/gram) to equal to or less than 500 ml washing liquid per gram of catalyst (500 ml/gram). More preferably the volume of washing liquid applied per

weight of catalyst ranges from equal to or more than 10ml/gram to equal to or less than 100 ml/grams.

[0068] In order to achieve optimal results, it can be advantageous to sequentially apply two or more portions, more preferably 2 to 5 portions, of washing liquid. That is, preferably the washing of the spent heterogeneous catalyst comprises two or more, more preferably 2 to 5, washing steps. Preferably each washing step would include washing of the spent heterogeneous catalyst with a washing liquid and optionally subsequent drying of the washed spent heterogeneous catalyst. After washing and drying a subsequent washing step could then be initiated. It can also be advantageous to wash the spent heterogeneous catalyst in a continuous manner by applying a continuous stream of washing liquid to the spent heterogeneous catalyst.

[0069] If two or more portions of washing liquid are applied, it is possible to use one and the same type of washing liquid for each portion, but one could also use different types of washing liquid for different portions or washing liquids with different concentrations for different portions. It can be advantageous to use a combination of washing liquids. For example the heterogeneous catalyst can first be washed with one washing liquid and can subsequently be washed with another, different washing liquid.

[0070] The time during which the catalyst is washed, also herein referred to as the "washing time", can also vary widely. Preferably the washing of the spent heterogeneous catalyst is carried out whilst applying washing times in the range from equal to or more than 15 minutes to equal to or less than 16 hours, more preferably in the range from equal to or more than 0.5 hour to equal to or less than 12 hours, and most preferably in the range from equal to or more than 1 hour to equal to or less than 8 hours.

[0071] Subsequently the fixed bed of heterogeneous catalyst is suitably dried under an atmosphere and/or in a flow of inert gas. The inert gas can for example be helium, argon or nitrogen. Nitrogen is preferred as inert gas. Preferably the washed and/or regenerated catalyst is dried in a flow of inert gas.

[0072] The drying preferably includes the application of heat. Preferably the washed and/or regenerated catalyst is dried at a temperature, herein also referred to as the "drying temperature" in the range from equal to or more than 100 °C, more preferably equal to or more than 150 °C, to equal to or less than 300 °C, more preferably equal to or less than 250 °C and most preferably equal to or less than 230 °C.

[0073] Preferably therefore step (ii) comprises or consists of:

- washing the spent heterogeneous catalyst with a washing liquid, for example with a washing liquid as described herein, to yield a washed, regenerated, heterogeneous catalyst;

- drying the washed, regenerated, heterogeneous catalyst, under an atmosphere and/or in a flow of inert gas, preferably by applying a temperature in the range from equal to or more than 100 °C to equal to or less than 300 °C, to yield a dried, regenerated, heterogeneous catalyst.

5 [0074] Suitably the dried, regenerated, heterogeneous catalyst can be kept under an inert gas flow, such as a nitrogen flow, at room temperature (about 20 °C) until re-use thereof.

[0075] Step (ii) is preferably carried out "in-situ". By "in-situ" is understood that step (ii) is carried out inside of the reactor, in contrast to an "ex-situ" step which would be carried out outside the reactor.

10 [0076] When the regeneration is carried out "in-situ", at least a portion of the deposited tungsten species is removed from the spent heterogeneous catalyst inside the reactor. Such is advantageous, as the heterogeneous catalyst in the reactor is present in a fixed bed.

[0077] Preferably the washing is carried out intermittently. For example, preferably the process according to the invention is carried out such that the reactor is supplied in an
15 alternating manner with: (i) a stream containing the one or more polyols chosen from the group consisting of sorbitol, glycerol, and erythritol; and (ii) a stream comprising a washing liquid.

[0078] The above advantageously allows one to operate the process in a plurality of two or more reactors, each reactor comprising a fixed bed of heterogeneous catalyst, which two or
20 more reactors may be operated in swing-mode. That is, where at any one time, one or more reactors are operated in a reaction mode where one or more polyols chosen from the group consisting of sorbitol, glycerol, and erythritol are reacted, whilst in one or more other reactors deposited tungsten species are removed from the spent heterogeneous catalyst, for example by washing.

25 [0079] Step (ii) suitably yields a regenerated heterogeneous catalyst. The regenerated heterogeneous catalyst may still comprise some residual tungsten deposited onto the transition metal. The tungsten species remaining in the regenerated heterogeneous catalyst are preferably tungsten species wherein the tungsten has an oxidation state of +4, +5 and/or +6. More preferably the tungsten species contain or consist of tungsten dioxide (also known
30 as tungsten (IV) oxide) and/or tungsten trioxide (also known as tungsten (VI) oxide). That is, suitably the regenerated heterogeneous catalyst comprises remaining tungsten dioxide and/or tungsten trioxide deposited onto the transition metal(s). The average weight percentage of tungsten, calculated as metal, of such regenerated heterogeneous catalyst, however, may suitably be lower than the average weight percentage of tungsten, calculated
35 as metal, of the spent heterogeneous catalyst. More suitably the weight ratio of total amount of tungsten species (calculated on tungsten metal basis) to transition metal (calculated on

metal basis) in the regenerated heterogeneous catalyst is lower than the weight ratio of total amount of tungsten species (calculated on tungsten metal basis) to transition metal (calculated on metal basis) in the spent heterogeneous catalyst. Preferably the weight ratio of weight tungsten to the total weight of transition metal, all calculated on metal basis, in the regenerated heterogeneous catalyst is equal to or lower than 30:1, more preferably equal to or lower than 20:1, even more preferably equal to or lower than 10:1, still more preferably equal to or lower than 5:1(wt/wt), and most preferably equal to or lower than 2:1 (wt/wt). Suitably the weight ratio of weight tungsten to the total weight of transition metal, all calculated on metal basis, in the regenerated heterogeneous catalyst is equal to or higher than 1:1000, more suitably equal to or higher than 1:100.

[0080] As illustrated by the examples, such regenerated heterogeneous catalyst may under certain circumstances even perform better in step (i) than a fresh heterogeneous catalyst.

[0081] Optional step (iii) suitably comprises re-using at least a portion of the regenerated heterogeneous catalyst as heterogeneous catalyst another reaction.

[0082] The invention therefore further provides a process for the conversion of one or more polyols including the step of reacting one or more polyols chosen from the group consisting of sorbitol, glycerol, and erythritol, at a temperature in the range from equal to or more than 200°C to equal to or less than 280°C, in the presence of hydrogen and in the presence of a homogeneous catalyst, which homogeneous catalyst contains tungsten, in a reactor comprising a fixed bed of regenerated heterogeneous catalyst, which heterogeneous catalyst contains one or more transition metals from groups 8, 9 and 10 of the Periodic Table of the Elements, yielding one or more reaction products, wherein the heterogeneous catalyst is a regenerated heterogeneous catalyst obtained by a process as described above.

[0083] The process is herein below further illustrated by the following non-limiting examples.

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Example 1

A feed having the composition as listed in Table 1A was converted in a small-scale plug flow reactor comprising a fixed bed comprising a heterogeneous catalyst comprising 10 wt. % ruthenium on activated carbon.

30 The feed was converted during 18 days at a reaction temperature of 240 °C. Conversion slowly decreased over time and also yields to the desired reaction products ethylene and propylene slowly decreased. After a runtime of 18 days the reaction temperature was increased but kept within the range of 240 - 255°C. The total runtime was about 30 days. After 30 days the feed was stopped. The total pressure applied was about 5 Megapascal.

35 The feed was provided to the reactor at a flow rate of about 0.05 milliliter per minute. Hydrogen was provided at a flow rate of about 83 milliliter per minute.

The conversions at a runtime of 18 days are listed in Table 1B. The yields of desired reaction products ethylene glycol and propylene glycol at such runtime of 18 days are also listed.

5 Table 1A: Feed composition

Component	Weight percentage in the feed (wt%)
Ethylene glycol	0.3
Glycerol	60.7
Erythritol	15.0
Sorbitol	21.3
Glucose	0.2
1,3-Propylene glycol	0.3
1, 4- Butylene glycol	0.2
Tungstic acid (H ₂ WO ₄)	2.0

Table 1B: Conversion rate at 18 days of operation

Component	Conversion (wt/wt)
Sorbitol	52.8
Erythritol	39.1
Glycerol	39.7

Table 1C: Yields at 18 days of operation

Product	Yield (wt/wt) based on weight of the effluent (gram specified product per gram of effluent)
Ethylene glycol	2
1,2-Propylene glycol	4.1

Example 2

The fixed bed comprising the heterogeneous catalyst comprising 10 wt. % ruthenium on activated carbon as obtained after the reaction in example 1, was washed, in-situ within the reactor by pumping a washing liquid consisting of glycerol through the reactor, under an air atmosphere of about 0.1 Megapascal, and at a temperature of about 200 °C, in the absence of hydrogen. Before the washing there was a period of 38 minutes in which the system was warmed up and glycerol was pumped in to fill the dead volume before the catalyst bed and then glycerol was pumped at 0.5 milliliters per minute for about 4.2 hours to keep a ratio 36 liter glycerol/ kilogram of catalyst. Samples were taken from the resulting spent washing liquid were taken during the washing step at a time of 26 minutes (t1), a time of 86 minutes (t2), a time of 146 minutes (t3), a time of 206 minutes (t4) and a time of 246 minutes (t5) and analyzed to determine tungsten (W) content, determined as metal, in weight percent (wt. %) on the basis of the total sample, by means of Inductively coupled Plasma (ICP) analysis. The results are summarized in Table 2.

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Table 2: Analysis of samples of spent washing liquid

Sample time	Tungsten (W) content (wt. %)
26 (t1)	0.41-0.43 (in duplo)
86 (t2)	0.12
146 (t3)	0.07
206 (t4)	0.05
246 (t5)	0.04

Subsequently the fixed bed comprising the washed heterogeneous catalyst was dried with a flow of nitrogen, applied at a flow rate of 20 milliliters per minute, at a temperature of 200 °C for a period of 3 hours, to remove all of the washing liquid (glycerol).

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Example 3

The fixed bed comprising the regenerated heterogeneous catalyst comprising 10 wt. % ruthenium on activated carbon as obtained after the washing, drying and regeneration in example 2, was reused in a reaction.

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A feed having the composition as listed in Table 3A was converted in the fixed bed as obtained in example 2. The feed was converted during 3 days at a reaction temperature of 240 °C at a total pressure of about 5 Megapascal. The feed was provided to the reactor at a flow rate of about 0.05 milliliter per minute. Hydrogen was provided at a flow rate of about 83 milliliter per minute.

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The conversions respectively the yields obtained at a runtime of the 3 days are listed in Table 3B, respectively Table 3C.

Table 3A: Feed composition

Component	Weight percentage in the feed (wt%)
Ethylene glycol	0.30
Glycerol	59.85
Erythritol	15.38
Sorbitol	21.81
Glucose	0.10
1,3-Propylene glycol	0.30
1, 4- Butylene glycol	0.30
Tungstic acid (H ₂ WO ₄)	1.96

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Table 3B: Conversion rate after 3 days of operation

Component	Conversion (wt/wt)
Sorbitol	73.8
Erythritol	64.1
Glycerol	64

Table 3C: Yields after 3 days of operation

Product	Yield (wt/wt) based on weight of the effluent (gram specified product per gram of effluent)
Ethylene glycol	3
Propylene glycol	6.4

CLAIMS

1. A process for the conversion of one or more polyols including the steps of:
 - (i) reacting one or more polyols chosen from the group consisting of sorbitol, glycerol, and erythritol, at a temperature in the range from equal to or more than 200°C to equal to or less than 280°C, in the presence of hydrogen and in the presence of a homogeneous catalyst, which homogeneous catalyst contains tungsten, in a reactor comprising a fixed bed of heterogeneous catalyst, which heterogeneous catalyst contains one or more transition metals from groups 8, 9 and 10 of the Periodic Table of the Elements, yielding one or more reaction products and a spent heterogeneous catalyst;
 - (ii) regenerating the spent heterogeneous catalyst by washing the fixed bed of heterogeneous catalyst with a washing liquid and subsequently drying the fixed bed of heterogeneous catalyst under an atmosphere and/or in a flow of inert gas, yielding a regenerated heterogeneous catalyst; and
 - (iii) optionally re-using at least a portion of the regenerated heterogeneous catalyst as heterogeneous catalyst.
2. The process according to claim 1, wherein the homogeneous catalyst contains tungsten which tungsten is present as a tungsten compound or tungsten derived from a tungsten compound.
3. The process according to claim 1 or 2, wherein the homogeneous catalyst contains or consists of a complex of hexavalent tungsten and pentavalent tungsten.
4. The process according to any one of claims 1 to 3, wherein step (ii) comprises the in-situ removal of deposited tungsten species from the spent heterogeneous catalyst.
5. The process according to any one of claims 1 to 4, wherein the washing is carried out at a washing temperature in the range from equal to or more than 100 °C to equal to or less than 300 °C.
6. The process according to any one of claims 1 to 5, wherein the drying is carried out at a drying temperature in the range from equal to or more than 100 °C to equal to or less than 300 °C.

7. The process according to any one of claims 1 to 6, wherein the washing liquid is chosen from the group consisting of alkylene glycols or mixtures thereof, a mixture of water and alkylene glycol, glycerol, a mixture of water and glycerol, an alkali metal hydroxide solution or an alkali earth metal hydroxide solution.
8. The process according to any one of claims 1 to 7, wherein the washing liquid comprises or consists of ethylene glycol, propylene glycol, butylene glycol or a mixture thereof.
9. The process according to any one of claims 1 to 8, wherein step (ii) comprises two or more washing steps, wherein the fixed bed of heterogeneous catalyst is washed and/or two or more drying steps wherein the fixed bed of heterogeneous catalyst is dried.
10. The process according to any one of claims 1 to 9, wherein step (ii) is carried out in the absence of hydrogen.
11. The process according to any one of claims 1 to 10, wherein the inert gas is nitrogen.
12. The process according to any one of claims 1 to 11, wherein the reactor is supplied in an alternating manner with: (i) a stream containing the one or more polyols chosen from the group consisting of sorbitol, glycerol, and erythritol; and (ii) a stream comprising a washing liquid.
13. The process according to any one of claims 1 to 12, wherein the process is carried out in a plurality of two or more reactors, each reactor comprising a fixed bed of heterogeneous catalyst, which two or more reactors are operated in swing-mode.
14. A process for the conversion of one or more polyols including the step of reacting one or more polyols chosen from the group consisting of sorbitol, glycerol, and erythritol, at a temperature in the range from equal to or more than 200°C to equal to or less than 280°C, in the presence of hydrogen and in the presence of a homogeneous catalyst, which homogeneous catalyst contains tungsten, in a reactor comprising a fixed bed of regenerated heterogeneous catalyst, which heterogeneous catalyst contains one or more transition metals from groups 8, 9 and 10 of the Periodic Table of the Elements, yielding one or more reaction products, wherein the heterogeneous catalyst is a regenerated heterogeneous catalyst obtained by a process according to anyone of claims 1 to 13.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2020/054820

A. CLASSIFICATION OF SUBJECT MATTER
 INV. C07C29/60 C07C29/00 C07C31/20
 ADD.
 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
 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
 EPO-Internal, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2016/114658 A1 (AVANTIUM KNOWLEDGE CENTRE BV [NL]) 21 July 2016 (2016-07-21) cited in the application abstract claims 1-23	1-14
A	US 2011/313209 A1 (KALNES TOM N [US] ET AL) 22 December 2011 (2011-12-22) abstract examples 1-17 claims 1,12	1-14

Further documents are listed in the continuation of Box C.

See patent family annex.

- * Special categories of cited documents :
- | | |
|---|---|
| <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> | <p>"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</p> <p>"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</p> <p>"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</p> <p>"&" document member of the same patent family</p> |
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Date of the actual completion of the international search 15 June 2020	Date of mailing of the international search report 25/06/2020
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2020/054820

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