



## Process for reducing the oxygen content of biomass using vanadium-based catalysts

Dethlefsen, Johannes Rytter; Fristrup, Peter

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(71) Applicant: DANMARKS TEKNISKE UNIVERSITET  
[DK/DK]; Anker Engélundsvej 1, Bygning 101A, 2800  
Lyngby (DK).

(72) Inventors: DETHLEFSEN, Johannes Rytter; Korsager  
Allé 53, 2700 Brønshøj (DK). FRISTRUP, Peter;  
Bernhard Olsens Vej 25, 2830 Virum (DK).

(74) Agent: PLOUGMANN VINGTOFT A/S; Rued Lang-  
gaards Vej 8, 2300 Copenhagen S (DK).

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(54) Title: PROCESS FOR REDUCING THE OXYGEN CONTENT OF BIOMASS USING VANADIUM-BASED CATALYSTS

(57) Abstract: The present invention concerns a process for converting biomass into useful organic building blocks for the chemical industry. The process involves the use of vanadium-based catalysts of the formula  $A^{a+}a(V_vX_xR^1yR^2z)^{a+a-}$ , which may be readily prepared from industrial vanadium compounds, for converting a polyol in a solvent.



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## **PROCESS FOR REDUCING THE OXYGEN CONTENT OF BIOMASS USING VANADIUM-BASED CATALYSTS**

### **Field of the invention**

The present invention concerns a process for converting biomass into useful building blocks for the chemical industry. The process involves the use of vanadium-based catalysts, which are commercially available or may be readily prepared from industrial vanadium compounds.

### **Background of the invention**

- 10 The chemistry building blocks used in industrial polymers, fine chemicals etc. are typically prepared from fossil fuels. However, the use of fossil fuel-based building blocks is not sustainable, and it is therefore desirable to find alternative ways of preparing these building blocks.
- 15 Biomass and waste products from processes including biomass contain more oxygen than the products obtained from fossil resources, and they are therefore not immediately useful in preparing organic chemistry building blocks. One example of a waste product obtained from processing biomass is glycerol, which is a byproduct from biodiesel production. According to Ullmann's Encyclopedia of
- 20 Industrial Chemicals, the production of glycerol will be six times higher than the demand by 2020. Glycerol is not useful as such as a building block, but if it is reduced to allyl alcohol, or even propylene, it could serve as a building block.

- US 8,273,926 concerns a method for converting a polyol to the corresponding olefin by heating with formic acid. One of the polyols tested in this patent is glycerol. The disadvantages of the method include the need of carrying out three formic acid treatment/distillation/cooling-to-room-temperature cycles, the use of an inert atmosphere, and the separation of allyl alcohol from formic acid.
- 30 Yi et al., *ChemSusChem*, 2012, 5, 1401–1404, describe rhenium-catalyzed deoxydehydration of glycerol, erythritol, and threitol. The disadvantage of using rhenium-based catalysts is the high and volatile price of the non-abundant metal.

Dethlefsen et al., *ChemSusChem*, 2014, 7, 425–428, disclose a process for converting polyols using molybdenum-based catalysts in the neat polyol or using a solvent that cannot be oxidized.

- 5 EP 2179981, Rajan et al., *Catalysis Science & Technology*, vol. 4 (2014), 81-92, and Suprun et al., *J. Mol. Catalysis A*, vol. 342 (2011), 91-100, disclose attempts at dehydrating glycerol using vapour phase reactions with phosphate-modified vanadium catalysts. However, they do not disclose solvent-based reactions.
- 10 Chapman and Nicholas, *Chem. Commun.*, 2013, 49, 8199–8201, disclose a process for reducing model vicinal diols using various vanadium-based catalysts to the corresponding unsaturated compounds. The only effective catalyst employed by Chapman and Nicholas was the  $\text{Bu}_4\text{N}(\text{dipic})\text{VO}_2$  catalyst (Bu is butyl and  $\text{dipic}^{2-}$  is the tridentate 2,6-pyridinedicarboxylate ligand) using either triphenylphosphine
- 15 or sodium sulfite as the reductant and benzene or chlorobenzene as the solvent. Most notably, 2,4-dimethyl-3-pentanol, a secondary alcohol, failed to provide any significant conversion of the activated styrene diol model compound.

- Hence, there exists a need for an improved process for reducing biomass and
- 20 biomass-derived compounds in an efficient and cost-effective manner. Preferably, the process should involve a catalyst that is either already commercially available or is readily prepared from commercially available compounds.

### Summary of the invention

- 25 Accordingly, the present invention concerns in one aspect a process for the conversion of a polyol, said polyol defined as an alcohol containing a plurality of hydroxyl groups, wherein at least two of the hydroxyl groups are located on adjacent carbon atoms, comprising the reaction of the polyol with a reactant selected from a polyol and a primary or secondary  $\text{C}_1\text{-C}_{10}$  alcohol in a solvent in
- 30 the presence of a vanadium-based catalyst at a temperature of at least 185 °C,

wherein said vanadium-based catalyst has the formula:



wherein

- 5  $A^{a+}$  is a mono-, di-, or trivalent counterion;  
 X is O, OH, S, or Se;  
 $R^1$  is selected from the group consisting of H, F, Cl, Br, I, CN,  $N_3$ , NCS, dithiocarbamates,  $CH_3$ ,  $BF_4$ ,  $PF_6$ ,  $CF_3SO_3$ ,  $CH_3CH_2SO_3$ ,  $CH_3O$ ,  $CH_3CH_2O$ ,  $CH_3CH_2CH_2O$ ,  $CH_3CH(O)CH_3$ ,  $SbF_6$ , and  $AsF_6$ ;  
 10  $R^2$  is a mono-, bi- or tridentate ligand;
- a is 0, 1, 2, 3, 4, 5, or 6;  
 v is 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10;  
 x is in the range 0 to 5v;  
 15 y is 0, 1, 2, 3, or 4; and  
 z is 0, 1, 2, 3, or 4;

wherein transition metals different from vanadium are present in a molar amount less than the molar amount of vanadium, wherein said polyol, said reactant, and

- 20 said vanadium-based catalyst are dissolved in said solvent, and wherein said solvent may be identical to or different from said polyol or said reactant.

## Detailed disclosure of the invention

### Definitions

- 25 In the present context, the term "primary or secondary  $C_1$ - $C_{10}$  alcohol" is intended to mean a linear or branched hydrocarbon with one or more primary or secondary OH groups and having 1 to 10 carbon atoms. The "primary or secondary  $C_1$ - $C_{10}$  alcohol" may also contain other functional groups than OH groups, such as e.g. CHO groups.

30

In the present context, the term "primary or secondary monohydric  $C_1$ - $C_{10}$  alcohol" is intended to mean a linear or branched hydrocarbon with one primary or secondary OH group and having 1 to 10 carbon atoms, such as methanol, ethanol, *n*-propanol, isopropyl alcohol, *n*-butanol, isobutyl alcohol, *sec*-butanol, *n*-

pentanol, isopentyl alcohol, 2-pentanol, 3-pentanol, neopentyl alcohol, *n*-hexanol, isohexyl alcohol, and *n*-heptanol.

In the context of the present invention, the term "glycerol" is intended to mean  
5 the chemical compound  $\text{HOCH}_2\text{CHOHCH}_2\text{OH}$ , which is also commonly referred to as 1,2,3-trihydroxypropane or glycerin.

In the context of the present invention, the term "diol" is intended to mean an organic chemical compound containing two hydroxyl groups.

10

In the context of the present invention, the term "triol" is intended to mean an organic chemical compound containing three hydroxyl groups.

In the context of the present invention, the term "polyol" refers to a polyhydric  
15 alcohol, or polyalcohol, that is, an alcohol containing a plurality of hydroxyl groups, wherein at least two of the hydroxyl groups are located on adjacent carbon atoms.

In the context of the present invention, the term "sugar alcohol", also known as  
20 alditol, is intended to mean a reduced form of a carbohydrate where the carbonyl group (aldehyde or ketone) has been reduced to a primary or secondary hydroxyl group.

In the context of the present invention, the term "donor atom" is intended to  
25 mean the atom directly attached to the vanadium atom. The term "monodentate ligand" is intended to mean a ligand having one donor atom. The term "bidentate ligand" is intended to mean a ligand having two donor atoms. The term "tridentate ligand" is intended to mean a ligand having three donor atoms.

30 In the context of the present invention, a "reductant" is intended to mean a reactant of the process of the invention that serves to reduce another reactant, such as the polyol. In the context of the present invention, an "oxidant" is intended to mean a reactant of the process of the invention that serves to oxidize another reactant, such as the polyol.

35

In the context of the present invention, the term "transition metal" is intended to mean an element in groups 3 to 12 of the periodic table, including lanthanides and actinides. Thus, elements 21 thru 30 (Sc thru Zn), elements 39 thru 48 (Y thru Cd), elements 57 thru 80 (La thru Hg), and elements 89 thru 112 (Ac thru 5 Cn) are considered transition metals in the context of the present invention.

In the context of the present invention, the term "polar solvent" is intended to mean a solvent with a dielectric constant of 15 or more at 25 °C. Similarly, a "non-polar" solvent is intended to mean a solvent with a dielectric constant of less 10 than 15 at 25 °C.

In one aspect of the present invention, it concerns a process for the conversion of a polyol, said polyol defined as an alcohol containing a plurality of hydroxyl groups, wherein at least two of the hydroxyl groups are located on adjacent 15 carbon atoms, comprising the reaction of the polyol with a reactant selected from a polyol and a primary or secondary C<sub>1</sub>-C<sub>10</sub> alcohol in a solvent in the presence of a vanadium-based catalyst at a temperature of at least 185 °C, wherein said vanadium-based catalyst has the formula:



wherein

A<sup>a+</sup> is a mono-, di-, or trivalent counterion;

X is O, OH, S, or Se;

25 R<sup>1</sup> is selected from the group consisting of H, F, Cl, Br, I, CN, N<sub>3</sub>, NCS, dithiocarbamates, CH<sub>3</sub>, BF<sub>4</sub>, PF<sub>6</sub>, CF<sub>3</sub>SO<sub>3</sub>, CH<sub>3</sub>CH<sub>2</sub>SO<sub>3</sub>, CH<sub>3</sub>O, CH<sub>3</sub>CH<sub>2</sub>O, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>O, CH<sub>3</sub>CH(O)CH<sub>3</sub>, SbF<sub>6</sub>, and AsF<sub>6</sub>;

R<sup>2</sup> is a mono-, bi- or tridentate ligand;

30 a is 0, 1, 2, 3, 4, 5, or 6;

v is 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10;

x is in the range 0 to 5v;

y is 0, 1, 2, 3, or 4; and

z is 0, 1, 2, 3, or 4;

35

wherein transition metals different from vanadium are present in a molar amount less than the molar amount of vanadium, wherein said polyol, said reactant, and said vanadium-based catalyst are dissolved in said solvent.

## 5 Temperature

As mentioned above, the temperature of the process of the present invention has been found to be an important parameter in obtaining a yield of reaction products. It has been found that the reaction temperature is advantageously at least 185 °C. There is in principle no upper limit on the reaction temperature, except  
10 for the critical point of the reaction mixture. However, it would be less than economical to run the reaction at a higher temperature than the temperature necessary to optimize the yield.

Accordingly, in one embodiment, the temperature is in the range 185 to 350 °C.  
15 In another embodiment, the temperature is in the range 195 to 300 °C. In yet another embodiment, the temperature is in the range 200 to 290 °C. In a further embodiment, the temperature is in the range 210 to 280 °C. In still a further embodiment, the temperature is in the range 210 to 270 °C.

## 20 Polyol

The process of the present invention achieves the reduction of biomass material or biomass-derived byproducts. Common to these biomass products is that they are polyols in the meaning used in the present context. Biomass-derived material may contain larger molecules, such as macromolecules, wherein only parts of the  
25 molecule contain a plurality of hydroxyl groups. The present invention is also intended to encompass these molecules in the process. Examples of such molecules are amylose, amylopectin, cellulose and hemicellulose.

The polyol can be cyclic or acyclic. In one embodiment of the invention, the polyol  
30 contains at least two hydroxyl groups located on adjacent carbon atoms, wherein both said hydroxyl groups are primary or secondary alcohol groups. In another embodiment, the polyol is a diol or triol. In a further embodiment, the polyol is selected from the group consisting of 1,2-hexanediol, 1,2-decanediol, and



glycerol. In still a further embodiment, the polyol is a diol. In yet a further embodiment, the polyol is a triol.

In another embodiment of the invention, the diol is 1,2-propanediol, 1,2-  
5 butanediol, 1,2-pentanediol, 1,2-hexanediol, 3,4-hexanediol, 2-ethyl-1,2-  
butanediol, 3-ethyl-3,4-hexanediol, 2,3-dimethyl-2,3-butanediol, 1,2-octanediol,  
1,2-decanediol, 1,2-dodecanediol, 1,2-tetradecanediol, *cis*-1,2-cyclooctanediol,  
*trans*-1,2-cyclooctanediol, *cis*-1,2-cyclohexanediol, *trans*-1,2-cyclohexanediol, *cis*-  
1,2-cyclopentanediol, *trans*-1,2-cyclopentanediol, 1,4-anhydroerythritol, or a  
10 mixture thereof.

In yet another embodiment of the invention, the triol is glycerol, 1,2,6-  
hexanetriol, 1,2,3-butanetriol, 1,2,3-hexanetriol, 1,2,3-cyclohexanetriol, or a  
mixture thereof.

15

An important byproduct in biodiesel production is glycerol. Hence, in still another embodiment, the polyol is glycerol.

In a further embodiment of the invention, the polyol is a sugar alcohol,  
20 monoanhydro sugar alcohol, sugar, or a mixture thereof. In yet a further  
embodiment of the invention, the polyol is xylitol, sorbitol, arabinitol, ribitol,  
mannitol, galactitol, iditol, erythritol, threitol, isomalt, lactitol, quinic acid, shikimic  
acid, or a mixture thereof. In still a further embodiment of the invention, the  
polyol is glucose, fructose, sucrose, lactose, maltose, xylose, or a mixture thereof.

25

### Reactant

A reduction reaction requires a reductant, which in turn is oxidized in the reaction. Similarly, an oxidation reaction requires an oxidant, which in turn is reduced in the reaction. A number of different reactants will be reduced or oxidized in the  
30 presence of the polyol and vanadium catalysts according to the present invention. The versatility of the vanadium catalyst in the process of the present invention is illustrated by the fact that the polyol itself may serve both as oxidant and reductant, i.e., for each two molecules of polyol one is reduced and the other oxidized. Hence, in one embodiment of the present invention, the reactant is the

polyol itself. In another embodiment, the reactant is a polyol different from the polyol being converted in the process. As an example, the polyol being converted may be glycerol, while the reactant may be propylene glycol.

- 5 Furthermore, it has been found that primary and secondary alcohols with just one OH group may serve as the reactant. Hence, in one embodiment, the reactant is a primary or secondary monohydric C<sub>1</sub>-C<sub>10</sub> alcohol.

10 It has been found that the primary and secondary monohydric alcohols used in the process of the invention may serve both as reductants and as solvents for the polyol and the vanadium-based catalyst. Hence, two advantageous properties are achieved with the primary and secondary monohydric alcohols used in the process of the invention.

- 15 The primary or secondary monohydric C<sub>1</sub>-C<sub>10</sub> alcohol used in the present invention may in one embodiment be a C<sub>1</sub>-C<sub>8</sub> alcohol, such as a C<sub>2</sub>-C<sub>5</sub> alcohol, e.g. a C<sub>2</sub>-C<sub>4</sub> alcohol, such as a C<sub>3</sub> alcohol. C<sub>x</sub> indicates that the alcohol in question has x carbon atoms. Hence, in a further embodiment, the primary or secondary monohydric C<sub>1</sub>-C<sub>10</sub> alcohol is selected from the group consisting of methanol, 20 ethanol, *n*-propanol, isopropyl alcohol, *n*-butanol, *sec*-butanol, isobutyl alcohol, *n*-pentanol, 2-pentanol, 3-pentanol, and mixtures thereof. In another embodiment, the primary or secondary monohydric C<sub>1</sub>-C<sub>10</sub> alcohol is isopropyl alcohol. In yet another embodiment the primary or secondary monohydric C<sub>1</sub>-C<sub>10</sub> alcohol is ethanol.

25

- It should be understood that when referring to "the primary or secondary monohydric C<sub>1</sub>-C<sub>10</sub> alcohol", this also includes mixtures of said alcohols. Thus, in one embodiment, a mixture of two or more primary or secondary monohydric C<sub>1</sub>-C<sub>10</sub> alcohols is used. In another embodiment, only one primary or secondary 30 monohydric C<sub>1</sub>-C<sub>10</sub> alcohol is used. In a particular embodiment, a mixture of isopropyl alcohol and ethanol is used. In a further embodiment, a mixture of isopropyl alcohol and methanol is used.

- Another example of a reactant, which does not necessarily meet the definition of 35 polyol in the context of the present invention, is a diol. The diol reactant may or

may not have hydroxyl groups on adjacent carbon atoms. Accordingly, in one embodiment of the present invention, the reactant is a diol different from the polyol, such as 1,5-pentanediol or 1,6-hexanediol, in particular 1,5-pentanediol.

## 5 Solvent

The polyol being converted in the process according to the present invention may also act as the solvent. Hence, the process may be carried out with or without an additional solvent. Accordingly, in one embodiment the process is carried out without a solvent in addition to the polyol. The reactant may also act as a solvent.

- 10 Thus, in another embodiment, the reactant is the only other solvent than the polyol. In still a further embodiment, the solvent is a solvent different from both the polyol and the reactant.

- If an additional solvent is used, it should preferably be chosen so that the
- 15 solubility of the polyol, the reactant, and the vanadium-based catalyst is high enough to fully dissolve all of these components. Suitable solvents for the process of the present invention include 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, diethyleneglycol, triethyleneglycol, *N,N*-dimethylformamide, *N*-methyl-2-pyrrolidone, dimethyl sulfoxide, acetone, acetaldehyde, or mixtures thereof.

20

- It has been found that polar solvents dissolve the polyol and the reactant better than non-polar solvents and therefore provide higher yields than non-polar solvents. Hence, in one embodiment, the solvent, such as in the case of using an additional solvent, is a polar solvent. In a further embodiment, if an additional
- 25 solvent is used, the volume of non-polar solvent is less than the combined volume of the polyol and the reactant.

- The solvent employed in the process according to the present invention is preferably in liquid form during the process. Hence, in one embodiment, the
- 30 boiling point of the solvent at the highest pressure employed during the process is higher than the highest reaction temperature employed during the process.

Vanadium-based catalyst

The vanadium-based catalyst employed in the process of the present invention has the formula:



wherein

$A^{a+}$  is a mono-, di-, or trivalent counterion;

X is O, OH, S, or Se;

- 10  $R^1$  is selected from the group consisting of H, F, Cl, Br, I, CN,  $N_3$ , NCS, dithiocarbamates,  $CH_3$ ,  $BF_4$ ,  $PF_6$ ,  $CF_3SO_3$ ,  $CH_3CH_2SO_3$ ,  $CH_3O$ ,  $CH_3CH_2O$ ,  $CH_3CH_2CH_2O$ ,  $CH_3CH(O)CH_3$ ,  $SbF_6$ , and  $AsF_6$ ;  
 $R^2$  is a mono-, bi- or tridentate ligand;

- 15 a is 0, 1, 2, 3, 4, 5, or 6;  
 v is 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10;  
 x is in the range 0 to 5v;  
 y is 0, 1, 2, 3, or 4; and  
 z is 0, 1, 2, 3, or 4;

20

wherein transition metals different from vanadium are present in a molar amount less than the molar amount of vanadium.

The element vanadium can exist in a number of oxidation states from -1 to +5.

- 25 The vanadium used in the vanadium-based catalyst according to the present invention may be in any one of these oxidation states. However, some oxidation states are more frequently encountered than others. Thus, in one embodiment V is V(III), V(IV), or V(V). In another embodiment, V is V(V) or V(IV), in particular V(V).

30

The vanadium-based catalyst may contain a mono-, di-, or trivalent cationic counterion,  $A^{a+}$ . This counterion may be selected from the group consisting of simple metal cations ( $Li^+$ ,  $Na^+$ ,  $K^+$ ,  $Rb^+$ ,  $Cs^+$ ,  $Be^{2+}$ ,  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Sr^{2+}$ ,  $Ba^{2+}$ ,  $Al^{3+}$ ,  $Ga^{3+}$ ,  $In^{3+}$ ,  $Tl^+$ ,  $Sn^{2+}$ ,  $Pb^{2+}$ ,  $Bi^{3+}$ ,  $Sc^{3+}$ ,  $Y^{3+}$ ,  $Ti^{2+}$ ,  $Ti^{3+}$ ,  $Cr^{2+}$ ,  $Cr^{3+}$ ,  $Mn^{2+}$ ,  $Mn^{3+}$ ,  $Fe^{2+}$ ,  
 35  $Fe^{3+}$ ,  $Ru^{2+}$ ,  $Ru^{3+}$ ,  $Co^{2+}$ ,  $Co^{3+}$ ,  $Rh^{3+}$ ,  $Ir^{3+}$ ,  $Ni^{2+}$ ,  $Pd^{2+}$ ,  $Pt^{2+}$ ,  $Cu^+$ ,  $Cu^{2+}$ ,  $Ag^+$ ,  $Au^+$ ,

$\text{Au}^{3+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{La}^{3+}$ , and other lanthanides),  $\text{H}^+$ ,  $\text{NH}_4^+$ , alkyl-substituted ammonium ions, pyridinium, and combinations thereof. In one embodiment,  $\text{A}^{q+}$  is  $\text{Na}^+$ ,  $\text{NH}_4^+$ , or  $\text{Bu}_4\text{N}^+$ , wherein Bu is butyl.

- 5 The X component may be any one of O, OH, S, Se, or mixtures thereof. In one embodiment, X is O.

- $\text{R}^1$  may be selected from any one of H, F, Cl, Br, I, CN,  $\text{N}_3$ , NCS, dithiocarbamates,  $\text{CH}_3$ ,  $\text{BF}_4$ ,  $\text{PF}_6$ ,  $\text{CF}_3\text{SO}_3$ ,  $\text{CH}_3\text{CH}_2\text{SO}_3$ ,  $\text{CH}_3\text{O}$ ,  $\text{CH}_3\text{CH}_2\text{O}$ ,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{O}$ ,  $\text{CH}_3\text{CH}(\text{O})\text{CH}_3$ ,  
 10  $\text{SbF}_6$ , and  $\text{AsF}_6$ ; . In one embodiment,  $\text{R}^1$  is selected from the group consisting of  $\text{CF}_3\text{SO}_3$ , Cl, and  $\text{CH}_3\text{CH}_2\text{SO}_3$ . In a further embodiment,  $\text{R}^1$  is  $\text{CH}_3\text{CH}_2\text{SO}_3$ . In yet a further embodiment,  $\text{R}^1$  is  $\text{CF}_3\text{SO}_3$ . In still a further embodiment,  $\text{R}^1$  is Cl.

- The  $\text{R}^2$  ligand may in principle have any electron pair-donating element as the  
 15 donor atom. In one embodiment,  $\text{R}^2$  has one or more donor atoms selected from the group consisting of N, O, and S. In another embodiment,  $\text{R}^2$  has one or more oxygen atoms as donor atoms. This embodiment also includes peroxide ( $\text{O}_2^{2-}$ ). In a further embodiment,  $\text{R}^2$  has one or more nitrogen atoms as donor atoms. In still a further embodiment,  $\text{R}^2$  is an organic ligand, such as 2,2'-bipyridine or  
 20 acetylacetonate. In yet another embodiment,  $\text{R}^2$  is 2,2'-bipyridine. In still a further embodiment,  $\text{R}^2$  is acetylacetonate (acac).

- The  $\text{R}^2$  ligand may be mono-, bi-, or tridentate. In one embodiment,  $\text{R}^2$  is a bidentate ligand.

25

In one embodiment,  $\text{R}^2$  is not cinnamate. In another embodiment,  $\text{R}^2$  is not dipicolinate (dipic). In yet another embodiment,  $\text{R}^2$  is neither cinnamate nor dipicolinate (dipic). In still another embodiment,  $\text{R}^2$  is not a phosphate, such as a hydrogen phosphate ( $\text{HPO}_4^{2-}$ ), phosphate ( $\text{PO}_4^{3-}$ ), or pyrophosphate ( $\text{P}_2\text{O}_7^{4-}$ ).

30

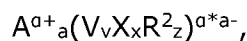
- The value of the various parameters, a, v, x, y, and z, may vary. In one embodiment, a is 0, 1, or 3. In another embodiment, v is 1, 2, or 10, in particular 1. The parameter x is in the range 0 to 5v, i.e. in the range of 0 to 5 times the number v. Thus, in an embodiment wherein v is 2, x is in the range 0 to 10. In  
 35 one embodiment, x is 0, 3, 4, 5, or 28.

R<sup>1</sup> may be present in the catalyst or it may be absent. Accordingly, y is 0, 1, 2, 3, or 4. In one embodiment, y is 0 or 1. The ligand R<sup>2</sup> may also be absent in the vanadium-based catalyst. Accordingly, z is 0, 1, 2, 3, or 4. In one embodiment, z is 0 or 2.

5

The individual embodiments for each of the parameters a, v, x, y, and z, may be combined according to the present invention. Hence, in one further embodiment, a is 0, 1, or 3, v is 1, 2, or 10, x is 3, 4, 5, or 28, y is 0, and z is 0 or 2. Thus, in this embodiment, the vanadium-based catalyst has the formula:

10



wherein

A<sup>a+</sup> is a mono-, di-, or trivalent counterion;

15 X is O, OH, S, or Se;

R<sup>2</sup> is a mono-, bi- or tridentate ligand;

a is 0, 1, or 3;

v is 1, 2, or 10;

x is 3, 4, 5, or 28; and

20 z is 0 or 2.

In a further embodiment X is O, and the vanadium-based catalyst has the formula:

25



wherein

A<sup>a+</sup> is a mono-, di-, or trivalent counterion;

R<sup>2</sup> is a mono-, bi- or tridentate ligand;

30 a is 0, 1, or 3;

v is 1, 2, or 10;

x is 3, 4, 5, or 28; and

z is 0 or 2.

Concrete examples of vanadium-based catalysts effective in the process of the invention are  $\text{NH}_4\text{VO}_3$ ,  $\text{Bu}_4\text{NVO}_3$ ,  $\text{Na}_3\text{VO}_4$ ,  $\text{VO}(\text{acac})_2$ ,  $\text{VO}_2$ ,  $\text{V}_2\text{O}_5$ ,  $\text{V}(\text{acac})_3$ , and salts of  $\text{V}_{10}\text{O}_{28}^{6-}$ , wherein acac is acetylacetonate and Bu is butyl. Accordingly, in one embodiment, the vanadium-based catalyst is selected from the group

5 consisting of  $\text{NH}_4\text{VO}_3$ ,  $\text{Bu}_4\text{NVO}_3$ ,  $\text{Na}_3\text{VO}_4$ ,  $\text{VO}(\text{acac})_2$ ,  $\text{VO}_2$ ,  $\text{V}_2\text{O}_5$ ,  $\text{V}(\text{acac})_3$ , and mixtures thereof, wherein acac is acetylacetonate and Bu is butyl.

In a further embodiment, the vanadium-based catalyst has the formula:



wherein

$\text{A}^{a+}$  is a mono-, di-, or trivalent counterion;

a is 0, 1, or 3;

15 v is 1, 2, or 10; and

x is 3, 4, 5, or 28.

In still a further embodiment, the vanadium-based catalyst is selected from the group consisting of  $\text{NH}_4\text{VO}_3$ ,  $\text{Bu}_4\text{NVO}_3$ ,  $\text{Na}_3\text{VO}_4$ ,  $\text{VO}((\text{CH}_3)_2\text{CHO})_3$ ,  $\text{V}_2\text{O}_5$ ,  $\text{VO}(\text{acac})_2$ ,  
 20  $\text{VO}_2$ , and  $\text{V}(\text{acac})_3$ , and mixtures thereof, wherein Bu is butyl. In yet a further embodiment, the vanadium-based catalyst is  $\text{NH}_4\text{VO}_3$ . In another embodiment, the vanadium-based catalyst is  $\text{V}_2\text{O}_5$ .

The amount of vanadium-based catalyst used in the process of the invention may

25 vary within a wide range. The amount is balanced by the requirement that enough catalyst is present to catalyze the process on the one hand and the requirement that the process remains economical on the other hand. Accordingly, in one embodiment, the amount of vanadium-based catalyst is in the range 0.1 to 20 mol%. In another embodiment, the amount of vanadium-based catalyst is in the

30 range 0.3 to 15 mol%. In yet another embodiment, the amount of vanadium-based catalyst is in the range 0.5 to 10 mol%. In still another embodiment, the amount of vanadium-based catalyst is in the range 0.7 to 8 mol%. In a further embodiment, the amount of vanadium-based catalyst is in the range 0.8 to 5 mol%, such as approximately 1 mol%.

The molar amount of transition metals different from vanadium present in the vanadium-based catalyst according to the invention is less than the molar amount of vanadium. When referring to the "molar amount of transition metals different from vanadium", it means the combined molar amounts of all transition metals different from vanadium. In one embodiment, the molar amount of transition metals different from vanadium is 50% or less of the molar amount of vanadium. In another embodiment, the molar amount of transition metals different from vanadium is 40% or less of the molar amount of vanadium. In yet another embodiment, the molar amount of transition metals different from vanadium is 30% or less of the molar amount of vanadium. In still another embodiment, the molar amount of transition metals different from vanadium is 20% or less of the molar amount of vanadium. In a further embodiment, the molar amount of transition metals different from vanadium is 10% or less of the molar amount of vanadium. In yet a further embodiment, the molar amount of transition metals different from vanadium is 5% or less of the molar amount of vanadium. In still a further embodiment, the molar amount of transition metals different from vanadium is 2% or less of the molar amount of vanadium.

#### The product

Depending on the exact reaction conditions, the product of the process may vary. In one embodiment, the resulting product of the process according to the present invention having the highest molar percentage is the compound corresponding to the polyol wherein at least one  $\alpha,\beta$ -dihydroxyl group has been converted into an  $\alpha,\beta$ -carbon-carbon double bond.

25

An example of the latter is when the polyol has at least three adjacent hydroxyl groups and is converted into the corresponding allylic alcohol. Hence, in a further embodiment, the resulting product of the process according to the invention having the highest molar percentage is the allylic alcohol corresponding to a polyol having at least three adjacent hydroxyl groups. In yet a further embodiment the polyol is glycerol and it is converted into allyl alcohol. The allyl alcohol may under some circumstances of the process of the invention be reduced further to propylene. Hence, in still a further embodiment, the polyol is glycerol



and it is converted into a mixture of allyl alcohol and propylene. In still another embodiment, the polyol is glycerol and it is converted into propylene.

Additional embodiments

- 5 The inventors of the present invention have found that the yield does not depend significantly on whether it is carried out under an inert atmosphere or not. However, circumstances may dictate that an inert atmosphere is used. Thus, in one embodiment, the process is carried out under an inert atmosphere.

## Examples

### Example 1 – Deoxydehydration of 1,2-decanediol

In the following examples, unless something else is stated, 40 mmol of diol, 2.0 mmol of catalyst (5 mol%, calculated with respect to the amount of vanadium),  
5 500 mg of hexadecane (internal standard), and 100 ml of solvent were mixed in a 300 ml PTFE cup and placed in a 400 ml autoclave with a magnetic stir bar and computer-controlled heating plate. The autoclave was sealed, pressurized with 10–25 bar of H<sub>2</sub>, N<sub>2</sub>, or CO and heated to 230 °C for 1000 min (corresponding to ~16 h at the reaction temperature); the temperature typically stabilized between  
10 225 and 235 °C. When the system had cooled to room temperature, the pressure was released, the reaction mixture was filtered to remove a black precipitate and analyzed by GC (for determination of conversion and yields) and GC-MS (for observation and identification of other products).

#### 15 *Comparison of solvents*

A number of primary or secondary monohydric C<sub>1</sub>-C<sub>10</sub> alcohol solvents were tested together with NH<sub>4</sub>VO<sub>3</sub> as the catalyst. In addition, their performance was compared to that of acetone and hexane as solvents. The yields of 1-decene (**C=C**), 2-decanone (**C=O**), 2-decanol (**2°OH**), and 1-decanol (**1°OH**) are  
20 provided below in Table 1.

It is evident that using a primary or secondary monohydric C<sub>1</sub>-C<sub>10</sub> alcohol as the solvent results in a better selectivity of 1-decene than any of the comparative solvents.

Table 1 – Comparison of organic solvents in the deoxydehydration of 1,2-decanediol using  $\text{NH}_4\text{VO}_3$  as the catalyst.<sup>[a]</sup>

Solvent	Conv. [%]	Yields [%]			
		<b>C=C</b>	<b>C=O</b>	<b>2°OH</b>	<b>1°OH</b>
MeOH	35	6	1	1	0
EtOH	64	17	4	1	3
<i>n</i> PrOH	78	27	2	1	3
<i>i</i> PrOH	97	51	2	1	8
3-pentanol	97	46	2	1	6
2,4-dimethyl-3-pentanol	full	38	7	0	0
Cyclohexanol	98	43	2	2	5
Acetone	13	5	7	8	1
Hexane	full	30	9	3	3
2,2,2-Trifluoroethanol <sup>[b]</sup>	67	19	0	0	3
Hexafluoroisopropanol <sup>[b]</sup>	61	13	0	0	4

[a] The autoclave was pressurized with 15 bar of nitrogen. [b] The substrate was 1,2-hexanediol and the experiments were conducted on half scale in a 150 ml cylinder.

### Example 2 – The influence of the gas phase

In order to confirm that the composition of the gas phase had little effect on the 1-decene yield and the product distribution, a comparison of nitrogen, hydrogen, and carbon monoxide gas was made. Using the same reaction conditions as in Example 1, including the  $\text{NH}_4\text{VO}_3$  catalyst, the results are summarized in Table 2 below. It is evident that neither the hydrogen gas nor the carbon monoxide gas act as reductants during the reaction.

Table 2 - Comparison of nitrogen, hydrogen, and carbon monoxide gas in the deoxydehydration of 1,2-decanediol in the solvents hexane and *i*PrOH using  $\text{NH}_4\text{VO}_3$  as the catalyst.

Gas	Solvent	Conv. [%]	Yields [%] of			
			<b>C=C</b>	<b>C=O</b>	<b>2° OH</b>	<b>1° OH</b>
10 bar of $\text{N}_2$	Hexane	Full	31	7	1	1
22 bar of $\text{H}_2$	Hexane	Full	32	6	1	1
10 bar of $\text{N}_2$	<i>i</i> PrOH	91	48	1	1	6
20 bar of $\text{H}_2$	<i>i</i> PrOH	93	48	2	2	6
14 bar of CO	<i>i</i> PrOH	full	51	5	2	1

Example 3 – Varying the vanadium-based catalyst

In addition to ammonium metavanadate,  $\text{NH}_4\text{VO}_3$ , a number of other vanadium-based catalysts were tested. The results are summarized in Table 3.

Table 3 – Test of vanadium-based catalysts in the deoxydehydration of 1,2-decanediol in *i*PrOH.<sup>[a]</sup>

Catalyst	Conv. [%]	Yields [%] of			
		C=C	C=O	2°OH	1°OH
$\text{NH}_4\text{VO}_3$	97	51	2	1	8
$\text{Bu}_4\text{NVO}_3$	90	45	2	1	7
$\text{Bu}_4\text{NVO}_2(\text{dipic})^{[\text{b}]}$	95	47	2	1	7
$\text{V}_2\text{O}_5$	93	47	2	1	8
$\text{VO}((\text{CH}_3)_2\text{CHO})_3$	92	48	2	1	8
$\text{VO}(\text{acac})_2^{[\text{c}]}$	full	54	4	2	10
$\text{V}(\text{acac})_3^{[\text{c}]}$	94	50	2	1	7
$\text{NH}_4\text{VO}_3 + \text{acid}^{[\text{d}]}$	93	50	2	1	7
$\text{VOSO}_4 \cdot x\text{H}_2\text{O}$	77	2	1	9	7
$\text{Na}_3\text{VO}_4$	37	1	1	0	1
$\text{VO}(\text{tpp})^{[\text{e}]}$	84	18	5	0	16
$(\text{Bu}_4\text{N})_3\text{H}_3\text{V}_{10}\text{O}_{28}^{[\text{f}]}$	92	23	6	0	19

[a] Standard reaction conditions were employed (as in Example 1). [b]  $\text{dipic}^{2-}$  = dipicolinate. [c]  $\text{acac}^-$  = acetylacetonate. [d] Acetic acid (1.2 equiv with respect to 1,2-decanediol) was added. [e] The substrate was 1,2-hexanediol, the experiments were conducted on half scale in a 150 ml cylinder, the amount of catalyst was 4 mol%, and the reaction time was 900 min. [f] The substrate was 1,2-hexanediol, the experiments were conducted on half scale in a 150 ml cylinder, and the reaction time was 1260 min.

5

Example 4 – Variations in temperature

The effect of changing the temperature was screened under reaction conditions otherwise identical to those in Example 1. At a temperature of 246 °C, the conversion of the diol was complete and the alkene yield was 51%; at a  
 10 temperature of 209 °C, the conversion of the diol was 14% and the alkene yield was 5%.

Example 5 – Reduction of glycerol

- In a 50 ml round-bottomed flask, 23 g (0.25 mol) of glycerol and 1 mol% of a vanadium-based catalyst was placed. The reaction mixture was heated to 220–290 °C and some of the volatile products were condensed at 5 °C. The reaction
- 5 was stopped, when the magnetic stir bar could not stir any more (or after 5 h) – at that point, pyrolysis of the residue had probably been going on for some time, as some of it had already solidified. The incondensable, volatile products comprise propylene. The yield of volatile products was calculated as the mass loss in the reaction flask divided by the mass of glycerol; the yield of condensable products
- 10 was calculated as the mass of products collected after cooling of the volatile products to 5 °C divided by the mass of glycerol. The yields of allyl alcohol and acrolein were determined by <sup>1</sup>H-NMR using 1,4-dioxane as internal standard. The yields are summarized below in Table 4.
- 15 It was found that the reaction generated water as one of the condensable volatile products, i.e. water was removed from glycerol during the reaction. It was further found that while the glycerol used in the process burns very poorly (could not be ignited using a Bunsen burner), the residue remaining in the reaction flask could in fact be burned. Hence, the process, in addition to providing useful chemical
- 20 building blocks from the glycerol waste product, also provides a residue that is more easily disposed of than the glycerol waste product.

Table 4 – Test of vanadium-based catalysts and additives in the deoxydehydration of glycerol using glycerol as polyol, reactant, and solvent.

Catalyst	Additive <sup>[a]</sup>	Time [h]	Yield [%] of <sup>[b]</sup>			
			vol. prod.	cond. prod.	allyl alcohol	acrolein
NH <sub>4</sub> VO <sub>3</sub>		4	80.6	63.8	21.6	4.2
Bu <sub>4</sub> NVO <sub>3</sub>		3	82.0	66.7	19.7	4.7
Na <sub>3</sub> VO <sub>4</sub> <sup>[c]</sup>		2	61.1	49.6	11.4	0.6
V <sub>2</sub> O <sub>5</sub>		4	80.6	65.5	20.5	4.9
VO(acac) <sub>2</sub>		5	81.5	64.3	18.9	4.6
V(acac) <sub>3</sub>		2	82.3	70.6	20.2	6.4
VO <sub>2</sub>		5 <sup>[d]</sup>		48.9	14.9	3.3
NH <sub>4</sub> VO <sub>3</sub>	NaCl	5	80.7	66.4	17.2	2.8
NH <sub>4</sub> VO <sub>3</sub>	NH <sub>4</sub> Cl	2.5	73.3	62.8	9.9	5.8
NH <sub>4</sub> VO <sub>3</sub>	NaOH <sup>[e]</sup>	4	37.9	32.2	8.9	~0
NH <sub>4</sub> VO <sub>3</sub>	NaHCO <sub>3</sub> <sup>[f]</sup>	2	63.1	52.6	12.3	~0
NH <sub>4</sub> VO <sub>3</sub>	citric acid	3.5	85.2	69.3	21.5	5.1

[a] Unless otherwise noted, the amount of additive was 1 mol%. [b] The yield of volatile products (vol. prod.) was calculated as the mass loss in the reaction flask divided by the mass of glycerol; the yield of condensable products (cond. prod.) was calculated as the mass of products collected after cooling of the volatile products to 5 °C divided by the mass of glycerol; the yields of allyl alcohol and acrolein were calculated as the number of moles of allyl alcohol or acrolein in the condensed products divided by the number of moles of glycerol. [c] Purity ≥90%. [d] Conversion not complete; yield of volatile products not measured [e] 2.2 mol% of NaOH was added to account for the neutralization of the ammonium ion in NH<sub>4</sub>VO<sub>3</sub>. [f] 1.7 mol% of NaHCO<sub>3</sub> was added to account for the neutralization of the ammonium ion in NH<sub>4</sub>VO<sub>3</sub>.

#### Example 6 – Large-scale reduction of glycerol

- In a 1000 ml three-necked, round-bottomed flask equipped with a mechanical stirrer, 587 g of technical-grade glycerin (499 g glycerol, 88 g water) and 5.0 g of
- 5 V<sub>2</sub>O<sub>5</sub> was placed. Under a slow stream of nitrogen gas, the reaction mixture was heated to 220–290 °C and some of the volatile products were condensed at 5 °C. The reaction was stopped, when no more volatiles. The incondensable, volatile products comprise propylene. The solid residue had a mass of 33 g corresponding; after subtraction of the mass of the catalyst, to 5.6 % by weight of the glycerol.
  - 10 The condensable products contained glycerol that distilled over due to the stream of nitrogen; this amount was not quantified but is not negligible. The condensable

products were purified by a second distillation and found to contain 16% of allyl alcohol and 7% of acrolein (not taking the incomplete conversion of glycerol into account).



**Claims**

1. A process for the conversion of a polyol, said polyol defined as an alcohol containing a plurality of hydroxyl groups, wherein at least two of the hydroxyl groups are located on adjacent carbon atoms, comprising the reaction of the
- 5 polyol with a reactant selected from a polyol and a primary or secondary C<sub>1</sub>-C<sub>10</sub> alcohol in a solvent in the presence of a vanadium-based catalyst at a temperature of at least 185 °C, wherein said vanadium-based catalyst has the formula:



wherein

A<sup>a+</sup> is a mono-, di-, or trivalent counterion;

X is O, OH, S, or Se;

- 15 R<sup>1</sup> is selected from the group consisting of H, F, Cl, Br, I, CN, N<sub>3</sub>, NCS, dithiocarbamates, CH<sub>3</sub>, BF<sub>4</sub>, PF<sub>6</sub>, CF<sub>3</sub>SO<sub>3</sub>, CH<sub>3</sub>CH<sub>2</sub>SO<sub>3</sub>, CH<sub>3</sub>O, CH<sub>3</sub>CH<sub>2</sub>O, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>O, CH<sub>3</sub>CH(O)CH<sub>3</sub>, SbF<sub>6</sub>, and AsF<sub>6</sub>;
- R<sup>2</sup> is a mono-, bi- or tridentate ligand;

- 20 a is 0, 1, 2, 3, 4, 5, or 6;  
 v is 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10;  
 x is in the range 0 to 5v;  
 y is 0, 1, 2, 3, or 4; and  
 z is 0, 1, 2, 3, or 4;

25

wherein transition metals different from vanadium are present in a molar amount less than the molar amount of vanadium, wherein said polyol, said reactant, and said vanadium-based catalyst are dissolved in said solvent, and wherein said solvent may be identical to or different from said polyol or said reactant.

30

2. The process according to claim 1, wherein the temperature is in the range 185 to 350 °C, such as in the range 195 to 300 °C, e.g. in the range 200 to 290 °C, preferably in the range 210 to 280 °C, even more preferably in the range 210 to 270 °C.

35

3. The process according to any one of the preceding claims, wherein the polyol is selected from the group consisting of 1,2-hexanediol, 3,4-hexanediol, *cis*-1,2-cyclohexanediol, 1,2-decanediol, and glycerol.
- 5 4. The process according to claim 3, wherein the polyol is glycerol.
5. The process according to any one of the preceding claims, wherein said solvent and said reactant is a primary or secondary monohydric C<sub>1</sub>-C<sub>10</sub> alcohol.
- 10 6. The process according to claim 5, wherein the primary or secondary monohydric C<sub>1</sub>-C<sub>10</sub> alcohol, is a C<sub>1</sub>-C<sub>8</sub> alcohol, such as a C<sub>2</sub>-C<sub>5</sub> alcohol, e.g. a C<sub>2</sub>-C<sub>4</sub> alcohol, such as a C<sub>3</sub> alcohol.
7. The process according to claim 6, wherein the primary or secondary
- 15 monohydric C<sub>1</sub>-C<sub>10</sub> alcohol is selected from the group consisting of methanol, ethanol, *n*-propanol, isopropyl alcohol, 3-pentanol, and mixtures thereof; in particular isopropyl alcohol or ethanol, preferably isopropyl alcohol.
8. The process according to any one of the preceding claims, wherein the amount
- 20 of vanadium-based catalyst is in the range 0.1 to 20 mol%, such as in the range 0.3 to 15 mol%, e.g. in the range 0.5 to 10 mol%, preferably in the range 0.7 to 8 mol%, more preferably in the range 0.8 to 5 mol%.
9. The process according to any one of the preceding claims, wherein said
- 25 vanadium-based catalyst has the formula:



wherein

A<sup>a+</sup> is a mono-, di-, or trivalent counterion;

30 X is O, OH, S, or Se;

R<sup>2</sup> is a mono-, bi- or tridentate ligand;

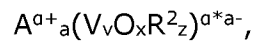
a is 0, 1, or 3;

v is 1, 2, or 10;

x is 3, 4, 5, or 28; and

35 z is 0 or 2.

10. The process according to claim 9, wherein the vanadium-based catalyst has the formula:



5

wherein

$A^{a+}$  is a mono-, di-, or trivalent counterion;

$R^2$  is a mono-, bi- or tridentate ligand;

$a$  is 0, 1, or 3;

10  $v$  is 1, 2, or 10;

$x$  is 3, 4, 5, or 28; and

$z$  is 0 or 2.

11. The process according to claim 10, wherein the vanadium-based catalyst has  
15 the formula:



wherein

20  $A^{a+}$  is a mono-, di-, or trivalent counterion;

$a$  is 0, 1, or 3;

$v$  is 1, 2, or 10; and

$x$  is 3, 4, 5, or 28.

25 12. The process according to any one of claims 1 to 10, wherein the vanadium-based catalyst is selected from the group consisting of  $NH_4VO_3$ ,  $Bu_4NVO_3$ ,  $NaVO_3$ ,  $Na_3VO_4$ ,  $VO(acac)_2$ ,  $VO_2$ ,  $V_2O_5$ , and mixtures thereof, wherein  $acac$  is acetylacetonate and  $Bu$  is butyl.

30 13. The process according to any one of claims 1 to 11, wherein  $A^{a+}$  is  $Na^+$ ,  $Bu_4N^+$ , or  $NH_4^+$ , wherein  $Bu$  is butyl.

14. The process according to any one of the preceding claims, wherein the vanadium-based catalyst is selected from the group consisting of  $NH_4VO_3$ ,  
35  $Bu_4NVO_3$ ,  $NaVO_3$ ,  $Na_3VO_4$ , and mixtures thereof, wherein  $Bu$  is butyl.

15. The process according to any one of the preceding claims, wherein the solvent is a polar solvent.

## INTERNATIONAL SEARCH REPORT

International application No  
PCT/DK2015/050411

## A. CLASSIFICATION OF SUBJECT MATTER

INV. C07C1/20 C07C29/60 C07C11/02 C07C33/02  
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, WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 2 179 981 A1 (ARKEMA FRANCE [FR]) 28 April 2010 (2010-04-28) paragraph [0025] - paragraph [0032] paragraph [0064] - paragraph [0067] claims	1-4,8,15
X	N. PETHAN RAJAN ET AL: "Vapour phase dehydration of glycerol over VPO catalyst supported on zirconium phosphate", CATALYSIS SCIENCE & TECHNOLOGY, vol. 4, no. 1, 1 January 2014 (2014-01-01) , pages 81-92, XP055193440, ISSN: 2044-4753, DOI: 10.1039/C3CY00430A tables 4, 5	1-4,8,15



Further documents are listed in the continuation of Box C.



See patent family annex.

## \* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

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"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

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Date of the actual completion of the international search

15 February 2016

Date of mailing of the international search report

24/02/2016

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040,  
Fax: (+31-70) 340-3016

Authorized officer

Patteux, Claudine

## INTERNATIONAL SEARCH REPORT

International application No

PCT/DK2015/050411

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>WLADIMIR SUPRUN ET AL: "Catalytic activity of bifunctional transition metal oxide containing phosphated alumina catalysts in the dehydration of glycerol", JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL, ELSEVIER, AMSTERDAM, NL, vol. 342, 29 April 2011 (2011-04-29), pages 91-100, XP028225194, ISSN: 1381-1169, DOI: 10.1016/J.MOLCATA.2011.04.020 [retrieved on 2011-05-08] page 95; table 2 page 97, column 1, paragraph 2</p> <p>-----</p>	1-4,8,15
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