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(54) Title: PROCESS FOR OXIDATION OF ALCOHOLS

(57) Abstract: Provided is a process for oxidation of alcohols in the presence of a noble metal catalyst. The process allows desired alcohol oxidation reaction to obtain the corresponding carboxylic acid with a high yield and avoids problems associated with inorganic salt by-products.



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Process for Oxidation of Alcohols

The present invention relates to a process for oxidation of alcohols in the presence of a noble metal catalyst.

5 **BACKGROUND**

The following discussion of the prior art is provided to place the invention in an appropriate technical context and enable the advantages of it to be more fully understood. It should be appreciated, however, that any discussion of the prior art throughout the specification should not be considered as an express or
10 implied admission that such prior art is widely known or forms part of common general knowledge in the field.

Direct oxidation of fatty alcohols in the presence of noble metal catalyst(s) is known in the art and draws considerable interest, because this type of reaction
15 has the potential to generate numerous fatty acid end-products which can be used for various applications, in particular for detergent and cosmetics applications.

For example, it is known that ether carboxylic acids or their salts can be produced by oxidation of their corresponding ether alcohols, usually with the
20 help of a noble metal catalyst. Oxidizing ether alcohols by using oxygen or oxygen-containing gas in the presence of a noble metal catalyst (such as palladium and platinum) is disclosed, for example, in US Patent No. 3342858, US Patent No. 8093414 and US Patent Application No. 2010056735 A. However, one drawback is that these known processes involve the use of bases in the
25 reactions. The bases will react with the ether carboxylic acids generated in the oxidation reaction and salts will be formed in the reaction products. It thus requires additional steps to separate such salts from the desired ether carboxylic acid products, which increases the time and costs for the processes.

30 Chinese Patent Publication No.101905158 B discloses a modified liquid-phase reaction to oxidize alkoxyalkanol, using hydrogen peroxide as oxidant and a carbon-supported palladium catalyst containing at least one main group metal of

Sn or Bi. However, the final yield of the desired ether carboxylic acid is fairly low (roughly 50% or lower according to the Examples).

INVENTION

5 It is an objective of the present invention to provide a process for oxidation of alcohols which requires minimal level of bases in the reaction. It is an objective of the present invention to provide a process for oxidation of alcohols which can provide high yield in ether carboxylic acids.

10 In one aspect, the present invention pertains to a process for oxidizing an alcohol of formula (I):



wherein R^1 represents a saturated or unsaturated, linear, branched or cyclic C_3 - C_{85} hydrocarbon group which is optionally substituted with a heteroatom,
15 the process is performed in a liquid medium in the presence of a catalyst comprising:

- (i) noble metal A being platinum,
 - (ii) noble metal B chosen from the group consisting of Ru, Rh, Pd, Au, Ag and a mixture thereof, and
 - 20 (iii) a support;
- wherein the liquid medium comprises:

- an oxidant,
- a solvent comprising the alcohol of formula (I),
- from 0 to 2 wt %, of an alkaline substance based on the total weight of
- 25 the alcohol, the oxidant and the alkaline substance.

In another aspect, the present invention relates to a composition comprising:

- a solvent comprising an alcohol of formula (I):
 $R^1OH \quad (I)$
- 30 wherein R^1 represents a saturated or unsaturated, linear, branched or cyclic C_3 - C_{85} hydrocarbon group which is optionally substituted with a heteroatom,
- an oxidant,
- from 0 to 2 wt % of an alkaline substance based on the total weight of the alcohol, the oxidant and the alkaline substance,
- 35 - a catalyst comprising:
 - (i) noble metal A being platinum,

- (ii) noble metal B chosen in the group consisting of Ru, Rh, Pd, Au, Ag, and a mixture thereof, and
- (iii) a support.

5 DEFINITIONS

For convenience, before further description of the present disclosure, certain terms employed in the specification, and examples are collected here. These definitions should be read in the light of the remainder of the disclosure and understood as by a person of skill in the art. The terms used herein have the
10 meanings recognized and known to those of skill in the art, however, for convenience and completeness, particular terms and their meanings are set forth below.

The articles “a”, “an” and “the” are used to refer to one or to more than one (i.e.,
15 to at least one) of the grammatical object of the article.

The term “and/or” includes the meanings “and”, “or” and also all the other possible combinations of the elements connected to this term.

20 Throughout the description, including the claims, the term "comprising one" should be understood as being synonymous with the term "comprising at least one", unless otherwise specified, and "between" should be understood as being inclusive of the limits.

25 It should be noted that in specifying any range of concentration, any particular upper concentration can be associated with any particular lower concentration.

It is specified that, in the continuation of the description, unless otherwise indicated, the values at the limits are included in the ranges of values which are
30 given.

As used herein, "alkaline substance" refers to any substance falls into the Arrhenius definition, Brønsted definition or Lewis definition.

35 As used herein, the term "hydrocarbon group" refers to a group which contains carbon and hydrogen bonds. A hydrocarbon group may be linear, branched, or

cyclic, and may contain a heteroatom such as oxygen, nitrogen, sulfur, halogen, etc.

5 As used herein, the term "alkyl" means a saturated hydrocarbon radical, which may be straight, branched or cyclic, such as, methyl, ethyl, n-propyl, iso-propyl, n-butyl, sec-butyl, t-butyl, pentyl, n-hexyl, cyclohexyl.

10 As used herein, the term "alkenyl" as a group or part of a group denotes an aliphatic hydrocarbon group containing at least one carbon-carbon double bond and which may be straight or branched. The group may contain a plurality of double bonds in the normal chain and the orientation about each is independently E or Z. Exemplary alkenyl groups include, but are not limited to, ethenyl, propenyl, butenyl, pentenyl, hexenyl, heptenyl, octenyl and nonenyl. The group may be a terminal group or a bridging group.

15 As used herein, the term "aryl" refers to a monovalent aromatic hydrocarbon group, including bridged ring and/or fused ring systems, containing at least one aromatic ring. Examples of aryl groups include phenyl, naphthyl and the like. The term "arylalkyl" or the term "aralkyl" refers to alkyl substituted with an aryl.
20 The term "arylalkoxy" refers to an alkoxy substituted with aryl.

As used herein, the term "cyclic group" means a closed ring hydrocarbon group that is classified as an alicyclic group, aromatic group, or heterocyclic group. The term "alicyclic group" means a cyclic hydrocarbon group having properties
25 resembling those of aliphatic groups.

As used herein, the term "cycloalkyl" as used herein means cycloalkyl groups containing from 3 to 8 carbon atoms, such as for example cyclohexyl.

30 As used herein, the term "heterocyclic" as used herein means heterocyclic groups containing up to 6 carbon atoms together with 1 or 2 heteroatoms which are usually selected from O, N and S, such as for example radicals of : oxirane, oxirene, oxetane, oxete, oxetium, oxalane (tetrahydrofuran), oxole, furane, oxane, pyrane, dioxine, pyranium, oxepane, oxepine, oxocane, oxocinc groups,
35 aziridine, azirine, azirene, azetidione, azetine, azete, azolidine, azoline, azole, azinane, tetrahydropyridine, tetrahydrotetrazine, dihydroazine, azine, azepane,

azepine, azocane, dihydroazocine, azocinic groups and thiirane, thiirene, thiethane, thiirene, thietane, thiete, thietium, thiolane, thiole, thiophene, thiane, thiopyrane, thiine, thiinium, thiepane, thiepine, thiocane, thiocinic groups.

"Heterocyclic" may also mean a heterocyclic group fused with a benzene-ring wherein the fused rings contain carbon atoms together with 1 or 2 heteroatom's which are selected from N, O and S.

As used herein, the terminology "(C_n-C_m)" in reference to an organic group, wherein n and m are each integers, indicates that the group may contain from n carbon atoms to m carbon atoms per group.

10

DETAILS OF THE INVENTION

The present invention relates to a process for oxidizing an alcohol of formula (I):



wherein R¹ represents a saturated or unsaturated, linear, branched or cyclic C₃-C₈₅ hydrocarbon group which is optionally substituted with a heteroatom, the process is performed in a liquid medium in the presence of a catalyst comprising:

- (i) noble metal A being platinum,
- (ii) noble metal B chosen from the group consisting of Ru, Rh, Pd, Au, Ag and a mixture thereof, and
- (iii) a support;

20

wherein the liquid medium comprises:

- an oxidant,
- a solvent comprising the alcohol of formula (I),
- from 0 to 2 wt %, of an alkaline substance based on the total weight of the alcohol, the oxidant and the alkaline substance.

25

As discovered by inventors, the combination of two noble metal elements can effectively facilitate the desired oxidation of the alcohol of formula (I) with minimal amount of alkaline substance or no alkaline substance. Advantageously, said combination of two noble metals makes it possible to perform the desired alcohol oxidation reaction with high yields of desired products which avoids problems associated with inorganic salt by-products. Particularly, the catalyst mentioned above can be conveniently recycled without loss of catalytic activity. Notably, the process of the present invention is suited for preparing detergent range alkoxyalkanols.

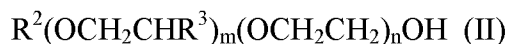
35

The term "alcohol", as used herein, includes primary alcohols and secondary alcohols. Notably, the reaction encompassed in the "process of oxidizing an alcohol" includes a process of obtaining carboxylic acid from a primary alcohol, a process of obtaining aldehyde from a primary alcohol, and a process of obtaining ketone from a secondary alcohol.

Preferably, R^1 may be a saturated or unsaturated, linear, branched or cyclic C_3 - C_{30} hydrocarbon group which is optionally substituted with a heteroatom.

The heteroatom comprised in R^1 may be nitrogen, oxygen, sulfur, phosphorus, chlorine, bromine or iodine. Preferably, the heteroatom is oxygen.

Preferably, the alcohol subjected to oxidation is an ethoxylated fatty alcohol of formula (II):



wherein:

- R^2 represents a linear or branched alkyl radical having 1 to 22 carbon atoms or a linear or branched alkenyl radical having 2 to 22 carbon atoms, optionally comprising at least a substituent and/or a heteroatom such as N and O,
- R^3 represents a hydrogen atom or a methyl group,
- m is an integer from 0 to 19,
- n is an integer from 1 to 20, and
- the sum of m and n is from 1 to 20.

R^2 in formula (II) preferably represents an alkyl group having from 3 to 22, more preferably from 8 to 20, most preferably from 10 to 16 carbon atoms. Particular preference for R^2 is given to methyl, butyl and lauryl, of which lauryl is further preferred. The R^2 group can be an alkyl group substituted with any substituent which does not interfere with the oxidation of the hydroxyl group. For example, R^2 in formula (II) may be an alkyl group substituted with at least one substituent selected from a group consisting of $-OR^4$, $-CH_3$, $-CH_2CH_3$, $-COOH$, $-CONH_2$ and $-COOR^4$, wherein R^4 represents an alkyl or aryl group.

Preferably, n is an integer from 4 to 12, more preferably from 4 to 9.

In some embodiments, m is 0 and n is an integer from 1 to 9.

5

In particular, when the alcohol subjected to oxidation is an ethoxylated fatty alcohol of formula (II), the invention provides a process for producing compounds of formula (III):



10

R^2 , R^3 , m, n having the same meaning given above, and/or of the corresponding protonated carboxylic acids by oxidizing one or more ethoxylated fatty alcohols of formula (II), characterized in that the oxidation is performed in a liquid medium in the presence of a catalyst comprising:

- 15 (i) noble metal A being platinum,
(ii) noble metal B chosen in the group consisting of Ru, Rh, Pd, Au, Ag, and a mixture thereof, and
(iii) a support;

wherein the liquid medium comprises:

- 20 - an oxidant,
- a solvent comprising the alcohol of formula (II),
- from 0 to 2 wt % of an alkaline substance based on the total weight of the alcohol, the oxidant and the alkaline substance.

25 According to the present invention, the catalyst comprises:

- (i) noble metal A being platinum,
(ii) noble metal B chosen from the group consisting of Ru, Rh, Pd, Au, Ag and a mixture thereof, and
(iii) a support.

30

Noble metal B is preferably one or more selected from Ru, Rh or Pd, more preferably noble metal B is Pd.

35 Noble metal A and noble metal B contained in the catalyst are preferably in the form of elementary substance.

In some embodiments, catalyst according to the invention may further comprise oxides of noble metal A and/or oxides of noble metal B.

5 The support of catalyst is not particularly limited. It may be Kieselguhr, silica, alumina, silica-alumina, clay, titania, zirconia, magnesia, calcia, lanthanum oxide, niobium oxide, carbon and any combination thereof. Preferably, the support could be selected from silica, titania, zirconia, lanthanum oxide, niobium oxide or carbon. Among these, carbon is more preferable.

10 The supported catalyst can be produced by known methods such as adsorption, deposition-precipitation, and incipient wetness impregnation approach.

The supported catalyst may have average particles size in nanometer range, preferably from 0.1 to 15 nm, more preferably from 2 to 5 nm. The particle size can be measured, e.g., by transmission electron microscopy or light scattering
15 methods known in the art.

The supported catalyst may have any shape such as powder, grains or pellets.

20 Noble metal A may be comprised from 1.0 wt% to 10.0 wt% based on total weight of the catalyst and preferably from 2 wt% to 6 wt%; notably 2 wt%, 3 wt%, 4 wt%, 5 wt%, or any range obtained between these values.

25 Noble metal B may be comprised from 0.1 wt% to 3.0 wt% based on total weight of the catalyst and preferably from 0.3 wt% to 1.5 wt%; notably 0.2 wt%, 0.3 wt%, 0.4 wt%, 0.5 wt%, 0.6 wt%, 0.7 wt%, 0.8 wt% or any range obtained between these values.

30 It should be understood by the people in the ordinary skill that alkaline substance falls into Arrhenius definition is a substance that gives the OH⁻ when dissolved in H₂O, such as alkali metal hydroxide: lithium hydroxide (LiOH), sodium hydroxide (NaOH), potassium hydroxide (KOH), rubidium hydroxide (RbOH), caesium hydroxide (CsOH).

35 Alkaline substance falls into Brønsted definition is a substance that can accept an H⁺ ion from an acid, such as sodium carbonate (Na₂CO₃), sodium

bicarbonate(NaHCO_3), potassium carbonate(K_2CO_3), potassium bicarbonate(KHCO_3).

5 Alkaline substance falls into Lewis definition is a substance that can donate a pair of nonbonding electrons, such as NH_3 , pyridine, Et_3N .

In some embodiments, alkaline substance in the liquid medium is comprised from 0 to 1.0 wt %, based on the total weight of the alcohol, the oxidant and the alkaline substance, and preferably from 0 to 0.5 wt %.

10

In a preferred embodiment, the liquid medium contains no alkaline substance.

Advantageously, the inventive process is performed in an aqueous reaction medium, the pH value of the liquid medium prior to the oxidation reaction being preferably from 1.0 to 7.0, more preferably from 2.0 to 5.0 and most preferably from 2.5 to 3.5; notably pH is equal to 2.5, 2.6, 2.7, 2.8, 2.9, 3.0, 3.1, 3.2, 3.3, 3.4, 3.5 or any range obtained between these values. The pH value could be measure by a pH meter, such as fisher scientific XL200. Three buffer solutions from Fisher Scientific with pH 4.0, 7.0 and 10.0 could be used for calibration before measurement.

20

Preferably, at least part of the supported catalyst used in the process of the invention may be recycled. More preferably, all the supported catalyst is recycled to a fresh reaction solution.

25

Preferably, the recycled catalyst may be directly reused after physical separation from reaction solution.

The oxidant according to the invention could notably be oxygen, organic peroxy acid, such as peracetic acid and peroxide.

30

According to the present invention, oxygen is a preferred oxidant for safety consideration. It could be introduced in the form of suitable oxygen containing gases, such as air, oxygen gas, and mixtures of oxygen gas with other gases such as nitrogen or argon. In some embodiments, the oxygen containing gas is a flowing oxygen containing gas. Alternatively, the reaction vessel is charged with

35

the oxygen containing gas. The oxidation reaction in such case may be, but is not limited to, conducted at a total pressure comprised from 1 bar to 20 bar, such as 5 bar to 20 bar or 10 bar to 20 bar.

Suitable peroxide is not particularly limited. It can be organic or inorganic
5 peroxide and may be selected from hydroperoxides, such as hydrogen peroxide, *tert*-butyl hydroperoxide, or cumene hydroperoxide; diacyl peroxides, such as benzoyl peroxide, lauroyl peroxide, and the like; and ketone peroxides, such as methyl ethyl ketone peroxide, methyl isobutyl ketone peroxide, cyclohexanone peroxide, and the like. Particular preference is given to hydrogen peroxide and
10 *tert*-butyl hydroperoxide, of which hydrogen peroxide is further preferred.

Suitable solvent is not particularly limited as long as its presence does not bring undesired by-products. Preferred solvents to be used in the process of the invention are polar solvents, such as for instance acetonitrile, tetrahydrofuran,
15 dimethylformamide, isopropanol, acetic acid and water. The process of the invention is preferably carried out in water.

These solvents may be used in any amount with no specific restrictions, but desirably in an amount ranging from 0.5 to 50 times the weight of alcohol used,
20 and more preferably in an amount of 2 to 10 times the weight of alcohol used.

The oxidation reaction according to the invention is usually carried out at a temperature from 30°C to 150°C, preferably from 60°C to 140°C. The reaction pressure is generally atmospheric pressure, although higher pressure is also
25 possible. The reaction time is generally between 1 hour and 20 hours, preferably between 5 hours and 15 hours.

In a preferred embodiment, the present invention concerns a process of obtaining carboxylic acid from a primary alcohol. The conversion of alcohol may be of at
30 least 70%, preferably comprised from 75% to 100%, more preferably from 85% to 95%. The selectivity of carboxylic acid may be at least 80%, preferably from 85% to 95%.

When an alcohol is to be subjected to oxidation according to the process of the invention, the reaction can be allowed to proceed by successively adding the
35 oxidant and the catalyst to a solution containing the alcohol. Alternatively, the

reaction can also be allowed to proceed conveniently by successively adding the oxidant to a mixture containing the alcohol and the catalyst.

The present invention also relates to a composition comprising:

- 5 - a solvent comprising an alcohol of formula (I):
 R^1OH (I)
wherein R^1 represents a saturated or unsaturated, linear, branched or cyclic C_3 - C_{85} hydrocarbon group which is optionally substituted with a heteroatom,
- 10 - an oxidant,
- from 0 to 2 wt % of an alkaline substance based on the total weight of the alcohol, the oxidant and the alkaline substance;
- a catalyst comprising:
(i) noble metal A being platinum,
(ii) noble metal B chosen in the group consisting of Ru, Rh, Pd, Au, Ag, and
15 a mixture thereof, and
(iii) a support.

In one preferred embodiment, the composition comprising:

- 20 - a solvent comprising an alcohol of formula (I):
 R^1OH (I)
wherein R^1 represents a saturated or unsaturated, linear, branched or cyclic C_3 - C_{85} hydrocarbon group which is optionally substituted with a heteroatom,
- an oxidant,
- from 0 to 2 wt % of an alkaline substance based on the total weight of
25 the alcohol, the oxidant and the alkaline substance;
- a catalyst consisting of:
(i) noble metal A being platinum,
(ii) noble metal B chosen in the group consisting of Ru, Rh, Pd, Au, Ag, and
a mixture thereof, and
30 (iii) a support.

The following examples are included to illustrate embodiments of the invention. Needless to say, the invention is not limited to the described examples.

EXPERIMENTAL PART

Raw materials and products:

Triethylene glycol monomethyl ether (C1EO3): CAS 112-35-6

2-[2-(2-methoxyethoxy)ethoxy]acetic acid (C1EO2CA): CAS 16024-58-1

5 Diethylene glycol monomethyl ether (C1EO2): CAS 111-77-3

2-(2-methoxyethoxy)acetic acid (C1EOCA): CAS 16024-56-9

EXAMPLE 1:

Pt-Pd/C catalyst was prepared by the impregnation method. In a typical
10 preparation, 0.2015 g $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ (Sinopharm) and 0.05 g $\text{Pd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$
(Aldrich) were mixed with 2 g activated carbon (Norit SX-ULTRA), in which
10 g water was added to dissolve metal precursor and disperse activated carbon.
The mixture was heated to 80°C under stirring until the full evaporation of water.
The solid was then dried at 110°C for overnight. Finally, the catalyst was
15 calcined in air at 250°C (3°C/min ramping) for 2 h. Before catalytic use, the
calcined sample was treated by feeding of N_2 (27ml/min) and H_2 (3ml/min) at
250 °C for 2 h. Finally, an activated carbon supported catalyst that comprised 4
wt% Pt and 1wt% Pd was obtained.

EXAMPLE 2:

C1EO3 was used as the substrate to evaluate catalytic performance of catalyst
prepared by Example 1. C1EO2CA was desirable product. C1EO2 and C1EOCA
were side products.

25 In a typical reaction, the oxidation reaction was performed in an autoclave
reactor. 0.4 g catalyst prepared by Example 1 and 0.6844 g triethylene glycol
monomethyl ether (C1EO3) 5.4711 g H_2O were added into the reactor. The pH
value was measured to be 3.1. The reactor was exchanged with O_2 three times to
remove residue air and O_2 was finally regulated at 10 bar. At last, the reaction
30 proceeded at 100°C for 5 h.

Conversion and selectivity were measured by Agilent 7890A GC equipped with
FFAP column. 75% C1EO3 conversion and 85% selectivity for C1EO2CA were
obtained.

35

EXAMPLE 3:

Pt-Pd/C was separated from reactants in example 2, washed with H₂O and ethanol, dried at 100 °C and used for next consecutive reaction runs under the same reaction conditions. Results in Table 1 shows catalyst could be recycled for more times without loss of catalytic activity.

5

Table 1

| Cycle | C1EO3 conversion (%) | C1EO2CA selectivity (%) | C1EO2CA yield (%) |
|-------|----------------------|-------------------------|-------------------|
| 1 | 75 | 85 | 64 |
| 2 | 85 | 88 | 74 |
| 3 | 85 | 90 | 76 |
| 4 | 94 | 91 | 85 |
| 5 | 94 | 85 | 80 |
| 6 | 86 | 86 | 74 |
| 7 | 86 | 86 | 74 |
| 8 | 91 | 92 | 84 |

COMPARATIVE EXAMPLE:

Monometallic catalysts, namely 5 wt% Pt/C or 5 wt% Pd/C were prepared by the same method as described in example 1, in which only H₂PtCl₆ or Pd(NO₃)₂ precursor was added. Then Pt/C or Pd/C catalyst was utilized under identical reaction conditions of Example 2. When Pt/C was used as catalyst, 66% conversion of C1EO3 and 77% selectivity for C1EO2CA were achieved. In the case of Pd/C, 41% conversion of C1EO3 and 33% selectivity for C1EO2CA were obtained.

10

15

CLAIMS

1. A process for oxidizing an alcohol of formula (I):



wherein R^1 represents a saturated or unsaturated, linear, branched or cyclic
5 C_3 - C_{85} hydrocarbon group which is optionally substituted with a heteroatom,

the process is performed in a liquid medium in the presence of a catalyst comprising:

(i) noble metal A being platinum,

(ii) noble metal B chosen from the group consisting of Ru, Rh, Pd, Au, Ag
10 and a mixture thereof, and

(iii) a support;

wherein the liquid medium comprises:

- an oxidant,
- a solvent comprising the alcohol of formula (I),
- 15 - from 0 to 2 wt %, of an alkaline substance based on the total weight of the alcohol, the oxidant and the alkaline substance.

2. The process according to claim 1, wherein noble metal B is Pd.

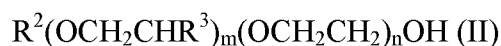
3. The process according to claim 1 or 2, wherein noble metal A is comprised from 2.0 wt% to 6.0 wt% based on total weight of the catalyst.

20 4. The process according to any one of claims 1 or 3, wherein noble metal B is comprised from 0.5 wt% to 1.5 wt% based on total weight of the catalyst.

5. The process according to any one of claims 1 or 4, wherein the pH value of the liquid medium prior to the oxidation reaction is from 2.0 to 5.0.

25 6. The process according to any one of claims 1 or 5, wherein the oxidant is oxygen.

7. The process according to any one of claims 1 or 6, wherein alcohol subjected to oxidation is an ethoxylated fatty alcohol of formula (II):



wherein:

- 5
- R^2 represents a linear or branched alkyl radical having 1 to 22 carbon atoms or a linear or branched alkenyl radical having 2 to 22 carbon atoms, optionally comprising at least a substituent and/or a heteroatom,
 - R^3 represents a hydrogen atom or a methyl group,
 - m is an integer from 0 to 19,
- 10
- n is an integer from 1 to 20, and
 - the sum of m and n is from 1 to 20.

8. The process according to claim 7, wherein the product is a compound of formula (III):



15 wherein:

- R^2 represents a linear or branched alkyl radical having 1 to 22 carbon atoms or a linear or branched alkenyl radical having 2 to 22 carbon atoms, optionally comprising at least a substituent and/or a heteroatom being N or O,
- R^3 represents a hydrogen atom or a methyl group,
- m is an integer from 0 to 19,
- n is an integer from 1 to 20, and
- the sum of m and n is from 1 to 20.

9. A composition comprising:

- 25
- a solvent comprising an alcohol of formula (I):



wherein R^1 represents a saturated or unsaturated, linear, branched or cyclic C_3 - C_{85} hydrocarbon group which is optionally substituted with a heteroatom,

- an oxidant,
- 5 - from 0 to 2 wt %, of an alkaline substance based on the total weight of the alcohol, the oxidant and the alkaline substance,
- a catalyst comprising:
 - (i) noble metal A being platinum,
 - (ii) noble metal B chosen from the group consisting of Ru, Rh, Pd, Au, Ag
10 and a mixture thereof, and
 - (iii) a support.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2017/100936

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| A. CLASSIFICATION OF SUBJECT MATTER C07C 51/235(2006.01)i; C07C 59/125(2006.01)i According to International Patent Classification (IPC) or to both national classification and IPC | | |
| B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) C07C 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) CNPAT,EPODOC,WPI,USTXT,CNTXT,CNKI,Caplus(STN),Registry(STN),alcohol, oxidation, carboxylic acid, platinum, palladium, base,alkaline | | |
| C. DOCUMENTS CONSIDERED TO BE RELEVANT | | |
| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
| X | JP 5398923 A (KAWAKEN FINE CHEMICALS CO) 29 August 1978 (1978-08-29) see columns 4, 5, example 1 | 1-6, 9 |
| Y | JP 5398923 A (KAWAKEN FINE CHEMICALS CO) 29 August 1978 (1978-08-29) see columns 4, 5, example 1 | 7, 8 |
| X | CN 104364010 A (ENNOVIA IN) 18 February 2015 (2015-02-18) see example 1, table 1 | 1-6, 9 |
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| Y | US 3342858 A (ALLIED CHEM) 19 September 1967 (1967-09-19) see claim 1 | 7, 8 |
| A | US 3929873 A (EASTMAN KODAK CO) 30 December 1975 (1975-12-30) see claims 1-16 | 1-9 |
| A | US 4804777 A (EASTMAN KODAK CO) 14 February 1989 (1989-02-14) see abstract, claims 1-12 | 1-9 |
| <input type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> 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 "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) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family | | |
| Date of the actual completion of the international search 04 May 2018 | | Date of mailing of the international search report 25 May 2018 |
| Name and mailing address of the ISA/CN STATE INTELLECTUAL PROPERTY OFFICE OF THE P.R.CHINA 6, Xitucheng Rd., Jimen Bridge, Haidian District, Beijing 100088 China | | Authorized officer CUI,Yan |
| Facsimile No. (86-10)62019451 | | Telephone No. 86-(10)-53962310 |

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

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