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PREPARATION OF WATER-SOLUBLE SULPHONATED
ORGANOPHOSPHORUS COMPOUNDS



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The present invention relates to a process
5 for preparing water-soluble sulphonated
organophosphorus compounds which is particularly
suitable for organic reactions carried out with two-
phase catalysis.

Organophosphorus compounds find a
10 particularly important application as ligands for
transition metal elements to prepare catalytic systems
for various organic reactions such as carbonylation,
hydroformylation, hydrocyanation and the isomerization
of olefinic compounds.

15 These catalytic systems are generally used in
reactions involving a single phase and thus an
occasionally complex step of separation and recovery of
the catalyst is required.

At the start of the 1970s, water-soluble
20 compounds able to form complexes with metal elements in
oxidation state zero were proposed. These water-soluble
compounds generally belong to the family of
organophosphorus compounds comprising at least one
sulphonate group. Thus, F. Joes and M.T. Beck in an
25 article published in React. Kim. Catal. Letters 2
(1975) 257 and Bawoski et al. in an article published
in the review Nouv. J. Chem. 2 (1978) 137 describe a

water-soluble monosulphonated triphenylphosphine which cannot be extracted with organic solvents.

The synthesis of these products allowed the development of a new method of catalysis referred to as
5 two-phase catalysis. Specifically, the catalyst, consisting of transition metal elements complexed with water-soluble organophosphorus compounds, is present in an aqueous phase while the reagents are in an organic phase. Stirring and emulsification of the medium gives
10 efficient catalysis. At the end of the reaction, the catalyst is recovered by simple separation by decantation of the two phases.

The company Rhône-Poulenc has developed this technique for the preparation of several important
15 organic reactions such as the hydroformylation of olefins for the production of aldehydes, as described in French patents 2 505 322 and 2 541 675. Another important application of this catalytic system, described in particular in French patents
20 Nos. 2 338 253 and 2 366 237, concerns the hydrocyanation reaction of olefins and the isomerization of the nitriles obtained, for example for the synthesis of adiponitrile, which is a major chemical intermediate in particular for the manufacture
25 of polyamide monomers.

Investigations are constantly being undertaken to improve the cost-effectiveness of these processes, in particular by increasing the cycle time

and the lifetime of the catalytic system, as well as reducing the consumption of catalyst per quantity of adiponitrile produced.

In the course of these investigations,
5 degradation of the water-soluble sulphonated organophosphorus compounds has been observed.

One of the aims of the present invention is, in particular, to overcome these drawbacks by proposing a water-soluble sulphonated organophosphorus ligand
10 which is resistant to degradation, and thus to propose a more stable two-phase catalytic system.

To this end, the invention relates to a process for carrying out organic reactions by two-phase catalysis comprising an organic phase containing the reagents and the reaction products, an aqueous phase
15 comprising a catalyst and a water-soluble sulphonated organophosphorus compound, characterized in that the water-soluble sulphonated organophosphorus compound comprises an amount of sulphite of less than 100 ppm and has undergone a
20 removal of sulphite compounds or radicals.

According to one preferred characteristic of the invention, the sulphonated organophosphorus compound has a weight concentration of sulphite of less than 50 ppm.

According to another characteristic of the
25 invention, the removal of sulphites is obtained by converting them into sulphurous gas.

Among the organic reactions catalysed by a two-phase catalysis, mention may be made of

hydroformylation, carbonylation, oxidation, isomerization and hydrocyanation reactions, in particular applied to unsaturated compounds.

According to one preferred embodiment, mention will be made in particular of the hydrocyanation reaction of organic compounds comprising at least one ethylenic bond, making it possible to manufacture nitrile compounds such as adiponitrile for the synthesis in particular of lactam, amino acid or amine monomers for polyamides. This synthetic process in particular comprises a hydrocyanation of 3-pentenitrile (unsaturated organic compound comprising a nitrile function) into adiponitrile, for which the catalyst comprising a sulphite-freed organophosphine in accordance with the invention as a component is particularly suitable.

Thus, in the case of such an application, the lifetime of the catalyst can be greatly improved. This improvement is observed, in the case of the hydrocyanation of organic compounds comprising several ethylenic bonds and in particular dienes, both for the hydrocyanation reaction of the first ethylenic bond and in that of the second ethylenic bond.

The process of the invention makes it possible to carry out the hydrocyanation of butadiene for the synthesis of adiponitrile with a catalyst based on water-soluble sulphonated organophosphorus ligands and on at least one metal element in oxidation state zero, with a consumption of catalyst per kg of

adiponitrile produced which is markedly lower than that found with a catalyst or a ligand which has not undergone a removal of sulphites.

According to one preferred embodiment of the invention, and this is another subject of the invention, removal of the sulphites contained in the water-soluble sulphonated organophosphorus compound is obtained by lowering the pH of the solution of organophosphorus compounds to a value of less than or equal to 4 and maintenance of the solution at a pH of less than or equal to 4 until a sulphite concentration in the solution of less than 100 ppm is obtained.

Assay of the sulphite compounds in the solution is carried out, for example, by ionic chromatography.

The lowering of the pH of the solution can be carried out by any suitable means. However, according to one preferred embodiment of the invention, this lowering is obtained by addition of a strong inorganic or organic acid in pure form or, more preferably, in solution.

The acidic solution can be a concentrated or dilute solution.

As acids which are suitable for the invention, mention may be made of acids with, for example, a pKa of less than or equal to 4, the corresponding anhydrides and more generally any compound which is chemically inert with respect to the

organophosphorus compound and which can lower the pH of a solution.

By way of non-limiting example, acids which may be mentioned are sulphuric acid, hydrochloric acid, 5 trifluoroacetic acid, para-toluenesulphonic acid, perchloric acid and nitric acid.

Moreover, the solution of water-soluble sulphonated organophosphorus compounds is preferably an aqueous solution. However, solutions using 10 water/alcohol mixtures as solvent are also suitable. The alcohol can be replaced with any water-miscible solvent.

According to another characteristic of the invention, the solution is maintained at a pH of less 15 than or equal to 4, at a temperature below 100°C and advantageously between 40°C and 90°C.

The sulphurous gas produced by converting the sulphites is, in one preferred embodiment of the invention, removed from the medium by entrainment with 20 a carrier fluid. This carrier fluid is preferably non-oxidizing. Thus, carrier fluids which are suitable for the invention are, for example, nitrogen, carbon dioxide, water vapour, rare or inert gases, and oxygen-depleted air.

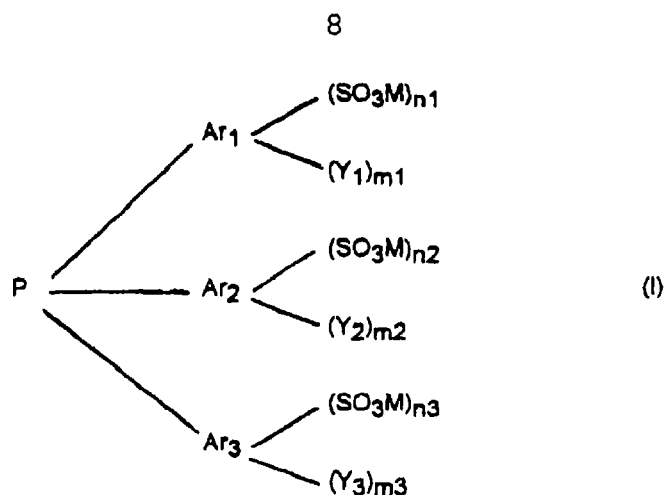
25 The water-soluble sulphonated organophosphorus compounds which are suitable for treatment according to the process of the invention and which are useful as ligands in the processes of two-

phase catalysis are generally the sulphonated organophosphorus compounds prepared by carrying out one or more sulphonation steps as described in the article published in J. Chem. Soc. pages 276 - 288 (1958) or
5 GB patent No. 1 066 261. They can also be prepared by reacting sodium p-chlorobenzenesulphonate with diphenylchlorophosphine as described in the article H. Schindlbauer, Monatsch. Chem. 96, pages 2051 - 2057 (1965).

10 Generally, these processes for synthesizing sulphonated organophosphorus compounds do not make it possible to obtain a compound which is free of sulphite compounds or radicals. Consequently, in order to avoid degradation of these compounds during their use as a
15 catalyst or a ligand of a catalytic system, it is necessary according to the process of the invention to remove these sulphites at least partially.

 As water-soluble sulphonated phosphine compounds which are suitable for carrying out the
20 invention, mention may be made of the compounds belonging to the family of phosphine compounds described in French patent No. 2 338 253 or in patent applications WO 97/12857 and EP 0 650 959.

 Thus, phosphines which are suitable for the
25 invention correspond to the general formula (I) below:



in which:

* Ar₁, Ar₂ and Ar₃, which may be identical or different, represent aryl groups,

* Y₁, Y₂ and Y₃, which may be identical or different, represent

- an alkyl radical containing 1 to 4 carbon atoms,

- an alkoxy radical containing 1 to 4 carbon atoms,

- a halogen atom,

- a CN radical,

- an NO₂ radical,

- an OH radical,

- a radical NR₁R₂, in which formula R₁ and R₂, which may be identical or different, represent an alkyl radical containing 1 to 4 carbon atoms,

* M is an inorganic or organic cationic

residue chosen such that the compound of formula (I) is soluble in water, in the group comprising:

- H^+ ,
 - cations derived from alkali metals or alkaline-earth metals,
 - $N(R_3R_4R_5R_6)^+$ with R_3 , R_4 , R_5 and R_6 , which
5 may be identical or different,
representing an alkyl radical containing
1 to 4 carbon atoms or a hydrogen atom,
 - other cations derived from metals whose benzenesulphonic acid salts are soluble
10 in water,
- * m_1 , m_2 and m_3 are integers, which may be identical or different, from 0 to 5,
- * n_1 , n_2 and n_3 are integers, which may be identical or different, from 0 to 3,
15 at least one of them being greater than or equal to 1.

As examples of metals whose benzenesulphonic acid salts are soluble in water, mention may be made of lead, zinc and tin.

20 In the present text, the expression "soluble in water" generally means a compound which is soluble to at least 0.01 g per litre of water.

Among the phosphines of formula (1) which are preferred are those for which:

- 25 - Ar_1 , Ar_2 and Ar_3 are phenyl groups,
- Y_1 , Y_2 and Y_3 represent groups chosen from
 - alkyl radicals containing 1 or 2 carbon atoms,

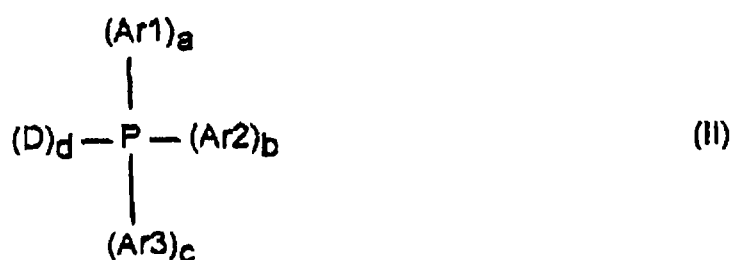
- alkoxy radicals containing 1 or 2 carbon atoms,
- M represents a cation chosen from the group comprising
 - H^+
 - cations derived from Na, K, Ca or Ba,
 - NH_4^+
 - tetramethylammonium, tetraethylammonium, tetrapropylammonium and tetrabutylammonium cations
- m_1 , m_2 and m_3 are integers from 0 to 3
- n_1 , n_2 and n_3 are integers from 0 to 3, at least one also being greater than 1.

Among these phosphines, the ones which are most particularly preferred are the sodium, potassium, calcium, barium, ammonium, tetramethylammonium and tetraethylammonium salts of mono(sulphophenyl)diphenylphosphine, di(sulphophenyl)phenylphosphine and tri(sulphophenyl)phosphine, in which formulae the SO_3 groups are preferably in the meta position.

As other examples of phosphines of formula (I) which can be used in the process of the invention, mention may be made of alkali metal or alkaline-earth metal salts, ammonium salts, and quaternary ammonium salts of (3-sulpho-4-methylphenyl)bis(4-methylphenyl)phosphine; (3-sulpho-4-methoxyphenyl)bis(4-methoxyphenyl)phosphine; (3-sulpho-4-chlorophenyl)bis(4-chlorophenyl)phosphine;

bis(3-sulphophenyl)phenylphosphine;
 bis(4-sulphophenyl)phenylphosphine; bis(3-sulpho-
 4-methylphenyl)(4-methylphenyl)phosphine; bis(3-sulpho-
 4-methoxyphenyl)(4-methoxyphenyl)phosphine;
 5 bis(3-sulpho-4-chlorophenyl)(4-chlorophenyl)phosphine;
 tris(3-sulphophenyl)phosphine; tris(4-sulphophenyl)-
 phosphine; tris(3-sulpho-4-methylphenyl)phosphine;
 tris(3-sulpho-4-methoxyphenyl)phosphine; tris(3-sulpho-
 4-chlorophenyl)phosphine; (2-sulpho-4-methylphenyl)(3-
 10 sulpho-4-methylphenyl)(3,5-disulpho-4-methylphenyl)-
 phosphine; (3-sulphophenyl)(3-sulpho-4-chlorophenyl)
 (3,5-disulpho-4-chlorophenyl)phosphine.

Needless to say, it is possible to use a
 mixture of these phosphines. In particular, it is
 15 possible to use a mixture of mono-, di- and tri-meta-
 sulphonated phosphines. Monodentate or bidentate
 phosphines of general formula (II) or (III) below are
 also suitable for the invention:



20 in which:

- Ar1 and Ar2, which may be identical or different,
 represent aryl groups or aryl groups comprising one or
 more substituents such as:

- alkyl or alkoxy radical containing 1 to 4 carbon atoms,
- halogen atom,
- at least one hydrophilic group:

5 $-\text{SO}_3\text{M}$, M representing an inorganic or organic cationic residue chosen from a proton, cations derived from alkali metals or alkaline-earth metals, ammonium cations $-\text{N}(\text{R})_4$ in which formula the symbols R,

 which may be identical or different,

10 represent a hydrogen atom or an alkyl radical containing from 1 to 4 carbon atoms, other cations derived from metals whose arylcarboxylic acid, arylsulphonic acid or arylphosphonic acid salts are soluble in water,

15 $-\text{N}(\text{R})_4$ in which formula the symbols R, which may be identical or different, represent a hydrogen atom or an alkyl radical containing from 1 to 4 carbon atoms,

$-\text{OH}$

20 - Ar_3 represents an aryl group comprising one or more substituents such as:

- alkyl or alkoxy radical containing 1 to 4 carbon atoms,
- halogen atom,

25 - hydrophilic group such as:

$-\text{COOM}$ or $-\text{PO}_3\text{M}$, M representing an inorganic or organic cationic residue chosen from a proton, cations derived from alkali metals or alkaline-earth metals,

ammonium cations $-N(R)_4$ in which formula the symbols R, which may be identical or different, represent a hydrogen atom or an alkyl radical containing from 1 to 4 carbon atoms, other cations derived from metals whose arylcarboxylic acid or arylphosphonic acid salts are soluble in water,

$-N(R)_4$ in which formula the symbols R, which may be identical or different, represent a hydrogen atom or an alkyl radical containing from 1 to 4 carbon atoms,

$-OH$,

at least one of the said substituents of Ar₃ being a hydrophilic group as defined above,

- a represents 0 or 1,
- 15 - b represents 0 or 1,
- c represents an integer from 0 to 3,
- D represents an alkyl group, a cycloalkyl group, an alkyl or cycloalkyl group comprising one or more substituents such as:

- 20 - alkoxy radical containing 1 to 4 carbon atoms,
- halogen atom,
- hydrophilic group such as:

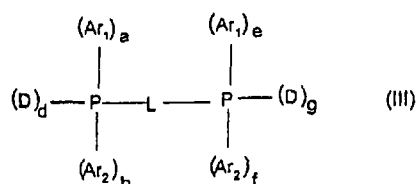
$-COOM$, $-SO_3M$ or $-PO_3M$, M representing an inorganic or organic cationic residue chosen from a proton, cations derived from alkali metals or alkaline-earth metals, ammonium cations $-N(R)_4$ in which formula the symbols R, which may be identical or different, represent a hydrogen atom or an alkyl radical

containing from 1 to 4 carbon atoms, other cations derived from metals whose arylcarboxylic acid, arylsulphonic acid or arylphosphonic acid salts are soluble in water,

- 5 $-N(R)_4$ in which formula the symbols R, which may be identical or different, represent a hydrogen atom or an alkyl radical containing from 1 to 4 carbon atoms,

$-OH$

- 10 - d represents an integer from 0 to 3,
 - the sum $(a+b+c+d)$ is equal to 3;
 or,



in which:

- 15 - Ar1, Ar2 and d have the meanings given above for formula (II),
 - a, b, e and f each represent 0 or 1,
 - d and g each represent an integer from 0 to 2,
 - the sum $(a+b+d)$ is equal to 2,
 - the sum $(e+f+g)$ is equal to 2,
 - L represents a single valency bond or a divalent hydrocarbon-based radical such as an alkylene radical, a cycloalkylene radical, an arylene radical, a radical derived from a heterocycle comprising one or two
 25 oxygen, nitrogen or sulphur atoms in the ring, these

various cyclic radicals being linked directly to one of the phosphorus atoms or to the two phosphorus atoms or being linked to one of the phosphorus atoms or to the two via a linear or branched alkylene radical

5 containing from 1 to 4 carbon atoms, it being possible for the ring(s) optionally forming part of the divalent radical L to comprise one or more substituents such as an alkyl group containing 1 to 4 carbon atoms.

As non-limiting examples of phosphines of
10 general formula (III), mention may be made in particular of the sodium salt of 2,2'-bis[di(sulphonatophenyl)phosphino]-1,1'-binaphthyl, the sodium salt of 1,2-bis[di(sulphonatophenyl)phosphinomethyl]-cyclobutane (CBDTS) and the sodium salt of
15 2,2'-bis[di(sulphonatophenyl)phosphinomethyl]-1,1'-binaphthyl.

Some of the water-soluble phosphines of formulae (I) to (III) are commercially available.

For the preparation of the others, reference
20 may be made to the general or specific processes for synthesizing phosphines described in general texts such as Houben-Weyl, Methoden der organischen Chemie, organische Phosphor-Verbindungen, part 1 (1963).

Finally, for the preparation of the water-
25 soluble derivatives not described, it is possible, starting with phosphines not comprising any water-soluble substituents defined above, to carry out the introduction of one or more of these hydrophilic

substituents. Thus, the sulphonate groups, for example, can be introduced by the reaction of SO₃ in sulphuric acid. The carboxylate, phosphonate and quaternary ammonium groups can similarly be introduced by applying
5 chemical methods known for this type of synthesis.

As water-soluble sulphonated organophosphorus compounds which are suitable for the invention, mention may also be made of the compounds BISBIS, NORBOS and BINAS described in the article by Boy Cornils and
10 Emile G. Kuntz published in "Journal of Organometallic Chemistry" No. 502 (1995) pp. 177-186. Similarly, the water-soluble furylphosphine compounds described in French patent application No. 98/06559 filed on 20/05/98 - not yet published - fall within the context
15 of the invention.

As mentioned above, these sulphite-freed organophosphorus compounds are used in particular as components of catalysts comprising a transition metal element chosen, for example, from the group comprising
20 nickel, cobalt, iron, ruthenium, rhodium, palladium, osmium, iridium, platinum, copper, silver, gold, zinc, cadmium and mercury in variable oxidation states.

As examples, it may be mentioned that, in these catalysts, generally, rhodium is in oxidation
25 state (I), ruthenium is in oxidation state (II), platinum is in oxidation state (I), palladium is in oxidation state (II), osmium is in oxidation state (0),

iridium is in oxidation state (0) and nickel is in oxidation state (0).

The catalyst can also comprise metallic elements as promoter or dopant.

5 Other details and advantages of the invention will become apparent in the light of the examples below, given purely as a guide.

EXAMPLE 1

19.2 kg of an aqueous solution containing 30%
10 by weight of the sodium salt of triphenylphosphine trisulphonate and initially containing 1540 ppm of sulphites (pH = 6.2) is placed in a 20 litre reactor stirred using a turbomixer (180 rpm) and fitted with an ascending condenser, a nitrogen inlet via a dipping
15 cannula and a bubbler containing an aqueous sodium hydroxide solution (1 mol/litre). This solution is degassed. 222 g of an aqueous sulphuric acid solution at 2 mol/litre is then introduced, which leads to a pH

of 1.8. This mixture is heated to 80°C with stirring and under a stream of nitrogen so as to entrain the sulphurous gas. Assay of the sulphites by ionic chromatography on samples taken every 15 minutes makes it possible to monitor the conversion of the sulphites into sulphur dioxide. After 1 hour at 80°C, the assay in question gives the following result: 80 ppm of sulphites. After 1 h 45 minutes, the sulphite content becomes less than or equal to 40 ppm (detection limit of the ionic chromatography analysis). After 2 hours at 80°C, the mixture is cooled with stirring to room temperature. 324 g of an aqueous sodium hydroxide solution at 1 mol/litre are then introduced and a sulphite-freed aqueous solution of TPPTS (pH = 5.4) is obtained.

EXAMPLE 2

500 cm³ of the sulphite-freed aqueous solution of TPPTS at 30% by weight, of Example 1, is placed in a 1 litre glass round-bottomed flask fitted with a magnetic stirring bar and an ascending condenser. The solution is degassed. 20 g of Ni(cyclooctadiene)₂ are then introduced, with stirring and under a stream of nitrogen, followed by 350 cm³ of pre-degassed ortho-xylene. This mixture is heated at 45°C for 15 h. After cooling, the two-phase system is decanted. About 35 cm³ of the aqueous phase, which is a strong red colour, are taken and introduced into a 150 cm³ glass reactor fitted with a turbomixer and purged with argon. This aqueous

phase is heated to 90°C and 3.2 cm³ of an aqueous solution of zinc chloride at 70% by weight are then added. The mixture is maintained at 90°C with stirring for 48 hours. After cooling to room temperature, a
5 sample of the aqueous solution is taken and analysed by phosphorus-31 NMR (nuclear magnetic resonance). The analysis, performed on a Bruker AMX 300 II[®] spectrometer at a frequency of 121 MHz, shows that the TPPTS contains no TPPTS sulphide (content less than the
10 detection limit of the analysis technique, i.e. less than 0.1 mol% of the total phosphorus in solution).

EXAMPLE 3

500 cm³ of the aqueous solution of TPPTS at 30% by weight, initially containing 1540 ppm of
15 sulphites, are placed in a 1 litre glass round-bottomed flask fitted with a magnetic stirring bar and an ascending condenser. The solution is degassed. 20 g of Ni(cyclooctadiene)₂ are then introduced, with stirring and under a stream of argon, followed by 350 cm³ of pre-
20 degassed ortho-xylene. This mixture is heated at 45°C for 15 h. After cooling, the two-phase system is decanted. About 35 cm³ of the aqueous phase, which is a strong red colour, are taken and introduced into a 150 cm³ glass reactor fitted with a turbomixer and
25 purged with argon. This aqueous phase is heated to 90°C and 3.2 cm³ of an aqueous solution of zinc chloride at 70% by weight are then added. The mixture is maintained at 90°C with stirring at 48 hours. After cooling to

room temperature, a sample of the aqueous solution is taken and analysed by phosphorus-31 NMR (nuclear magnetic resonance). The analysis in question, performed on a Bruker AMX 300 II[®] spectrometer at a
5 frequency of 121 MHz, shows that it contains TPPTS sulphide (peak at 43.7 ppm) to an extent of 4.5 mol% of the total phosphorus in solution.

CLAIMS

1. Process for carrying out organic reactions by two-phase catalysis comprising an organic phase containing the reagents and the reaction products, an aqueous phase comprising a catalyst and a water-soluble sulphonated organophosphorus compound, characterized in that the water-soluble sulphonated organophosphorus compound comprises an amount of sulphite of less than 100 ppm and undergoes a treatment for at least partially removing the sulphite compounds or radicals.

2. Process according to claim 1, characterized in that the weight concentration of sulphite compounds or radicals after treatment is less than 50 ppm.

3. Process according to claim 1 or 2, characterized in that the water-soluble sulphonated organophosphorus compound is treated to convert the sulphite radicals into sulphurous gas.

4. Process according to one of the preceding claims, characterized in that the organic reaction is chosen from the group comprising hydroformylation, carbonylation, oxidation, isomerization and hydrocyanation reactions.

5. Process according to claim 4, characterized in that the organic reaction is a hydrocyanation of organic compounds comprising at least one ethylenic unsaturation.

6. Process according to claim 5, characterized in that the organic compound is a diolefin or an unsaturated organic compound comprising a nitrile function.

5 7. Process according to one of the preceding claims, characterized in that the catalyst comprises the water-soluble sulphonated organophosphorus compound and at least one transition metal.

10 8. Process according to claim 7, characterized in that the transition metal is chosen from the group comprising nickel, cobalt, iron, ruthenium, rhodium, palladium, osmium, iridium, platinum, copper, silver, gold, zinc, cadmium and
15 mercury.

9. Process according to claim 7 or 8, characterized in that the catalyst comprises promoter or dopant metal elements.

10 10. Process for preparing water-soluble sulphonated organophosphorus compounds, characterized in that it consists in at least partially removing the sulphite compounds or groups by lowering the pH of a solution of the said compounds to a value of less than or equal to 4, and maintenance of the pH of this
25 solution at a value of less than or equal to 4 down to a weight concentration of sulphite in the solution at a value of less than 100 ppm.

11. Process according to claim 10, characterized in that the lowering of the pH is carried out by addition of an acidic compound.

12. Process according to claim 11,
characterized in that the acid is a strong inorganic or
organic acid.

13. Process according to claim 12,
5 characterized in that the acid has a pKa of less than
or equal to 4.

14. Process according to one of claims 11 to
13, characterized in that the acidic compound is chosen
from the group comprising sulphuric acid, hydrochloric
10 acid, trifluoroacetic acid, para-toluenesulphonic acid,
perchloric acid and nitric acid.

15. Process according to one of claims 10 to
14, characterized in that the solution is maintained at
a temperature below 100°C, preferably between 40 and
15 90°C.

16. Process according to one of claims 10 to
15, characterized in that the sulphurous gas is removed
by entrainment with a carrier fluid.

17. Process according to claim 16,
20 characterized in that the carrier fluid is chosen from
the group comprising nitrogen, carbon dioxide, water
vapour, rare or inert gases, and oxygen-depleted air.

18. Process according to one of claims 10 to
17, characterized in that the solution of the said
25 sulphonated organophosphorus compound is an aqueous
solution or a solution in a water/alcohol mixture.