

PROCESS FOR THE ELECTROCHEMICAL PREPARATION OF
CATALYSTS BASED ON A TRANSITION METAL
AND ON A PHOSPHINE

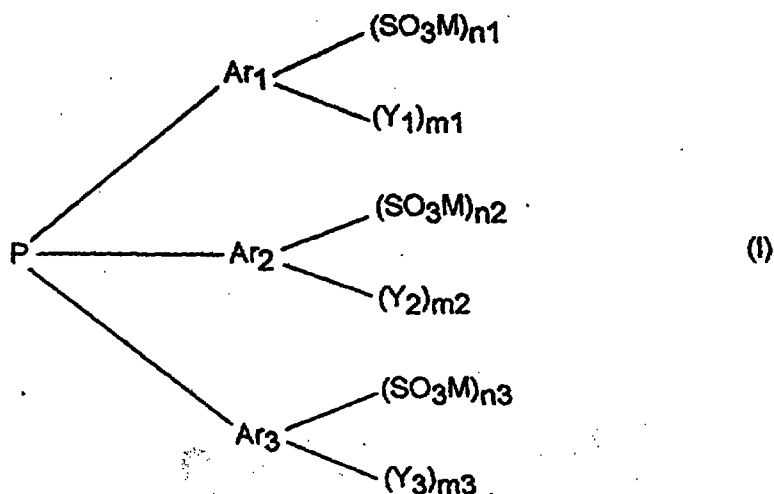
5 The present invention relates to an electrochemical process for the preparation of compounds which can be used as catalysts. These compounds comprise at least one transition metal having an oxidation number of 0 or 1, combined with at least one water-soluble sulphonated phosphine.

10 Such compounds can be used, for example, as catalysts in the ethylene-compound hydrocyanation reaction described in FR-A-2,338,253. In the present text, they will be called catalysts without thereby limiting their field of use.

15 The present invention provides a process for the electrochemical synthesis of a catalyst comprising at least one transition metal having an oxidation number of 0 or 1, combined with at least one sulphonated phosphine, which comprises electrolytically treating, in the cathode compartment of an electrolysis cell of an electrolyser, an aqueous solution comprising at least one compound of a transition metal and a sulphonated phosphine.

20 The present invention also provides a catalyst obtained by a process as defined above.

25 The sulphonated phosphine employed in the process of the invention generally has the formula (I):



in which:

- * Ar_1 , Ar_2 and Ar_3 , which may be the same or different, represent aryl groups;
- * Y_1 , Y_2 and Y_3 , which may be the same or different, represent
 - . an alkyl radical having 1 to 4 carbon atoms,
 - . an alkoxy radical having 1 to 4 carbon atoms,
 - . a halogen atom,
 - . a CN radical,
 - . an NO_2 radical,
 - . an OH radical, or
 - . an NR_1R_2 radical, in which R_1 and R_2 , which may be the same or different, represent an alkyl radical having 1 to 4 carbon atoms;
- * each M, which may be the same or different, is an inorganic or organic cationic residue chosen such that the compound of formula (I) is soluble in water, for example:
 - . H^+ ,
 - . a cation derived from an alkali metal or alkaline-earth metal,
 - . $N(R_3R_4R_5R_6)^+$ with R_3 , R_4 , R_5 and R_6 , which may be the same or different, representing an alkyl radical having 1 to 4 carbon atoms or a hydrogen atom,
 - . another cation derived from a metal whose salts with benzenesulphonic acid are soluble in water;
- * m_1 , m_2 and m_3 , which may be the same or different, are integers of from 0 to 5; and
- * n_1 , n_2 and n_3 , which may be the same or different, are integers of from 0 to 3, one of them at least being equal to or greater than 1.

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

By the expression "water soluble", it is generally meant in the present text a compound which is soluble to at least 0.01 g per litre of water.

Among the phosphines of formula (I), it is preferred to use those for which:

- Ar_1 , Ar_2 and Ar_3 are phenyl groups;
- Y_1 , Y_2 and Y_3 , which may be the same or different, represent groups chosen from
 - . alkyl radicals having 1 or 2 carbon atoms, or
 - . alkoxy radicals having 1 or 2 carbon atoms;
- each M, which may be the same or different, represents a cation chosen from:
 - . H^+ ,
 - . cations derived from Na, K, Ca, Ba,
 - . NH_4^+ , and
 - . tetramethylammonium, tetraethylammonium, tetrapropylammonium or tetrabutylammonium cations;
- m_1 , m_2 and m_3 , which may be the same or different, are integers of from 0 to 3; and
- n_1 , n_2 and n_3 , which may be the same or different, are integers of from 0 to 3, one at least also being greater than 1.

Among these phosphines, the 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 the formulae of which the SO_3 groups are preferably in the meta position.

Mention may be made, as other examples of phosphines of formula (I) which can be employed in the process of the invention, of alkali salts or alkaline-earth salts, ammonium salts, quaternary ammonium salts of

- (3-sulpho-4-methylphenyl)di(4-methylphenyl)phosphine;
- (3-sulpho-4-methoxyphenyl)di(4-methoxyphenyl)phosphine;
- (3-sulpho-4-chlorophenyl)di(4-chlorophenyl)phosphine;

di(3-sulphophenyl)phenylphosphine;
di(4-sulphophenyl)phenylphosphine;
di(3-sulpho-4-methylphenyl)(4-methylphenyl)phosphine;
di(3-sulpho-4-methoxyphenyl)(4-methoxyphenyl)phosphine;
5 di(3-sulpho-4-chlorophenyl)(4-chlorophenyl)phosphine;
tri(3-sulphophenyl)phosphine; tri(4-sulphophenyl)phosphine;
tri(3-sulpho-4-methylphenyl)phosphine;
tri(3-sulpho-4-methoxyphenyl)phosphine;
tri(3-sulpho-4-chlorophenyl)phosphine;
10 (2-sulpho-4-methylphenyl)(3-sulpho-4-methylphenyl)
(3,5-disulpho-4-methylphenyl)phosphine; and
(3-sulphophenyl)(3-sulpho-4-chlorophenyl)
(3,5-disulpho-4-chlorophenyl)phosphine.

Of course, a mixture of these phosphines may be
15 used. In particular, a mixture of mono-, di- and
tri-metasulphonated phosphines may be used.

As transition-metal compounds, it is preferable to
use nickel, cobalt, iron, palladium, platinum, rhodium and
iridium compounds. Water soluble compounds or compounds
20 capable of passing into solution under the reaction
conditions are generally used. The remaining ligands bonded
to the metal are not critical, as long as they satisfy these
conditions.

Among the aforementioned compounds, the most
25 preferred compounds are those of nickel. By way of
non-limiting examples, mention may be made of nickel
carboxylates (especially nickel acetate, formate and
citrate), nickel carbonate, nickel bicarbonate, nickel
borate, nickel bromide, nickel chloride, nickel iodide,
30 nickel thiocyanate, nickel cyanide, nickel hydroxide, nickel
hydrophosphite, nickel phosphite, nickel phosphate and its
derivatives, nickel nitrate, nickel sulphate, nickel
sulphite, nickel arylsulphonates and nickel alkylsulphonates.

It is not necessary for the nickel compound itself
35 to be water-soluble. For example, nickel cyanide, which is
not very soluble in water, dissolves very well in an aqueous
solution of sulphonated phosphine.

The electrolysis cell of the electrolyser, used in
the present process, comprises a cathode compartment and an

anode compartment which are separated by a separator element.

The cathode of the electrolysis cell may be made of a material such as platinum, gold, iridium, ruthenium, palladium, nickel, graphite, vitreous carbon, iron, a stainless steel, a special steel, lead, mercury or an amalgam. It may also comprise titanium, tantalum, nickel or a stainless steel, coated with a layer of platinum, of gold, of iridium, of ruthenium, of a mixture of several of these metals, of platinum, palladium, iridium, rhodium, ruthenium, osmium or tantalum oxides or of a mixture of several of these oxides.

The cathode may have a plane structure, such as a plate or grid, or a voluminal structure; it can in particular be perforated or opened out. As types of voluminal structures, granular stacks of the previously mentioned materials, or felts or foams of these materials may be used.

The anode may be made of a material such as platinum, gold, iridium, ruthenium, palladium, nickel, graphite, vitreous carbon, a stainless steel, a special steel or lead. It may also comprise titanium or tantalum coated with a layer of platinum, of gold, of iridium, of ruthenium, of a mixture of several of these metals, of platinum, palladium, iridium, rhodium, ruthenium, osmium or tantalum oxides or of a mixture of several of these oxides.

The structure of the anode may be of different types from that which has been defined for the cathode.

The separator element of the electrolysis cell generally comprises an ion-exchange membrane or a porous diaphragm.

The membranes may be of the cationic type, especially those prepared from cation-exchange resins possessing acid groups such as sulphonic groups or carboxylic groups. Preferably, membranes prepared with sulphonic resins will be used. As membranes of this kind, mention may be made, for example, of those which are sold under the Nafion® (perfluorinated sulphonic membranes) or Selemion® trademarks.

The membranes may also be of the anionic type, but cationic membranes are generally preferred since they have a

certain number of advantages. In particular, they are stronger than anionic membranes and they also enable higher current strengths to be used.

5 The porous diaphragms may be especially diaphragms made of porous ceramic, diaphragms made of woven or non-woven synthetic fibres or deposited diaphragms based on asbestos fibres or on synthetic fibres.

The separator element may be arranged so as to bear on the anode or on the cathode.

10 As indicated previously, the aqueous solution containing the sulphonated phosphine and the transition-metal compound is in the cathode compartment. The initial concentration of sulphonated phosphine lies generally from 10^{-3} mol/litre to 1 mol/litre. The initial concentration of
15 transition-metal compound, especially of nickel compound, lies generally from 10^{-5} mol/litre to 1 mol/litre.

Other compounds enabling the conductivity of the electrolyte to be increased, such as soluble salts for example, may be added to the cathode compartment.

20 Complexing agents capable of modifying the potential at which the reduction of the transition metal takes place may also be added. As examples of such complexing agents, mention may be made of cyanides.

The solution in the cathode compartment may
25 furthermore include compounds whose role is to complement the catalyst prepared by the process of the invention. These compounds are especially Lewis acids.

By "Lewis acid" is meant, according to the usual definition, compounds which can accept electron pairs.

30 The Lewis acids mentioned in the work, edited by G.A. Olah, "Friedel-Crafts and related reactions", volume 1, pages 191 to 197 (1963), may, for example, be employed.

The Lewis acids which may be employed in the cathode compartment are generally chosen from compounds of the
35 elements in Groups Ib, IIb, IIIa, IIIb, IVa, IVb, Va, Vb, VIb, VIIb and VIII of the Periodic Table of the Elements, insofar as the said compounds are at least partially soluble and stable in water or, more generally, in the aqueous solution to be electrolytically treated. These compounds are

usually, but non-limitingly, salts, especially halides, preferably chlorides and bromides, sulphates, nitrates, sulphonates, especially trifluoromethanesulphonates, carboxylates, acetylacetonates, tetrafluoroborates and phosphates.

By way of non-limiting examples of such Lewis acids, mention may be made of zinc chloride, zinc bromide, zinc iodide, zinc trifluoromethanesulphonate, zinc acetate, zinc nitrate, zinc tetrafluoroborate, manganese chloride, manganese bromide, nickel chloride, nickel bromide, nickel cyanide, nickel acetylacetonate, cadmium chloride, cadmium bromide, stannous chloride, stannous bromide, stannous sulphate, stannous tartrate, chlorides, bromides, sulphates, nitrates, carboxylates or trifluoromethanesulphonates of the rare-earth elements such as lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium and lutetium, cobalt chloride, ferrous chloride and yttrium chloride.

Of course, mixtures of several Lewis acids may be employed.

Among the Lewis acids which may be used, most particular mention may be made of zinc chloride, zinc bromide, zinc sulphate, zinc tetrafluoroborate, stannous chloride, stannous bromide, zinc chloride/stannous chloride mixtures, nickel chloride, nickel bromide and nickel acetylacetonate.

The Lewis acid employed represents generally from 0 to 50 mol per mole of transition-metal compound, more particularly of nickel compound, and preferably from 0 to 10 mol per mole.

The anode compartment contains an aqueous solution of an anolyte which may consist of a salt, an acid such as especially sulphuric acid, nitric acid, water-soluble carboxylic acids such as acetic acid, of their salts especially sodium, potassium, ammonium or quaternary ammonium salts, or of a base such as especially sodium hydroxide or potassium hydroxide. Preferably, the anolyte will be chosen from sulphuric acid and its salts, especially dipotassium sulphate, potassium hydrogen sulphate, disodium sulphate and

sodium hydrogen sulphate.

The anolyte may also consist of one or more sulphonated phosphines defined above.

5 The initial concentration of the anolyte in the solution in the anode compartment is generally from 10^{-2} mol/litre to 3 mol/litre.

10 The electric current employed in the process of the invention is defined by its intensity and the cathode potential. The potential may, for example, be kept constant throughout the electrolysis (potentiostatic process). Another possibility, for example, is to keep the intensity constant (galvanostatic process). In continuous operation of the process of the invention, these two variants are equivalent.

15 When the process is carried out at constant potential, the value of the latter may easily be determined by one skilled in the art from the trace of current/potential curves.

20 The current density may reach 30 A/dm². It is adjusted depending on the amount of transition metal to be reduced.

The temperature at which the process is carried out generally lies from 0°C to 95°C.

25 An advantageous variant of the process of the invention consists in regenerating a spent catalyst, that is to say a catalyst which has been used and has become at least partially inactive. Thus, a catalyst based on a sulphonated phosphine and on a transition metal, in particular nickel, having an oxidation number of 0 or 1, optionally also
30 containing one or more Lewis acids, which is used in the butadiene and/or pentenenitrile hydrocyanation reaction, progressively becomes deactivated, in particular by oxidation of the transition metal. The transition metal is converted, at least partly, into a cyanide. At the end of the
35 hydrocyanation reaction, the aqueous phase containing especially the sulphonated phosphine and the transition-metal compound may be easily separated from the organic phase. This aqueous phase may contain relatively small amounts of compounds which are initially introduced, such as butadiene

and/or pentenenitriles, or are formed during the reaction, such as adiponitrile, methylglutaronitrile, ethylsuccinonitrile, pentenenitriles and methylbutenenitriles. The aqueous phase is electrochemically
5 treated, as described previously, so as to regenerate the catalyst.

The following Examples further illustrate the invention.

EXAMPLES

10 Apparatus used.

The electrolysis cell is composed of a cylindrical glass container having a working volume of approximately 100 ml, in which there is a cathode in the form of a platinum grid and a cylindrical anode well which is placed inside the
15 cathode grid and which comprises, at its base, a membrane made of resin of the Nafion 417® type and in which the anode in the form of a platinum plate is immersed.

The electrolyser is connected to a potentiostat which enables the cathode potential to be kept at a value of
20 -1.2 volts with respect to an Ag/AgCl reference electrode.

Abbreviations used:

TSTPP = sodium salt of trisulphonated triphenylphosphine
3PN = 3-pentenenitrile
25 ADN = adiponitrile
2M3 = 2-methyl-3-butenitrile
BD = butadiene
DC = degree of conversion
RT = selectivity of a compound obtained with respect
30 to the converted initial compound
t.o. = turn-over = number of mmol of nitriles or of dinitriles formed per mmol of Ni(0) involved
COD = cyclooctadiene

Examples 1 to 5 - Synthesis of an Ni(0)/TSTPP catalyst by
35 electrochemical reduction of Ni(CN)₂ in an aqueous solution of TSTPP.

50 ml of an aqueous solution of nickel cyanide ($\text{Ni}(\text{CN})_2$; 10.6 g/kg) and of TSTPP (300 g/kg of water) are put into the cathode compartment.

20 ml of anolyte (having the composition in Table 1 below) are put in the anode compartment. The electrolysis is carried out at 25°C at the controlled potential of -1.2 volts. Samples are regularly removed so as to assay the remaining $\text{Ni}(\text{II})$ by polarography.

Examples	Anolyte	Duration (min)	DC $\text{Ni}(\text{CN})_2$ (%)
1	0.6M TSTPP	220	50
2	1.5M KHSO_4	400	92
3	saturated K_2SO_4	400	48
4	saturated K_2SO_4	1350	75
5	0.1N H_2SO_4	75	77

15

Table 1

3-Pentenitrile hydrocyanation tests (a, b, c and d) on the solutions 1, 2, 4 and 5 of electrochemically generated catalysts.

Tests	Catalyst	$\text{Ni}(\text{O})$ (mmol)	HCN (mmol/h)	RT_{ADW} (%)	t.o.
CT1*	$\text{Ni}(\text{COD})_2/\text{TSTPP}$	5	67.4	61	30
CT2**	$\text{Ni}(\text{CN})_2(\text{TSTPP})_2$	0	67.4	0	0
a	solution 1	3	55.7	64	38
b	solution 2	3.8	50.5	63	37
c	solution 4	3.2	54.7	63	35
d	solution 5	2.9	39.1	61	37

25

Table 2

The operating conditions for the hydrocyanation tests are:

- 3PN : 320 mmol; ZnCl_2 : 20 mmol; 65°C; 3 h.

30

CT1* = comparative test with a catalyst prepared by exchange of the COD ligands of $\text{Ni}(\text{COD})_2$ by TSTPP;

CT2** = comparative test with a solution of $\text{Ni}(\text{CN})_2(\text{TSTPP})_2$, which is not electrochemically treated.

Butadiene hydrocyanation test (e) on the electrochemically generated catalyst solution 1.

Tests	Catalyst	BD (mmol)	Ni(0) (mmol)	HCN (mmol/h)	RT _{3PN+2H3} (%)	t.o.
CT3*	Ni(COD) ₂ /TSTPP	400	5.5	350	97	70
CT4**	Ni(CN) ₂ (TSTPP) ₂	400	0	350	0	0
e	solution 1	530	4	386	90	60

Table 3

The operating conditions for the hydrocyanation tests are:

- TSTPP : 25 mmol; 90°C; 1.2 h.

CT3* = comparative test with a catalyst prepared by exchange of the COD ligands of Ni(COD)₂ by TSTPP;

CT4** = comparative test with a solution of Ni(CN)₂(TSTPP)₂ which is not electroreductively treated.

Example 6 - Synthesis of Ni(0)/TSTPP by reduction of NiCl₂ in an aqueous solution of TSTPP.

50 ml of an aqueous solution of nickel chloride (NiCl₂: 17.4 g/kg), TSTPP (300 g/kg of water) and sodium cyanide (NaCN: 6.6 g/kg) are put in the cathode compartment.

20 ml of a saturated aqueous solution of K₂SO₄ are put in the anode compartment. The electrolysis is carried out at 25°C at a controlled potential of -1.2 volts. Samples are regularly removed so as to assay the remaining Ni(II) by polarography.

Example	Anolyte	Duration (min)	DC Ni(II) (%)
6	Saturated K ₂ SO ₄	1000	80

3PN hydrocyanation test (f) on solution 6 of the electrochemically regenerated catalyst.

Test	Catalyst	Ni(0) (mmol)	HCN (mmol/h)	RT _{adm} (%)	t.o.
f	solution 6	4.45	57.5	59	25

Example 7 - Regeneration of an aqueous solution of Ni/TSTPP coming from the hydrocyanation of 3-pentenitrile.

5 a) Placed in a 150 ml glass reactor, stirred using a turbine, are:

- 38 ml of an aqueous solution containing 5 mmol of nickel (0), 20 mmol of TSTPP and 20 mmol of zinc chloride;
- 32.4 ml of 3PN (320 mmol).

10 The entire system is heated to 65°C and pure hydrocyanic acid (condensed at -10°C) is injected at a flow rate of 67 mmol/h for 3.5 h. After cooling, degassing and settling, the two phases are separated. The organic phase is assayed by gas phase chromatography (GPC):

- 15
- 3-pentenitrile: 177 mmol
 - ethylsuccinonitrile: 13 mmol
 - methylglutaronitrile: 35 mmol
 - adiponitrile: 92 mmol

28 mmol of dinitriles being formed per mmol of nickel.

20 b) The completely inactive aqueous phase is electrolysed at a potential of -1.2 volts with respect to an Ag/AgCl reference electrode for 3 h.

c) Replaced in the reactor are:

25 regenerated;

- 10 mmol of ZnCl₂;
- 32.4 ml of 3PN (320 mmol).

30 The entire system is heated to 65°C and hydrocyanic acid is injected at a flow rate of 34 mmol/h for 6 h. After cooling and degassing, the various nitriles are assayed by GPC:

- 35
- 3-nitrilepentene: 183 mmol
 - ethylsuccinonitrile: 14 mmol
 - methylglutaronitrile: 39 mmol
 - adiponitrile: 78 mmol

32 mmol of dinitriles being formed per mmol of nickel.

These results indicate that the catalyst is completely regenerated.

CLAIMS

1. Process for the electrochemical synthesis of a catalyst comprising at least one transition metal having an oxidation number of 0 or 1, combined with at least one
5 sulphonated phosphine, which comprises electrolytically treating, in the cathode compartment of an electrolysis cell of an electrolyser, an aqueous solution comprising at least one compound of a transition metal and a sulphonated phosphine.
- 10 2. Process according to Claim 1, wherein the electrolysis cell of the electrolyser comprises a cathode compartment and an anode compartment which are separated by a separator element comprising an ion-exchange membrane or a porous diaphragm.
- 15 3. Process according to Claim 2, wherein the separator element is a cationic-type membrane prepared from cation-exchange resins possessing acid groups.
4. Process according to Claim 3, wherein the acid groups are sulphonic groups or carboxylic groups.
- 20 5. Process according to Claim 3 or 4, wherein the membrane is prepared from sulphonic resins.
6. Process according to Claim 2, wherein the separator element is a diaphragm made of porous ceramic, a diaphragm made of woven or non-woven synthetic fibres, or a
25 deposited diaphragm based on asbestos fibres or on synthetic fibres.
7. Process according to any one of Claims 1 to 6, wherein the cathode of the electrolysis cell is made of platinum, gold, iridium, ruthenium, palladium, nickel,
30 graphite, vitreous carbon, iron, a stainless steel, a special steel, lead, mercury or an amalgam or comprises titanium, tantalum, nickel or a stainless steel, coated with a layer of platinum, of gold, of iridium, of ruthenium, of a mixture of several of these metals, of platinum, palladium, iridium,
35 rhodium, ruthenium, osmium or tantalum oxides or of a mixture of several of these oxides.
8. Process according to any one of Claims 1 to 7, wherein the cathode and the anode of the electrolysis cell





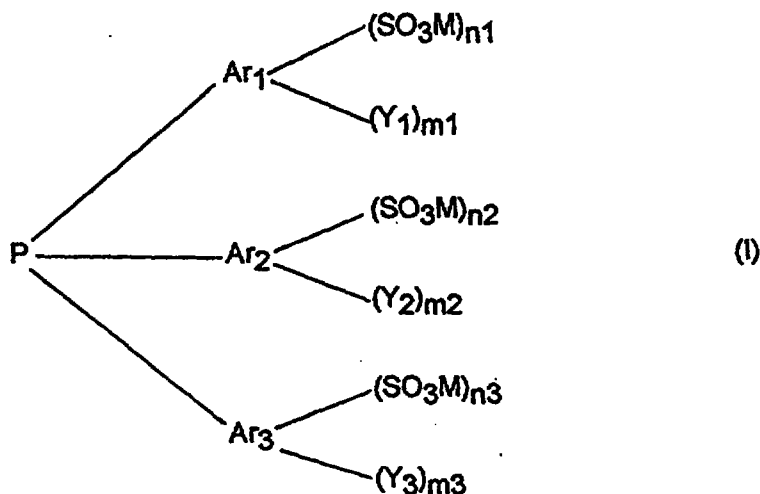
have a plane structure or a voluminal structure and are perforated or opened out.

9. Process according to Claim 8 wherein the cathode and the anode have a plate or grid plane structure.

5 10. Process according to Claim 8, wherein the cathode or the anode has a voluminal structure chosen from granular stacks of the materials of which it is composed, felts or foams of these said materials.

10 11. Process according to any one of Claims 1 to 10, wherein the anode is made of platinum, gold, iridium, ruthenium, palladium, nickel, graphite, vitreous carbon, a stainless steel, a special steel, or lead or comprises titanium or tantalum coated with a layer of platinum, of gold, of iridium, of ruthenium, of a mixture of several of
15 these metals, of platinum, palladium, iridium, rhodium, ruthenium, osmium or tantalum oxides or of a mixture of several of these oxides.

12. Process according to any one of Claims 1 to 11, wherein the sulphonated phosphine has the formula (I):



20 in which:

* Ar_1 , Ar_2 and Ar_3 , which may be the same or different, represent aryl groups;

* Y_1 , Y_2 and Y_3 , which may be the same or different, represent

25 . an alkyl radical having 1 to 4 carbon



- atoms,
- . an alkoxy radical having 1 to 4 carbon atoms,
 - . a halogen atom,
 - . a CN radical,
 - . an NO₂ radical,
 - . an OH radical, or
 - . an NR₁R₂ radical, in which R₁ and R₂, which may be the same or different, represent an alkyl radical having 1 to 4 carbon atoms;
- * each M, which may be the same or different, is an inorganic or organic cationic residue chosen such that the compound of formula (I) is soluble in water;
- * m₁, m₂ and m₃, which may be the same or different, are integers of from 0 to 5; and
- * n₁, n₂ and n₃, which may be the same or different, are integers of from 0 to 3, one of them at least being equal to or greater than 1.
13. Process according to Claim 12, in which each M, which may be the same or different, is:
- . H⁺,
 - . a cation derived from an alkali metal or alkaline-earth metal,
 - . N(R₃R₄R₅R₆)⁺ with R₃, R₄, R₅ and R₆, which may be the same or different, representing an alkyl radical having 1 to 4 carbon atoms or a hydrogen atom, or
 - . another cation derived from a metal whose salts with benzenesulphonic acid are soluble in water.
14. Process according to Claim 13, in which the sulphonated phosphine is one in which:
- Ar₁, Ar₂ and Ar₃ are phenyl groups;
 - Y₁, Y₂ and Y₃, which may be the same or different, represent groups chosen from:
 - . alkyl radicals having 1 or 2 carbon atoms, and

- . alkoxy radicals having 1 or 2 carbon atoms;
- each M, which may be the same or different, represents a cation chosen from:
 - 5 . H^+ ,
 - . cations derived from Na, K, Ca, Ba,
 - . NH_4^+ , and
 - . tetramethylammonium, tetraethylammonium, tetrapropylammonium or tetrabutylammonium cations;
- 10 - m_1 , m_2 and m_3 , which may be the same or different, are integers of from 0 to 3; and
- n_1 , n_2 and n_3 , which may be the same or different, are integers of from 0 to 3, one at least being greater than 1.

15 15. Process according to Claim 14, in which the sulphonated phosphine is chosen from the sodium, potassium, calcium, barium, ammonium, tetramethylammonium and tetraethylammonium salts of

20 mono(sulphophenyl)diphenylphosphine, di(sulphophenyl)phenylphosphine and tri(sulphophenyl)phosphine.

16. Process according to Claim 15, in which the SO_3 groups are in the meta position of the sulphonated phosphine.

25 17. Process according to any one of Claims 1 to 16, wherein the transition-metal compound is chosen from nickel, cobalt, iron, palladium, platinum, rhodium and iridium compounds which are soluble in water or capable of passing into solution under the reaction conditions.

30 18. Process according to any one of Claims 1 to 17, wherein the transition-metal compound is a nickel compound.

19. Process according to Claim 18, wherein the transition-metal compound is a nickel carboxylate, nickel carbonate, nickel bicarbonate, nickel borate, nickel bromide,

35 nickel chloride, nickel iodide, nickel thiocyanate, nickel cyanide, nickel hydroxide, nickel hydrophosphite, nickel phosphite, nickel phosphate or a derivative thereof, nickel nitrate, nickel sulphate, nickel sulphite, nickel arylsulphonate or nickel alkylsulphonate.



20. Process according to Claim 19, wherein the nickel carboxylate is nickel acetate, nickel formate or nickel citrate.

5 21. Process according to any one of Claims 1 to 20, wherein, in the cathode compartment, the initial concentration of the sulphonated phosphine is from 10^{-3} mol/litre to 1 mol/litre and the initial concentration of the transition-metal compound is from 10^{-5} mol/litre to 1 mol/litre.

10 22. Process according to any one of Claims 1 to 21, wherein the cathode compartment contains other compounds enabling the conductivity of the electrolyte to be increased.

15 23. Process according to Claim 22, wherein the other compounds in the cathode compartment are soluble salts or complexing agents capable of modifying the potential at which the reduction of the transition metal takes place.

24. Process according to Claim 23, wherein the complexing agent is a cyanide or Lewis acid.

20 25. Process according to Claim 24, wherein the Lewis acid is chosen from compounds of elements in Groups Ib, IIb, IIIa, IIIb, IVa, IVb, Va, Vb, VIb, VIIb and VIII of the Periodic Table of the Elements, insofar as the said compounds are at least partially soluble and stable in water or, more generally, in the aqueous solution to be electrolytically
25 treated.

26. Process according to Claim 25, wherein the Lewis acid is a salt.

30 27. Process according to Claim 26, wherein the salt is a halide, sulphate, nitrate, sulphonate, carboxylate, acetylacetonate, tetrafluoroborate or phosphate.

28. Process according to Claim 27, wherein the halide is a chloride or bromide and the sulphonate is a trifluoromethanesulphonate.

35 29. Process according to any one of Claims 24 to 28, wherein the Lewis acid is zinc chloride, zinc bromide, zinc iodide, zinc trifluoromethanesulphonate, zinc acetate, zinc nitrate, zinc tetrafluoroborate, manganese chloride, manganese bromide, nickel chloride, nickel bromide, nickel cyanide, nickel acetylacetonate, cadmium chloride, cadmium



* C L H S *

bromide, stannous chloride, stannous bromide, stannous sulphate, stannous tartrate, chlorides, bromides, sulphates, nitrates, carboxylates or trifluoromethanesulphonates of a rare-earth element, cobalt chloride, ferrous chloride or yttrium chloride.

30. Process according to Claim 30, wherein the rare earth element is lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium or lutetium.

31. Process according to any one of Claims 24 to 29, wherein the Lewis acid is zinc chloride, zinc bromide, zinc sulphate, zinc tetrafluoroborate, stannous chloride, stannous bromide, a zinc chloride/stannous chloride mixture, nickel chloride, nickel bromide or nickel acetylacetonate.

32. Process according to any one of Claims 24 to 30, wherein the Lewis acid represents from 0 to 50 mol per mole of transition-metal compound.

33. Process according to Claim 32, wherein the Lewis acid represent from 0 to 10 mol per mole of transition metal compound.

34. Process according to any one of Claims 1 to 33, wherein the anode compartment contains an aqueous solution of an anolyte comprising an acid, a salt or a base.

35. Process according to Claim 34, wherein the anolyte is sulphuric acid, nitric acid, a water-soluble carboxylic acid, a salt thereof, sodium hydroxide or potassium hydroxide.

36. Process according to Claim 35, wherein the carboxylic acid is acetic acid.

37. Process according to Claim 35 or 36, wherein the anolyte is a sodium, potassium, ammonium or quaternary ammonium salt.

38. Process according to Claim 37, wherein the anolyte is sulphuric acid or a salt thereof.

39. Process according to any one of Claims 1 to 33, wherein the anode compartment contains an aqueous solution of an anolyte comprising one or more sulphonated phosphines.

40. Process according to any one of Claims 1 to 39, wherein the initial concentration of the anolyte in the



solution in the anode compartment of the electrolysis cell is from 10^{-2} mol/litre to 3 mol/litre.

41. Process according to any one of Claims 1 to 40, wherein the cathode compartment contains an aqueous solution of a spent catalyst, based on a sulphonated phosphine and on a transition metal, converted at least partly into a cyanide, said spent catalyst also containing, optionally, one or more Lewis acids, and it being possible for said solution to contain relatively small amounts of compounds such as butadiene and/or pentenenitriles or such as adiponitrile, methylglutaronitrile, ethylsuccinonitrile or methylbutenenitriles.

42. A catalyst obtained by a process as defined in any one of Claims 1 to 41.



ABSTRACT

PROCESS FOR THE ELECTROCHEMICAL PREPARATION OF
CATALYSTS BASED ON A TRANSITION METAL
AND ON A PHOSPHINE

- 5 Process for the electrochemical synthesis of a catalyst
comprising at least one transition metal having an oxidation
number of 0 or 1, combined with at least one sulphonated
phosphine, which comprises electrolytically treating, in the
cathode compartment of an electrolysis cell of an
10 electrolyser, an aqueous solution comprising at least one
compound of a transition metal and a sulphonated phosphine.