

**PROCESS FOR THE PREPARATION BY HYDROGENATION OF
CATALYSTS BASED ON TRANSITION METAL AND PHOSPHINE**

The present invention relates to a process
5 for the preparation, by reduction using hydrogen, of
compounds which can be used as catalysts.

The compounds towards which the process of
the invention is directed contain at least one
transition metal in oxidation state 0 or 1 combined
10 with at least one monodentate or bidentate water-
soluble phosphine.

Such compounds can be used, for example, as
catalysts in place of the catalysts used in the
hydrocyanation reaction of ethylenic compounds, as
15 described in patent FR-A-2,338,253. In the present
text, they will be referred to as catalysts without
this limiting their field of use.

Besides the synthesis of such catalysts, the
present invention allows their regeneration. The reason
20 for this is that during the use of such catalysts for
the hydrocyanation of ethylenic compounds, gradual
oxidation of the transition metal they contain occurs,
thus leading in the long- or short-term to at least
partial deactivation of the said catalysts.

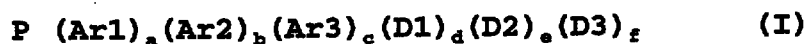
25 The process for the preparation of catalysts
containing at least one transition metal in oxidation
state 0 or 1, combined with at least one monodentate or
bidentate water-soluble phosphine, consists in treating

an aqueous solution containing at least one transition metal compound and at least one monodentate or bidentate water-soluble phosphine with hydrogen in the absence of carbon monoxide.

5 The expression "in the absence of carbon monoxide" means that industrial-grade hydrogen possibly containing only very low residual amounts of carbon monoxide, i.e. amounts usually less than 0.01 mol% per mole, is used in the process of the invention, and that
10 no additional amount of the said carbon monoxide is added.

The water-soluble phosphine used in the process of the invention is a monodentate phosphine corresponding to the general formula (I):

15



in which:

- Ar1, Ar2 and Ar3, which are identical or different,
20 represent aryl groups or aryl groups containing one or more substituents such as:
 - alkyl or alkoxy radical having 1 to 4 carbon atoms,
 - halogen atom,
 - nitrile group,
 - 25 - nitro group,
 - hydrophilic group such as:
 - COOM, -SO₃M, -PO₃M, 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 are identical or different, represent a hydrogen atom or an alkyl radical having from 1 to 4 carbon atoms, the other cations derived from metals whose arylcarboxylic acid, arylsulphonic acid or arylphosphonic acid salts are water-soluble,
- 5 - $N(R)_3$, in which formula the symbols R, which are identical or different, represent a hydrogen atom or an alkyl radical having from 1 to 4 carbon atoms,
- 10 - OH,
- a, b and c represent, independently of each other, 0 or 1,
- 15 - D1, D2 and D3, which are identical or different, represent an alkyl group, a cycloalkyl group, an alkyl or cycloalkyl group containing one or more substituents such as:
- 20 - alkoxy radical having 1 to 4 carbon atoms,
- halogen atom,
- nitrile group,
- nitro group,
- hydrophilic group such as:
- 25 - COOM, $-SO_3M$, $-PO_3M$, 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 are identical or different, represent a hydrogen atom or an alkyl radical having from 1 to 4 carbon atoms, the other cations derived from metals whose
 5 carboxylic acid, sulphonic acid or phosphonic acid salts are water-soluble,

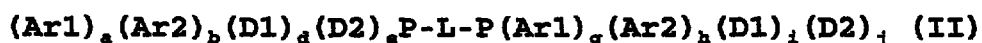
- $N(R)_3$, in which formula the symbols R, which are identical or different, represent a hydrogen atom or an alkyl radical having from 1 to 4 carbon
 10 atoms,

- OH,

- d, e and f represent, independently of each other, 0 or 1,

- the sum $(a+b+c+d+e+f)$ is equal to 3

15 or a bidentate phosphine corresponding to the general formula (II):



20 in which:

- Ar1, Ar2, D1 and D2 have the meanings indicated above for formula (I),

- a, b, d, e, g, h, i and j each represent 0 or 1,

- the sum $(a+b+d+e)$ is equal to 2,

25 - the sum $(g+h+i+j)$ is equal to 2,

- L represents a single valency bond or a divalent hydrocarbon radical such as an alkylene radical, a cycloalkylene radical, an arylene radical, a radical

derived from a heterocycle containing one or two oxygen, nitrogen or sulphur atoms in the ring, these various cyclic radicals being bonded directly to one of the phosphorus atoms or to the two phosphorus atoms or being bonded to one of the phosphorus atoms or to the two via a linear or branched alkylene radical having from 1 to 4 carbon atoms, it being possible for the ring or rings which may form part of the divalent radical L to contain one or more substituents such as those defined for Ar1, Ar2, Ar3, D1, D2 and D3.

As examples of metals whose carboxylic acid, sulphonic acid or phosphonic acid salts are water-soluble, mention may be made of lead, zinc and tin.

In the present text, the expression water-soluble is understood to refer to a compound which is soluble to at least 0.01 g per litre of water.

The preferred water-soluble phosphines are the phosphines of formula (I) or of formula (II) in which Ar1, Ar2 and Ar3 are phenyl groups or phenyl groups containing one or two substituents as defined above. D1, D2 and D3 represent an alkyl group having from 1 to 6 carbon atoms, a cycloalkyl group having 5 to 8 carbon atoms, an alkyl group having from 1 to 6 carbon atoms or a cycloalkyl group having 5 to 8 carbon atoms containing one or more substituents as defined above, L is a single valency bond, an alkylene radical having from 1 to 6 carbon atoms, a monocyclic or

bicyclic cycloalkylene radical having from 4 to 12 carbon atoms, a phenylene radical, a diphenylene radical, a naphthylene radical, a dinaphthylene radical, a radical derived from a heterocycle

5 containing one or two oxygen, nitrogen or sulphur atoms in the ring, these various cyclic radicals being bonded directly to one of the phosphorus atoms or to the two phosphorus atoms or being bonded to one of the phosphorus atoms or to the two via a linear or branched

10 alkylene radical having from 1 to 4 carbon atoms, it being possible for the ring or rings which may form part of the divalent radical L to contain one or more substituents such as an alkyl group having from 1 to 4 carbon atoms.

15 The preferred water-soluble phosphines are the phosphines of formula (I) or of formula (II) in which:

- the substituent or substituents of Ar, Ar₂ and Ar₃, which are identical or different, represent groups
- 20 such as:
 - alkyl or alkoxy radical having from 1 to 2 carbon atoms,
 - chlorine atom,
 - hydrophilic group such as:
 - 25 - COOM, -SO₃M, -PO₃M, M representing an inorganic or organic cationic residue chosen from a proton, cations derived from sodium, from potassium, from calcium or from barium, ammonium,

tetramethylammonium, tetraethylammonium,
tetrapropylammonium and tetrabutylammonium
cations, cations derived from zinc, from lead or
from tin,

- 5 - N(R)₃, in which formula the symbols R, which are
identical or different, represent a hydrogen atom
or an alkyl radical having from 1 to 4 carbon
atoms,

- OH

- 10 overall at least two of the said substituents of Ar₁,
Ar₂, Ar₃, D₁, D₂ and D₃ for the phosphines of formula
(I) and of Ar₁, Ar₂, D₁ and D₂ for the phosphines of
formula (II) being a hydrophilic group as defined
above.

- 15 Non-limiting examples of phosphines of
general formula (I) which may be mentioned in
particular are the alkali metal or alkaline-earth metal
salts, the ammonium salts and the quaternary ammonium
salts of (3-sulpho-

- 20 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-
25 4-methylphenyl) (4-methylphenyl)phosphine; di(3-sulpho-
4-methoxyphenyl) (4-methoxyphenyl)phosphine;
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; (2-sulpho-
 5 4-methylphenyl)(3-sulpho-4-methylphenyl)(3,5-disulpho-
 4-methylphenyl)phosphine; (3-sulphophenyl)(3-sulpho-
 4-chlorophenyl)(3,5-disulpho-4-chlorophenyl)phosphine,
 tris(hydroxymethyl)phosphine,
 tris(2-hydroxyethyl)phosphine,
 10 tris(3-hydroxypropyl)phosphine,
 tris(2-carboxymethyl)phosphine, the sodium salt of
 tris(3-carboxylatophenyl)phosphine,
 tris(3-carboxyethyl)phosphine,
 tris(4-trimethylammoniumphenyl)phosphine iodide, the
 15 sodium salt of tris(2-phosphonatoethyl)phosphine,
 bis(2-carboxyethyl)phenylphosphine,
 hydroxymethylbis(2-hydroxyethyl)phosphine, the sodium
 salt of tris(para-phosphonophenyl)phosphine, the sodium
 salt of bis(meta-sulphophenyl)-para-
 20 carboxyphenylphosphine and the sodium salt of bis(meta-
 sulphophenyl)-2-sulphoethylphosphine.

Non-limiting examples of phosphines of
 general formula (II) which may be mentioned in
 particular are the sodium salt of

- 25 2,2'-bis[di(sulphonatophenyl)phosphino]1,1'-binaphthyl,
 the sodium salt of
 1,2-bis[di(sulphonatophenyl)phosphinomethyl]cyclobutane
 (CBDTS), 1,2-bis(dihydroxymethylphosphino)ethane,

1,3-bis(dihydroxymethylphosphino)propane and the sodium salt of 2,2'-bis[di(sulphonatophenyl)phosphinomethyl]-1,1'-binaphthyl.

Obviously, it is possible to use a mixture of several of these phosphines.

Some of these water-soluble phosphines of formula (I) or (II) are commercially available.

For the preparation of the others, reference may be made to the general or specific phosphine synthesis processes described in general texts such as Houben-Weyl, Method der organischen Chemie, organische Phosphor Verbindungen, Volume 1 (1963).

Lastly, for the preparation of the water-soluble derivatives not described, it is possible, starting with phosphines containing no water-soluble substituents defined above, to readily introduce one or more of these hydrophilic substituents. Thus, the sulphonate groups, for example, may be introduced by the reaction of SO_3 in sulphuric acid. The carboxylate, phosphonate and quaternary ammonium groups may likewise be introduced by applying the chemical methods known for this type of synthesis.

Transition metal compounds which are preferably used are nickel, cobalt, iron, palladium, platinum, rhodium and iridium compounds, at least partially in an oxidation state other than 0. Water-soluble compounds or compounds capable of passing into solution under the reaction conditions are used. The

residue bonded to the metal is not essential provided that it satisfies these conditions.

Among the abovementioned compounds, the compounds most preferred are those of nickel. Non-
5 limiting examples which may be mentioned are compounds such as nickel carboxylates (in particular acetate, formate and citrate), nickel carbonate, nickel bicarbonate, nickel borate, nickel bromide, nickel chloride, nickel iodide, nickel thiocyanate, nickel
10 cyanide, nickel hydroxide, nickel hydrophosphite, nickel phosphite, nickel phosphate and derivatives, nickel nitrate, nickel sulphate, nickel sulphite and nickel aryl and alkyl sulphonates.

It is not necessary for the nickel compound
15 itself to be water-soluble. For example, nickel cyanite, which is sparingly soluble in water, dissolves well in an aqueous solution of water-soluble phosphine, in particular one which is sulphonated.

The reduction with hydrogen of the transition
20 metal compound in the presence of at least one monodentate or bidentate water-soluble phosphine may be carried out in homogeneous phase, optionally in the presence of a homogeneous catalyst which is soluble in the reaction medium, or in heterogeneous phase in the
25 presence of a catalyst which is insoluble in the reaction medium.

Homogeneous catalysts which may be used are the usual catalysts for this type of catalysis, such

as, for example, water-soluble phosphine complexes of rhodium, iridium, cobalt, ruthenium, nickel or palladium.

Heterogeneous catalysts which may be used are
5 the various metals or compounds of these metals, which are or are not deposited on a support, and which are generally employed in catalytic hydrogenation. Among these metals, those most commonly used are the metals of group VIII of the Periodic Table of the Elements, as
10 published in the Handbook of Chemistry and Physics, 51st Edition (1970-1971) of The Chemical Rubber Co. Among the metals of this group VIII which are more particularly suitable, mention may be made of platinum, palladium, ruthenium and nickel.

15 Supported catalysts are advantageously used. The supports are very varied. Among these, mention may be made, without any limitation, of aluminas, carbon black, silicas, various metal oxides such as cerine, zirconia and titanium dioxide, and metal salts such as
20 calcium carbonate and barium sulphate.

Among the non-supported heterogeneous catalysts, Raney nickel and Raney cobalt are preferably used. Raney nickel is most particularly suitable.

The catalytic reduction is generally carried
25 out at a hydrogen pressure, measured at 25°C, of from 1 to 200 bar and at a temperature of from 5°C to 200°C. Preferably, the hydrogen pressure measured at 25°C is from 1 to 150 bar and the temperature is from 10°C to

120°C.

The solution of the transition metal compound to be reduced may also comprise compounds whose role is to complement the catalyst prepared by the process of the invention. These compounds are, in particular, Lewis acids.

In the present text, the term Lewis acid is understood, according to the usual definition, to refer to electron-pair-acceptor compounds.

The Lewis acids mentioned in the text edited by G.A. Olah "Friedel-Crafts and Related Reactions", Volume 1, pages 191 to 197 (1963) may be used in particular.

The Lewis acids which may be used in the reaction mixture are chosen from compounds of the elements of groups Ib, IIb, IIIa, IIIb, IVa, IVb, Va, Vb, VIb, VIIb and VIII of the Periodic Table of the Elements, as published in Handbook of Chemistry and Physics, 51st Edition (1970-1971), insofar as the said compounds are at least partially soluble and stable in water or more generally in the aqueous solution to be treated. These compounds are usually, but with no limitation being implied, salts, in particular halides, preferably chlorides and bromides, sulphates, nitrates, sulphonates, in particular trifluoromethanesulphonates, carboxylates, acetylacetonates, tetrafluoroborates and phosphates.

Non-limiting examples of such Lewis acids

which may be mentioned are 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, the chlorides, bromides, sulphates, nitrates, carboxylates or trifluoromethanesulphonates of 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.

Obviously, mixtures of several of these Lewis acids may be used.

Among the Lewis acids which may be used, mention may be made most particularly 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 used generally represents 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.

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 monodentate or bidentate water-soluble phosphine and on a transition metal in oxidation state 0 or 1, optionally also containing one or more Lewis acids, used in the hydrocyanation reaction of butadiene and/or of pentenenitriles becomes gradually deactivated, in particular by oxidation of the transition metal. The latter, and more particularly nickel, is at least partly converted into cyanide. At the end of the hydrocyanation reaction, the aqueous phase containing in particular the monodentate or bidentate water-soluble phosphine and the compound of the transition metal which is at least partially in an oxidation state higher than 0, may readily be separated from the organic phase. This aqueous phase may contain variable amounts of compounds initially introduced, such as butadiene and/or pentenenitriles, or formed during the reaction, such as adiponitrile, methylglutaronitrile, ethylsuccinonitrile, pentenenitriles and methylbutenenitriles. The aqueous phase is treated as described above in order to regenerate the catalyst by reduction of the transition metal which is found in an oxidation state higher than 0.

The examples which follow illustrate the invention.

Abbreviations used:

3PN = 3-pentenitrile

ADN = adiponitrile

RC = selectivity towards a compound obtained

5 relative to the starting compound converted

t.o. = turnover = number of mmol of dinitriles formed
per mmol of Ni(0) employed

COD = cyclooctadiene.

10 Examples 1 to 10: Reduction of Ni(CN)₂ on a
heterogeneous catalyst

The following are loaded into a 5 ml glass ampule:

- the hydrogenation catalyst (10 mol% of metal relative
to the Ni(CN)₂ to be reduced) (mass indicated in the
15 table hereinbelow),
 - 2.4 g of an aqueous solution of Ni(CN)₂,
(0.127 mol/kg), of sodium triphenylphosphine
trisulphonate (TPPTSNa₃) (0.5 mol/kg) and ZnCl₂,
(0.41 mol/kg),
 - 20 - 100 µl of 3-pentenitrile (3PN) (0.42 mol/kg).
- (These concentrations are expressed relative to the
whole reaction mixture).

The ampule is placed in an autoclave which is
pressurized to 50 bar of hydrogen and heated at 100°C
25 for 1 hour. At the end of the test, the reactor is
depressurized and the aqueous solution is analysed by
polarography. The nickel (0) concentration is
calculated by the difference between the total nickel

concentration and the residual nickel (II)
concentration.

	Example	Catalyst	Mass of catalyst (mg)	[Ni(0)] (mol/kg)
5	Example 1	Pd/C containing 2.5% Pd	134.6	0.05
	Example 2	Pd/ α Al ₂ O ₃ containing 0.5% Pd	680	0.029
	Example 3	Pd/ γ Al ₂ O ₃ containing 5% Pd	74.3	0.024
	Example 4	Pd/CaCO ₃ containing 5% Pd	79.1	0.025
	Example 5	Pd/BaSO ₄ containing 5% Pd	78.8	0.023
10	Example 6	Pt/C containing 2.5% Pt	270	0.115
	Example 7	Pt/ α Al ₂ O ₃ containing 0.1% Pt	1257	0.026
	Example 8	Pt/ γ Al ₂ O ₃ containing 0.1% Pt	1272	0.007
	Example 9	Ru/C containing 2.55% Pd	136	0.040
	Example 10	Ru/ γ Al ₂ O ₃ containing 5% Ru	69	0.035

Table 1

**Example 11: Reduction of $\text{Ni}(\text{CN})_2$ on Pt/C and
hydrocyanation of 3-pentenitrile**

a) preparation of the catalyst

- 5 The following are loaded into a 125 ml glass ampule:
- 60 g of an aqueous solution of $\text{Ni}(\text{CN})_2$ (0.135 mol/kg)
in TPPTSNa₃ (0.5 mol/kg)
 - 3.39 g of ZnCl_2 (24.9 mmol of Zn)
 - 6.25 g of Pt/C (0.8 mmol of Pt)
- 10 - 1 g of 3-pentenitrile (12.3 mmol).

The ampule is placed in an autoclave which is
pressurized to 50 bar of hydrogen and heated at 100°C
for 1 hour. At the end of the test, the reactor is
decompressed and polarographic analysis of the aqueous
15 solution indicates a nickel (0) concentration of
0.051 mol/kg (= solution 11a).

b) test of the solution 11a in the hydrocyanation of
3-pentenitrile

Test	Catalyst	Ni(0)	HCN	RC ADN	t.o.
		(mmol)	(mmol/h)	(%)	
CT1*	Ni(COD) ₂ /TPPTSNa ₃	5	67.4	61	30
CT2**	Ni(CN) ₂ (TPPTSNa ₃) ₂	0	67.4	0	0
test	solution 11a	2.15	28	67	25

Table 2

10

Operating conditions of the hydrocyanation test: 3PN =
 300 mmol, 65°C, 3 h.

CT1* = comparative test with a catalyst prepared by
 exchanging the COD ligands of Ni(COD)₂ for TPPTSNa₃ +
 15 ZnCl₂ (0.5 mol/kg).

CT2* = comparative test with a solution of
 Ni(CN)₂(TPPTSNa₃)₂ + ZnCl₂ (0.5 mol/kg) not treated with
 hydrogen.

20 Examples 12 to 16: Reduction of Ni(CN)₂ in homogeneous
phase

The following are loaded into a 5 ml glass ampule:

- 2.4 g of an aqueous solution containing Ni(CN)₂,
 (0.09 mol/kg), Ni(0) (0.03 mol/kg) and TPPTSNa₃,
 25 (0.5 mol/kg),

- optionally, a zinc derivative (see Table 3),
- 25 μ l of 3-pentenitrile (0.25 mmol).

The ampule is placed in an autoclave which is pressurized to 100 bar of hydrogen and heated to 100°C

5 (duration indicated in Table 3). At the end of the test, the autoclave is depressurized and the aqueous solution is analysed by polarography. The nickel (0) concentration is calculated by the difference between the total nickel concentration and the concentration of
10 residual nickel (II).

Test	Zinc compound	mmol of zinc	Duration (h)	[Ni(0)] (mol/kg)
Example 12	ZnSO ₄	0.6	1	0.055
Example 13	ZnCl ₂	1.1	1	0.069
15 Example 14	none	0	0.25	0.052
Example 15	none	0	0.5	0.067
Example 16	none	0	1	0.106

Table 3

Example 17: Reduction of $\text{Ni}(\text{CN})_2$ in homogeneous phase and hydrocyanation of 3-pentenitrile

a) preparation of the catalyst

- 5 The following are loaded into a 125 ml glass ampule:
- 45 g of an aqueous solution of $\text{Ni}(\text{CN})_2$ (0.135 mol/kg) in TPPTSNa₃ (0.5 mol/kg)
 - 15 g of an aqueous solution of $\text{Ni}(0)$ (0.11 mol/kg) in TPPTSNa₃ (0.5 mol/kg)
 - 10 - 2 g of ZnCl_2 (14.7 mmol of Zn)
 - 0.6 g of 3-pentenitrile (7.4 mmol).

The ampule is placed in an autoclave which is pressurized to 100 bar of hydrogen and heated at 100°C for 1 hour. At the end of the test, the autoclave is

15 depressurized and polarographic analysis of the aqueous solution indicates a nickel (0) concentration of 0.078 mol/kg (= solution 17a).

**b) test of the solution 17a in the hydrocyanation of
3-pentenitrile**

	Test	Catalyst	Ni(0)	HCN	RC ADN	t.o.
			(mmol)	(mmol/h)	(%)	
5	CT3*	Ni(COD) ₂ /TPPTSNa ₃	5	67.4	61	30
	CE4**	Ni(CN) ₂ (TPPTSNa ₃) ₂	0	67.4	0	0
	test	solution 17a	3.3	42.9	67	28

Table 4

10

Operating conditions of the hydrocyanation test: 3PN =
300 mmol, 65°C, 3 h.

CT3* = comparative test with a catalyst prepared by
exchanging the COD ligands of Ni(COD)₂ for TPPTSNa₃ +
15 ZnCl₂ (0.5 mol/kg).

CT4* = comparative test with a solution of
Ni(CN)₂(TPPTSNa₃)₂ + ZnCl₂ (0.5 mol/kg) not treated with
hydrogen.

20 **Examples 18 to 20: Reduction of Ni(CN)₂ on a
heterogeneous catalyst**

The following are loaded into a 5 ml glass ampule:

- the hydrogenation catalyst (mass indicated in Table 5
below),
- 25 - 2.2 g of an aqueous solution of Ni(CN)₂ (0.12 to

0.13 mol/kg), sodium triphenylphosphine trisulphonate (TPPTSNa₃) (0.5 mol/kg) and ZnCl₂ (0.100 g),
- 100 µl of 3-pentenitrile (3PN) (0.42 mol/kg).

(These concentrations are expressed relative to the
5 whole reaction mixture).

The ampule is placed in an autoclave which is
pressurized to 100 bar of hydrogen and stirred at room
temperature (about 25°C) for 1 hour. At the end of the
10 test, the reactor is depressurized and the aqueous
solution is analysed by polarography. The nickel (0)
concentration is calculated by the difference between
the total nickel concentration and the concentration of
residual nickel (II).

15 No precipitate of nickel is observed and in
each test the amount of total nickel assayed
corresponds, within the accuracy limits of the
analysis, to the amount introduced at the start of the
test.

Example	Catalyst	Total Ni assayed (mol/kg)	Ni(0) assayed (mol/kg)
Example 18	Pt/C at 5% by weight (0.234 g)	0.130	0.063
Example 19	Pt/C at 5% by weight (0.269 g)	0.135	0.074
Example 20	Pt/C at 0.88% by weight (0.401 g)	0.119	0.053

5

Table 5

Examples 21 to 25: Reduction of Ni(CN)₂ on a heterogeneous catalyst

- 10 The following are loaded into a 5 ml glass ampule:
- the hydrogenation catalyst (nature and mass indicated in Table 6 below),
 - 2.2 g of an aqueous solution of Ni(CN)₂ (0.112 mol/kg) and sodium triphenylphosphine trisulphonate (TPPTSNa₃)
 - 15 (0.5 mol/kg),
 - 130 to 150 µl of 3-pentenitrile (3PN).
- (These concentrations are expressed relative to the whole reaction mixture).

- 20 The ampule is placed in an autoclave which is

pressurized to 100 bar of hydrogen and stirred at different temperatures (indicated in Table 6 below under the abbreviation T°C) for different durations. At the end of the test, the reactor is depressurized and
5 the aqueous solution is analysed by polarography. The nickel (0) concentration is calculated by the difference between the total nickel concentration and the concentration of residual nickel (II).

No nickel precipitate is observed (except a
10 very slight one in Example 23 corresponding to less than 0.003 mol/kg) and in each test the amount of total nickel assayed corresponds, within the accuracy limits of the analysis, to the amount introduced at the start of the test.

5

10

Example	Catalyst	T° C	Duration	Total Ni assayed (mol/kg)	Ni(0) assayed (mol/kg)
Example 21	Pt/C at 5% by weight (0.26 g)	65	1 h 30	0.113	0.091
Example 22	Pt/C at 5% by weight (0.23 g)	25	4 h	0.113	0.089
Example 23	Pt/alumina at 0.5% by weight (0.99 g)	25	4 h	0.109	0.044
Example 24	wet Raney nickel (0.09 g)	40	1 h 30	0.108	0.103
Example 25	wet Raney nickel (0.06 g)	65	1 h 30	0.109	0.099

Table 6

CLAIMS

1. Process for the preparation of catalysts containing at least one transition metal in oxidation state 0 or 1, combined with at least one monodentate or bidentate water-soluble phosphine, characterized in that it consists in treating an aqueous solution containing at least one transition metal compound and at least one monodentate or bidentate water-soluble phosphine with hydrogen in the absence of carbon monoxide.

2. Process according to Claim 1, characterized in that the water-soluble phosphine used is a monodentate phosphine corresponding to the general formula (I):



in which:

- Ar1, Ar2 and Ar3, which are identical or different, represent aryl groups or aryl groups containing one or more substituents such as:
 - alkyl or alkoxy radical having 1 to 4 carbon atoms,
 - halogen atom,
 - nitrile group,
 - nitro group,
 - hydrophilic group such as:
 - COOM, -SO₃M, -PO₃M, 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 are identical or different, represent a hydrogen atom or an alkyl radical having from 1 to 4 carbon atoms, the
- 5 other cations derived from metals whose arylcarboxylic acid, arylsulphonic acid or arylphosphonic acid salts are water-soluble,
- $N(R)_4$, in which formula the symbols R, which are identical or different, represent a hydrogen atom
- 10 or an alkyl radical having from 1 to 4 carbon atoms,
- OH,
- a, b and c represent, independently of each other, 0 or 1,
- 15 - D1, D2 and D3, which are identical or different, represent an alkyl group, a cycloalkyl group, an alkyl or cycloalkyl group containing one or more substituents such as:
- alkoxy radical having 1 to 4 carbon atoms,
- 20 - halogen atom,
- nitrile group,
- nitro group,
- hydrophilic group such as:
- COOM, $-SO_3M$, $-PO_3M$, M representing an inorganic or
- 25 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 are identical or



- different, represent a hydrogen atom or an alkyl radical having from 1 to 4 carbon atoms, the other cations derived from metals whose carboxylic acid, sulphonic acid or phosphonic acid salts are water-soluble,
- 5 - N(R), in which formula the symbols R, which are identical or different, represent a hydrogen atom or an alkyl radical having from 1 to 4 carbon atoms,
- 10 - OH,
- d, e and f represent, independently of each other, 0 or 1,
- the sum (a+b+c+d+e+f) is equal to 3
- or a bidentate phosphine corresponding to the general
- 15 formula (II):
- $$(Ar1)_a(Ar2)_b(D1)_d(D2)_eP-L-P(Ar1)_g(Ar2)_h(D1)_i(D2)_j \quad (II)$$
- in which:
- Ar1, Ar2, D1 and D2 have the meanings indicated above for formula (I),
- 20 - a, b, d, e, g, h, i and j each represent 0 or 1,
- the sum (a+b+d+e) is equal to 2,
- the sum (g+h+i+j) is equal to 2,
- L represents a single valency bond or a divalent hydrocarbon radical such as an alkylene radical, a
- 25 cycloalkylene radical, an arylene radical, a radical derived from a heterocycle containing one or two oxygen, nitrogen or sulphur atoms in the ring, these various cyclic radicals being bonded directly to one



of the phosphorus atoms or to the two phosphorus atoms or being bonded to one of the phosphorus atoms or to the two via a linear or branched alkylene radical having from 1 to 4 carbon atoms, it being possible for the ring or rings which may form part of the divalent radical L to contain one or more substituents such as those defined for Ar1, Ar2, Ar3, D1, D2 and D3.

3. Process according to either of Claims 1 and 2, characterized in that the transition metal compound is chosen from nickel, cobalt, iron, palladium, platinum, rhodium and iridium compounds, which are water-soluble or capable of passing into solution under the reaction conditions.

4. Process according to one of Claims 1 to 3, characterized in that the transition metal compound is chosen from nickel compounds such as nickel carboxylates, in particular acetate, formate and citrate, nickel carbonate, nickel bicarbonate, nickel borate, nickel bromide, nickel chloride, nickel iodide, nickel thiocyanate, nickel cyanide, nickel hydroxide, nickel hydrophosphite, nickel phosphite, nickel phosphate and its derivatives, nickel nitrate, nickel sulphate, nickel sulphite and nickel aryl and alkyl sulphonates.

5. Process according to one of Claims 1 to 4, characterized in that the reduction with hydrogen is performed in a homogeneous medium.



6. Process according to Claim 5, characterized in that the reaction is carried out in the presence of a homogeneous catalyst which is soluble in the reaction medium.

5 7. Process according to Claim 6, characterized in that the homogeneous catalyst is chosen from water-soluble phosphine complexes of rhodium, iridium, cobalt, ruthenium, nickel or palladium.

8. Process according to one of Claims 1 to 4,
10 characterized in that the reduction with hydrogen is carried out in a heterogeneous medium in the presence of a heterogeneous catalyst which is insoluble in the reaction medium.

9. Process according to Claim 8, characterized
15 ized in that the heterogeneous catalyst is chosen from the various metals of group VIII of the Periodic Table of the Elements or compounds of these metals, which are or are not deposited on a support.

10. Process according to either of Claims 8
20 and 9, characterized in that the heterogeneous catalyst is chosen from platinum, palladium, ruthenium and nickel.

11. Process according to one of Claims 1 to
10, characterized in that the water-soluble phosphine
25 is chosen from phosphines of formula (I) or of formula (II) in which Ar₁, Ar₂ and Ar₃ are phenyl groups or phenyl groups containing one or two substituents as defined above, D₁, D₂ and D₃ represent an alkyl group



having from 1 to 6 carbon atoms, a cycloalkyl group having 5 to 8 carbon atoms, an alkyl group having from 1 to 6 carbon atoms or a cycloalkyl group having 5 to 8 carbon atoms containing one or more substituents as defined above, L is a single valency bond, an alkylene radical having from 1 to 6 carbon atoms, a monocyclic or bicyclic cycloalkylene radical having from 4 to 12 carbon atoms, a phenylene radical, a diphenylene radical, a naphthylene radical, a dinaphthylene radical, a radical derived from a heterocycle containing one or two oxygen, nitrogen or sulphur atoms in the ring, these various cyclic radicals being bonded directly to one of the phosphorus atoms or to the two phosphorus atoms or being bonded to one of the phosphorus atoms or to the two via a linear or branched alkylene radical having from 1 to 4 carbon atoms, it being possible for the ring or rings which may form part of the divalent radical L to contain one or more substituents such as an alkyl group having from 1 to 4 carbon atoms.

12. Process according to one of Claims 1 to 11, characterized in that the water-soluble phosphine is chosen from phosphines of formula (I) or of formula (II) in which:

- 25 - the substituent or substituents of Ar, Ar₂ and Ar₃, which are identical or different, represent groups such as:
- alkyl or alkoxy radical having from 1 to 2 carbon



atoms,

- chlorine atom,

- hydrophilic group such as:

- COOM, -SO₃M, -PO₃M, M representing an inorganic or

5 organic cationic residue chosen from a proton, cations derived from sodium, from potassium, from calcium or from barium, ammonium,

tetramethylammonium, tetraethylammonium,

tetrapropylammonium and tetrabutylammonium

10 cations, cations derived from zinc, from lead or from tin,

- N(R)₃, in which formula the symbols R, which are identical or different, represent a hydrogen atom or an alkyl radical having from 1 to 4 carbon

15 atoms,

- OH

overall at least two of the said substituents of Ar₁, Ar₂, Ar₃, D₁, D₂ and D₃ for the phosphines of formula (I) and of Ar₁, Ar₂, D₁ and D₂ for the phosphines of
20 formula (II) being a hydrophilic group as defined above.

13. Process according to one of Claims 1 to 12, characterized in that the water-soluble phosphine is chosen from the alkaline metal or alkaline-earth
25 metal salts, the ammonium salts and the 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-
5 4-methoxyphenyl) (4-methoxyphenyl) phosphine;
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-
10 4-methoxyphenyl) phosphine; tri (3-sulpho-
4-chlorophenyl) phosphine; (2-sulpho-
4-methylphenyl) (3-sulpho-4-methylphenyl) (3,5-disulpho-
4-methylphenyl) phosphine; (3-sulphophenyl) (3-sulpho-
4-chlorophenyl) (3,5-disulpho-4-chlorophenyl) phosphine,
15 tris (hydroxymethyl) phosphine,
tris (2-hydroxyethyl) phosphine,
tris (3-hydroxypropyl) phosphine,
tris (2-carboxymethyl) phosphine, the sodium salt of
tris (3-carboxylatophenyl) phosphine,
20 tris (3-carboxyethyl) phosphine, tris (4-
trimethylammoniumphenyl) phosphine iodide, the sodium
salt of tris (2-phosphonatoethyl) phosphine,
bis (2-carboxyethyl) phenylphosphine,
hydroxymethylbis (2-hydroxyethyl) phosphine, the sodium
25 salt of tris (para-phosphonophenyl) phosphine, the sodium
salt of bis (meta-sulphophenyl) -para-
carboxyphenylphosphine and the sodium salt of bis (meta-
sulphophenyl) -2-sulphoethylphosphine.



14. Process according to one of Claims 1 to 12, characterized in that the water-soluble phosphine is chosen from the sodium salt of 2,2'-bis[di(sulphonatophenyl)phosphino]1,1'-binaphthyl, 5 the sodium salt of 1,2-bis[di(sulphonatophenyl)phosphinomethyl]cyclobutane (CBDTS), 1,2-bis(dihydroxymethylphosphino)ethane, 1,3-bis(dihydroxymethylphosphino)propane and the sodium salt of 2,2'-bis[di(sulphonatophenyl)phosphinomethyl]- 10 1,1'-binaphthyl.

15. Process according to one of Claims 1 to 14, characterized in that the solution of the transition metal compound to be reduced comprises at least one Lewis acid chosen from compounds of the 15 elements of 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 treated preferably from 20 the salts, in particular the halides, sulphates, nitrates, sulphonates, in particular trifluoromethanesulphonates, carboxylates, acetylacetonates, tetrafluoroborates and phosphates.

16. Process according to Claim 15, character- 25 ized in that the Lewis acid is chosen from 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, the chlorides,
5 bromides, sulphates, nitrates, carboxylates or
trifluoromethanesulphonates of rare-earth elements such
as lanthanum, cerium, praseodymium, neodymium,
samarium, europium, gadolinium, terbium, dysprosium,
holmium, erbium, thulium, ytterbium and lutetium,
10 cobalt chloride, ferrous chloride and yttrium chloride.

17. Process according to either of Claims 15
and 16, characterized in that the Lewis acid used
represents from 0 to 50 mol per mole of transition
metal compound, more particularly of nickel compound,
15 and preferably from 0 to 10 mol per mole.

18. Process according to one of Claims 1 to
17, characterized in that it consists in using an
aqueous solution of a spent catalyst to be regenerated,
based on monodentate or bidentate water-soluble
20 phosphine and on a transition metal, and more
particularly nickel, which is at least partly converted
into cyanide, the said spent catalyst optionally
containing one or more Lewis acids and optionally
containing variable amounts of compounds such as
25 butadiene and/or pentenenitriles or such as
adiponitrile, methylglutaronitrile, ethylsuccinonitrile
and methylbutenenitriles.

19. Process according to one of Claims 1 to



18, characterized in that the catalytic reduction is carried out at a hydrogen pressure, measured at 25°C, of from 1 to 200 bar and at a temperature of from 5°C to 200°C and preferably at a hydrogen pressure, 5 measured at 25°C, of from 1 to 150 bar and at a temperature of from 10°C to 120°C.

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(54) Title: PROCESS FOR THE PREPARATION BY HYDROGENATION OF CATALYSTS BASED ON A TRANSITION METAL AND PHOSPHINE (54) Titre: PROCEDE DE PREPARATION PAR HYDROGENATION DE CATALYSEURS A BASE DE METAL DE TRANSITION ET DE PHOSPHINE (57) Abstract The present invention relates to a process for the preparation through hydrogenation of compounds which can be used as catalysts. The disclosed compounds comprise more specifically at least one transition metal with an oxydation degree of 0 or 1 associated to at least one monodentate or bidentate hydrosoluble phosphine. The process for the synthesis of catalysts comprises the hydrogenation of an aqueous solution containing at least one compound of a transition metal and a monodentate or bidentate hydrosoluble phosphine. (57) Abrégé La présente invention concerne un procédé de préparation, mettant en oeuvre une hydrogénation, de composés pouvant être utilisés comme catalyseurs. Les composés visés comportent plus spécifiquement au moins un métal de transition au degré d'oxydation 0 ou 1 associé à au moins une phosphine hydrosoluble monodentate ou bidentate. Le procédé de synthèse des catalyseurs consiste à hydrogéner une solution aqueuse contenant au moins un composé d'un métal de transition et une phosphine hydrosoluble monodentate ou bidentate.		

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