PROCESS FOR THE MANUFACTURE OF A HYDROCYANATION CATALYST

The present invention relates to a process for the manufacture of a catalyst for the hydrocyanation of an organic compound comprising ethylenic unsaturation.

It relates more particularly to a process for the manufacture of a hydrocyanation catalyst comprising in particular nickel and a water-soluble phosphine.

The hydrocyanation reaction, in particular of organic compounds comprising at least one ethylenic unsaturation, is an important industrial reaction allowing the manufacture of numerous compounds. Thus, this reaction is employed in the synthesis of organic intermediates, such as 3-pentenenitrile, which is used in the manufacture of monomers such as aminocapronitrile or hexamethylenediamine.

This reaction is disclosed in particular in French Patents No. 1,599,761 and No. 2,338,253 and United States Patents US 3,655,723, US 3,850,973, US 3,925,445 or US 3,686,264.

This reaction is generally carried out in the presence of a catalyst comprising a transition metal. Such catalysts are disclosed in the above patents.

Thus, French Patent No. 2,338,253 discloses in particular a nickel-based catalyst which is formed

This catalyst is obtained by addition, to an aqueous solution of phosphine, of a nickel compound which is soluble or insoluble in water. The amount of nickel in the aqueous phase then corresponds to that of nickel extracted or complexed by the water-soluble phosphine compound. However, in a preferred embodiment, it is advantageous to use a nickel compound which is soluble in the phosphine/water mixture. Thus, French Patent No. 2,338,253 specifies that the nickel cyanide compound, which is insoluble in water but soluble in the aqueous solution of phosphine, is a preferred compound in the manufacture of such a catalyst. Other compounds, such as organic complexes or salts of nickel, can advantageously be used to manufacture the catalyst.

These various methods for the preparation of a hydrocyanation catalyst exhibits the major disadvantage of using a nickel compound which may be either very difficult to manufacture with a sufficient degree of purity or may have a cost and an availability which affect the economics of the industrial operation of the hydrocyanation reaction.

An objective of the invention is to overcome these disadvantages by providing a novel process for the manufacture of a hydrocyanation catalyst which can be of high purity using accessible nickel compounds as starting materials.

To this end, the invention provides a process for the preparation of a catalyst for the hydrocyanation of an organic compound composed of an aqueous solution of at least one water-soluble phosphine and of nickel, characterized in that it consists in bringing an aqueous solution of a water-soluble phosphine and a nickel hydroxide into contact, in adding hydrogen cyanide or a compound which generates hydrogen cyanide to the mixture, and in keeping the mixture stirred until the nickel has dissolved and in then subjecting the mixture to a reduction in order to at least partially convert the dissolved nickel to a 0 oxidation state.

According to a preferred characteristic of the invention, the mixture, after addition of the hydrogen cyanide, is kept stirred at a temperature of less than 100°C, preferably of between 20°C and 80°C.

The amount of hydrogen cyanide added is at least equal to the stoichiometric amount for converting the nickel hydroxide to nickel cyanide.

The amount of hydrogen cyanide added will advantageously be from 30% to 200% greater than the stoichiometric amount.

After at least partial dissolution of the nickel hydroxide, the aqueous solution is subjected to a stage of reduction of the nickel with an oxidation state of greater than zero in order to obtain nickel with the zero oxidation state.

This reduction reaction is advantageously carried out after addition, to the mixture, of a small amount of nickel in the zero oxidation state. This addition can be carried out by the addition of a small amount of catalyst comprising nickel in the zero oxidation state.

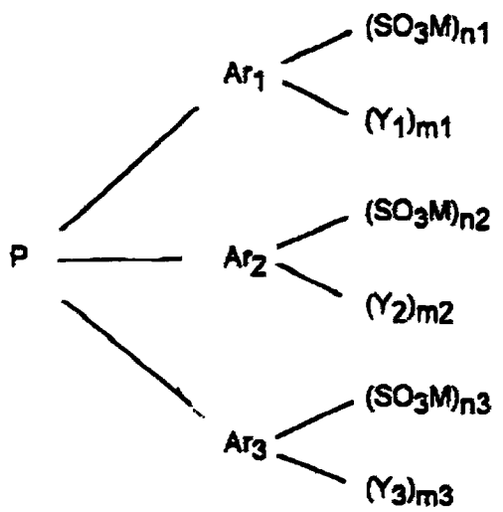
The stage of regeneration of the catalyst, or in other words the reduction of the nickel to the 0 oxidation state, can be carried out by several processes, such as a reduction by gaseous hydrogen, an electrochemical reduction or addition of an organic or inorganic reducing agent. The reduction processes are known and are disclosed in particular in Patents WO 97/24184, EP 0,715,890 and FR 1,599,761.

The amount of nickel compound used is chosen so that there is, per litre of reaction solution, between 10^{-4} and 1, and preferably between 0.005 and 0.5, mol of nickel.

The amount of water-soluble phosphine used to prepare the reaction solution is chosen so that the number of moles of this compound with respect to 1 mol of nickel is from 0.5 to 2000 and preferably from 2 to 300.

Mention may be made, as suitable water-soluble phosphine compounds, of the compounds disclosed in Patent 2,338,253 or in Patent Applications WO 97/12857 and EP 0,650,959. This listing does not have any limiting nature.

Thus, suitable phosphines for the invention correspond to the following general formula (I):



(I)

in which:

* Ar_1, Ar_2 and Ar_3, which are identical or different, represent aryl groups
* Y_1, Y_2 and Y_3, which are identical 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,
    - an NR_1R_2 radical, in the formula of which R_1 and R_2, which are identical or different, represent an alkyl radical having 1 to 4 carbon atoms,

* M is an inorganic or organic cationic residue chosen, so that the compound of formula (I) is soluble in water, from the group consisting of:
  . H^+,
  . cations derived from alkali metals or alkaline earth metals,
  . $N(R_3R_4R_5R_6)^+$, where R_3, R_4, R_5 and R_6, which are identical or different, represent an alkyl radical having 1 to 4 carbon atoms or a hydrogen atom,
  . other cations derived from metals, the benzenesulphonic acid salts of which are soluble in water,
* m_1, m_2 and m_3 are identical or different integers from 0 to 5,
* n_1, n_2 and n_3 are identical or different integers from 0 to 3, at least one of them being equal to or greater than 1.

Mention may be made, as examples of metals, the benzenesulphonic acid salts of which are soluble in water, of lead, zinc and tin.

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

Preference is given, among phosphines of formula (I), to those in which:

- Ar_1, Ar_2 and Ar_3 are phenyl groups,
- Y_1, Y_2 and Y_3 represent groups chosen from

. alkyl radicals having from 1 to 2 carbon atoms,

. alkoxy radicals having from 1 to 2 carbon atoms,

- M represents a cation chosen from the group consisting of

. H^+

. cations derived from Na, K, Ca and 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.

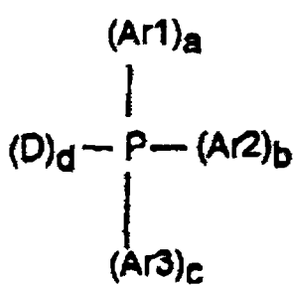
The more particularly preferred among these phosphines are the sodium, potassium, calcium, barium, ammonium, tetramethylammonium and tetraethylammonium salts of mono(sulphophenyl)diphenylphosphine, di(sulphophenyl)phenylphosphine and tri(sulphophenyl)-phosphine, in the formulae of which the SO_3 groups 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 metal or alkaline earth metal salts, ammonium salts or 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, 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-4-methylphenyl)(3-sulpho-4-methylphenyl)(3,5-disulpho-4-methylphenyl)-phosphine or (3-sulphophenyl)(3-sulpho-4-chlorophenyl)-(3,5-disulpho-4-chlorophenyl)phosphine.

It is very clearly possible to use a mixture of these phosphines. In particular, it is possible to use a mixture of mono-, di- and tri-meta-sulphonated phosphines.

Monodentate and bidentate phosphines of following general formulae (II) and (III) are also suitable for the invention:



(II)

in which:

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

  - alkyl or alkoxy radical having 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 proton, cations derived from alkali metals or alkaline earth metals, ammonium cations $-N(R)_4$ in the formula of which the R symbols, which are identical or different, represent a hydrogen atom or an alkyl radical having from 1 to 4 carbon atoms, and other cations derived from metals, the arylcarboxylic acid, arylsulphonic acid or arylphosphonic acid salts of which are soluble in water,

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

  -OH

- Ar3 represents an aryl group comprising one or more substituents, such as:

  - alkyl or alkoxy radical having 1 to 4 carbon atoms,
  - halogen atom,
  - hydrophilic group, such as:

-COOM or -PO_3M, M representing an inorganic or organic cationic residue chosen from proton, cations derived from alkali metals or alkaline earth metals, ammonium cations -$N(R)_4$ in the formula of which the R symbols, which are identical or different, represent a hydrogen atom or an alkyl radical having from 1 to 4 carbon atoms, and other cations derived from metals, the arylcarboxylic acid or arylphosphonic acid salts of which are soluble in water,

-$N(R)_4$, in the formula of which the R symbols, which are identical or different, represent a hydrogen atom or an alkyl radical having 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,
- b represents 0 or 1,
- c represents an integer from 0 to 3,
- D represents an alkyl group, a cycloalkyl group or an alkyl or cycloalkyl group comprising one or more substituents, such as:
  - alkoxy radical having 1 to 4 carbon atoms,
  - halogen atom,
  - hydrophilic group, such as:

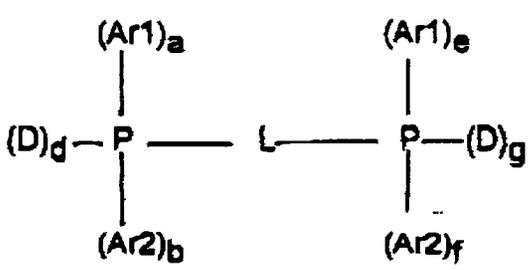
-COOM, -SO_3M or -PO_3M, M representing an inorganic or organic cationic residue chosen from proton, cations derived from alkali metals or alkaline

earth metals, ammonium cations $-N(R)_4$ in the formula of which the R symbols, which are identical or different, represent a hydrogen atom or an alkyl radical having from 1 to 4 carbon atoms, and other cations derived from metals, the arylcarboxylic acid, arylsulphonic acid or phosphonic acid salts of which are soluble in water,

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

-OH

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



(III)

in which:

- Ar1, Ar2 and D have the meanings indicated above for the 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 hydrocarbonaceous radical, such as an alkylene radical, a cycloalkylene radical, an arylene radical or a radical deriving from a heterocycle comprising 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 both phosphorus atoms or being bonded to one of the phosphorus atoms or to both via a linear or branched alkylene radical having from 1 to 4 carbon atoms, it being possible for the ring or rings which are optionally parts of the divalent radical L to comprise one or more substituents, such as [lacuna] alkyl group having 1 to 4 carbon atoms.

The expression "soluble in water" means a compound soluble to at least 0.01 g per litre of water.

Mention may in particular be made, as non-limiting examples of phosphines of general formula (II), of tris(hydroxymethyl)phosphine, tris(2-hydroxyethyl)phosphine, 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 sodium salt of tris(2-phosphonatoethyl)phosphine or bis(2-carboxyethyl)phenylphosphine.

Mention may in particular be made, as non-limiting examples of phosphines of general formula (III), of the sodium salt of 2,2'-bis[di(sulphonato-

phenyl)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 or the sodium salt of 2,2'-bis[di(sulphonatophenyl)phosphinomethyl]-1,1'-binaphthyl.

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

For the preparation of the others, reference may be made to the general or specific processes for the synthesis of phosphines described in the general literature, such as Houben-Weyl, Method der organischen Chemie, organische Phosphor Verbindungen [Methods of Organic Chemistry, Organic Phosphorus Compounds], Part 1 (1963).

Finally, for the preparation of water-soluble derivatives which have not been described, it is possible, starting with phosphines not comprising water-soluble substituents defined above, to introduce one or more of these hydrophilic substituents. Thus, sulphonate groups, for example, may be introduced by the reaction of SO_3 in sulphuric acid. Carboxylate, phosphonate and quaternary ammonium groups can likewise be introduced by applying the chemical methods known for this type of synthesis.

The organic compounds comprising at least one ethylenic bond which can be subjected to a hydrocyanation in the presence of a catalyst prepared

according to the process of the invention are diolefins, such as butadiene, isoprene, 1,5-hexadiene or 1,5-cyclooctadiene, aliphatic nitriles comprising ethylenic unsaturation, particularly linear pentenenitriles, such as 3-pentenenitrile or 4-pentenenitrile, monoolefins, such as styrene, methylstyrene, vinylnaphthalene, cyclohexene or methylcyclohexene, and mixtures of several of these compounds.

The pentenenitriles in particular can comprise amounts, generally minor amounts, of other compounds, such as 2-methyl-2-butenenitrile, 2-methyl-2-butenenitrile, 2-pentenenitrile, valeronitrile, adiponitrile, 2-methylglutaronitrile, 2-ethylsuccinonitrile or butadiene, originating, for example, from the prior hydrocyanation reaction of butadiene.

Not insignificant amounts of 2-methyl-3-butenenitrile and 2-methyl-2-butenenitrile are formed, with the linear pentenenitriles, during the hydrocyanation of butadiene.

The process for the preparation of a catalytic solution in accordance with the invention is, in a preferred embodiment, carried out before the introduction of the catalytic solution into the reaction region for hydrocyanation of an ethylenically unsaturated organic compound.

The hydrocyanation reaction is generally carried out at a temperature from 10°C to 200°C and preferably from 30°C to 120°C.

The process of the invention can be carried out continuously or batchwise.

The hydrogen cyanide employed can be prepared from metal cyanides, in particular sodium cyanide, or from cyanohydrins.

The hydrogen cyanide is introduced into the reactor in the gaseous form or in the liquid form. It can also be dissolved beforehand in an organic solvent.

Within the context of a batchwise implementation, it is possible, in practice, to charge to a reactor which has been purged beforehand using an inert gas (such as nitrogen or argon) either an aqueous solution comprising all or part of the various constituents, such as the water-soluble phosphine, the transition metal compound, the optional reducing agent and the optional solvent, or the said constituents separately. Generally, the reactor is then brought to the chosen temperature and then the compound to be hydrocyanated is introduced. The hydrogen cyanide is then itself introduced, preferably continuously and uniformly.

When the reaction (the progress of which can be monitored by quantitative determination of samples withdrawn) has finished, the reaction mixture is drawn off after cooling and the reaction products are isolated by separation by settling, optionally followed by extraction of the aqueous layer using an appropriate

solvent, such as, for example, the abovementioned water-immiscible solvents.

The aqueous catalytic solution can then be recycled in a fresh reaction for the hydrocyanation of organic compounds comprising at least one ethylenic double bond, after having been optionally treated by a regeneration process.

It is also possible to use the catalyst in combination with a Lewis acid.

The Lewis acid used as cocatalyst makes it possible in particular, in the case of the hydrocyanation of aliphatic nitriles comprising ethylenic unsaturation, to improve the linearity of the dinitriles obtained, that is to say the percentage of linear dinitrile with respect to all the dinitriles formed, and/or to increase the lifetime of the catalyst.

The term "Lewis acid" means in the present text, according to the usual definition, compounds which are electron-pair acceptors.

The Lewis acids cited in the work edited by G.A. Olah, "Friedel-Crafts and Related Reactions", Volume I, pages 191 to 197 (1963), can in particular be employed.

The Lewis acids which can be employed as cocatalysts in the present process are chosen from compounds of the elements from groups Ib, IIb, IIIa, IIIb, IVa, IVb, Va, Vb, VIb, VIIb and VIII of the

Periodic Classification of the Elements, in so far as the said compounds are at least partially soluble in water. These compounds are generally salts, in particular halides, preferably chlorides and bromides, sulphates, carboxylates and phosphates.

Mention may be made, as non-limiting examples of such Lewis acids, of zinc chloride, zinc bromide, zinc iodide, manganese chloride, manganese bromide, cadmium chloride, cadmium bromide, stannous chloride, stannous bromide, stannous sulphate, stannous tartrate, chlorides or bromides of rare earth metal elements, such as lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium and lutetium, cobalt chloride, ferrous chloride or yttrium chloride.

It is, of course, possible to employ mixtures of several Lewis acids.

It is also advantageous, if appropriate, to stabilize the Lewis acid in aqueous solution by the addition of an alkali metal or alkaline earth metal halide, such as lithium chloride, sodium chloride, calcium chloride or magnesium chloride, in particular. The alkali metal or alkaline earth metal halide/Lewis acid molar ratio varies very widely, for example from 0 to 100, it being possible for the specific ratio to be adjusted depending on the stability of the Lewis acid in water.

Preference is very particularly given, among the Lewis acids, to zinc chloride, zinc bromide, stannous chloride, stannous bromide, stannous chloride stabilized with lithium chloride, stannous chloride stabilized with sodium chloride and zinc chloride/stannous chloride mixtures.

The Lewis acid cocatalyst employed generally represents from 0.01 to 50 mol per mole of nickel compound and preferably from 1 to 10 mol per mole.

As for the implementation of the process which forms the basis of the invention, the catalytic solution used for the hydrocyanation in the presence of Lewis acid can be prepared before it is introduced into the reaction region, for example by addition, to the aqueous solution of the water-soluble phosphine, of the appropriate amount of nickel hydroxide, of the Lewis acid and optionally of the reducing agent.

It is also possible, under the conditions of the hydrocyanation process of the present invention, and in particular by carrying out the reaction in the presence of the catalyst described above comprising at least one water-soluble phosphine and at least one nickel compound, to isomerize 2-methyl-3-butenenitrile to pentenenitriles in the absence of hydrogen cyanide.

The 2-methyl-3-butenenitrile subjected to the isomerization according to the invention can be employed alone or as a mixture with other compounds.

Thus, it is possible to use 2-methyl-3-butenenitrile as a mixture with 2-methyl-2-butenenitrile, 4-pentenenitrile, 3-pentenenitrile, 2-pentenenitrile, butadiene, adiponitrile, 2-methylglutaroronitrile, 2-ethylsuccinonitrile or valeronitrile.

Thus, it is particularly advantageous to treat the reaction mixture originating from the hydrocyanation of butadiene with HCN in the presence of an aqueous solution of at least one water-soluble phosphine [lacuna] of at least one nickel compound, more preferably of a nickel compound in the 0 oxidation state, as defined above.

Within the context of this preferred alternative form, as the catalytic system is already present for the hydrocyanation reaction of butadiene, it is sufficient to stop any introduction of hydrogen cyanide in order to allow the isomerization reaction to take place.

It is possible, if appropriate, in this alternative form, to gently flush the reactor using an inert gas, such as nitrogen or argon, for example, in order to drive off the hydrocyanic acid which might still be present.

The isomerization reaction is generally carried out at a temperature of from 10°C to 200°C and preferably from 60°C to 120°C.

In the preferred case of an isomerization immediately following the hydrocyanation reaction of butadiene, it will be advantageous to carry out the isomerization at the temperature at which the hydrocyanation has been carried out.

As for the process for the hydrocyanation of compounds comprising ethylenic unsaturation, the catalytic solution used for the isomerization can be prepared before it is introduced into the reaction region, for example by addition, to the aqueous solution of a water-soluble phosphine, of the appropriate amount of nickel compound and optionally of the reducing agent. It is also possible to prepare the catalytic solution "in situ" by simple mixing of these various constituents. The amount of nickel compound and the amount of water-soluble phosphine are the same as for the hydrocyanation reaction. This catalyst can also be prepared by the process of the invention before it is introduced into the reaction region.

Although the isomerization reaction is generally carried out without a third solvent, it can be advantageous to add an inert water-immiscible organic solvent which can be that of the subsequent extraction. This is in particular the case when such a solvent has been employed in the hydrocyanation reaction of butadiene which has been used to prepare the mixture subjected to the isomerization reaction.

Such solvents can be chosen from those which have been mentioned above for the hydrocyanation.

At the end of the reaction, it is very easy to separate the catalyst from the isomerization reaction products, as has been indicated for the hydrocyanation, and to recycle it, if appropriate, in one of the hydrocyanation reactions described above or in a fresh isomerization reaction, after treatment of the aqueous phase and/or of the solid phase according to the process of the invention with a hydrogen cyanide in order to dissolve the said solid phase.

Other advantages and details of the invention which become more clearly apparent in the light of the examples given below solely by way of indication.

EXAMPLE 1

150 cm^3 of a 1 mol/litre aqueous nickel chloride solution are charged to a 1 litre Erlenmeyer flask equipped with a magnetic bar. 170 cm^3 of a 2 mol/litre aqueous sodium hydroxide solution are run in, with stirring at room temperature, over a period of 3 hours and then the mixture is kept stirred for 1 hour. The system is subsequently left standing for the time necessary for the nickel hydroxide precipitated to settle out and for the supernatant aqueous solution to become clear. The nickel hydroxide precipitate is then washed. To do this, as much as possible of the supernatant aqueous phase is siphoned off, 200 ml of distilled water are added, stirring of

the system is resumed for 1 hour and then the system is again left standing for the time necessary for the separation by settling of the solid phase; this series of operations is repeated until a supernatant aqueous phase of neutral pH is obtained. The solid phase is then recovered by filtration through a sintered glass of porosity 4. The said filtration is carried out so as to obtain the nickel hydroxide in the form of a paste which will be subsequently described as freshly precipitated and wet nickel hydroxide. Quantitative determination of the Ni on 3 withdrawn samples of this wet paste stored in a closed container results in a mean assay by weight of 25.2 wgt % of Ni.

57.5 g of a 30 wgt % solution of sodium salt of trisulphonated triphenylphosphine (TSTPP) in water are charged to a 150 cm^3 glass reactor purged with argon and equipped with an auto-suction turbine. This solution is degassed. 1.445 g of freshly precipitated and wet nickel hydroxide obtained above are subsequently introduced. With stirring (1200 revolutions/minute) and at room temperature, 0.640 ml of hydrocyanic acid is injected into the reactor head space, with a constant flow rate and over a duration of one hour, via a syringe thermostatically controlled at -10°C. During the injection of the HCN, the solution rapidly becomes orangey and then red. After injection, the mixture is kept stirred for 3 hours at 80°C and then cooled to room temperature,

where it is kept stirred for 12 hour. After flushing the head space of the reactor with argon for approximately 1 hour, a homogeneous and clear solution with a dark red colouring is recovered. Quantitative determination of the Ni on a withdrawn sample filtered by means of a Millipore Millex-HV® filter (Hydrophilic PVDF, 0.45 μm) gives the following result: 106 mmol/kg.

The solution thus recovered can be used as catalytic solution after having been subjected to a stage of electrochemical reduction after addition of nickel in the (0) oxidation state.

EXAMPLE 2

57.8 g of a 30 wgt % solution of sodium salt of trisulphonated triphenylphosphine (TSTPP) in water are charged to a 150 cm^3 glass reactor purged with argon and equipped with an auto-suction turbine. This solution is degassed. 606 mg of a commercial nickel hydroxide (Aldrich) comprising approximately 61 wgt % of Ni are subsequently introduced. With stirring (1200 revolutions/minute) and at room temperature, 0.640 ml of hydrocyanic acid is injected into the reactor head space, with a constant flow rate and over a duration of one hour, via a syringe thermostatically controlled at -10°C. During the injection of the HCN, the solution rapidly becomes orangey and then red. After injection, the mixture is kept stirred for 3 hours at 80°C and then cooled to room temperature, where it is kept stirred for 12 hours. After flushing

the head space of the reactor with argon for approximately 1 hour, a homogeneous and clear solution with a dark red colouring is recovered. Quantitative determination of the Ni on a withdrawn sample filtered by means of a Millipore Millex-HV® filter (Hydrophilic PVDF, 0.45 μm) gives the following result: 103 mmol/kg.

The solution thus recovered can be used as catalytic solution after having been subjected to a stage of electrochemical reduction after addition of nickel in the (0) oxidation state.

CLAIMS

1. Process for the manufacture of a catalyst for the hydrocyanation of [lacuna] organic compound composed of an aqueous solution of at least one water-soluble phosphine and of nickel, characterized in that it consists in bringing an aqueous solution of at least one water-soluble phosphine and a nickel hydroxide into contact, in adding hydrogen cyanide or a compound which generates hydrogen cyanide to the mixture, in keeping the mixture stirred until the nickel has at least partially dissolved and in subjecting the said mixture to a reduction of at least a portion of nickel with an oxidation state of greater than zero to the zero oxidation state.

2. Process according to claim 1, characterized in that the solution is kept stirred at a temperature of less than 100°C, preferably between 20°C and 80°C.

3. Process according to claim 1 or 2, characterized in that, before the stage of reduction of the nickel, nickel in the zero oxidation state is added to the mixture.

4. Process according to one of the preceding claims, characterized in that the amount of hydrogen cyanide added is at least equal to the

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5. Process according to claim 4, characterized in that the amount of hydrogen cyanide added is greater by 30% to 200% than the stoichiometric amount.

6. Process according to one of the preceding claims, characterized in that the amount of water-soluble phosphine, expressed as number of moles per 1 mol of nickel, is between 0.5 and 2000, preferably between 2 and 300.

7. Process according to one of the preceding claims, characterized in that the reduction of the nickel is carried out by treatment with gaseous hydrogen, electrochemical reduction or reduction by inorganic or organic reducing agents.

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