



159159

WO 03/000651

1

PCT/FR02/02023

**METHOD FOR THE HEMIHYDROGENATION OF DINITRILES IN ORDER
TO FORM AMINONITRILES**

The present invention relates to the
hemihydrogenation of dinitriles to corresponding
5 aminonitriles.

The hydrogenation of dinitriles is generally
carried out in order to prepare the corresponding
diamines; thus, particularly, the hydrogenation of
adiponitrile results in hexamethylenediamine, itself
10 one of the two base compounds for the preparation of
polyamide-6,6.

However, it can sometimes prove necessary to
prepare not the diamine but the intermediate
aminonitrile. This is the case, for example but not
15 limitingly, in the hemihydrogenation of adiponitrile to
aminocapronitrile, which is capable of subsequently
being converted to caprolactam, the base compound for
polyamide-6, or directly to polyamide-6.

Thus, Patent US 4 389 348 discloses a process
20 for the hydrogenation of dinitrile to ω -aminonitrile by
hydrogen in ammonia and aprotic solvent medium in the
presence of rhodium deposited on a basic support.

Patent US 5 151 543 discloses a process for
the partial hydrogenation of dinitriles to
25 aminonitriles in a solvent in molar excess of at least
2/1 with respect to the dinitrile, comprising liquid
ammonia or an alkanol comprising an inorganic base



G00002

which is soluble in the said alkanol, in the presence of a catalyst of Raney cobalt or nickel type.

Patent US 5 981 790 relates to a process for the partial hydrogenation of dinitriles to
5 aminonitriles in the presence of a catalyst based on Raney nickel or Raney cobalt in the presence of at least 0.5% by weight of water in the reaction medium comprising the products to be hydrogenated and the hydrogenated compounds. The catalyst is used in
10 conjunction with a base.

These various processes make it possible to jointly produce an aminonitrile and a diamine in relatively high ratios and with relatively high production of by-products which are difficult to
15 separate. Studies are continually being carried out to modify this ratio in order in particular to increase the production of aminonitrile at the expense of that of diamine and also to reduce the formation of by-products.

20 Thus, Patent Application WO 00/64862 discloses a process for the partial hydrogenation of a dinitrile for the production of aminonitriles in the presence of a hydrogenation catalyst, of an alkanol or a liquid ammonia solvent and of a compound which makes
25 it possible to improve the selectivity of the reaction for aminonitriles. However, the production of undesirable by-products remains high.

One of the objects of the present invention

is to provide a novel process for the selective hydrogenation of a single nitrile functional group of a dinitrile (referred to in the present text as hemihydrogenation), so as to prepare predominantly the
5 corresponding aminonitrile and only to a minor extent the diamine, with minimal formation of by-products.

More specifically, the invention relates to a process for the hemihydrogenation of aliphatic dinitriles to corresponding aminonitriles using
10 hydrogen in the presence of a hydrogenation catalyst, for example based on nickel, on cobalt, on Raney nickel or on Raney cobalt, optionally comprising a doping element chosen from the elements from Groups 3 to 12 of the Periodic Table of the Elements according to the
15 IUPAC nomenclature published in the Handbook of Chemistry and Physics, 80th edition, 1999-2000, and of a strong inorganic base deriving from an alkali metal or alkaline earth metal or from an ammonium. The starting hydrogenation medium comprises water at a
20 content of at least 0.5% by weight with respect to all of the liquid compounds of the said medium, diamine and/or aminonitrile capable of being formed from the dinitrile to be hydrogenated, and unconverted dinitrile, the content by weight of the combination of
25 these three compounds in the medium being between 80% and 99.5%.

According to the invention, the hemihydrogenation reaction is carried out in the

presence of at least one additive which increases the selectivity for aminonitrile with respect to that obtained with the additive-free system described above, while maintaining the overall selectivity for
5 aminonitrile and diamine at a level at least substantially equivalent to that obtained without the additive.

The term "selectivity for a product" is understood to mean the yield of this product obtained,
10 calculated with respect to the amount of dinitrile converted at the end of the reaction.

This additive is a compound chosen from the group consisting of:

- a compound comprising at least one cyanide
15 radical not bonded to a carbon atom,
- an organic isonitrile compound,
- a tetraalkylammonium or tetraalkyl-phosphonium hydroxide or fluoride compound,
- a complex compound from coordination
20 between at least one metal atom and at least carbonyl radicals,
- an alkali metal or alkaline earth metal fluoride compound.

Mention may be made, as compounds comprising
25 at least one cyanide radical not bonded to a carbon atom, of inorganic cyanides, organic/inorganic cyanides, cyanide complexes or salts, such as hydrogen cyanide, lithium, sodium, potassium or copper cyanide,

the cyanide complexes $K_3[Fe(CN)_6]$, $K_4[Fe(CN)_4]$,
 $K_3[Co(CN)_6]$, $K_2[Pt(CN)_6]$ or $K_4[Ru(CN)_6]$, or ammonium or
 alkali metal thiocyanides. Mention may be made, as
 organic/inorganic cyanide, of tetraalkylammonium
 5 cyanides, such as tetrabutylammonium cyanide,
 tetramethylammonium thiocyanide or tetrapropylammonium
 thiocyanide.

Mention may be made, as organic isonitrile
 compounds suitable for the invention, of tert-
 10 octylisonitrile, tert-butylisonitrile,
 n-butylisonitrile, isopropylisonitrile,
 benzylisonitrile, ethylisonitrile, methylisonitrile and
 amylisonitrile.

Mention may be made, as coordination complex
 15 compounds, of the complexes comprising, as complexing
 compounds, organic compounds comprising carbonyl,
 phosphine, arsine or mercapto functional groups
 connected to the metal. Mention may be made, as
 suitable metals, of in particular the metals from
 20 Groups 7, 8, 9 and 10 of the Periodic Table of the
 Elements mentioned above, such as, for example, iron,
 ruthenium, cobalt, osmium, rhenium, iridium or rhodium.

Mention may be made, as organic
 tetraalkylonium hydroxide or fluoride compounds, of
 25 tetraalkylammoniums or tetraalkylphosphoniums
 comprising hydroxyl groups or fluorine atoms connected
 to the ammonium or phosphonium groups. The alkyl
 radicals are preferably hydrocarbonaceous groups

comprising from 1 to 8 carbon atoms. These radicals can be linear or branched. By way of examples, tetramethylammonium, tetraethylammonium, tetrapropylammonium, tetrabutylammonium and
5 tetrabutylphosphonium are suitable for the invention.

According to a preferred characteristic of the invention, the ratio by weight of the selectivating agent with respect to the weight of catalytic element, expressed as weight of metal, such as nickel, is
10 between 0.001:1 and 2:1, advantageously between 0.005:1 and 1:1. This ratio varies according to the nature of the selectivating agent.

The process of the invention makes it possible to obtain, for degrees of conversion of the
15 dinitrile of greater than 70%, a selectivity for aminonitrile of greater than 65% and an overall selectivity for aminonitrile and diamine of greater than 90%.

The aliphatic dinitriles which can be
20 employed in the process of the invention are more particularly the dinitriles of general formula (I):



in which R represents a linear or branched alkylene or alkenylene group having from 1 to 12 carbon atoms.

25 Use is preferably made, in the process of the invention, of the dinitriles of formula (I) in which R represents a linear or branched alkylene radical having from 2 to 6 carbon atoms.

Mention may in particular be made, as examples of such dinitriles, of adiponitrile (AdN), methylglutaronitrile, ethylsuccinonitrile, malononitrile, succinonitrile, glutaronitrile and their
5 mixtures, in particular the mixtures of adiponitrile and/or of methylglutaronitrile and/or of ethylsuccinonitrile capable of originating from the same process for the synthesis of adiponitrile.

In practice, the case where $R = (CH_2)_4$ will be
10 the commonest, as this corresponds to the use of adiponitrile (AdN) in the present process.

The strong inorganic base is generally composed of alkali metal or alkaline earth metal or ammonium hydroxides, carbonates and alkoxides. It is
15 preferably chosen from alkali metal hydroxides, carbonates and alkoxides.

Preferably, the strong inorganic base employed is chosen from the following compounds: LiOH, NaOH, KOH, RbOH, CsOH and their mixtures.

20 In practice, NaOH and KOH are generally used, although RbOH and CsOH can give very good results.

Water is usually present in the reaction medium in an amount of less than or equal to 20% by weight. Preferably, the content of water in the
25 reaction medium is between 2% and 15% by weight with respect to the combined liquid constituents of the said medium.

The overall concentration of targeted

aminonitrile and/or of the corresponding diamine and of the unconverted dinitrile in the reaction medium is generally between 85% and 99% by weight with respect to the combined liquids included in the said reaction

5 medium.

The amount of strong inorganic base is advantageously greater than or equal to 0.05 mol/kg of catalyst. Preferably, it is between 0.1 mol and 3 mol per kg of catalyst and more preferably still between
10 0.15 and 2 mol/kg of catalyst.

The catalyst used in the process can be nickel, cobalt, a Raney nickel or a Raney cobalt. The latter Raney metals comprise, in addition to the nickel or the cobalt and the residual amounts of the metal
15 removed from the starting alloy during the preparation of the catalyst, that is to say generally aluminium, one or more other elements, often referred to as dopants, such as, for example, chromium, titanium, molybdenum, tungsten, iron, zinc, copper, rhodium,
20 iridium, cobalt and nickel. Among these doping elements, chromium and/or iron and/or titanium are regarded as the most advantageous. These dopants usually represent, as weight by weight of nickel, from 0% to 10% and preferably from 0% to 5%. These dopants
25 are also used with the catalysts based on nickel and/or on cobalt.

The amount of catalyst employed can vary very widely according in particular to the method of

operation adopted or the reaction conditions chosen. By way of indication, use may be made of 0.5% to 50% by weight of catalyst with respect to the total weight of the reaction medium and generally of 1% to 35%.

5 According to a preferred embodiment of the invention, the catalyst is preconditioned before it is introduced into the hemihydrogenation medium. This preconditioning is advantageously carried out according to the process disclosed in the unpublished French
10 Patent Application No. 00 02997. This process consists briefly in mixing the hydrogenation catalyst with a predetermined amount of strong inorganic base and a solvent in which the strong inorganic base is not very soluble. According to the invention, the medium
15 comprising the catalyst thus conditioned is fed to the hydrogenation reactor, the hydrogenation reaction being carried out according to the usual conditions and procedures already disclosed in the literature.

 The selectivating agent can be added to the
20 reaction medium separately from the catalyst. In a preferred embodiment, the selectivating agent is added to the catalyst before the introduction of the latter into the reaction medium, for example at the stage of conditioning the latter.

25 The optimum for the selectivity for aminonitrile, at a constant degree of conversion of the dinitrile, depends on the nature and on the content of dopant, on the amount of water in the reaction medium,

on the temperature and on the nature and content of base and/or selectivating agent.

The process of the invention is generally carried out at a reaction temperature of less than or
5 equal to 150°C, preferably of less than or equal to 120°C and more preferably still of less than or equal to 100°C.

In practical terms, this temperature is between ambient temperature (approximately 20°C) and
10 100°C.

Prior to, simultaneously with or subsequent to the heating, the reaction chamber is brought to the appropriate hydrogen pressure, that is to say, in practice, between 1 bar (0.10 MPa) and 100 bar (10 MPa)
15 and preferably between 5 bar (0.5 MPa) and 50 bar (5 MPa).

The duration of the reaction can vary as a function of the reaction conditions and of the catalyst.

20 In a batchwise method of operation, it can vary from a few minutes to several hours.

It should be noted that a person skilled in the art can vary the order of occurrence of the stages of the process according to the invention, according to
25 the operating conditions.

The other conditions which govern the hydrogenation (continuous or batchwise) in accordance with the invention relate to conventional technical

arrangements known per se.

The examples which follow illustrate the invention.

In these examples, the following
5 abbreviations are used;

- AdN = adiponitrile
- ACN = aminocapronitrile
- HMD = hexamethylenediamine
- DC = degree of conversion
- 10 - CY = selectivity with respect to the
converted starting substrate (in this instance with
respect to the AdN).

COMPARATIVE EXAMPLE 1

15 The following are charged to a 100 ml
stainless steel reactor equipped with a stirrer of
self-suction type, with means for introducing the
reactants and hydrogen and with a temperature
regulation system:

- | | | |
|----|------------------------------------|--------------|
| 20 | - hexamethylenediamine | 24 g |
| | - water | 5.3 g |
| | - KOH | 0.33 mmol |
| | - Raney Ni (comprising 1.7% of Cr) | 0.65 g of Ni |

In this example, there is 0.5 mol KOH/kg Ni.

25 After having purged the reactor with nitrogen
and then with hydrogen, the pressure is adjusted to 2
MPa of hydrogen. The reaction mixture is heated to
50°C.

24 g of adiponitrile are subsequently introduced instantaneously via a dropping funnel pressurized to 2.5 MPa by a pressure reducer placed on a hydrogen supply at 5 MPa. The time is taken as equal
 5 to 0 at this point. The progress of the reaction is monitored by the consumption of hydrogen in the supply, the pressure in the reactor being kept constant at 2.5 MPa, and by the analysis by gas chromatography (GC) of a withdrawn sample of the reaction mixture. When the
 10 optimum aminocapronitrile yield is reached, the reaction is halted by halting the stirring, cooling the reaction mixture and then depressurizing.

The following results are obtained:

	- duration of the reaction	33 min
15	- DC of the AdN:	79.6%
	- CY for ACN:	70.1%
	- CY for HMD	29.5%
	- CY for various other products:	0.4%

EXAMPLE 2

20 Example 1 is repeated but charging the following reactants:

	- hexamethylenediamine	24 g
	- water	5.3 g
	- KOH	0.18 mmol
25	- Raney Ni (comprising 1.7% of Cr) 0.65 g of Ni	
	- Selectivating agent $(C_2H_5)_4N^+F^- \cdot H_2O$	1.09 mmol (0.162 g)

In this example, there are 0.3 mol KOH/kg Ni and a selectivating agent/nickel ratio equal to 0.25:1.

The results obtained are as follows:

	- duration of the reaction	63 min
	- DC of the AdN:	83.8%
	- CY for ACN:	81.6%
5	- CY for HMD	17.8%
	- CY for various other products:	0.6%

This test shows the improvement in the selectivity for ACN and a stability in the selectivity for by-products.

CLAIMS

1. Process for the hemihydrogenation of dinitriles to corresponding aminonitriles using hydrogen in the presence of a catalyst based on nickel, on cobalt, on Raney nickel or on Raney cobalt, optionally comprising a doping element chosen from the elements from Groups 3 to 12 of the Periodic Table of the Elements according to the IUPAC nomenclature published in the Handbook of Chemistry and Physics, 80th edition, 1999-2000, and of a strong inorganic base deriving from an alkali metal or alkaline earth metal or ammonia, the starting hydrogenation medium comprising water at a concentration by weight of at least 0.5% by weight with respect to all of the liquid compounds of the said medium, diamine and/or aminonitrile capable of being formed from the dinitrile to be hydrogenated, and unconverted dinitrile, the concentration by weight of the combination of these three compounds being from 80% to 99.5%, characterized in that the hemihydrogenation reaction is carried out in the presence of at least one selectivating agent chosen from the group consisting of:
- a compound comprising at least one cyanide radical not bonded to a carbon atom,
 - an organic isonitrile compound,
 - a tetraalkylammonium or tetraalkylphosphonium hydroxide or fluoride compound,

- a complex compound from coordination between at least one metal atom and at least carbonyl radicals,
- an alkali metal or alkaline earth metal fluoride compound.

5 2. Process according to Claim 1, characterized in that the inorganic base is chosen from alkali metal, alkaline earth metal or ammonium hydroxides, carbonates and alkoxides.

10 3. Process according to either of Claims 1 and 2, characterized in that the strong inorganic base employed is chosen from the following compounds: LiOH, NaOH, KOH, RbOH, CsOH and their mixtures.

15 4. Process according to one of Claims 1 to 3, characterized in that the amount of inorganic base present in the reaction medium is greater than or equal to 0.05 mol per kilogram of catalyst.

 5. Process according to one of Claims 1 to 4, characterized in that aliphatic dinitriles are the dinitriles of general formula (I):



in which R represents a linear or branched alkylene or alkenylene group having from 1 to 12 carbon atoms and preferably R represents a linear or branched alkylene radical having from 2 to 6 carbon atoms.

25 6. Process according to one of Claims 1 to 5, characterized in that water is present in the reaction medium in an amount of less than or equal to

20% and preferably of between 2% and 15% by weight with respect to the combined liquid constituents of the said medium.

7. Process according to one of Claims 1
5 to 6, characterized in that the concentration of the targeted aminonitrile and/or of the corresponding diamine and of the unconverted dinitrile in the reaction medium is between 85% and 99% by weight with respect to the combined liquids constituting the said
10 reaction medium.

8. Process according to one of Claims 1
to 7, characterized in that the catalyst used is chosen from a Raney nickel, a Raney cobalt, a Raney nickel and a Raney cobalt comprising one or more other doping
15 elements, such as chromium, titanium, molybdenum, tungsten, iron, zinc, copper, rhodium, iridium, cobalt or nickel.

9. Process according to one of Claims 1
to 8, characterized in that the catalyst used is chosen
20 from a Raney nickel comprising at least one doping element chosen from chromium and/or iron and/or titanium.

10. Process according to one of Claims 1
to 9, characterized in that the catalyst used is chosen
25 from a Raney nickel comprising at least one doping element in a proportion of 0% to 10%.

11. Process according to one of Claims 1

to 10, characterized in that the catalyst employed represents from 0.5% to 50% by weight with respect to the total weight of the reaction medium.

12. Process according to one of Claims 1
5 to 11, characterized in that it is carried out at a reaction temperature of less than or equal to 150°C.

13. Process according to one of Claims 1
to 12, characterized in that it is carried out at a hydrogen pressure of between 1 bar (0.10 MPa) and
10 100 bar (10 MPa).

14. Process according to one of the preceding claims, characterized in that the ratio by weight of the selectivating agent to the catalyst, expressed as weight of catalytic metal element, is
15 between 0.001:1 and 2:1.

15. Process according to one of the preceding claims, characterized in that the selectivating agent is a compound comprising at least one cyanide radical not bonded to a carbon atom chosen
20 from the group consisting of hydrogen cyanide, lithium, sodium, potassium or copper cyanide, the cyanide complexes $K_3[Fe(CN)_6]$, $K_4[Fe(CN)_4]$, $K_3[Co(CN)_6]$, $K_2[Pt(CN)_6]$ and $K_4[Ru(CN)_6]$, ammonium or alkali metal thiocyanides, tetrabutylammonium cyanide,
25 tetramethylammonium thiocyanide and tetrapropylammonium thiocyanide.

16. Process according to one of Claims 1

to 14, characterized in that the selectivating agent is an organic isonitrile compound chosen from the group consisting of tert-octylisonitrile, tert-butyl-isonitrile, n-butylisonitrile, isopropylisonitrile, 5 benzylisonitrile, ethylisonitrile, methylisonitrile and amylisonitrile.

17. Process according to one of Claims 1 to 14, characterized in that the selectivating agent is a tetraalkylammonium or tetraalkylphosphonium hydroxide 10 or fluoride compound chosen from the group consisting of tetramethylammonium, tetraethylammonium, tetrapropylammonium, tetrabutylammonium and tetrabutylphosphonium.

18. Process according to one of Claims 1 15 to 14, characterized in that the selectivating agent is a complex compound from coordination between at least one metal atom and at least carbonyl radicals chosen from the group consisting of organic compounds comprising carbonyl, phosphine, arsine or mercapto 20 functional groups connected to a metal chosen from the group consisting of iron, ruthenium, cobalt, osmium, rhenium, iridium and rhodium.