

PROCESS FOR THE PARTIAL HYDROGENATION OF DINITRILES

The present invention relates to the hydrogenation of a nitrile function of a dinitrile, in order to obtain the corresponding aminonitrile.

Generally, the hydrogenation of dinitriles is carried out to prepare the corresponding diamines; thus, particularly, the hydrogenation of adiponitrile leads to hexamethylenediamine, which is one of the two base compounds in the preparation of polyamide 6,6.

However, it is occasionally found to be necessary to prepare not the diamine, but the intermediate aminonitrile. This is the case, for example, but in a non-limiting manner, for the partial hydrogenation of adiponitrile into aminocapronitrile, which compound may then be converted into caprolactam, a base product of polyamide 6, or directly into polyamide 6.

Thus, patent US 4 389 348 discloses a process for the hydrogenation of dinitrile into ω -aminonitrile, with hydrogen, in an aprotic solvent medium and ammonia and in the presence of rhodium deposited on a basic support.

Patent US 5 151 543 discloses a process for the partial hydrogenation of dinitriles into aminonitriles in a solvent in a molar excess of at least 2/1 relative to the dinitrile, comprising liquid ammonia or

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

Patent application WO-A-96/18603 discloses a
5 process for the partial hydrogenation of aliphatic dinitriles into the corresponding aminonitriles, using hydrogen and in the presence of a catalyst chosen from Raney nickel and Raney cobalt, said Raney nickel or Raney cobalt preferably comprising a dopant element
10 such as chromium, iron, titanium or zinc, and a strong mineral base derived from an alkali metal or alkaline-earth metal, the initial hydrogenation medium comprising water in a proportion of at least 0.5% by weight relative to the total amount of liquid compounds
15 in said medium, diamine and/or aminonitrile which may be formed from the dinitrile to be hydrogenated, and also unconverted dinitrile in a proportion for these three compounds together of from 80% to 99.5% by weight relative to the total amount of liquid compounds in
20 said medium.

As emerges from the preceding analysis, the processes for the partial hydrogenation of dinitriles into aminonitriles usually involve a catalyst of Raney nickel or Raney cobalt type, preferably doped by the
25 presence of one or more other elements.

It has now been found that the presence of copper and/or silver and/or gold in Raney nickel or

Raney cobalt gives, unexpectedly, excellent results in terms of selectivity toward aminonitrile.

The selective hydrogenation of only one nitrile function of a dinitrile is by nature very
5 difficult to achieve, since the aminonitrile is the intermediate compound of the complete hydrogenation into diamine. This intermediate thus enters into competition with the starting dinitrile as a compound which may be hydrogenated. Consequently, the overall
10 distribution between aminonitrile and diamine obtained results from the ratio of the kinetic hydrogenation coefficients for the first nitrile function (k_1) and for the second nitrile function (k_2).

It has been found that the use of a Raney
15 cobalt or Raney nickel doped with at least one metal chosen from copper, silver and gold makes it possible to improve the ratio k_1/k_2 of these kinetic coefficients and thus the selectivity of the hydrogenation toward aminonitrile relative to the
20 complete hydrogenation to diamine, in comparison with the use of a Raney catalyst doped with the elements most frequently used such as, for example, chromium, iron or titanium.

The present invention relates to the
25 preferential hydrogenation of only one nitrile function of a dinitrile (also referred to in the present text as partial hydrogenation) so as to prepare predominantly

the corresponding aminonitrile and, in only a minor amount, the diamine.

More specifically, the invention relates to a process for the partial hydrogenation of a dinitrile
5 into the corresponding aminonitrile, in a liquid medium, characterized in that the process is performed in the presence of a Raney nickel or a Raney cobalt catalyst containing at least one metal chosen from copper, silver and gold and in the presence of an
10 alkali metal hydroxide or alkaline-earth metal hydroxide.

Raney nickels are catalysts that are widely used in industry for hydrogenation reactions. They are prepared by alkaline attack of aluminum-rich Al/Ni or
15 Al/Co alloys containing, as may be the case, other metals, generally referred to as dopants or promoters. The catalyst consists of aggregates of nickel or cobalt crystallites with a large specific surface area and a variable residual aluminum concentration.

20 This catalyst generally comprises an aluminum content, expressed by weight relative to the weight of the nickel or cobalt, of less than or equal to 10%.

Advantageously, the weight ratio (Cu + Ag + Au)/Ni or (Cu + Ag + Au)/Co of the catalyst used in the
25 present invention is between 0.05% and 10% and preferably between 0.1% and 5%.

With copper and/or silver and/or gold, the catalyst used in the process may contain amounts, generally smaller amounts, of one or more other elements also grouped under the generic term dopant or
5 promoter.

These additional dopants which may be present are preferably chosen from the following elements: titanium, chromium, iron, zirconium, vanadium, manganese, bismuth, tantalum, rhodium, ruthenium,
10 iridium, platinum, palladium, niobium, hafnium and rare-earth elements. When the catalyst used is Raney nickel, cobalt may also be present as additional dopant.

Similarly, when the catalyst used is Raney
15 cobalt, nickel may also be present as additional dopant. Titanium, chromium, iron and zirconium are particularly preferred.

The amount of dopant other than copper, silver and gold which the catalyst may contain
20 generally represents from 0% to 5% by weight relative to the weight of the nickel or cobalt.

Among the Raney-type catalysts used, the Raney nickel as defined above will be preferred.

The catalyst used in the present invention
25 may also be used in the form of grains.

The process of the invention applies, more particularly but in a non-limiting manner, to the dinitrile substrates of formula (I):



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

Dinitriles of formula (I) in which R represents a linear or branched alkylene radical containing from 1 to 6 carbon atoms are preferably used
10 in the process of the present invention.

As examples of such dinitriles, mention may be made in particular of adiponitrile, methylglutaronitrile, ethylsuccinonitrile, malono-
nitrile, succinonitrile and glutaronitrile and also
15 mixtures of several of these dinitriles, in particular the mixtures adiponitrile, methylglutaronitrile, ethylsuccinonitrile which are derived from the same adiponitrile synthesis process.

The concentration of dinitriles in the
20 reaction medium, in particular of adiponitrile, may vary within a wide range depending on the mode of implementation of the invention, continuous or batch-wise operation, initial load or gradual introduction, for example. In the preferred context of an industrial
25 process in continuous operation, the average concentration of dinitriles is usually between 10% and 45% on a weight for weight basis.

The alkali metal hydroxides LiOH, NaOH, KOH, RbOH and CsOH and mixtures thereof are preferably used.

In practice, NaOH and KOH is preferentially used, for a good performance/price compromise.

5 The hydrogenation reaction medium is liquid. It contains at least one solvent capable of at least partially dissolving the dinitrile substrate to be hydrogenated.

 According to one advantageous embodiment of
10 the process according to the invention, a liquid reaction medium which is at least partially aqueous is used. The water generally represents an amount of from 1% to 25% by weight relative to the weight of the total reaction medium. Preferably, the water content of the
15 reaction medium is between 1% and 15% on a weight for weight basis.

 In addition to or in replacement for the water, at least one other solvent, generally of alcohol type, may be provided. The alcohols which are more
20 particularly suitable are, for example, methanol, ethanol, propanol, isopropanol and butanol and mixtures of said compounds.

 When it is used with water, the alcoholic solvent represents from two to four parts by weight per
25 one part by weight of water and preferably three parts per one part of water.

According to another preferred characteristic of the invention, the initial hydrogenation medium comprises, in particular in the context of a continuous implementation of the process, diamine which is
5 coproduced by the hydrogenation. This is, for example, hexamethylenediamine when the dinitrile substrate is adiponitrile.

The average concentration of aminonitrile and/or of diamine in the reaction medium in a
10 continuous regime is advantageously between 35% and 90% by weight relative to the total weight of the solvent included in said reaction medium and is more preferably between 45% and 89% on a weight for weight basis.

The reaction medium may comprise liquid or
15 dissolved ammonia. Generally, the ammonia represents from 0% to 50% by weight of the reaction medium and preferably from 0% to 15%.

The amount of alkali metal hydroxide or alkaline-earth metal hydroxide in the reaction medium
20 varies as a function of the nature of said reaction medium.

Since the reaction medium contains only water, the reaction products and optionally ammonia, as liquid solvent medium, the amount of alkali metal
25 hydroxide or alkaline-earth metal hydroxide is advantageously greater than or equal to 0.1 mol/kg of catalyst, preferably between 0.1 and 2 mol/kg of

catalyst and even more preferably between 0.2 and 1.0 mol/kg of catalyst.

When the reaction medium also comprises an alcohol, the amount of alkali metal hydroxide or
5 alkaline-earth metal hydroxide is greater than or equal to 0.05 mol/kg of catalyst, preferably between 0.1 and 10.0 mol/kg and even more preferably between 1.0 and 8.0 mol/kg.

The temperature at which the partial
10 hydrogenation process is carried out is generally less than or equal to 150°C, preferably less than or equal to 120°C and even more preferably less than or equal to 100°C.

In concrete terms, this temperature is
15 usually between room temperature (about 20°C) and 100°C.

Prior to, simultaneously with or subsequent to the heating, the reaction chamber is brought to a suitable hydrogen pressure, that is to say, in
20 practice, between 0.10 and 10 MPa.

The reaction time is variable as a function of the reaction conditions and of the catalyst.

In a batchwise operating mode, it may range from a few minutes to several hours.

25 In a continuous operating mode, which is preferred for the process according to the invention, the time is obviously not a settable parameter.

It should be noted that a person skilled in the art can modify the order of the steps of the process according to the invention, depending on the operating conditions. The order given above corresponds
5 merely to a preferred, but non-limiting, form of the process according to the invention.

The other conditions which govern the hydrogenation (in continuous or batchwise mode) in accordance with the invention consist of technical
10 arrangements that are conventional and known per se.

By means of all the advantageous arrangements mentioned above, the process of the invention makes it possible to hydrogenate dinitrile substrates into corresponding aminonitriles, selectively, rapidly,
15 conveniently and economically.

The partial hydrogenation of adiponitrile gives 6-aminocapronitrile, which compound is easy to convert by cyclizing hydrolysis into caprolactam, a starting material in the synthesis of polyamide 6.

20 The invention is illustrated by the examples which follow for the partial hydrogenation of adiponitrile into 6-aminocapronitrile.

In these examples, the following abbreviations may be used:

- 25
- ADN = adiponitrile
 - ACN = aminocapronitrile
 - HMD = hexamethylenediamine

- ACA = aminocaproamide
- CVA = cyanovaleramide
- DC = degree of conversion
- RC = selectivity relative to the starting
5 substrate converted (in this case relative
to the ADN)
- RY = yield relative to the starting
substrate (ADN) used
- IPOL = polarographic index, reflecting the
10 presence of impurities especially of imine
type which in particular cause colorations
and branching during the polymerization of
caprolactam (prepared by hydrolysis of
ACN), if they are found in said compound;
15 this polarographic index is thus determined
by polarography and is expressed as moles
of imine function per ton of sample to be
assayed.

EXAMPLE 1

20 The following are loaded in a 100 ml
stainless-steel reactor equipped with a stirrer of
rushtone cavitator type, means for introducing reagents
and the hydrogen and a temperature regulation system:

- | | | |
|----|------------------------|---------|
| | - adiponitrile | 24.0 g |
| 25 | - hexamethylenediamine | 24.0 g |
| | - water | 5.3 g |
| | - KOH | 0.064 g |

- Raney Ni (containing 1.7% Cu) 1.35 g

After purging the reactor with nitrogen and then with hydrogen, the reaction mixture is heated to 50°C; the pressure is then adjusted to 2.5 MPa at this
5 temperature by continuous addition of hydrogen. The reaction progress is monitored by the consumption of hydrogen and analysis by gas chromatography (GC) of a sample of the reaction mixture. When the optimum yield is reached, the reaction is stopped by switching off
10 the stirring and cooling the reaction mixture.

The following results are obtained:

	- reaction time:	321 min
	- DC of the ADN:	82.3%
	- RY of ACN:	60.3%
15	- RY of HMD:	20.9%
	- sum of the RCs into ACN and HMD:	98.7%
	- IPOL index:	15.0

The remainder to 100% of the RCs and of the compounds evaluated by the IPOL index is represented by
20 ACA and CVA which are compounds which may be upgraded during the cyclizing hydrolysis of ACN into caprolactam.

EXAMPLE 2

Example 1 is repeated in the same apparatus, with the same amounts of reagents and under the same conditions, but using Raney Ni comprising 3% by weight
5 of Cu.

The following results are obtained:

- reaction time: 395 min
- DC of the ADN: 85.7%
- RY of ACN: 58.9%
- 10 - RY of HMD: 21.0%
- sum of the RCs into ACN and HMD: 93.2%
- IPOL index: 19.6

The remainder to 100% of the RCs and of the compounds evaluated by the IPOL index is represented by
15 ACA and CVA.

EXAMPLE 3

Example 1 is repeated in the same apparatus, with the same amounts of reagents and under the same conditions, but using Raney Ni comprising 3% by weight
20 of copper and 2.1% by weight of chromium.

The following results are obtained:

- reaction time: 29 min
- DC of the ADN: 80.3%
- RY of ACN: 56.3%
- 25 - RY of HMD: 24.5%
- sum of the RCs into ACN and HMD: 100%
- IPOL index: 26

COMPARATIVE TEST 1

Example 1 is repeated in the same apparatus,
with the same amounts of reagents and under the same
conditions, but using Raney Ni comprising 1.7% by
5 weight of chromium.

The following results are obtained:

	- reaction time:	30 min
	- DC of the ADN:	81.7%
	- RY of ACN:	56.9%
10	- RY of HMD:	22.4%
	- sum of the RCs into ACN and HMD:	97.1%
	- IPOL index:	72.5

The remainder to 100% of the RCs and of the
compounds evaluated by the IPOL index is represented by
15 by-products not taken into account in the IPOL index
and other than ACA and CVA (for example bis-hexa-
methylenetriamine).

CLAIMS

1. Process for the partial hydrogenation of a dinitrile into the corresponding aminonitrile, in a liquid medium, characterized in that the process is performed in the presence of a Raney nickel or a Raney cobalt catalyst containing at least one metal chosen from copper, silver and gold and in the presence of an alkali metal hydroxide or alkaline-earth metal hydroxide.

2. Process according to claim 1, characterized in that the weight ratio $(\text{Cu} + \text{Ag} + \text{Au})/\text{Ni}$ or $(\text{Cu} + \text{Ag} + \text{Au})/\text{Co}$ of the catalyst used is between 0.05% and 10% and preferably between 0.1% and 5%.

3. Process according to either of claims 1 and 2, characterized in that the catalyst contains one or more additional dopants chosen from titanium, chromium, iron, zirconium, vanadium, manganese, bismuth, tantalum, rhodium, ruthenium, iridium, platinum, palladium, niobium, hafnium and rare-earth elements, and also cobalt when the catalyst is Raney nickel and nickel when the catalyst is Raney cobalt.

4. Process according to one of claims 1 to 3, characterized in that the amount of dopant other than copper, silver and gold which the catalyst contains represents from 0% to 5% by weight relative to the weight of the nickel or cobalt.



5. Process according to one of claims 1 to 4, characterized in that the catalyst used is preferably a Raney nickel.

6. Process according to one of claims 1 to 5, characterized in that the catalyst is used in the form of grains.

7. Process according to one of claims 1 to 6, characterized in that it applies to the dinitrile substrates of formula (I):



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

15 8. Process according to one of claims 1 to 7, characterized in that the average concentration of dinitrile in the reaction medium in the context of an industrial process in continuous operation is between 10% and 45% on a weight for weight basis.

20 9. Process according to one of claims 1 to 8, characterized in that it is carried out in the presence of LiOH, NaOH, KOH, RbOH or CsOH and mixtures thereof.

10. Process according to one of claims 1 to 9, characterized in that the liquid reaction medium is at least partially aqueous and the water represents an amount of from 1% to 25% by weight relative to the



weight of the total reaction medium and is preferably between 1% and 15% on a weight for weight basis.

11. Process according to one of claims 1 to 10, characterized in that the reaction medium comprises, in addition to or in replacement for the water, at least one other solvent of alcohol type.

12. Process according to claim 11, characterized in that the reaction medium comprises an alcohol chosen from methanol, ethanol, propanol, isopropanol and butanol and mixtures of said compounds.

13. Process according to one of claims 1 to 12, characterized in that the reaction medium comprises diamine which is coproduced by the hydrogenation.

14. Process according to claim 13, characterized in that the average concentration of aminonitrile and/or of diamine in the reaction medium in a continuous regime is between 35% and 90% by weight relative to the total weight of the solvent included in said reaction medium and is more preferably between 45% and 89% on a weight for weight basis.

15. Process according to one of claims 1 to 14, characterized in that the reaction medium comprises liquid or dissolved ammonia.

16. Process according to one of claims 1 to 15, characterized in that the ammonia represents



from 0% to 50% by weight of the reaction medium and preferably from 0% to 15%.

17. Process according to one of claims 1 to 10 and 13 to 16, characterized in that the amount of alkali metal hydroxide or alkaline-earth metal hydroxide is greater than or equal to 0.1 mol/kg of catalyst, preferably between 0.1 and 2 mol/kg of catalyst and even more preferably between 0.2 and 1.0 mol/kg of catalyst.

18. Process according to either of claims 11 and 12, characterized in that the amount of alkali metal hydroxide or alkaline-earth metal hydroxide is greater than or equal to 0.05 mol/kg of catalyst, preferably between 0.1 and 10.0 mol/kg of catalyst and more preferably between 1.0 and 8.0 mol/kg of catalyst.

19. Process according to one of claims 1 to 18, characterized in that it is carried out at a temperature of less than or equal to 150°C, preferably less than or equal to 120°C and more preferably between room temperature (about 20°C) and 100°C.

20. Process according to one of claims 1 to 19, characterized in that it is carried out at a hydrogen pressure of between 0.10 and 10 MPa.

