

PROCESS FOR HEMIHYDROGENATION OF DINITRILES
TO 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 produces hexamethylenediamine, itself one
10 of the two base compounds for the preparation of polyamide 6,6.

However, it may sometimes be found necessary to prepare not the diamine but the intermediate aminonitrile. This, for example, is the case - although
15 no limitation is implied thereby - of the hemihydrogenation of adiponitrile to aminocapronitrile, a compound capable of being subsequently converted into caprolactam, a base compound for polyamide 6, or directly into polyamide 6.

20 Thus, US patent 4 389 348 describes a process for hydrogenation of dinitrile to omega-aminonitrile, using hydrogen in an aprotic solvent medium and ammonia in the presence of rhodium deposited on a basic support.

25 US patent 5 151 543 describes a process for partial hydrogenation of dinitriles to aminonitriles in a solvent in a molar excess of at least 2/1 in relation to the dinitrile, including liquid ammonia or an

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

The present invention deals with the preferential hydrogenation of a single nitrile functional group of a dinitrile (called hemihydrogenation in this text), so as to prepare the corresponding aminonitrile as a major product and the diamine only as a minor product.

More precisely, the invention relates to a process for the hemihydrogenation of aliphatic dinitriles to the corresponding aminonitriles, with the aid of hydrogen and in the presence of a catalyst chosen from Raney nickel, Raney cobalt, Raney nickel comprising a doping element chosen from the elements of groups IVb, VIb, VIIb and VIII of the Periodic Classification of the elements, as published in the Handbook of Chemistry and Physics (Weast, 5th edition of 1970-1971) and zinc and Raney cobalt comprising a doping element chosen from the elements of groups IVb, VIb, VIIb and VIII of the Periodic Classification of the elements and zinc, and of a strong inorganic base derived from an alkali or alkaline-earth metal, characterized in that:

- the initial hydrogenation mixture comprises water in a proportion of at least 0.5 % by weight relative to the total of the liquid compounds of the said mixture, the diamine and/or the aminonitrile which

are liable to be formed from the dinitrile to be hydrogenated and the unconverted dinitrile in a proportion of 80 % to 99.5 % for the combined total of these three compounds by weight relative to the total
5 of the liquid compounds of the said mixture,

- the degree of conversion of the dinitrile can reach 95 %

- and in that the said process makes it possible to obtain a selectivity for the aminonitriles
10 being aimed at of at least 60 %.

The degree of conversion of the dinitrile is preferably at least 70 %.

The aliphatic dinitriles which may be used in the process of the invention are more particularly the
15 dinitriles of general formula (I):



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

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

Examples of such dinitriles which may be mentioned are especially adiponitrile,
25 methylglutaronitrile, ethylsuccinonitrile malononitrile, succinonitrile and glutaronitrile and

mixtures thereof, especially the mixtures of adiponitrile and/or methylglutaronitrile and/or ethylsuccinonitrile that are liable to originate from the same process for the synthesis of adiponitrile.

5 In practice, the case where $R = (CH_2)_4$ will be the most frequent one, because this corresponds to the use of adiponitrile (ADN) in the present process.

 The strong inorganic base generally consists of alkali metal or alkaline-earth metal hydroxides, carbonates and alkanolates. It is preferably chosen
10 from alkali metal hydroxides, carbonates and alkanolates.

 As a matter of priority, the strong inorganic base used is chosen from the following compounds: LiOH, NaOH, KOH, RbOH, CsOH and mixtures thereof.
15

 NaOH and KOH are employed most frequently in practice as a good performance-price compromise, although RbOH and CsOH can give very good results.

 The reaction mixture has a composition which
20 varies depending on the type of implementation of the process.

 In fact, if the process is carried out noncontinuously, as is the case especially in the laboratory embodiments or small intermittent
25 manufacture, the initial reaction mixture will become gradually enriched in aminonitrile and, in a lesser proportion, in diamine, while the dinitrile concentration will be capable either of decreasing if

all or most of the said dinitrile is charged at the very beginning of the hemihydrogenation, or of remaining relatively constant if the dinitrile is introduced gradually during the reaction.

5 On the other hand, if the process is conducted continuously, the composition of the reaction mixture leaving the reactor reaches values that are determined by the selectivities of the reaction.

 Water is generally present in a quantity
10 which is smaller than or equal to 20 %. The water content of the reaction mixture is preferably between 2 % and 15 % by weight relative to the combined total of the liquid constituents of the said mixture.

 The concentration of the aminonitrile aimed
15 at and/or of the corresponding diamine and of the unconverted dinitrile in the reaction mixture is generally between 85 % and 98 % by weight relative to the combined total of the liquids included in the said reaction mixture.

20 In continuous operation of the process of the invention the composition leaving the reactor will be determined by the ratio of the respective selectivities for aminonitrile and for diamine and by the rate of introduction of the dinitrile.

25 The quantity of strong inorganic base is advantageously greater than or equal to 0.1 mol/kg of catalyst. It is preferably between 0.1 mol and 3 mol per kg of catalyst and still more preferably between

0.2 and 2 mol/kg of catalyst.

To obtain an optimum selectivity for aminonitrile the strong inorganic base/catalyst ratio may be modified according to the base used. Thus, with
5 KOH, RbOH and CsOH, this ratio will be still more preferably from 0.2 to 1.0 mol per kg of catalyst, particularly of Raney nickel, whether doped or not. With NaOH and LiOH, this ratio will be still more preferably from 0.2 to 1.5 mol per kg of catalyst,
10 particularly of Raney nickel, whether doped or not.

The catalyst employed in the process may be a Raney nickel, a Raney cobalt, a Raney nickel or a Raney cobalt comprising, besides the nickel or the cobalt and the residual quantities of the metal removed from the
15 original alloy during the preparation of the catalyst, that is to say generally aluminium, one or several other elements, often called dopants, such as, for example, chromium, titanium, molybdenum, tungsten, iron or zinc. Among these doping elements, chromium,
20 titanium, iron and their mixtures are considered to be the most advantageous ones. These dopants usually represent from 0 % to 15 % and preferably from 0 % to 10 % by weight per weight of nickel or of cobalt.

When the catalyst contains a dopant such as
25 chromium or titanium, it is also advantageous to take the strong base/dopant ratio into account. Thus, a KOH/dopant ratio of 12 to 30 mol per kg of dopant and an NaOH/dopant ratio of 12 to 50 mol per kg of dopant

are preferably used.

The quantity of catalyst which is used may vary very widely as a function especially of the method of operation which is adopted or of the reaction conditions which are chosen. Thus, if the dinitrile is introduced gradually into the reaction mixture, the weight ratio of catalyst/dinitrile to be hydrogenated will be much higher than if all the dinitrile is used at the very beginning of the reaction. To give an indication, from 0.5 % to 50 % by weight of catalyst may be employed relative to the total weight of the reaction mixture, and in most cases from 1 % to 35 %.

With a given catalyst and with a given degree of conversion of the dinitrile, the yield of aminonitrile passes through a maximum that is determined by the base/Ni or base/Co ratio chosen in the ranges of values indicated above.

The overall selectivity for aminonitrile is improved by the increase in the value of the rate constant of hydrogenation of the dinitrile to aminonitrile and not by the decrease in the value of the rate constant of hydrogenation of the aminonitrile to diamine. It is essentially the rate constant of the first of the two consecutive reactions that is affected by the various parameters indicated above.

The process of the invention is generally carried out at a reaction temperature which is lower than or equal to 150°C, preferably lower than or equal

to 120°C and, still more preferably, lower than or equal to 100°C.

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

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

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

In noncontinuous operation it may vary from a few minutes to several hours.

In continuous operation, which is the preferable industrial method for the process according to the invention, the duration is obviously not a tangible parameter.

It should be noted that, according to the operating conditions, a person skilled in the art may modify the chronology of the stages of the process according to the invention.

The other conditions which control the hydrogenation (using a continuous or noncontinuous method) in accordance with the invention, are related to technical arrangements which are conventional and known per se.

The examples which follow illustrate the invention.

The following abbreviations may be employed in these examples:

- 5 - ADN = adiponitrile
- ACN = aminocapronitrile
- HMD = hexamethylenediamine
- DC = degree of conversion
- CY = selectivity based on the initial
- 10 substrate converted (based on ADN
- in this case).

EXAMPLE 1

Into a 300-ml stainless steel reactor fitted with stirring of the Rushtone Cavitator type, means for introducing reactants and hydrogen and a temperature control system, are charged:

- | | | |
|----|-------------------------------------|---------|
| | - adiponitrile | 95.1 g |
| | - hexamethylenediamine | 94.2 g |
| | - water | 21.1 g |
| 20 | - KOH | 0.056 g |
| | - Raney Ni (containing 1.7 % of Cr) | 2.5 g |

In this example there is 0.4 mol KOH/kg Raney Ni.

The reaction mixture is heated to 50°C after
25 the reactor has been purged with nitrogen and then with
hydrogen; the pressure is then adjusted to 2 MPa at

this temperature by continuous addition of hydrogen.

The progress of the reaction is followed by using the consumption of hydrogen and analysis by vapour phase chromatography (GC) of a sample of the reaction

5 mixture. When the optimum yield is reached, the reaction is stopped by stopping the stirring and cooling of the reaction mixture.

The following results are obtained:

	- reaction time:	80 min
10	- DC of ADN:	83.5 %
	- CY of ACN:	77.5 %

EXAMPLE 2

Example 1 is repeated in the same operating
15 conditions with the following charges:

	- adiponitrile	95.1 g
	- hexamethylenediamine	95.4 g
	- water	21.1 g
	- KOH	0.113 g
20	- Raney Ni (containing 1.7 % of Cr)	2.5 g

In this example there is 0.8 mol KOH/kg
Raney Ni.

The following results are obtained:

	- reaction time:	80 min
25	- DC of ADN:	81.9 %
	- CY of ACN:	68.3 %

EXAMPLE 3

Example 1 is repeated in the same operating conditions with the following charges:

- | | | |
|---|-------------------------------------|---------|
| | - adiponitrile | 27.4 g |
| 5 | - hexamethylenediamine | 166.4 g |
| | - water | 19.4 g |
| | - KOH | 0.115 g |
| | - Raney Ni (containing 1.7 % of Cr) | 2.5 g |

In this example there is 0.8 mol KOH/kg

10 Raney Ni.

The following results are obtained:

- | | |
|------------------|--------|
| - reaction time: | 20 min |
| - DC of ADN: | 71.2 % |
| - CY of ACN: | 77.0 % |

15 EXAMPLE 4

Example 1 is repeated in the same operating conditions with the following charges:

- | | | |
|----|-------------------------------------|---------|
| | - adiponitrile | 142.4 g |
| | - hexamethylenediamine | 47.75 g |
| 20 | - water | 21.1 g |
| | - KOH | 0.053 g |
| | - Raney Ni (containing 1.7 % of Cr) | 2.5 g |

In this example there is 0.4 mol KOH/kg

Raney Ni.

25 The following results are obtained:

- reaction time: 103 min
- DC of ADN: 76.2 %
- CY of ACN: 77.2 %

EXAMPLE 5

5 Example 1 is repeated in the same operating conditions with the following charges:

- adiponitrile 95.1 g
- hexamethylenediamine 97.1 g
- water 21.1 g
- 10 - KOH 0.056 g
- Raney Ni (containing 2.4 % of Cr and
1.3 % of Fe) 2.5 g

In this example there is 0.4 mol KOH/kg Raney Ni and 16.7 mol KOH/kg Cr.

15 The following results are obtained:

- reaction time: 45 min
- DC of ADN: 82.4 %
- CY of ACN: 74.3 %

EXAMPLE 6

20 Example 1 is repeated in the same operating conditions with the following charges:

- adiponitrile 95.0 g
- hexamethylenediamine 97.3 g
- water 21.1 g
- 25 - KOH 0.056 g

- Raney Ni (containing 3.0 % of Cr and
1.6 % of Fe) 2.5 g

In this example there is 0.4 mol KOH/kg Raney Ni and 13.3 mol KOH/kg Cr.

5 The following results are obtained:

- reaction time: 85 min
- DC of ADN: 84.5 %
- CY of ACN: 65.9 %

EXAMPLE 7

10 Into a 150-ml stainless steel reactor fitted with magnetic stirring, means for introducing reactants and hydrogen and a temperature control system, are charged:

- adiponitrile 21.65 g
- 15 - hexamethylenediamine 21.65 g
- water 4.75 g
- NaOH 0.0372 g
- Raney Ni (containing 1.7 % of Cr) 0.58 g

In this example there is 1.6 mol NaOH/kg
20 Raney Ni.

The reaction mixture is heated to 50°C after the reactor has been purged with nitrogen and then with hydrogen; the pressure is then adjusted to 2 MPa at this temperature by continuous addition of hydrogen.

25 The progress of the reaction is followed by using the

consumption of hydrogen and analysis by vapour phase chromatography (GC) of a sample of the reaction mixture. When the optimum yield is reached, the reaction is stopped by stopping the stirring and
5 cooling of the reaction mixture.

The following results are obtained:

- reaction time:	90 min
- DC of ADN:	70 %
- CY of ACN:	62 %

10

EXAMPLE 8

Example 7 is repeated in the same operating conditions with the following charges:

- adiponitrile	21.6 g
15 - hexamethylenediamine	21.8 g
- water	4.75 g
- NaOH	0.0046 g
- Raney Ni (containing 1.7 % of Cr)	0.58 g

20

In this example there is 0.2 mol NaOH/kg Raney Ni.

The following results are obtained:

- reaction time:	107 min
- DC of ADN:	76 %
25 - CY of ACN:	62 %

EXAMPLE 9

Example 7 is repeated in the same operating

conditions with the following charges:

	- adiponitrile	21.6 g
	- hexamethylenediamine	21.7 g
	- water	4.78 g
5	- NaOH	0.0094 g
	- Raney Ni (containing 1.7 % of Cr)	0.58 g

In this example there is 0.4 mol NaOH/kg
Raney Ni.

10 The following results are obtained:

- reaction time:	67 min
- DC of ADN:	80 %
- CY of ACN:	69 %

EXAMPLE 10

15 Example 7 is repeated in the same operating
conditions with the following charges:

	- adiponitrile	21.6 g
	- hexamethylenediamine	21.6 g
	- water	4.75 g
20	- NaOH	0.0187 g
	- Raney Ni (containing 1.7 % of Cr)	0.58 g

In this example there is 0.8 mol NaOH/kg
Raney Ni.

25 The following results are obtained:

- reaction time:	69 min
- DC of ADN:	75 %

- CY of ACN:

73 %

EXAMPLE 11

Example 7 is repeated in the same operating conditions with the following charges:

5	- adiponitrile	21.65 g
	- hexamethylenediamine	21.65 g
	- water	4.75 g
	- KOH	0.026 g
	- Raney Ni (containing 3.6 % of Cr)	0.58 g

10

In this example there is 0.8 mol KOH/kg Raney Ni.

The following results are obtained:

	- reaction time:	51 min
15	- DC of ADN:	75 %
	- CY of ACN:	67 %

EXAMPLE 12

Into a metal reactor fitted with stirring of the cavitator type, means for introducing reactants and hydrogen and with various control systems there are introduced with the following charges:

	- adiponitrile	2856 kg
	- hexamethylenediamine	1151 kg
	- water	588 kg
25	- KOH	0.83 kg
	- Raney Ni (containing 1.7 % of Cr)	37 kg

The operation is carried out in the conditions described for Example 1.

The following results are obtained:

- reaction time: 3 h 30
- 5 - DC of ADN: 86 %
- CY of ACN: 64 %

EXAMPLE 13

Into a 150-ml stainless steel reactor fitted with magnetic stirring, means for introducing reactants and hydrogen and a temperature control system, are charged:

- adiponitrile 6 g
- hexamethylenediamine 41.16 g
- water 0.84 g
- 15 - CsOH 0.054 g
- Raney Ni (containing 12 % of Fe) 0.4 g

In this example there is 0.9 mol CsOH/kg Raney Ni.

The reaction mixture is heated to 80°C after the reactor has been purged with nitrogen and then with hydrogen; the pressure is then adjusted to 2.5 MPa at this temperature by continuous addition of hydrogen. The progress of the reaction is followed by using the consumption of hydrogen and analysis by vapour phase chromatography (GC) of a sample of the reaction

mixture. When the optimum yield is reached, the reaction is stopped by stopping the stirring and cooling of the reaction mixture.

The following results are obtained:

- | | | |
|---|------------------|--------|
| 5 | - reaction time: | 50 min |
| | - DC of ADN: | 89 % |
| | - CY of ACN: | 65 % |

EXAMPLE 14

Example 13 is repeated in the same operating conditions with the following charges:

- | | | |
|----|-------------------------------------|---------|
| | - adiponitrile | 6 g |
| | - hexamethylenediamine | 37.8 g |
| | - water | 4.2 g |
| | - CsOH | 0.036 g |
| 15 | - Raney Ni (containing 1.5 % of Ti) | 0.4 g |

In this example there is 0.6 mol CsOH/kg Raney Ni.

The following results are obtained:

- | | | |
|----|------------------|--------|
| | - reaction time: | 20 min |
| 20 | - DC of ADN: | 90 % |
| | - CY of ACN: | 60 % |

CLAIMS

1. Process for the hemihydrogenation of dinitriles to the corresponding aminonitriles, with the aid of hydrogen and in the presence of a catalyst
5 chosen from Raney nickel, Raney cobalt, Raney nickel comprising a doping element chosen from the elements of groups IVb, VIb, VIIb and VIII of the Periodic Classification of the elements and zinc and Raney cobalt comprising a doping element chosen from the
10 elements of groups IVb, VIb, VIIb and VIII of the Periodic Classification of the elements and zinc, and of a strong inorganic base derived from an alkali or alkaline-earth metal, characterized in that:

- the initial hydrogenation mixture comprises
15 water in a proportion of at least 0.5 % by weight relative to the total of the liquid compounds of the said mixture, the diamine and/or the aminonitrile which are liable to be formed from the dinitrile to be hydrogenated and the unconverted dinitrile in a
20 proportion of 80 % to 99.5 % for the combined total of these three compounds by weight relative to the total of the liquid compounds of the said mixture,

- the degree of conversion of the dinitrile can reach 95 %

25 - and in that the said process makes it possible to obtain a selectivity for the aminonitriles being aimed at of at least 60 %.

2. Process according to Claim 1,



characterized in that the degree of conversion of the dinitrile is at least 70 %.

3. Process according to either of Claims 1 and 2, characterized in that the inorganic base is
5 chosen from alkali metal or alkaline-earth metal hydroxides, carbonates and alkanolates and preferably from alkali metal hydroxides, carbonates and alkanolates.

4. Process according to one of Claims 1 to
10 3, characterized in that the strong inorganic base used is chosen from the following compounds: LiOH, NaOH, KOH, RbOH, CsOH and mixtures thereof.

5. Process according to one of Claims 1 to 4, characterized in that the quantity of organic base
15 which is present in the reaction mixture is greater than or equal to 0.1 mole per kilogram of catalyst and preferably between 0.1 and 3 moles per kilogram of catalyst.

6. Process according to one of Claims 1 to
20 5, characterized in that the quantity of KOH, RbOH or CsOH inorganic base present in the reaction mixture is from 0.2 to 1.0 mol per kg of catalyst, particularly of Raney nickel, whether doped or not.

7. Process according to one of Claims 1 to
25 5, characterized in that the quantity of NaOH or LiOH inorganic base present in the reaction mixture is from 0.2 to 1.5 mol per kg of catalyst, particularly of Raney nickel, whether doped or not.



8. Process according to one of Claims 1 to 7, characterized in that the aliphatic dinitriles which may be used in the process of the invention are the dinitriles of general formula (I):

5



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

10

9. Process according to one of Claims 1 to 8, characterized in that water is present in the reaction mixture in a quantity lower than or equal to 20 % and preferably between 2 % and 15 % by weight relative to the combined total of the liquid constituents of the said mixture.

15

10. Process according to one of Claims 1 to 9, characterized in that the concentration of the aminonitrile aimed at and/or of the corresponding diamine and of the unconverted dinitrile in the reaction mixture is between 85 % and 98 % by weight relative to the combined total of the liquids included in the said reaction mixture.

20

11. Process according to one of Claims 1 to 10, characterized in that the catalyst employed is chosen from a Raney nickel, a Raney cobalt, a Raney nickel or a Raney cobalt comprising one or several

25



other doping elements such as chromium, titanium, molybdenum, tungsten, iron or zinc.

12. Process according to one of Claims 1 to 11, characterized in that the catalyst employed is
5 chosen from a Raney nickel comprising at least one doping element chosen from chromium, titanium, iron and mixtures thereof.

13. Process according to one of Claims 1 to 12, characterized in that the catalyst employed is
10 chosen from a Raney nickel comprising from 0 % to 15 % and preferably from 0 % to 10 % of at least one doping element by weight per weight of nickel.

14. Process according to one of Claims 1 to 13, characterized in that the catalyst contains a
15 dopant chosen from chromium or titanium and that a KOH/dopant ratio of 12 to 30 mol per kg of dopant or an NaOH/dopant ratio of 12 to 50 mol per kg of dopant is used.

15. Process according to one of Claims 1 to 14, characterized in that the catalyst used represents
20 from 0.5 % to 50 % by weight relative to the total weight of the reaction mixture, and in most cases from 1 % to 35 %.

16. Process according to one of Claims 1 to 15, characterized in that it is carried out at a
25 reaction temperature which is lower than or equal to 150°C, preferably lower than or equal to 120°C and, still more preferably, lower than or equal to 100°C.



17. Process according to one of Claims 1 to 16, characterized in that the operation is carried out at a hydrogen pressure of between 1 bar (0.10 MPa) and 100 bar (10 MPa) and preferably between 5 bar (0.5 MPa) and 50 bar (5 MPa).

