

Preparation of aliphatic alpha,omega-aminonitriles in the gas phase

- 5 The present invention relates to an improved process for the preparation of aliphatic alpha,omega-aminonitriles by partial hydrogenation of aliphatic alpha,omega-dinitriles at elevated temperatures in the presence of a catalyst in the gas phase.
- 10 J. Mol. Cat. 61 (1990), 197-205 describes the gas-phase hydrogenation of adiponitrile over iron and nickel catalysts doped with alkali metal, in the absence of ammonia. Furthermore, J. Chem. Soc. Faraday Trans. 89 (1993), 3981-3986 describes the partial hydrogenation of adiponitrile over catalysts which con-
- 15 tain 30% by weight of nickel and are doped with potassium. At reaction temperatures of 170°C and atmospheric pressure, yields of up to 85% are obtained at a conversion of 65%. However, the disadvantage of these methods is that the catalysts are in powder form and therefore unsuitable for large-scale industrial realiza-
- 20 tion in a fixed bed, particularly because of the short catalyst life. Furthermore, a large excess of hydrogen is used, and the catalyst space velocity of 0.02 kg of dinitrile per l of catalyst per hour is also useless for commercial use.
- 25 It is an object of the present invention to provide an improved process for the preparation of aliphatic alpha,omega-aminonitriles by partial hydrogenation of adiponitrile, which does not have the abovementioned disadvantages. In particular, it was intended to find a catalyst which has a longer life than the cat-
- 30 alysts used to date.

We have found that this object is achieved by a process for the preparation of aliphatic alpha,omega-aminonitriles by partial hydrogenation of aliphatic alpha,omega-dinitriles at elevated

35 temperatures in the presence of a catalyst in the gas phase by carrying out the hydrogenation with a catalyst based on at least one metal selected from the group consisting of nickel, cobalt, ruthenium and rhodium and with the proviso that the catalyst is not a powder.

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Aliphatic alpha,omega-dinitriles of the general formula I



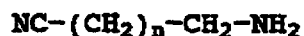
I

- 45 where n is an integer from 1 to 10, in particular 2, 3, 4, 5 or 6, are used as starting materials in the novel process. Particularly preferred compounds I are succinonitrile, glutaronitrile,

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adiponitrile, pimelonitrile and suberonitrile, very particularly preferably adiponitrile.

In the novel process, the dinitriles I described above are partially hydrogenated in the presence of a catalyst to give alpha,omega-aminonitriles of the general formula II



II

10 where n has the abovementioned meanings. Particularly preferred aminonitriles II are those in which n is 2, 3, 4, 5 or 6, in particular 4, ie. 4-aminobutyronitrile, 5-aminopentanenitrile, 6-aminohexanenitrile (6-aminocapronitrile), 7-aminoheptanenitrile and 8-aminooctanenitrile, very particularly preferably 6-amino-15 capronitrile.

The reaction is carried out as a rule at from 100 to 250°C, preferably from 150 to 220°C, particularly preferably from 160 to 200°C; the pressure is chosen in general in the range from 0.01 to 20 3, preferably from 0.07 to 1, particularly preferably from 0.09 to 0.5, MPa.

The hydrogen concentration in the inlet gas depends essentially on the dinitrile concentration. Usually, the molar ratio of 25 hydrogen to dinitrile is chosen in the range from 2:1 to 300:1, preferably from 10:1 to 200:1.

In a preferred embodiment, ammonia or an amine, particularly preferably ammonia, is additionally used. Particularly when ammonia 30 is used, observations to date have shown that the catalyst life is increased. The amount of ammonia or amine is usually from 5 to 50, preferably from 10 to 30 % by weight, based on dinitrile used.

35 According to the invention, the catalysts used are those based on at least one metal selected from the group consisting of nickel, cobalt, ruthenium and rhodium, preferably those based on nickel.

The catalysts may be used in the form of unsupported or supported 40 catalysts, suitable carriers being, for example, alumina, silica, aluminosilicates, titanium dioxide, zirconium dioxide, and magnesium oxide, preferably alumina, silica and aluminosilicates, particularly preferably alumina.

45 In a preferred embodiment, the catalysts may be modified with a modifier based on a metal selected from the group consisting of lithium, sodium, potassium, rubidium, cesium, magnesium, calcium,

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strontium, barium, scandium, yttrium, lanthanides, silver, cadmium, aluminum, tin and zinc, preferably with the oxides thereof. Alkali metal oxides, such as lithium oxide, sodium oxide, potassium oxide, rubidium oxide and cesium oxide, and zinc oxide are particularly preferred, cesium oxide being very particularly preferred.

The amount of catalyst is chosen in general so that the catalyst space velocity is from 0.03 to 10, preferably from 0.05 to 3, kg of dinitrile per kg of catalyst per hour.

When supported catalysts are used, the metal content of the catalyst is usually chosen in the range from 0.1 to 80, preferably from 0.2 to 70, particularly preferably from 0.5 to 50, % by weight, based on the carrier.

According to the invention, the catalysts are not used in the form of powder but as moldings, such as extrudates, pellets and beads, depending on the intended use.

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The reaction is preferably carried out continuously as fixed-bed reaction using a fixed catalyst, for example by the liquid-phase or trickle-bed procedure. By changing the residence time, the conversion and hence the selectivity can be controlled.

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The preparation of the catalysts is known per se (cf. Appl. Het. Cat., (1987), 106-122; Catalysis 4 (1981), 1-30; DE-A 2 260 978). The preparation is usually carried out by precipitating water-soluble salts, such as nitrates, sulfates, chlorides, formates or acetates, of the corresponding metals in the presence or absence of a carrier, if desired processing the resulting catalyst precursor to give extrudates or pellets, drying the product and then calcining it. Supported catalysts are in general also obtainable by impregnating the carrier with an aqueous salt of the corresponding metal or of the corresponding metals, if desired in the presence of the abovementioned modifiers, in particular cesium compounds, or by spraying the corresponding metal salt solutions onto the carrier.

40 The precipitation is effected in general either by adding precipitating reagents or by changing the pH or the temperature.

The preliminary catalyst material thus obtained is usually dried, in general at from 80 to 150°C, preferably from 80 to 120°C.

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The calcination is effected, as a rule, at from 150 to 700°C, preferably from 200 to 650°C, in a gas mixture comprising hydrogen and nitrogen.

5 In the novel process, the catalysts used, in particular supported catalysts, exhibit high activity over a longer period than in the past. Alpha,omega-aminonitriles are obtained in high yield and with good selectivities. The alpha,omega-aminonitriles are important starting compounds for the preparation of cyclic lactams, in
10 particular 6-aminocapronitrile for caprolactam.

Examples

Example 1

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67 ml of an aqueous nickel/nitrate solution (nickel content 16.72 g, calculated as nickel metal) were added to 225 g of alumina extrudates (diameter 4 mm, BET surface area 1 m²/g) and the mixture was left to stand for two hours at room temperature with
20 repeated, thorough stirring. The resulting catalyst precursor was then dried for 16 hours at 120°C and calcined for 4 hours at 350°C. The total process was then repeated.

After cooling, the extrudates were placed in a reduction apparatus and flushed for 2 hours with 20 l of nitrogen per hour.
25 Thereafter, the extrudates were heated to 300°C at 2°C/min and while passing in 20 l of hydrogen per hour and were kept at this temperature for 20 hours. After cooling in a stream of nitrogen, the catalyst was passivated with an air/nitrogen mixture, the
30 temperature increasing not more than 20°C.

The catalyst extrudates obtained contained 13% by weight of nickel (calculated as metal and based on alumina).

35 Example 2

Example 1 was repeated, except that impregnation with lithium nitrate (32 ml of 3.4% strength by weight solution) was carried out before the impregnation with nickel nitrate.

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The catalyst extrudates obtained contained 13% by weight of nickel and 0.1% by weight of lithium, the percentage in each case being calculated as metal and based on alumina.

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Example 3

Example 1 was repeated, except that impregnation with sodium nitrate (32 ml of a 1.4% strength by weight solution) was carried out before the impregnation with nickel nitrate.

The catalyst extrudates obtained contained 13% by weight of nickel and 0.1% by weight of sodium, the percentage in each case being calculated as metal and based on alumina.

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Example 4

Example 1 was repeated, except that impregnation with potassium nitrate (32 ml of a 1.0% strength by weight solution) was carried out before the impregnation with nickel nitrate.

The catalyst extrudates obtained contained 13% by weight of nickel and 0.1% by weight of potassium, the percentage in each case being calculated as metal and based on alumina.

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Example 5

Example 1 was repeated, except that impregnation with cesium nitrate (32 ml of a 0.5% strength by weight solution) was carried out before the impregnation with nickel nitrate.

The catalyst extrudates obtained contained 13% by weight of nickel and 0.1% by weight of cesium, the percentage in each case being calculated as metal and based on alumina.

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Example 6

Example 5 was repeated with an alumina which had a BET surface area of 5.5 m²/g (SCS 9 (Pechiney)).

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The catalyst extrudates obtained contained 13% by weight of nickel and 0.1% by weight of cesium, the percentage in each case being calculated as metal and based on alumina.

40 Example 7

Example 5 was repeated with an alumina which had a BET surface area of 7.7 m²/g (SPH 512 B (Rhone-Poulenc)).

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The catalyst extrudates obtained contained 13% by weight of nickel and 0.1% by weight of cesium, the percentage in each case being calculated as metal and based on alumina.

5 Example 8

From 3 to 20 g of adiponitrile per hour were passed into an evaporator (300°C) and from there, with from 100 to 200 l/h of hydrogen, over 100 ml of catalyst by the trickle-bed procedure. The 10 gaseous reacted mixture was condensed in cold traps and analyzed by gas chromatography. Further reaction parameters and the results are shown in the table below.

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Table

Catalyst from:	Temperature [°C]	H ₂ /ADN-Molar ratio	Catalyst space velocity [g of ADN per g of cat. x h]	ACN-yield [%]	HMD-yield [%]	ACN-selectivity [%]	Conversion [%]
Example 1	a 180	60	0.07	54	4	75	72
	b 200	60	0.07	56	13	59	95
Example 2	180	45	0.08	22	0.3	85	26
Example 3	180	45	0.08	5	0	71	7
Example 4	180	45	0.08	16	0.2	89	18
Example 5	a 180	45	0.08	49	1	88	56
	b 200	45	0.08	60	4	79	76
Example 6	a 180	45	0.1	25	0.5	89	28
	b 180	60	0.1	21	0.3	91	23
	c 200	45	0.1	29	0.4	85	34
	d 180	150	0.05	46.4	1.4	92	50.7
Example 7	a 180	45	0.1	71	3	91	78
	b 180	90	0.1	54	2	93	58
	c 180	50	0.2	34	1	92	37
	d 180	60	0.2	28	0.5	93	30

THIS SHEET HAS BEEN
REPLACED

We claim:-

1. A process for the preparation of aliphatic alpha,omega-aminonitriles by partial hydrogenation of aliphatic alpha,omega-dinitriles at elevated temperatures in the presence of a catalyst in the gas phase, which comprises carrying out the hydrogenation with a catalyst based on at least one metal selected from the group consisting of nickel, cobalt, ruthenium and rhodium, and with the proviso that the catalyst is not a powder.
2. A process as claimed in claim 1, wherein the catalyst is modified with at least one modifier based on a metal selected from the group consisting of lithium, sodium, potassium, rubidium, cesium, magnesium, calcium, strontium, barium, scandium, yttrium, lanthanides, silver, cadmium, aluminum, tin and zinc.
3. A process as claimed in claim 1 or 2, wherein the hydrogenation is carried out at from 100 to 250°C.
4. A process as claimed in any of claims 1 to 3, wherein the hydrogenation is carried out at from 0.01 to 3 MPa.
5. A process as claimed in any of claims 1 to 4, wherein adiponitrile is used as the aliphatic alpha,omega-dinitrile and 6-aminocapronitrile is obtained.



This Sheet Has Been Replaced



Preparation of aliphatic alpha,omega-aminonitriles in the gas phase

5 Abstract

Aliphatic alpha,omega-aminonitriles are prepared by partial hydrogenation of aliphatic alpha,omega-dinitriles at elevated temperatures in the presence of a catalyst in the gas phase by a process which comprises carrying out the hydrogenation with a catalyst based on at least one metal selected from the group consisting of nickel, cobalt, ruthenium and rhodium and with the proviso that the catalyst is not a powder.

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