

The preparation of caprolactam

The present invention relates to a novel process for preparing
5 cyclic lactams by reacting amino carbonitriles with water in the presence of catalysts.

US-A 4 628 085 discloses the reaction of 6-aminocapronitrile with water in the gas phase on acidic silica gel at 300°C. The reaction
10 takes place quantitatively with an initial selectivity of 95 % to produce caprolactam, but a rapid decline in productivity and selectivity is to be found. A similar process is described in US-A 4 625 023, in which a highly diluted gas stream comprising 6-aminocapronitrile, adiponitrile, ammonia, water and carrier gas
15 is passed over a silica gel and a copper/chromium/barium-titanium oxide catalyst bed. Caprolactam is obtained with a selectivity of 91 %, with 85 % conversion. Once again there is observed to be a rapid deactivation of the catalyst.

20 US-A 2 301 964 relates to the uncatalyzed conversion of 6-aminocapronitrile into caprolactam in aqueous solution at 285°C. The yields are below 80 %.

FR-A 2 029 540 describes a process for the cyclization of 6-aminocapronitrile to caprolactam using homogeneous metal catalysts
25 from the zinc and copper group in aqueous solution, resulting in caprolactam in yields of up to 83 %. However, complete removal of the catalyst from the required product caprolactam is problematic because the latter forms complexes with the metals used.

30

It is an object of the present invention to provide a process for preparing cyclic lactams by reacting amino carbonitriles with water which does not involve the disadvantages described above.

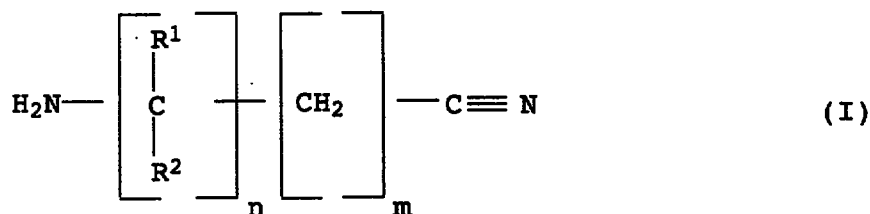
35 We have found that this object is achieved by carrying out the reaction in liquid phase in the presence of heterogeneous catalysts based on titanium dioxide with a rutile content in the range from 0.1 to 95 % by weight and an anatase content of from 99.9 to 5 % by weight, in each case based on the total content of
40 titanium dioxide.

Preferred embodiments of the process according to the invention are evident from the dependent claims.

2

The starting materials employed in the process according to the invention are amino carbonitriles, preferably those of the general formula I

5



10

where n and m can each have the values 0, 1, 2, 3, 4, 5, 6, 7, 8 and 9, and the total of n + m is at least 3, preferably at

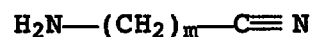
15 least 4.

R¹ and R² can in principle be substituents of any type, it merely being necessary to ensure that the required cyclization reaction is unaffected by the substituents. R¹ and R² are preferably, inde-

20 ppendently of one another, C₁-C₆-alkyl or C₅-C₇-cycloalkyl groups or C₆-C₁₂-aryl groups.

Particularly preferred starting compounds are amino carbonitriles of the general formula

25



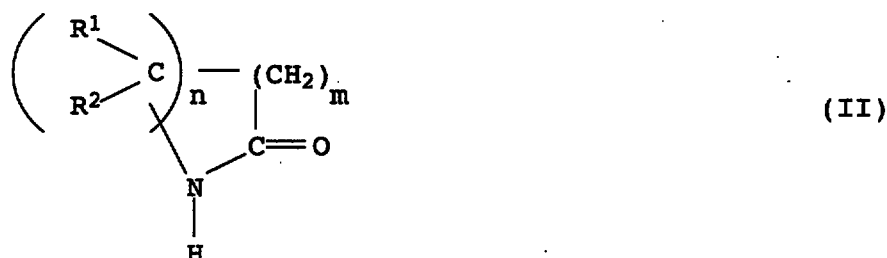
where m has a value of 3, 4, 5 or 6, in particular 5. Where m = 5, the starting compound is 6-aminocapronitrile.

30

In the process according to the invention, the amino carbonitriles described above are reacted with water in liquid phase using heterogeneous catalysts to give cyclic lactams. Use of amino carbonitriles of the formula I results in the corresponding cy-

35 clic lactams of the formula II

40



45

3

where n, m, R¹ and R² have the abovementioned meanings. Particularly preferred lactams are those where n is 0 and m has a value of 4, 5 or 6, in particular 5 (in the latter case, caprolactam is obtained).

5

The reaction is carried out in liquid phase at temperatures of, in general, 140 to 320°C, preferably 160 to 280°C; the pressure is generally in the range from 1 to 250 bar, preferably from 5 to 150 bar, it being necessary to take care that the reaction mix-

10 ture is mainly, ie. without the catalyst which is present in solid phase, liquid under the conditions used. The holdup times are generally in the range from 1 to 120, preferably 1 to 90 and, in particular, 1 to 60, min. In some cases, holdup times of from 1 to 10 min have proven entirely adequate.

15

In general, at least 0.01 mol, preferably 0.1-20 and, in particular, 1-5, mol of water are employed per mol of amino carbonitrile.

20 The amino carbonitrile is advantageously employed in the form of a 1-50 % by weight, in particular 5-50 % by weight, particularly preferably 5-30 % by weight, solution in water (in which case the solvent is also a reactant) or in water/solvent mixtures. Examples of solvents which may be mentioned are alkanols such as

25 methanol, ethanol, n- and i-propanol, n-, i- and t-butanol and polyols such as diethylene glycol and tetraethylene glycol, hydrocarbons such as petroleum ether, benzene, toluene, xylene, lactams such as pyrrolidone or caprolactam or alkyl-substituted lactams such as N-methylpyrrolidone, N-methylcaprolactam or

30 N-ethylcaprolactam, and carboxylic esters, preferably of carboxylic acids with from 1 to 8 carbon atoms. Ammonia may also be present in the reaction. It is, of course, also possible to use mixtures of organic solvents. Mixtures of water and alkanols in the water/alkanol ratio by weight of 1-75 to 25-99, preferably

35 1-50 to 50-99, have emerged as particularly advantageous in some cases.

The process according to the invention is generally carried out in the presence of titanium dioxide catalysts which have a rutile
40 content in the range from 0.1 to 95, preferably from 1 to 90, % by weight and an anatase content in the range from 99.9 to 5, preferably from 99 to 10, % by weight, in each case based on the total content of titanium dioxide.

45

4

In a preferred embodiment, the reaction is carried out in a fixed bed using the catalysts in the form of extrudates or tablets, with the tablets and extrudates preferably having a diameter of from 1 to 10 mm.

5

The extrudates and tablets can be produced by conventional methods using titanium dioxide powder which already has the required content of anatase and rutile, or which is obtained by pyrolysis starting either from a pure anatase modification or a mixed form containing anatase and rutile phases or a mixture of pure anatase and rutile modifications, pyrolyzing with an appropriate temperature and holdup time (both are known to the skilled worker, for example from Catalysis Today 14 (1992) 225-242) until the required anatase to rutile ratio is reached.

15

Corresponding powders are commercially obtainable, for example the titanium dioxide powders P25® (20-30 % by weight rutile and 80-70 % by weight anatase) from Degussa and S150® and S140® (each 100 % by weight anatase) from Fintti-Kemira.

20

The titanium dioxide can be used as such or as supported catalyst, in which case it can be applied to a mechanically and chemically stable support, usually with a high surface area.

25 The titanium dioxide can have been prepared by precipitation from aqueous solutions, eg. by the sulfate process or by other processes such as pyrogenic preparation of fine titanium dioxide powders which can be bought.

30 If required, the rutile/anatase-containing titanium dioxide can be mixed with other oxides such as aluminum oxide, zirconium oxide or cerium oxide. Several methods are available for preparing mixtures of various oxides. The oxides or their precursor compounds which can be converted into the oxides by calcination can
35 be prepared, for example, by precipitation together from solution. This generally results in a very good dispersion of the two oxides used. Precipitation of the oxide or precursor mixtures can also take place by precipitating one oxide or precursor in the presence of the second oxide or precursor which is in the form of
40 a suspension of finely dispersed particles. Another method comprises mechanically mixing the oxide or precursor powders, in which case this mixture can be used as starting material for producing extrudates or tablets.

45 Various methods are available for producing supported catalysts. Thus, the titanium dioxide can be applied in the form of a sol to the support by simple impregnation. Drying and calcination

5

normally remove the volatile constituents of the sol from the catalyst. Sols of this type for titanium dioxide can be bought.

Another possibility for applying layers of the active titanium dioxide comprises hydrolysis or pyrolysis of organic or inorganic compounds. Thus, a ceramic support can be coated with titanium dioxide in a thin layer by hydrolyzing titanium isopropylate or other Ti alkoxides. Another suitable compound is TiCl_4 . Suitable supports are powders, extrudates or tablets of titanium dioxide itself or other stable oxides such as silicon dioxide. The supports used can be designed to be macroporous to improve material transport. It is important to take care during the pyrolysis of the titanium dioxide that both rutile and anatase phases result in the abovementioned ranges.

15

The process according to the invention results in cyclic lactams, in particular caprolactam, in high yield with good selectivities and constancy of catalytic activity.

20 Examples

Examples 1 to 7

A solution of 6-aminocapronitrile (ACN) in water and ethanol in the ratios by weight stated in the table was passed under 100 bar in a heated tubular reactor of capacity 25 ml (diameter 6 mm; length 800 mm) packed with titanium dioxide in the form of tablets or extrudates. The product stream leaving the reactor was analyzed by gas chromatography. The results are likewise to be found in the table.

35

40

45

Table

Ex.	Catalyst	Form	Sulfate content [%]	Rutile [%]	Anatase [%]	BET [m ² /g]	Y	C	S
1	P25	3 mm extrudate	0.01	93	7	15	92	95	97
2	P25/DT51 ¹	3 mm extrudate	0.5	18	82	41	90	98	93
3	P25/S150 ²	3 mm extrudate	0.06	16	84	50	89	97	92
4	P25	1.5 mm extrudate	n.d.	20	80	48	91	99	93
for comparison									
5	VKR611® ³	1.5 mm extrudate	n.d.	100	0	5	5	10	53
6	DT51	4 mm extrudate	n.d.	0	100	36	78	90	85
7	S150	3 mm extrudate	0.17	0	100	108	90	99	91

¹ Mixture of 2/3 parts by weight of P25® powder, remainder DT51® (Rhône-Poulenc)

² Mixture of 2/3 parts by weight of P25® powder, remainder S150® (Finti-Kemira)

³ Rutile from Sachtleben, treated by heating at 875°C for 2 h

n.d.= not determined

Y= yield; S = selectivity; C = conversion

BET= BET surface area by DIN 66 131 method

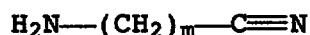


We claim:

1. A process for preparing cyclic lactams by reacting amino carbonitriles with water in the presence of catalysts, wherein the reaction is carried out in liquid phase in the presence of heterogeneous catalysts based on titanium dioxide with a rutile content in the range from 0.1 to 95 % by weight and an anatase content in the range from 99.9 to 5 % by weight, in each case based on the total content of titanium dioxide.

2. A process as claimed in claim 1, wherein the reaction is carried out at a temperature in the range from 140 to 320°C.

3. A process as claimed in either of claims 1 and 2, wherein amino carbonitriles of the formula



where

m is 3, 4, 5 or 6,

are employed.

4. A process as claimed in claim 3, wherein 6-aminocapronitrile is employed as amino carbonitrile.

5. A process as claimed in any of claims 1 to 4, wherein a 1-50 % by weight solution of the amino carbonitrile in water or in water/org. solvent mixtures is employed.

THIS SHEET HAS BEEN
REPLACED

The preparation of caprolactam

Abstract

5

Cyclic lactams are prepared by reacting amino carbonitriles with water, in liquid phase in the presence of heterogeneous catalysts based on titanium dioxide with a rutile content in the range from 0.1 to 95 % by weight and an anatase content in the range from 10 99.9 to 5 % by weight, in each case based on the total content of titanium dioxide.

15

20

25

30

35

40

45

THIS SHEET HAS BEEN REPLACED
