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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 the productivity and selectivity are
found to decline rapidly. A similar process is described in
US-A 4 625 023, in which a highly diluted gas stream composed of
6-aminocapronitrile, adiponitrile, ammonia, water and carrier gas
15 is passed over a silica gel catalyst bed and a copper/chromium/
barium/titanium oxide catalyst bed. Caprolactam is obtained with
a selectivity of 91% and a conversion of 85%. In this case too
there is rapid inactivation of the catalyst.

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

FR-A 2 029 540 describes a process for cyclization of 6-amino-
25 capronitrile to caprolactam using homogeneous metal catalysts
from the zinc and copper group in aqueous solution, caprolactam
being obtained in yields of up to 83%. However, there are
problems in complete removal of the catalyst from the required
caprolactam because the latter forms complexes with the metals
30 used.

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 entail the disadvantages described above.

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We have found that this object is achieved by carrying out the
reaction in liquid phase in the presence of heterogeneous cata-
lysts based on titanium dioxide, zirconium oxide, cerium oxide
and aluminum oxide.

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

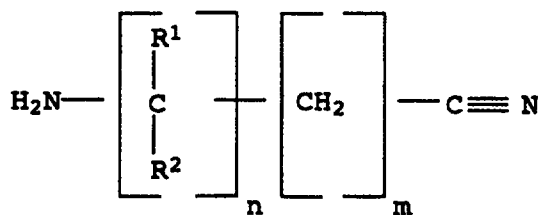
The starting materials employed in the process according to the
45 invention are amino carbonitriles, preferably those of the
general formula I

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(I)

where n and m are each 0, 1, 2, 3, 4, 5, 6, 7, 8 or 9, and n + m
total at least 3, preferably at least 4.

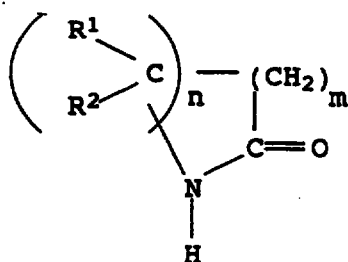
R¹ and R² can, in principle, be substituents of any type, it
merely being necessary to ensure that the required cyclization is
unaffected by the substituents. R¹ and R² are preferably, indepen-
dently of one another, each C₁-C₆-alkyl, C₅-C₇-cycloalkyl or
C₆-C₁₂-aryl.

Particularly preferred starting compounds are amino carbonitriles
of the general formula



where m is 3, 4, 5 or 6, in particular 5. The starting compound
when m = 5 is 6-aminocapronitrile.

In the process according to the invention, the amino carbo-
nitriles 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
cyclic lactams of the formula II



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where n, m, R¹ and R² have the abovementioned meanings. Particu-
larly preferred lactams are those where n is 0 and m is 4, 5 or
6, in particular 5 (in the latter case, caprolactam is obtained).

The reaction is carried out in liquid phase at, in general, from
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

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being necessary to ensure that the reaction mixture is predominantly liquid under the conditions employed. 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 5 1 - 10 min have proved to be entirely sufficient.

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

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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 reactant) or in water/solvent mixtures. Examples 15 of solvents which may be mentioned are alkanols such as 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 20 N-methylpyrrolidone, N-methylcaprolactam or N-ethylcaprolactam, as well as esters of carboxylic acids with, preferably, 1-8 carbon atoms. Ammonia can also be present in the reaction. Mixtures of organic solvents can, of course, also be used. Mixtures of water and alkanols in the water/alkanol ratio by weight of 25 1 - 75/25 - 99, preferably 1 - 50/50 - 99, have emerged in some cases as particularly advantageous.

It is, in principle, equally possible to employ the amino carbonitriles simultaneously as reactant and as solvent.

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Catalysts which, under the reaction conditions described above, have very high conversions, yields, selectivities and useful lives are heterogeneous catalysts based on titanium oxide, zirconium oxide, cerium oxide and aluminum oxide. These can be used 35 in the form of powders, granules, chips, pellets or tablets. The form required for the oxides generally depends on the requirements of the particular reaction procedure, using powder or granules in suspension. In a fixed bed procedure, tablets or pellets with diameters of from 1 mm to 10 mm are normally used.

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Aluminum oxide is suitable in all modifications which can be obtained by heating the precursor aluminum hydroxide or aluminum oxide hydroxide (gibbsite, boehmite, pseudoboehmite, bayerite and diaspore) at various temperatures. These include in particular 45 gamma- and alpha-aluminum oxide and mixtures thereof.



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The oxides can be used in pure form (> 80% by weight content of the particular oxide), as mixture of the abovementioned oxides, in which case the total of the abovementioned oxides should be more than 80% by weight, or as supported catalyst, in which case
5 the abovementioned oxides can be applied to a mechanically and chemically stable support, usually with a large surface area.

The pure oxides can have been prepared by precipitation from aqueous solutions, eg. titanium dioxide by the sulfate process,
10 or by other processes, eg. the pyrogenic production of fine aluminum oxide, titanium dioxide or zirconium dioxide powders, which are commercially available.

Several methods are available for preparing mixtures of the various oxides. The oxides, or their precursors which can be converted into the oxides by calcination, can be prepared, for example, by coprecipitation from solution. This generally results in very good dispersion of the two oxides used. The oxide or precursor mixtures can also be prepared by precipitating one oxide
20 or precursor onto a second oxide or precursor in a suspension of finely dispersed particles thereof. Another method comprises mechanically mixing the oxide or precursor powders, and this mixture can be used as starting material for preparing pellets or tablets.

25 Various methods are available for preparing supported catalysts. Thus, for example, the oxides can be applied in the form of their sols to the support by simple impregnation. Drying and calcination are normally carried out to remove the volatile constituents of the sol from the catalyst. Sols of titanium dioxide, aluminum
30 oxide and zirconium dioxide are commercially available.

Another possibility for applying layers of active oxides comprises hydrolysis or pyrolysis of organic or inorganic compounds. Thus, a ceramic support can be coated with titanium
35 dioxide in a thin layer by hydrolyzing titanium isopropylate or other titanium alkoxides. Other suitable compounds include TiCl_4 , zirconyl chloride, aluminum nitrate and cerium nitrate. Suitable supports are powders, extrudates or tablets of the said oxides themselves or other stable oxides such as silicon dioxide. The
40 supports can be made macroporous to improve transport of matter.

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

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EXAMPLES

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EXAMPLES 1 TO 6

5 A solution of 6-aminocapronitrile (ACN) in water and ethanol in the ratios by weight stated in the table was passed under 100 bar into a heated tubular reactor with a capacity of 25 ml (diameter 6 mm, length 800 mm) which was packed with titanium dioxide (anatase) in the form of 1.5 mm pellets. The product stream leaving
10 the reactor was analyzed by gas chromatography and high-pressure liquid chromatography (HPLC). The results are likewise to be found in the table.

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Table

Ex.	ACN [% by wt.]	Water [% by wt.]	ACN/H ₂ O molar ratio	Ethanol [% by wt.]	Temp. [°C]	Holdup time [min]	Conversion [%]	Sel. [%]
1	10	6.4	1:4	83.6	180	30	90	98
2	10	6.4	1:4	83.6	200	30	100	88
3	10	6.4	1:4	83.6	220	30	100	94
4	10	6.4	1:4	83.6	240	30	100	88
5	15	9.6	1:4	75.4	220	30	100	86
6	10	1.6	1:1	88.4	220	30	99	93

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Comparative test

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A solution of 10% aminocapronitrile, 6.4% water and 83.6% ethanol
5 was reacted as in the tests described in Example 1 without a
heterogeneous catalyst at 250°C with a holdup time of 30 min in an
empty tubular reactor. The conversion was 28% and the selectivity
for caprolactam was 74%.

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EXAMPLES 7 TO 16

Examples 7 to 16 were carried out as in Examples 1 to 6 using the same tubular reactor and employing 13.3 g of TiO_2

Bsp.	ACN [Gew.-%]	ACN [Gew.-%]	Wasser (Gew.-%]	Molverh. ACN/ H_2O [%]	Ethanol [%]	Temp. [°C]	Temp. [°C]	Ums. [%]	Sel. [%]
Ex.	Cat.	Solvent	Temp. [°C]	Water/ ACN [mol/mol]	Feed rate [ml/h]	Free volume [ml]	HUT [min]	Conv. [%]	Sel. [%]
7	TiO_2	EtOH	180	2	9.3	9.3	60	96	92
8	TiO_2	EtOH	230	2	62	9.3	9	100	91
9	TiO_2	EtOH	260	2	139.5	9.3	4	99	91
10	TiO_2	EtOH	180	4	9.3	9.3	60	98	93
11	TiO_2	EtOH	230	4	80	9.3	7	92	94
12	TiO_2	EtOH	230	4	56	9.3	10	100	90
13	TiO_2	EtOH	260	4	139.5	9.3	4	98	91
14	TiO_2	EtOH	180	10	9.3	9.3	60	98	91
15	TiO_2	EtOH	230	10	56	9.3	10	97	93
16	TiO_2	EtOH	260	10	62	9.3	9	100	93

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EXAMPLES 17 TO 22

Examples 17 to 22 were carried out as in Examples 1 to 6 using the same tubular reactor and employing 20 g of TiO_2

Ex.	Cat.	Solvent	Temp. [°C]	Water/ ACN [mol/mol]	Feed rate [ml/h]	Free volume [ml]	HUT [min]	Conv. [%]	Sel. [%]
17	TiO_2	MeOH	220	2	29	14.2	30	100	91
18	TiO_2	EtOH	220	2	29	14.2	30	100	89
19	TiO_2	n-PrOH	220	2	29	14.2	30	100	79
20	TiO_2	i-PrOH	220	2	29	14.2	30	100	87
21	TiO_2	n-BuOH	220	2	29	14.2	30	100	81
22	TiO_2	TEG	220	2	29	14.2	30	99	89

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EXAMPLES 23 TO 27

Examples 23 to 27 were carried out as in Examples 1 to 6 using the same tubular reactor and employing different catalysts.

Ex.	Cat.	Solvent	Temp. [°C]	Water/ ACN [mol/mol]	Feed rate [ml/h]	Free volume [ml]	HUT [min]	Conv. [%]	Sel. [%]
23	ZrO ₂	EtOH	220	2	27	13.3	30	90	83
24	γ-Al ₂ O ₃	EtOH	240	4	27	13.6	30	84	91
25	γ-Al ₂ O ₃	EtOH	260	4	27	13.6	30	97	93
26	α-Al ₂ O ₃	EtOH	240	4	25	12.6	30	91	84
27	CeO ₂	EtOH	220	4	20	10.3	30	100	90

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We claim:

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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, zirconium oxide, cerium oxide and aluminum oxide.
2. A process as claimed in claim 1, wherein the reaction is carried out at from 140 to 320°C.
3. A process as claimed in either of claims 1 and 2, wherein amino carbonitriles of the formula
- $$\text{H}_2\text{N}-(\text{CH}_2)_m-\text{C}\equiv\text{N}$$
- 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.

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