

PROCESS FOR THE PREPARATION OF LACTAM

The present invention relates to the preparation of lactam by ring-closing hydrolysis of the corresponding aminonitrile.

5 Aliphatic lactams such as especially epsilon-caprolactam are basic compounds for the preparation of polyamides (polyamide 6 from caprolactam).

One of the known means for preparing these lactams consists in performing a ring-closing
10 hydrolysis of the corresponding aminonitriles, more particularly of unbranched aliphatic aminonitriles, by passing them in vapour phase with water over a solid catalyst.

Thus, US Patent 2 357 484 describes a process
15 for the vapour phase preparation of lactam, consisting in passing a mixture of water and of aminonitrile over a dehydration catalyst such as activated alumina, silica gel and titanium oxide or borophosphoric acid.

US Patent 4 628 085 has proposed a process
20 for the preparation of lactams in vapour phase, consisting in bringing an aliphatic or aromatic aminonitrile and water into contact with a catalyst based on silica in the form of spherical particles which have a BET surface greater than 250 m²/g and a
25 mean pore diameter smaller than 20 nm, and generally in the presence of hydrogen and ammonia.

In general the catalysts employed in the processes of the prior art enable good selectivity for lactam to be obtained. On the other hand, it is often

found that they are rapidly deactivated and this constitutes a very great handicap for an industrial application of the said processes.

Moreover, the process according to
 5 US 4 628 085 employs a very complex reaction mixture requiring, when the reaction has ended, separation and recycling operations which greatly complicate the said process.

The present invention proposes new catalysts
 10 which, while resulting in a good selectivity of the reaction of conversion of aminonitriles to lactams, have a longer life and therefore require less frequent regeneration.

More precisely, the invention consists of a
 15 process for the preparation of lactam by vapour phase reaction of an aliphatic aminonitrile of general formula (I):



in which R denotes an alkylene radical containing from
 20 3 to 12 carbon atoms, with water, in the presence of a solid catalyst, characterized in that the catalyst is a metal phosphate of general formula (II):



in which:

25 - M denotes a divalent, trivalent, tetravalent or pentavalent element chosen from groups 2a, 3b, 4b, 5b, 6b, 7b, 8, 2b, 3a, 4a and 5a of the Periodic Classification of the elements or a mixture of

several of these elements, or $M = 0$,

- Imp denotes a basic impregnating compound consisting of an alkali metal or alkaline-earth metal or of mixtures of several of these metals, used in
5 combination with a counteranion to ensure electrical neutrality,

- n denotes 1, 2 or 3,

- h denotes 0, 1 or 2,

- p denotes a number between 0 and $1/3$ and
10 corresponds to a molar ratio of the impregnating compound Imp and the impregnated compound $MH_n(PO_4)_n$.

Among the most important aminonitriles of formula (I) are those which produce lactams that are used as raw material for the preparation of polyamides
15 4, 5, 6 and 10, that is to say those in whose formula the symbol R denotes a linear alkylene radical containing 3, 4, 5 or 9 carbon atoms. The preferred compound of formula (I) is 6-aminocapronitrile (or epsilon capronitrile), which produces caprolactam, the
20 polymerization of which yields polyamide 6.

Among the metals of groups 2a, 3b, 4b, 5b, 6b, 7b, 8, 2b, 3a, 4a and 5a of the Periodic Classification of the elements there may be mentioned especially beryllium, magnesium, calcium, strontium,
25 barium, aluminium, boron, gallium, indium, yttrium, lanthanides such as lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium and

lutetium, zirconium, titanium, vanadium, niobium, iron, germanium, tin and bismuth.

Among the lanthanide phosphates, a first class may be distinguished, which includes the orthophosphates of light rare earths, also called ceric rare earths, including lanthanum, cerium, praseodymium, neodymium, samarium and europium. These orthophosphates are dimorphic. They have a hexagonal structure and change to a monoclinic structure when heated to a temperature of 600 to 800°C.

A second class of lanthanide phosphates includes gadolinium, terbium and dysprosium orthophosphates. These orthophosphates have the same structure as the orthophosphates of ceric rare earths but, in addition, have a third crystalline phase of tetragonal structure at high temperature (at about 1700°C).

A third class of lanthanide phosphates includes the orthophosphates of heavy rare earths, also called yttric rare earths, including yttrium, holmium, erbium, thulium, ytterbium and lutetium. These compounds crystallize only in the tetragonal form.

Among the different abovementioned classes of rare-earth orthophosphates, those preferably used are the ceric rare-earth orthophosphates.

It is possible to use metal phosphates of formula (II) which are mixtures of phosphates of several of the metals indicated above or mixed

phosphates of several of the metals indicated above or else mixed phosphates containing one or several of the metals indicated above and one or several other metals such as the alkali or alkaline-earth metals.

5 The counteranions forming part of the formula of the impregnating compound Imp are basic. In particular, the hydroxide, phosphate, hydrogenphosphate, dihydrogenphosphate, chloride, fluoride, nitrate, benzoate and oxalate ions may be
10 used, without any limitation being implied by these mentions.

The molar ratio p is preferably between 0.02 and 0.2.

If reference is made to the general
15 techniques for preparing phosphates (as described especially in P. Pascal "Nouveau traité de chimie minérale", vol. X (1956), pages 821-823 and in "Gmelins Handbuch der anorganischen Chemie" (8th edition) volume 16 (C), pages 202-206 (1965), two main routes of access
20 to phosphates can be discerned. On the one hand, the precipitation of a soluble salt of the metal (chloride, nitrate) using ammonium hydrogenphosphate or phosphoric acid. On the other hand, dissolving the metal oxide or carbonate (which are insoluble) using phosphoric acid,
25 generally with heating, followed by a reprecipitation.

The precipitated phosphates obtained according to one of the routes indicated may be dried, treated with an organic base (such as aqueous ammonia)

or an inorganic one (such as an alkali metal hydroxide) and may be subjected to calcining, it being possible for these three operations to be carried out in the order shown or in a different order.

5 The metal phosphates of formula (II) in the case of which the symbol p is greater than 0 may be prepared by impregnating the compound $MH_n(PO_4)_n$, prepared according to one of the techniques described above, with a solution or a suspension of Imp in a
10 volatile solvent, such as preferably water.

The results are correspondingly better the more soluble Imp is and the more freshly manufactured is the compound $MH_n(PO_4)_n$.

Thus, an advantageous process for preparing
15 the phosphates of formula (II) consists:

- a) in carrying out the synthesis of the compound $MH_n(PO_4)_n$ and then, preferably without isolating $MH_n(PO_4)_n$ from the reaction mixture;
- b) in introducing the impregnating compound
20 Imp into the reaction mixture;
- c) in separating any residual liquid from the reaction solid;
- d) in drying and optionally in calcining.

The performance of the catalyst of formula
25 (II) and especially its resistance to deactivation can be improved further by a calcination. The calcination temperature will be advantageously between 300°C and 1000°C and preferably between 400°C and 900°C. The

duration of the calcination may vary within wide limits. By way of guidance, it is generally between 1 hour and 24 hours.

Among the catalysts of formula (II) which are preferred in the process of the invention there may be mentioned more particularly lanthanum phosphate, calcined lanthanum phosphate, lanthanum phosphate used in combination with a caesium, rubidium or potassium derivative, calcined cerium phosphate, cerium phosphate used in combination with a caesium, rubidium or potassium compound, samarium phosphate used in combination with a caesium, rubidium or potassium compound, aluminium phosphate, aluminium phosphate used in combination with a caesium, rubidium or potassium compound, calcined niobium phosphate, niobium phosphate used in combination with a caesium, rubidium or potassium compound, calcined zirconium hydrogenphosphate, and zirconium hydrogenphosphate used in combination with a caesium, rubidium or potassium compound.

The catalyst is generally used in the form of powder, tablets, beads or extrudates, it being optionally possible for the said forming to be carried out with the aid of a binder. In some cases it may be advantageous for at least a part of the free volume of the reactor to be occupied by an inert solid such as, for example, quartz, in order to promote the vaporization and the dispersion of the reactants.

The ring-closing hydrolysis reaction requires the presence of water. The molar ratio of water to the aminonitrile introduced is usually between 0.5 and 50 and preferably between 1 and 20.

5 The aminonitrile and the water may be introduced in the form of their mixtures in vapour state or may be introduced separately into the reactor. A prevaporization of the reactants may be carried out, and these subsequently pass through a mixing chamber.

10 Any inert gas such as nitrogen, helium or argon may be employed as carrier, without any disadvantage.

 The temperature at which the process of the invention is carried out must be sufficient for the
15 reactants to be entirely in the vapour state. It generally lies between 200°C and 450°C and preferably between 250°C and 400°C.

 The contact time between the aminonitrile and the catalyst is not critical. It may vary, especially
20 depending on the equipment employed. Contact times of 1 to 200 seconds are preferred, and, still more preferably, of 50 to 100 seconds.

 Pressure is not a critical parameter of the process. It is thus possible to operate at pressures of
25 10^{-3} bar to 200 bars. The process will be preferably carried out at a pressure of 0.1 to 20 bars.

 There is nothing to prevent the use of a solvent which is inert in the reaction conditions, such

as, for example, an alkane, a cycloalkane, an aromatic hydrocarbon or a halogenated derivative of one of these preceding hydrocarbons, and thus to have a liquid phase in the reaction stream.

5 The examples which follow illustrate the invention.

EXAMPLES 1 TO 6

 Into a 20-ml cylindrical reactor made of Pyrex glass, arranged vertically and fitted with means
10 for heating, openings for the entry and the exit of the gas streams and with a system for injecting the reactants, are charged, in succession: 10 ml of quartz, 1 ml of the catalyst in the form of powder from 0.8 to 1.25 micrometres (nature of the catalyst shown in
15 Table 1 below) and, again, 10 ml of quartz.

 Thus charged, the reactor is heated to 400°C under a stream of air (at a flow rate of 1.5 litres/hour) for 2 hours. The reactor is then cooled to 320°C (chosen reaction temperature) and
20 placed under a stream of nitrogen (flow rate of 1 litre/hour).

 A mixture of 6-aminocapronitrile (ACN) and water (weight ratio 50/50, that is a water/ACN molar ratio of 6.2) is then injected with the aid of a pump.
25 The rate of injection of the mixture is 1.2 ml/h.

 On leaving the reactor the vapour is condensed in a glass trap at ambient temperature, for a

period of 2 hours.

The final reaction mixture is analysed quantitatively by vapour phase chromatography.

The degree of conversion (DC) of aminocapronitrile, the yield (RY) of caprolactam (CPL) based on the aminocapronitrile converted, and the activity of the catalyst, measured in grams of caprolactam formed/millilitre of catalyst $\times$ hour are determined.

The results obtained are collected in Table 1 below.

Examples	Catalyst	DC ACN %	RY CPL %	Activity
Example 1	LaPO ₄	63	91	0.49 g
Example 2	LaPO ₄ calcined 4 h at 700°C	90	92	0.47 g
Example 3	LaPO ₄ /CS*	69	97	0.63 g
Example 4	AlPO ₄	88	93	0.70 g
Example 5	Zr(HPO ₄) ₂	45	77	0.32 g
Example 6	NbOPO ₄	39	100	0.33 g

* La phosphate doped with Cs hydrogenphosphate
(Cs/LaPO₄ molar ratio = 0.053)

Table 1

EXAMPLES 7 TO 9

Examples 1 to 3 are repeated, the change in

the activity of the various catalysts being followed over periods of up to 35 hours.

The values of the activity are assembled in Table 2 below for each catalyst and for increasing reaction periods (ND = value not determined).

Examples	Catalyst	Activity of the catalyst for periods of						
		4 h	6 h	8 h	10 h	25 h	30 h	35 h
Example 7	LaPO ₄	0.45	0.40	0.35	ND	ND	ND	ND
Example 8	LaPO ₄ /Cs	0.60	0.55	0.60	0.68	0.60	0.55	0.63
Example 9	Calcined LaPO ₄	0.62	0.70	0.63	0.50	0.35	0.37	0.42

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Table 2EXAMPLES 10 AND 11

Example 1 is repeated in the same conditions, but with the ring-closing hydrolysis reaction being carried out at different temperatures.

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The results obtained are assembled in Table 3 below, and the results of Example 1 are also repeated by way of comparison.

Examples	Temperature	DC ACN %	RY CPL %	Activity
Example 10	280°C	44 %	90 %	0.4
Example 11	300°C	46 %	100 %	0.5
Example 1	320°C	63 %	91 %	0.5

20

Table 3

COMPARATIVE EXAMPLE A

Example 1 is repeated, La phosphate being replaced with silica (marketed under the trademark Aerosil 200) calcined for 16 h at 600°C.

- 5 The operating conditions are the same as in Example 1 (temperature of 320°C; water/ACN molar ratio of 6.2; duration of 2 h).

The following results were obtained:

- 10 - DC of ACN: 17.6 %
 - RY of CPL: 53 %
 - Catalyst activity: 0.04 g CPL/ml catalyst x h

Silica produces a low yield of caprolactam and exhibits an extremely low activity.

CLAIMS

1. Process for the preparation of lactam by vapour phase reaction of an aliphatic aminonitrile of general formula (I):



in which R denotes an alkylene radical containing from 3 to 12 carbon atoms, with water, in the presence of a solid catalyst, characterized in that the catalyst is a metal phosphate of general formula (II):



in which:

- M denotes a divalent, trivalent, tetravalent or pentavalent element chosen from groups 2a, 3b, 4b, 5b, 6b, 7b, 8, 2b, 3a, 4a and 5a of the
15 Periodic Classification of the elements or a mixture of several of these elements, or $\text{M} = \text{O}$,

- Imp denotes a basic impregnating compound consisting of an alkali metal or alkaline-earth metal or of mixtures of several of these metals, used in
20 combination with a counteranion to ensure electrical neutrality,

- n denotes 1, 2 or 3,
- h denotes 0, 1 or 2,
- p denotes a number between 0 and 1/3 and
25 corresponds to a molar ratio of the impregnating compound Imp and the impregnated compound $\text{MH}_h(\text{PO}_4)_n$.

2. Process according to Claim 1, characterized in that the aminonitrile of formula (I) is



6-aminocapronitrile.

3. Process according to either of Claims 1 and 2, characterized in that in the formula (II) of the metal phosphates the metals of groups 2a, 3b, 4b, 5b, 5 6b, 7b, 8, 2b, 3a, 4a and 5a of the Periodic Classification of the elements, denoted by M, are chosen from beryllium, magnesium, calcium, strontium, barium, aluminium, boron, gallium, indium, yttrium, lanthanides such as lanthanum, cerium, praseodymium, 10 neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium and lutetium, zirconium, titanium, vanadium, niobium, iron, germanium, tin and bismuth.
4. Process according to one of Claims 1 to 3, 15 characterized in that metal phosphates of formula (II) are used, which are mixtures of phosphates of several of the metals M or mixed phosphates of several of the metals M or else mixed phosphates containing one or several of the metals M and one or several other 20 metals, such as the alkali or alkaline-earth metals.
5. Process according to one of Claims 1 to 4, characterized in that the counteranions forming part of the formula of the impregnating compound Imp are basic and are preferably chosen from hydroxide, phosphate, 25 hydrogenphosphate, dihydrogenphosphate, chloride, fluoride, nitrate, benzoate and oxalate ions.
6. Process according to one of Claims 1 to 5, characterized in that the molar ratio p is preferably



between 0.02 and 0.2.

7. Process according to one of Claims 1 to 6, characterized in that the catalyst of formula (II) is subjected to a calcination at a temperature of between
5 300°C and 1000°C and preferably between 400°C and 900°C.

8. Process according to one of Claims 1 to 7, characterized in that the catalyst is chosen more particularly from lanthanum phosphate, calcined
10 lanthanum phosphate, lanthanum phosphate used in combination with a caesium, rubidium or potassium derivative, calcined cerium phosphate, cerium phosphate used in combination with a caesium, rubidium or potassium compound, samarium phosphate used in
15 combination with a caesium, rubidium or potassium compound, aluminium phosphate, aluminium phosphate used in combination with a caesium, rubidium or potassium compound, calcined niobium phosphate, niobium phosphate used in combination with a caesium, rubidium or
20 potassium compound, calcined zirconium hydrogenphosphate, and zirconium hydrogenphosphate used in combination with a caesium, rubidium or potassium compound.

9. Process according to one of Claims 1 to 8,
25 characterized in that the molar ratio of the water to the aminonitrile introduced is between 0.5 and 50 and preferably between 1 and 20.

10. Process according to one of Claims 1 to 9,



characterized in that the temperature at which the process of the invention is carried out lies between 200°C and 450°C and preferably between 250°C and 400°C.



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