

PROCESS FOR THE PREPARATION OF PENTENENITRILES

The present invention relates to a process for the preparation of pentenenitriles.

Pentenenitriles, more particularly 3-pentenenitrile and
5 4-pentenenitrile, can result in adiponitrile by reaction with hydrogen cyanide.

The invention more specifically consists of a process for the preparation of pentenenitriles by the use, in the vapour phase, of 2-methylglutarimide and/or
10 of ethylsuccinimide and/or of their precursors, in the presence of an acidic solid catalyst chosen in particular from acidic molecular sieves, acidic clays, bridged clays (or pillared clays), bulk oxides and acidic phosphates.

15 During the preparation of adiponitrile by hydrocyanation of butadiene, with the intermediate production of pentenenitriles, large amounts of methylglutaronitrile and ethylsuccinonitrile are inevitably obtained. These by-products currently have
20 only very few industrial outlets and must largely be incinerated.

It is therefore entirely desirable to enhance the value of such by-products and this is one of the aims of the present invention. This is because the
25 compounds employed in the present process, 2-methylglutarimide and/or ethylsuccinimide, as well as their precursors, can be prepared from methylglutaronitrile or from ethylsuccinonitrile.

2-Methylglutarimide can be employed directly or in the form of one of its precursors, such as in particular 4-cyanovaleramide, 2-methyl-4-cyano-butylamide, 4-cyanovaleric acid or 2-methyl-4-cyanovaleric acid.

Likewise, ethylsuccinimide can be employed directly or in the form of one of its precursors, such as in particular 3-cyanovaleramide, 2-ethyl-3-cyanopropionamide, 3-cyanovaleric acid or 2-ethyl-3-cyanopropionic acid.

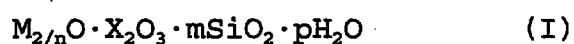
2-Methylglutarimide and its precursors are the most important and the preferred substrates among those which can be employed in the present process, in particular because of the higher proportion of methylglutaronitrile available and because of the better results which they provide.

2-Methylglutarimide can be prepared, for example, by reaction of methylglutaronitrile with dodecanoic acid, as described in an article in the Journal of Organic Chemistry, 36, pages 3050 et seq. (1971). It can also be prepared by reaction of methylglutaric acid with ammonia, as described in another article in the Journal of Organic Chemistry, 22, pages 1728 et seq. (1957).

The acidic molecular sieves employed are in particular acidic zeolites of pentasil structure, such as, for example, ZSM-5, ZSM-11, ZSM-12, ZSM-22, ZSM-23, ZSM-48, mordenite or ferrierite, and acidic zeolites of

faujasite structure, such as, for example, zeolite X or zeolite Y.

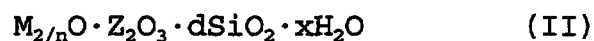
The zeolites of pentasil structure are more particularly zeolites of ZSM-5, ZSM-12, ZSM-11, ZSM-22, 5 ZSM-23, ZSM-48, mordenite and ferrierite type having the general formula (I) expressed in terms of ratios of oxides:



in which:

- 10 - M represents a component chosen from hydrogen, NH_4 and mono-, di-, tri- and tetravalent metals, M being at least in part a hydrogen atom,
- X represents a trivalent element chosen from
- 15 Al, Ga, Fe and B,
- n represents a number from 1 to 4,
- m represents a number equal to or greater than 2,
- p represents a number from 0 to 40.

20 The zeolites of faujasite structure are more particularly those having the general formula (II) expressed in terms of ratios of oxides:



in which:

- M represents a component chosen from hydrogen, NH_4 and mono-, di-, tri- and tetravalent metals, M being at least in part a hydrogen atom,
- 5 - Z represents a trivalent element chosen from Al, Ga, Fe and B,
- n represents a number from 1 to 4,
- d represents a number equal to or greater than 2,
- 10 - x represents a number from 5 to 100.

The zeolites used in the context of the invention are preferably those in the formula (I) or (II) of which the oxide used in combination with silica is that of a trivalent metal, in particular Al or Ga.

- 15 Preference is generally given to the acidic zeolites in the formula (I) or (II) of which M is chosen from hydrogen, NH_4 , alkali metals, such as, for example, Na, K, Li, Rb or Cs, alkaline-earth metals, such as, for example, Be, Mg, Ca, Sr or Ba, rare-earth
- 20 metals, such as, for example, La or Ce, or transition metals, such as, for example, Fe.

For a more detailed description of acidic clays, reference may be made to Patent FR-A-2,622,575, which is incorporated in the present text by reference.

- 25 Preference is given, in the process of the invention, to the use of smectites, such as, for example, montmorillonites, beidellites, nontronites, hectorites, stevensites and saponites.

Bridged clays, which can be used as catalysts in the present process, are clays between the sheets of which have been introduced bridges or pillars which maintain a basal spacing. The basal spacing is the sum
5 of the thickness of a sheet of the clay and of the interfoliar spacing.

The preparation of these bridged clays has been described in particular in Patent FR-A-2,563,446 and in Patent FR-A-2,618,143.

10 Preference will generally be given, as starting clay, to beidellites.

Bridging of the clays can be achieved in particular using aluminium, vanadium, molybdenum, zirconium, iron, niobium, tantalum, chromium, lanthanum,
15 cerium, titanium and gallium hydroxides or mixed hydroxides of a number of these metals.

These bridged clays can be modified, in particular by the action of a dihalogen, of an ammonium halide or of an acid, such as sulphuric acid or
20 hydrohalic acids. The halogen thus optionally introduced is preferably chlorine or fluorine.

Use is preferably made, in the process of the invention, of clays, particularly beidellites, bridged using aluminium hydroxide.

25 The bulk oxides are metal oxides, mixtures of metal oxides or modified metal oxides, in particular modified by the action of a dihalogen, of an ammonium halide or of an acid, such as sulphuric acid or

hydrohalic acids. The halogen thus optionally introduced is preferably chlorine or fluorine.

Mention may be made, as non-limiting examples, of $\text{SiO}_2/\text{Al}_2\text{O}_3$, $\text{SiO}_2/\text{Ga}_2\text{O}_3$, $\text{SiO}_2/\text{Fe}_2\text{O}_3$ and
5 $\text{SiO}_2/\text{B}_2\text{O}_3$ mixtures, halogenated aluminas, such as in particular chlorinated aluminas and fluorinated aluminas, sulphated zirconia, niobium oxide or tungsten oxide.

The acidic phosphates which can be used in
10 the process of the invention are in particular, by way of examples, boron phosphates, alone or as a mixture with alumina or with silica, corresponding to various $\text{H}_3\text{BO}_3/\text{H}_3\text{PO}_4$ molar ratios introduced during the synthesis, lanthanum phosphate, aluminium phosphates corresponding
15 to various $\text{Al}_2\text{O}_3/\text{H}_3\text{PO}_4$ molar ratios introduced during the synthesis, phosphorus pentoxide/silica mixtures (generally known as UOP catalysts), aluminophosphates of zeolite structure (AlPO) and silicoaluminophosphates of zeolite structure (SAPO).

20 The process is implemented continuously.

The catalyst used can be arranged in a stationary bed or be employed in a fluidized bed. It can be used as a mixture with inert solids, in order to increase the contact surface area.

25 The process is generally implemented at a temperature of 200°C to 600°C and preferably of 250°C to 500°C .

The contact time, defined as the ratio

between the volume of the catalyst and the total gas flow rate (2-methylglutarimide and/or ethylsuccinimide and/or their precursors + solvent, if appropriate + carrier gas, if appropriate) at the chosen temperature, generally varies from 0.1 second to 50 seconds and most often from 0.2 second to 10 seconds.

The pressure is not critical. It is generally between a pressure lower than atmospheric pressure and 10 MPa (100 bar) and preferably between 0.01 MPa (0.1 bar absolute) and 5 MPa (50 bar).

The 2-methylglutarimide and/the ethylsuccinimide and/or their precursors can be introduced into the reactor containing the catalyst either in the molten state or in solution in a solvent which is substantially inert under the reaction conditions.

Use may be made, as solvents, of any compound which is vaporized under the reaction conditions, which does not induce harmful side reactions and in which the substrate or substrates employed are soluble. In the present text, a substrate is regarded as soluble in a compound when it can be dissolved in the proportion of at least 5 grams per litre of the said compound at 50°C.

Mention may be made, as non-limiting examples of solvents, of nitriles, such as acetonitrile, propionitrile, valeronitrile, adiponitrile or methylglutaronitrile, ketones, such as acetone or

methyl isobutyl ketone, or ethers, such as dibutyl ether or dimethoxyethane. Water can also be used as solvent when precursors of 2-methylglutarimide or of ethylsuccinimide are employed.

5 They can also be introduced in conjunction with an inert carrier gas; this joint introduction can be carried out in the form of a mixture or in the form of separate simultaneous introductions.

 The inert carrier gas can consist of a gas or
10 a mixture of gases which are inert under the reaction conditions, such as, for example, nitrogen or argon.

 The substrate employed, in particular 2-methylglutarimide and/or its precursors, represents from 5% to 100% by weight with respect to the total
15 weight of gases introduced into the reaction and preferably from 10% to 100%.

 The process of the invention generally results in the formation of a mixture of pentenenitriles, 2-pentenenitrile, 3-pentenenitrile and
20 4-pentenenitrile. These last two pentenenitriles can be converted into adiponitrile by reaction with hydrogen cyanide.

 The following examples illustrate the invention.

25 The following procedure will be used, except when otherwise mentioned, in the examples.

 The following are successively charged, onto the sintered glass, in a reactor arranged vertically

(tube made of Pyrex glass with a length = 15 cm and with a diameter = 2 cm): quartz grains (from 0.63 to 1.25 mm) over a height of 1.2 cm, the catalyst of ZSM-5 type (0.25 cm³, 0.5 cm³, 1 cm³ or 2 cm³, depending on the 5 examples) having a particle size of 0.25-1.25 mm, and then a second layer of quartz with a height of 1.2 cm.

The catalyst is then calcined overnight at 475°C.

The reaction is carried out under a 10 0.3 litre/hour nitrogen stream at a temperature of 450°C, except when otherwise mentioned.

The dissolved substrate is then injected via a syringe driver.

The injection flow rates will be specified 15 for each example: they are expressed in grams of solution per hour.

After running for approximately 1 hour, the test proper lasts 1 hour, during which the products exiting from the reactor are trapped in a series of 20 three receivers, the first at room temperature and the following ones cooled by ice.

Analysis of the reaction products and of the unconverted substrate is carried out by gas chromatography (GC).

25 The following are calculated for each test:

- the degree of conversion (DC) of the substrate: % of the substrate converted with respect to that which has been charged;
- the yields (YY) of pentenenitriles and of methylglutaronitrile formed: molar % of these compounds formed with respect to the substrate charged;
- isomeric distribution of the pentenenitriles formed.

10 EXAMPLES 1 TO 11

These tests were carried out by using 2-methylglutarimide as substrate.

Tests of various acidic zeolites of ZSM-5 type of general formula (I) in which X represents Al and exhibiting various $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratios (value of m in the formula (I)):

Zeolite 1: $\text{SiO}_2/\text{Al}_2\text{O}_3 = 51$

100% of the components M in the formula (I) are H

20 $n = 1$

Zeolite 2: $\text{SiO}_2/\text{Al}_2\text{O}_3 = 350$

100 % of the components M in the formula (I) are H

$n = 1$

25 The operating conditions are those given in the general procedure described above.

The concentration of 2-methylglutarimide in the injected solution is 15 % by weight/weight and the

injection flow rate of this solution is 3.5 g/h.

The contact time (ct) is indicated (in seconds) for each of the examples.

The results obtained are combined in Table 1
5 below.

The abbreviations MGI, PN, PN2, PN3, PN4 and MGN used have the following meanings:

- MGI = 2-methylglutarimide
- PN = pentenenitriles
- 10 - PN2 = 2-pentenenitrile
- PN3 = 3-pentenenitrile
- PN4 = 4-pentenenitrile
- MGN = methylglutaronitrile.

EXAMPLES 12 AND 13

15 These tests were carried out by using 2-methylglutarimide as substrate.

The operating conditions are those given in the general procedure described above but the tests are carried out at different temperatures.

20 The concentration of 2-methylglutarimide in the injected solution is 15 % by weight/weight and the injection flow rate of this solution is 3.5 g/h.

The catalyst used is zeolite 1 (1 cm³).

The contact time (ct) is indicated for each
25 of the examples.

The results obtained are collated in Table 2 below.

Examples	Catalyst (volume)	Solvent	DC % MGI	YY % PN PN2/PN3/PN4 distri- bution	YY % MGN	ct (in s)
Example 1	Zeolite 2 (2 cm ³)	Aceto- nitrile	98	75 40/44/16	0	1.6
Example 2	Zeolite 2 (1 cm ³)	Aceto- nitrile	96	77 28/53/19	6	0.8
Example 3	Zeolite 2 (0.5 cm ³)	Aceto- nitrile	80	65 16/61/23	4	0.4
Example 4	Zeolite 2 (0.25 cm ³)	aceto- nitrile	62	47 10/63/27	1	0.2
Example 5	Zeolite 1 (0.25 cm ³)	Aceto- nitrile	79	60 15/61/24	6	0.2
Example 6	Zeolite 1 (0.5 cm ³)	Aceto- nitrile	89	63 28/52/20	9	0.4
Example 7	Zeolite 1 (1 cm ³)	Aceto- nitrile	99	67 41/44/15	12	0.8
Example 8	Zeolite 2 (0.5 cm ³)	Acetone	36	26 4/60/36	1	0.5
Example 9	Zeolite 2 (2 cm ³)	Acetone	68	52 11/62/27	0	1.8
Example 10	Zeolite 2 (0.25 cm ³)	Acetone	28	17 4/59/37	0	0.2
Example 11	Zeolite 2 (1 cm ³)	Acetone	50	39 7/61/32	1	0.9

TABLE 1

Examples	Temp. (in °C)	Solvent	DC % MGI	YY % PN PN2/PN3/PN4 distri- bution	YY % MGN	ct (in s)
Example 12	400	Aceto- nitrile	68	41 15/64/21	14	0.8
Example 13	350	Aceto- nitrile	22	9 6/71/23	9	0.8

TABLE 2EXAMPLES 14 TO 17

These tests were carried out by using various substrates which are precursors of 2-methylglutarimide:

- Example 14, carried out with 4-cyanovaleramide
- Example 15, carried out with 2-methyl-4-cyanobutyramide
- Example 16, carried out with 4-cyanovaleric acid
- Example 17, carried out with 2-methyl-4-cyanobutyric acid.

The operating conditions are those given in the general procedure described above.

The concentration of substrate in the injected solution is 50 % by weight/weight and the injection flow rate of this solution is 1 g/h.

The contact time (ct) is indicated for each of the examples.

The results obtained are collated in Table 3 below.

Examples	Catalyst (volume)	Solvent	DC % sub- strate	YY % PN PN2/PN3/PN4 distri- bution	YY % MGN	ct (in s)
Example 14	Zeolite 1 (2 cm ³)	Water	82	17 51/37/12	18	2.7
Example 15	Zeolite 1 (2 cm ³)	Water	81	17 52/35/13	19	2.7
Example 16	Zeolite 1 (2 cm ³)	Aceto- nitrile	100	17 65/24/11	6	4.5
Example 17	Zeolite 2 (2 cm ³)	Aceto- nitrile	100	40 51/37/12	11	4.5

TABLE 3

EXAMPLES 18 AND 19

These tests were carried out by using 2-methylglutarimide as substrate.

The operating conditions are those given in the general procedure described above but the tests are carried out with different concentrations of 2-methylglutarimide in the injected solution.

The injection flow rate of these solutions is 3.5 g/h.

The catalyst used is zeolite 2 (0.5 cm³).

The contact time (ct) is indicated for each of the examples.

The results obtained are collated in Table 4 below.

Examples	MGI (% w/w)	Solvent	DC % MGI	YY % PN PN2/PN3/PN4 distri- bution	YY % MGN	ct (in s)
Example 18	20	Aceto- nitrile	66	55 9/64/27	3	0.4
Example 19	30	Aceto- nitrile	54	43 7/64/29	2	0.4

TABLE 4EXAMPLES 20 TO 25

These tests were carried out by using
2-methylglutarimide as substrate and by employing
different acidic catalysts.

These catalysts are commercially available
products.

Only boron phosphate was prepared in the
laboratory, according to the following procedure:

- 417.4 g of H_3PO_4 (2.9 mol) are introduced
into a 1 l reactor equipped with a central stirrer and
a reflux condenser;
- then 180 g (2.9 mol) of boric acid H_3BO_3 ,
sieved at 300 μm , are introduced with stirring;
- the mixture is heated at reflux for one
hour and is then cooled to room temperature;
- the mixture is calcined for 3 h at
500°C.

The operating conditions are those given in.

the general procedure described above, with a catalyst volume of 1 cm³, a concentration of 2-methylglutarimide in the injected solution of 33 % by weight/weight, a nitrogen flow rate of 1 litre/hour and an injection
 5 flow rate of 1.5 g/h, acetonitrile being used as solvent.

The contents of the traps are analysed after the first hour of operation.

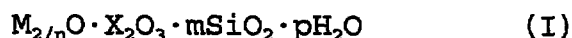
The results obtained are collated in Table 5
 10 below: degree of conversion (DC) of the substrate and the yield (YY) of pentenenitriles formed.

Examples	Catalyst		DC %	YY %
			MGI	PN
Example 20	BPO4	B/P = 0.85	60	27
Example 21	Mordenite ZM760	SiO ₂ /Al ₂ O ₃ = 25	59	25
15 Example 22	Zeolite β	SiO ₂ /Al ₂ O ₃ = 6	80	23
Example 23	Faujasite HY ZF520	SiO ₂ /Al ₂ O ₃ = 10	61	10
Example 24	Mordenite ZM510	SiO ₂ /Al ₂ O ₃ = 5	44	9
Example 25	HCl-treated montmorillonite	All of Ca ²⁺ exchanged	47	7

TABLE 5

CLAIMS

1. Process for the preparation of pentenenitriles, characterized by the use, in the vapour phase, of 2-methylglutarimide and/or of ethylsuccinimide and/or of their precursors, in the presence of an acidic solid catalyst chosen from acidic molecular sieves, acidic clays, bridged clays (or pillared clays), bulk oxides and acidic phosphates.
2. Process according to claim 1, characterized in that the 2-methylglutarimide is employed directly or in the form of one of its precursors, such as 4-cyanovaleramide, 2-methyl-4-cyanobutyramide, 4-cyanovaleric acid or 2-methyl-4-cyanobutyric acid.
3. Process according to one of claims 1 and 2, characterized in that the acidic molecular sieves employed are zeolites of pentasil structure, such as ZSM-5, ZSM-11, ZSM-12, ZSM-22, ZSM-23, ZSM-48, mordenite or ferrierite, and zeolites of faujasite structure, such as zeolite X or zeolite Y.
4. Process according to claim 3, characterized in that the zeolites of pentasil structure are zeolites of ZSM-5, ZSM-11, ZSM-12, ZSM-22, ZSM-23, ZSM-48, mordenite and ferrierite type having the general formula (I) expressed in terms of ratios of oxides:

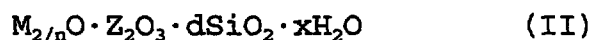




in which:

- M represents a component chosen from hydrogen, NH_4 and mono-, di-, tri- and tetravalent metals, M being at least in part a hydrogen atom,
- X represents a trivalent element chosen from Al, Ga, Fe and B,
- n represents a number from 1 to 4,
- m represents a number equal to or greater than 2,
- p represents a number from 0 to 40.

5. Process according to claim 3, characterized in that the zeolites of faujasite structure are more particularly those having the general formula (II) expressed in terms of ratios of oxides:



in which:

- M represents a component chosen from hydrogen, NH_4 and mono-, di-, tri- and tetravalent metals, M being at least in part a hydrogen atom,
- Z represents a trivalent element chosen from Al, Ga, Fe and B,
- n represents a number from 1 to 4,
- d represents a number equal to or greater



than 2,

- x represents a number from 5 to 100.

6. Process according to one of claims 3 to 5, characterized in that the zeolites used are preferably those in the formula (I) or (II) of which the oxide used in combination with silica is that of a trivalent metal, such as Al or Ga.

7. Process according to one of claims 1 and 2, characterized in that the clays used are smectites, such as montmorillonites, beidellites, nontronites, hectorites, stevensites and saponites.

8. Process according to one of claims 1 and 2, characterized in that the bridged clays used are clays between the sheets of which have been introduced bridges or pillars which maintain a basal spacing, by bridging using aluminium, vanadium, molybdenum, zirconium, iron, niobium, tantalum, chromium, lanthanum, cerium, titanium and gallium hydroxides or mixed hydroxides of a number of these metals, and are preferably beidellites, bridged using aluminium hydroxide.

9. Process according to claim 8, characterized in that the bridged clays used are modified by the action of a dihalogen, of an ammonium halide or of an acid, such as sulphuric acid or hydrohalic acids, the halogen thus optionally introduced preferably being chlorine or fluorine.

10. Process according to one of claims 1 and



2, characterized in that the bulk oxides used are metal oxides, mixtures of metal oxides or metal oxides modified by the action of a dihalogen, of an ammonium halide or of an acid, such as sulphuric acid or
5 hydrohalic acids, the halogen thus optionally introduced preferably being chlorine or fluorine.

11. Process according to claim 10, characterized in that the bulk oxides used are chosen from $\text{SiO}_2/\text{Al}_2\text{O}_3$, $\text{SiO}_2/\text{Ga}_2\text{O}_3$, $\text{SiO}_2/\text{Fe}_2\text{O}_3$ and $\text{SiO}_2/\text{B}_2\text{O}_3$
10 mixtures, halogenated aluminas, such as chlorinated aluminas and fluorinated aluminas, sulphated zirconia, niobium oxide or tungsten oxide.

12. Process according to one of claims 1 and 2, characterized in that the acidic phosphates are
15 chosen from boron phosphates, alone or as a mixture with alumina or with silica, corresponding to various $\text{H}_3\text{BO}_3/\text{H}_3\text{PO}_4$ molar ratios introduced during the synthesis, lanthanum phosphate, aluminium phosphates corresponding to various $\text{Al}_2\text{O}_3/\text{H}_3\text{PO}_4$ molar ratios introduced during the
20 synthesis, phosphorus pentoxide/silica mixtures (generally known as UOP catalysts), aluminophosphates of zeolite structure (AlPO) and silicoaluminophosphates of zeolite structure (SAPO).

13. Process according to one of claims 1 to 12, characterized in that the process is implemented at
25 a temperature of 200°C to 600°C and preferably of 250°C to 500°C .

14. Process according to one of claims 1 to



13, characterized in that the 2-methylglutarimide
and/the ethylsuccinimide and/or their precursors are
introduced into the reactor containing the catalyst
either in the molten state or in solution in a solvent
5 which is substantially inert under the reaction
conditions.

15. Process according to claim 14,
characterized in that the 2-methylglutarimide and/the
ethylsuccinimide and/or their precursors are introduced
10 in solution in a solvent chosen from nitriles, such as
acetonitrile, propionitrile, valeronitrile,
adiponitrile or methylglutaronitrile; ketones, such as
acetone or methyl isobutyl ketone, ethers, such as
dibutyl ether or dimethoxyethane, and water when
15 precursors of 2-methylglutarimide or of
ethylsuccinimide are employed.

16. Process according to one of claims 1 to
15, characterized in that the 2-methylglutarimide
and/or the ethylsuccinimide and/or their precursors
20 employed represent from 5% to 100% by weight with
respect to the total weight of the gases introduced
into the reaction and preferably from 10% to 100%.