

PROCESS FOR THE DEHYDROCYANATION OF ALIPHATIC
DINITRILES

The present invention relates to a process for the dehydrocyanation of aliphatic dinitriles in the vapour phase.

It is more particularly directed towards the dehydrocyanation of branched saturated aliphatic dinitriles, which constitute, in certain cases, by-products which have little enhanced value from the production of linear saturated dinitriles. The dehydrocyanation of such compounds makes it possible to obtain ethylenic nitriles which can be reused, especially in the processes for the synthesis of linear dinitriles.

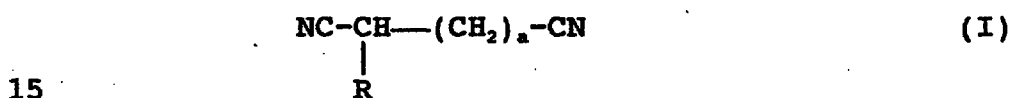
Patent US-A-3,795,694 describes the production of 1,4-dicyanobutene and of 2-methyleneglutaronitrile by dehydrocyanation, generally in a liquid phase, of 1,2,4-tricyanobutane in the presence of a basic catalyst. The same patent also describes the conversion of 2-methyleneglutaronitrile to 1-4-dicyanobutene by hydrocyanic acid in the presence of a basic catalyst.

Such a process does not apply to the saturated branched aliphatic dinitriles, which represent among the most significant amounts of by-products available and which are currently generally destroyed.

The present invention proposes to provide a means of enabling the value of such by-products to be enhanced.

More precisely, it consists of a process for
 5 the dehydrocyanation of branched saturated dinitriles, characterised in that vapours of one or a number of the said branched saturated dinitriles are brought into contact with an acidified cation exchanger.

The branched saturated dinitriles which are
 10 subjected to the dehydrocyanation according to the present process are more particularly those which correspond to the general formula (I):



in which:

- R represents a linear or branched alkyl radical having 1 to 4 carbon atoms,
- a represents an integer from 1 to 6.

20 Among the dinitriles of formula (I), those which are produced in relatively significant amounts in the industrial synthesis of adiponitrile by hydrocyanation of butadiene and whose enhanced valuation constitutes a crucial problem, are more
 25 particularly 2-methylglutaronitrile and 2-ethylsuccinonitrile.

The process of the invention will thus

preferably apply to these dinitriles, to their mixtures with each other and to their industrial mixtures with adiponitrile and/or pentenenitriles.

5 The temperature at which the process is carried out must be sufficient for the saturated dinitriles to be dehydrocyanated to be in the vapour state.

Preferably, it will be situated between 300°C and 600°C and more preferentially between 350°C and 10 500°C.

A preferred variation of the inventor consists in introducing water simultaneously with the introduction of the saturated dinitrile(s).

15 The water/branched saturated dinitrile molar ratio generally varies from 0 to 10 and preferably from 0 to 5.

In order to facilitate the introduction of the saturated dinitrile, it is convenient to use a carrier gas which is inert under the operating 20 conditions.

Nitrogen, alone or mixed with other inert gases, is the most often used.

The catalyst used in the present process is chosen from the partially or completely acidified 25 cation exchangers and more particularly from the solids having a cation-exchanging capacity of 0.001 to 5 milliequivalents per gram.

The partially or completely acidified cation

exchangers belong essentially to the following families:

- the molecular sieves,
- the clays,
- 5 - the pillared clays or bridged clays,
- the acid oxides,
- the bridged or unbridged lamellar phosphates.

The acidic molecular sieves are more particularly the zeolites of pentasil structure (such as, for example, ZSM-5, ZSM-11, ZSM-22, ZSM-23, ZSM-48, ferrierite and mordenite) and the zeolites of faujasite structure.

The acidic zeolites of pentasil structure are preferred in the context of the invention, especially those of the formula in which the oxide combined with the silica is that of a trivalent metal.

These are more particularly:

- the zeolites of ZSM-5 type having the general formula (II) expressed in terms of ratios of oxides:



in which:

- M represents an element chosen from hydrogen and the mono-, di-, tri- and tetraivalent 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 20,
- p represents a number from 0 to 40;
- the zeolites of ZSM-11 type having the general formula (III) expressed in terms of ratios of oxides:



in which:

- M represents an element chosen from hydrogen and the 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,
- m represents a number equal to or greater than 20,
- x represents a number from 6 to 12.

There are generally preferred the zeolites of formula (II) or (III) in which M is chosen from

hydrogen, the alkali metals such as, for example, Na, K, Li or Rb, the alkaline-earth metals such as, for

example, Be, Mg, Ca, Sr or Ba, the rare-earth metals such as, for example, La or Ce, or the transition metals, M being at least in part hydrogen.

For these zeolites, those of formula (II) or
5 (III) in which the symbols X and Z represent Al, Ga or B will be preferred.

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

In the process of the invention, it will be preferred to use the smectites such as, for example the montmorillonites, the beidellites, the nontronites, the hectorites, the stevensites and the saponites.

15 The bridged clays, which can be used as catalysts in the present process, are clays between the lamellae of which have been introduced bridges or pillars which maintain a basal spacing. The basal spacing is the sum of the thickness of a lamella of the
20 clay and of the interlamellar spacing.

The preparation of these bridged clays has been described especially in the Patent FR-A-2,543,446 and in the Patent FR-A-2,618,143.

The beidellites will generally be preferred
25 as the starting clay.

The bridging of the clays can be carried out especially using hydroxides of aluminium, vanadium, molybdenum, zirconium, iron, niobium, tantalum,

chromium, lanthanum, cerium, titanium or gallium or mixed hydroxides of a number of these metals.

Preferably, clays are used in the process of the invention, particularly beidellites, which are
5 bridged using aluminium hydroxide.

The bridged or unbridged lamellar phosphates which can be used as catalysts in the present process are more particularly phosphates, hydrogenphosphates or sulphophosphonates of zirconium, cerium, thorium,
10 uranium, hafnium, lead, titanium, antimony, germanium or tin or mixtures of a number of these compounds.

The metal sulphophosphonates (or MELS = Molecularly Engineered Layered Structures) are especially those which are described in the Patent
15 US-A-4,235,990.

Among these compounds, there may be more particularly mentioned the zirconium sulphophosphonates described in Reactive Polymers, 5 (1987), pages 13 to
21.

20 The process of the invention is used continuously and the flow rate of introduction of the saturated dinitrile into the equipment is such that there is from 0.1 to 10 grams of dinitrile per gram of catalyst per hour (this is the hourly weight
25 productivity or HWP expressed in h^{-1}).

The contact time between the saturated dinitrile and the catalyst usually varies between 0.1 second and 20 seconds.

The examples which follow illustrate the invention.

EXAMPLES 1 to 5

Into a quartz tubular reactor with a length of 230 mm and an internal diameter of 15 mm, containing in its lower part a sintered disc and equipped with a casing containing 3 thermocouples, 3 fluid supplies (nitrogen inlet and 2 syringe drivers) and a cylindrical oven, there are successively introduced onto the sintered disc:

- quartz grains (with a diameter of 0.8 to 1.2 mm) to a height of 1 to 2 cm,
- the catalyst: 2.31 g (4 cm³) of zeolite of ZSM-5 type (having a cation-exchanging capacity of 0.63 milliequivalent H⁺/g, a general formula (II) in which M represents H and X represents Al, a SiO₂/Al₂O₃ molar ratio of 51 and a particle size range of 0.2 to 1.0 mm),
- a second layer of quartz grains to a height of 1 to 2 cm.

The reactants are supplied at a temperature of 450°C.

The supply flow rates are the following:

- nitrogen : 1 litre/hour
- 2-methylglutaronitrile (MGN) : 1 gram/hour

- H₂O : from 0 to 0.2 gram/hour

The operating parameters are the following:

- hourly weight productivity (HWP) : 0.43 h⁻¹

- contact times at 450°C:

5 · MGN/N₂ 17/83 : 4.9 seconds

 · H₂O/MGN/N₂ 17/14/69 : 4.1 seconds.

The operating time is of the order of 1 to 2 hours. The products are recovered at the outlet of the apparatus in 3 successive traps (the first cooled to
10 room temperature, the following two by acetone/solid carbon dioxide).

The table below shows the values of the parameters, which vary depending on the tests, and the results obtained.

15 In this table, the following conventions have been used:

ct = MGN/catalyst contact time

DC (%) = degree of conversion of the MGN in %

RY (%) DHCN = dehydrocyanation yield in %

20 (sum of pentenenitriles and butenenitriles obtained) with respect to the MGN charged

RY (%) C = cracking yield in % (sum of the cracking compounds

25 obtained) with respect to the MGN charged

Sel (%) DHCN = selectivity in % of the
dehydrocyanation reaction:

RY (%) DHCN

5

RY (%) DHCN + RY (%) C

Examples	Composition of the supply stream (molar %)			H ₂ O/MGN Molar ratio	ct (in sec)	DC (%) MGN	RY (%) DHCN	RY (%) C	sel (%) DHCN
	H ₂ O	MGN	N ₂						
Example 1	0	17	83	0	4.9	28	3.5	6.4	35
Example 2	2	17	81	0.12	4.8	17	6.6	7.2	48
Example 3	4	17	79	0.24	4.7	15	7.7	5.3	59
Example 4	12	15	73	0.78	4.3	15	9.1	3.8	71
Example 5	17	14	69	1.2	4.1	18	13.4	4	77

TABLE 1

CLAIMS

1. Process for the dehydrocyanation of branched saturated dinitriles, characterised in that vapours of one or a number of the said branched
5 saturated dinitriles are brought into contact with a partially or completely acidified cation exchanger.

2. Process according to claim 1, characterised in that the branched saturated dinitriles which are subjected to the dehydrocyanation are those
10 which correspond to the general formula (I):



in which:

- 15 - R represents a linear or branched alkyl radical having 1 to 4 carbon atoms,
 - a represents an integer from 1 to 6.

3. Process according to one of claims 1 or 2, characterised in that dinitriles of formula (I) are
20 2-methylglutaronitrile or 2-ethylsuccinonitrile, their mixtures with each other and their industrial mixtures with adiponitrile and/or pentenenitriles.

4. Process according to one of claims 1 to 3, characterised in that the temperature at which it is
25 carried out is sufficient for the saturated dinitriles to be dehydrocyanated to be in the vapour state,



preferably between 300°C and 600°C and more preferentially between 350°C and 500°C.

5. Process according to one of claims 1 to 4, characterised in that water is introduced simultaneously with the introduction of the saturated dinitrile(s).

6. Process according to one of claims 1 to 5, characterised in that the water/branched saturated dinitrile molar ratio varies from 0 to 10 and preferably from 0 to 5.

7. Process according to one of claims 1 to 6, characterised in that, in order to facilitate the introduction of the saturated dinitrile, a carrier gas is used which is inert under the operating conditions, preferably nitrogen, alone or mixed with other inert gases.

8. Process according to one of claims 1 to 7, characterised in that the catalyst used is chosen from the partially or completely acidified cation exchangers and more particularly from the solids having a cation-exchanging capacity of 0.001 to 5 milliequivalents per gram.

9. Process according to one of claims 1 to 8, characterised in that the acidified cation exchangers belong essentially to the following families:

- the molecular sieves,
- the clays,



- the pillared clays or bridged clays,
- the acid oxides,
- the bridged or unbridged lamellar phosphates.

5 10. Process according to claim 9,
characterised in that the acidic molecular sieves are
zeolites of pentasil or faujasite structure and
preferably the acidic zeolites of pentasil structure,
especially those of the formula in which the oxide
10 combined with the silica is that of a trivalent metal.

11. Process according to one of claims 9 or
10, characterised in that the acid zeolites of pentasil
structure are:

- the zeolites of ZSM-5 type having the
15 general formula (II) expressed in terms
of ratios of oxides:



in which:

- M represents an element chosen from
20 hydrogen and the 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 20,

- p represents a number from 0 to 40;
- the zeolites of ZSM-11 type having the general formula (III) expressed in terms of ratios of oxides:

5



in which:

10

- M represents an element chosen from hydrogen and the 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,
- m represents a number equal to or greater than 20,
- x represents a number from 6 to 12;

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and preferably those of formula (II) or (III) in which the symbols X and Z represent Al, Ga or B.

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12. Process according to one of claims 9 to 11, characterised in that the zeolites have a general formula (II) or (III) in which M is chosen from hydrogen, the alkali metals such as Na, K, Li or Rb, the alkaline-earth metals such as Be, Mg, Ca, Sr or Ba, 25 the rare-earth metals such as La or Ce, or the transition metals, M being at least in part hydrogen.

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ABSTRACT

The present invention relates to a process for the dehydrocyanation of aliphatic dinitriles in the vapour phase.

It consists more precisely of a process for the dehydrocyanation of branched saturated dinitriles, characterised in that vapours of one or a number of the said branched saturated dinitriles are brought into contact with a partially or completely acidified cation exchanger.

The branched saturated dinitriles which are subjected to the dehydrocyanation according to the present process are more particularly 2-methylglutaronitrile or 2-ethylsuccinonitrile, their mixtures with each other or the industrial mixtures containing them.