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PROCESS FOR ISOMERIZATION OF 2-PENTENOIC ACID TO
3-PENTENOIC AND 4-PENTENOIC ACIDS BY ACIDIC,
BASIC OR AMPHOTERIC CATALYSIS

5 The present invention relates to a process
for isomerization of 2-pentenoic acid to 3-pentenoic
and 4-pentenoic acids.

Hydroxycarbonylation of butadiene to
pentenoic acids generally results in the formation of
the various position isomers: 2-pentenoic, 3-pentenoic
10 and 4-pentenoic.

3-Pentenoic and 4-pentenoic acids themselves
can be subsequently hydroxycarbonylated to adipic acid,
whereas 2-pentenoic acid cannot be thus converted.

It would therefore be industrially useful to
15 isomerize this 2-pentenoic acid to 3-pentenoic and/or
4-pentenoic acids in order to improve the overall
production efficiency of a process for the preparation
of adipic acid by a double hydroxycarbonylation of
butadiene.

20 When the very high level of investments that
are necessary for a process of this type is known, any
improvement in the overall yield assumes an enormous
importance.

In Patent EP-A-0,291,033 a process has been
25 described for isomerization of 3-pentenoic acid or of
its derivatives, essentially methyl 3-pentenoate, to
4-pentenoic acid or its derivatives, by passing over a
perfluorinated acidic ion exchange resin.

This process does not apply to 2-pentenoic acid and, furthermore, the type of resin employed does not stand up to relatively elevated temperatures and therefore makes it necessary to work in liquid phase.

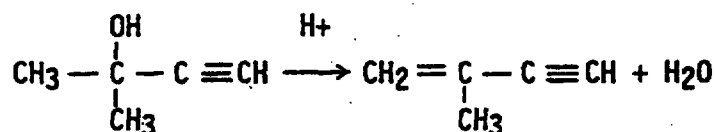
5 Moreover, it results in the formation of a very high proportion of lactone from 3-pentenoic acid, this not being wanted.

The problem of enhancing the value of 2-pentenoic acid by its isomerization to 3-pentenoic
10 and/or 4-pentenoic acids is therefore not solved.

The present invention proposes to solve precisely this problem by permitting the conversion of 2-pentenoic acid to the other pentenoic acids which can again be hydroxycarbonylated to adipic acid.

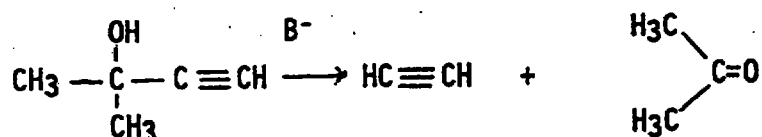
15 It consists of a process for isomerization of 2-pentenoic acid to 3-pentenoic and/or 4-pentenoic acids, characterized in that the said 2-pentenoic acid in vapour phase is placed in contact with an acidic, basic or amphoteric solid catalyst.

20 In the present text acidic solid catalysts will be understood to mean solid compounds, in most cases metal oxides or metal salts, which result in the dehydration of methylbutynol to methylbutenyne ("methylbutynol" test) according to the reaction:

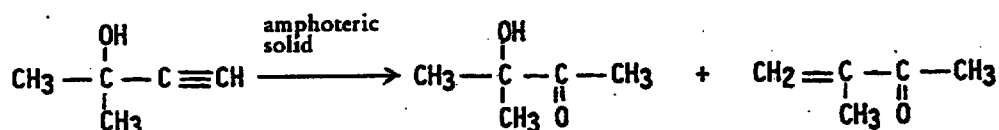


25 Basic solid catalysts will be understood to

mean solid compounds, in most cases metal oxides or metal salts, which result in the reversion of methylbutynol to acetylene and acetone ("methylbutynol" test) according to the reaction:



5 Amphoteric solid catalysts will be understood to mean solid compounds, in most cases metal oxides, which result in the conversion of methylbutynol to 3-hydroxy-3-methyl-2-butanone and 3-methyl-3-buten-2-one ("methylbutynol" test) according to the reaction:



10 For further details on this test reference can be made to the paper in "Applied Catalysis, 78 (1991), pages 213 to 225.

The 2-pentenoic acid which is employed in the process of the invention may originate from any source.

15 In most cases it will originate, as has already been indicated above, from the hydroxycarbonylation of butadiene, but the present process is not restricted to the product from this source alone. Thus, for example, it may itself
20 originate from the isomerization of lactones containing 5 carbon atoms and more particularly of gamma-valerolactone, to a mixtures [sic] of pentenoic acids,

in the presence of the acidic or basic catalysts described below.

2-Pentenoic acid can be used by itself, but it may also contain various proportions of other compounds such as other pentenoic acids, lactones such as gamma-valerolactone, delta-valerolactone or 2-methylbutyrolactone, adipic acid, 2-methylglutaric acid or 2-ethylsuccinic acid. 2-Pentenoic acid generally constitutes more than half of the weight of such a mixture but, if appropriate, a lower proportion can be employed. In what follows, the term 2-pentenoic acid will also include the mixtures of this compound with one or more of the compounds referred to above.

Among acidic solid catalysts there may be mentioned acidic molecular sieves, acidic clays, bridged clays (or pillar clays), solid oxides and acidic phosphates.

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

Zeolites of pentasil or mordenite structure are more particularly the zeolites of ZSM-5, ZSM-11, ZSM-22, ZSM-23 and ZSM-48 and mordenite type, which have the general formula (I) expressed in terms of oxide ratios:



in which:

- M denotes an element chosen from hydrogen, NH_4 and mono-, di-, tri- and tetravalent metals,
- X denotes a trivalent element chosen from Al, Ga, Fe and B,
- n denotes a number from 1 to 4,
- m denotes a number equal to or greater than 10,
- p denotes a number from 0 to 40.

Zeolites of the faujasite structure type are more particularly those which have the general formula (II) expressed in terms of oxide ratios:



in which:

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

The acidic zeolites employed within the scope of the invention are especially those in whose formula

the oxide used in combination with silica is that of a trivalent metal.

Preference is generally given to the zeolites in whose formula (I) or (II) M is chosen from hydrogen, NH₄, 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 metals such as, for example, La or Ce and 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 by reference in the present text.

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

Bridged clays which may be employed as catalysts in the present process are clays between whose leaflets bridges or pillars have been introduced which maintain a basal spacing. The basal spacing is the sum of the thickness of a clay leaflet and of the interleaflet spacing.

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

Beidellites will be generally preferred as starting clay.

The bridging of clays can be performed

especially with the aid of aluminium, vanadium, molybdenum, zirconium, iron, niobium [sic], tantalum, chromium, lanthanum, cerium, titanium or gallium hydroxides or of mixed hydroxides of a number of these
5 metals.

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

Clays, particularly beidellites, bridged with the aid of aluminium hydroxide are preferably employed in the process of the invention.

15 The solid oxides are metal oxides, mixtures of metal oxides or metal oxides which have been modified, especially by the action of a dihalogen, of an ammonium halide or of an acid such as sulphuric acid or hydrogen halide acids. The halogen thus optionally
20 introduced is preferably chlorine or fluorine.

By way of nonlimiting examples there may be mentioned the mixtures $\text{SiO}_2/\text{Al}_2\text{O}_3$, $\text{SiO}_2/\text{Ga}_2\text{O}_3$, $\text{SiO}_2/\text{Fe}_2\text{O}_3$ and $\text{SiO}_2/\text{B}_2\text{O}_3$, halogenated aluminas such as especially chlorinated aluminas and fluorinated aluminas,
25 sulphated zirconia, niobium oxide or tungsten oxide.

The acidic phosphates which can be employed in the process of the invention are especially, by way of examples, boron phosphates, by themselves or mixed

with alumina or with silica, corresponding to different H_3BO_3/H_3PO_4 molar ratios introduced during the synthesis, lanthanum phosphate, aluminium phosphates corresponding to different Al_2O_3/H_3PO_4 molar ratios introduced during the synthesis, phosphorus pentoxide/-silica mixtures (usually called UOP catalysts), aluminophosphates with a zeolite structure (AlPO) and silicoaluminophosphates with a zeolite structure (SAPO).

The basic solid catalysts which can be employed in the process of the invention are especially basic metal phosphates, basic metal oxides, metal carbonates and basic molecular sieves.

The basic metal phosphates are in particular the phosphates, the hydrogenphosphates and the dihydrogenphosphates of general formula (III):



in which:

- A denotes a metal atom, a group of metal atoms or partially a hydrogen atom;
- y denotes a whole or fractional number from 3/4 to 3 depending on the valency of the elements A;
- Imp corresponds to a basic impregnating compound consisting of metal chosen from the alkaline-earth metals, the alkali metals and their mixtures used in combination with a counteranion to

ensure electrical neutrality;

- the coefficient z denotes the weight ratio of the impregnant to the impregnated material (A_zPO_4) and is between 0 % and 20 % and preferably between 2 % and 10 %.

The basic phosphates employed in the process of the invention are preferably compounds of general formula (III) in which:

- 10 - A denotes more particularly calcium, zirconium, lanthanum, cerium, samarium, aluminium, boron, iron and partially hydrogen;
- 15 - y denotes a whole or fractional number from $3/4$ to 3 depending on the valency of the elements A;
- Imp consists of an alkali metal or of a mixture of alkali metals and of a basic counteranion;
- 20 - the coefficient z is between 2 % and 10 %.

By way of nonlimiting examples of basic phosphates there may be mentioned lanthanum phosphate used in combination with a caesium, rubidium or
25 potassium compound, cerium phosphate used in combination with a caesium, rubidium or potassium compound, samarium phosphate in used combination with a caesium, rubidium or potassium compound, calcium

phosphate used in combination with a caesium, rubidium or potassium compound, calcium hydrogenphosphate used in combination with a caesium, rubidium or potassium compound or zirconium hydrogenphosphate used in combination with a caesium, rubidium or potassium compound.

The basic phosphates of formula (III) can be prepared by impregnating a compound of formula (IV) A'_yPO_4 , in which A' has the same meaning as A , with a solution or a suspension of Imp in a volatile solvent such as preferably water.

The results are proportionately better when Imp is more soluble and when the compound A'_yPO_4 is more freshly manufactured.

Thus, an advantageous process for the preparation of the phosphates of formula (III) consists:

a) in carrying out the synthesis of the compound A'_yPO_4 ; then preferably without isolating A'_yPO_4 from the reaction mixture;

b) in introducing the impregnant Imp into the reaction mixture;

c) in separating off any residual liquid from the reaction solid;

d) in drying and optionally in calcining.

If reference is made to the general techniques for the preparation of phosphates (as described especially in "P. Pascal Nouveau traité de

chimie minérale" volume 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 to the phosphates can be discerned. On the one hand, the precipitation of a soluble metal salt (chloride, nitrate) using ammonium hydrogenphosphate and a finishing treatment with aqueous ammonia, optionally followed by an additional neutralization. On the other hand, the reaction of the metal oxide with phosphoric acid with heating and an optional finishing treatment with an alkali metal hydroxide.

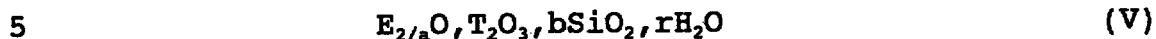
The basic metal oxides employed in the process of the invention are the oxides of a basic nature or those which are made basic by a treatment with the aid of a base such as an alkali metal or alkaline-earth metal hydroxide.

As basic metal oxides there may be mentioned - no limitation being implied - the oxides of the alkali metals, of alkaline-earth metals, of metals of group IIIa of the Periodic Classification of the elements, of transition elements or of rare earths, treated or untreated with an alkali metal hydroxide.

By way of examples there may be mentioned more particularly alumina treated with sodium hydroxide, zinc oxide and calcium oxide.

The basic molecular sieves employed in the process of the invention are more particularly the zeolites of pentasil structure such as, for example,

ZSM-5, ZSM-11, ZSM-22, ZSM-23 or ZSM-48, of mordenite structure, of ferrierite structure or of faujasite structure, such as zeolite X or zeolite Y, of general formula (V) expressed in terms of oxides:



in which:

- E denotes an alkali or alkaline-earth metal, completely or with a small proportion of hydrogen,
- T denotes a trivalent metal chosen from Al, Ga, Fe and B,
- a denotes a number from 1 to 2,
- b denotes a number equal to or greater than 2,
- r denotes a number from 0 to 100.

In the general formula (V) the expression "low proportion of hydrogen" for the meaning of the symbol E means that the optional presence of protons in the molecular sieve must not be such that the latter has an acidic reaction in the test indicated above.

Among the basic molecular sieves of formula (V) those preferably employed will be the ones in which E denotes an alkali metal.

By way of nonlimiting examples of basic molecular sieves there may be mentioned zeolite NaZSM-5, zeolite NaMOR, zeolite 13XCs, zeolite NaY, zeolite KY and zeolite CsY.

The amphoteric solid catalysts which can be

employed in the process of the invention are especially amphoteric metal oxides.

The amphoteric metal oxides employed in the process of the invention are oxides of an amphoteric nature or those which are made amphoteric by their method of preparation or by a subsequent treatment.

As amphoteric metal oxides there may be mentioned, by way of nonlimiting examples, thoria (ThO_2), zirconia (ZrO_2), titanium dioxide (TiO_2), ceria (CeO_2), silica (SiO_2), alumina (Al_2O_3) and mixtures of a number of these oxides.

The process is used continuously.

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

The isomerization process is generally used at a temperature of 200°C to 500°C and preferably from 250°C to 400°C .

The contact time, defined as the ratio of the volume of catalyst to the total gas flow rate (2-pentenoic acid + carrier gas where appropriate) at the chosen temperature, usually varies from 0.1 second to 50 seconds and in most cases from 1 second to 10 seconds.

The pressure is not critical. It is generally situated from atmospheric pressure to 10 MPa (100 bar) and preferably from atmospheric pressure to 1.5 MPa

(15 bar).

The 2-pentenoic acid can be introduced by itself into the reactor containing the catalyst.

It can also be introduced together with an
5 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 may consist of a gas or a mixture of gases which are inert under the reaction
10 conditions, such as, for example, nitrogen, argon, air, steam and carboxylic acids which are gaseous at the temperature at which the reaction is operated.

2-Pentenoic acid represents from 10 % to 100 % by weight relative to the total weight of the
15 gases introduced into the reaction, and preferably from 40 % to 100 %.

The process of the invention generally results in the formation of a mixture of pentenoic acids, 3-pentenoic acid and 4-pentenoic acid, both of
20 which can be hydroxycarbonylated to adipic acid by reaction with carbon monoxide and water, as has already been indicated above. The formation of gamma-valerolactone can also be observed.

The examples which follow illustrate the
25 invention.

The following operating method will be employed in the examples (unless stated otherwise).

A reactor arranged vertically (quartz tube of

length = 15 cm and diameter = 2 cm) is charged in succession with 2cm³ of quartz, an intimate mixture of 2 cm³ of catalyst and 10 cm³ of quartz and then 5 cm³ of quartz. The packing of the reactor is then finished
5 with glass beads (diameter: 2 to 3 mm).

The catalyst is conditioned at the temperature chosen for the reaction (300°C unless stated otherwise), by passing a stream of nitrogen for 2 hours (2 litres/hour at normal pressure and
10 temperature conditions).

2-Pentenoic acid is then injected by means of a syringe driver.

The injection rates of 2-pentenoic acid will be stated for each example: they are expressed in cm³ (ml) of 2-pentenoic acid in the liquid state.
15

After establishing a steady state for approximately 15 minutes, the test generally lasts 1 hour. The products leaving the reactor are trapped in a receiver containing 10 cm³ of acetonitrile.

20 Analysis of the reaction products and of the unconverted 2-pentenoic acid is carried out by gas phase chromatography (GC).

The following are calculated for each test:

- the hourly weight production efficiency (HWE): weight of 2-pentenoic acid introduced relative to the weight of the catalyst and per hour (expressed in h⁻¹);
 - the degree of conversion (DC) of
- 25

2-pentenoic acid; % of 2-pentenoic acid converted relative to what has been introduced;

- the yields (RY) of the various pentenoic acids and of gamma-valerolactone: mol% of each pentenoic acid or of gamma-valerolactone formed relative to the 2-pentenoic acid introduced.

EXAMPLES 1 TO 3

10 Tests of different zeolites of type ZSM-5 of general formula (I) exhibiting different Si/Al molar ratios:

- zeolite 1: Si/Al = 30
75 % of the elements M in the formula (I) are H,
- zeolite 2: Si/Al = 52
75 % of the elements M in the formula (I) are H,
- zeolite 3: Si/Al = 120
75 % of the elements M in the formula (I) are H.

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

25 The contact time (t_c) is approximately 1.4 seconds for each of the examples.

The results obtained are collated in Table 1 below.

The abbreviations P2, P3, P4 and VAL which

are employed have the following meanings:

P2 = 2-pentenoic acid

P3 = 3-pentenoic acid

P4 = 4-pentenoic acid

5 VAL = gamma-valerolactone.

EXAMPLES	CATALYST	DC % P2	RY %			HWE (h ⁻¹)
			P4	P3	VAL	
Example 1	Zeolite 1	34	0	26	7	4.3
Example 2	Zeolite 2	55	2	30	20	3.1
Example 3	Zeolite 3	33	1	25	5	4.9

10

TABLE 1

EXAMPLES 4 TO 11

Tests of various acidic catalysts:

- SiO₂/Al₂O₃ (marketed by Degussa)
containing 16 % by weight of Al₂O₃,
- 15 - zeolite Y which has an SiO₂/Al₂O₃ ratio
of 5 and is exchanged with Fe³⁺,
- LaPO₄,
- Montmorillonite Volclay clay (Montmo),
- Montmorillonite Volclay bridged clay
20 (Montmo-P),
- chlorinated Al₂O₃,
- sulphated ZrO₂,
- niobium oxide.

The operating conditions are those described above. The reaction period is 1 hour with the exception of Example 9 with chlorinated alumina where this period is 0.5 h, the temperature may be other than 300°C, the
5 nitrogen flow rate may be other than 2 litres/hour and the rate of introduction of 2-pentenoic acid may be other than 3.2 ml/h of liquid/hour.

Table 2 below shows the values of some parameters which vary, as well as the results obtained.

Examples	Catalyst	Temp. (°C)	N ₂ flow rate l/h	P2 flow rate ml/h	DC P2 %	RY %			tc (s)	HWE (h ⁻¹)
						P4	P3	VAL		
Example 4	SiO ₂ /Al ₂ O ₃ (2 cm ³)	300	2	3.2	38	1	30	6	1.4	4.9
Example 5	Zeolite Y (1.5 cm ³)	300	3	3.2	40	0	30	2	0.7	5.9
Example 6	LaPO ₄ (2 cm ³)	300	2	3.2	88	2	15	45	1.4	1.9
Example 7	Montmo (2 cm ³)	320	2	3.2	35	0	25	2	1.3	2.0
Example 8	Montmo-P (4 cm ³)	280	2	6.4	81	1	10	32	5.5	0.4
Example 9	Chlorinated Al ₂ O ₃ (2 cm ³)	380	0.5	9.6	76	2	40	6	1.2	8.6
Example 10	Sulphated ZrO ₂ (4 cm ³)	300	0.5	0.96	69	2	40	7	10.2	0.4
Example 11	Nb oxide (2 cm ³)	380	2	3.2	79	25	30	9	1.2	1.9

TABLE 2

EXAMPLES 12 TO 21

Tests of various basic solid catalysts:

- Ce phosphate doped with 3 % of Cs
hydrogenphosphate
- 5 - Ca hydrogenphosphate (hydroxyapatite)
- zeolite 13XCs
- alumina treated with sodium hydroxide
(10 % of sodium hydroxide on weight per
weight basis)
- 10 - La phosphate doped with 3 % of Cs
hydrogenphosphate
- Al phosphate doped with 3 % of Cs
hydrogenphosphate
- La phosphate doped with 3 % of K
15 dihydrogenphosphate
- magnesium oxide
- zinc oxide
- ceria.

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

The results obtained are collated in Table 3
below together with the values of the parameters which
were changed in relation to the general operating
method.

25 EXAMPLES 22 TO 25

Tests of various amphoteric solid catalysts:

- zirconia (ZrO_2)
- thorium (ThO_2)

- titanium dioxide (TiO_2)
- Condea alumina (Al_2O_3).

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

5 The results obtained are collated in Table 4 below together with the values of the parameters which were changed in relation to the general operating method.

Examples	Catalyst	Temp. (°C)	N ₂ flow rate l/h	P2 flow rate ml/h	DC P2 %	RY %			tc (s)	HWE (h ⁻¹)
						P4	P3	VAL		
Example 12	CePO ₄ /CsHPO ₄ (2 cm ³)	300	2	1.6	70	1	40	11	1.3	1.3
Example 13	Hydroxyapatite (2 cm ³)	330	1	6.4	43	0	36	1	1.4	10.9
Example 14	Zeolite 13XCs (2 cm ³)	320	2	3.2	82	0	23	8	1.3	2.1
Example 15	Al ₂ O ₃ /NaOH (4 cm ³)	320	1	1.6	73	2	40	3	5.2	0.6
Example 16	LaPO ₄ /Cs ₂ HPO ₄ (2 cm ³)	300	2	3.2	62	2	45	10	1.4	1.8
Example 17	AlPO ₄ /CsHPO ₄ (2 cm ³)	320	2	6.4	56	0	50	0	1.0	3.9
Example 18	LaPO ₄ /KH ₂ PO ₄ (4 cm ³)	350	2	1.6	57	0	50	0	1.4	0.8
Example 19	MgO (2 cm ³)	300	2	3.2	87	0	20	0	1.4	1.8
Example 20	ZnO (2 cm ³)	370	2	3.2	97	1	3	3	1.2	2.0
Example 21	Ceria (2 cm ³)	380	2	3.2	94	0	10	3	1.2	1.9

TABLE 3

Examples	Catalyst	Temperature (°C)	DC P2 %	RY %			tc (s)	HWE (h ⁻¹)
				P4	P3	VAL		
Example 22	ZrO ₂	300	50	0	45	0	1.4	3.1
Example 23	ThO ₂	300	60	0	40	2	1.4	0.5
Example 24	TiO ₂	300	70	1	40	2	1.3	1.9
Example 25	Al ₂ O ₃	350	74	2	40	5	1.3	2.1

TABLE 4

CLAIMS

1. Process for isomerization of 2-pentenoic acid to 3-pentenoic and/or 4-pentenoic acids, characterized in that the said 2-pentenoic acid in vapour phase is placed in contact with an acidic, basic or amphoteric solid catalyst.

2. Process according to claim 1, characterized in that 2-pentenoic acid is used by itself or it contains various proportions of other compounds such as the other pentenoic acids, lactones such as gamma-valerolactone, delta-valerolactone or 2-methylbutyrolactone, adipic acid, 2-methylglutaric acid or 2-ethylsuccinic acid.

3. Process according to either of claims 1 and 2, characterized in that the catalyst is an acidic solid catalyst chosen from acidic molecular sieves, acidic clays, bridged clays (or pillar clays), solid oxides and acidic phosphates.

4. Process according to claim 3, characterized in that the acidic molecular sieves are zeolites of pentasil structure, such as ZSM-5, ZSM-11, ZSM-22, ZSM-23, ZSM-48, ferrierite, mordenites and zeolites of faujasite structure, such as zeolite X or zeolite Y.

5. Process according to either of claims 3 and 4, characterized in that the acidic zeolites of pentasil or mordenite structure are zeolites of ZSM-5, ZSM-11, ZSM-22, ZSM-23 and ZSM-48 or mordenite type



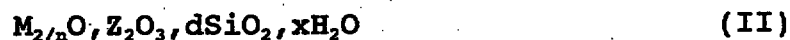
which have the general formula (I) expressed in terms of oxide ratios:



in which:

- 5 - M denotes an element chosen from
 hydrogen, NH_4 and mono-, di-, tri- and
 tetravalent metals,
- X denotes a trivalent element chosen
 from Al, Ga, Fe and B,
- 10 - n denotes a number from 1 to 4,
- m denotes a number equal to or greater
 than 10, .
- p denotes a number from 0 to 40.

- 6. Process according to claim 3,
- 15 characterized in that the acidic molecular sieves are
 zeolites of faujasite structure of zeolite X or zeolite
 Y type which have the general formula (II) expressed in
 terms of oxide ratios:



20 in which:

- M denotes an element chosen from
 hydrogen, NH_4 and mono-, di-, tri- and
 tetravalent metals, M being at least
 partially a hydrogen atom,
- 25 - Z denotes a trivalent metal chosen from
 Al, Ga, Fe and B,
- n denotes a number from 1 to 4,
- d denotes a number equal to or greater



than 2,

- x denotes a number from 5 to 100.

7. Process according to one of claims 3 to 6, characterized in that the acidic molecular sieves are acidic zeolites in whose formula the oxide used in combination with the silica is that of a trivalent metal.

8. Process according to claim 3, characterized in that the clays employed are smectites such as montmorillonites, beidellites, nontronites, hectorites, stevensites and saponites.

9. Process according to claim 3, characterized in that the bridged clays employed are clays between whose leaflets bridges or pillars have been introduced which maintain a basal spacing, by bridging with the aid of aluminium, vanadium, molybdenum, zirconium, iron, niobium [sic], tantalum, chromium, lanthanum, cerium, titanium or gallium hydroxides or of mixed hydroxides of a number of these metals and are preferably beidellites bridged with the aid of aluminium hydroxide.

10. Process according to either of claims 3 and 9, characterized in that the bridged clays employed are modified by the action of a dihalogen, of an ammonium halide or of an acid such as sulphuric acid or the hydrogen halide acids, the halogen thus optionally introduced being preferably chlorine or fluorine.

11. Process according to claim 3,



characterized in that the solid oxides employed are metal oxides, mixtures of metal oxides or metal oxides which have been modified by the action of a dihalogen, of an ammonium halide or of an acid such as sulphuric acid or the hydrogen halide acids, the halogen thus optionally introduced being preferably chlorine or fluorine.

12. Process according to either of claims 3 and 11, characterized in that the solid oxides employed are chosen from the mixtures $\text{SiO}_2/\text{Al}_2\text{O}_3$, $\text{SiO}_2/\text{Ga}_2\text{O}_3$, $\text{SiO}_2/\text{Fe}_2\text{O}_3$, $\text{SiO}_2/\text{B}_2\text{O}_3$, halogenated aluminas such as chlorinated aluminas and fluorinated aluminas, sulphated zirconia, niobium oxide or tungsten oxide.

13. Process according to claim 3, characterized in that the acidic phosphates are chosen from boron phosphates, by themselves or mixed with alumina or with silica, corresponding to different $\text{H}_3\text{BO}_3/\text{H}_3\text{PO}_4$ molar ratios introduced during the synthesis, lanthanum phosphate, aluminium phosphates corresponding to different $\text{Al}_2\text{O}_3/\text{H}_3\text{PO}_4$ molar ratios introduced during the synthesis, phosphorus pentoxide/silica mixtures (usually called UOP catalysts), aluminophosphates with a zeolite structure (AlPO) and silicoaluminophosphates with a zeolite structure (SAPO).

14. Process according to either of claims 1 and 2, characterized in that the catalyst is a basic solid catalyst chosen from basic metal phosphates, basic metal oxides, metal carbonates and basic



molecular sieves.

15. Process according to claim 14, characterized in that the basic metal phosphates are more particularly the phosphates of general formula

5 (III):



in which:

- A denotes a metal atom, a group of metal atoms or partially a hydrogen atom;
- 10 - y denotes a whole or fractional number from 3/4 to 3 depending on the valency of the elements A;
- Imp corresponds to a basic impregnating compound consisting of metal chosen from the alkaline-earth metals, the alkali
- 15 metals and their mixtures used in combination with a counteranion to ensure electrical neutrality;
- the coefficient z denotes the weight
- 20 ratio of the impregnant to the impregnated material (A_yPO_4) and is between 0 % and 20 % and preferably between 2 % and 10 %.

16. Process according to either of claims 14 and 15, characterized in that the basic metal phosphates are more particularly the phosphates of general formula (III):





in which:

- A denotes more particularly calcium, zirconium, lanthanum, cerium, samarium, aluminium, boron, iron and partially hydrogen;
- y denotes a whole or fractional number from $3/4$ to 3 depending on the valency of the elements A;
- Imp consists of an alkali metal or of a mixture of alkali metals and of a basic counteranion;
- the coefficient z is between 2 % and 10 %.

17. Process according to one of claims 14 to 16, characterized in that the basic metal phosphates are more particularly lanthanum phosphate used in combination with a caesium, rubidium or potassium compound, cerium phosphate used in combination with a caesium, rubidium or potassium compound, samarium phosphate used in combination with caesium, rubidium or potassium compound, calcium phosphate used in combination with a caesium, rubidium or potassium compound, calcium hydrogenphosphate used in combination with a caesium, rubidium or potassium compound, or zirconium hydrogenphosphate used in combination with a caesium, rubidium or potassium compound.

18. Process according to one of claims 14 to 17, characterized in that the basic metal phosphates



are prepared by impregnating a compound of formula (IV) A'_yPO_4 , in which A' has the same meanings as A , with a solution or a suspension of Imp in a volatile solvent such as preferably water.

5 19. Process according to one of claims 14 to 18, characterized in that the basic metal phosphates are prepared by a process which consists :

 a) in carrying out the synthesis of the compound A'_yPO_4 ; then preferably without isolating A'_yPO_4 ,
10 from the reaction mixture;

 b) in introducing the impregnant Imp into the reaction mixture;

 c) in separating any residual liquid from the reaction solid;

15 d) in drying and optionally in calcining.

 20. Process according to claim 14, characterized in that the basis metal oxides are more particularly the oxides of a basic nature or those which are made basic by a treatment with the aid of a
20 base such as an alkali metal or alkaline-earth metal hydroxide.

 21. Process according to one of claims 14 and 20, characterized in that the basis metal oxides are chosen from the oxides of the alkali metals, of
25 alkaline-earth metals, of metals of group IIIa of the Periodic Classification of the elements, of transition elements or of rare earths, treated or untreated with an alkali metal hydroxide.



22. Process according to claim 14,
characterized in that the basic molecular sieves are
more particularly the zeolites of pentasil structure
such as ZSM-5, ZSM-11, ZSM-22, ZSM-23 or ZSM-48, of
5 mordenite structure, of ferrierite structure or of
faujasite structure, such as zeolite X or zeolite Y, of
general formula (V) expressed in terms of oxides:



in which:

- 10 - E denotes an alkali or alkaline-earth
metal, completely or with a small
proportion of hydrogen,
- T denotes a trivalent metal chosen from
Al, Ga, Fe and B,
- 15 - a denotes a number from 1 to 2,
- b denotes a number equal to or greater
than 2,
- r denotes a number from 0 to 100.

23. Process according to claim 14,
20 characterized in that the basic molecular sieves are
more particularly the zeolites ZSM-5, ZSM-11, ZSM-22,
ZSM-23 and ZSM-48, mordenites, ferrierites and
faujasites such as zeolite X and zeolite Y.

24. Process according to either of claims 1
25 and 2, characterized in that the catalyst is an
amphoteric solid catalyst chosen from amphoteric metal
oxides.

25. Process according to claim 24,



characterized in that the amphoteric metal oxides are oxides of an amphoteric nature or those which are made amphoteric by their method of preparation or by a subsequent treatment, such as thoria (ThO_2), zirconia
5 (ZrO_2), titanium dioxide (TiO_2), ceria (CeO_2), silica (SiO_2), alumina (Al_2O_3) and mixtures of a number of these oxides.

26. Process according to one of claims 1 to 25, characterized in that it is used at a temperature
10 of 200°C to 500°C and preferably from 250°C to 400°C .

27. Process according to one of claims 1 to 26, characterized in that 2-pentenoic acid is introduced by itself into the reactor containing the catalyst.

15 28. Process according to one of claims 1 to 26, characterized in that 2-pentenoic acid is introduced together with an inert carrier gas which consists of a gas or a mixture of gases which are inert under the reaction conditions, such as nitrogen, argon,
20 air, steam or carboxylic acids which are gaseous at the temperature at which the reaction is operated.

29. Process according to either of Claims 27 and 28, characterized in that 2-pentenoic acid represents from 10 % to 100 % by weight relative to the
25 total weight of the gases introduced into the reaction, and preferably from 40 % to 100 %.