

PROCESS FOR ISOMERIZATION OF LACTONES TO
PENTENOIC ACIDS BY ACIDIC OR BASIC CATALYSIS

The present invention relates to a process for isomerization of lactones, more particularly of
5 different valerolactones and their isomers, to pentenoic acids.

Hydroxycarbonylation of 3-pentenoic acid to prepare adipic acid always results in the formation of gamma-valerolactone as byproduct.

10 The conversion of gamma-valerolactone (or 4-methylbutyrolactone) into a valuable product therefore presents a considerable problem to be solved within the scope of a possible industrial process for the preparation of adipic acid by hydroxycarbonylation
15 of 3-pentenoic acid.

One of the methods that can be envisaged for conversion into a valuable product consists in trying to carbonylate gamma-valerolactone. Thus, Patent EP-A-0 395 038 describes this carbonylation, at a
20 temperature higher than or equal to 190°C and in the presence of rhodium/HI or rhodium/HBr.

This process is relatively selective for adipic acid, but with the formation of valeric acid; but the production efficiency of adipic acid is low,
25 despite a high rhodium concentration.

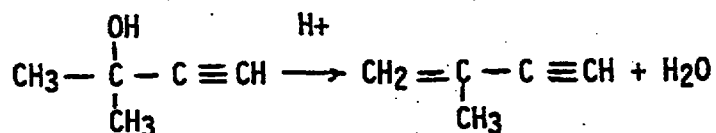
The problem of increasing the efficiency of a 3-pentenoic acid hydroxycarbonylation process by the conversion of gamma-valerolactone into compounds that

can be profitably exploited has therefore not found any satisfactory solution.

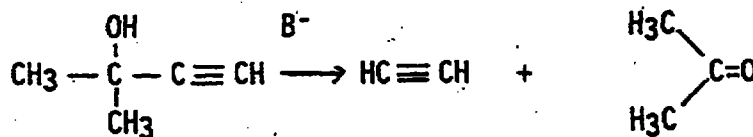
The present invention proposes to solve precisely this problem by permitting the isomerization of gamma-valerolactone or of its isomers to pentenoic acids, which can be hydroxycarbonylated again to adipic acid.

It consists of a process for isomerization of at least one lactone containing 5 carbon atoms to pentenoic acid, characterized in that the said lactone in vapour phase is placed in contact with an acidic or basic solid catalyst.

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:



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:



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

5 The lactones which can be employed in the process of the invention are more particularly gamma-valerolactone (or 4-methylbutyrolactone), delta-valerolactone, 2-methylbutyrolactone, 3-ethylpropiolactone, 2-ethylpropiolactone and 2,3-dimethylpropiolactone.

10 Among these lactones, gamma-valerolactone is the most advantageous one because of its formation in the processes of hydroxycarbonylation of 3-pentenoic acid to adipic acid.

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

20 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.

25 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 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 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.

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 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, 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).

10 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.

15 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_yPO_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:

- 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 %.

By way of nonlimiting examples of basic phosphates there may be mentioned 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 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

5 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
10 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
15 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
20 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
25 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
 5 formula (V) expressed in terms of oxides:



in which:

- E denotes an alkali or alkaline-earth metal, completely or with a small
 10 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
 15 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
 20 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.

25 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 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
5 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
10 volume of catalyst to the total gas flow rate (lactone + 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
15 situated from atmospheric pressure to 10 MPa (100 bar) and preferably from atmospheric pressure to 1.5 MPa (15 bar).

The lactone can be introduced by itself into the reactor containing the catalyst.

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

The lactone represents from 10 % to 100 % by weight relative to the total weight of the gases introduced into the reaction, and preferably from 40 % to 100 %.

5 The process of the invention generally results in the formation of a mixture of pentenoic acids, 2-pentenoic acid, 3-pentenoic acid and 4-pentenoic acid.

10 3-Pentenoic and 4-pentenoic acids can be hydroxycarbonylated to adipic acid by reaction with carbon monoxide and water.

2-Pentenoic acid itself can be isomerized to 3-pentenoic and 4-pentenoic acids which can be directly used profitably as indicated above.

15 Since the isomerization reaction according to the invention is a thermodynamically difficult reaction, the degree of conversion of the lactone will in practice be generally limited to less than 80 % and in most cases less than 60 %, it then being possible
20 for the unconverted lactone to be easily recycled.

The examples which follow illustrate the invention.

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

25 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 with glass beads (diameter: 2 to 3 mm).

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

The lactone is then injected by means of a syringe driver.

10 The injection rates of the lactone will be stated for each example: they are expressed in cm^3 (ml) of lactone in the liquid state.

After establishing a steady state for approximately 15 minutes, the test generally lasts 1
15 hour. The products leaving the reactor are trapped in a receiver containing 10 cm^3 of acetonitrile.

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

20 The following are calculated for each test:

- the hourly weight production efficiency (HWE): weight of lactone introduced relative to the weight of the catalyst and per hour (expressed in h^{-1});
- 25 - the degree of conversion (DC) of the lactone; % of the lactone converted relative to the lactone introduced;
- the yields (RY) of the various pentenoic

acids: mol% of each pentenoic acid
formed relative to the lactone
introduced.

EXAMPLES 1 TO 7 (substrate: gamma-valerolactone)

5 Tests of different zeolites of type ZSM-5 of
general formula (I) exhibiting different Si/Al molar
ratios and more or less acidified:

- zeolite 1: Si/Al = 30
75 % of the elements M in the
10 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
15 75 % of the elements M in the
formula (I) are H,

- zeolite 4: Si/Al = 30
M in formula (I) represents
predominantly NH_4 and a
20 minority of H,

- zeolite 5: Si/Al = 50

- zeolite 6: Si/Al = 120
M in formula (I) represents
predominantly NH_4 and a
25 minority of H,

- zeolite 7: Si/Al = 50
M in formula (I) represents
entirely H.

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

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

5 The results obtained are collated in Table 1 below.

The abbreviations P2, P3 and P4 which are employed have the following meanings:

P2 = 2-pentenoic acid

10 P3 = 3-pentenoic acid

P4 = 4-pentenoic acid

15

EXAMPLES	CATALYST	DC %	RY %			HWE (h ⁻¹)
			P4	P3	P4	
Example 1	Zeolite 1	14	2	8	3	6.9
Example 2	Zeolite 2	22	2	10	5	3.9
Example 3	Zeolite 3	9	2	5	1	4.9
Example 4	Zeolite 4	10	2	7	3	4.2
Example 5	Zeolite 5	18	3	9	4	2.7
Example 6	Zeolite 6	15	2	9.5	3.5	3.1
Example 7	Zeolite 7	21	2.5	10.5	4.5	3.3

20

TABLE 1

EXAMPLES 8 TO 15 (substrate: gamma-valerolactone)

Tests of various acidic catalysts:

- $\text{SiO}_2/\text{Al}_2\text{O}_3$ (marketed by Degussa)
containing 16 % by weight of SiO_2 ,
- 5 - zeolite Y which has an $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio
of 5 (marketed by Toyo Soda),
- BPO_4 (B/P ratio = 1),
- LaPO_4 ,
- Montmorillonite Volclay clay (Montmo),
- 10 - zeolite of ZSM-5 type of formula (I)
with X denoting Fe and with an $\text{SiO}_2/\text{Fe}_2\text{O}_3$
ratio = 120 (ZSM-5/Fe),
- chlorinated Al_2O_3 ,
- niobium oxide.

15 The operating conditions are those described
above. The reaction period is 1 hour with the exception
of Example 14 with chlorinated alumina where this
period is 0.5 h, the temperature may be other than
300°C, the nitrogen flow rate may be other than
20 2 litres/hour and the rate of introduction of
gamma-valerolactone 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	Temperature in °C	N ₂ flow rate l/h	Lactone flow rate ml/h	DC %	RY %			t _c (s)	HWE (h ⁻¹)
						P4	P3	P2		
Example 8	SiO ₂ /Al ₂ O ₃	300	2	3.2	9	2	6	3	1.4	4.1
Example 9	Zeolite Y	300	2	3.2	8	2	5	2	1.4	4.6
Example 10	BPO ₄	300	2	3.2	5	2	5	2	1.4	2.1
Example 11	LaPO ₄	300	2	3.2	38	2	9	6	1.4	1.9
Example 12	Montmo	275	2	3.2	4.5	1	3.5	0	1.4	1.9
Example 13	ZSM-5/Fe	300	2	6.4	10.5	2	6	2.5	1.0	6.1
Example 14	Chlorinated Al ₂ O ₃	380	0.45	9.6	11.5	4	4.5	2.5	1.1	10.6
Example 15	Nb oxide	380	2	3.2	39	5	9	5	1.1	2.0

TABLE 2

EXAMPLE 16 (substrate: delta-valerolactone)

Tests on zeolite Y exchanged with Fe
($\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio = 5 and $M = \text{Fe}$).

The operating conditions are those described
5 previously in the general operating method, with the
following differences:

- reaction temperature: 370°C
- catalyst volume: 1.5 cm³
- N₂ flow rate: 3 l/h
- 10 - lactone flow rate: 3.2 ml/h.

The following results are obtained:

	DC of the lactone:	10 %
	P ₂ RY:	4.3 %
	P ₃ RY:	0 %
15	P ₄ RY:	1.3 %
	Tc:	0.8 s
	HWE:	7.3 h ⁻¹ .

EXAMPLES 17 TO 20 (Substrate: gamma-valerolactone)

Tests of various basic solid catalysts:

- 20 - Ce phosphate doped with 3 % of Cs
hydrogenphosphate
- Ca hydrogenphosphate (hydroxyapatite)
- zeolite 13XCs
- alumina treated with sodium hydroxide
- 25 (10 % of sodium hydroxide on weight per
weight basis) (value of 4 cm³ instead of
2 cm³).

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.

EXAMPLES 21 TO 24 (substrate: gamma-valerolactone)

Tests on La phosphate used in combination with various impregnants (the percentage of impregnant in relation to La phosphate is expressed as weight per weight).

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

The results obtained are collated in Table 4 below together with the values of the reaction temperature and the injection flow rate of the lactone.

Examples	Catalyst	Temperature in °C	N ₂ flow rate l/h	Lactone flow rate ml/h	DC %	RY %			tc (s)	HWE (h ⁻¹)
						P4	P3	P2		
Example 17	CePO ₄ , CsHPO ₄ 3 % by weight	300	2	3.2	11	3	4	3	1.3	1.5
Example 18	Hydroxyapatite	380	1	6.4	14	5	2.5	1.5	1.2	13.9
Example 19	Zeotite 13XCs	300	2	3.2	29	2.5	5	3.5	1.3	2.2
Example 20	Alumina treated with NaOH	320	1	1.6	20	3.5	3	2	5.1	0.6

TABLE 3

Examples	Catalyst	Temperature in °C	Lactone flow rate l/h	DC %	RY %			tc (s)	HWE (h ⁻¹)
					P4	P3	P2		
Example 21	LaPO ₄ , 3 % Na ₂ HPO ₄	300	3.2	4	3	2	1	1.4	1.8
Example 22	LaPO ₄ , 3 % Cs ₂ HPO ₄	300	3.2	8	3	3	2	1.4	2.2
Example 23	LaPO ₄ , 3 % KH ₂ PO ₄	300	3.2	20	3	7	5	1.4	1.5
Example 24	LaPO ₄ , 3 % Rb ₂ CO ₃	300	3.2	11	3	5	3	1.4	1.6

TABLE 4

CLAIMS

1. Process for isomerization of at least one lactone containing 5 carbon atoms to pentenoic acid, characterized in that the said lactone in vapour
5 phase is placed in contact with an acidic or basic solid catalyst.

2. Process according to claim 1, characterized in that the lactone is chosen from gamma-valerolactone (or 4-methylbutyrolactone),
10 delta-valerolactone, 2-methylbutyrolactone, 3-ethylpropiolactone, 2-ethylpropiolactone and 2,3-dimethylpropiolactone.

3. Process according to either of claims 1 and 2, characterized in that the catalyst is an acidic
15 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
20 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
25 pentasil or mordenite structure are zeolites of ZSM-5, ZSM-11, ZSM-22, ZSM-3 and ZSM-48 or 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.

6. Process according to claim 3,
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:



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 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
5 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 $\text{SiO}_2/\text{Al}_2\text{O}_3$, $\text{SiO}_2/\text{Ga}_2\text{O}_3$,
10 $\text{SiO}_2/\text{Fe}_2\text{O}_3$, $\text{SiO}_2/\text{B}_2\text{O}_3$, 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
15 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
20 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
25 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
(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
10 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 ratio of the impregnant to the
20 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
25 phosphates are more particularly the phosphates of general formula (III):



in which:



* C L M S *

- A denotes more particularly calcium, zirconium, lanthanum, cerium, samarium, aluminium, boron, iron and partially hydrogen;
- 5 - 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;
- 10 - 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
15 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 a caesium, rubidium
20 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
25 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.

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 from the reaction mixture:
- 10 b) in introducing the impregnant Imp into the reaction mixture;
- c) in separating any residual liquid from the reaction solid;
- d) in drying and optionally in calcining.

15 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 base such as an alkali metal or alkaline-earth metal
20 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 alkaline-earth metals, of metals of group IIIa of the
25 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 mordenite structure, of ferrierite structure or of
 5 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
 10 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,
- 15 - b denotes a number equal to or greater than 2,
- r denotes a number from 0 to 100.

23. Process according to claim 14,
 characterized in that the basic molecular sieves are
 20 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 one of claims 1 to 23, characterized in that it is used at a temperature
 25 of 200°C to 500°C and preferably from 250°C to 400°C.

25. Process according to one of claims 1 to



26. Process according to one of claims 1 to 24, characterized in that the lactone 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, air, steam or carboxylic acids which are gaseous at the temperature at which the reaction is operated.

27. Process according to either of Claims 25 and 26, characterized in that the lactone represents from 10 % to 100 % by weight relative to the total weight of the gases introduced into the reaction, and preferably from 40 % to 100 %.

