

MICROPOROUS CRYSTALLINE MATERIAL, ZEOLITE ITQ-33,
METHOD OF PREPARATION AND USE

5

Field of technology

The present application relates to a novel microporous crystalline material, ITQ-33, to the method of preparation thereof and to its use in the catalytic
10 conversion of organic compounds.

Background

The zeolites are porous crystalline aluminosilicates that have found important applications as catalysts,
15 adsorbents and ion exchangers. Many of these zeolitic materials have well-defined structures that form channels and cavities within them of uniform size and shape that allow certain molecules to be adsorbed, whereas they prevent other molecules, that are too
20 large to diffuse through the pores, from passing through to the interior of the crystal. This characteristic endows these materials with molecular sieve properties. The lattice of these molecular sieves can incorporate Si and other elements of group IIIA of
25 the periodic table, all of them in tetrahedral coordination, with the tetrahedra joined at their vertices via oxygen atoms, forming a three-dimensional network. The negative charge generated by the group IIIA elements at lattice sites is compensated by the
30 presence of cations in the crystal, for example cations of alkali metals or alkaline earth metals. A cation of one type can be exchanged totally or partially by cations of another type by techniques of ion exchange, so that the properties of a given silicate can be
35 varied by selecting the desired cations.

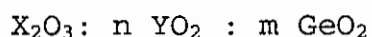
Many zeolites have been synthesized in the presence of an organic molecule that acts as a structure-controlling agent. The organic molecules that act as

structure-controlling agents (SCAs) generally include nitrogen in their composition, and can give rise to organic cations that are stable in the reaction mixture.

- 5 Mobilization of silica can be accomplished in the presence of OH⁻ groups and a basic medium, which can be introduced as the hydroxide of said SCA, for example tetrapropylammonium hydroxide in the case of zeolite ZSM-5.

10 Description of the invention

The present invention relates to a novel microporous crystalline material ITQ-33, which in its calcined form has a chemical composition represented by the formula:



- 15 in which (n + m) is at least 5, X is a trivalent element, Y represents one or more tetravalent elements other than Ge, and the ratio Y/Ge is greater than 1, and it has an X-ray diffraction pattern with the following principal lines for its uncalcined
20 synthesized form:

(d ± 0.2) (Å)	Relative intensity
16.59	vs
11.63	vw
9.57	vw
8.31	vw
6.76	vw
4.81	vw
4.62	vw
4.27	w
3.64	w
3.15	w

where "vs" denotes relative intensity 80-100, "w" denotes relative intensity 20-40 and "vw" denotes relative intensity 0-20, calculated as a percentage relative to the peak with greatest intensity.

- 5 The novel porous crystalline material can therefore be obtained in the absence of germanium.

This novel material, designated ITQ-33, both in its calcined form and uncalcined synthesized form, has an X-ray diffraction pattern that is different from that
10 of other known zeolitic materials whose most important diffraction lines are given in Table 1 for the calcined form.

Table 1

(d ± 0.2) (Å)	Relative intensity
16.81	vs
11.50	vw
9.71	vw
8.41	vw
6.79	vw
4.84	vw
4.65	vw
4.24	vw
4.01	vw
3.84	w
3.81	vw
3.66	vw
3.36	w
3.17	vw
2.81	vw
2.56	vw
2.37	vw
2.27	vw

The interplanar spacings, d , were calculated in angstroms, and the relative intensity of the lines is calculated as a percentage relative to the peak of highest intensity, and is regarded as very strong (vs)=80-100, strong (s)=60-80, medium (m)=40-60, weak (w)=20-40, and very weak (vw)=0-20.

Preferred embodiments of ITQ-33 have, in their uncalcined form, the diffraction lines shown in Table 2.

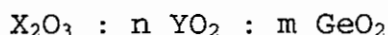
10 Table 2

$(d \pm 0.2)$ (Å)	Relative intensity
16.59	vs
11.63	vw
9.57	vw
8.31	vw
6.76	vw
4.81	vw
4.62	vw
4.27	w
4.02	vw
3.86	vw
3.82	vw
3.64	w
3.33	vw
3.15	w
2.78	vw
2.75	vw
2.54	vw
2.38	vw
2.27	vw

These diffraction patterns were obtained with a Philips X'Pert diffractometer equipped with a graphite monochromator and an automatic divergence slit using

copper K_{α} radiation. The diffraction data were recorded with a step 2θ of 0.01° where θ is the Bragg angle and a count time of 10 seconds per step. The interplanar spacings, d , were calculated in angstroms, and the
5 relative intensity of the lines is calculated as a percentage relative to the peak of highest intensity, and is regarded as very strong (vs)=80-100, strong (s)=60-80, medium (m)=40-60, weak (w)=20-40, and very weak (vw)=0-20.

- 10 It must be taken into account that the diffraction data listed for this sample as single or unique lines may be formed by multiple overlaps or superposition of reflections which, in certain conditions, such as differences in crystallographic changes, may appear as
15 resolved or partially resolved lines. Generally, the crystallographic changes may include small variations in the parameters of the unit cell and/or changes in crystal symmetry, without producing a change in the structure. These modifications, which also include
20 changes in relative intensities, may also be due to differences in the type and quantity of compensating cations, lattice composition, crystal size and habit, preferential orientation or the type of thermal or hydrothermal treatments that have been carried out.
- 25 The crystalline material preferably has, in its anhydrous, calcined form, a composition represented by:



- in which $(n+m)$ is at least 5, and the value of n/m is at least 1, X represents one or more trivalent elements
30 selected from the group comprising Al, B, In, Ga, Fe and Cr; and Y represents one or more tetravalent elements selected from Si, Sn, Ti, V.

In an especially preferred embodiment, the crystalline material has the formula stated previously in calcined

form, in which X is selected from B, Al and a mixture of the two; and Y is Si.

It is clear from the values given that the crystalline material ITQ-33 can be synthesized in the absence of
5 added trivalent elements.

The organic component of the material as synthesized can be removed, for example by extraction or by thermal treatment by heating to a temperature above 250°C for a period of time between 2 minutes and 25 hours.

10 The compensating cations in the material in its uncalcined form, or after thermal treatment, can be replaced, if they are present, by other cations such as metal ions, H^+ and precursors of H^+ , for example NH_4^+ . Among the cations that can be introduced by ion
15 exchange, those are preferred that can have a positive effect on the activity of the material as a catalyst, and more specifically cations such as H^+ , cations of rare earths, and metals of group VIII, as well as of group IIA, IIIA, IVA, VA, IB, IIB, IIIB, IVB, VB, VIIB
20 of the periodic table of the elements, are preferred.

The crystalline material of the present invention can also be combined intimately with hydrogenating-dehydrogenating components such as platinum, palladium, nickel, rhenium, cobalt, tungsten, molybdenum,
25 vanadium, chromium, manganese, iron and combinations thereof. Introduction of these elements can take place in the crystallization stage, by exchange (if it occurs), and/or by impregnation, or by physical mixing. These elements can be introduced in their cationic form
30 and/or from salts or other compounds which, on decomposition, generate the metallic or oxide component in its appropriate catalytic form.

The present invention also relates to a method of preparation of the crystalline material defined

previously, comprising at least:

- preparing a synthesis mixture that comprises at least H_2O , a source of one or more tetravalent elements Y and an organic compound as structure-controlling agent (R),
- 5 - holding the synthesis mixture at a temperature between 80 and 200°C until the crystals of the porous crystalline material form; and
- recovering the crystalline material.

10 According to a preferred embodiment, the method of preparation of the crystalline material defined previously comprises at least:

- preparing a synthesis mixture that comprises at least:
 - H_2O ,
 - 15 - an oxide of one or more tetravalent elements Y,
 - and an organic compound as structure-controlling agent (R),

with molar ratios of oxides:

$H_2O/(YO_2)$	1-50
$R/(YO_2)$	0.1-3.0

20

- holding the synthesis mixture at a temperature between 80 and 200°C until the crystals of the porous crystalline material form; and

- recovery of the crystalline material.

In this embodiment, and especially preferably, the molar ratios of oxides are:

$$\text{H}_2\text{O}/(\text{YO}_2) \quad 2-20$$

$$\text{R}/(\text{YO}_2) \quad 0.1-1.0$$

- 5 A further preferred embodiment of the method comprises:

- preparing a synthesis mixture that comprises at least H_2O , a source of one or more tetravalent elements Y, a source of Ge and an organic compound as structure-controlling agent (R),
- 10 - holding the synthesis mixture at a temperature between 80 and 200°C until the crystals of the porous crystalline material form; and
- recovering the crystalline material.

- 15 According to a preferred embodiment, the method of preparation of the crystalline material defined previously comprises at least:

- preparing a synthesis mixture that comprises at least:
 - H_2O ,
- 20 - an oxide of one or more tetravalent elements Y,
- oxide of Ge,
 - and an organic compound as structure-

controlling agent (R),

with molar ratios of oxides:

$H_2O/(YO_2 + GeO_2)$	1-50
$R/(YO_2 + GeO_2)$	0.1-3.0
YO_2/GeO_2	greater than 1

5 - holding the synthesis mixture at a temperature between 80 and 200°C until the crystals of the porous crystalline material form; and

- recovery of the crystalline material.

In this embodiment, and especially preferably, the molar ratios of oxides are:

$H_2O/(YO_2 + GeO_2)$	2-20
$R/(YO_2 + GeO_2)$	0.1-1.0
YO_2/GeO_2	greater than 1

10

Another additional preferred embodiment of the method comprises at least:

15 - preparing a synthesis mixture that comprises at least H_2O , a source of one or more trivalent elements X; a source of one or more tetravalent elements Y and an organic compound as structure-controlling agent (R),

- holding the synthesis mixture at a temperature between 80 and 200°C until the crystals of the porous

crystalline material form; and

- recovery of the crystalline material.

Another additional preferred embodiment of the method comprises at least:

- 5 - preparing a synthesis mixture that comprises at least H_2O , an oxide of one or more trivalent elements X; an oxide of one or more tetravalent elements Y and an organic compound as structure-controlling agent (R), with molar ratios of oxides:

YO_2/X_2O_3 at least 5

H_2O/YO_2 between 1 and 50

R/YO_2 between 0.1 and 3.0

10

- holding the synthesis mixture at a temperature between 80 and 200°C until the crystals of the porous crystalline material form; and

- recovery of the crystalline material.

- 15 According to the preceding embodiment, the preferred molar ratios of oxides are:

YO_2/X_2O_3 greater than 7

H_2O/YO_2 between 2 and 20

R/YO_2 between 0.1 and 1.0

Another preferred additional embodiment of the method

comprises:

- preparing a synthesis mixture that comprises at least H₂O, a source of one or more trivalent elements X; a source of one or more tetravalent elements Y, oxide of Ge, and an organic compound as structure-controlling agent (R),
- holding the synthesis mixture at a temperature between 80 and 200°C until the crystals of the porous crystalline material form; and
- 10 - recovery of the crystalline material.

A further preferred embodiment of the method comprises:

- preparing a synthesis mixture that comprises at least H₂O, an oxide of one or more trivalent elements X; an oxide of one or more tetravalent elements Y, oxide of Ge, and an organic compound as structure-controlling agent (R), with molar ratios of oxides:

$$(Y\text{O}_2 + \text{GeO}_2)/X_2\text{O}_3 \quad \text{greater than 5}$$

$$\text{H}_2\text{O}/(Y\text{O}_2 + \text{GeO}_2) \quad \text{between 1 and 50}$$

$$\text{R}/(Y\text{O}_2 + \text{GeO}_2) \quad \text{between 0.1 and 3.0}$$

$$Y\text{O}_2/\text{GeO}_2 \quad \text{greater than 1}$$

- holding the synthesis mixture at a temperature between 80 and 200°C until the crystals of the porous crystalline material form; and
- 20 - recovery of the crystalline material.

According to this embodiment, the molar ratios of

oxides are preferably:

$(\text{YO}_2 + \text{GeO}_2) / \text{X}_2\text{O}_3$ greater than 7

$\text{H}_2\text{O} / (\text{YO}_2 + \text{GeO}_2)$ between 2 and 20

$\text{R} / (\text{YO}_2 + \text{GeO}_2)$ between 0.1 and 1.0

$\text{YO}_2 / \text{GeO}_2$ greater than 1

In any embodiment of the method of the present invention, crystals of zeolite ITQ-33 (up to 20 wt.%),
5 which act as seed crystals, can be added to the synthesis mixture.

In any embodiment of the method of the present invention the organic compound used as structure-controlling agent is preferably selected from an amine
10 and a tetraalkylammonium salt, preferably the hydroxide.

The method of the present invention, when production of the calcined crystalline material is intended, comprises a stage of removal of the organic matter
15 trapped within the material, which can be carried out by extraction and/or thermal treatment at temperatures above 250°C for a period of time between 2 minutes and 25 hours.

According to a further preferred embodiment of the
20 method of the present invention, it comprises:

- preparing a synthesis mixture that comprises at least H_2O , an oxide of one or more trivalent elements X selected from Al, B and a mixture of the two, an oxide of Si, oxide of Ge, a hexamethonium salt as R, with
25 molar ratios of oxides:

$(\text{SiO}_2 + \text{GeO}_2)/\text{X}_2\text{O}_3$ at least 5

$\text{H}_2\text{O}/(\text{SiO}_2 + \text{GeO}_2)$ between 1 and 50

$\text{R}/(\text{SiO}_2 + \text{GeO}_2)$ between 0.1 and 3.0

$\text{SiO}_2/\text{GeO}_2$ greater than 1

- holding the synthesis mixture at a temperature between 80 and 200°C until the crystals of the porous crystalline material form; and

5 - recovery of the crystalline material.

The crystallization of ITQ-33 can be carried out in static conditions or with stirring, in autoclaves at a temperature between 80 and 200°C, for times sufficient to achieve crystallization, for example between 12
10 hours and 60 days.

On completion of the crystallization stage, the crystals of ITQ-33 are separated from the mother liquor, and are recovered. It must be borne in mind that the components of the synthesis mixture can come
15 from different sources, and the crystallization times and conditions can vary depending on these. For the purpose of facilitating synthesis, crystals of ITQ-33 can be added as seeds, in amounts of up to 20 wt.% relative to the total of oxides, to the synthesis
20 mixture. These can be added before or during crystallization of ITQ-33.

The material produced by means of this invention can be pelletized in accordance with known techniques, and can be used in catalytic cracking of hydrocarbons,
25 catalytic hydrocracking of hydrocarbons, alkylation of aromatics with olefins and in processes of

esterification, acylation, reaction of aniline with formaldehyde in its acid form and/or exchange with suitable cations. Preferably the material is present as a component of other catalysts.

- 5 The present invention further relates to a method of converting feeds formed from organic compounds, characterized in that it comprises bringing said feed into contact with an active form of the porous crystalline material of the invention.
- 10 Preferably said method is selected from catalytic cracking of hydrocarbons, catalytic hydrocracking of hydrocarbons, alkylation of aromatics with olefins, esterification, acylation and reaction of aniline with formaldehyde, and comprises the pelletization of the
- 15 material in a form selected from its acid form, exchange with cations and a combination of the two. Even more preferably, said material is present as a component of catalysts.

EXAMPLES

20 Example 1: Synthesis of ITQ-33

- Dissolve 0.174 g of GeO_2 in 0.373 g of a solution of hexamethonium hydroxide (16.3 wt.%) and 0.843 g of solution of hexamethonium bromide (50 wt.%). Add 6.8 mg of Al_2O_3 and 0.533 g of Ludox AS-40 to the previous
- 25 solution, leaving the synthesis mixture to evaporate while stirring until the final composition is reached:

$0.68 \text{ SiO}_2 : 0.32 \text{ GeO}_2 : 0.019 \text{ Al}_2\text{O}_3 : 0.10 \text{ R(OH)}_2 : 0.16$
 $\text{R(Br)}_2 : 2.63 \text{ H}_2\text{O}$

where R is hexamethonium.

- 30 Heat the gel for 4 days in Teflon-lined steel autoclaves at 175°C in static conditions. The solid obtained after filtration, washing with distilled water and drying at 100°C is ITQ-33.

Calcine the material at 540°C for 3 hours in an air stream to remove the organic matter. The X-ray powder diffraction pattern of the solid obtained coincides with the values in Table 1.

5 Example 2:

Dissolve 0.174 g of GeO_2 in 0.353 g of a solution of hexamethonium hydroxide (16.6 wt.%) and 0.895 g of solution of hexamethonium bromide (50 wt.%). Add 7.3 mg of Al_2O_3 and 0.542 g of Ludox AS-40 to the previous
10 solution, stirring the synthesis mixture until the following composition is reached by evaporation:

0.68 SiO_2 : 0.32 GeO_2 : 0.020 Al_2O_3 : 0.09 R(OH)_2 : 0.17
 R(Br)_2 : 2.3 H_2O

where R is hexamethonium.

15 Heat the gel for 14 days in Teflon-lined steel autoclaves at 175°C in static conditions. The solid obtained after filtration, washing with distilled water and drying at 100°C is ITQ-33.

Example 3:

20 Dissolve 0.174 g of GeO_2 in 0.359 g of solution of hexamethonium hydroxide (16.3 wt.%) and 0.824 g of solution of hexamethonium bromide (50 wt.%). Add 0.151 g of solution of H_3BO_3 (5 wt.%) and 0.497 g of Ludox AS-40 to the solution obtained, and leave to
25 evaporate, while stirring, until the synthesis mixture reaches the composition:

0.66 SiO_2 : 0.34 GeO_2 : 0.025 B_2O_3 : 0.10 R(OH)_2 : 0.16
 R(Br)_2 : 3.13 H_2O

where R is hexamethonium.

30 Heat the gel for 5 days in Teflon-lined steel autoclaves at 175°C in static conditions. The solid

obtained after filtration, washing with distilled water and drying at 100°C is zeolite ITQ-33.

Example 4:

5 Dissolve 0.174 g of GeO_2 in 0.381 g of solution of hexamethonium hydroxide (15.4 wt.%) and 0.854 g of solution of hexamethonium bromide (50 wt.%). Add 7.0 mg of Al_2O_3 and 0.516 g of Ludox AS-40 to the solution obtained, and leave to evaporate, while stirring, until the mixture reaches the composition:

10 $0.67 \text{ SiO}_2 : 0.33 \text{ GeO}_2 : 0.020 \text{ Al}_2\text{O}_3 : 0.10 \text{ R(OH)}_2 : 0.17 \text{ R(Br)}_2 : 1.91 \text{ H}_2\text{O}$

where R is hexamethonium.

Heat the gel for 8 days in Teflon-lined steel autoclaves at 175°C in static conditions. The solid
15 obtained after filtration, washing with distilled water and drying at 100°C is zeolite ITQ-33.

Example 5:

Dissolve 0.174 g of GeO_2 in 0.384 g of a solution of hexamethonium hydroxide (15.4 wt.%) and 0.897 g of
20 solution of hexamethonium bromide (50 wt.%). Add 11.2 mg of Al_2O_3 and 0.515 g of Ludox AS-40 to the previous solution, and leave the mixture to evaporate, while stirring, until the final composition is reached:

$0.67 \text{ SiO}_2 : 0.33 \text{ GeO}_2 : 0.032 \text{ Al}_2\text{O}_3 : 0.10 \text{ R(OH)}_2 : 0.18$
25 $\text{R(Br)}_2 : 2.80 \text{ H}_2\text{O}$

where R is hexamethonium.

Heat the gel for 8 days in Teflon-lined steel autoclaves at 175°C in static conditions. The solid
30 obtained after filtration, washing with distilled water and drying at 100°C is ITQ-33.

Example 6:

Dissolve 0.174 g of GeO_2 in 0.317 g of solution of hexamethonium hydroxide (18.3 wt.%) and 0.830 g of solution of hexamethonium bromide (50 wt.%). Add 6.9 mg
5 of Al_2O_3 and 0.513 g of Ludox AS-40 to the solution obtained, and leave to evaporate, while stirring, until the mixture reaches the composition:

0.67 SiO_2 : 0.33 GeO_2 : 0.020 Al_2O_3 : 0.10 $\text{R}(\text{OH})_2$: 0.16
 $\text{R}(\text{Br})_2$: 2.78 H_2O

10 where R is hexamethonium.

Heat the gel for 25 days in Teflon-lined steel autoclaves at 150°C in static conditions. The solid obtained after filtration, washing with distilled water and drying at 100°C is zeolite ITQ-33.

15 Example 7:

Dissolve 0.176 g of GeO_2 in 0.322 g of solution of hexamethonium hydroxide (18.3 wt.%) and 0.882 g of solution of hexamethonium bromide (50 wt.%). Add 0.122 g of solution of H_3BO_3 (5 wt.%) and 0.525 g of
20 Ludox AS-40. Leave the mixture to evaporate, while stirring, until the reaction mixture reaches a final composition:

0.67 SiO_2 : 0.33 GeO_2 : 0.01 B_2O_3 : 0.10 $\text{R}(\text{OH})_2$: 0.16
 $\text{R}(\text{Br})_2$: 4.2 H_2O

25 where R is hexamethonium.

Heat the gel at 175°C in static conditions for 14 days in Teflon-lined steel autoclaves. The solid obtained after filtration, washing with distilled water and drying at 100°C is a mixture of the phases ITQ-33 and
30 ITQ-24.

Example 8:

Dissolve 0.174 g of GeO_2 in 0.320 g of solution of hexamethonium hydroxide (18.3 wt.%) and 0.823 g of solution of hexamethonium bromide (50 wt.%). Add 0.311 g of solution of H_3BO_3 (5 wt.%) and 0.507 g of Ludox AS-40 to the solution obtained, and leave to evaporate, while stirring, until the mixture reaches the composition:

0.67 SiO_2 : 0.33 GeO_2 : 0.025 B_2O_3 : 0.10 $\text{R}(\text{OH})_2$: 0.15 $\text{R}(\text{Br})_2$: 4.7 H_2O

10 where R is hexamethonium.

Heat the gel for 14 days in Teflon-lined steel autoclaves at 175°C in static conditions. The solid obtained after filtration, washing with distilled water and drying at 100°C is a mixture of the phases ITQ-33 and ITQ-24.

Example 9:

Dissolve 0.105 g of GeO_2 in 0.586 g of solution of hexamethonium hydroxide (17.6 wt.%) and 0.239 g of solution of hexamethonium bromide (50 wt.%). Add 0.010 g of Al_2O_3 and 0.303 g of Ludox AS-40. Finally add 0.332 g of solution of ammonium fluoride (10 wt.%) and leave the mixture to evaporate, while stirring, until the reaction mixture reaches a final composition:

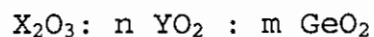
0.67 SiO_2 : 0.33 GeO_2 : 0.025 Al_2O_3 : 0.15 $\text{R}(\text{OH})_2$: 0.10 $\text{R}(\text{Br})_2$: 0.30 NH_4F : 3 H_2O

where R is hexamethonium.

Add 0.018 g of crystals of ITQ-33 and homogenize the mixture. Heat the gel at 175°C in static conditions for 20 hours in Teflon-lined steel autoclaves. The solid obtained after filtration, washing with distilled water and drying at 100°C is ITQ-33.

Patent claims

1. A porous crystalline material, characterized in
5 that it has a chemical composition in the calcined form
represented by the formula:



in which (n + m) is at least 5, X is a trivalent
element, Y represents one or more tetravalent elements
10 other than Ge, and the ratio Y/Ge is greater than 1,
and has a X-ray diffraction pattern whose principal
lines for its uncalcined synthesized form are

(d ± 0.2) (Å)	Relative intensity
16.59	vs
11.63	vw
9.57	vw
8.31	vw
6.76	vw
4.81	vw
4.62	vw
4.27	w
3.64	w
3.15	w

in which "vs" denotes relative intensity 80-100, "w"
15 denotes relative intensity 20-40 and "vw" denotes
relative intensity 0-20, calculated as a percentage
relative to the peak with greatest intensity.

2. The porous crystalline material as claimed in
claim 1, characterized by an X-ray diffraction pattern
20 whose principal lines for its calcined form are:

(d ± 0.2) (Å)	Relative intensity
16.81	vs
11.50	vw
9.71	vw
8.41	vw
6.79	vw
4.84	vw
4.65	vw
4.24	vw
4.01	vw
3.84	w
3.81	vw
3.66	vw
3.36	w
3.17	vw
2.81	vw
2.56	vw
2.37	vw
2.27	vw

where "vs", "w" and "vw" have the meanings stated in claim 1.

5 3. The crystalline material as claimed in one of
 claims 1 or 2, characterized in that X represents one
 or more trivalent elements selected from the group
 comprising Al, B, In, Ga, Fe and Cr; and Y represents
 one or more tetravalent elements selected from Si, Sn,
10 Ti, V.

4. The crystalline material as claimed in claim 3,
 characterized in that X is selected from B, Al and a
 mixture of the two; and Y is Si.

5. A catalyst, characterized in that it comprises

the material as claimed in one of the preceding claims, combined with hydrogenating-dehydrogenating components.

6. The catalyst as claimed in claim 5, characterized in that said hydrogenating-
5 dehydrogenating components are selected from platinum, palladium, nickel, rhenium, cobalt, tungsten, molybdenum, vanadium, chromium, manganese, iron and combinations thereof.

7. A method of synthesis of the crystalline
10 material as claimed in one of claims 1 to 4, characterized in that it comprises at least:

- preparing a synthesis mixture that comprises at least H_2O , a source of one or more tetravalent elements Y and an organic compound as structure-controlling agent (R),
- 15 - holding the synthesis mixture at a temperature between 80 and 200°C until the crystals of the porous crystalline material form; and
- recovering the crystalline material.

8. The method as claimed in claim 7, characterized
20 in that it comprises at least:

- preparing a synthesis mixture that comprises at least:
 - H_2O ,
 - an oxide of one or more tetravalent
25 elements Y,
 - and an organic compound as structure-controlling agent (R),

with molar ratios of oxides:

$H_2O/(YO_2)$ 1-50

$R/(YO_2)$ 0.1-3.0

- holding the synthesis mixture at a temperature between 80 and 200°C until the crystals of the porous crystalline material form; and

- recovery of the crystalline material.

- 5 9. The method as claimed in claim 8, characterized in that the molar ratios of oxides are:

$H_2O/(YO_2)$ 2-20

$R/(YO_2)$ 0.1-1.0

10. The method as claimed in claim 7, characterized in that it comprises at least:

- 10 - preparing a synthesis mixture that comprises at least H_2O , a source of one or more tetravalent elements Y, a source of Ge and an organic compound as structure-controlling agent (R),

15 - holding the synthesis mixture at a temperature between 80 and 200°C until the crystals of the porous crystalline material form; and

- recovering the crystalline material.

11. The method as claimed in claim 10, characterized in that it comprises at least:

- 20 - preparing a synthesis mixture that comprises at least H_2O , an oxide of one or more tetravalent elements Y, oxide of Ge and an organic compound as structure-

controlling agent (R), with molar ratios of oxides:

$$\text{H}_2\text{O}/(\text{YO}_2 + \text{GeO}_2) \quad 1-50$$

$$\text{R}/(\text{YO}_2 + \text{GeO}_2) \quad 0.1-3.0$$

$$\text{YO}_2/\text{GeO}_2 \quad \text{greater than } 1$$

- holding the synthesis mixture at a temperature between 80 and 200°C until the crystals of the porous crystalline material form; and

5 - recovery of the crystalline material.

12. The method as claimed in claim 11, characterized in that the molar ratios of oxides are:

$$\text{H}_2\text{O}/(\text{YO}_2 + \text{GeO}_2) \quad 2-20$$

$$\text{R}/(\text{YO}_2 + \text{GeO}_2) \quad 0.1-1.0$$

$$\text{YO}_2/\text{GeO}_2 \quad \text{greater than } 1$$

10 13. The method as claimed in claim 7, characterized in that it comprises at least:

- preparing a synthesis mixture that comprises at least H_2O , a source of one or more trivalent elements X; a source of one or more tetravalent elements Y and an organic compound as structure-controlling agent (R),

15 - holding the synthesis mixture at a temperature between 80 and 200°C until the crystals of the porous crystalline material form; and

- recovery of the crystalline material.

14. The method as claimed in claim 13, characterized in that it comprises:

- preparing a synthesis mixture that comprises at least H₂O, an oxide of one or more trivalent elements X; an
5 oxide of one or more tetravalent elements Y and an organic compound as structure-controlling agent (R), with molar ratios of oxides:

YO_2/X_2O_3 at least 5

H_2O/YO_2 between 1 and 50

R/YO_2 between 0.1 and 3.0

- holding the synthesis mixture at a temperature between 80 and 200°C until the crystals of the porous
10 crystalline material form; and
- recovery of the crystalline material.

15. The method as claimed in claim 14, characterized in that the molar ratios of oxides are:

YO_2/X_2O_3 greater than 7

H_2O/YO_2 between 2 and 20

R/YO_2 between 0.1 and 1.0

15 16. The method as claimed in claim 10, characterized in that it comprises at least:

- preparing a synthesis mixture that comprises at least H₂O, a source of one or more trivalent elements X; a
source of one or more tetravalent elements Y, oxide of
20 Ge, and an organic compound as structure-controlling

agent (R),

- holding the synthesis mixture at a temperature between 80 and 200°C until the crystals of the porous crystalline material form; and

5 - recovery of the crystalline material.

17. The method as claimed in claim 16, characterized in that it comprises:

- preparing a synthesis mixture that comprises at least H₂O, an oxide of one or more trivalent elements X; an
10 oxide of one or more tetravalent elements Y, oxide of Ge, and an organic compound as structure-controlling agent (R), with molar ratios of oxides:

$(\text{YO}_2 + \text{GeO}_2) / \text{X}_2\text{O}_3$ at least 5

$\text{H}_2\text{O} / (\text{YO}_2 + \text{GeO}_2)$ between 1 and 50

$\text{R} / (\text{YO}_2 + \text{GeO}_2)$ between 0.1 and 3.0

$\text{YO}_2 / \text{GeO}_2$ greater than 1

- holding the synthesis mixture at a temperature between 80 and 200°C until the crystals of the porous
15 crystalline material form; and

- recovery of the crystalline material.

18. The method as claimed in claim 17, characterized in that the molar ratios of oxides are:

$(\text{YO}_2 + \text{GeO}_2)/\text{X}_2\text{O}_3$ greater than 7

$\text{H}_2\text{O}/(\text{YO}_2 + \text{GeO}_2)$ between 2 and 20

$\text{R}/(\text{YO}_2 + \text{GeO}_2)$ between 0.1 and 1.0

YO_2/GeO_2 greater than 1

19. The method as claimed in one of claims 7 to 18,
characterized in that crystals of zeolite ITQ-33, which
5 act as seed crystals, are added to the synthesis
mixture.

20. The method as claimed in claim 19,
characterized in that said crystals of zeolite ITQ-33
that act as seed are added in a proportion up to
10 20 wt.% relative to the total weight of oxides.

21. The method as claimed in one of claims 7 to 19,
characterized in that the organic compound used as
structure-controlling agent is selected from an amine
and a tetraalkylammonium salt.

15 22. The method as claimed in one of claims 7 to 19,
characterized in that the organic compound used as
structure-controlling agent is hexamethonium hydroxide.

23. The method as claimed in claim 7, characterized
in that it comprises:

20 - preparing a synthesis mixture that comprises at least
 H_2O , an oxide of one or more trivalent elements X
selected from Al, B and a mixture of the two, an oxide
of Si, oxide of Ge, a hexamethonium salt as structure-
controlling agent R, with molar ratios of oxides:

$(\text{SiO}_2 + \text{GeO}_2)/\text{X}_2\text{O}_3$ at least 5

$\text{H}_2\text{O}/(\text{SiO}_2 + \text{GeO}_2)$ between 1 and 50

$\text{R}/(\text{SiO}_2 + \text{GeO}_2)$ between 0.1 and 3.0

$\text{SiO}_2/\text{GeO}_2$ greater than 1

- holding the synthesis mixture at a temperature between 80 and 200°C until the crystals of the porous crystalline material form; and

- recovery of the crystalline material.

5 24. The method as claimed in one of claims 7 to 23, characterized in that it comprises a stage of removal of the organic matter trapped inside the material, which is carried out by extraction, thermal treatment at temperatures above 250°C for a period of time
10 between 2 minutes and 25 hours, or a combination of the two.

25. The use of an active form of the porous crystalline material as claimed in one of claims 1 to 4, as catalyst in the conversion of feeds comprising
15 organic compounds.

26. The use as claimed in claim 25, characterized in that said conversion is selected from catalytic cracking of hydrocarbons, catalytic hydrocracking of hydrocarbons, alkylation of aromatics with olefins, esterification, acylation and reaction of aniline with
20 formaldehyde, which comprises pelletization of the material in a form selected from its acid form, exchange with cations and a combination of the two.

27. The use as claimed in claim 26, characterized
25 in that the material is a component of a catalyst.