Title: HYDROCRACKING OF ORGANIC COMPOUNDS USING ZEOLITE ITQ-33

Abstract: The present invention relates to a process for hydrocracking organic compounds characterized in that it comprises at least: a. introducing a catalyst comprising at least the zeolitic material ITQ-33 into a reactor, b. feeding the reactor with at least one organic compound, c. allowing the catalyst comprising at least the zeolitic material ITQ-33 and the organic compound to remain in contact the time necessary for the reaction to occur.
HYDROCRACKING OF ORGANIC COMPOUNDS USING ZEOLITE ITQ-33

TECHNICAL FIELD OF THE INVENTION

5 Heterogeneous catalysis.

PRIOR ART

Hydrocracking of heavy oil fractions is a very important process within current refinery practices, since it allows a wide variety of light products such as jet fuel, middle distillates and light gas oils to be obtained from heavier feeds of low intrinsic value. One advantage of the hydrocracking process with regard to other reforming processes such as catalytic cracking is that it produces middle distillates of excellent quality, whereas hydrocracked gasoline usually has a lower octane number than that obtained by catalytic cracking. On the other hand, the great flexibility of the hydrocracking process allows the production of the different fractions to be adapted to the market demand.

Conventional hydrocracking catalysts are of a bifunctional nature, i.e. they are formed by the combination of a hydrogenating function and an acid function. The hydrogenating function comes from the presence of one or more metals from group VIII of the periodic table such as palladium or platinum, from the presence in the catalyst of one or more metals from group VIB of the elements such as molybdenum and tungsten, or from a combination of one or more group VIII metals (usually non-noble metals) such as nickel, cobalt and iron, with group VIB metals. The acid function is usually associated with a porous substrate with a large specific surface area with surface acidity, such as halogenated alumina, mixed oxides, such as amorphous silica-alumina, and zeolites.

Both the activity and the selectivity to different products of a bifunctional hydrocracking catalyst are determined largely by the balance between the hydrogenating function and the acid function. When the acid function is weak and the hydrogenating function is strong the catalyst is characterized by having low hydrocracking activity, which forces it to work at high reaction temperatures (above 400°C) or at very low (usually below 2 h⁻¹) space velocities (feed volume to be treated per unit volume of catalyst per hour), and high selectivity to middle distillates. In contrast, if the acid function is strong and the hydrogenating function is weak the catalyst is characterized by having high hydrocracking activity but low selectivity to middle distillates. Therefore, a good hydrocracking catalyst must
have a suitable balance between the acid function and the hydrogenating function.

Amorphous silica-alumina is of note amongst the substrates with a low acid function that are currently most used in formulating conventional hydrocracking catalysts. Hydrocracking catalysts based on amorphous silica-alumina exhibit good selectivity to middle distillates, but, as mentioned above, they are characterized by presenting low activity.

Zeolites are among the substrates with a stronger acid function. Zeolites, and specifically zeolite Y with a Faujasite-type structure, form part of the formulation of last-generation hydrocracking catalysts. Hydrocracking catalysts based on zeolite Y thus exhibit greater activity than conventional catalysts based on amorphous silica-alumina, although their selectivity to middle distillates is usually less than for the latter. Some hydrocracking processes using zeolite Y-based catalysts are disclosed, for example, in patents US-3,269,934 and US-3,524,809.

The activity and selectivity of a zeolite Y-based hydrocracking catalyst may be altered by modifying zeolite acidity, which depends largely on its chemical composition, and more specifically on the ratio between silicon and aluminum atoms (Si/Al ratio) forming part of its crystalline structure. It is well known that the presence of an aluminum atom in tetrahedral coordination in the crystalline lattice of zeolite generates a charge deficiency that is compensated by a proton, thus giving rise to the formation of a Brønsted-type acid center. It is thus possible, in principle, to control zeolite acidity by varying the Si/Al ratio in the lattice.

Zeolite Y-based hydrocracking catalysts with a high Al content in the lattice (low Si/Al ratio) exhibit high activity since they have a large concentration of Brønsted acid centers. Nevertheless, these catalysts exhibit low selectivity to middle distillates since the presence of a large amount of acid centers favors secondary cracking reactions favoring the formation of lighter products, such as gases and naphtha. In contrast, hydrocracking catalysts containing zeolite Y with a low Al content in the lattice (high Si/Al ratio), and therefore a low concentration of acid centers, are more selective to middle distillates although they exhibit lower hydrocracking activity. In order to reduce Al concentration in the lattice and to achieve the adequate range of Si/Al ratios in cracking catalysts, zeolite Y must be subjected to post-synthesis dealumination treatments since this zeolite cannot be synthesized with a high Si/Al ratio. Said dealumination treatments usually require the use of severe hydrothermal conditions that lead to a partial loss of zeolite crystallinity.
Thus, it would be highly desirable to have a hydrocracking catalyst with good
activity and selectivity to middle distillates, based on a zeolitic material with a
topology such that it provides it with equal accessibility to or greater accessibility
than that of zeolite Y, and that may be obtained with a high Si/Al ratio in a single
synthesis step, preventing subsequent dealumination processes.

The present invention relates to a hydrocracking process for organic compounds
and preferably for oil-derived or synthetic hydrocarbon fractions, using the zeolitic
material called ITQ-33 as the active zeolitic component, the structure of which is
defined by a characteristic X-ray diffractogram. The relative positions, widths and
intensities of the diffraction peaks may be modified according to the chemical
composition of the material, as well as by the degree of hydration and the crystal
size of the zeolite.

The specific pore topology and acidity of this zeolite ITQ-33 will be shown to
provide it with activity for the hydrocracking process for organic compounds and
good selectivity to products in the range of middle distillates.

DESCRIPTION OF THE INVENTION

The present invention relates to a hydrocracking process for organic compounds.
One of the characteristics of this process is that a catalyst is used comprising at
least one zeolitic material called ITQ-33.

This zeolitic material used as a component of the catalyst in the process of the
present invention has a composition in its calcined and anhydrous forms provided
by the following formula:

$$X_2O_3: n \text{YO}_2: m \text{GeO}_2$$

wherein \((n + m)\) is at least 5, \(X\) is a trivalent element, \(Y\) corresponds to one or
several tetravalent elements other than Ge, the \(Y/Ge\) ratio is more than 1, and with
an X-ray diffraction pattern the main lines of which for its synthesized uncalcined
form are those included in Table 1:

<table>
<thead>
<tr>
<th>((d \pm 0.2) (\text{Å}))</th>
<th>Relative Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>16.59</td>
<td>vs</td>
</tr>
</tbody>
</table>

Table 1: Uncalcined zeolite ITQ-33.
wherein "vs" means a relative intensity of 80-100, "w" means a relative intensity of 20-40 and "vw" means a relative intensity of 0-20, calculated as a percentage with respect to the most intense peak.

Once calcined, the crystalline structure of zeolite ITQ-33 is characterized by an X-ray diffraction pattern the most characteristic lines of which are shown in Table 2.

Table 2: Calcined Zeolite ITQ-33.

<table>
<thead>
<tr>
<th>d ± 0.2 (Å)</th>
<th>I_rel</th>
</tr>
</thead>
<tbody>
<tr>
<td>16.81</td>
<td>vs</td>
</tr>
<tr>
<td>11.50</td>
<td>vw</td>
</tr>
<tr>
<td>9.71</td>
<td>vw</td>
</tr>
<tr>
<td>8.41</td>
<td>vw</td>
</tr>
<tr>
<td>6.79</td>
<td>vw</td>
</tr>
<tr>
<td>4.84</td>
<td>vw</td>
</tr>
<tr>
<td>4.65</td>
<td>vw</td>
</tr>
<tr>
<td>4.24</td>
<td>vw</td>
</tr>
<tr>
<td>3.66</td>
<td>vw</td>
</tr>
<tr>
<td>3.17</td>
<td>vw</td>
</tr>
</tbody>
</table>

wherein "vs" means a relative intensity of 80-100, "w" means a relative intensity of 20-40 and "vw" means a relative intensity of 0-20, calculated as a percentage with respect to the most intense peak.

Zeolite ITQ-33 may be synthesized in fluoride medium or in OH⁻ medium, using an organic structure-directing agent, such as for example the hexamethonium cation, and forming a gel containing in its composition the source of at least one T⁴⁺ element, amongst which Si and Ge are preferred, and of one or more T³⁺ elements, amongst which Al, B, Fe and Ga are preferred, preferably Al, B or a
mixture of both, the $T^{IV}/T^{III}$ ratio being at least 5. According to this synthesis process organic molecules and fluoride ions will be occluded inside the structure, which can be eliminated by conventional means. The organic component may thus be eliminated, for example, by extraction and/or by thermal treatment by heating at a temperature exceeding 250°C for a period of time comprised between 2 minutes and 25 hours. In either case, the acid form is finally obtained, which is the preferred form in the catalytic composition, either directly or through conventional ion exchanges. The catalyst of the present invention may optionally comprise some promoter elements, such as for example phosphorus and/or boron, and at least one element from group VIIA, preferably fluorine.

The proton (acid) form of the zeolitic material is preferred for its application as an acid component of a hydrocracking catalyst. Optionally, the zeolitic material can be subjected to a calcination treatment in the presence of steam and/or a mixture of steam and air or any of its components, at temperatures between 200 and 700°C for a time comprised between 10 minutes and 5 hours.

The zeolitic material ITQ-33 present in the catalyst used in the process of the present invention exhibits a structure with a three-directional channel system, with straight ultra-large pore channels parallel to the $c$ axis, defined by circular openings formed by 18 atoms in tetrahedral coordination. These channels are interconnected by a system of channels or windows formed by 10 atoms in tetrahedral coordination located in the $ab$ plane, and with openings of $6.1 \times 4.3$ Å.

The catalyst used in the process of the present invention is characterized in that it may comprise, as well as a zeolitic material called ITQ-33, at least one metal from the elements of groups VIB and VIII, and at least one substrate formed by a matrix of an amorphous or low crystallinity oxide (such as alumina or silica-alumina) among others.

The present invention relates to a process for hydrocracking organic compounds characterized in that it comprises at least:

a. introducing a catalyst comprising at least the zeolitic material ITQ-33 into a reactor,

b. feeding the reactor with at least one organic compound,

c. allowing the catalyst comprising at least the zeolitic material ITQ-33 and the organic compound to remain in contact the time necessary for the reaction to occur.
According to the hydrocracking process of the present invention, the catalyst used may also comprise at least one matrix of at least one oxide chosen from amorphous oxide, low crystallinity oxide and combinations thereof.

Preferably the matrix may be chosen from alumina, silica-alumina, silica, clays, magnesium oxide, titanium oxide, boric oxide, zirconia, aluminum phosphates, zirconium phosphates, coal, aluminates and combinations thereof. More preferably said matrix is chosen from an oxide comprising at least one form of alumina, and even more preferably that matrix is gamma-alumina.

According to the hydrocracking process of the present invention the catalyst may also comprise at least one hydrogenating component.

This hydrogenating component may be chosen from metals of groups VIB and VIII of the periodic table and combinations thereof.

Preferably, the metals from group VIB are chosen from molybdenum, tungsten and combinations thereof and the elements from group VIII are preferably chosen from iridium, ruthenium, rhodium, rhenium, palladium, platinum, iron, cobalt, nickel and combinations thereof.

According to a particular embodiment of the process of the present invention in which the hydrogenating function of the catalyst is provided by a combination of at least one non-noble metal from group VIII and at least one metal from group VIB, amongst the metals from group VIII non-noble metals are preferred, preferably cobalt and nickel, and amongst the metals from group VIB molybdenum and tungsten are preferred. The preferred combinations are: nickel-molybdenum, cobalt-molybdenum and nickel-tungsten, although optionally combinations of three elements may be used, such as nickel-cobalt-molybdenum. On the other hand, when the hydrogenating function is only given by at least one metal from group VIII, these metals from group VIII are chosen from platinum, palladium, iridium, ruthenium, rhodium and rhenium and combinations thereof, and preferably from palladium, platinum and combinations thereof. The metals from group VIII and from group VIB may be totally or partially in metallic and/or oxide form and/or in sulfide form.

According to the process of the present invention, the catalyst may also comprise at least one promoter element, which may be chosen from phosphorus, boron and combinations thereof. Said promoter element is preferably phosphorus.
Also, the catalyst used in the present invention may comprise at least one element from group VIIA, preferably fluorine.

According to the process of the present invention, the catalyst described may have percentages by weight with respect to the total weight of the catalyst between:

- 0.1 and 99% of the zeolitic material ITQ-33;
- 0.1 and 99% of at least one matrix formed by at least one oxide chosen from an amorphous oxide and a low crystallinity oxide;
- 0.1 and 60% of a hydrogenating component.

And preferably said percentages range between:

- 0.1 and 60% of the zeolitic material ITQ-33;
- 0.1 and 98% of at least one matrix formed by at least one oxide chosen from an amorphous oxide and a low crystallinity oxide;
- 0.1 and 50% of a hydrogenating component.

According to a preferred embodiment of the present invention, the percentage by weight with respect to the total weight of the catalyst ranges between 0.1 and 40% of a hydrogenating component.

According to another preferred embodiment, the percentages by weight with respect to the total weight of the catalyst of the promoter element and of the element of group VIIA range between:

- 0 and 20% of at least one promoter element;
- 0 and 20% of at least one element from group VIIA.

The catalyst of the present invention may be prepared by any of the methods that are well known by those skilled in the art. An advantageous manner for preparing the catalyst consists in admixing the zeolitic material ITQ-33 with the chosen matrix and then forming the mixture.

According to a particular embodiment, the hydrogenating component may be incorporated onto a mixture of the matrix and the zeolitic material ITQ-33.

According to another particular embodiment, the hydrogenating component is directly incorporated on the matrix before admixing with the zeolitic material ITQ-33. According to this particular embodiment, the hydrogenating component is first incorporated on the chosen matrix which is then mixed with the zeolitic material ITQ-33 in order subsequently to form the mixture.
The forming can be carried out by extrusion, pelleting, by the oil drop method or by any other method that is well known to those skilled in the art. A calcination step is carried out after forming. The hydrogenating component may be totally or partially incorporated (e.g. in the case of using a combination of elements from groups VIII and VIB) before or after calcination. Catalyst preparation is completed with a calcination step at temperatures comprised between 150°C and 800°C.

Incorporation of the hydrogenating component may be performed by means of one or more ion exchange steps in the case where the incorporation is performed on the mixture of the zeolitic material and the matrix.

When the incorporation of the hydrogenating component is performed on the matrix or on the mixture of the matrix and the zeolitic material, it can be carried out by means of one or more impregnation processes with a solution comprising at least one precursor of at least one oxide of at least one metal chosen from the metals from groups VIB, VIII and combinations thereof. When the hydrogenation function is formed by the combination of at least one element from group VIB and at least one element from group VIII, the impregnation of the precursor (or precursors) of the oxide(s) of the element(s) from group VIII is performed preferably after or at the same time as the impregnation of the precursor(s) of the oxide(s) of the element(s) from group VIB.

Impregnation of these elements can be carried out by means of the pore volume method, also known as "dry" impregnation, wherein the pore volume of the substrate is filled with a solution containing at least one precursor of at least one of the metals from groups VIB and VIII. Impregnation may also be performed with excess solution comprising at least one precursor from at least one of the metals from groups VIB and VIII. In this case the excess solvent is eliminated slowly by evaporation in controlled conditions.

In the case where the incorporation of these elements is carried out in several impregnation steps, it is preferable to perform an intermediate calcination step between each impregnation at a temperature comprised between 150°C and 800°C.

Different precursors can be used for the elements from group VIB. For example, in the case of molybdenum and tungsten different oxides and salts may be used, such as ammonium molybdate, ammonium heptamolybdate and ammonium tungsten.

Corresponding nitrates, sulfates and halides amongst others are usually used as
sources of the elements from group VIII.

In the particular case where the catalyst comprises at least one promoter element such as for example phosphorus and/or boron, and at least one element from group VIIA, such as for example fluorine, these may be incorporated at any time during catalyst preparation, preferably on the substrate already comprising the zeolitic material and the matrix and more preferably after incorporation of at least one of the elements chosen from the elements from groups VIB and VIII. It is also possible to incorporate the promoter element(s) and those from group VIIA on the matrix, preferably after incorporation of at least one of the elements from groups VIB and VIII, and then perform the mixture with the zeolitic material.

These elements may be incorporated by means of any known method, although the impregnation method is preferred, at pore volume ("dry" impregnation) or in excess solvent.

Orthophosphoric acid, H₃PO₄, is preferred as the source of phosphorus, although some of its salts and esters, such as ammonium phosphates, may also be used.

Any source well known to a person skilled in the art may be used as the source of the element from group VIIA. For example, hydrofluoric acid or its salts may be used as the source in the case of fluorine. It is also possible to use fluorine compounds that may give rise to the formation of fluoride by hydrolysis in the presence of water, such as ammonium fluorosilicate (NH₄)₂SiF₆, silicon tetrafluoride SiF₄, or sodium tetrafluoride Na₂SiF₆. Fluorine may be incorporated into the catalyst, for example, by impregnation from an aqueous solution of hydrofluoric acid or ammonium fluoride.

As a final step in preparing the catalyst, calcination is performed at a temperature between 150°C and 800°C.

According to the process of the present invention, the catalyst described in the preceding paragraphs may be subjected to a pretreatment step such as for example a sulfuration step or a reduction step.

Reaction temperature according to the process of the present invention may be greater than 200°C, and preferably between 250°C and 500°C. Reaction pressure may be greater than 0.1 MPa, preferably between 0.1 and 20 MPa, and more preferably greater than between 2.0 and 20 MPa. The H₂/hydrocarbon ratio of the
process of the present invention, i.e. the amount of hydrogen with respect to the amount of feed, may be at least 10 Nm³ hydrogen per m³ of feed, preferably between 20 and 5000 Nm³ of hydrogen per m³ of feed, and more preferably between 30 and 1500 Nm³ of hydrogen per m³ of feed. Space velocity (LHSV) may be comprised between 0.01 and 20 feed volumes per catalyst volume per hour and preferably the space velocity is comprised between 0.05 and 5 feed volumes per catalyst volume per hour.

According to a preferred embodiment, the feed stream according to the process of the present invention is made up of hydrocarbons; preferably said feed is made up of hydrocarbon heavy fractions.

Preferably, the hydrocarbon feed is placed in contact with the hydrocracking catalyst in the presence of hydrogen, usually in a fixed bed reactor. The conditions of the hydrocracking process may vary according to the nature of the feed, the intended quality of the products, and the particular facilities of each refinery.

According to a particular embodiment, the feed stream may be subjected to a hydrotreatment process prior to the hydrocracking process of the present invention.

According to another particular embodiment, the catalyst used in the process of the present invention may be subjected to a sulfuration step.

Preferably, said sulfuration is performed in a stream chosen from a neat hydrogen sulfide stream, a mixture of hydrogen sulfide and hydrogen, a mixture of hydrogen and liquid hydrocarbons that in turn contain at least one compound containing sulfur in its composition, and combinations thereof.

This sulfuration is performed preferably at a temperature between 150 and 800°C.

According to this particular embodiment, the hydrogenating component may be at least one element from group VIII chosen from iron, cobalt, nickel and combinations thereof and at least one element from group VIB chosen from molybdenum, tungsten and combinations thereof.

Preferred combinations may be the binary combinations nickel-molybdenum, cobalt-molybdenum, nickel-tungsten, or the ternary combination nickel-cobalt-molybdenum. The metals from group VIII and from group VIB may be totally or partially in metallic and/or oxide form and/or in sulfide form.
According to this particular embodiment, the catalyst of the present invention is preferably subjected to the sulfuration treatment before coming in contact with the feed in order to transform, at least partially, the group VIB and VIII metals into corresponding sulfides. The sulfuration treatment may be performed by any of the methods described in the literature.

A typical sulfuration method consists in heating the catalyst in the presence of a stream of neat hydrogen sulfide or a mixture of hydrogen sulfide and hydrogen or a stream containing hydrogen and liquid hydrocarbons that in turn contain at least one compound containing sulfur in its composition, at a preferred temperature of between 150 and 800°C. This process is usually performed in a continuous fixed bed reactor.

According to this particular embodiment a hydrocracking process of hydrocarbon heavy fractions is preferred. These fractions may be from different sources. Preferably said feed is formed by a vacuum gas oil. These fractions usually contain at least 80% by volume of compounds with boiling points greater than 350°C, and preferably between 350°C and 580°C. These fractions usually contain heteroatoms, such as sulfur and nitrogen. Nitrogen content is usually comprised between 1 and 5000 ppm (by weight), and sulfur content is usually from 0.01% to 5% by weight. These fractions can optionally be subjected to a hydrotreatment process prior to hydrocracking in order to reduce the concentration of heteroatoms or to eliminate any pollutant metals that they may contain.

According to this particular embodiment, the hydrocarbon feed is placed in contact with the hydrocracking catalyst in the presence of hydrogen, usually in a fixed bed reactor. The conditions of the hydrocracking process may vary according to the nature of the feed, the intended quality of the products, and the particular facilities of each refinery. The temperature is usually greater than 200°C, and is often comprised between 250°C and 500°C. Pressure is usually greater than 0.1 MPa and often greater than 1 MPa. The H₂/hydrocarbon ratio is usually greater than 10 and usually between 20 and 5000 Nm³ of hydrogen per m³ of feed. Space velocity (LHSV) is usually comprised between 0.01 and 20 feed volumes per catalyst volume per hour. The hydrocracking process is preferably performed at temperatures from 300°C to 500°C, pressures from 5 to 20 MPa, H₂/hydrocarbon ratios from 30 to 1500 Nm³/m³ and LHSV from 0.05 to 5 h⁻¹.

According to another particular embodiment, the catalyst of the present invention is subjected to a reduction treatment in a hydrogen stream before coming in contact
with the feed, in order to transform the oxides of noble metals from group VIII into their metal form maintaining good dispersion of the metal on the substrate. The reduction treatment may be performed by any of the methods described in the literature.

A typical reduction method consists in heating the catalyst in the presence of a stream of hydrogen at a temperature of between 100 and 600°C, and preferably between 300 and 500°C, for from 10 minutes to 5 hours, preferably from 30 minutes to 3 hours. This process is usually performed in a continuous fixed bed reactor.

The reduction treatment according to this particular embodiment of the process of the present invention is preferably performed at a temperature of between 100 and 600°C.

Moreover, according to this particular embodiment, the hydrogenating component of the catalyst used in the process of the present invention is an element from group VIII chosen from iridium, ruthenium, rhodium, rhenium, palladium, platinum and combinations thereof, and preferably from palladium, platinum and combinations thereof.

According to this particular embodiment a hydrocracking process of hydrocarbon heavy fractions is preferred. These fractions may be from different sources. The feed is preferably made up of heavy products obtained by means of the Fischer-Tropsch process. These fractions usually contain hydrocarbons with at least 20 carbon atoms, and they usually do not contain heteroatoms, such as sulfur and nitrogen.

According to this particular embodiment, the hydrocarbon feed is placed in contact with the hydrocracking catalyst in the presence of hydrogen, usually in a fixed bed reactor. The conditions of the hydrocracking process may vary according to the nature of the feed, the intended quality of the products, and the particular facilities of each refinery. The temperature is usually greater than 200°C, and is often comprised between 250°C and 480°C. Pressure is usually greater than 0.1 MPa and often greater than 1 MPa. The H₂/hydrocarbon ratio is usually greater than 10 and usually between 20 and 2000 Nm³ of hydrogen per m³ of feed. Space velocity (LHSV) is usually comprised between 0.01 and 20 feed volumes per catalyst volume per hour. The hydrocracking process according to this particular embodiment is preferably performed at temperatures from 250°C to 320°C,
pressures from 2 to 20 MPa, H₂/hydrocarbon ratios from 30 to 1000 Nm³/m³ and LHSV from 0.05 to 5 h⁻¹.

**BRIEF DESCRIPTION OF THE DRAWINGS**

5 **Figure 1:** X-ray diffraction pattern for uncalcined ITQ-33.

**Figure 2:** Product distribution (molar %) obtained in hydrocracking n-hexadecane with the catalyst described in Example 3, under the experimental conditions described in Example 6.

10 **Figure 3:** Product distribution (molar %) obtained in hydrocracking n-hexadecane with the catalyst described in Example 4, under the experimental conditions described in Example 7.

15 Examples are shown below that illustrate the essence of this invention, which cannot be considered limiting thereof.

**EXAMPLES**

**Example 1: Synthesis of a sample of the zeolitic component ITQ-33.**

A typical process for the synthesis of a sample of zeolitic component ITQ-33 according to this invention is shown in this example.

3.484 g of GeO₂ are dissolved in 14.543 g of hexamethonium hydroxide solution (24.5% by weight) and 8.035 g of hexamethonium bromide solution (50% by weight). 1.043 g of aluminum isopropoxide and 14.205 g of tetraethyl orthosilicate (TEOS) are added. Finally, having hydrolyzed the alkoxides, 1.254 g of hydrofluoric acid solution (48% by weight) are added and the mixture is kept stirring whilst being allowed to evaporate until the reaction mixture reaches a final composition of:

30 0.67 SiO₂ : 0.33 GeO₂ : 0.025 Al₂O₃ : 0.15 R(OH)₂ : 0.10 R(Br)₂ : 0.30 HF : 1.5 H₂O

wherein R is hexamethonium.

The gel is heated up to 175°C without stirring for 20 hours in steel autoclaves with an internal Teflon sheath. The solid obtained after filtering, washing with distilled water and drying at 100°C is ITQ-33.

The X-ray powder diffraction pattern from the solid obtained after filtering, washing and drying at 100°C is shown in Figure 1 and in Table 3.
Table 3: Uncalcined zeolite ITQ-33.

<table>
<thead>
<tr>
<th>(d ± 0.2) (Å)</th>
<th>Relative Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>16.59</td>
<td>VS</td>
</tr>
<tr>
<td>11.63</td>
<td>VW</td>
</tr>
<tr>
<td>9.57</td>
<td>VW</td>
</tr>
<tr>
<td>8.31</td>
<td>VW</td>
</tr>
<tr>
<td>6.76</td>
<td>VW</td>
</tr>
<tr>
<td>4.81</td>
<td>VW</td>
</tr>
<tr>
<td>4.62</td>
<td>VW</td>
</tr>
<tr>
<td>4.27</td>
<td>W</td>
</tr>
<tr>
<td>4.02</td>
<td>VW</td>
</tr>
<tr>
<td>3.86</td>
<td>VW</td>
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<td>3.82</td>
<td>VW</td>
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<td>3.64</td>
<td>W</td>
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<tr>
<td>3.33</td>
<td>VW</td>
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<td>3.15</td>
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<tr>
<td>2.54</td>
<td>VW</td>
</tr>
<tr>
<td>2.38</td>
<td>VW</td>
</tr>
<tr>
<td>2.27</td>
<td>VW</td>
</tr>
</tbody>
</table>

The relative intensity of the lines is calculated as the percentage with respect to the most intense peak, and is considered very strong (VS)= 80-100, strong (S)=60-80, medium (M)= 40-60, weak (W)=20-40, and very weak (VW)= 0-20.

Example 2: Activation by means of calcination of the zeolitic component ITQ-33.

The zeolite obtained from Example 1 is calcined in air flow at 540°C for 3 hours.

The X-ray diffraction pattern of the calcined material is shown in Table 4.

Table 4: Calcined zeolite ITQ-33.

<table>
<thead>
<tr>
<th>(d ± 0.2) (Å)</th>
<th>Relative Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>16.81</td>
<td>VS</td>
</tr>
<tr>
<td>11.50</td>
<td>VW</td>
</tr>
<tr>
<td>9.71</td>
<td>VW</td>
</tr>
</tbody>
</table>
The relative intensity of the lines is calculated as the percentage with respect to the most intense peak, and is considered very strong (VS) = 80-100, strong (S) = 60-80, medium (M) = 40-60, weak (W) = 20-40, and very weak (VW) = 0-20.

5

Example 3: Preparation of a hydrocracking catalyst containing zeolite ITQ-33.

This example illustrates the preparation of a hydrocracking catalyst according to the invention, containing zeolite ITQ-33 obtained according to the process described in Example 1, a gamma-alumina and platinum matrix as a hydrogenating component, in which the hydrogenating component is incorporated exclusively on the gamma-alumina matrix.

The gamma-alumina matrix is first impregnated by means of the pore volume or "dry" impregnation method, with an aqueous solution of 0.1 N HCl, containing the amount of hexachloroplatinic acid necessary to obtain a final platinum content of 1% by weight. The solid is then dried in a heat cabinet at 100°C for 12 hours and is calcined in a crucible furnace at 450°C for 3 hours.

20 The gamma-alumina matrix containing platinum oxide is mixed with the zeolite ITQ-33 in suitable proportions to obtain a catalyst with the following chemical composition, indicated as % by weight:

0.5 % platinum (as oxide)
49.5 % of γ-alumina
Example 4: Preparation of a hydrocracking catalyst containing a USY zeolite.
This example illustrates the preparation of a hydrocracking catalyst according to the invention, containing a commercial USY zeolite (Zeolyst CBV712) with a unit cell of 24.33 Å, a gamma-alumina matrix, and platinum as a hydrogenating component, in which the hydrogenating component is exclusively incorporated on the gamma-alumina matrix.

The gamma-alumina matrix is first impregnated following the process described in Example 3.

The gamma-alumina matrix containing platinum oxide is mixed with the USY zeolite in suitable proportions to obtain a catalyst with the following chemical composition, indicated as % by weight:

- 0.5 % platinum (as oxide)
- 49.5 % of γ-alumina
- 50.0% of USY

Example 5: Preparation of a hydrocracking catalyst containing a silica-alumina.
This example illustrates preparing a hydrocracking catalyst according to the invention, containing silica-alumina with 13% by weight of Al₂O₃, and platinum as a hydrogenating component, in which the hydrogenating component is incorporated exclusively on the gamma-alumina matrix.

The silica-alumina is impregnated by means of the pore volume or "dry" impregnation method, with an aqueous solution of 0.1 N HCl, containing the amount of hexachloroplatinic acid necessary to obtain a final platinum content of 1% by weight. The solid is then dried in a heat cabinet at 100°C for 12 hours and is calcined in a crucible furnace at 450°C for 3 hours. A catalyst is thus obtained with the following chemical composition, indicated as % by weight:

- 1.0 % platinum (as oxide)
- 99 % silica-alumina

Example 6: Hydrocracking of n-hexadecane with a catalyst containing ITQ-33
This example illustrates the activity and selectivity of the catalyst prepared according to Example 3 according to the invention, for hydrocracking n-hexadecane.
Hydrocracking experiments were performed in a continuous fixed bed reactor loaded with 2.0 grams of catalyst sieved to a particle size of 0.2-0.4 mm, and diluted with CSi, with a particle size of 0.6-0.8 mm, up to a total volume of 5.5 cm³.

Before bringing the catalyst in contact with the n-hexadecane the catalyst was calcined “in situ” for 4 hours at 540°C in air flow (100 ml/min). It was then subjected to a reduction step at 400°C for 2 hours in hydrogen flow (300 ml/min) at atmospheric pressure. Having completed the calcination and reduction steps, the n-hexadecane was then hydrocracked in the presence of hydrogen under the following reaction conditions: total pressure of 4.0 MPa, molar ratio H₂/n-hexadecane of 95 mol.mol⁻¹, space velocity (WHSV) of 3.6 h⁻¹, referred to the zeolitic component, and a temperature of 300°C.

In these reaction conditions, and using the catalyst containing zeolitic material ITQ-33 the preparation of which is described in Example 3, a transformation of n-hexadecane of 72% was obtained, with a yield of hydrocracking products of 62% by weight. The distribution of products obtained (in molar %) is shown in Figure 2, that of the C1-C6 fraction being 49 molar %.

**Example 7: Hydrocracking of n-hexadecane with a catalyst containing USY.**

This example illustrates the activity and selectivity of the catalyst prepared according to Example 4 according to the invention, for hydrocracking n-hexadecane.

As in Example 6, hydrocracking experiments were performed in a continuous fixed bed reactor loaded with 2.0 grams of catalyst sieved to a particle size of 0.2-0.4 mm, and diluted with CSi, with a particle size of 0.6-0.8 mm, up to a total volume of 5.5 cm³.

Before bringing the catalyst in contact with the n-hexadecane the catalyst was calcined "in situ" and then subjected to a reduction step under the same conditions as those described in Example 6. Having completed the calcination and reduction steps, the n-hexadecane was then hydrocracked in the presence of hydrogen under the following reaction conditions: total pressure of 4.0 MPa, molar ratio H₂/n-hexadecane of 95 mol.mol⁻¹, space velocity (WHSV) of 3.6 h⁻¹, referred to the zeolitic component, and a temperature of 230°C.

Under these reaction conditions, and using the catalyst containing the USY zeolite
the preparation of which is described in Example 4, a transformation of n-hexadecane of 84% was obtained, with a yield of hydrocracking products of 62% by weight. The distribution of products obtained (in molar %) is shown in Figure 3, that of the C\textsubscript{1}-C\textsubscript{6} fraction being 55 molar %.

Comparing the product distribution obtained with the catalysts prepared in Examples 3 and 4, provided in Figures 2 and 3, we can observe that with the catalyst containing zeolitic material ITQ-33, claimed in the present invention, fewer light reocracking products (C\textsubscript{1}-C\textsubscript{6}) and more C\textsubscript{6+} products are obtained, especially in the C\textsubscript{10}-C\textsubscript{15} fraction.

**Example 8: Hydrocracking of n-hexadecane with a catalyst containing silica-alumina.**

This example illustrates the activity and selectivity of the catalyst prepared according to Example 5 according to the invention, for hydrocracking n-hexadecane.

As in Example 6, hydrocracking experiments were performed in a continuous fixed bed reactor loaded with 1.0 grams of catalyst sieved to a particle size of 0.2-0.4 mm, and diluted with CSi, with a particle size of 0.6-0.8 mm, up to a total volume of 5.5 cm\textsuperscript{3}.

Before bringing the catalyst in contact with the n-hexadecane the catalyst was subjected to a reduction step at 400\textdegree C for 2 hours in hydrogen flow (300 ml/min) at atmospheric pressure. Having completed this reduction step, the n-hexadecane was then hydrocracked in the presence of hydrogen under the following reaction conditions: total pressure of 4.0 MPa, molar ratio \textit{H}_2/n-hexadecane of 95 mol.mol\textsuperscript{-1}, space velocity (WHSV) of 3.6 h\textsuperscript{-1} and a temperature of 300\textdegree C.

Under these reaction conditions, and using the catalyst containing the silica-alumina with 13% of Al\textsubscript{2}O\textsubscript{3} the preparation of which is described in Example 5, a transformation of n-hexadecane of 32% was obtained, with a yield of hydrocracking products of 40% by weight.

Comparing the transformation obtained in this example with the transformation obtained with the catalyst prepared in Example 3, containing zeolitic material ITQ-33, at the same reaction temperature, we can observe that the latter, containing the zeolite the use of which is claimed in the present patent, is more active than that based on silica-alumina.
CLAIMS

1. Hydrocracking process for organic compounds characterized in that it comprises at least:
   a. introducing a catalyst comprising at least the zeolitic material ITQ-33 into a reactor,
   b. feeding the reactor with at least one organic compound,
   c. allowing the catalyst comprising at least the zeolitic material ITQ-33 and the organic compound to remain in contact the time necessary for the reaction to occur.

2. Hydrocracking process according to Claim 1, characterized in that the catalyst also comprises at least one matrix of at least one oxide chosen from amorphous oxide, low crystallinity oxide and combinations thereof.

3. Hydrocracking process according to Claim 2, characterized in that said matrix is chosen from alumina, silica-alumina, silica, clays, magnesium oxide, titanium oxide, boric oxide, zirconia, aluminum phosphates, zirconium phosphates, coal, aluminates and combinations thereof.

4. Hydrocracking process according to one of Claims 2 and 3, characterized in that said matrix is chosen from an amorphous oxide comprising at least one form of alumina.

5. Hydrocracking process according to Claim 4, characterized in that said matrix is gamma-alumina.

6. Hydrocracking process according to one of Claims 1 to 5, characterized in that the catalyst also comprises at least one hydrogenating component.

7. Hydrocracking process according to Claim 6, said hydrogenating component being characterized in that it is at least one element chosen from the elements from groups VIB, VIII and combinations thereof.

8. Hydrocracking process according to Claim 7, characterized in that the element from group VIB is chosen from molybdenum, tungsten and combinations thereof.

9. Hydrocracking process according to Claim 7, characterized in that the element from group VIII is chosen from iridium, ruthenium, rhodium, rhenium,
palladium, platinum, iron, cobalt, nickel and combinations thereof.

10. Hydrocracking process according to one of Claims 1 to 9, characterized in that the catalyst also comprises at least one promoter element chosen from phosphorus, boron and combinations thereof.

11. Hydrocracking process according to Claim 10, characterized in that said promoter element is phosphorus.

12. Hydrocracking process according to one of Claims 1 to 11, characterized in that the catalyst also comprises at least one element from group VIIA.

13. Hydrocracking process according to Claim 12, characterized in that said element from group VIIA is fluorine.

14. Hydrocracking process according to some of the preceding claims characterized by percentages by weight with respect to the total weight of catalyst of between:

- 0.1 and 99% of the zeolitic material ITQ-33;
- 0.1 and 99% of at least one matrix formed by at least one oxide chosen from an amorphous oxide and a low crystallinity oxide;
- 0.1 and 60% of a hydrogenating component.

15. Hydrocracking process according to Claim 14 characterized by percentages by weight with respect to the total weight of catalyst of between:

- 0.1 and 60% of the zeolitic material ITQ-33;
- 0.1 and 98% of at least one matrix formed by at least one oxide chosen from an amorphous oxide and a low crystallinity oxide;
- 0.1 and 50% of a hydrogenating component.

16. Hydrocracking process according to Claim 15 characterized by a percentage by weight with respect to the total weight of catalyst of between 0.1 and 40% of a hydrogenating component.

17. Hydrocracking process according to one of Claims 14 to 16, characterized by percentages by weight with respect to the total weight of catalyst of between:

- 0 and 20% of at least one promoter element;
- 0 and 20% of at least one element from group VIIA.
18. Hydrocracking process according to one of the preceding claims, characterized in that the hydrogenating component is incorporated on a mixture of the matrix and the zeolitic material ITQ-33.

19. Hydrocracking process according to one of Claims 1 to 17, characterized in that the hydrogenating component is incorporated directly on the matrix before admixing with the zeolitic material ITQ-33.

20. Hydrocracking process according to one of the preceding claims, characterized in that it is performed at a temperature greater than 200°C.

21. Hydrocracking process according to Claim 20, characterized in that it is performed at a temperature between 250 and 500°C.

22. Hydrocracking process according to one of the preceding claims, characterized in that it is performed at a pressure greater than 0.1 MPa.

23. Hydrocracking process according to Claim 22, characterized in that it is performed at a pressure from 0.1 to 20 MPa.

24. Hydrocracking process according to Claim 23, characterized in that it is performed at a pressure from 2.0 to 20 MPa.

25. Hydrocracking process according to one of the preceding claims, characterized in that it is performed with an amount of hydrogen of at least 10 Nm³ per m³ of feed.

26. Hydrocracking process according to Claim 25, characterized in that it is performed with an amount of hydrogen of between 20 and 5000 Nm³ per m³ of feed.

27. Hydrocracking process according to Claim 26, characterized in that it is performed with an amount of hydrogen of between 30 and 1500 Nm³ per m³ of feed.

28. Hydrocracking process according to one of the preceding claims, characterized in that it is performed at a space velocity between 0.01 and 20 feed volumes per catalyst volume per hour.
29. Hydrocracking process according to Claim 28, characterized in that it is performed at a space velocity between 0.05 and 5 feed volumes per catalyst volume per hour.

30. Hydrocracking process according to one of the preceding claims, characterized in that the feed stream is made up of hydrocarbons.

31. Hydrocracking process according to Claim 30, characterized in that said feed stream is made up of hydrocarbon heavy fractions.

32. Hydrocracking process according to one of the preceding claims, characterized in that the feed is subjected to a hydrotreatment process prior to the hydrocracking process.

33. Hydrocracking process according to one of the preceding claims, characterized in that the catalyst is subjected to a sulfuration step.

34. Hydrocracking process according to Claim 33, characterized in that said sulfuration is performed in a stream chosen from a neat hydrogen sulfide stream, a mixture of hydrogen sulfide and hydrogen, a mixture of hydrogen and liquid hydrocarbons that in turn contain at least one compound containing sulfur in its composition, and combinations thereof.

35. Hydrocracking process according to one of Claims 33 and 34, characterized in that the sulfuration is performed at a temperature between 150 and 800°C.

36. Hydrocracking process according to one of Claims 33 to 35, characterized in that the hydrogenating component is at least one element from group VIII chosen from iron, cobalt, nickel and combinations thereof and at least one element from group VIB chosen from molybdenum, tungsten and combinations thereof.

37. Hydrocracking process according to one of Claims 33 to 36, characterized in that the feed stream is made up of a vacuum gas oil.

38. Hydrocracking process according to one of Claims 1 to 32, characterized in that the catalyst is subjected to a reduction step in a hydrogen stream.

39. Hydrocracking process according to Claim 38, characterized in that said reduction is performed at a temperature between 100 and 600°C.
40. Hydrocracking process according to either of Claims 38 and 39, characterized in that the hydrogenating component is an element from group VIII chosen from iridium, ruthenium, rhodium, rhenium, palladium, platinum and combinations thereof.

41. Hydrocracking process according to Claim 40, characterized in that the hydrogenating component is chosen from palladium, platinum and combinations thereof.

42. Hydrocracking process according to one of Claims 38 to 41, characterized in that the feed is made up of heavy products obtained by means of the Fischer-Tropsch process.
Figure 2

Product Distribution (molar %)

Number of Carbon Atoms
Figure 3