(12) DEMANDE INTERNATIONALE PUBLIÉE EN VERTU DU TRAITÉ DE COOPÉRATION EN MATIÈRE DE BREVETS (PCT)

(19) Organisation Mondiale de la Propriété Intellectuelle
Bureau international

(43) Date de la publication internationale
30 novembre 2000 (30.11.2000)

PCT

(10) Numéro de publication internationale
WO 00/71250 A1

(51) Classification internationale des brevets⁷: B01J 29/16, C10G 47/16, 45/12

(21) Numéro de la demande internationale:
PCT/FR00/01389

(22) Date de dépôt international: 19 mai 2000 (19.05.2000)

(25) Langue de dépôt: français

(26) Langue de publication: français

(30) Données relatives à la priorité:
99/06445 19 mai 1999 (19.05.1999) FR

(71) Déposant: INSTITUT FRANCAIS DU PETROLE [FR/FR]; 1 & 4, avenue de Bois Préau, F-92852 Rueil Malmaison Cedex (FR).

(72) Inventeurs: BENAZZI, Eric; 44, rue le Val Sablons, F-78400 Chatou (FR). DEVES, Jean-Marie; 30, allée des Vergers, F-78540 Vernouillet (FR). KASZTELAN, Slavik; 27, rue Queneau, F-92500 Rueil Malmaison (FR).

(74) Mandataire: ANDREEFF, François; Institut Français du Pétrole, 1 et 4, avenue de Bois Préau, F-92852 Rueil Malmaison Cedex (FR).

(81) États désignés *(national)*: BR, IN, JP, KR, SG.

(84) États désignés *(régional)*: brevet européen (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Publiée:
— *Avec rapport de recherche internationale.*

En ce qui concerne les codes à deux lettres et autres abréviations, se référer aux "Notes explicatives relatives aux codes et abréviations" figurant au début de chaque numéro ordinaire de la Gazette du PCT.

(54) Title: CATALYST COMPRISING A PARTIALLY AMORPHOUS ZEOLITE Y, AN ELEMENT OF GROUP V B AND ITS USE FOR HYDROCONVERTING AND HYDROREFINING HYDROCARBON OIL FEEDSTOCKS

(54) Titre: CATALYSEUR COMPRENANT UNE ZEOLITHE Y PARTIELLEMENT AMORPHE, UN ELEMENT DU GROUPE VB ET SON UTILISATION EN HYDROCONVERSION ET HYDRORAFFINAGE DE CHARGES PETROLIERES HYDROCARBONEES

(57) Abstract: The invention concerns a catalyst containing at least a partially amorphous zeolite Y, at least a metal of group VB, preferably niobium, at least an amorphous or poorly crystallised matrix, optionally an element selected from group VIB and group VIII, optionally at least an element selected from the group consisting of P, B, Si, optionally at least an element of group VIIA. The invention also concerns the use of said catalyst for hydrocracking and hydrorefining hydrocarbon feedstocks.

(57) Abrégé: L'invention concerne un catalyseur renfermant au moins une zéolithe Y partiellement amorphe, au moins un métal du groupe VB, de préférence le niobium, au moins une matrice amorphe ou mal cristallisée, éventuellement au moins un métal choisi dans le groupe VIB et le groupe VIII, éventuellement au moins un élément choisi dans le groupe formé par P, B, Si, éventuellement au moins un élément du groupe VIIA. L'invention concerne également l'utilisation de ce catalyseur en hydrocraquage et en hydroraffinage des charges hydrocarbonées.

WO 00/71250 A1

A CATALYST COMPRISING A PARTIALLY AMORPHOUS Y ZEOLITE, A GROUP VB ELEMENT, AND USE THEREOF IN HYDROCONVERSION AND HYDROREFINING OF HYDROCARBON PETROLEUM FEEDSTOCKS

The present invention is concerned with a catalyst of hydrocarbon feedstocks, said catalyst comprising at least one partially amorphous Y zeolite, at least one group VB metal, preferably niobium, at least one oxide-type amorphous or poorly crystallized matrix, possibly at least one metal selected from group VIB and group VIII of the periodic table, preferably molybdenum and tungsten, cobalt, nickel and iron. The matrix of the catalyst possibly contains at least one element selected from the group P, B, Si, and possibly at least one group VIIA element (group 17 of the halogens), such as fluorine, for example.

More particularly, the present invention is concerned with a catalyst comprising at least one matrix, at least one group VB element and at least one partially amorphous Y zeolite, having a peak rate of less than 0.4 and a crystalline fraction, expressed in relation to a reference zeolite in sodium (Na) form, which is less than 60%.

The present invention is also concerned with processes for the preparation of said catalyst, as well as use thereof for the hydrocracking of hydrocarbon feedstocks, such as petroleum fractions, the fractions obtained from carbon containing aromatic compounds, and/or olefinic compounds and/or naphthenic compounds and/or paraffinic compounds, said feedstocks possibly containing metals and/or nitrogen and/or oxygen and/or sulphur. The invention is also concerned with use of the catalyst for the hydrorefining of hydrocarbon feedstocks.

The hydrocracking of heavy petroleum fractions is a very important refining process permitting the production, starting from excess, heavy feedstocks which cannot be readily upgraded, of lighter fractions such as gasolines, jet fuels and light gas oils which the refiner looks for in order to adapt his production to the structure of demand. Certain hydrocracking processes also make it possible to obtain a greatly purified residue which can constitute excellent base for oils. In comparison with catalytic cracking, the advantage of catalytic

hydrocracking is to provide middle distillates, jet fuels and gas oils of very good quality. The gasoline which is produced has a much lower octane number than that obtained from catalytic cracking.

The catalysts which are used in hydrocracking are all bifunctional in type which link an acid function to a hydrogenating function. The acid function is provided by large-surface

substrates (generally from 150 to 800 $m^2.g^{-1}$) which have a surface acidity, such as halogenated aluminas (in particular, chlorinated or fluorinated), combinations of boron oxides and aluminium oxides, amorphous silica-aluminas and zeolites. The hydrogenating function is provided either by one or more metals of group VIII of the periodic table, such as iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium and platinum, or by a combination of at least one metal of group VI of the periodic table, such as molybdenum and tungsten, and at least one group VIII metal.

The balance between the two acid and hydrogenating functions is the basic parameter governing the activity and selectivity of the catalyst. A weak acid function and a strong hydrogenating function provide catalysts which are not very active and which work at a temperature which is usually high (above or equal to 390°C) and at a low feed volumetric flow rate (the VVH expressed by volume of feedstock to be treated per unit of volume of catalyst and per hour is generally less than or equal to 2) but provided with very good selectivity of middle distillates. Conversely, a strong acid function and a weak hydrogenating function provide catalysts which are active but which have less favourable selectivities of middle distillates. The search for a suitable catalyst will therefore be centered on a judicious choice of each of the functions for adjusting the activity/selectivity pair of the catalyst.

Thus, one of the great advantages of hydrocracking is the exhibiting of great flexibility at various levels: flexibility with regard to the catalysts used, which brings about flexibility of the feedstocks which are to be treated, and with regard to the products which are obtained. An easy parameter to control is the acidity of the substrate of the catalyst.

The conventional catalysts for catalytic hydrocracking, for the large part, consist of weakly acidic substrates, such as amorphous silica-aluminas, for example. These systems are used more particularly for producing middle distillates of very good quality and also oil bases when their acidity is very weak.

The family of amorphous silica-aluminas is found in slightly acid substrates. Many catalysts on the hydrocracking market have a silica-alumina base combined either with a group VIII metal, or, preferably, when the heteroatomic poison contents of the feedstock to be treated exceed 0.5% by weight, with a combination of sulfides of group VIB and VIII metals. These systems have very good selectivity in middle distillates, and the products formed are of good

quality. These catalysts, as far as the less acidic among them are concerned, can also produce lubricating bases. As mentioned, the drawback of all these catalytic systems which have an amorphous substrate base is their weak activity.

The catalysts comprising the FAU-structural-type Y zeolite or the catalysts comprising a beta-type zeolite, for example, admittedly have a higher catalytic activity than those of the amorphous silica-aluminas. However, they have higher selectivities in light products. In the prior art, the zeolites used for the preparation of hydrocracking catalysts are characterised by several magnitudes like their SiO_2/Al_2O_3 framework molar ratio, their crystalline parameter, their pore distribution, their specific surface area, their sodium ion uptake capacity, or else their water vapour adsorption capacity. Thus, the above patents of the Applicant (French Patents FR-A-2,754,742, FR-A-2,754,826) use a zeolite, the crystalline parameter of which is between 24.15 and 24.38A, the SiO_2/Al_2O_3 framework molar ratio between 500 and 21, the sodium content less than 0.15% by weight, the sodium ion uptake capacity greater than 0.85 g Na/100 g zeolite, the specific surface area greater than 400 m^2/g, the water vapour adsorption capacity greater than 6%, and 1 and 20% of the pore volume is contained in the pores with a diameter of between 20 and 80A.

In all prior art instances, the zeolites used have high crystalline fractions (or degree of crystallinity) and high peak rates.

Moreover, simple sulfides of group VB elements have been described as components of hydrorefining catalysts of hydrocarbon feedstocks, such as, for example, niobium trisulfide in US-A-5.294.333. Mixtures of simple sulfides comprising at least one group VB element and one group VIB element have also been tested as components of hydrorefining catalysts of hydrocarbon feedstocks, such as, for example, in US-A-4.910.181 or US-A-5.275.994. US-A-4.777.157 describes a catalyst comprising a niobium compound and a cracking compound which can be a Y zeolite, and use thereof in hydrocracking for the production of gasolines and kerosene.

The current processes for catalytic hydrorefining use catalysts which are able to promote the main reactions useful in exploiting heavy fractions, in particular hydrogenation of the aromatic cores (HAR), hydrodesulfurization (HDS), hydrodenitrating (HDN) and other hydroeliminations. Hydrorefining is used to treat feedstocks such as gasolines, vacuum gas

oils, atmospheric residues or vacuum residues deasphalted or otherwise. For example, cracking and catalytic hydrocracking processes are indicated for the treatment of the feedstocks. The nitrogen-containing heterocyclic compounds which are encountered in the heavy fractions act as poisons with very marked toxicity for the cracking or hydrocracking catalysts. Consequently, the denitrating of the catalytic hydrocracking feedstocks constitutes one of the possible means of improving the overall yield of these processes, and it is then desirable to reduce as much as possible the nitrogen content of the feedstocks before cracking them. At least one hydrorefining stage is usually integrated into each of the known sequences for upgrading heavy petroleum fractions.

The research work which has been carried out by the Applicant on a number of zeolites and microporous solids and on hydrogenating active phases has led him to discover, surprisingly, that selectivities of middle distillates (kerosene + gas oil) were obtained which were higher than with known prior art catalysts containing a Y zeolite if a catalyst according to the invention was used comprising at least one partially amorphous Y zeolite, at least one amorphous or poorly crystallised mineral matrix which is usually porous, such as alumina, at least one group VB element of the periodic table, such as tantalum, niobium, or vanadium, preferably niobium, and possibly at least one group VIB element of said periodic table, such as chromium, molybdenum, or tungsten, preferably molybdenum or tungsten, even more preferably molybdenum, possibly one group VIII element, i.e. an element selected from the group constituted by: Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, preferably iron, cobalt or nickel, possibly one element selected from the group formed by P, B and Si, possibly one group VIIA element, and preferably fluorine.

It could be seen that this catalyst has a more significant hydrocracking and hydrorefining activity than those of the catalytic formulae known in the prior art.

The catalyst of the present invention generally contains in % by weight in relation to the total mass of the catalyst:

- 0.1 to 99.8%, preferably 0.1 to 90%, and still more preferably 0.1 to 80%, of a partially amorphous Y zeolite,
- 0.1 to 60%, preferably 0.1 to 50%, and still more preferably 0.1 to 40%, of at least one metal selected from group VB,

- 0.1 to 99.8%, preferably 0.1 to 99%, preferably 1 to 98%, of an oxide-type amorphous or poorly crystallized porous mineral matrix,
  said catalyst being characterised in that it possibly contains:
- 0 to 60%, advantageously 0.1 to 60%, preferably 0.1 to 50%, and still more preferably 0.1 to 40% of at least one hydro-dehydrogenating metal preferably selected from the group VIII and group VIB elements.
- 0 to 20%, preferably 0.1 to 15%, and still more preferably 0.1 to 10%, of at least one promoter element selected from the group constituted by silicon, boron and phosphorus, not including the silicon which is possibly contained in the zeolite framework, the element preferably being boron and/or silicon,
- 0 to 20%, preferably 0.1 to 15%, and still more preferably 0.1 to 10%, of at least one element selected from group VIIA, preferably fluorine.

The partially amorphous Y zeolite used in the present invention is a solid with the following characteristics:

i. a peak rate which is less than about 0.40, preferably less than about 0.30,
ii. a crystalline fraction, expressed in relation to a reference Y zeolite in sodium form (Na) which is less than about 60%, preferably less than about 50%.

Preferably, the solid, partially amorphous Y zeolites forming part of the composition of the catalyst according to the invention have at least one (and preferably all) of the other following characteristics:

iii) an overall Si/Al ratio greater than 15, preferably greater than 20 and less than 150,
iv) an Si/Al^{IV} framework ratio greater than, or equal to, the overall Si/Al ratio.
v) a pore volume at least equal to 0.20 ml/g of solid whose fraction, between 8% and 50%, is constituted by pores with a diameter of at least 5 nm (nanometer) or 50 Å,
vi) a specific surface area of 210-800 m^2/g, preferably 250-750 m^2/g, and advantageously 300-600 m^2/g.

The peak rates and crystalline fractions are determined by x-ray diffraction using a procedure which is derived from the ASTM D3906-97 method, "Determination of Relative X-ray Diffraction Intensities of Faujasite-Type-Containing Materials." It is possible to refer to this

method for the general conditions of application of the procedure, and, in particular, for the preparation of samples and references.

A diffractogramme consists of lines which are characteristic of the crystallized fraction of the sample and a bottom, essentially produced by the diffusion of the amorphous or microcrystalline fraction of the sample (a weak diffusion signal is linked to the equipment, air, sample holder, etc.). The peak rate of a zeolite is the ratio, in a predefined angular zone (typically 8 to 40° 2θ when Kα radiation of copper is used, $\lambda = 0.154$ nm), of the area of the lines of the zeolite (peaks) to the overall area of the diffractogramme (peaks + trough). This peaks/(peaks + trough) ratio is proportional to the amount of crystallized zeolite in the material.

To estimate the crystalline fraction of a Y zeolite sample, the peak rate of the sample will be compared to that of a reference considered as being 100% crystallized (NaY, for example). The peak rate of a perfectly crystallized NaY zeolite is in the order of 0.55 to 0.60.

The peak rate of a standard USY zeolite is 0.45 to 0.55; its crystalline fraction in comparison with a perfectly crystallized NaY is 80 to 95%. The peak rate of the solid which is the object of the present invention is less than 0.4, and preferably less than 0.35. Its crystalline fraction is therefore less than 70%, preferably less than 60%.

The partially amorphous zeolites are prepared in accordance with techniques used generally for dealuminification, starting with commercially available Y zeolites, i.e. which usually have high crystallinities (at least 80%). More generally, it is possible to start with zeolites with a crystalline fraction of at least 60% or at least 70%.

The Y zeolites generally used in the hydrocracking catalysts are produced by modifying the commercially available Na-Y zeolite. This modification permits so-called stabilized, ultra-stabilized, or else dealuminified zeolites to be obtained. The modification is carried out by at least one of the dealuminification techniques, e.g. the hydrothermic treatment, acid attack. Preferably, the modification takes place by combining three types of operations known to the skilled person: hydrothermic treatment, ion exchange and acid attack. The hydrothermic treatment is perfectly defined by the union of operating variables, such as temperature, duration, total pressure and partial pressure of water vapour. This treatment has

the effect of extracting aluminium atoms from the silico-aluminium framework of the zeolite. The consequence of this treatment is an increase in the SiO_2/Al_2O_3 framework molar ratio and a reduction in the crystalline mesh parameter.

The ion exchange usually takes place by immersing the zeolite into an aqueous solution containing ions which can be fixed to the cationic exchange sites of the zeolite. In this way, the sodium cations present in the zeolite following crystallisation are removed.

The acid attack operation consists in contacting the zeolite with an aqueous solution of a mineral acid. The severity of the acid attack is adjusted by the acid concentration, duration and temperature. When carried out on a hydrothermically treated zeolite this treatment has the effect of eliminating the aluminium species which are extracted from the framework and which block the micropores of the solid.

The partially amorphous Y zeolite which is used in the catalysts according to the invention is at least in part in hydrogen form or acid (H+) form or ammonium (NH_4+) or cationic form, said cation being selected from the group formed by groups IA, IB, IIA, IIB, IIIA, IIIB (including rare earths), Sn, Pb and Si; it is preferably at least in part in H+ form, or it can also be used at least in part in cationic form (as defined above).

The partially amorphous Y zeolite which is at least partly in acid form (and preferably in H form in its entirety) or partially exchanged with cations, e.g. alkaline cations and/or alkaline-earth cations, will preferably be used.

The catalyst comprising at least one partially amorphous Y zeolite also contains a hydrogenating function. The hydrogenating function, as defined hereinabove, preferably comprises at least one metal selected from the group formed by the metals of groups VIB and VIII of the periodic table.

In one realisation of the invention, the catalyst preferably contains at least one element selected from the group formed by boron, silicon and phosphorus. The catalyst possibly contains at least one group VIIA element, preferably chlorine and fluorine, and also possibly at least one group VIIB element.

The boron, silicon and/or phosphorus can be in the matrix, the zeolite, or are preferably deposited on the catalyst and then mainly located on the matrix.

The element introduced, and, in particular, the silicon which is located mainly on the matrix of the substrate, can be characterised by techniques such as Castaing microprobe (distribution profile of various elements), transmission electron microscopy coupled with X analysis of the components of the catalysts, or else by establishing a cartograph for the distribution of elements present in the catalyst by electron microprobe.

The group VB, VIB and VIII metals of the catalyst of the present invention can be present completely or partially in metallic form and/or oxide form and/or sulfide form.

The porous mineral matrix which is usually amorphous or poorly crystallised is generally constituted by at least one refractory oxide in amorphous or poorly crystallized form. Said matrix is preferably selected from the group formed by alumina, silica-alumina, or a mixture of at least two of the oxides cited hereinabove. It is also possible to select aluminates. It is preferable to use matrices which contain alumina in all these forms known to the skilled person, e.g the gamma-alumina.

The catalysts according to the invention can be prepared in accordance with all of the methods well-known to the skilled person.

A preferred process for preparation of the catalyst according to the present invention comprises the following steps:

a) the drying and weighing takes place of a solid, referred to hereinafter as the precursor, and containing at least one of the following components: at least one matrix, at least one partially amorphous Y zeolite, possibly at least one element selected from the group VIB and group VIII elements, possibly at least one element selected from the phosphorus, boron and silicon group, possibly at least one group VIIA element, the whole preferably being shaped,

b) the dry solid obtained in step a) is calcined at a temperature of at least 150°C.

c) the precursor solid, defined in step b) is impregnated with a solution containing a group VB element, preferably niobium,

d) the moist solid is left in a moist atmosphere at a temperature of between 10 and 120°C,

e) the moist solid obtained in step d) is dried at a temperature of between 60 and 150°C.

The precursor of step c) above can be prepared in accordance with all conventional methods known to the skilled person. In accordance with another preferred preparation process, the precursor is obtained by mixing at least one matrix and at least one partially amorphous Y zeolite, followed by shaping, drying and calcination. The group VIB, VIII elements and those selected from phosphorus, boron, silicon and the group VIIA elements are then possibly introduced by way of any method known to the skilled person at any of stages a) to e), before or after shaping and before or after calcination of the precursor or catalyst.

Shaping can be carried out, by way of example, by extrusion, pelletizing, by the oil-drop method, by turntable granulation, or by any other method well-known to the skilled person. At least one calcination operation can be performed after any one of the preparation steps; it is usually performed in air at a temperature of at least 150°, preferably of at least 300°C. In this way, the product obtained at the end of stage a) and/or stage e) and/or possibly following introduction of the group VIB, VIII element(s), those selected from phosphorus, boron, silicon, and the group VIIA elements, is then possibly calcined in air, usually at a temperature of at least 150°C, preferably of at least 250°C, currently of about 350 to 1000°C.

The hydrogenating element can be introduced at any stage of the preparation, preferably during the mixing, or most preferably following the shaping. The shaping is followed by calcination, and the hydrogenating element can also be introduced before or after this calcination. The preparation usually ends with calcination at a temperature of between 250 and 600°C. Another of the preferred methods according to the present invention consists in mixing at least one partially amorphous Y zeolite in a moist alumina gel for several tens of minutes, then in passing the paste thus obtained through a die in order to form extrudes of between 0.4 and 4 mm in diameter. The hydrogenating function can thus be introduced in part only (for example, in the case of combinations of oxides of group VIB and VIII metals) or completely at the time of mixing at least one partially amorphous Y zeolite, with at least

one oxide gel selected as matrix. It can also be introduced by one or more ion exchange operations on the calcined substrate constituted by at least one partially amorphous Y zeolite which is dispersed in at least one matrix with solutions containing the precursor salts of the chosen metals, when these latter belong to group VIII. It can also be introduced by one or more impregnation operations of the shaped and calcined support, by a solution of the precursors of the oxides of group VIII metals (in particular, cobalt and nickel) when the precursors of the oxides of group VIB metals (notably molybdenum or tungsten) have been previously introduced when the substrate was mixed. Finally, it can also be introduced by way of one or more impregnation operations of the calcined substrate constituted by at least one partially amorphous Y zeolite and by at least one matrix, with solutions containing the precursors of the oxides of the group VI and/or VIII metals, the precursors of the oxides of the group VIII metals preferably being introduced after those of group VIB or at the same time as these latter.

Preferably, the substrate is impregnated with an aqueous solution. The support is preferably impregnated by way of the so-called "dry" impregnation method which is well-known to the skilled person. The impregnation can be carried out in one single stage by a solution containing all the constituent elements of the final catalyst.

The boron and/or silicon and/or phosphorus, and possibly the element selected from group VIIA, preferably fluorine, can be introduced into the catalyst at any level of the preparation and in accordance with any technique known to the skilled person.

A preferred method of the invention consists in depositing the promoter element(s) selected, e.g. the boron-silicon pair, onto the precursor which may, or may not, be calcined. To that end, an aqueous solution is prepared of at least one boron salt, such as ammonium biborate or ammonium pentaborate in alkaline medium and in the presence of hydrogen peroxide, and so-called "dry" impregnation is carried out in which the pore volume of the precursor is filled with the solution which contains, for example, boron. If silicon, for example, is also deposited, a solution will be used of a silicone-type silicon compound.

The boron and silicon can also be deposited simultaneously by the use of a solution containing a boron salt and a silicone-type silicon compound, for example. Thus, for example, if the precursor is a catalyst of the nickel-molybdenum type which is supported on

alumina and partially amorphous Y zeolite, then it is possible to impregnate the precursor with the aqueous solution of ammonium biborate and Rhodorsil E1P silicone of Rhône-Poulenc, to undertake drying at, for example, 80°C, followed by impregnation with an ammonium fluoride solution, to undertake drying at, for example, 80°C, and to carry out calcination, for example and preferably in air, in a flushed bed, for example at 500°C for 4 hours. The group VB element is then deposited by way of any method known to the skilled person.

The promoter element which is selected from the group formed by silicon, boron and phosphorus and the element which is selected from the group VIIA halide ions can be introduced by way of one or more impregnation operations with excess solution on the calcined precursor.

Thus, for example, it is possible to impregnate the precursor with an aqueous solution of ammonium biborate or Rhodorsil E1P silicone by Rhône-Poulenc, to carry out drying, for example at 80°C, then to carry out impregnation with an ammonium fluoride solution, to carry out drying, for example at 80°C, and to carry out calcination, by way of example and preferably in air in a flushed bed, for example at 500°C for 4 hours. The group VB element is then deposited by way of any method known to the skilled person.

Other impregnation sequences can be used in order to obtain the catalyst according to the invention.

For example, it is possible to impregnate the precursor with a solution containing one of the promoter elements (P, B, Si), to dry, calcine, and then impregnate the solid obtained with the solution containing another promoter element, to dry it, to calcine it. It is also possible to impregnate the precursor with a solution containing two of the promoter elements, to dry, calcine and then impregnate the solid obtained with the solution containing another promoter element, to dry it and to carry out final calcination. The group VB element is then deposited in accordance with any method known to the skilled person.

The catalyst of the present invention can thus possibly contain at least one group VIII element, such as iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium or platinum. Of the group VIII metals, it is preferable to use a metal selected from the group

formed by iron, cobalt, nickel and ruthenium. The catalyst according to the invention can also contain at least one group VIB element, preferably tungsten and molybdenum. Advantageously, the combinations of the following metals are used: nickel-molybdenum, cobalt-molybdenum, iron-molybdenum, iron-tungsten, nickel-tungsten, cobalt-tungsten, and the preferred combinations are : nickel-molybdenum, cobalt-molybdenum, and nickel-tungsten. It is also possible to use combinations of three metals, for example nickel-cobalt-molybdenum. Advantageously, the following combinations of metals are used: nickel-niobium-molybdenum, cobalt-niobium-molybdenum, iron-niobium-molybdenum, nickel-niobium-tungsten, cobalt-niobium-tungsten, iron-niobium-tungsten, the preferred combinations being: nickel-niobium-molybdenum, cobalt-niobium-molybdenum. It is also possible to use combinations of four metals, for example nickel-cobalt-niobium-molybdenum. It is also possible to use combinations containing a noble metal, such as ruthenium-niobium-molybdenum, or ruthenium-nickel-niobium-molybdenum.

If the elements are introduced in several impregnations of the corresponding precursor salts, an intermediate calcination stage of the catalyst has to be carried out at a temperature of, by way of example and preferably, between 250 and 600°C.

Impregnation of the molybdenum can be facilitated by adding phosphoric acid to the ammonium paramolybdate solutions, which also permits the introduction of phosphorus so as to promote catalytic activity. Other phosphorus compounds can be used, as is well-known to the skilled person.

Impregnation of the niobium can be facilitated by adding oxalic acid, and possibly ammonium oxalate, to the niobium oxalate solutions. Other compounds can be used for improving solubility and for facilitating impregnation of the niobium, as is well-known to the skilled person.

The sources of the group VB element which can be used are well-known to the skilled person. For example, of the niobium sources oxides can be used, such as diniobium pentaoxide Nb_2O_5, niobic acid $Nb_2O_5.H_2O$, niobium hydroxides and polyoxoniobates, niobium alkoxydes of formula $Nb(OR_1)_3$ where R_1 is an alkyl radical, niobium oxalate $NbO(HC_2O_4)_5$, ammonium niobate. Niobium oxalate or ammonium niobate are preferably used.

The preferred phosphorus source is orthophosphoric acid H_3PO_4, but the salts and esters thereof, such as the ammonium phosphates, are also suitable. The phosphorus can be introduced, for example, in the form of a mixture of phosphoric acid and a basic organic compound containing nitrogen, such as ammonia, primary and secondary amines, cyclic amines, compounds of the pyridine family, and quinolines, and compounds of the pyrrole family.

Numerous silicon sources can be used. Thus, it is possible to use ethyl orthosilicate $Si(OEt)_4$, siloxanes, polysiloxanes, silicones, silicone emulsions, halide silicates, such as ammonium fluorosilicate $(NH_4)_2SiF_6$ or sodium fluorosilicate Na_2SiF_6. Silicomolybdic acid and the salts thereof, and silicotungstic acid and the salts thereof can also advantageously be used. The silicon can also be added, for example, by impregnation of ethyl silicate in solution in a water/alcohol mixture. The silicon can also be added, for example, by impregnation of a silicone-type silicon compound which is placed in suspension in water.

The boron source can be boric acid, preferably orthoboric acid H_3BO_3, ammonium biborate or pentaborate, boron oxide, and boric esters. The boron can be introduced, for example, in the form of a mixture of boric acid, hydrogen peroxide and a basic organic compound containing nitrogen, such as ammonia, primary and secondary amines, cyclic amines, compounds of the pyridine family and quinolines and compounds of the pyrrole family. Boron can be introduced, for example, by way of a boric acid solution in a water/alcohol mixture.

The sources of group VIIA elements which can be used are well-known to the skilled person. For example, fluoride anions can be introduced in the form of hydrofluoric acid or the salts thereof. These salts are formed with alkaline metals, ammonium or an organic compound. In the latter case, the salt is advantageously formed in the reaction mixture by reaction between the organic compound and the hydrofluoric acid. It is also possible to use hydrolysable compounds which can release fluoride anions in water, such as ammonium fluorosilicate $(NH_4)_2SiF_6$, silicon tetrafluoride SiF_4 or sodium tetrafluoride Na_2SiF_6. The fluorine can be introduced, for example, by impregnation of an aqueous solution of hydrofluoric acid or of ammonium fluoride.

The sources of group VIB elements which can be used are well-known to the skilled person. For example, of the molybdenum and tungsten sources it is possible to use oxides and

hydroxides, molybdic and tungstic acids and salts thereof, in particular ammonium salts such as ammonium molybdate, ammonium heptamolybdate, ammonium tungstate, phosphomolybdic acid, phosphotungstic acid and salts thereof, silicomolybdic acid, silicotungstic acid and salts thereof. Preferably, ammonium oxides and salts are used, such as ammonium molybdate, ammonium heptamolybdate and ammonium tungstate.

The sources of group VIII elements which can be used are well-known to the skilled person. For example, for the non-noble metals, nitrates, sulfates, phosphates, halides, e.g. chlorides, bromides and fluorides, carboxylates, e.g. acetates and carbonates are used. For the noble metals, halides will be used, e.g. chloride, nitrates, acids such as chloroplatinic acid, and oxychlorides such as ruthenium ammoniacal oxychloride.

The catalysts which are obtained by way of the present invention are generally shaped. The grains thus obtained are of different shapes and sizes. They are generally used in the form of cylindrical or multilobar extrudes, such as bilobar, trilobar, polylobar extrudates of straight or twisted shape, but they can possibly be produced and used in the form of crushed powder, tablets, rings, balls, and wheels. They have a specific surface area, measured by nitrogen adsorption according to the BET method (Brunauer, Emmett, Teller, J. Am. Chem. Soc., Vol. 60, 308-316 (1938)) of between 50 and 600 m^2/g, a pore volume measured by mercury porosimetry of between 0.2 and 1.5 cm^3/g and a pore size distribution which can be monomodal, bimodal or polymodal.

The catalysts which are obtained by way of the present invention are used for conversion, in particular hydroconversion, of hydrocarbon feedstocks, such as petroleum feedstocks, and, for example, hydrocracking. The hydroconversion catalyst then contains at least one hydro-dehydrogenating element. The feedstocks which are used in the process are gasolines, kerosenes, gas oils, vacuum gas oils, atmospheric residues, vacuum residues, atmospheric distillates, vacuum distillates, heavy fuels, oils, waxes and paraffins, used oils, residues or deasphalted crude oils, feedstocks obtained from thermal or catalytic conversion processes, and mixtures thereof. They contain heteroatoms such as sulfur, oxygen, and nitrogen, and possibly metals.

The catalysts which are thus obtained are used advantageously for the hydrocracking, in particular of vacuum distillate-type heavy hydrocarbon fractions, deasphalted or hydrotreated

residues, or the equivalent. The heavy fractions preferably consist of at least 80% by volume of compounds with boiling points of at least 350°C, preferably of between 350 and 580°C (i.e. corresponding to compounds which contain at least 15 to 20 carbon atoms). They generally contain heteroatoms, such as sulfur and nitrogen. The nitrogen content is usually between 1 and 5000 ppm by weight, and the sulfur content is between 0.01 and 5% by weight.

The hydrocracking conditions, such as temperature, pressure, hydrogen recycling rate and hourly volumetric flow rate can be very variable depending upon the nature of the feedstock, the quality of the desired products and the installations available to the refiner. The temperature is generally above 200°C, and often between 250°C and 480°C. The pressure is greater than 0.1 MPa and often greater than 1 MPa. The quantity of hydrogen is at least 50 litres of hydrogen per litre of feedstock, and often between 80 and 5000 litres of hydrogen per litre of feedstock. The hourly volumetric flow rate is generally between 0.1 and 20 volumes of feedstock per volume of catalyst and per hour (h^{-1}).

The catalysts of the present invention are preferably subjected to a sulfurization treatment which permits at least partial transformation of the metallic species into sulfide prior to contacting them with the feedstock which is to be treated. This activation treatment by sulfurization is well-known to the skilled person, and can be carried out using any method already described in the literature.

Sulfurization of solids (catalysts) which contain at least one group VB element in oxide form proves to be very difficult by the majority of conventional sulfurization methods known to the skilled person. Indeed, catalysts which contain at least one group VB element supported on an alumina-type matrix are known to be very difficult to sulfurize once the group VB element-alumina combination has been calcined at a temperature of above 200°C.

Sulfurization can be carried out by way of any method known to the skilled person and at any stage of the preparation. The preferred method according to the invention consists in heating the non-calcined catalyst in a stream of a hydrogen-hydrogen sulfide mixture, or in a stream of a nitrogen-hydrogen sulfide mixture, or in pure hydrogen sulfide, at a temperature of between 150 and 800°C, preferably of between 250 and 600°C, generally in a flushed-bed reaction zone. Thus, by way of example, in the preferred case where the group VB metal is niobium and where the group VIB metal is molybdenum, it is possible to impregnate the

substrate with ammonium heptamolybdate, to carry out drying at 80°C, and then to carry out impregnation with niobium oxalate, to carry out drying at 80°C, and to carry out sulfurization for example and preferably by H_2S in a flushed bed, for example at 500°C for 10 hours.

The sulfur source can be elementary sulfur, carbon sulfide, hydrogen sulfide, sulfur-containing hydrocarbons, such as dimethyl sulfide, dimethyl disulfide, mercaptans, thiophene compounds, thiols, polysulfides such as di-tert-nonylpolysulfide or TPS-37 by ATOCHEM, petroleum fractions with a high sulfur content, such as gasoline, kerosene, gas oil, alone or mixed with one of the sulfur-containing compounds cited hereinabove. The preferred sulfur source is carbon sulfide or hydrogen sulfide.

The catalyst of the present invention can be used advantageously for the hydrocracking of hydrocarbon feedstocks, in particular vacuum distillate-type fractions, more particularly fractions with a sulfur content greater than 0.1% by weight and with a nitrogen content which is greater than 10 ppm.

In a first embodiment for partial hydrocracking, also called gentle hydrocracking, the conversion level is less than 55%. The catalyst according to the invention is then used at a temperature which is generally above or equal to 230°C, and preferably between 300°C and 480°C, and most often between 350°C and 450°C. The pressure is generally above 2 MPa, and preferably above 3 MPa, and less than 12 MPa, and preferably less than 10 MPa. The amount of hydrogen is at least 100 litres of hydrogen per litre of feedstock, and often between 200 and 3000 litres of hydrogen per litre of feedstock. The hourly volumetric flow rate is generally between 0.1 and 10 h^{-1}. Under these conditions, the catalysts of the present invention have better activity in conversion, hydrodesulfurization, and hydrodenitrating than commercial catalysts.

In a second embodiment, the catalyst of the present invention can be used for partial hydrocracking, advantageously under moderate hydrogen pressure conditions, of, for example, vacuum distillate-type fractions which have a high sulfur and nitrogen content, and which have previously been subjected to hydrotreatment. In this hydrocracking mode, the conversion level is less than 55%. In this case, the conversion process of the petroleum fraction takes place in two stages, the catalysts according to the invention being used in the second stage. The catalyst of the first stage can be any hydrotreatment catalyst and comprises

a matrix preferably with an alumina base, and preferably not containing zeolite, and at least one metal with a hydrogenating function. Said matrix is an oxide-type amorphous, or poorly crystallised, porous mineral matrix. By way of non-limitative example, the aluminas, silicas, and silica-aluminas can be cited. It is also possible to select aluminates. It is preferable to use matrices containing alumina, in all forms known to the skilled person, and, still more preferably, aluminas, e.g. the gamma-alumina. The hydrotreatment function is provided by at least one metal or group VIII metal compound, such as nickel and cobalt, for example. It is possible to use a combination of at least one metal or metal compound of group VIB (e.g. molybdenum or tungsten) and of at least one metal or metal compound of group VIII (e.g. cobalt or nickel) of the periodic table. The total concentration of metal oxides of groups VIB and VIII is preferably between 5 and 40% by weight, and, very preferably, between 7 and 30% by weight, and the ratio expressed in terms of weight of metal oxide of group VIB metal(s) to group VIII metal(s) is preferably between 1.25 and 20, and, very preferably, between 2 and 10. In addition, this catalyst can possibly contain phosphorus. The phosphorus content, expressed as a concentration of diphosphorus pentaoxide P_2O_5 is preferably at most 15%, more preferably between 0.1 and 15% by weight, and, very preferably, between 0.15 and 10% by weight. It can also contain boron in a B/P ratio = 1.05 - 2 (atomic), the sum of the B and P contents, expressed in terms of oxides, preferably being between 5 and 15% by weight.

The first stage generally takes place at a temperature of between 350 and 460°C, preferably of between 360 and 450°C, a pressure of at least 2 MPa, and preferably of at least 3 MPa, an hourly volumetric flow rate of 0.1-5 h^{-1}, and preferably 0.2-2 h^{-1}, and with an amount of hydrogen of at least 100 litres of hydrogen per litre of feedstock, and preferably 260-3000 litres of hydrogen per litre of feedstock.

For the conversion stage with the catalyst according to the invention (or second hydrocracking stage), the temperatures are generally above or equal to 230°C, and often between 300°C and 480°C, preferably between 330°C and 450°C. The pressure is generally at least 2 MPa, and preferably at least 3 MPa, and less than 12 MPa, preferably less than 10 MPa. The amount of hydrogen is at least 100 litres of hydrogen per litre of feedstock, and often between 200 and 3000 litres of hydrogen per litre of feedstock. The hourly volumetric flow rate is generally between 0.15 and 10 h^{-1}. Under these conditions, the catalysts of the present invention have a better activity in conversion, in hydrodesulfurisation, in

hydrodenitrating and a better selectivity in middle distillates than commercial catalysts. The service life of the catalysts is also improved in the moderate pressure range.

In another embodiment in two stages, the catalyst of the present invention can be used for hydrocracking under high hydrogen pressure conditions of at least 5 MPa. The treated fractions are, for example, vacuum distillate types with a high content of sulfur and nitrogen, and have previously been subjected to hydrotreatment. In this hydrocracking mode, the conversion level is above 55%. In this case, the conversion level of the petroleum fraction takes place in two stages, the catalyst according to the invention being used in the second stage.

The catalyst of the first stage has a hydrotreatment function and comprises a matrix, preferably with an alumina base, and preferably not containing any zeolite, and at least one metal which has a hydrogenating function. Said matrix can also be constituted by, or contain, silica, silica-alumina, boron oxide, magnesium, zirconium, titanium oxide, or a combination of these oxides. The hydro-dehydrogenating function is provided by at least one metal or metal compound of group VIII, such as nickel and cobalt, in particular. It is possible to use a combination of at least one metal or metal compound of group VI (in particular, molybdenum or tungsten) and at least one metal or metal compound of group VIII (in particular, cobalt or nickel) of the periodic table. The total concentration of oxides of group VI and VIII metals is between 5 and 40% by weight, and preferably between 7 and 30% by weight, and the weight ratio expressed in terms of metallic oxide of metal (or metals) of group VI to metal (or metals) of group VIII is between 1.25 and 20, and preferably between 2 and 10. Furthermore, this catalyst can contain phosphorus. The content of phosphorus, expressed in terms of the concentration of diphosphorus pentaoxide P_2O_5 generally will be at most 15%, preferably between 0.1 and 15% by weight, and preferably between 0.15 and 10% by weight. It can also contain boron in a B/P ratio of 1.02-2 (atomic), the sum of the B and P contents, expressed in terms of oxides, being 5-15% by weight.

The first stage generally takes place at a temperature of between 350 and 460°C, preferably of between 360 and 450°C, a total pressure of at least 2 MPa, and preferably of at least 3 MPa, an hourly volumetric flow rate of 0.1-5 h^{-1}, and preferably 0.2-2 h^{-1}, and with an amount of hydrogen of at least 100 litres of hydrogen per litre of feedstock, and preferably 260-3000 litres of hydrogen per litre of feedstock.

For the conversion stage with the catalyst according to the invention (or second stage), the temperatures are generally above or equal to 230°C, and often between 300°C and 480°C, preferably between 300°C and 440°C. The pressure is generally greater than 5 MPa, and preferably greater than 7 MPa. The amount of hydrogen is at least 100 litres of hydrogen per litre of feedstock and often between 200 and 3000 litres of hydrogen per litre of feedstock. The hourly volumetric flow rate is generally between 0.15 and 10 h^{-1}.

Under these conditions, the catalysts of the present invention have a better conversion activity than commercial catalysts, even when the zeolite contents are considerably lower than those of the commercial catalysts.

The catalysts obtained by way of the present invention are also used for the hydrorefining of hydrocarbon feedstocks, such as petroleum fractions, fractions obtained from carbon, or hydrocarbons produced from natural gas. The main reactions used are hydrogenation of aromatic compounds, hydrodenitrating, hydrodeoxygenation, hydrodesulfurization, hydrodemetallization, accompanied most frequently by hydrocracking. The hydrocarbon feedstocks contain aromatic compounds and/or olefinic compounds and/or napthenic compounds and/or paraffinic compounds, and possibly metals and/or nitrogen and/or oxygen and/or sulfur. In these uses, the catalysts which are obtained by way of the present invention have an improved activity in comparison with the prior art.

The feedstocks used in the process are gasolines, gas oils, vacuum gas oils, atmospheric residues, vacuum residues, atmospheric distillates, vacuum distillates, heavy fuels, oils, waxes, and paraffins, used oils, deasphalted residues or crude oils, feedstocks which are obtained from thermal or catalytic conversion processes and their mixtures. They contain heteroatoms, such as sulphur, oxygen and nitrogen, and at least one metal. The heavy fractions, as such and by way of non-limitative example, vacuum distillates, deasphalted or hydrotreated residues, or equivalents, preferably consist of at least 80% by volume of compounds with boiling points of at least 350°C, and preferably of between 350 and 580°C (i.e. corresponding to compounds which contain at least 15 to 20 carbon atoms). They generally contain heteroatoms like sulfur and nitrogen. The nitrogen content is usually between 1 and 5000 ppm by weight, and the sulfur content is between 0.01 and 5% by weight.

The catalysts of the present invention are also advantageously used preferably during the pretreatment of catalytic cracking feedstocks and in the first stage of a gentle hydrocracking or hydroconversion operation. They are then usually used in combination with an acid catalyst which may or may not be zeolitic for the second treatment stage.

The hydrorefining conditions, such as temperature, pressure, hydrogen recycling rate, hourly volumetric flow rate, can be very variable depending upon the nature of the feedstock, quality of the desired products, and installation available to the refiner. The temperature is usually above 200°C, and often between 250°C and 480°C. The pressure is above 0.05 MPa and often above 1 MPa. The hydrogen recycling rate is at least 80, and often between 50 and 5000 normal litres of hydrogen per litre of feedstock. The hourly volumetric flow rate is generally between 0.1 and 20 volumes of feedstock per volume of catalyst and per hour.

The catalysts of the present invention are preferably subjected to a sulfurization treatment permitting at least partial transformation of the metallic species into sulfide before they are brought into contact with the feedstock to be treated. This activation treatment by sulfurization is well-known to the skilled person, and can be carried out using any method which has already been described in the literature.

A conventional sulfurization method well-known to the skilled person consists in heating the mixture of solids in a stream of a hydrogen and hydrogen sulfide mixture, or in a stream of a nitrogen and hydrogen sulfide mixture, at a temperature of between 150 and 800°C, preferably of between 250 and 600°C, generally in a flushed bed reaction zone.

The results which are of importance to the refiner are the HDS activity, the HDN activity, and the conversion activity. The desired goals should be achieved under conditions which are compatible with economic reality. Thus, the refiner seeks to decrease the temperature, the pressure, and the hydrogen recycling rate, and to maximise the hourly volumetric flow rate. It is known that the activity can be increased by a temperature increase, but this is often to the detriment of the stability of the catalyst. The stability or service life improves with an increase in pressure or in hydrogen recycling rate, but this is to the detriment of the economy of the process.

The following examples illustrate the present invention, but without limiting the scope thereof.

Example 1: Preparation of a Hydrocracking Catalyst Substrate which contains a Partially Amorphous Y Zeolite

A USY commercial ultrastable dealuminified zeolite with an overall Si/Al molar ratio of 15.2, an Si/Al framework ratio of 29, a crystalline parameter of 24.29Å, containing 0.03% by weight Na, with a peak rate of 0.48 and with a crystalline fraction of 85%, is amorphized by a hydrothermic treatment at 620°C for 5 hours in the presence of a partial water vapour pressure of 0.5 bar absolute. The zeolite is then subjected to acid attack carried out under the following conditions: normality of the acid: 0.85N, duration: 3 hours; and temperature : 95°C. A final hydrothermic treatment which is identical to the first one, with a partial water vapour pressure of 0.02 bar is applied to the zeolite. At the end of these treatments, the partially amorphous zeolite has a peak rate of 0.26, a crystalline fraction of 44%, an overall Si/Al ratio of 72, and an Si/Al^{IV} framework ratio of 80, a pore volume of 0.35 ml liquid nitrogen per gramme, 29% of which consists of pores of at least 5 nanometres (50 Å) in diameter. A hydrocracking catalyst substrate containing this Y zeolite is produced in the following way:

50 g of the partially amorphous Y zeolite described hereinabove is mixed with 50 g of a matrix consisting of ultrafine tabular boehmite or alumina gel marketed under the name SB3 by Condéa Chemie GmbH. This powder mixture was then mixed with an aqueous solution containing nitric acid at 66% (7% by weight acid per gramme of dry gel), then mixed for 15 minutes. At the end of this mixing, the paste which is obtained is passed through a die with cylindrical orifices of 1.4 mm in diameter. The extrudates are then dried for one night at 120°C in air, and then calcined at 550°C in air.

Example 2: Preparation of Catalysts which contain a Partially Amorphous Y Zeolite

The substrate extrudates, prepared in Example 1, which contain a partially amorphous Y zeolite are impregnated in the dry state with an aqueous solution of ammonium heptamolybdate and nickel nitrate, dried for one night at 120°C in air, and finally calcined in air at 550°C. The contents by weight of the oxides of the $NiMoY_2$ catalyst obtained are given in Table 1.

The extrudates are impregnated in the dry state with an aqueous solution of a mixture of ammonium heptamolybdate, nickel nitrate and orthophosphoric acid, dried for one night at

120°C in air, and finally calcined in air at 550°C. The contents by weight of $NiMoPY_2$ catalyst oxides obtained are given in Table 1.

We then impregnated the sample of the $NiMoPY_2$ catalyst with an aqueous solution containing ammonium biborate and Rhodorsil EP1 silicone emulsion, and obtained the $NiMoPBSiY_2$ catalyst. The final contents of oxides of the catalysts thus prepared are shown in Table 1.

Electron microprobe analysis of the $NiMoPBSiY_2$ and $NiMoNbPBSiY_2$ catalysts reveals that the silicon added to the catalyst according to the invention is located mainly on the matrix and is in the form of amorphous silica.

Example 3: Preparation of Catalysts containing a Partially Amorphous Y Zeolite and Niobium

The catalysts of Example 2 hereinabove are impregnated with an aqueous solution of niobium oxalate $Nb(HC_2O_4)_5$, oxalic acid and ammonium oxalate. The aqueous solution containing niobium is prepared from 1330 ml water in which 33 g oxalic acid, 37.2 g ammonium oxalate and 92.3 g niobium oxalate are dissolved. This makes it possible to deposit approximately 5% by weight Nb on the catalyst. In order to prepare the solution, the mixture of oxalic acid and ammonium oxalate is firstly dissolved, and when the solution is clear said solution is heated to 55°C, and niobium oxalate is added. Water is then added in order to obtain 1330 mm of solution.

The catalysts of Example 2 hereinabove are impregnated by the so-called excess solution method. The 1330 ml of solution are brought into contact with 380 g of catalyst. After two hours, the extrudates are recovered. These latter are then dried for one night at 120°C in a stream of dry air. The final contents of oxides of the $NiMoNbY_2$, $NiMoNbPY_2$ and $NiMoNbPBSiY_2$ catalysts thus obtained are indicated in Table 1.

Table 1 : Characteristics of the Catalysts of the Y_2 Series

Catalyst	$NiMoY_2$	$NiMoNbY_2$	$NiMoPY_2$	$NiMoNbPY_2$	$NiMoPBSiY_2$	$NiMoNbPBSiY_2$
MoO_3 (% by weight)	13.9	12.8	13.4	12.2	12.3	11.6
Nb_2O_5 (% by weight)	0	3.0	0	6.4	0	6.4
NiO (% by weight)	2.9	3.0	2.9	2.9	2.8	2.8
P_2O_5 (% by weight)	0	0	4.6	4.4	4.2	4.3
B_2O_3 (% by weight)	0	0	0	0	1.4	1.5
SiO_2 (% by weight)	41.0	38.3	39.0	36.5	40.7	37.6
Complement up to 100% consisting mainly of Al_2O_3 (% by weight)	42.2	39.4	40.1	37.6	38.6	35.8

Example 4 : Comparison of Catalysts in the Hydrocracking of a Vacuum Gas Oil with Partial Conversion.

The catalysts, preparation of which is described in Examples 1 to 3, are used under moderate pressure hydrocracking conditions on a petroleum feedstock, the main characteristics of which are as follows:

Density (20/4)	0.921
Sulphur (% by weight)	2.46
Nitrogen (ppm by weight)	1130
Simulated distillation	
Starting point	365°C
10% point	430°C

50% point	472°C
90% point	504°C
Final point	539°C
Pour point	+ 39°C

The catalytic test unit comprises two fixed-bed reactors, with upward circulation of the feedstock ("up-flow"). In the first reactor, i.e. that in which the feedstock passes first, the HTH548 hydrotreatment first-stage catalyst sold by Procatalyse is introduced which comprises a group VI element and a group VIII element which are deposited on alumina. In a second reactor, i.e. that in which the feedstock passes second, one of the hydrocracking catalysts prepared in Examples 1 to 3 is introduced. In each of the reactors, 40 ml of catalyst is introduced. The two reactors operate at the same temperature and at the same pressure. The operating conditions of the test unit are as follows:

Total pressure	5 MPa
Hydrotreatment catalyst	40 cm^3
Hydrocracking catalyst	40 cm^3
Temperature	400°C
Hydrogen flow rate	20 l/h
Feedstock flow rate	40 cm^3/h

The two catalysts undergo an in-situ sulfurization stage before reaction. It should be noted that any in-situ or ex-situ sulfurization method is suitable. Once the sulfurization has been carried out, the afore-described feedstock can be transformed.

The catalytic performances are expressed in terms of gross conversion at 400°C (GC), in terms of the coarse selectivity of middle distillates (CS) and in terms of hydrodesulfurization conversions (HDS) and in terms of hydrodenitration (HDN). These catalytic performances are measured on the catalyst after a stabilisation period, usually of at least 48 hours, has elapsed.

Hydrodesulfurization conversion HDS is assumed to be equal to:

$$HDS = (S_{initial} - S_{effluent}) / S_{initial} * 100 = (24600 - S_{effluent}) / 24600 * 100$$

Hydrodenitrating conversion HDN is assumed to be equal to:

$$HDN = (N_{initial} - N_{effluent}) / N_{initial} * 100 = (1130 - N_{effluent}) / 1130 * 100$$

The following table gives the hydrodesulfurization conversion HDS and the hydrodenitrating conversion HDN for the catalysts.

Table 2 : Catalytic activities of the partially amorphous Y zeolite-based catalysts in partial hydrocracking at 400°C

		HDS (%)	HDN (%)
$NiMoY_2$	$NiMo/Y_2$	98.6	95.3
$NiMoNbY_2$	$NiMoNb/Y_2$	98.9	96.8
$NiMoPY_2$	$NiMoP/Y_2$	99.4	96.4
$NiMoNbPY_2$	$NiMoNbP/Y_2$	99.5	97.2
$NiMoPBSiY_2$	$NiMoPBSi/Y_2$	99.55	98.5

The results of Table 2 reveal that the adding of niobium to the NiMo, NiMoP and NiMoPBSi catalysts based on substrates containing alumina and a partially amorphous Y zeolite brings about an improvement in the performances of the catalyst in terms of hydrodesulfurization, and, particularly, in terms of hydrodenitrating.

Example 5 : Comparison of Partially Amorphous Y-Based Catalysts in the Hydrocracking of a High-Conversion Vacuum Gas Oil

The catalysts containing partially amorphous Y zeolite and niobium, preparation of which has been described in Examples 1 to 3, are used under high-conversion hydrocracking conditions (60-100%). The petroleum feedstock is a hydrotreated vacuum distillate, the main characteristics of which are as follows:

Density (20/4)	0.869
Sulfur (ppm by weight)	502
Nitrogen (ppm by weight)	10
Simulated distillation	

Initial point	298°C
10% point	369°C
50% point	427°C
90% point	481°C
Final point	538°C

This feedstock was obtained by hydrotreatment of a vacuum distillate on a HR360 catalyst sold by Procatalyse and comprising a group VIB element and a group VIII element which are deposited on alumina.

Prior to the hydrotreatment, the feedstock contained 1500 ppm nitrogen and 3.2% sulfur. A H_2S precursor sulfur-containing compound and an ammonia precursor nitrogen-containing compound are added to the hydrotreated feedstock in order to simulate the partial pressures of H_2S and NH_3 in the hydrocracking stage. The feedstock thus prepared is injected into the hydrocracking test unit which comprises a fixed-bed reactor, with upward circulation of the feedstock ("up-flow"), into which 80 ml catalyst is introduced. Before injecting the feedstock, the catalyst is sulfurized by an n-hexane/DMDS + aniline mixture up to 320°C. Any in-situ or ex-situ sulfurization method can be used. Once sulfurization has been carried out, the afore-described feedstock can be transformed. The operating conditions of the test unit are as follows:

Total pressure	9 MPa
Catalyst	80 cm^3
Temperature	360-420°C
Hydrogen flow rate	80 l/h
Feedstock flow rate	8 cm^3/h

The catalytic performances are expressed in terms of the temperature which makes it possible to reach a gross conversion level of 70% and in terms of the coarse selectivity of 150-380°C middle distillates. These catalytic performances are measured on the catalyst after a stabilisation period, usually of at least 48 hours, has elapsed.

The gross conversion (GC) is assumed to be equal to:

GC = % by weight of 380°C ^{less} of the effluent

The coarse selectivity CS of middle distillate is assumed to be equal to:
CS = 100* by weight of the fraction (150°C-380°C) / weight of the 380°C^{less} fraction of the effluent

The reaction temperature is fixed in order to reach a gross conversion GC of 70% by weight. Table 3 hereinafter gives the reaction temperature and coarse selectivity for the catalysts described in Table 1.

Table 3: Catalytic Activities of the High-Conversion Hydrocracking Catalysts (70%)

		T (°C)	Selectivity of Middle Distillate (150-380°C) (% by weight)
$NiMoY_2$	$NiMo/Y_2$	394	70.4
$NiMoNbY_2$	$NiMoNb/Y_2$	392	70.7
$NiMoPY_2$	$NiMoP/Y_2$	393	71.2
$NiMoNbP\ Y_2$	$NiMoNbP/Y_2$	389	71.5
$NiMoPBSiY_2$	$NiMoPBSi/Y_2$	387	72.5
$NiMoNbPBSiY_2$	$NiMoNbPBSi/Y_2$	384	72.8

Table 3 reveals that the use of a catalyst according to the invention which contains partially amorphous Y zeolite and niobium results in higher conversion levels (i.e. lower conversion temperatures for a given conversion of 70% by weight) in comparison with catalysts which contain the same zeolite but which do not contain niobium. Moreover, at an iso-conversion of 70% by weight, all of the catalysts containing a partially amorphous Y zeolite and niobium according to the invention result in middle distillate selectivities (150-380°C fraction) which are better than those recorded in the case of catalysts containing the same zeolite but not containing any niobium.

CLAIMS

1. A catalyst comprising at least one matrix, at least one group VB element and at least one partially amorphous Y zeolite, having a peak rate of less than 0.4 and a crystalline fraction, expressed in relation to a reference zeolite in sodium (Na) form, which is less than 60%.

2. A catalyst according to claim 1 which also comprises at least one hydrodehydrogenating element.

3. A catalyst according to any one of the preceding claims, wherein the zeolite has :

- an overall Si/Al ratio greater than 15,
- an Si/Al^{IV} framework ratio greater than, or equal to, the overall Si/Al ratio,
- a pore volume at least equal to 0.20 ml/g of solid whose fraction, between 8% and 50%, is constituted by pores with a diameter of at least 5 nm.

4. A catalyst according to any one of the preceding claims, wherein the group VB element is niobium.

5. A catalyst according to any one of the preceding claims which also contains at least one element selected from the group formed by phosphorus, boron, and silicon.

6. A catalyst according to claim 5 wherein the element is deposited on the catalyst and mainly located on the matrix.

7. A catalyst according to any one of the preceding claims which also contains at least one group VIIA element.

8. A catalyst according to any one of the preceding claims which also contains at least one group VIIB element.

9. A catalyst according to claim 8 in which the group VIIB element is manganese.

10. A catalyst according to any one of the preceding claims which contains in % by weight in relation to the total mass of the catalyst:
    - 0.1 to 99.8% of at least one oxide-type amorphous or poorly crystallized porous mineral matrix,
    - 0.1 to 99.8% of partially amorphous Y zeolite,
    - 0 to 60% of at least one group VB element,
    - 0 to 60% of at least one hydro-dehydrogenating element,
    - 0 to 20% of at least one element selected from the group formed by boron, silicon, phosphorus;
    - 0 to 20% of at least one group VIIA element.

11. A catalyst according to any one of the preceding claims, wherein the matrix is selected from alumina, silica-alumina, aluminates, silica.

12. A process for the conversion of hydrocarbon feedstock with a catalyst according to any one of the preceding claims.

13. A process according to claim 12 for hydrocracking with a catalyst which also comprises at least one hydro-dehydrogenating element.

14. A process according to claim 13 for hydrocracking at a temperature of above 200°C, a pressure of above 0.1 MPa, a volumetric flow rate of 0.1-20h^{-1}, and a hydrogen recycling of at least 50Nl/l of feedstock.

15. A process according to claim 14, wherein the pressure is greater than 2 MPa and less than 12 MPa, the temperature is at least 230°C, the volumetric flow rate is 0.1-10h-1, and the hydrogen recycling is at least 100 Nl/l of feedstock, the conversion being less than 55%.

16. A process according to claim 14, in which the pressure is at least 5 MPa, and the conversion is greater than 55%.

17. A process according to claim 12 for hydro-refining with a catalyst which also

comprises at least one hydro-dehydrogenating element.

18. A process according to claim 17 which is carried out at a temperature of above 200°C, a pressure of above 0.05 MPa, a hydrogen recycling rate of at least 80 Nl/l of feedstock, and an hourly volumetric flow rate of 0.1-20 h^{-1}.

19. A process according to any one of claims 12 to 16, wherein the catalyst is sulfurized beforehand.

20. A process according to any one of claims 14 to 16, wherein the feedstock is subjected to a hydrotreatment before being hydrocracked.

21. A catalyst, according to one of the preceding claims, comprising:

(1) at least one matrix and at least one partially amorphous Y zeolite that has a peak ratio that is less than 0.4, a crystalline fraction, expressed relative to a reference zeolite in sodium form (Na), that is less than 60%,

(2) at least one element selected from group VB,

(3) at least one hydro-dehydrogenating element selected from the group consisting of the elements of group VIB and group VIII, and

(4) at least one promoter element that is selected from the group consisting of phosphorus, boron, and silicon, wherein the zeolite has the following characteristics:

- an overall Si/Al ratio that is greater than 15,
- an Si/Al^{IV} framework ratio that is greater than 15,
- a pore volume that is at least equal to 0.20 ml/g wherein between 8% and 50% of the pore volume consists of pores that have a diameter of at least 5 nm.