

**A CATALYST WHICH COMPRISES A PARTIALLY AMORPHOUS
Y ZEOLITE AND USE THEREOF IN HYDROCONVERSION OF
HYDROCARBON PETROLEUM FEEDSTOCKS**

The present invention relates to a catalyst which contains at least one matrix, a partially amorphous Y zeolite, possibly at least one hydro-dehydrogenating metal, preferably selected from the group formed by the metals of group VIB and group VIII of the periodic table, possibly at least one element selected from the group formed by phosphorus, boron and silicon, possibly at least one element of group VIIA, and possibly at least one element of group VIIB. The invention also relates to the use of this catalyst in hydroconversion, in particular hydrocracking of hydrocarbon feedstocks, and, very particularly, for obtaining high viscosity oils with viscosity numbers (VN) greater than 95-100, preferably between 95 and 150, and more particularly between 120 and 140.

The catalyst can also be used in 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 bases 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 m².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, or by a

combination of at least one metal of group VIB of the periodic table and at least one metal of group VIII.

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 h⁻¹) 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 beta-type catalysts admittedly have a higher catalytic activity than those of the amorphous silica-aluminas. However, they have higher selectivities in light products.

Hydrotreatment takes on increasing importance in the practice of refining, with the growing need to reduce the amount of sulfur in the petroleum fractions and to convert heavy fractions into lighter fractions which can be upgraded as fuels. On the one hand, this results in the growing demand for fuels with the resultant need to convert increasingly rich imported crude oils into heavy fractions and into heteroatoms, including nitrogen and sulfur, and, on the other hand, this results in specifications which are imposed on the contents of sulfur and aromatic compounds in various countries for commercial fuels. This upgrading involves a relatively significant reduction to the molecular weight of the heavy components, which can be obtained by means of cracking reactions, for example.

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, gas oils, vacuum gas oils, atmospheric residues and vacuum residues deasphalted or otherwise. For example, cracking and catalytic hydrocracking processes are indicated for the pretreatment 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 diagrams for upgrading heavy petroleum fractions.

In the prior art, the zeolites used for the preparation of hydrocracking catalysts are characterised by several magnitudes, such as their $\text{SiO}_2/\text{Al}_2\text{O}_3$ framework molar ratio, their crystalline parameter, their pore distribution, the 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 and FR-A-2,754,826) use a zeolite whose crystalline parameter is between 24.15 and 24.38 Å ($1\text{Å} = 0.1\text{ nm}$), the $\text{SiO}_2/\text{Al}_2\text{O}_3$

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 of Na/100 g of zeolite, the specific surface area greater than 400 m²/g, the water vapour adsorption capacity greater than 6%, and 1 to 20% of the pore volume is contained in pores with a diameter of between 20 and 80 Å.

Patent US-A-4,857,170 describes the use in hydrocracking of a modified zeolite with a crystalline parameter of less than 24.35 Å but on whose degree of crystallinity there is no effect, or little effect, by the modifying treatments.

Moreover, the prior art shows that an effort has always been made to maintain high crystalline fractions (or degree of crystallinity) and peak rates in the zeolites used.

The research work carried out by the Applicant on numerous zeolites and microporous solids led him to discover that, on the contrary and surprisingly, a catalyst which contains at least one partially crystallised FAU-structural-type Y zeolite enables middle distillate selectivities (kerosene and gas oil) to be obtained which are clearly better than catalysts containing a Y zeolite which are known in the prior art.

In addition, the same work made it possible for the Applicant to note, surprisingly, that Y zeolite samples which are modified differently, despite having characteristics identical or very close to those cited in the prior art, can in contrast exhibit different peak rates and different crystalline fractions and have different reactivities.

More specifically, the invention relates to a catalyst comprising at least one matrix and possibly at least one element selected from the group formed by the group VIII and group VIB elements, said catalyst being characterised in that it contains a partially amorphous Y zeolite.

The term, "partially amorphous Y zeolite", as used in the present invention, is understood to be a solid having:

- i) a peak rate of less than 0.40, preferably of 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%.

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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 m²/g, preferably 250-750 m²/g, and advantageously 300-600 m²/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 $\text{SiO}_2/\text{Al}_2\text{O}_3$ 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 crystallization 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.

The catalyst of this invention can contain at least one noble or non-noble element of group VIII, such as iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium or platinum. Among the metals of group VIII, the use of non-noble metals, such as iron, cobalt and nickel, is preferred. The catalyst according to the invention can contain at least one group VIB element, preferably tungsten and molybdenum. The combinations of the following metals are advantageously 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, e.g. nickel-cobalt-molybdenum.

The catalyst of the present invention also contains at least one oxide-type amorphous or poorly crystallized porous mineral matrix. Aluminas, silicas, and silica-aluminas can be cited by way of non-limiting example. It is also possible to select aluminates. Preferably, matrices are used which contain alumina under all of these forms known to the skilled person, and, even more preferably, aluminas, e.g. gamma-alumina.

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

- 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 formed by group VIB and group VIII metals,
- 0.1 to 99.9%, and preferably 0.1 to 99.8% or to 99.7% or to 99.6% or to 99%, preferably 1 to 98%, of at least one oxide-type amorphous or poorly crystallized porous mineral matrix,

said catalyst also contains 0.1 to 99.9%, preferably 0.1 to 99.8%, or to 99%, preferably 0.1 to 90%, preferably 0.1 to 80%, of partially amorphous Y zeolite,

said catalyst possibly containing

- 0 to 20%, preferably 0.1 to 15% and even more preferably 0.1 to 10% of at least one promoter element selected from the group formed by silicon, boron and phosphorus, and preferably boron and/or silicon,
- 0 to 20%, preferably 0.1 to 15%, and even more preferably 0.1 to 10%, of at least one element selected from group VIIA, preferably fluorine,
- 0 to 20%, preferably 0.1 to 15%, and even more preferably 0.1 to 10%, of at least one element selected from group VIIB.

The group VIB, VIII and VIIB 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.

This catalyst can be prepared using any methods well-known to the skilled person. It is advantageously obtained by mixing the matrix and zeolite, and the mixture is then shaped. The hydrogenating element is introduced during mixing, or, preferably, after shaping. The shaping is followed by calcination, and the hydrogenating element is introduced before or after this calcination. The preparation ends with calcination at a temperature of 250 to 600°C. One of the preferred methods according to this invention consists in mixing the partially

amorphous Y zeolite powder in a moist alumina gel for several tens of minutes, then in passing the paste thus obtained through a die in order to form extrudates of between 0.4 and 4 mm in diameter.

The hydrogenating function can be introduced in part only (e.g. in the case of combinations of oxides of group VIB and VIII metals) or completely at the time of mixing the zeolite, i.e. the partially amorphous Y zeolite, with the oxide gel selected as matrix.

The hydrogenating function can be introduced by one or more ion exchange operations onto the calcined substrate constituted by a partially amorphous Y zeolite which is dispersed in the selected matrix using solutions which contain the precursor salts of the selected metals.

The hydrogenating function can be introduced by one or more impregnation operations of the shaped and calcined substrate by way of a solution containing at least one precursor of at least one oxide of at least one metal selected from the group formed by the group VIII and VIB metals, the precursor(s) of at least one oxide of at least one metal of group VIII preferably being introduced after those of group VIB, or at the same time as the latter, if the catalyst contains at least one group VIB metal and at least one group VIII metal.

If the catalyst contains at least one group VIB element, e.g. molybdenum, it is possible to impregnate the catalyst, for example, with a solution containing at least one group VIB element, to dry it, and to calcine it. Impregnation of the molybdenum can be facilitated by adding phosphoric acid to the ammonium paramolybdate solutions, thereby permitting the introduction of phosphorus in order to promote catalytic activity.

In one preferred embodiment of the invention, the catalyst contains as promoter at least one element selected from silicon, boron and phosphorus. These elements are introduced onto a substrate which already contains at least one partially amorphous Y zeolite, at least one matrix, as defined hereinabove, and at least one metal selected from the group formed by the group VIB and group VIII metals.

If the catalyst contains boron, silicon and phosphorus, and possibly the element selected from group VIIA of the halide ions, and possibly at least one element selected from

group VIIB, these elements can be introduced into the catalyst at various stages of the preparation and in various ways.

The impregnation of the matrix is preferably carried out 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 using a solution containing all of the constituent elements of the final catalyst.

The P, B, Si and the element 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.

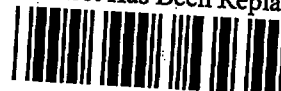
If the catalyst contains boron, a preferred method according to the invention consists in preparing an aqueous solution of at least one boron salt, such as ammonium baborate or ammonium pentaborate, in an alkaline medium and in the presence of hydrogen peroxide, and in undertaking a so-called dry impregnation operation in which the pore volume of the precursor is filled with the boron-containing solution.

If the catalyst contains silicon, a solution of a compound of the silicone-type silicon will be used.

If the catalyst contains boron and silicon, the boron and silicon can also be deposited simultaneously by using a solution which contains a boron salt and a silicone-type silicon compound. Thus, for example, if the precursor is a nickel-molybdenum-type catalyst which is supported on a substrate containing the partially amorphous Y zeolite and alumina, then it is possible to impregnate that precursor with the aqueous solution of ammonium baborate and Rhodorsil E1P silicone of Rhône-Poulenc, to undertake drying, e.g. at 80°C, followed by impregnation with an ammonium fluoride solution, to undertake drying, e.g. at 80°C, and to carry out calcination by way of example and preferably in air and in a flushed bed, e.g. at 500°C for 4 hours.

If the catalyst contains at least one group VIIA element, preferably fluorine, it is possible to impregnate the catalyst with an ammonium fluoride solution, for example, to

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undertake drying, e.g. at 80°C, and to carry out calcination, by way of example and preferably, in air and in a flushed bed, e.g. at 500°C for 4 hours.

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

If the catalyst contains phosphorus, it is possible, for example, to impregnate the catalyst with a solution which contains phosphorus, to dry it, and to calcine it.

If the elements contained in the catalyst, i.e. at least one metal selected from the group formed by group VIII and group VIB metals, possibly boron, silicon, phosphorus, at least one group VIIA element, and at least one group VIIB element, are introduced into several impregnation operations of the corresponding precursor salts, an intermediate drying stage of the catalyst is generally carried out at a temperature of between usually 60 and 250°C, and an intermediate calcination stage of the catalyst is usually carried out at a temperature of between 250 and 600°C.

In order to complete preparation of the catalyst, the moist solid is allowed to rest in a moist atmosphere at a temperature of between 10 and 80°C, and the moist solid obtained is then dried at a temperature of between 60 and 150°C, and finally the solid obtained is calcined at a temperature of between 150 and 800°C.

The sources of group VIB elements which can be used are well-known to the skilled person. For example, among the sources of molybdenum and tungsten, it is possible to use oxides and hydroxides, the molybdic and tungstic acids and salts thereof, in particular the ammonium salts such as ammonium molybdate, ammonium heptamolybdate, ammonium tungstate, phosphomolybdic acid, phosphotungstic acid and the salts thereof, silicomolybdic acid, silicotungstic acid and the salts thereof. The ammonium oxides and salts such as ammonium molybdate, ammonium heptamolybdate and ammonium tungstate are preferably used.

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, and carboxylates, e.g. acetates and carbonates, will be

used. For the noble metals, halides will be used, e.g. chlorides, nitrates, acids such as chloroplatinic acid, and oxychlorides such as ruthenium ammoniacal oxychloride.

The preferred source of phosphorus is H_3PO_4 orthophosphoric acid, but the salts and esters thereof, such as the ammonium phosphates, are also suitable. Phosphorus can be introduced, e.g. 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.

A number of silicon sources can be used. Thus, it is possible to use ethyl orthosilicate $\text{Si}(\text{OEt})_4$, siloxanes, polysiloxanes, halide silicates such as ammonium fluorosilicate $(\text{NH}_4)_2\text{SiF}_6$ or sodium fluorosilicate Na_2SiF_6 . Silicomolybdic acid and the salts thereof, and silicotungstic acid and the salts thereof can also advantageously be used. Silicon can be added, e.g. by impregnation of ethyl silicate in solution into a water/alcohol mixture. The silicon can be added, e.g. by impregnating 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 baborate 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 nitrogen-containing compound, 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, e.g. by 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. Those 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 $(\text{NH}_4)_2\text{SiF}_6$, silicon tetrafluoride SiF_4 , or sodium tetrafluoride Na_2SiF_6 . Fluorine can be introduced, e.g. by impregnation of an aqueous solution of hydrofluoric acid or ammonium fluoride.

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The sources of group VIIB elements which can be used are well-known to the skilled person. Ammonium salts, nitrates and chlorides are preferably used.

The catalysts thus obtained, in oxide form, can possibly be brought at least in part into metallic or sulfide form.

The catalysts which are obtained by way of the present invention are shaped into the form of grains 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 m²/g, a pore volume measured by mercury porosimetry of between 0.2 and 1.5 cm³/g and a pore size distribution which can be monomodal, bimodal or polymodal.

The catalysts which are thus obtained are used for the hydroconversion of hydrocarbon feedstocks (within the broad sense of conversion in the presence of hydrogen), and, in particular, for hydrocracking and hydrotreating. The hydroconversion catalyst then contains at least one hydro-dehydrogenating element.

The catalysts obtained by way of the present invention are used for hydrocracking hydrocarbon feedstocks, such as petroleum fractions. 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 hydrogen recycling rate is at least 50, and often between 80 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 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.

A conventional sulfurization method which is well-known to the skilled person consists in heating in the presence of hydrogen sulfide to a temperature of between 150 and 800°C, preferably of between 250 and 600°C, generally in a flushed bed reaction zone.

The catalyst of the present invention can be used advantageously for the hydrocracking of vacuum distillate-type fractions which have a high sulfur and nitrogen content. The desired products are middle distillates and/or oils. Advantageously, hydrocracking is used in combination with a preliminary hydrotreatment stage in a process for the improved production of middle distillates in conjunction with the production of oil bases which have a viscosity number of between 95 and 150.

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 300°C, generally at most 480°C, and often between 350°C and 450°C. The pressure is generally above 2 MPa,

and preferably 3 MPa; it is less than 12 MPa, and preferably less than 10 MPa. The amount of hydrogen is at least 100 normal litres of hydrogen per litre of feedstock, and often between 200 and 3000 normal 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, hydrosulfurization, and hydrodenitrating than commercial catalysts.

In a second embodiment, the process is carried out in two stages, the catalyst of the present invention being 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 contained in the prior art. This hydrotreatment catalyst advantageously comprises a matrix preferably with an alumina base and at least one metal with a hydrogenating function. The hydrotreatment function is ensured by at least one metal or metal compound, alone or in combination, selected in particular from among the group VIII and VIB metals, such as selected from nickel, cobalt, molybdenum and tungsten. In addition, this catalyst can possibly contain phosphorus and possibly boron.

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 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 NI/NI of feedstock, and preferably 260-3000 NI/NI 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 330°C and 450°C. The pressure is generally at least 2 MPa, and preferably 3 MPa; it is less than 12 MPa and preferably less than 10 MPa. The amount of hydrogen is at least 100 l/l of feedstock and often between 200 and 3000 l/l 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, hydrodesulfurization, and hydronitrating 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 takes place in two stages, the catalyst according to the invention being used in the second stage.

The catalyst of the first stage can be any hydrotreatment catalyst contained in the prior art. This hydrotreatment catalyst advantageously comprises a matrix preferably with an alumina base and at least one metal with a hydrogenating function. The hydrotreatment function is ensured by at least one metal or metal compound, alone or in combination, selected from the group VIII and group VIB metals, such as selected from nickel, cobalt, molybdenum and tungsten, in particular. In addition, this catalyst can possibly contain phosphorus and possibly boron.

The first stage generally takes place at a temperature of 350-460°C, preferably 360-450°C, a pressure above 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 NI/NI of feedstock, and preferably 260-3000 NI/NI of feedstock.

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

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

In a process for the production of oils which advantageously employs the hydrocracking process according to the invention, the operation is carried out in accordance with the teaching of the patent US-5,525,209 with a first hydrotreatment stage under conditions permitting the production of an effluent with a viscosity number of 90-130 and with a reduced nitrogen and polyaromatic compound content. In the subsequent hydrocracking stage, the effluent is treated in accordance with the invention in order to adjust the value of the viscosity number to that desired by the user.

The catalysts obtained by way of the present invention are also used for the hydrotreating 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 naphthenic 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, are 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 hydrotreating 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.

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Example 1: Preparation of a Hydrocracking or Hydrotreating 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 $24.29\text{\AA}$, 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 ($50\text{\AA}$) in diameter. A hydrocracking catalyst substrate containing this Y zeolite is produced in the following way:

60 g of the partially amorphous Y zeolite described hereinabove is mixed with 40 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 Hydrocracking and Hydrotreating Catalysts which contain a Partially Amorphous Y Zeolite, According to the Invention

The substrate extrudates which contain a partially amorphous Y zeolite of Example 1 are impregnated in the dry state with an aqueous solution of ammonium heptamolybdate, 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 Y_1Mo catalyst obtained are given in Table 1.

The Y_1Mo catalyst was then impregnated with an aqueous solution containing ammonium diborate in order to obtain a deposit of about 1.7% by mass of B_2O_3 . Following maturing at ambient temperature in a water-saturated atmosphere, the impregnated extrudates are dried for one night at 120°C and then calcined at 550°C for 2 hours in dry air. A catalyst

which is named Y_1MoB is obtained. In the same way, a Y_1MoSi catalyst was then prepared by impregnation of the Y_1Mo catalyst by a Rhodorsil EP1 silicone emulsion (Rhône-Poulenc) in such a way as to deposit about 2.0% of SiO_2 . The impregnated extrudates are then dried for one night at 120° and then calcined at $550^\circ C$ for 2 hours in dry air. Finally, a Y_1MoBSi catalyst achieved impregnation of the Y_1Mo catalyst by way of an aqueous solution containing ammonium baborate and the Rhodorsil EP1 (Rhône-Poulenc) silicone emulsion. The impregnated extrudates are then dried for one night at $120^\circ C$ and then calcined at $550^\circ C$ for 2 hours in dry air.

The substrate extrudates containing a partially amorphous Y zeolite, prepared in Example 1, are impregnated in the dry state with an aqueous solution of an ammonium heptamolybdate and nickel nitrate solution, dried for one night at $120^\circ C$ in air, and finally calcined in air at $550^\circ C$. The contents by weight of the Y_1NiMo catalyst oxides obtained are given in Table 3.

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 $120^\circ C$ in air, and finally calcined in air at $550^\circ C$. The contents by weight of Y_1NiMoP catalyst oxides obtained are given in Table 3.

We then impregnated the sample of the Y_1NiMoP catalyst with an aqueous solution containing ammonium baborate. After maturing at ambient temperature in a water-saturated atmosphere, the impregnated extrudates are dried for one night at $120^\circ C$, and then calcined for 2 hours in dry air. A catalyst named $Y_1NiMoPB$ is obtained.

A $Y_1NiMoPSi$ catalyst was obtained by way of the same procedure as the $Y_1NiMoPB$ catalyst above, but by replacing the boron precursor by the Rhodorsil EP1 silicone emulsion in the impregnation solution.

Finally, a $Y_1NiMoPBSi$ catalyst was obtained by way of the same procedure as the catalysts hereinabove but by using an aqueous solution containing ammonium baborate and the Rhodorsil EP1 silicone emulsion. Fluorine is then added to that catalyst by impregnation with a dilute hydrofluoric acid solution in such a way as to deposit about 1% by weight of fluorine. Following drying for one night at $120^\circ C$ and calcination at $550^\circ C$ for 2 hours in dry



air, the $Y_1NiMoPBSiF$ catalyst is obtained. The final contents of oxides of the Y_1NiMo catalysts are given in Table 1.

Table 1: Characteristics of the Y_1Mo and Y_1NiMo Catalysts

Catalyst	Y_1Mo	Y_1MoB	Y_1MoSi	Y_1MoBSi
MoO_3 (% by weight)	14.3	14.5	14.2	14.1
B_2O_3 (% by weight)	0	1.5	0	1.6
SiO_2 (% by weight)	50.7	49.7	52.3	51.4
Complement up to 100% consisting mainly of Al_2O_3 (% by weight)	35.0	34.3	33.5	32.9

Table 1 continued

Catalyst	Y_1NiNo	Y_1NiMoP	$Y_1NiMoPB$	$Y_1NiMoPSi$	$Y_1NiMoPBSi$	$Y_1NiMoPBSiF$
MoO_3 (% by weight)	13.5	13.9	12.8	12.9	12.9	12.85
NiO (% by weight)	3.05	2.2	2.95	2.9	3.0	2.95
P_2O_5 (% by weight)	0	4.4	4.3	4.5	4.5	4.4
B_2O_3 (% by weight)	0	0	1.4	0	1.5	1.6
SiO_2 (% by weight)	49.4	47.0	46.5	48.6	47.9	47.3
F (% by weight)	0	0	0	0	0	1.0
Complement up to 100% consisting mainly of Al_2O_3 (% by weight)	34.05	32.5	32.05	31.1	30.2	29.9

The Y_1NiMoP catalyst was then impregnated with an aqueous solution containing manganese nitrate. Following maturing at ambient temperature in a water-saturated atmosphere, the impregnated extrudates are dried for one night at $120^\circ C$ and then calcined at $550^\circ C$ for 2 hours in dry air. A catalyst named $Y_1NiMoPMn$ is obtained. That catalyst is then impregnated with an aqueous solution containing ammonium baborate and the Rhodorsil EP1 (Rhône-Poulenc) silicone emulsion. The impregnated extrudates are then dried for one night at $120^\circ C$ and then calcined at $550^\circ C$ for 2 hours in dry air, and the $Y_1NiMoPMnBSi$ catalyst is obtained. A dilute hydrofluoric acid solution is then added to that catalyst of fluorine by impregnation in such a way as to deposit 1% by weight of fluorine. Following drying for one night at $120^\circ C$ and calcination at $550^\circ C$ for 2 hours in dry air, the $Y_1NiMoPMnNBSiF$ catalyst is obtained. The contents by weight of these catalysts are given in Table 2.

Table 2: Characteristics of the Y_1NiMo Catalysts which contain Manganese

Catalyst	Y_1 NiMoPMn	Y_1 NiMoPMnBSi	Y_1 NiMoPMnBSiF
MoO ₃ (% by weight)	12.6	12.1	12.2
NiO (% by weight)	3.1	2.9	2.8
MnO ₂ (% by weight)	2.1	2.1	2.2
P ₂ O ₅ (% by weight)	4.4	4.5	4.9
B ₂ O ₃ (% by weight)	0	1.2	1.4
SiO ₂ (% by weight)	46.0	47.1	46.4
F (% by weight)	0	0	1.0
Complement up to 100% consisting mainly of Al ₂ O ₃ (% by weight)	31.8	30.1	29.1

The analysis, by electron microprobe, of the $Y_1NiMoPSi$, $Y_1NiMoPBSi$ and $Y_1NiMoPBSiF$ catalysts (Table 3) and of the $Y_1NiMoPMnBSi$ and $Y_1NiMoPMnBSiF$ catalysts (Table 3b) shows that the silicon which is added to the catalyst according to the invention is mainly located on the matrix and is in the form of amorphous silica.



Example 3: Preparation of a Substrate which contains a Y₁ Zeolite and a Silica-Alumina

We produced a silica-alumina powder by co-precipitation whose composition was 2% SiO₂ and 98% Al₂O₃. A hydrocracking catalyst substrate containing that silica-alumina and the partially amorphous Y zeolite of Example 1 was then produced. To that end, 50% by weight of the partially amorphous Y zeolite of Example 1, mixed with 50% by weight of a matrix consisting of the silica alumina prepared hereinabove, was used. That powder mixture was then mixed with an aqueous solution containing nitric acid at 66% (7% by weight of acid per gramme of dry gel) and then mixed for 15 minutes. After that mixing, the paste 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 and then calcined at 550°C for 2 hours in air.

Example 4: Preparation of Hydrocracking Catalysts which Contain a Partially Amorphous Y Zeolite and a Silica-Alumina

The substrate extrudates containing a silica-alumina and a partially amorphous Y zeolite of Example 3 are impregnated in the dry state with an aqueous solution of an ammonium heptamolybdate, nickel nitrate and orthophosphoric acid mixture, dried for one night at 120°C in air, and finally calcined in air at 550°C. The contents by weight of oxides of the Y₁-SiA1-NiMoP catalyst which are obtained are given in Table 4.

We impregnated the sample of Y₁-SiA1-NiMoP catalyst with an aqueous solution containing ammonium baborate in such a way as to impregnate 1.5% by mass of B₂O₃. Following maturing at ambient temperature in a water-saturated atmosphere, the impregnated extrudates are dried for one night at 120°C and then calcined at 550°C for 2 hours in dry air. A catalyst named Y₁-SiA1-NiMoPB which therefore contains silicon in the silica-alumina matrix is obtained.

The characteristics of the Y₁-SiA1-NiMo catalysts are given in Table 3:

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Table 3: Characteristics of the Y₁-SiAl-NiMo Catalysts

Catalyst	Y ₁ -SiAl-NiMoP	Y ₁ -SiAl-NiMoPB
MoO ₃ (% by weight)	13.1	13.5
NiO (% by weight)	2.9	2.7
P ₂ O ₅ (% by weight)	4.7	4.9
B ₂ O ₃ (% by weight)	0	1.4
SiO ₂ (% by weight)	47.6	46.5
Complement up to 100% consisting mainly of Al ₂ O ₃ (% by weight)	31.7	31.0

Example 5: Preparation of a Substrate which Contains a Prior Art Zeolite

A large amount of hydrocracking catalyst substrate containing a Y zeolite was produced in order to be able to prepare various catalysts which were based on the same substrate. To that end, 20.5% by weight of the same USY commercial zeolite is used as that used in Example 1. That zeolite is mixed with 79.5% by weight of a matrix consisting of ultrafine tabular boehmite or alumina gel marketed under the name SB3 by Condéa Chemie GmbH. That powder mixture was then mixed with an aqueous solution containing nitric acid at 66% (7% by weight of acid per gramme of dry gel), then mixed for 15 minutes. After mixing, the paste 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 and then calcined at 550°C for 2 hours in air. Cylindrical extrudates of 1.2 mm in diameter with a specific surface area of 223 m²/g and a monomodal pore size distribution centered at 10 nm are thus obtained.

Example 6: Preparation of Hydrocracking Catalysts which contain the Y Zeolite of Example 5

The substrate extrudates containing dealuminified Y zeolite of Example 5 are impregnated in the dry state with an aqueous solution of an ammonium heptamolybdate, nickel nitrate and orthophosphoric acid mixture, dried for one night at 120°C in air, and finally calcined in air at 550°C. The contents by weight of oxides of the YNiMoP catalyst obtained are given in Table 5. The final YNiMoP catalyst contains, in particular, 16.3% by

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weight of Y zeolite with a mesh parameter of 2.429 nm with an overall $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 30.4 and an $\text{SiO}_2/\text{Al}_2\text{O}_3$ framework ratio of 58.

We impregnated the sample of the YNiMoP catalyst with an aqueous solution containing ammonium baborate. Following maturing at ambient temperature in a water-saturated atmosphere, the impregnated extrudates are dried for one night at 120°C and then calcined at 550°C for 2 hours in dry air. An NiMoP/alumina-Y catalyst which is doped with boron is obtained.

A YNiMoPSi catalyst was obtained by way of the same procedure as the YNiMoPB catalyst above, but the boron precursor was replaced in the impregnation solution by the Rhodorsil EP1 (Rhône-Poulenc) silicone emulsion.

Finally, a YNiMoPBSi catalyst achieved impregnation of the catalyst with an aqueous solution containing ammonium baborate and Rhodorsil EP1 (Rhône-Poulenc) silicone emulsion. The other stages of the procedure are the same as those indicated above. The characteristics of the YNiMo catalysts are summarised in Table 4.

Table 4: Characteristics of the YNiMo Catalysts (Not in Accordance with the Invention)

Catalyst	YNiMo	YNiMoP	YNiMoPB	YNiMoPSi	YNiMoPBSi
MoO_3 (% by weight)	13.5	12.9	12.7	12.7	12.5
NiO (% by weight)	3.1	3.0	2.9	2.9	2.8
P_2O_5 (% by weight)	0	4.4	4.3	4.3	4.2
B_2O_3 (% by weight)	0	0	1.8	0	1.8
SiO_2 (% by weight)	16.2	15.4	15.2	17.0	16.7
Complement up to 100% consisting mainly of Al_2O_3 (% by weight)	67.2	64.3	63.1	63.1	62.0

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Analysis by electron microprobe of the YNiMoPSi and YNiMoPBSi catalysts (Table 5) shows that the silicon added to the catalyst according to the invention is mainly located on the matrix and is in the form of amorphous silica.

Example 7: Comparison of the Catalysts for Hydrocracking a Vacuum Gas Oil with Partial Conversion

The catalysts, preparation of which has been described in the above examples, are used under moderate pressure hydrocracking conditions on a petroleum feedstock whose main characteristics are as follows:

Density (20/4)	0.921
Sulfur (% 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 catalyst of the first HTH548 hydrotreatment stage sold by Procatalyse and comprising a group IV element and group VIII element which are deposited on the alumina is introduced. In the second reactor, i.e. that in which the feedstock passes last, a hydrocracking catalyst described hereinabove is introduced. In each of the reactors, 40 ml 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

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Feedstock flow rate 40 cm³/h

The two catalysts undergo an in-situ sulfurisation stage before reaction. We note that any in-situ or ex-situ sulfurization method is suitable. Once the sulfurization is carried out, the feedstock described hereinabove is able to be transformed.

The catalytic performances are expressed in terms of hydrodesulfurization conversions (HDS) and hydrodenitrating conversions (HDN). These catalytic performances are measured in the catalyst after a stabilization period, usually at least 48 hours, has elapsed.

Hydrosulfurization conversion HDS is assumed to be equal to:

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

Hydrodenitrating conversion HDN is assumed to be equal to:

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

In the following table, we recorded hydrodesulfurization conversion HDS and hydrodenitrating conversion HDN for the catalysts.

Table 5: Catalytic Activities of the Catalysts in Partial Hydrocracking at 400°C

References	Composition	HDS (%)	HDN (%)
YNiMoP	NiMoP/Y – Al ₂ O ₃	99.43	96.6
YNiMoPB	NiMoPB/Y	99.57	97.4
YNiMoPSi	NiMoPSi/Y	99.85	98.3
Y ₁ -SiAl-NiMoP	NiMoP/Y ₁ -SiAl	98.6	96.6
Y ₁ -SiAl-NiMoPB	NiMoPB/Y ₁ -SiAl	98.7	97.8
Y ₁ NiMo	NiMo/Y ₁ -Al ₂ O ₃	98.6	95.1
Y ₁ NiMoP	NiMoP/Y ₁	99.3	97.0
Y ₁ NiMoPB	NiMoPB/Y ₁	99.7	97.8
Y ₁ NiMoPSi	NiMoPSi/Y ₁	99.8	98.7
Y ₁ NiMoPBSi	NiMoPBSi/Y ₁	99.8	99.0

The results of Table 6 show that the use of a catalyst according to the invention, containing a partially amorphous Y zeolite, is more active in terms of hydrodesulfurization and in terms of hydrodenitrating than the prior art catalysts, and also that the addition of at least one element selected from the group formed by B, Si and P provides an improvement in performance levels of the catalyst according to the invention.

Furthermore, the results of Table 6 show that it is advantageous to introduce silicon onto the catalyst which has already been prepared (Y₁NiMo series) rather than in the form of a substrate containing silicon obtained from a silica-alumina (Y₁-SiAl-NiMo series). It is therefore particularly advantageous to introduce the silicon onto a precursor which already contains the group VIB and/or group VIII elements and possibly at least one of the elements P, B and F.

Example 8: Comparison of the Catalysts in the Hydrocracking of a High-Conversion Vacuum Gas Oil

The catalysts, the preparation of which has been described in the preceding examples, 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	
Starting point	298°C
10% point	369°C
50% point	427°C
90% point	481°C
Final point	538°C

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

An H_2S precursor sulfur-containing compound and an NH_3 precursor nitrogen-containing compound are added to the hydrotreated feedstock in order to simulate the partial pressures of H_2S and NH_3 present in the second hydrocracking stage. The feedstock which is thus prepared is injected into the hydrocracking test unit which comprises a fixed-bed reactor with upward circulation ("up-flow") of the feedstock, into which 80 ml of catalyst is introduced. Before the feedstock is injected, the catalyst is sulfurized by an n-hexane/DMDs + aniline mixture up to 320°C . Note that any in-situ or ex-situ sulfurization method is suitable. Once sulfurization has been carried out, the feedstock described hereinabove can be transformed. The operating conditions of the test unit are as follows:

Total pressure	9 MPa
Catalyst	80 cm^3
Temperature	360-420 $^\circ\text{C}$
Hydrogen flow rate	80 l/h
Feedstock flow rate	80 cm^3/h

The catalytic performances are expressed by the temperature permitting a gross conversion level of 70% and by the coarse selectivity of 150-380 $^\circ\text{C}$ middle distillates. These catalytic performances are measured in the catalyst after a stabilization period, generally at least 48 hours, has elapsed.

Gross conversion GC is assumed to be equal to:

$$\text{GC} = \% \text{ by weight of } 380^\circ\text{C}^{\text{less}} \text{ of the effluent}$$

Coarse selectivity CS of middle distillate is assumed to be equal to:

$$\text{CS} = 100 * \text{weight of the fraction } (150^\circ\text{C}-380^\circ\text{C}) / \text{weight of the fraction } 380^\circ\text{C}^{\text{less}} \text{ of the effluent.}$$

The middle distillates obtained consist of products which have a boiling point of between 150 and 380 $^\circ\text{C}$.

The reaction temperature is set to reach a gross conversion GC which is equal to 70% by weight. Table 6 hereinafter records the reaction temperature and the coarse selectivity for

the catalysts described in Tables 3 and 3b, as well as the values of the viscosity numbers which are determined in the 380°C+ fractions following removal of the paraffin from the solvent.

Table 6 shows that the use of a catalyst according to the invention which contains the partially amorphous Y zeolite results in coarse selectivities of middle distillate which are higher than those of anomalous prior art catalysts. In contrast, by adding at least one element selected from the group formed by P, B and Si to the catalysts according to the invention an increase in activity results. The improvement provided by the presence of manganese or fluorine to the activity is also noted.

In addition, it is clearly seen that the viscosity numbers of the 380°C+ fractions obtained with the catalysts according to the invention are clearly improved.

Generally, by adding to the catalyst according to the invention at least one element selected from the group P, B, Si, VIIB, VIIA to the catalyst containing the partially amorphous Y zeolite and the group VIB element the conversion activity can be improved, and this is reflected by a reduction in the reaction temperature which is needed in order to reach 70% conversion.

Table 6: Catalytic Activities of Catalysts in High-Conversion Hydrocracking (70%)

Reference	Composition	T(°C)	Coarse Selectivity of Middle Distillate (150-380°C) (% by weight)	Viscosity Number VI 380°C+ Removal of Paraffin
YNiMo	NiMo/Y-Al ₂ O ₃	375	65.8	112
YNiMo P	NiMoP/Y-Al ₂ O ₃	374	66.4	115
YNiMo PB	NiMoPB/Y-Al ₂ O ₃	374	67.1	116
YNiMo PSi	NiMoPSi/Y-Al ₂ O ₃	374	68.0	
Y ₁ MoB	MoB/Y ₁ -Al ₂ O ₃	386	69.4	
Y ₁ MpSi	MoSi/Y ₁ -Al ₂ O ₃	386	69.6	
Y ₁ MoBSi	MoBSi/Y ₁ -Al ₂ O ₃	384	70.1	



Y ₁ NiMo	NiMo/Y ₁ -Al ₂ O ₃	387	70.3	123
Y ₁ NiMoP	NiMoP/Y ₁ -Al ₂ O ₃	384	71.1	124
Y ₁ NiMoPB	NiMoPB/Y ₁ -Al ₂ O ₃	384	71.8	120
Y ₁ NiMoPSi	NiMoPSi/Y ₁ -Al ₂ O ₃	382	72.5	
Y ₁ NiMoPBSi	NiMoPBSi/Y ₁ -Al ₂ O ₃	380	72.6	
Y ₁ NiMoPBSiF	NiMoPBSiF/Y ₁ -Al ₂ O ₃	376	72.3	
Y ₁ NiMoPMn	NiMoPMn/Y ₁ -Al ₂ O ₃	382	72.0	
Y ₁ NiMoPMnBSi	NiMoPMnBSi/Y ₁ -Al ₂ O ₃	380	71.9	
Y ₁ NiMoPMnBSiF	NiMoPMnBSiF/Y ₁ -Al ₂ O ₃	377	71.7	

Example 9: Hydrotreatment Test of a Vacuum distillate

The Y₁NiMo, Y₁NiMoP, Y₁NiMoPB, Y₁NiMoPBSi and Y₁NiMoPBSiF catalysts, preparation of which has been described hereinabove, were compared in a hydrotreatment test of a vacuum distillate, the main characteristics of which are given in the following table:

Density at 15°C	:	0.938
Sulphur	:	3.12% by weight
Total nitrogen	:	1050 ppm by weight
Simulated distillation	:	
Starting point	:	345°C
10%	:	412°C
50%	:	488°C
90%	:	564°C
Final point	:	615°C

The test is carried out in an isothermal pilot reactor with a flushed fixed bed, with upward circulation of the fluids. Following in-situ sulfurization at 350°C in the pressurized unit with a direct distillation gas oil to which 2% by weight dimethyl disulfide is added, the hydrotreatment test was carried out under the following operating conditions:

Total pressure	:	12 MPa
Catalyst volume	:	40 cm ³
Temperature	:	380°C
Hydrogen flow rate	:	24 l/h
Feedstock flow rate	:	20 cm ³ /h

The catalytic performance levels of the catalysts tested are given in Table 7 hereinafter. They are expressed in terms of relative activity, assuming that that of the Y₁NiMo catalyst is equal to 1 and considering that they are of the order of 1.5. The equation linking activity and hydrodesulfurization conversion (% HDS) is as follows:

$$A_{HDS} = \left[\frac{100}{(100 - \% HDS)} \right]^{0.5-1}$$

The same equation is applicable to hydrodenitrating (% HDN and A_{HDN}).

The net conversion of the fraction of the feedstock which has a boiling point higher than 380°C (% 380°C⁺ by weight) which is obtained with each catalyst is also evaluated. It is expressed on the basis of simulated distillation results (ASTM D86 method) by the following equation:

$$Conv\ 380^{\circ}C^{-} = \frac{(\% 380^{\circ}C^{-})\ formula - (\% 380^{\circ}C^{-})\ feedstock}{(\% 380^{\circ}C^{+})\ feedstock}$$

Table 7 : Activity of Catalysts in Vacuum Distillate Hydrotreatment

Catalyst	A _{HDS} relative to Y ₁ NiMo	A _{HDN} relative to Y ₁ NiMo	Net Conv. 380°C (% by weight)
Y ₁ NiMo	1	1	53.4
Y ₁ NiMoP	1.07	1.2	55.2
Y ₁ NiMoPB	1.15	1.4	57.8
Y ₁ NiMoPBSi	1.3	1.7	59.5
Y ₁ NiMoPBSiF	1.25	1.65	62.8

These examples show every advantage in using a catalyst according to the invention which permits better hydrodesulfurization and hydrodenitrating activities as well as a better net conversion of products of 380°C (products with a boiling point of less than 380°C) than the catalysts known from the prior art.

The catalyst according to the invention is therefore significant in terms of its activity in hydrogenating aromatic hydrocarbons and in terms of hydrodenitrating and hydrodesulfurization. Without wanting to be tied to any theory, it seems that this particularly high activity of the catalysts of the present invention is due to the presence of the amorphized zeolite. It is reinforced by the joint presence of boron and silicon on the matrix which brings about an improvement in the hydrogenating, hydrodesulfurizing and hydrodenitrating properties, on the one hand, and an improvement in terms of the conversion, on the other hand.

CLAIMS



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

2. Catalyst according to claim 1 that also comprises at least one hydro-dehydrogenating element.

3. Catalyst according to one of the preceding claims in which the zeolite also has at least one of the following characteristics:

- an overall Si/Al ratio that is greater than 15,
- an Si/Al^{iv} framework ratio that is greater than or equal to the overall Si/Al ratio,
- a pore volume that is at least equal to 0.20 ml/g of solid whose fraction, between 8% and 50%, consists of pores that have a diameter of at least 5 nm,
- a specific surface area of 210-800 m²/g.

4. Catalyst according to claim 2, in which the hydro-dehydrogenating element is selected from among the elements of group VIII and the elements of group VI B.

5. Catalyst according to one of the preceding claims that also contains at least one element that is selected from the group that is formed by phosphorus, boron, and silicon.

6. Catalyst according to claim 5, in which the element is deposited on the catalyst and mainly located on the matrix.

7. Catalyst according to one of the preceding claims that also contains at least one element of group VII A.

8. Catalyst according to one of the preceding claims that also contains at least one element of group VII B.

9. Catalyst according to the claim in which the element of group VII B is manganese.

10. Catalyst according to one of the preceding claims that contain in % by weight relative to the total mass of the catalyst:

- 0.1 to 99.9% of at least one oxide-type amorphous or poorly crystallized porous mineral matrix,
- 0.1 to 99.9% of partially amorphous Y zeolite,
- 0 to 60% of at least one hydro-dehydrogenating element,
- 0 to 20% of at least one element that is selected from the group that is formed by boron, silicon and phosphorus,





-- 0 to 20% of at least one element of group VII A,

-- 0 to 20% of at least one element of group VII B.

11. Catalyst according to one of the preceding claims, in which the matrix is selected from among alumina, silica-alumina, aluminates and silica.

12. Catalyst according to one of the preceding claims, in which the partially amorphous Y zeolite is obtained by using dealuminification techniques on a Y zeolite that is available commercially.

13. Catalyst according to claim 12, in which the techniques that are used in combination are the hydrothermic treatment, ion exchange and acid attack.

14. Process for hydroconversion of hydrocarbon feedstock with a catalyst that comprises at least one matrix and at least one partially amorphous Y zeolite that has a peak rate that is less than 0.4 and a crystalline fraction that is expressed relative to a reference zeolite in sodium form (Na) which is less than 60% and that also comprises at least one hydro-dehydrogenating element.

15. Process according to claim 14 that is a hydrocracking.

16. Process according to claim 15 for hydrocracking at a temperature that is higher than 200°C, a pressure that is higher than 0.1 MPa, a volumetric flow rate of 0.1-20 h⁻¹ and a hydrogen recycling of at least 50 Nl/l of feedstock.

17. Process according to claim 15, in which the pressure is higher than 2 MPa and less than 12 MPa, the temperature is at least 230°C, the volumetric flow rate is 0.1-10 h⁻¹ and the hydrogen recycling is at least 100 Nl/l of feedstock, whereby the conversion is less than 55%.

18. Process according to claim 15, in which the pressure is at least 5 MPa, and the conversion is greater than 55%.

19. Process according to one of claims 15 to 18 in which the catalyst is previously sulfurized.

20. Process according to one of claims 15 to 18, in which the feedstock is subjected to a hydrotreatment before being hydrocracked.

21. Process according to claim 14, which is a hydrotreating.

22. Process according to claim 21 that operates at a temperature that is higher than 200°C, a pressure that is higher than 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.

23. Process according to claim 21, in which the catalyst is previously sulfurized.

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24. Process according to one of claims 14 to 23 that operates with a catalyst according to one of claims 3 to 13.

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